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STUDIES OF Π BONDED PHOSPHORUS COMPOUNDS

BY

DAVID GILBERT SCHMIDLING

A dissertation submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1970

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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To my professors at City College, to my mentor Dr. Neil McKelvie, to my first teachers, my parents, and to my partner in learning, my wife, I dedicate this thesis.

STUDIES OF π BONDED PHOSPHORUS COMPOUNDS

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DAVID SCHMIDLING

ABSTRACT

This thesis is an investigation of the carbon to trivalent phosphorus π bond. Such bonds are weaker than π bonds between second row elements, presumably due to 2p-3p π overlap being less efficient than 2p-2p π overlap. The stability of compounds containing carbon to phosphorus double bonds that are essentially unstabilized by resonance is investigated theoretically and experimentally.

Dewar's thermocycle method for calculation of the resonance integral β is examined, and modified so that the few accurately known parameters for carbon to phosphorus bonds may be used for calibration. In the process of modification the thermocycle method is transformed into an empirical bond energy, bond length, bond order and stretching force constant correlation, in addition to performing its original function. This correlation is tested on known multiple bonds (C-C, C-O, C-N), and prediction of heats of atomization of aromatic systems containing these bonds are found to be reasonably accurate. However, predictions made for triple bonds are poor.

Huckel, Pople-Pariser-Parr, CNDO and MINDO molecular

orbital methods are applied to compounds containing phosphorus to carbon bonds, giving generally good agreement with experimental or expected values for bond length and bond energy. The d orbitals of trivalent phosphorus are predicted to be extensively involved in π bonding to carbon.

The carbon to phosphorus double bond in CH_2PH is estimated to have a bond length of 1.677 Å. and a bond energy of 116.7 Kcal/mole. The dimerization of two CH_2PH molecules (two carbon to phosphorus double bonds yield four carbon to phosphorus single bonds) is predicted to be exothermic, $\Delta H = -26 \pm 10$ Kcal per mole of dimer.

The experimental work was directed at the preparation of a compound containing a C=P double bond that was essentially unconjugated.

9-Fluorenylidene-9-fluorenylmethylphenylphosphorane, Fl-P(Me)(Ø)=Fl (Fl- = 9-fluorenyl) reacts with sodium hydride to form an ylid-anion, Fl^{-}-P(Me)(Ø)=Fl.

Bromodi-9-fluorenylphenylphosphonium bromide, $Fl_2ØP^{+}Br\ Br^{-}$ reacts with the base 1,5 diazobicyclo[3.4.0]nonene-5 (DBN) to give an unstable green solution, believed to contain bis-9-fluorenylidenephenylphosphorane, Fl=P(Ø)=Fl. This is a new type of ylid with two double bonds to phosphorus, implying involvement of a phosphorus 3p as well as a 3d orbital in bonding. The green color is slowly discharged, and the final products are bis-9-fluorenylidene and phenylphosphorus polymer.

Sodium 9-fluorenylide reacts with phosphorus trichloride. After two moles of sodium fluorenylide per mole of phosphorus trichloride are added, the solution begins to turn green. Addition of a third mole of sodium 9-fluorenylide or a mole of DBN gives an intense green solution. The stoichiometry for the reaction is determined to be 3:1, and the proposed structure of the green material is that of 9-fluorenylidene-9-fluorenylphosphine, Fl=P-Fl.

The above compound is discussed from a theoretical standpoint and is compared with model compounds.

CNDO and PPP calculations on the 9-fluorenylidene-phosphorus moiety indicate substantial carbon-phosphorus double bond character, and the PPP calculations combined with the thermocycle data give a C=P bond energy of 110.7 Kcal/mole. 9-Fluorenylidene-9-fluorenylphosphine is predicted to be stable towards dimerization, by virtue of steric effects, some of which are quantitatively estimated.

The visible spectrum of 9-fluorenylidene-9-fluorenylphosphine is compared with that of thiofluorenone, which is isoelectronic with the 9-fluorenylidene-phosphorus grouping and they are found to be very similar.

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The constructive criticisms and suggestions of members of my committee and especially of Dr. Neil McKelvie, under whose guidance this work was conducted have been most helpful, and are gratefully acknowledged. I also acknowledge with thanks my wife Beverly, for help in preparation of this thesis.

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INTRODUCTION

This thesis consists of both a theoretical and an experimental study of the phosphorus to carbon π bond. While π bonds are common amongst second row elements, examples of π bonded elements of the third row are comparitively rare.

In π bonds between second and third row elements, the 2p orbital on one atom overlaps with a 3p and one or more 3d orbitals on the other atom. Such overlap is generally poor, but improves on increasing the atomic number of the third row element, producing orbital contraction. Thus, one finds stable carbon to sulfur double bonds (e.g. carbon disulfide, thioketones), but no stable species containing a double bond to silicon. The 3p and 3d orbitals of silicon are too diffuse for strong π bonding.

π bonded silicon is known in diatomic spectroscopic species. When dissociation energies of such molecules are compared with energies of single bonds between the same atoms, it becomes evident that the π bonds are much weaker than the σ bonds. Thus if a compound containing a silicon to carbon double bond was prepared, there would exist a great tendency for it to polymerize.

Compounds containing π bonds between two third row atoms would also be subject to the tendency to polymerize (SiS_2 exists as an infinite chain of SiS_4 tetrahedra), but σ and π bonds are more nearly of the same energy. Such compounds have not as yet been reported, except for diatomic spectroscopic species.

Phosphorus is in between silicon and sulfur in atomic number, and π bonds to it may be expected to be intermediate in stability. This appears to be the case, and some classes of compounds containing carbon to phosphorus π bonds are already known. A summary of these compounds follows.

1. CP radical is a well known spectroscopic species,[1] and simple molecular orbital theory suggests the electronic structure $(KL2s3s\sigma^2 2s3s\sigma^{*2} 2p3p\pi^2 2p3p\pi^2 2p3p\sigma)$. Clearly some appreciable electron density resides in two π bonds. The bond length is 1.562Å. in the ground state, which may be compared with the sum of the Pauling double and triple bond radii, 1.67Å. and 1.53Å.[2], and with the normal single bond distance, 1.863Å., in methyl phosphine.[3]

1. G. Hertzberg, Spectra of Diatomic Molecules, New York (1955)
2. L. Pauling, The Nature of the Chemical Bond, third edition, Ithica, N.Y., (1960)
3. N. Kajima, E.L. Breig and C. C. Lin, J. Chem. Phys. 35, 2139 (1961)

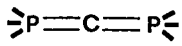
2. Methinophosphide, HCP has been reported[4,5] as a white solid, and as a gaseous species, stable below -150°C., prepared by passing phosphine gas through a carbon arc. The microwave spectrum of the vapor is consistent with a C-P bond length of 1.5421Å.,[6] indicating a triple bond (sum of Pauling triple bond radii = 1.53Å.). Infra-red[5] and mass spectral analysis[4] confirm the structure. HCP rapidly polymerizes on warming above -150°.

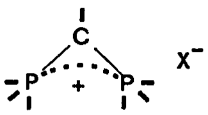
3. Pentavalent phosphorus ylids have been known for some time, the more reactive species being used extensively in the Wittig reaction. Carbon to phosphorus bond distances in various ylids of the structure $R_3P=CR_2$ have been reported in the range 1.66-1.74Å.[7]

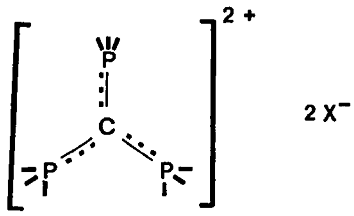
One ylid, $Ø_3P=C=C=O$, has a reported bond length of 1.648Å.,[8] less than the sum of the phosphorus and carbon double bond radii. This may be attributed in part to the small radius of the sp hybridized carbon, and partly to bonding between the d orbitals of phosphorus and the carbon one atom removed. The P-C-C bond angle is 145.5°.

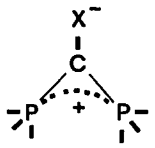
4. T. E. Gier, C. A., 58, 91406 (1963), U. S. 3,051,756
5. T. E. Gier, J. Am. Chem. Soc., 83, 1769 (1961)
6. J. K. Tyler, J. Chem. Phys., 40, 1170 (1964)
7. J. C. Bart, J. Chem. Soc., B, 350 (1969), and references therein.
8. J. J. Daly and P. J. Wheatley, J. Chem. Soc., A, 1703 (1966)

Carbophosphoranes of other structures have been reported, containing two and three phosphorus atoms bonded to carbon, each bond containing double bond character[9].





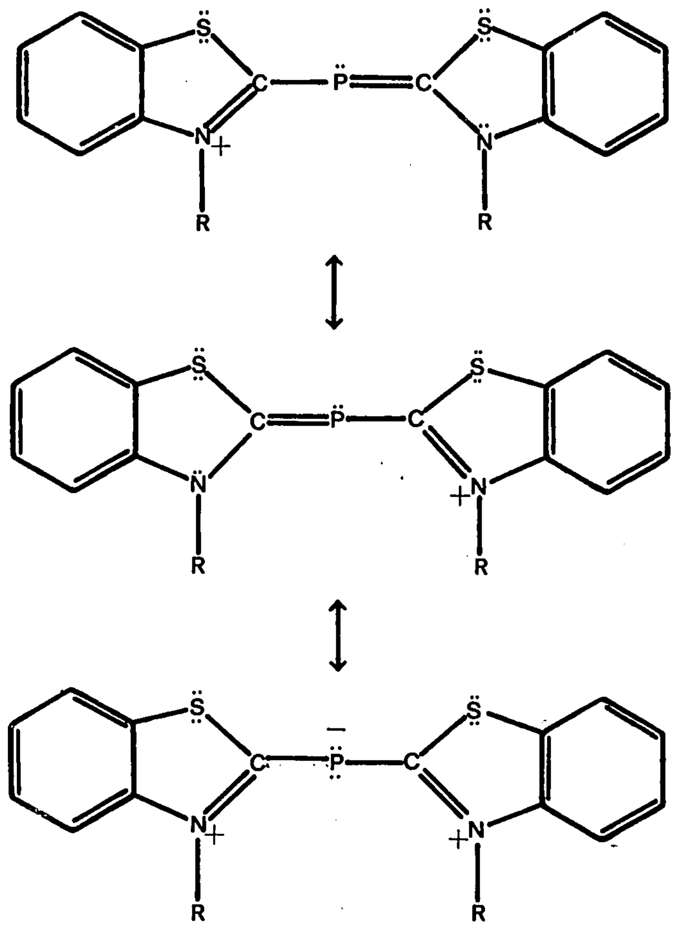




4. A series of phosphacyanines has been prepared by Dimroth and Hoffmann[10].

X-Ray diffraction demonstrates that the material is monomeric[11]. The carbon to phosphorus bond lengths are 1.76Å, and the C-P-C bond angle is 105°.

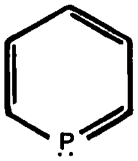
9. See a review article by C. N. Matthews and G. H. Birum, Accounts of Chemical Research, 2, 373 (1969)
10. K. Dimroth and P. Hoffmann, Angew. Chem., 76, 433 (1964)
11. R. Allman, Angew. Chem., 77, 134 (1965)



5. Substituted phospholes have been prepared[12,13], and there is some evidence of aromatic character[14,15], implying contribution of the lone pair of electrons on phosphorus to a 6 electron π system.

12. Pentaphenylphosphole, the first phosphole to be prepared, was reported by E. H. Braye and W. Hubel, Chem. Ind. (London), 1250 (1959)
13. Review article: G. Markl, Angew. Chem., 77, 1109 (1965)
14. L. D. Quin, J. G. Bryson and C. G. Morehead, J. Am. Chem. Soc., 91, 3308 (1969)
15. W. Egan, R. Tang, G. Zon and K. Mislow, J. Am. Chem. Soc., 92, 1442 (1970)

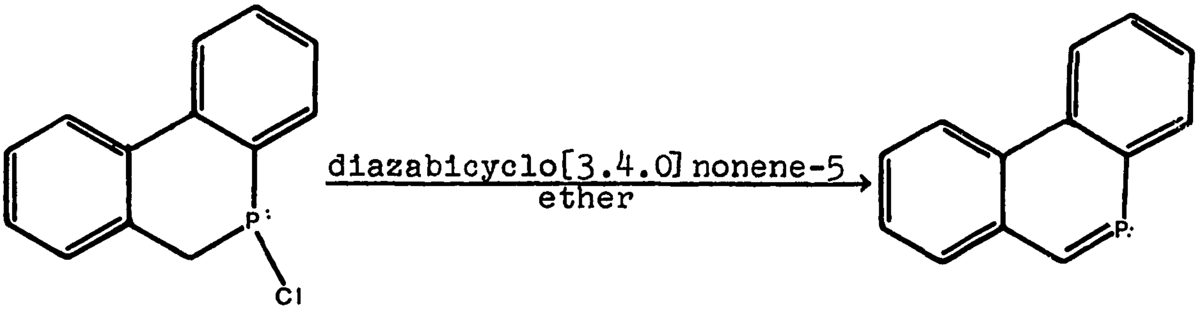
6. An exceptional series of compounds, substituted phosphabenzenes, have been prepared by Markl. 2,4,6-Triphenylphosphabenzene,



phosphabenzene

the first phosphabenzene reported[16], was prepared from 2,4,6-triphenylpyrylium tetrafluoroborate and tris-hydroxymethylphosphine. These also appear to be aromatic in character, and perfectly stable.

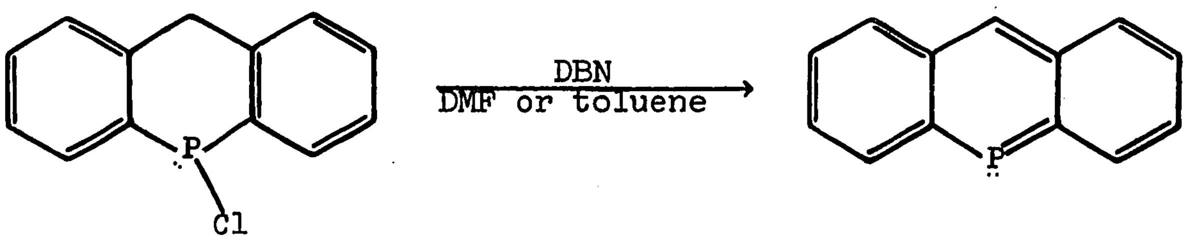
7. A material that has been reported in solution only is dibenzo [b, d] phosphorine[17]. It was prepared via 5-chloro-5,6-dihydrodibenzo [b, d] phosphorine.



The material is not stable. Comparison of the U. V. spectrum with that of phenanthrene and phenanthridene provides evidence for the assigned structure.

16. G. Markl, Angew. Chem., 78, 907 (1966)
17. P. deKoe, R. vanVeen and F. Bickelhaupt, Angew. Chem. internat. Edit., 7, 465 (1968)

Another material, also unstable, dibenzo [b, e] phosphorine was produced in analogous manner.[18]



The U. V. spectrum is similar to that of anthracene and acridene.

A number of conclusions may be drawn concerning the properties of compounds containing phosphorus to carbon π bonds.

1. Such compounds are capable of existence, and have some measure of stability.

2. Both 3p and 3d orbitals of phosphorus are involved in bonding, which can occur in both the trivalent and pentavalent state.

3. In the trivalent state, stability (criteria: resistance to autodissociation, disproportionation, polymerization) can be conferred by conjugation, i.e. resonance stabilization.

18. P. deKoe, Angew. Chem. internat. Edit., 6, 567 (1967)

4. The one stable compound discovered so far that has carbon to phosphorus π bonds unstabilized by resonance, HCP, polymerizes with great ease, indicating that such a π bond is weaker than a σ bond to trivalent phosphorus. This conclusion is confirmed by study of the CP radical.

Comparison of the heat of atomization of CP radical, 159 Kcal./mole, with the bond energy of a normal C-P single bond, 65 Kcal./mole, gives the result that a π bond is 18 Kcal./mole weaker than a σ bond, assuming a total bond order in CP of three[19]. This may be regarded as an upper limit. A lower limit on the σ-π bond energy difference is given by a CNDO calculation on CP radical[20], where the 2p-3pπ bond order (neglecting 2p-3dπ bonding) is 1.69. A π bond of unit order is then estimated to be 10 Kcal./mole weaker than a σ bond, assuming a linear bond order-bond energy relation.

In the present work, compounds containing phosphorus to carbon double bonds not stabilized by resonance, or those stabilized by resonance only to a small degree, will be investigated. These are compounds of the type $R_2C{=}PR$.

Since such compounds may well have a tendency to dimerize, synthetic work will be directed at such compounds for which dimerization is sterically hindered.

19. R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, New York, 1965, p. 20
20. Presented in this thesis, p. 74.

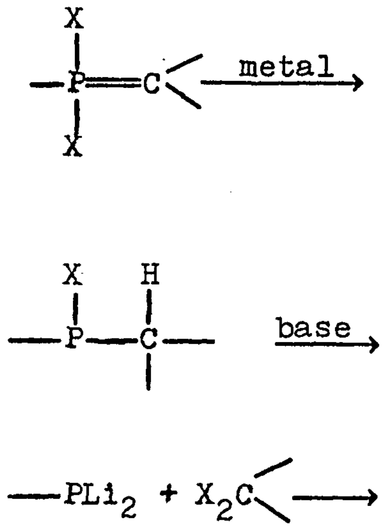
Theoretical estimates of the energy and other properties of carbon to phosphorus multiple bonds are made by several methods, to provide cross-checks.

One of the methods, empirical in nature, is a thermocycle method of evaluation of the resonance integral β, for use in Pople-Pariser-Parr SCF calculations. It is also itself a bond energy-bond length-bond order-stretching force constant correlation, which appears to be of general utility. It is discussed in the first section.

The second section is devoted to theoretical models for compounds containing carbon to phosphorus double bonds, including the Huckel, PPP, CNDO and MINDO molecular orbital methods, and also the application of the thermocycle method of Section 1 to the C=P system. Isoelectronic analogs, the feasibility of dimerization and U. V. spectra are other topics discussed here.

Section 3 embraces the experimental work, together with interpretive arguments, while Section 4 consists of the experimental details.

The experimental work consists of the preparation or attempted preparation of several carbon to phosphorus double bond containing compounds. The various reaction types are for the most part similar, with double bond formation proceeding via elimination of halogen, hydrogen halide or alkalai halide



In the only case where a reasonably stable product was obtained, structure proof is based on spectra and reactivity, as a method by which the product could be isolated was not devised.

EMPIRICAL BOND ENERGY, BOND LENGTH, BOND ORDER AND STRETCHING FORCE CONSTANT CORRELATIONS

A set of empirical bond property relationships was deemed necessary to calibrate SCF calculations on π bonded phosphorus compounds. The relationships evolved by Dewar in his thermocycle method[21a,b,c,d] for the calculation of the integral β and other bond properties provides very accurate values of heats of formation of π bonded compounds when used in conjunction with the Pople method. However, it contains a large number of empirical parameters, too many for direct application to π bonded phosphorus compounds, where little experimental data exists. It was therefore modified.

A description of the Dewar thermocycle method follows, using C-C bonds as an example.

BOND ENERGY VS. BOND LENGTH

An empirical bond energy-bond length relationship is proposed:

21a Alice L. H. Chung and Michael J. S. Dewar, J. Chem. Phys., 42, 755 (1965)
21b Michael J. S. Dewar and Gerald Jay Gleicher, J. Am. Chem. Soc., 87, 685 (1969)
21c Michael J. S. Dewar and Carlos de Llano, J. Am. Chem. Soc., 91, 789 (1969)
21d Michael J. S. Dewar and Toshifumi Morita, J. Am. Chem. Soc., 91, 796 (1969)

1) $$r = \frac{1}{b}\left\{a\left[\ln a\ (a^2-D^2)^{\frac{1}{2}}\right]-a \ln D-(a^2-D^2)^{\frac{1}{2}}\right\}$$

In this equation, r and D are the length and energy of a bond in a molecule, and a and b are adjustable parameters, determined from the bond lengths and energies of diamond and ethylene.

BOND ORDER VS. BOND LENGTH

A linear relationship between bond order and bond length for bonds between sp^2 hybridized atoms is found from the bond orders and bond lengths of ethylene, graphite and benzene, the bond orders of which are determined by symetry. This relation is then extrapolated to zero bond order, obtaining a bond length of 1.512Å. for a single bond between two sp^2 hybridized carbon atoms.

FORCE CONSTANT VS. BOND LENGTH

An empirical relationship between stretching force constant k and bond length r, containing three adjustable parameters is of the form:

2) $$k = \frac{C}{r^2}+\frac{D}{r^4}+\frac{E}{r^6}$$

where it is assumed that the force constant is a single valued function of bond length only.[22]

The values of C, D and E are computed via the force constants and bond lengths for ethane, ethylene and acetylene. The force constant for the bond between singly bonded sp^2 carbon atoms is computed using the value of the bond length obtained by extrapolating the bond order-bond length correlation to a π bond order of zero.

COMPRESSION ENERGIES

The energy change upon compressing a chemical bond from one bond length to another is approximated as a Morse potential:

3) $$C = D\{1 - \exp[a(r_1 - r_2)]\}^2$$

Where C = the compression energy

D = the dissociation energy of the bond from its equilibrium state (in actual calculations, the bond energy is used)

22. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London), A193, 456 (1948) have shown that the force constant is also dependent on bond polarity

a = the Morse constant = $(k/2D)^{\frac{1}{2}}$

r_1 = the initial (equilibrium) bond length

r_2 = the final (compressed bond) bond length

A distinction between equilibrium and non-equilibrium states is apparently not made by Dewar.

THE π BONDING ENERGY, E_π

The quantity E_π represents the energy change upon forming a double bond from a single bond of the same length and hybridization.

4) $$C \overset{r}{—} C \xrightarrow{E_\pi} C \overset{r}{=} C$$

In the Pople approximation, setting the repulsion between (+1) cores equal to (11,22):

5) $$E_\pi = 2\beta + \tfrac{1}{2}\left[(11,11)-(11,22)\right]$$

(11,11) and (11,22) are the one center and two center integrals:

6) $$(11,11) = \iint \phi_1{}^2(1)\,\frac{e}{r_{12}}\,\phi_1{}^2(2)\,d\tau_1 d\tau_2$$

7) $$(11,22) = \iint \phi_1{}^2(1)\frac{e}{r_{12}}\phi_2{}^2(2)\,d\tau_1\,d\tau_2$$

The expression for E_π may be derived as follows:[23]

For a π bond between two atoms, not interacting with other structures in a molecule, the elements in the F matrix in the Pople method are

8) $$F_{11} = W_1 + \tfrac{1}{2}q_1\,(11,11) + (q_2 - 1)(11,22)$$

$$F_{22} = W_2 + \tfrac{1}{2}q_2\,(22,22) + (q_1 - 1)(22,11)$$

$$F_{12} = F_{21} = \beta_{12} - \tfrac{1}{2}\,p_{12}\,(11,22)$$

where W's are the ground state valence state ionization potentials.

where q's are electron densities on atoms

where p_{12} is the bond order

where (11,22) = (22,11)

Also, for identical atoms,

23. Michael J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry." New York, 1969 p118

9) $$W_1 = W_2$$

$$(11,11) = (22,22)$$

Knowing in advance from the Huckel approximation that the charge densities on the atoms = 1, and that the bond order = 1 (In this case, the Huckel approximation must give correct results), we have

10) $$F_{11} = F_{22} = W + \tfrac{1}{2}(11,11)$$
$$F_{12} = F_{21} = \beta_{12} - \tfrac{1}{2}(11,22)$$

The secular equation is then

11) $$\begin{vmatrix} W+\tfrac{1}{2}(11,11)-E_{\pi} & \beta_{12}-\tfrac{1}{2}(11,22) \\ \beta_{12}-\tfrac{1}{2}(11,22) & W+\tfrac{1}{2}(11,11)-E_{\pi} \end{vmatrix} = 0$$

which has the solutions

12) $$E_{\pi\,\text{bonding orbital}} = W + \tfrac{1}{2}\left[(11,11)-(11,22)\right] + \beta$$
$$E_{\pi\,\text{antibonding orbital}} = W + \tfrac{1}{2}\left[(11,11)-(11,22)\right] - \beta$$

The total electronic energy of the two electrons in the bonding orbital is twice the energy of one electron occupying that orbital less the average repulsion between those electrons.

13) $$E_{\text{total electronic}} = 2E_{\text{bonding orbital}} - J_{11}$$

where

14) $$J_{11} = \iint \psi_1^{\,2}(1)\, \frac{e^2}{r_{12}}\, \psi_1(2)\, d\tau_1 d\tau_2 = \tfrac{1}{2}\left[(11,11)+(11,22)\right]$$

15) $$E_{\text{total electronic}} = 2W + 2\beta + \tfrac{1}{2}(11,11) - \tfrac{3}{2}(11,22)$$

The total energy is found by adding to the total electronic energy the repulsion between the singly charged cores, which is set equal to the repulsion of two positrons on adjacent centers.

16) $$E_{\text{core repulsion}} = (11,22)$$

17) $$E_{\text{total}} = E_{\text{total electronic}} + (11,22)$$

18) $$E_{\text{total}} = 2W + 2\beta + \tfrac{1}{2}\left[(11,11) - (11,22)\right]$$

The energy change on going to a single bond from a single bond with non interacting electrons already present, i.e. E_{π}, is then equal to E_{total} less the energy released on allowing two electrons to occupy the p orbitals (-2 times the valence state ionization potential)

19) $$E_{\pi} = E_{total} - 2W$$

20) $$E_{\pi} = 2\beta + \frac{1}{2}\left[(11,11) - (11,22)\right]$$

Note that this derivation is for formation of a bond from isolated atoms, but is also correct for formation of a π bond between already singly bonded atoms containing single electrons in non-interacting p orbitals on adjacent atoms. Implicit is the assumption already made that the σ and π bonds are independent of one another. That they are equivalent is seen from a thermocycle in which a single (σ) bond is broken, the π bond formed, and the σ bond is formed.

21)

$\dot{C}\overset{\sigma}{—}\dot{C}$ bond	$\longrightarrow$	$2\,\dot{C}\cdot$	ΔE = single bond energy
$2\,\dot{C}\cdot$	$\longrightarrow$	$\dot{C}\overset{\pi}{—}\dot{C}$ bond	$\Delta E = E_{\pi}$
$\dot{C}\overset{\pi}{—}\dot{C}$ bond	$\longrightarrow$	C═C double bond	ΔE = (-)single bond energy
$\dot{C}\overset{\sigma}{—}\dot{C}$ bond	$\longrightarrow$	C═C double bond	$\Sigma\Delta E = E_{\pi}$

(11,11) is set equal to I-A, the difference between the valence state ionization potential and the valence state electron affinity, the values of which are from Jaffe.[24]

(11,22) is approximated as a function of (11,11) and the bond length, r.[21c]

22) $$(11,22) = \frac{e^2}{\sqrt{r^2 + \frac{e^4}{(11,11)^2}}}$$

where e is the electronic charge in appropriate units.

24. Jurgen Hinze and H.H. Jaffe, J. Am. Chem. Soc., 84., 540 (1962)

21c. Michael J.S. Dewar and Carlos de Llano, J. Am. Chem. Soc., 91, 789 (1969)

23) $e = 4.80296 \pm .00006 \times 10^{-10}$ esu

$esu^2 = dyne\ cm^2$

$$e^2 = (4.80296 \pm .00006 \times 10^{-10})^2 \text{ dyne cm}^2 \times \frac{1 \text{ erg}}{\text{dyne cm}}$$

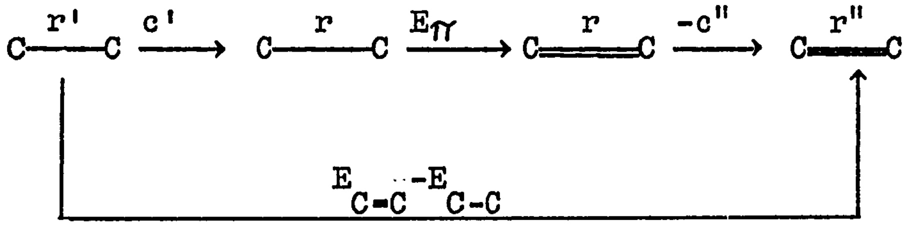
$$\times \frac{1 \text{ e.v.}}{1.602095 \pm .000022 \times 10^{-12} \text{ erg}} \times \frac{10^8 \text{Å.}}{\text{cm}}$$

$$= 14.389 \pm .006 \text{ e.v. Å.}$$

The value used in the calculation to facilitate comparison with older data was 14.297.

THERMOCYCLE FOR CALCULATION OF β

The value of β for use in Pariser-Parr-Pople SCF calculations is computed via a thermodynamic cycle using a two atoms system. A single bond between sp^2 hybridized atoms is compressed to a desired bond distance r. A π bond is added, and the bond is further compressed to the bond distance for a standard double bond. The sum of the energy changes in these steps is set equal to the bond energy for the standard double bond minus the bond energy for the standard single bond between sp^2 hybridized atoms.

24) 

For a carbon-carbon bond:

$r' = 1.512\text{Å}$

$r'' = 1.3380\text{Å}$ (bond length of ethylene)

E_{C-C} is computed from the bond length-bond energy relation, using the bond length r

$E_{C=C}$ is the bond energy of ethylene

25) $c' = E_{C-C}\left\{1-\exp\left[a'\ (r'-r)\right]\right\}^2, \quad a' = (k'/2E_{C-C})^{\frac{1}{2}}$

26) $-c'' = E_{C=C}\left\{1-\exp\left[a''\ (r''-r)\right]\right\}^2, \quad a'' = (k''/2E_{C=C})^{\frac{1}{2}}$

Recalling the expression for E_π,

20) $E_\pi = 2\beta + \frac{1}{2}\left[(11,11)-(11,22)\right]$

we may solve for β and substitute the quantities in the thermocycle for E_π.

27) $\beta = \frac{1}{2}E_\pi - \frac{1}{4}\left[(11,11)-(11,22)\right]$

28) $$\beta = \tfrac{1}{2}\left[(E_{C-C}-c') - (E_{C=C}-c'')\right] - \tfrac{1}{4}\left[(11,11)-(11,22)\right]$$

The energy of a single σ bond of length r is simply $E_{C-C} + c'(r)$.[21c]

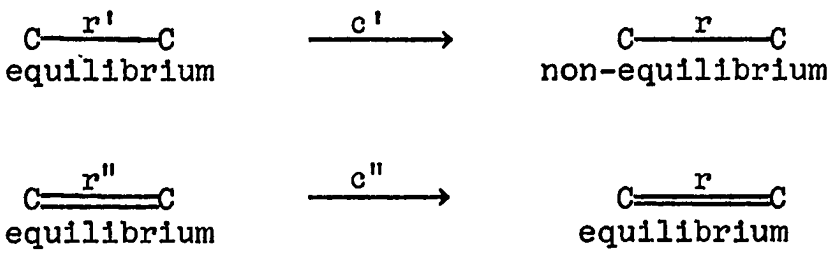
This thermocycle method was not used in the original form for phosphorus compounds for the following reasons:

1) The method requires a relatively large amount of experimental data. In particular, the linear bond order-bond length relationship requires accurate bond order and bond length data for at least two π bonded compounds. For C-C bonds, Dewar used graphite, benzene and ethylene. For bonds between other first row elements, he used an appropriate double bond and a zero π bond order bond, the length of which was estimated by assuming the contraction in bond length on going from an sp^3-sp^3 bond to an sp^2-sp^2 bond was the same as that for carbon, 0.032Å. It was felt that while this approximation apparently works well for first row elements, it is not necessarily sufficiently accurate for bond to phosphorus.

2) It was felt that the use of a Morse function to calculate c" was neither theoretically justified nor expedient.

A Morse function expresses a change in potential energy upon changing the bond distance. The altered bond is no longer in equilibrium, and cannot be in equilibrium without a change in both bond order and electron density. If a Morse function is appropriate in the calculation of c', where c' represents the energy in going from the (equilibrium) π bond order = 0, bond length r' state to the desired (non-equilibrium) π bond order = 0 state of bond length r, the same function is not appropriate in the calculation of c", the energy required to compress the ethylene type bond to the desired length r.

29)

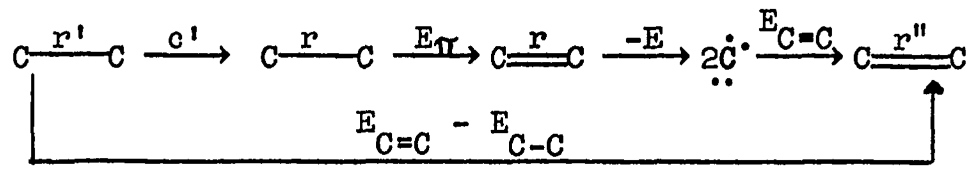


It was found that c" could be replaced by the difference between the bond energies of the desired bond and the standard ethylenic bond. An additional benefit of this assumption is that not only E_{π} but the total bond energy may be calculated from the thermocycle. An additional bond energy - bond length relation is not required. The total bond energy is then the sum of the σ and π bond energies, which was not found to be the case in Dewar's calculations.

3) The concept of a single bond between sp^2 hybridized atoms, the exact bond length of which is very critical to the calculations, was able to be dispensed with altogether by modification of the method.

MODIFIED THERMOCYCLE METHOD

The modified thermocycle is as follows:

30) 

where E is the bond energy of a double bond of length r and where other symbols have the same meaning as before in the Dewar thermocycle.

The standard single bond however is, in the case of C-C bonds, that of ethane. c' must therefore contain a rehybridization energy change (at the same bond length) as well as compression. This rehybridization energy must be small relative to the errors inherent in the approximation already made, or at worst, is largely compensated by differences in other errors between Dewar's thermocycle and my own. For comparison, the computed values of single σ bond energies for benzene, r=1.397Å, for Dewar's original and my modified thermocycle are 3.67 e.v. and 3.28 e.v. respectively.

β was calculated by setting it equal to the product of the stretching force constant and an adjustable parameter. The proportionality of β to k may be derived from theory, following Salem[25], with some added assumptions. These assumptions are not used in the thermocycle.

Assumption 1 For a stretching vibration of small amplitude the bond order remains constant.

Assumption 2 The σ bond energy is a unique function f of bond length.

Assumption 3 The π bond energy (core repulsion included) is given by the Huckel approximation.

31) $$E_{\pi} = 2p\beta$$

25. Lionel Salem, "The Molecular Orbital Theory of Conjugated Systems", New York, 1966, p142

The last assumption is made to simplify the second derivative of energy with respect to r. If the Pople expression is used, the results are similar to those obtained here, as $\partial^2(11,22)/\partial r^2$ is less than 25% of $\partial^2\beta/\partial r^2$ for systems of interest.

Assumption 4 There is a unique bond order-bond length relation p=P(r)

Assumption 5 σ - π separability

The total energy is the sum of σ and π bond energies.

32) $$E=E_\sigma + E_\pi = f + 2p\beta$$

Differentiating twice

33) $$\frac{\partial E}{\partial r} = \frac{\partial f}{\partial r} + 2p\frac{\partial \beta}{\partial r}$$

34) $$\frac{\partial^2 E}{\partial r^2} = \frac{\partial^2 f}{\partial r^2} + 2p\frac{\partial^2 \beta}{\partial r^2} = k$$ (expression valid at equilibrium only)

This expression may be further transformed by noting that to avoid collapse or expansion of a bond at equilibrium,[26]

26. ibid., p137

35) $$\frac{\partial f}{\partial r} = -2p\frac{\partial \beta}{\partial r}$$

On decreasing the bond distance an infinitesimal amount, the σ bond energy must decrease an infinitesimal amount, and must be exactly compensated by an infinitesimal increase in the π bond energy. Setting p=P(r) in (35), differentiating

36) $$\frac{\partial^2 f}{\partial r^2} = -2\frac{\partial P}{\partial r}\frac{\partial \beta}{\partial r} - 2p\frac{\partial^2 \beta}{\partial r^2}$$

Substituting (36) into the expression (34) for k

37) $$k = -2\frac{\partial P}{\partial r}\frac{\partial \beta}{\partial r}$$

Assumption 6 β is a unique function of r, the precise form being given by a relation suggested by Salem[25]

38) $$\beta = -b\ \exp(-r/a)$$

where a and b are constants. Differentiating (38) with respect to r gives

$$\frac{\partial \beta}{\partial r} = -b(-\frac{1}{a})\ \exp(-r/a) = -\frac{1}{a}\beta$$

25. Lionel Salem, "The Molecular Orbital Theory of Conjugated Systems", New York, 1966, p142

Substituting this result for $\partial \beta / \partial r$ in (37)

39) $$k = -2 \frac{\partial P}{\partial r}\left(-\frac{1}{a}\right)$$

Assumption 7 The relation p = P(r) is linear.

40) $$p = Cr + D$$

41) $$\frac{\partial p}{\partial r} = C$$

Substituting this result into (39)

42) $$k = \frac{2C}{a}\beta$$

This result shows that, under this set of approximations, the force constant is proportional to β. While these approximations are extreme, in practice the values of β are very similar to those calculated by Dewar. For example, the value of β for benzene (r=1.397Å.) in Dewar's calculation is -1.7882 e.v.. In my calculation the value is -1.7896 e.v..

NOTE: if Assumption 3 is not made (Huckel approximation), but the Pople method is used, the analog of (31) is

31a) $$E_\pi = -[2p\beta + \frac{1}{4}q_1 (11,11) + \frac{1}{4}q_2(22,22) + (q_1-1)(q_2-1)(11,22) - \frac{1}{2}p^2(11,22)]$$

which leads to an analog of (37)

37a) $$k = -2p \frac{\partial p}{\partial r} \frac{\partial \beta}{\partial r} + p \frac{\partial p}{\partial r} \frac{\partial (11,22)}{\partial r}$$

On the basis of thermocycle calculations in their final form, the second term of (37) is about 7% of the value of the first term for a C-C bond in benzene. At the level of approximation used here, this justifies leaving out the second term.

BOND ORDER

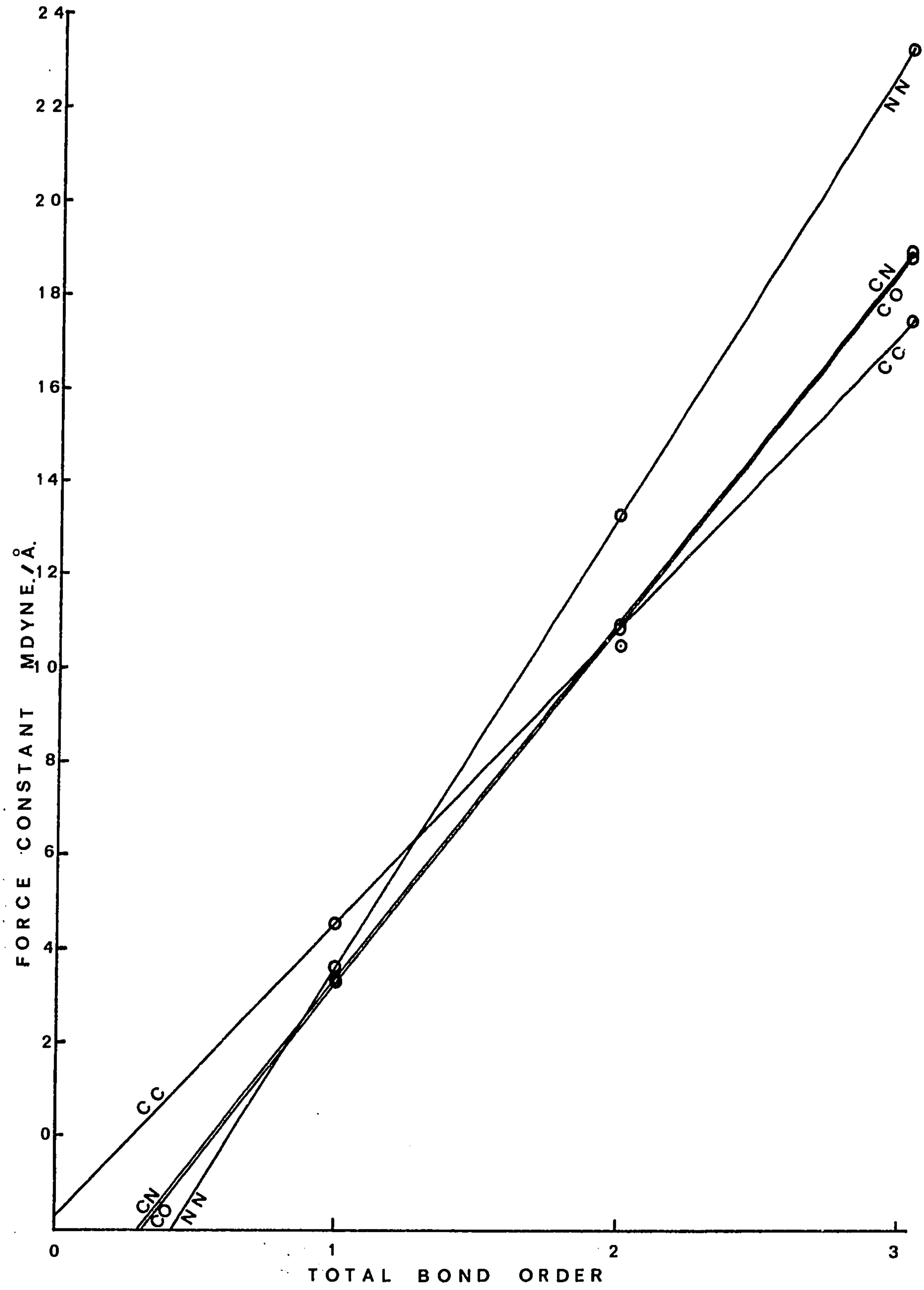
It was found that there exists an extremely good correlation between total bond order and stretching force constant, in cases where both are known unequivocally. This relation holds for both homonuclear and heteronuclear bonds, with the proviso that bond orders for heteronuclear bonds are treated as if bond polarity were nonexistant, e.g. the bond order for carbon monoxide would be exactly three. The validity of this correlation is demonstrated by plotting the data below. The force constants are those used by Dewar.[21c]

21c
Michael J. S. Dewar and Carlos de Llano, J. Am. Chem. Soc., 91, 789 (1969)

TABLE 1

BOND TYPE	COMPOUND	STRETCHING FORCE CONSTANT, MDYNE./Å.	BOND ORDER
C-C	Ethane	4.57	1.0
C=C	Ethylene	10.90	2.0
C≡C	Acetylene	17.20	3.0
C-N	Methylamine	3.347	1.0
C=N	Average of many Compounds	10.500	2.0
C≡N	Hydrogen Cyanide	18.583	3.0
C-O	Methanol	3.280	1.0
C=O	Formaldehyde	10.800	2.0
C≡O	Carbon Monoxide	18.530	3.0
N-N	Hydrazine	3.600	1.0
N=N	Average of many Compounds	13.250	2.0
N≡N	Nitrogen	22.900	3.0

FIGURE 1


24
22
20
18
16
14
12
10
8
6
4
2
0
FORCE CONSTANT MDYNE./Å.
NN
CN
CO
CC
CC
CN
CO
NN
0
1
2
3
TOTAL BOND ORDER

Only carbon to nitrogen bonds fail to fall on a straight line, the extrapolation of the straight line connecting the points for C-N and C=N bonds leads to a value of 17.80 for the stretching force constant of a triple bond between carbon and nitrogen.

Force constants for C≡N bonds vary from 16.2 to 18.6.[27] Further the stretching force constant for HCN is also reported as 18.07.[28] Also reliable values of the force constant of C=N bond do not exist.[29] Because of these considerations, C-N bonds will not be used as a test of the bond order-bond length correlation.

This correlation will be used to estimate bond orders, force constants being calculated, if desired, through Dewar's k=f(r) inverse power relation, which will be adopted for use here. Combining k=f(r) with k=g(p) gives

43) $f(r) = g(p),$

the bond length-bond order relation that will actually be used to estimate bond lengths.

27. E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", New York, 1955
28. W. J. Orville-Thomas, "The Structure of Small Molecules", London, 1966, p126
29. ibid, p54

CALIBRATION OF THERMOCYCLE

The thermocycle is calibrated as below, using carbon-carbon bonds as an example. The symbols used for the input data are as follows:

TABLE 2

COMPOUND	STRETCHING FORCE CONSTANT	BOND LENGTH	BOND ENERGY	BOND ORDER
Ethane	k'	r'	E'	p'
Ethylene	k''	r''	E''	p''
Acetylene	k'''	r'''		

The value of the integral (11,11) is also required. In the case of heteronuclear bonds, the value of (11,11) is taken to be the same for both atoms, the value being taken as the arithmetic mean of the value of (11,11) for the two atoms. (11,11) is set equal to I-A[30], the valence state ionization potential less the valence state electron affinity. The calibration procedure is given below.

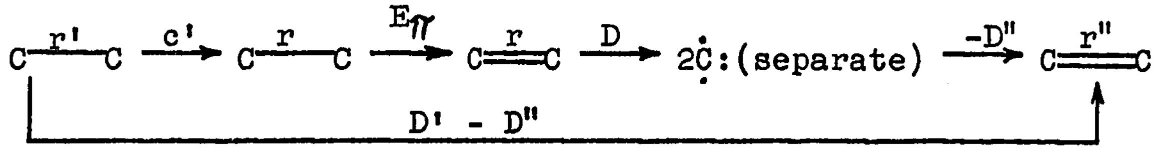
Using k', k'', k''', r' r'', r''' solve for the constants C, D and E in the relation

$$44) \qquad k = \frac{C}{r^2} + \frac{D}{r^4} + \frac{E}{r^6}$$

The thermocycle used is

30. Rudolph Pariser and Robert G. Parr, J. Chem. Phys., 21, 767, (1953)

45)



where D is the bond energy of the bond of desired length r, and E_π is the energy change upon forming a π bond. The expression for E_π is adopted unchanged from Dewar's calculations.

46) $$E_\pi = 2\beta + \tfrac{1}{2}[(11,11) - (11,22)]$$

Summing terms in the thermocycle

47) $$c' + E_\pi + D - D'' = D' - D''$$

Substituting for E_π in (46) and solving for β

48) $$\beta = -\tfrac{1}{2}\, c' - \tfrac{1}{2}D + \tfrac{1}{2}D' - \tfrac{1}{4}[(11,11) - (11,22)]$$

Since in this set of approximations β is proportional to k, the stretching force constant,

49) $$\beta = -\,A\,k$$

where (-A) is the constant of proportionality. Eliminating β from equations (48) and (49)

$$50)\qquad -A\,k = -\tfrac{1}{2}c' - \tfrac{1}{2}D + \tfrac{1}{2}D' - \tfrac{1}{4}[(11,11) - (11,22)]$$

(11,22) is approximated as a function of (11,11), as in the original Dewar thermocycle

$$51)\qquad (11,22) = \frac{14.397}{\sqrt{r^2 + \dfrac{(14.397)^2}{(11,11)^2}}}$$

The approximation for c' is also that used by Dewar.

$$52)\qquad c' = D'\left\{1 - \exp[(k'/2D')^{\frac{1}{2}}(r' - r)]\right\}^2$$

The constant A is calculated from equation (50) by using the constants for ethylene. Setting r=r" in (51) and (52),

$$53)\qquad -A\,k = -\tfrac{1}{2}c' - \tfrac{1}{2}D'' + \tfrac{1}{2}D' - \tfrac{1}{4}\left[(11,11) - (11,22)\right]$$

For carbon-carbon bonds,

$$54)\qquad A = 0.2057\,\frac{\text{e.v.}}{\text{millidyne/A.}}$$

The constants in the linear relation between k and p are calculated from the force constants and bond orders of the standard single and double bonds.

55) $$p = p' + \frac{p''-p'}{k''-k'}(k - k')$$

USE OF THE THERMOCYCLE

The thermocycle is used as follows. For a given value of the bond distance r:

<u>Step 1.</u> calculate the force constant k from the expression

56) $$k = \frac{C}{r^2} + \frac{D}{r^4} + \frac{E}{r^6}$$

<u>Step 2.</u> also calculate c' and (11,22)

57) $$c' = D'\left\{1- \exp\left[(k'/2D')^{\frac{1}{2}}(r' - r)\right]\right\}^2$$

58) $$(11,22) = \frac{14.397}{\sqrt{r^2 + \frac{(14.397)^2}{(11,11)^2}}}$$

The sigma bond energy is found immediately, as before

59) $D_\sigma = D' - c'$

<u>Step 3.</u> β and p, the bond order, are calculated using the computed value of k

60) $\beta = -A\ k$

61) $p = p' + \frac{p''-p'}{k''-k'}(k - k')$

<u>Step 4.</u> D_π, the π bond energy is computed as before ($D_\pi = -E_\pi$).

62) $D_\pi = -2\beta - \frac{1}{2}\left[(11,11) - (11,22)\right]$

<u>Step 5.</u> Finally the bond energy is found.

63) $D = D_\sigma + D_\pi$

In addition, it was found that triple bonds could be included in the scheme of the thermocycle by extending it to bond lengths shorter than r". It is assumed that p and

β bear the same relationship to r in triple bonds as in the case of double bonds, the term E in the thermocycle being the only one changed. Rehybridization energy is included by taking into account the fact that the values of (11,11) for sp and sp^2 hybrids are not necessarily the same. Also taken into account is the fact that two π bonds are formed instead of one.

The expression for D_π is derived as follows. First, it is assumed that the bonds are totally independent of one another. The electronic energy is then twice that of one π bond.

64) $$E_{electronic} = 2\,(2E_{bonding\ orbital} - J_{11})$$

The core repulsion is computed again as (11,22), so that

65) $$E_{total} = 4E_{bonding\ orbital} - 2J_{11} + (11,22)$$

From this must be subtracted the energy of four isolated p electrons in the two atoms.

66) $$E_{\pi,\ triple\ bond} = 4E_{bonding\ orbital} - 2J_{11} + (11,22) - 4W$$

As before,

67) $$E_{\text{bonding orbital}} = W + \tfrac{1}{2}(11,11) - \tfrac{1}{2}(11,22) + \beta$$

68) $J_{11} = \frac{1}{2}$ (11,11)+(11,22), where (11,11) is now found from the ionization potential and electron affinity of the $\text{didi}\pi\pi$ valence state.

From (66), (67), (68)

69)
$$E_{\pi,\text{ triple bond}} = 4\left\{W + \tfrac{1}{2}\left[(11,11) - (11,22)\right] + \beta\right\}$$
$$-2(\tfrac{1}{2})\left[(11,11) + (11,22)\right] + (11,22) - 4W$$

70) $$= 4\beta + (11,11) - 2(11,22)$$

In terms of a triple bond dissociation energy,

71) $$D = D_\sigma + D_\pi = D_\sigma - 4\beta - (11,11) + 2(11,22)$$

A computer program was devised to calculate bond properties for double bonds and triple bonds by this set of approximations. This program tabulated bond properties for successive incremented values of bond length at the rate of twenty bond lengths per second when run on an IBM 360/50. Initially, tables of bond properties were computed for C-C, C-O, C-N and N-N bonds for testing.

TESTING THE THERMOCYCLE METHOD

The first test of the thermocycle that will be discussed is the heat of atomization and bond order of graphite. The reported bond length is 1.4210±.0001 Å., and the bond order, fixed by theory is 1.525.[31] The thermocycle method yields a bond energy of 111.84 Kcal/mole, and a bond order of 1.526. Graphite sheets have each carbon atom connected to three others, for a total of 3/2 bonds per atom. The heat of atomization of a graphite sheet is then 167.67 Kcal/mole. Graphite consists of layers of these sheets, separated by 3.35Å.. The interlayer binding energy has been calculated to be 3.99 Kcal/mole.[32] This gives for the heat of atomization of solid graphite an estimate of 171.66 Kcal/mole, in excellent agreement with experiment (170.91 Kcal/mole).

The next test that the thermocycle was put to was the calculation of the heat of atomization of benzene. For r=1.397Å., the C-C bond energy is calculated to be 5.07397 e.v. (117.016 Kcal/mole). To the energy of six C-C bonds must be added the energy of six C-H bonds. The value for the C-H bond energy used by Dewar is 4.4375 e.v.,

31. C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London), A65, 815 (1952)
32. P. J. Durant and B. Durant, "Introduction to Advanced Inorganic Chemistry", London, 1962, p591

This value was apparently chosen to give the best over-all fit with experimental data for various aromatic hydrocarbons. Adding up these bond energies gives, for the heat of atomization of benzene 57.07 e.v.. The experimental value is 57.16 e.v.. This encouraging result was modified by integrating into the method the C-H bond energies. The error in the benzene heat of atomization was set equal to zero, the C-H bond energy being adjusted accordingly (the value used for benzene, and all aromatic hydrocarbons is 4.4527 e.v.). Also integrated into the method was an empirical bond energy-bond length relation, a version of one developed by McKelvie:[33]

72) $$Er^3 = \text{constant}$$

This relation was used only for bonds to hydrogen, and was employed in the following way. Using a standard bond energy and bond length (4.4527 e.v. and 1.084Å. in the case of C-H bonds), the constant in (72) is calculated. For different bond lengths, the bond energy is given by the constant divided by the cube of the bond length.

For purposes of testing the thermocycle, the Dewar value for the N-H bond energy (N is sp^2), 93.2 Kcal/mole

33. N. McKelvie, private communication

or 4.042 e.v.[21d] was adopted unchanged. A similar procedure will be used for P-H bonds, where there is no experimental value (sp^2 hybrid phosphorus).

It will be noted that this procedure for calculation of energies of bonds to hydrogen has the effect of partially compensating for systematic errors in the thermocycle. In the next table are presented predicted heats of atomization of various compounds, together with experimental values for comparison.[34]

21d. Michael J. S. Dewar and Toshifumi Morita, J. Am. Chem. Soc., 91, 796 (1969)

34. Experimental values used were those used by Dewar in references 21c and 21d.

TABLE 3

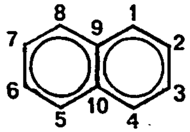
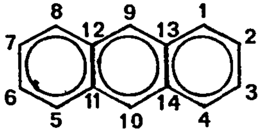
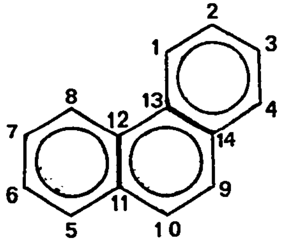
COMPOUND	BOND	BOND LENGTH EXP., Å.	CALCD. BOND ORDER	CALCD. BOND ENERGY e.v.	SUM OF. CALCD. BOND ENERGIES INCL. C-H e.v.	EXP. HEAT OF ATOMIZ. e.v.	ERROR
benzene	C1-C2	1.397	1.6521	5.0740			
					57.16	57.16	
napthalene	C1-C2	1.363	1.8458	5.3680			
	C2-C3	1.415	1.5568	4.9067			
	C1-C9	1.421	1.5261	4.8495			
	C9-C10	1.418	1.5414	4.8782			
					91.18	90.61	-.40 e.v. (.47%)
anthracene	C1-C2	1.366	1.8280	5.3433			
	C2-C3	1.419	1.5362	4.8686			
	C1-C13	1.434	1.4613	4.7233			
	C13-C14	1.428	1.4909	4.7819			
	C9-C13	1.399	1.6413	5.0557			
					124.32	123.93	.39 e.v. (.31%)
phenanthrene	C1-C2	1.373	1.7869	5.2848			
	C2-C3	1.406	1.6039	4.9912			
	C3-C4	1.373	1.7869	5.2848			
	C1-C13	1.409	1.6039	4.9912			
	C4-C14	1.411	1.5776	4.9445			
	C9-C10	1.352	1.9124	5.4552			
	C9-C14	1.444	1.4131	4.6246			
	C13-C14	1.394	1.6685	5.1011			
	C12-C13	1.445	1.4083	4.6146			
					123.80	124.20	.40 e.v. (.32%)

TABLE 3, cont.

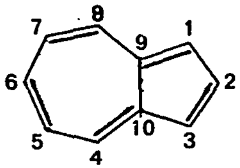
COMPOUND	BOND	BOND LENGTH EXP., Å.	CALCD. BOND ORDER	CALCD. BOND ENERGY e.v.	SUM OF CALCD. BOND ENERGIES INCL. C-H e.v.	EXP. HEAT OF ATOMIZ. e.v.	ERROR
azulene	C1-C2	1.391	1.6850	5.1281			
	C1-C9	1.413	1.5671	4.9256			
	C4-C5	1.401	1.6305	5.0374			
	C5-C6	1.385	1.7184	5.1813			
	C8-C9	1.383	1.7297	5.1989			
	C9-C10	1.483	1.2379	4.2281			
					90.79	89.19	1.60 e.v.(1.8%)
butadiene C=C-C=C	C1-C2	1.344	1.9621	5.5160			
	C2-C3	1.468	1.3029	4.3823			
					42.13	42.05	.08 e.v. (.19%)
Acetylene	C-C	1.205	2.995	9.3641			
	C-H	1.056		4.8164			
C≡C					19.00	16.93	2.07 e.v.(12.%)
carbon monoxide C≡O	C-O	1.1284	3.0279	18.4752	18.48	11.11	7.37 e.v.(66.%)
hydrogen cyanide	C-N	1.158	3.1300	11.9001			
	C-H	1.059		4.7755			
H-C≡N					16.68	14.65	2.03 e.v.(14.%)
nitrogen N≡N	N-N	1.095	3.0000	9.5688	9.57	9.79	-.22 (2.2%)

TABLE 3, cont.

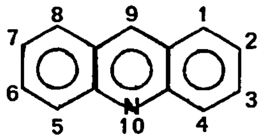
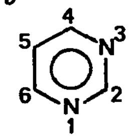
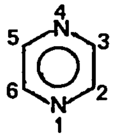
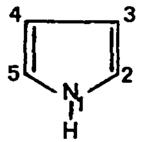
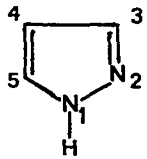
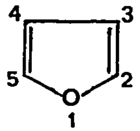
COMPOUND	BOND	BOND LENGTH EXP., Å.	CALCD. BOND ORDER	CALCD. BOND ENERGY e.v.	SUM OF CALCD. BOND ENERGIES INCL. C-H e.v.	EXP. HEAT OF ATOMIZ. e.v.	ERROR
pyridine	N1-C2	1.340	1.5540	4.0966			
	C2-C3	1.395	1.6630	5.0921			
	C3-C4	1.395	1.6630	5.0921			
					50.83	51.79	-.96 e.v.(1.8%)
acridine	C1-C2	1.360	1.8638	5.3920			
	C1-C13	1.429	1.4859	4.7722			
	C2-C3	1.428	1.4909	4.7819			
	C3-C4	1.359	1.8698	5.4001			
	C4-C14	1.434	1.4613	4.7234			
	N10-C11	1.348	1.5118	3.9860			
	C11-C12	1.434	1.4613	4.7234			
	C9-C12	1.398	1.6467	5.0649			
					119.76	118.64	1.12 e.v.(1.1%)
pyrimidine	N1-C2	1.335	1.5811	4.1668			
	N3-C4	1.355	1.4762	3.8911			
	C4-C5	1.395	1.6630	5.0921			
					44.11	46.99	-2.88 e.v.(6.1%)
pyrazine	N1-C2	1.334	1.5866	4.1810			
	C2-C3	1.388	1.7017	5.1548			
					44.84	46.44	-1.60 e.v.(3.4%)

TABLE 3, cont.

COMPOUND	BOND	BOND LENGTH EXP., Å.	CALCD. BOND ORDER	CALCD. BOND ENERGY e.v.	SUM OF CALCD. BOND ENERGIES INCL. C-H e.v.	EXP. HEAT OF ATOMIZ. e.v.	ERROR
pyrrole	N1-C2	1.383	1.3449	3.5272			
	C2-C3	1.371	1.7886	5.3017			
	C3-C4	1.429	1.4859	4.7722			
	N1-H			4.042			
					44.28	44.77	-.49 e.v.(1.1%)
pyrazole	N1-N2	1.361	1.3501	2.3273			
	N2-C3	1.314	1.7025	4.4725			
	C3-C4	1.414	1.5620	4.9161			
	C4-C5	1.335	2.019	5.5814			
	N1-C5	1.346	1.5222	4.0134			
	N1-H			4.042			
					38.71	39.26	-.55 e.v.(1.4%)
Furan	O1-C2	1.371	1.1992	3.8446			
	C2-C3	1.354	1.9001	5.4397			
	C3-C4	1.440	1.4322	4.6643			
					41.04	41.52	-.48 e.v.(1.2%)

The thermocycle is seen to give reasonable estimates of bond energies of double bonds. The results for triple bonds are very poor, perhaps singly as a consequence of their being essentially extrapolations from double bonds, thus compounding the felony of oversimplification without the redeeming quality of calibration. The thermocycle can be characterized as a poor theory for calculation of bond energies that nevertheless gives reasonable results as long as the bond is intermediate between the calibrated single and double bonds. Aside from an inadequate treatment of triple bonds the main failure of the method are the neglect of molecular geometry and bond polarity, i.e. strain energy and both σ and π bond polarization when they depart from the standard bond. It will be noticed that errors are larger for heterocycles than for pure carbocycles. Presumably this is due at least in part to bond polarity. Also, the relatively poor calibration of C=N bonds may contribute to the error.

Fortunately, C-P bonds may be safely predicted to be essentially non-polar, so that the bond energies of C-P bonds predicted by the thermocycle method should be fairly good (subject to separate verification).

SECTION 2

MODELS FOR CARBON TO PHOSPHORUS DOUBLE BONDS

CNDO Calculations:

The compounds $CH_2{=\!=}PH$ and $CH_2{=\!=}P\text{-}CH_3$ represent the simplest and most convenient models for the study of the carbon to phosphorus double bond. The CNDO molecular orbital method of Pople, Santry and Segal[35a,b,c,d] was the tool of choice for the following reasons.

First, it is a molecular orbital method sophisticated enough to take into account such features as d orbitals and a lone pair of electrons.

Second, the CNDO method has already been modified to include d orbitals, and has been calibrated in terms of spectral data of second row atoms, as opposed to calibration to fit experimental data of singly bonded compounds.

35a. J. A. Pople, D. P. Santry and G. A. Segal, J. Chem. Phys, 43, S 129 (1965)

35b. J. A. Pople and G. A. Segal, J. Chem. Phys, 43, S 136 (1965)

35c,d. Adaptation for Second row elements: D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967); D. P. Santry, J. Am. Chem. Soc., 90, 3309 (1968)

All of the electronic properties of doubly bonded compounds cannot necessarily be inferred from the properties of singly bonded compounds. Therefore, in any empirical calculation of molecular properties that is less than exact, if parameters are adjusted so that the method gives good results for one class of compounds, there is no guarantee that it will work nearly as well for another class of compounds. The more democratic calculation via atomic spectral parameters is preferable in the absence of experimental data for the particular class of compound under investigation. One may then take some comfort in the fact that the particular parameters used for calculations on an unknown class of compounds have been successful in predicting known properties of known compounds containing the same atoms.

Third, the inclusion of d orbitals in calculations on phosphorus containing molecules is essential, as d orbitals turn out to be heavily involved in bonding.

It may be noted here that explicit inclusion of d orbitals is necessary only when the parameters required for the calculation are not obtained from experimental data for the class of molecules under investigation.

For calculation of certain molecular parameters, even this requirement may be relaxed. For example, CNDO calculations without d orbitals successfully predict the shapes of such molecules as PCl_5, ClF_3 and SF_4.[35c] For prediction of bond orders, charge densities and energy levels however, d orbitals should be included.

If on the other hand, the calculations are calibrated to fit molecular experimental data, d orbitals may be safely excluded, provided one does not extrapolate too far beyond the range of calibration, and provided one verifies each predicted property independently.

A fourth reason for adoption of the CNDO method is that it is not so large a calculation that it cannot be used for anything except very small molecules. In fact it was used for calculation on the molecule fluorenylidenemethylphosphine, a model used for investigation of the interaction of the phosphorus atom with the fluorenylidene group. Only a direct calculation on fluorenylidenefluorenylphosphine, the particular compound under study, would have been preferable.

35c. D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967)

In calculations where most of the computing time is taken up in diagonalizing large square matrices, the computing time increases with the cube of the size of the matrices, i. e. the number of orbitals. The CNDO calculation for fluorenylidene methyl phosphine required 90 minutes on the 360/50 computer, using the entire core available for problem solving, which was only permitted by the City College Computer Center by special arrangement. The calculation for fluorenylidene fluorenyl phosphine would have had a running time that was entirely prohibitive (450 minutes not including the very large time losses incurred in overlay techniques made necessary by inability to fit the entire calculation into the computor storage at once). Fluorenylidene methyl phosphine was considered to be an adequate model for fluorenylidene fluorenyl phosphine, as the fluorenyl group's π structure is insulated from the π structure of the fluorenylidene-phosphorus moiety.

The CNDO method gives values for bond angles and dipole moments that are in good agreement with experiment. It may be expected therefore that the eigenvectors, charge densities and bond orders are reasonably accurate.

The ionization potential predictions are quantitatively poor, though qualitatively useful in predicting trends, so it may therefore be assumed that energy levels, in particular the energy levels of the highest occupied orbitals are qualitatively correctly positioned, although exact energies are beyond the scope of the method. This also implies that quantitative predictions concerning electronic spectra cannot be made accurately.

One exception to the accurate ordering of energy levels that has frequently been noted in the results of CNDO calculations is the particularly low energy of σ^* orbitals. Accordingly, no attempt was made to gain useful information from the position of this type of orbital.

Still another failure of the CNDO method is the inaccuracy of bond lengths predicted by minimizing the binding energy with respect to the nuclear coordinates. This may be due to the fact that the electronic energy varies very slowly with bond distance in this type of calculation. Bond lengths calculated via the CNDO method must be therefore used with great caution. If bond lengths calculated by the CNDO method are used as a basis for CNDO calculations on analogous compounds however, the effects of the improper bond length on other properties will tend to cancel out. It will be shown by direct comparison that the effect of bond length on bond order and charge density is not drastic for the type of compound under study.

$CH_2{=}PH$ and $CH_2{=}P\text{-}CH_3$

Methylidene phosphine and methylidene methyl phosphine were studied via CNDO. The carbon to phosphorus double bond distance, the carbon to phosphorus single bond distance and the angle between the bonds to phosphorus were varied in the calculations, the other distances and angles being assigned the appropriate values as follows.

H-C(sp^2) distance = 1.086Å.
H-C(sp^3) distance = 1.093Å.
H-C(sp^2)-H angle = 121.3 deg.
the methyl carbon is tetrahedral

The molecules were oriented in such a way with respect to the cartesian coordinates that only one of the d orbitals of the set d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2} could be used for π bonding to carbon.

The results are given in tables Four and Five, and in figures Two through Eleven.

TABLE 4

CNDO Calculations for $CH_2=PH$

C=P dist. Å.	C-P-H angle deg.	P-H dist. Å.	eigenvalues: π orbital	eigenvalues: lone pair*	bond order: 2p-3p	bond order: $2p\text{-}3d_{xz}$	electron density: on C	electron density: on P	total binding energy A. U.
1.677	102.96	1.395	-.4966	-.4884	.8372	.5363	4.2123	4.8163	-1.27820
1.677	102.96	1.400	-.4967	-.4883	.8372	.5363	4.2123	4.8160	-1.27921
1.677	102.96	1.405	-.4968	-.4882	.8372	.5363	4.2124	4.8157	-1.28016
1.677	102.96	1.410	-.4969	-.4882	.8372	.5363	4.2124	4.8154	-1.28107
1.677	102.96	1.415	-.4970	-.4881	.8372	.5363	4.2124	4.8152	-1.28192
1.677	102.96	1.420	-.4971	-.4880	.8372	.5363	4.2124	4.8149	-1.28273
1.677	102.96	1.425	-.4971	-.4878	.8372	.5363	4.2125	4.8146	-1.28350
1.677	102.96	1.430	-.4972	-.4877	.8372	.5363	4.2125	4.8143	-1.28421
1.677	102.96	1.435	-.4973	-.4876	.8372	.5363	4.2125	4.8140	-1.28489
1.677	102.96	1.440	-.4974	-.4875	.8372	.5363	4.2125	4.8138	-1.28551
1.675				does not converge					
1.67	95	1.425	-.4991	-.4946	.8381	.5365	4.2039	4.8143	-1.28179
1.67	95	1.420	-.4990	-.4948	.8380	.5365	4.2038	4.8146	-1.28102
1.67	95	1.415	-.4989	-.4949	.8380	.5365	4.2038	4.8149	-1.28021
1.67	95	1.410	-.4989	-.4951	.8380	.5365	4.2038	4.8152	-1.27936
1.67	95	1.405	-.4988	-.4952	.8380	.5365	4.2037	4.8155	-1.27845
1.67	95	1.400	-.4987	-.4953	.8380	.5365	4.2037	4.8158	-1.27750
1.67	120	1.420	-.4988	-.4700	.8319	.5411	4.2269	4.8159	-1.27504
1.67	100	1.420	-.4992	-.4903	.8366	.5377	4.2101	4.8146	-1.28239
1.67	100	1.415	-.4991	-.4905	.8366	.5377	4.2101	4.8149	-1.28158

* note: the orbital designated as "lone pair" is that orbital in which most of the non-bonding pair electron density resides. The lone pair is not localized in CNDO.

TABLE 4, cont.

CNDO Calculations for CH_2=PH

C=P dist. Å.	C-P-H angle deg.	P-H dist. Å.	eigenvalues		bond order		electron density		total binding energy A. U.
			π orbital	lone pair	2p-3p	$2p-3d_{xz}$	on C	on P	
1.67	100	1.410	-.4990	-.4906	.8365	.5377	4.2101	4.8152	-1.28073
1.67	100	1.405	-.4989	-.4907	.8365	.5377	4.2101	4.8155	-1.27982
1.67	100	1.400	-.4988	-.4908	.8365	.5377	4.2100	4.8158	-1.27887
1.67	100	1.395	-.4987	-.4908	.8365	.5377	4.2100	4.8161	-1.27786
1.67	120	1.415	-.4997	-.4701	.8319	.5411	4.2268	4.8161	-1.27422
1.67	120	1.410	-.4996	-.4701	.8319	.5411	4.2268	4.8164	-1.27335
1.67	120	1.405	-.4995	-.4702	.8318	.5411	4.2268	4.8167	-1.27244
1.67	120	1.400	-.4994	-.4702	.8318	.5411	4.2268	4.8170	-1.27147
1.65	120	1.414	-.5059	-.4688	.8278	.5465	4.2294	4.8172	-1.27298
1.66	120	1.414	-.5028	-.4694	.8298	.5438	4.2281	4.8167	-1.27369
1.67	120	1.414	-.4997	-.4701	.8319	.5411	4.2268	4.8162	-1.27405
1.68	120	1.414	-.4966	-.4707	.8340	.5383	4.2255	4.8158	-1.27408
1.69	120	1.414	-.4935	-.4713	.8363	.5352	4.2239	4.8157	-1.27379
1.55	120	1.414	-.5386	-.4610	.8102	.5689	4.2400	4.8262	-1.24428

TABLE 5

CNDO Calculations for CH_2=P-CH_3

C=P dist. Å.	C-P-C angle deg.	P-C dist. Å.	eigenvalues: π orbital	eigenvalues: lone pair	bond order: 2p-3p	bond order: $2p-3d_{xz}$	electron density: on Csp^2	electron density: on P	total binding energy A. U.
1.677	100	1.80	-.4712	-.4732	.8059	.5669	4.2168	4.8921	-2.53115
1.677	110	1.80	-.4731	-.4591	.8051	.5688	4.2250	4.9071	-2.53726
1.677	120	1.80	-.4742	-.4458	.8060	.5689	4.2299	4.9188	-2.53644
1.677	130	1.80	-.4748	-.4432	.8086	.5669	4.2327	4.9259	-2.52963
1.677	140	1.80	-.4752	-.4210	.8128	.5634	4.2353	4.9258	-2.51792
1.677	115	1.77	-.4714	-.4506	.8026	.5718	4.2287	4.9209	-2.53596
1.677	115	1.78	-.4722	-.4512	.8035	.5709	4.2285	4.9183	-2.53677
1.677	115	1.79	-.4730	-.4518	.8044	.5701	4.2283	4.9157	-2.53733
1.677	115	1.80	-.4738	-.4523	.8052	.5692	4.2280	4.9132	-2.53766
1.677	115	1.81	-.4745	-.4529	.8061	.5684	4.2278	4.9108	-2.53777
1.677	115	1.82	-.4753	-.4534	.8069	.5676	4.2276	4.9084	-2.53766
1.677	115	1.83	-.4760	-.4539	.8077	.5668	4.2274	4.9060	-2.53734
1.677	115	1.84	-.4768	-.4543	.8085	.5660	4.2271	4.9038	-2.53682
1.677	115	1.85	-.4775	-.4548	.8092	.5652	4.2269	4.9015	-2.53611
1.677	115	1.86	-.4782	-.4552	.8100	.5644	4.2267	4.8993	-2.53521
1.677	115	1.87	-.4789	-.4556	.8107	.5637	4.2265	4.8972	-2.53414
1.677	113.8	1.81	-.4744	-.4544	.8060	.5684	4.2273	4.9093	-2.53784

FIGURE 2 $CH_2=PH$

BINDING ENERGY AS A FUNCTION OF C-P-H ANGLE FOR VARIOUS P-H DISTANCES

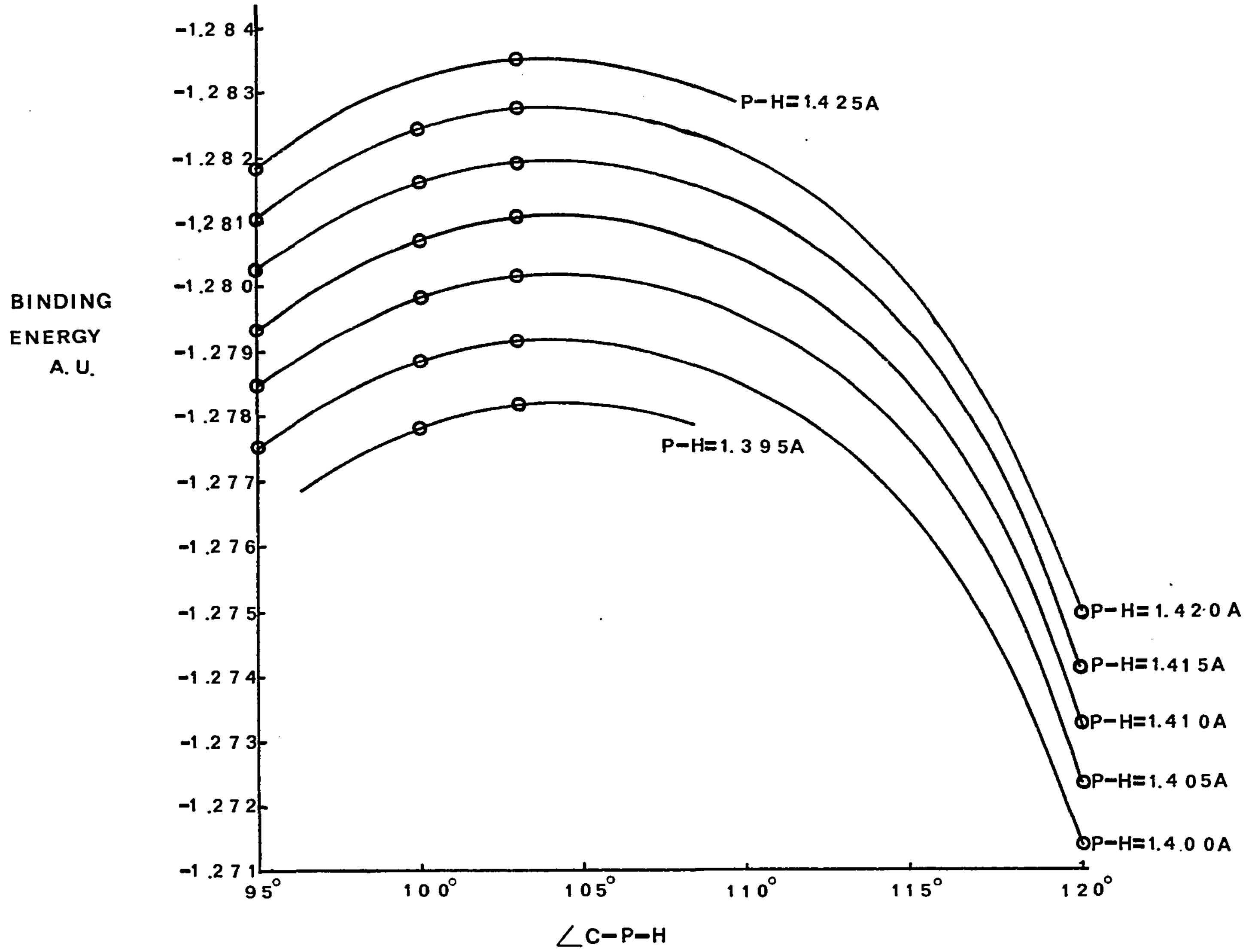
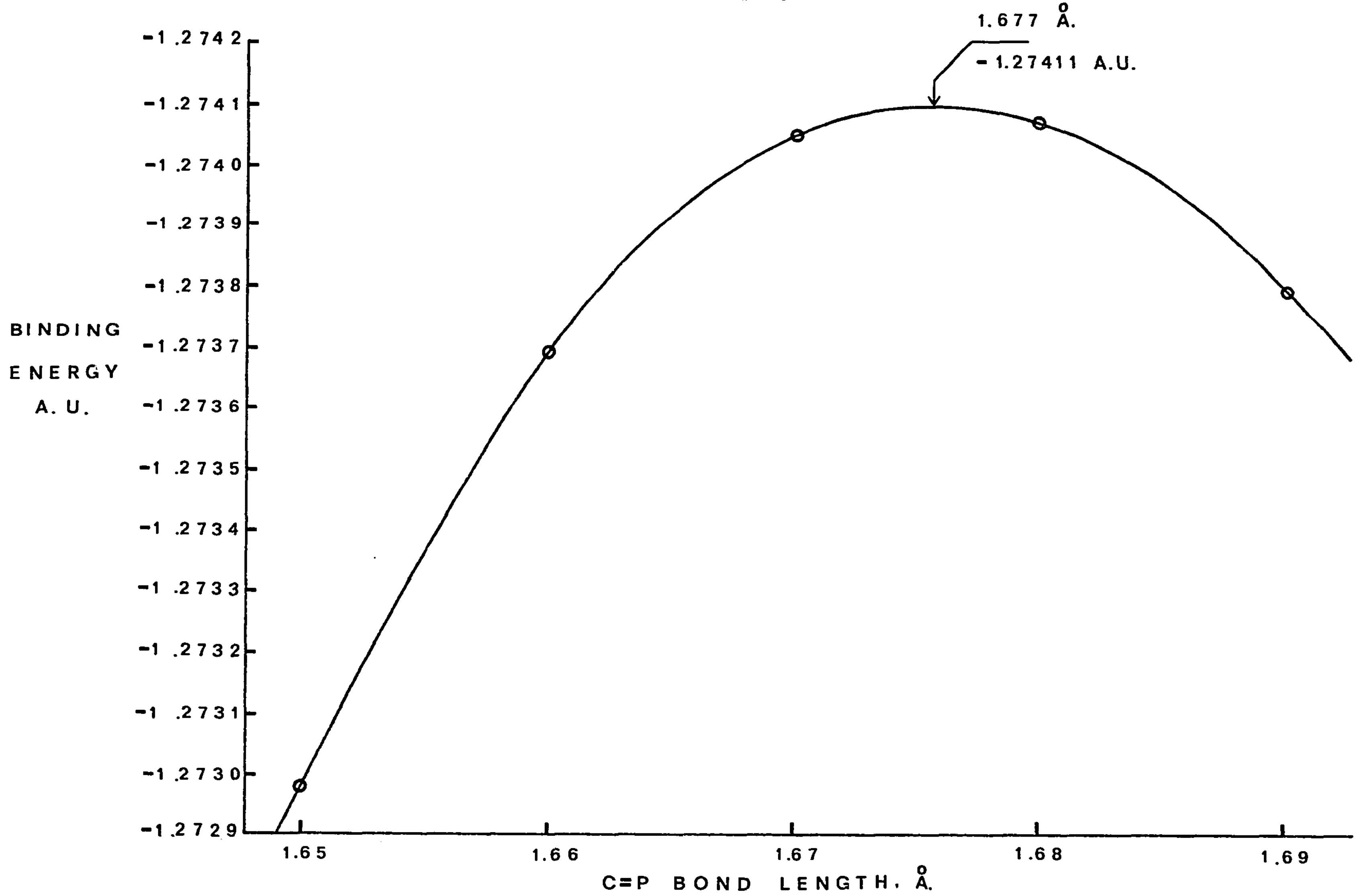


FIGURE 3



BINDING ENERGY OF CH_2=PH AS A FUNCTION OF C=P BOND LENGTH

FIGURE 4

BINDING ENERGY OF CH_2=PH AS A FUNCTION OF P-H BOND LENGTH AT VARIOUS C-P-H BOND ANGLES

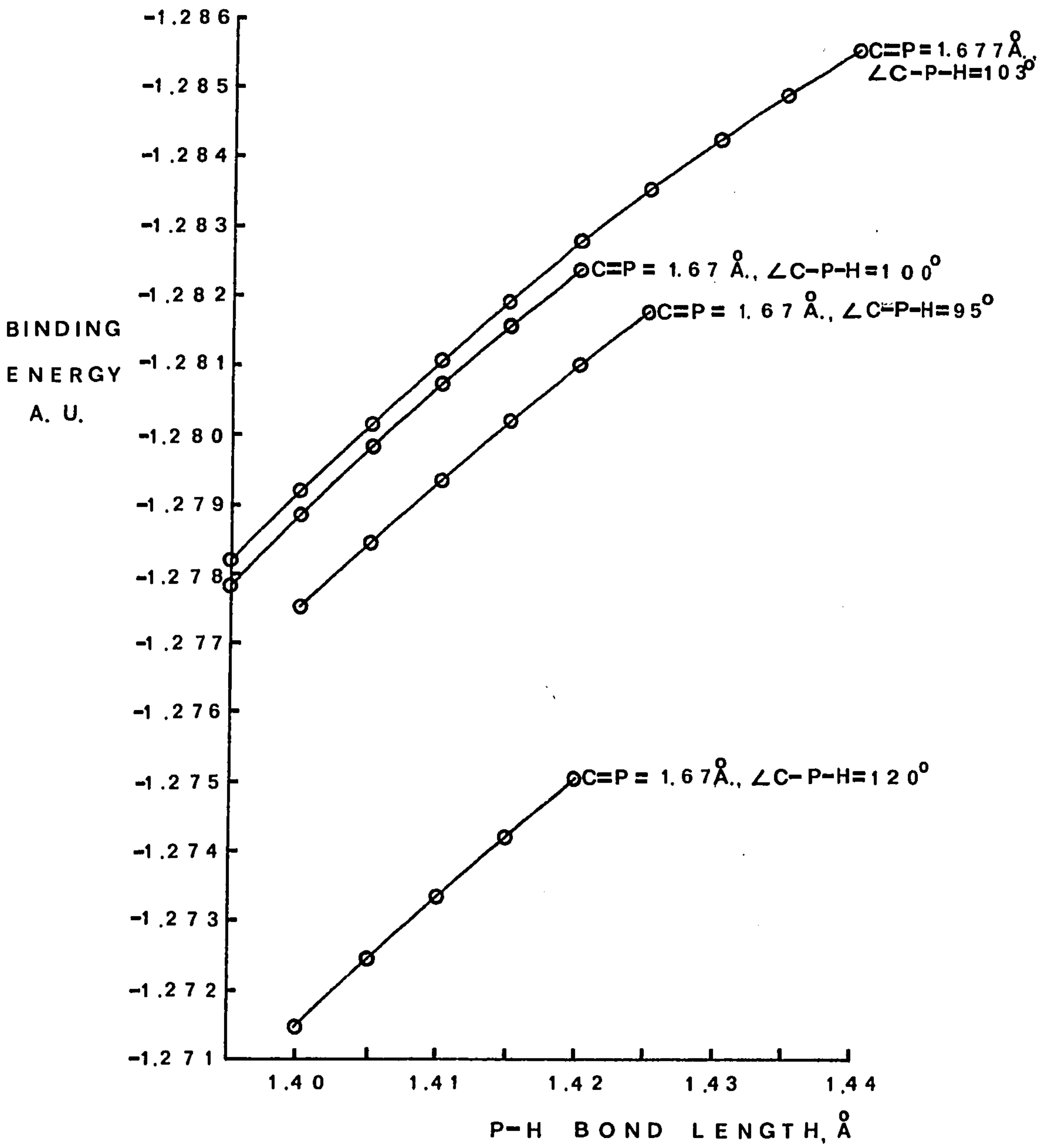


FIGURE 5

C=P π BOND ORDERS AS A FUNCTION OF C=P BOND LENGTH IN CH_2=PH

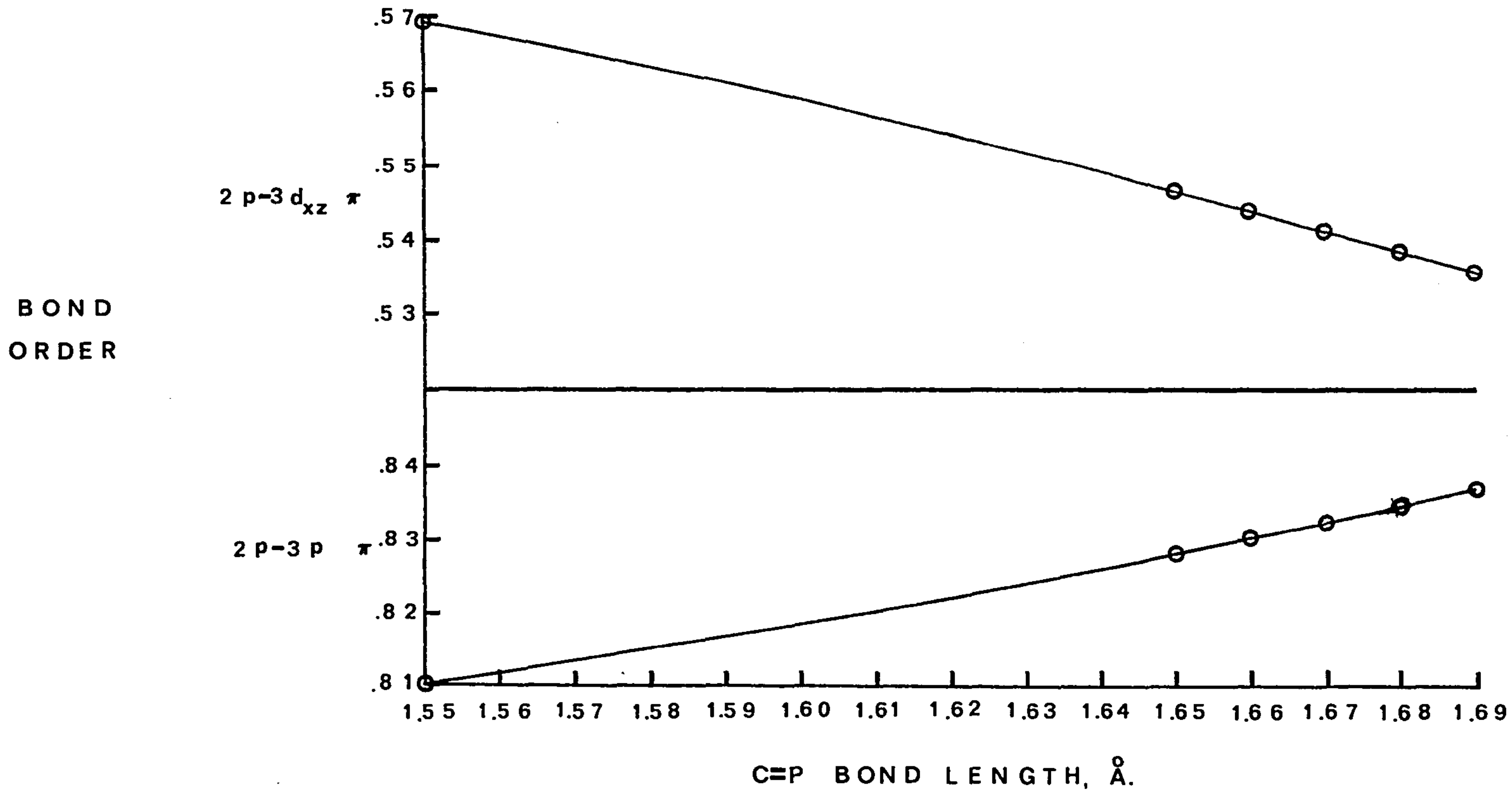


FIGURE 6

EIGENVALUES FOR π BOND AND LONE PAIR ORBITALS AS A FUNCTION OF C=P BOND LENGTH IN CH_2=PH

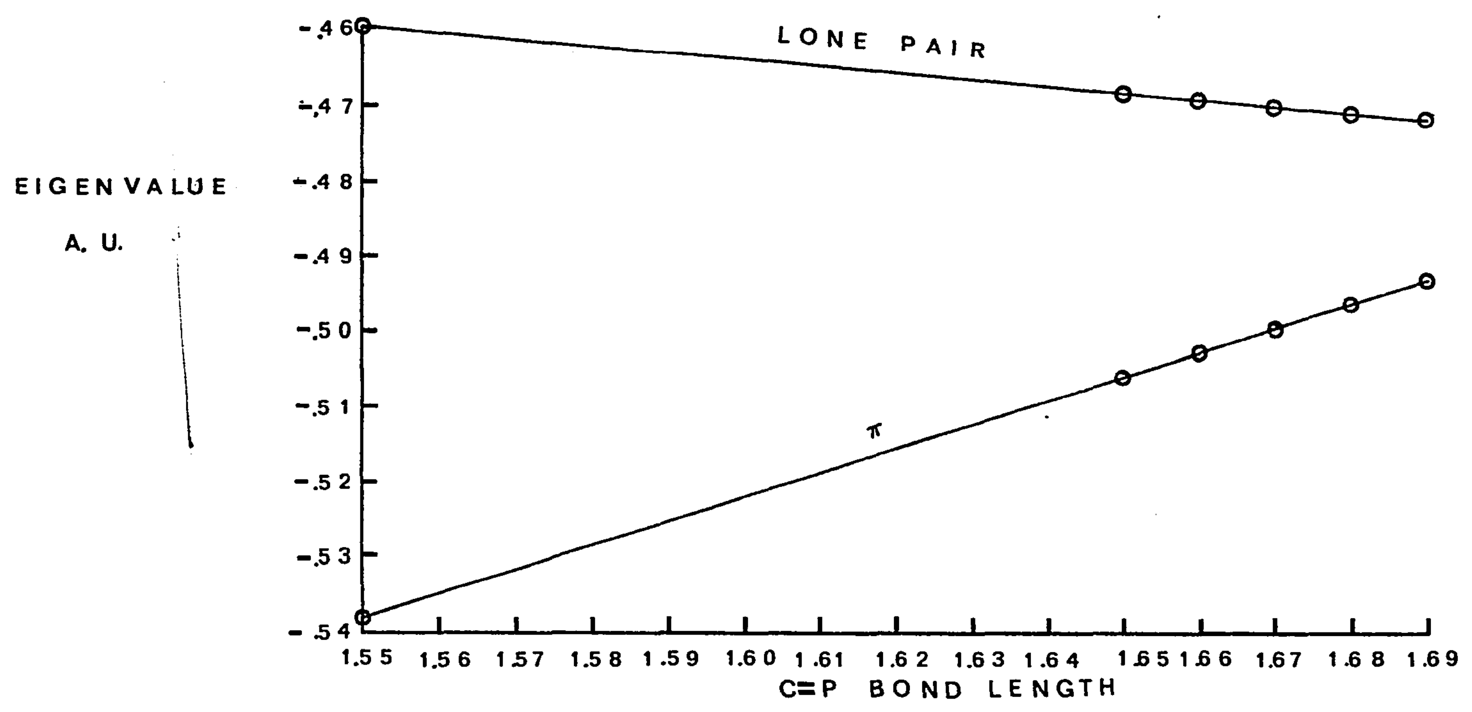


FIGURE 7

ELECTRON DENSITY ON PHOSPHORUS IN CH_2=PH AS A FUNCTION OF P–H BOND LENGTH

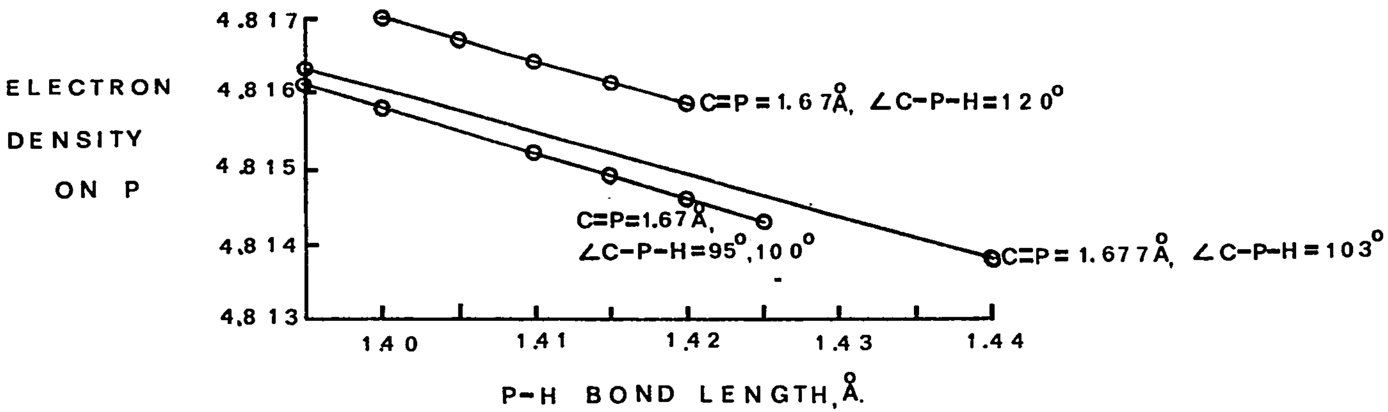


FIGURE 8

ELECTRON DENSITY ON CARBON IN CH_2=PH AS A FUNCTION OF P-H BOND LENGTH

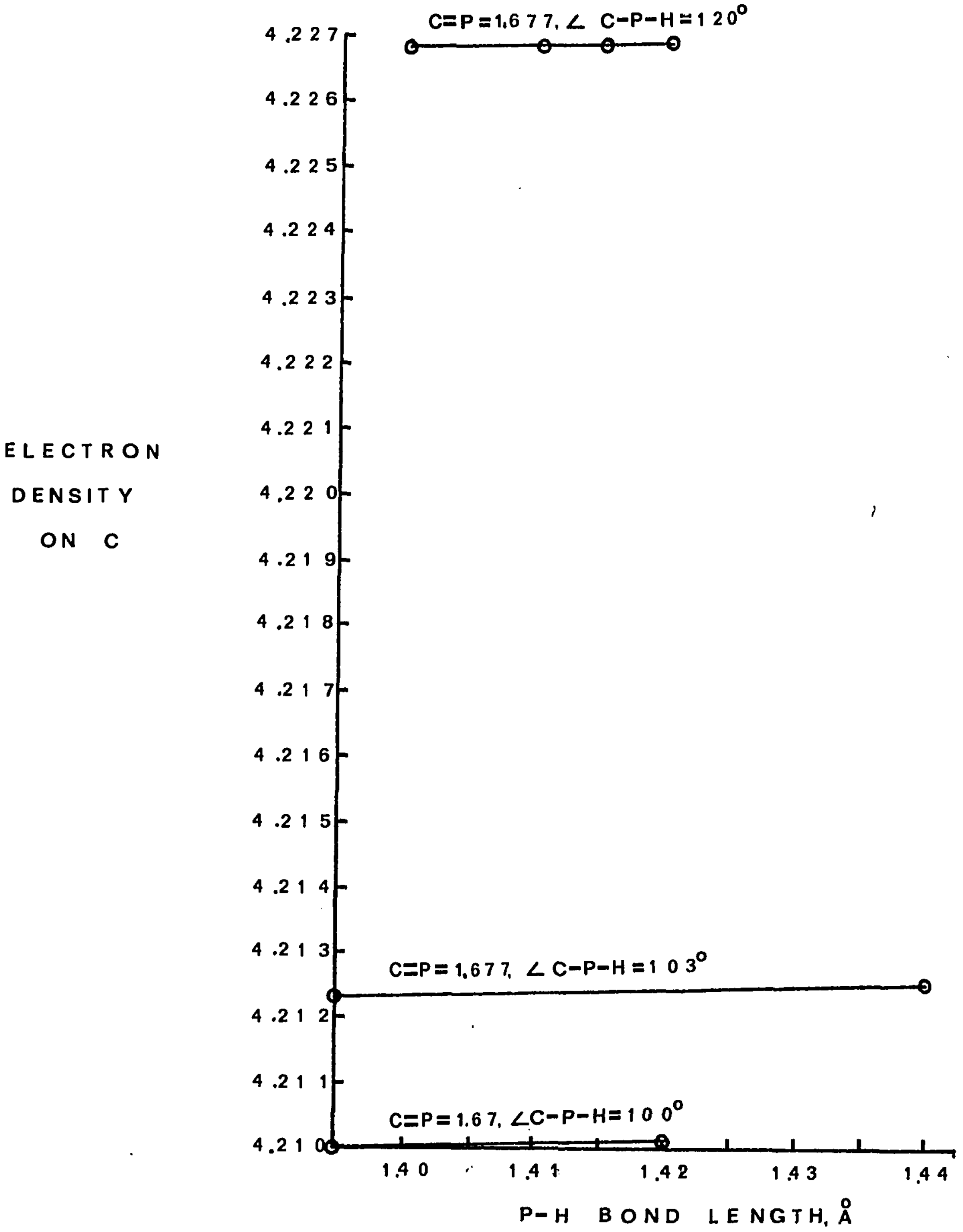


FIGURE 9

BINDING ENERGY OF $CH_2=P-CH_3$ AS A FUNCTION OF C–P–C ANGLE

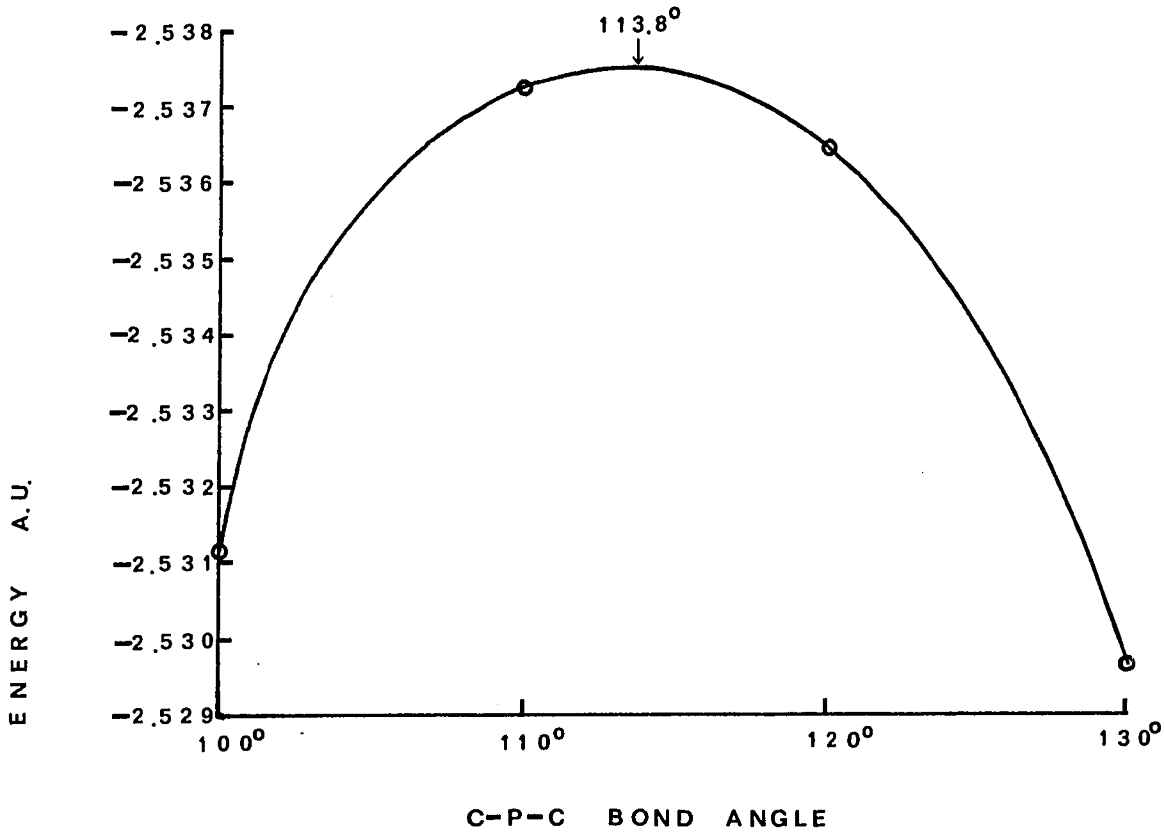


FIGURE 10

UPPERMOST ENERGY LEVELS AND BINDING ENERGY AS A FUNCTION OF C-P SINGLE BOND LENGTH IN $CH_2=P-CH_3$

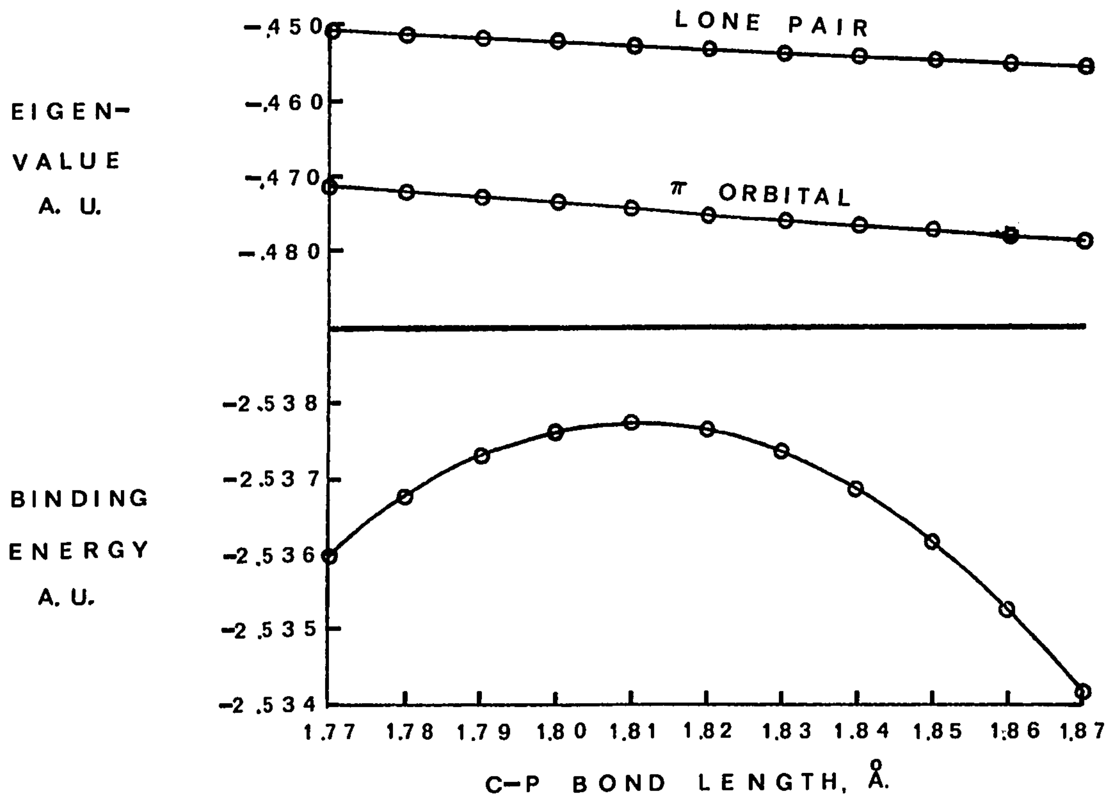
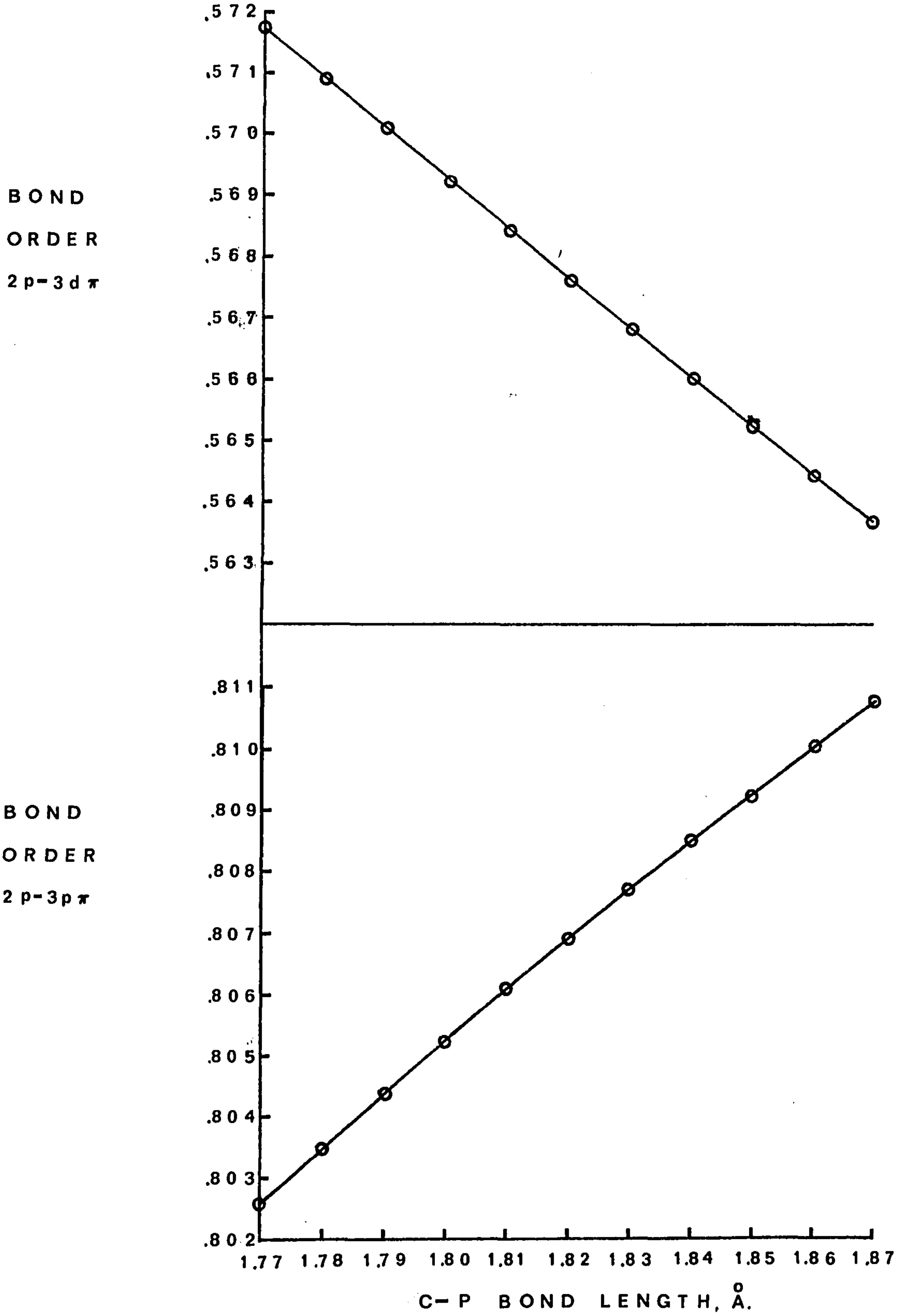


FIGURE 11

π BOND ORDERS IN $CH_2=P-CH_3$ AS A FUNCTION OF P-C SINGLE BOND LENGTH



The conclusions drawn from the CNDO calculations on CH_2=PH and CH_2=P-CH_3 are given below.

1. In CH_2=PH, the C-P-H angle is about 103° (see figure 2).

2. In CH_2=PH, the C-P distance is about 1.677Å. (see figure 3). This agrees well with the sum of the Pauling double bond radii, 1.67Å.

3. CNDO does not yield a reasonable value for the P-H distance in CH_2=PH. The plots of total binding energy vs. P-H distance (figure 4) do not have minima in the desired range of bond lengths. It will be necessary to assume a P-H bond length in order to estimate the C=P bond energy for this molecule.

4. The d orbitals of phosphorus make important contributions to the occupied π orbitals. The 2p-3dπ bond order is appreciable.

5. In both compounds, the eigenvalues of the wavefunctions that represent the lone pair on phosphorus and the π orbital are similar (figure 6 and 10).

6. In CH_2=PH, the total electron density on carbon is affected by the C-P-H bond angle, but not appreciably by the P-H bond length, while the electron density on phosphorus is effected by both the C-P-H bond angle and the P-H bond length (figure 7 and 8). This is in line with chemical intuition.

7. In CH_2=P-CH_3, the energy is a minimum for a (sp^2)P-C(sp^3) distance of 1.810Å. (figure 10). This is again reasonable, being slightly shorter than the C-P distance of 1.841Å. in the analogous saturated compound, trimethyl phosphine.

8. In CH_2=P-CH_3 the C-P-C bond angle is about 113.8 degrees (figure 9).

That the conclusions drawn solely from the CNDO calculations are reasonable results (with the exception of the P-H bond length in CH_2=PH) is an indication that the CNDO method is applicable to π bonded phosphorus compounds.

While CH_2=PH and CH_2=P-CH_3 are compounds of interest as models, they are not known species. In order to compare CNDO results with experiment, one must go further afield. Four compounds for which data are accurately known are HCP, CP radical, $MePH_2$ and Me_3P. While the last two are not π bonded species, single bond properties are also of use in interpreting CNDO results. The available experimental data are summarized in Table 6.

TABLE 6

	HCP	$CP(X^2\Sigma_g^+)$	$MePH_2$	Me_3P
bond distance H-C Å.	1.0667[6]		1.093[39]	----
bond distance C-P Å.	1.5421[6]	1.562[1]	1.863[39]	1.841[41]
bond distance P-H Å.			1.414[39]	
bond angle H-C-H			109°45[39]	----
bond angle C-P-H			97°30[39]	
heat of atomization Kcal/mole	----	159	----	1086.4[42]
heat of formation Kcal/mole	----	----	----	-30.1[42]
force constant C-P mdyne/A.	8.824[36]	7.8317[38]	2.882[40]	----
ionization potential e.v.	13.0±0.6[37]	----	----	----

6. J. K. Tyler, J. Chem. Phys., 40, 1170 (1964)
36. Recalculated from the data of T. E. Gier, J. Am. Chem. Soc., 83, 1769 (1961)
37. Indirect derivation by Yasno Wada and Robert W. Kiser, J. Phys. Chem., 68, 2290 (1964)
1. G. Hertzberg, Spectra of Diatomic Molecules, New York (1955)
38. T. L. Cottrell, Strength of Chemical Bonds, New York (1954)
39. N. Kajima, E. L. Breig, C. C. Lin, J. Chem. Phys., 35, 2139 (1961) (Microwave Spectrum)
40. Joseph A. Lannon and Eugene R. Nixon, Spectrochemical Acta, 23A, 2713 (1967).
41. Tables of Interatomic Distances and configuration in Molecules and Ions., Special Publication #11, The Chem. Soc. (London), (1958)
42. Calc. from heat of combustion (L.H. Long, J. F. Sackman, Trans. Faraday Soc., 53, 1606) and standard heat of formation.

H-C≡P

CNDO calculation on HCP were performed for various C≡P bond lengths, keeping the C-H bond distance equal to the experimental value of 1.0667Å.. The results are summarized in Table 7.

TABLE 7

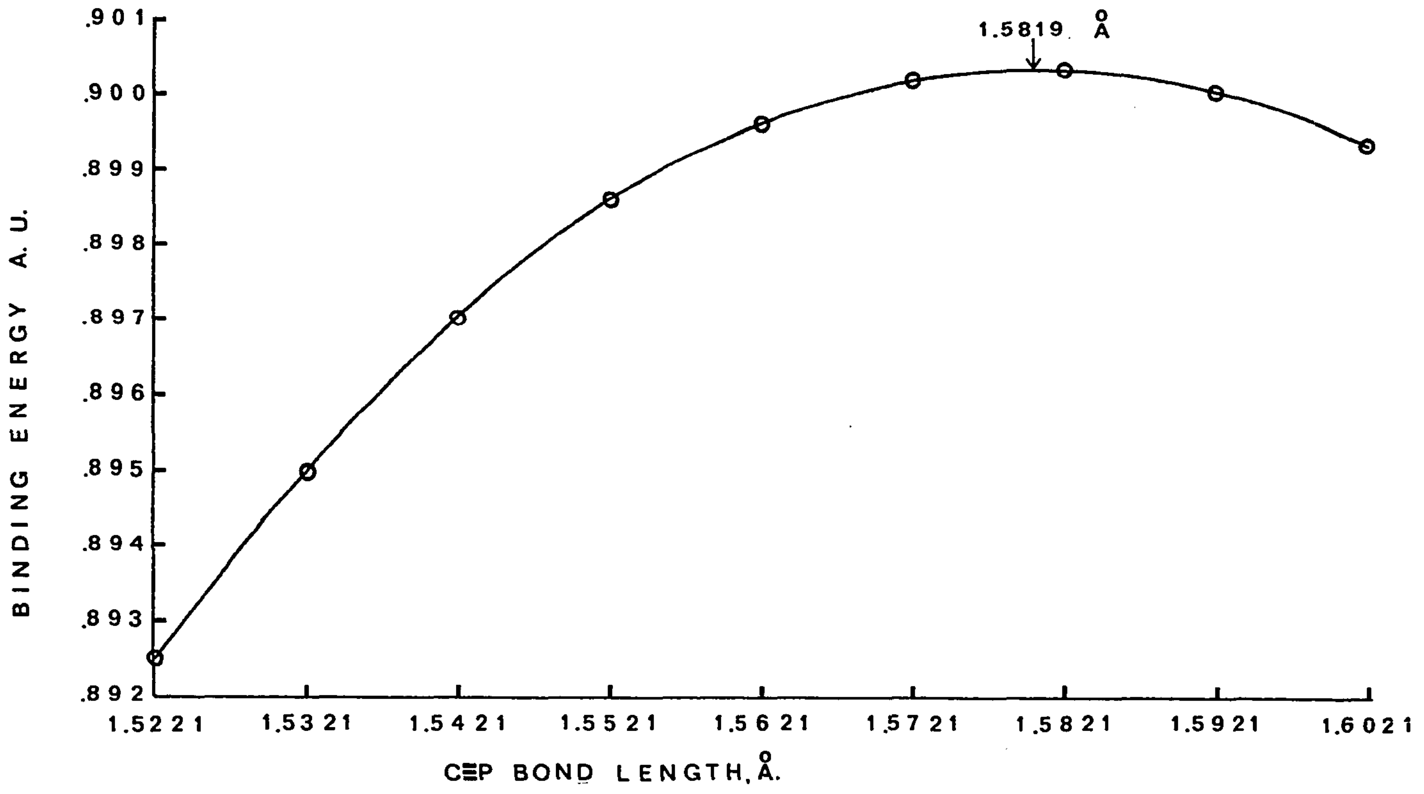
HCP CNDO Calculations

C-P bond length, Å.	Total binding energy, A. U.
1.5221	-.89251
1.5321	-.89505
1.5421	-.89707
1.5521	-.89860
1.5621	-.89965
1.5721	-.90023
1.5821	-.90037
1.5921	-.90008
1.6021	-.89937

These results are plotted in figure12 and are seen to give a minimum in the energy at about 1.582Å., or about .04Å. larger than the experimental value. The predicted heat of atomization at the energy minimum is 280.88 Kcal/mole, or 279.86 Kcal/mole if the experimental C≡P bond length is used. At the experimental bond length, 1.5421Å, the 2p-3p π and 2p-3d π bond orders are 1.6786 and 1.0872 respectively. The sum of the Pauling triple bond radii is 1.53Å.

FIGURE 12

BINDING ENERGY OF HC≡P AS A FUNCTION OF C≡P BOND LENGTH



C-P

A CNDO calculation was performed on ground state ($^2\Sigma_g^+$) CP, using the experimental bond distance of 1.562Å.. The heat of atomization was calculated to be 6.958 e.v., in excellent agreement with experiment (6.9 e.v.). The 2p-3p π bond order was calculated to be 1.6922. The 2p-3d π bond order was calculated to be 1.0648.

CH_3PH_2

A CNDO calculation was performed on methyl phosphine, using experimental bond lengths and bond angles, and yielded a heat of atomization of 527.36 Kcal/mole.

$(CH_3)_3P$

A CNDO calculation was performed on trimethyl phosphine, using experimental bond lengths and bond angles, and yielded a heat of atomization of 1303.14 Kcal/mole.

MINDO Calculations

MINDO calculations were performed for HCP, $MePH_2$ and Me_3P. The MINDO method of Dewar[43a,b] had not been calibrated for phosphorus compounds, but the literature was found to contain values for the parameters required. These are given below.

43a,b. N. C. Baird and M. J. S. Dewar, J. Chem. Phys., 50, 2362 (1969); ibid, 50, 1275 (1969)

TABLE 8

MINDO parameters for phosphorus

core integral s electrons	USS	-50.758 e.v.[44]
core integral p electrons	UPP	-43.362 e.v.[44]
Slater-Condon parameters	F^0	11.149 e.v.[45,46]
	F^2	5.105 e.v.[45,46]
	G^1	6.7744 e.v.[45,46]
atom energy	EISOL	-129.951 e.v.[46]

Values of the adjustable parameters BETA1 and BETA2 of 0.35 and 0.0 respectively yielded agreement of the calculated heat of formation of trimethylphosphine with experiment, but the bond orders and charge densities were far removed from reasonable values, perhaps indicating that some of the program modifications were incorrect. In particular, it may be that there is some requirement of self consistency amongst the parameters in table 8. The value of BETA1 that proved successful in the MINDO calculation for Me_3P was used in the calculation for HCP, a procedure that is liable to some error when BETA2 is set equal to zero. In the absence of experimental energy data for a molecule containing a short carbon to phosphorus bond there is no alternative (CP is excluded because the MINDO method does not handle radicals). Setting BETA2 equal to zero is equivalent to

44. G. Klopman, J. Am. Chem. Soc., 86, 1463, (1964)
45. calculated from data and formulas of Gerald J. Iafrate, J. Chem. Phys., 46, 728 (1967)
46. $EISOL = 2USS + 3UPP - 10F^0 + G^1 + 0.6F^2$
$(ss,ss)=(ss,pp)=F^0$; $(sp,sp)=G^1/3$; $(pp,pp)=F^0 + 4/25\ F^2$
$(pp,p'p')=F^0 - 2/25\ F^2$; $(pp',pp')=3/25\ F^2$

assuming that the resonance integral between two orbitals is proportional to the overlap integral, without an additional term involving an extra dependency on bond distance.

TABLE 9

MINDO calculations

	BETA1	HEAT OF ATOMIZATION, KCAL	HEAT OF FORMATION, KCAL
Me_3P	.16	918.521	138.245
Me_3P	.30	1058.570	-1.804
Me_3P	.35	1086.501	-20.735
Me_3P	.40	1116.735	-59.969
HCP	.35	295.193	-2.979
$MePH_2$	.35	526.692	-20.113

The experimental value for the heat of atomization of trimethyl phosphine, 1086.36±1.1 Kcal/mole[47], is the same as the value calculated when BETA1 for C-P bonds is assigned the value 0.35. This is then the value of BETA1 adopted for calculations on HCP and $MePH_2$. A MINDO calculation was attempted for CH_2=P-CH_3 but did not converge on a solution.

ESTIMATION OF BOND ENERGIES

Heats of atomization as calculated by the CNDO method tend to have positive errors, with larger errors for molecules with larger numbers of atoms, and so only those re-

47. Recalculated from the reported heat of combustion of Me_3P and data in "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-3, Washington, D. C., 1968.

sults for the smallest molecules, i.e. CH_3PH_2, CH_2PH, HCP and CP will be used in calculation of bond energies.

In order to calculate carbon to phosphorus bond energies it is necessary to specify the bond energies of the other bonds in the molecules of interest, which in themselves tend to change with the states of hybridization and bond length. For bonds to hydrogen, a simple expression due to McKelvie[33] was used in the section dealing with a Dewar-type thermocycle, and may be applied here. The expression is

$$\text{(bond energy) (bond distance)}^3 = \text{constant.}$$

The C-H bonds in benzene and the P-H bonds in phosphine were used as standards to calculate the constants for each bond. The lengths and energies for the pertinent bonds are listed in Table 10.

TABLE 10

BOND	BOND LENGTH Angstroms	BOND ENERGY Kcal/mole
(sp^3) C-H	1.093	100.17
(sp^2) C-H	1.086	102.17
(sp) C-H	1.0667	107.89
(sp^3) P-H	1.414	76.91
(sp^2) P-H	1.404 (assumed)	78.57 (assumed)

33. N. McKelvie, private communication.

In the absence of experimental data, the assumption of the (sp^2) phosphorus to hydrogen distance being .01Å. less than that in methylphosphine is perhaps the simplest. A decrease in the bond length by 0.01Å. is predicted to increase the P-H bond energy by less than two Kcal/mole.

The results so far for CNDO and MINDO calculations and the C-P bond energies calculated from them are compared with the experimental values in Table 11.

Various estimates of (E_σ-E_π), the difference between the σ and π bond energies, can be made. It is assumed in estimating this quantity that the σ bond energy is a constant whatever its length or environment.

1. E_σ-E_π =10-18 Kcal/mole: from the bond energy of CP (exp.) and the C-P bond energy in Me_3P (exp.)
2. E_σ-E_π =13 Kcal/mole: from the C-P bond energy in Me_3P (exp.) and the C=P bond energy in CH_2PH (CNDO)
3. E_σ-E_π =29.3 Kcal/mole: from the C-P bond energy in $MePH_2$ (CNDO) and the C=P bond energy in CH_2PH (CNDO)
4. E_σ-E_π =4.3 Kcal/mole: from the C-P bond energy in Me_3P (exp.) and the C≡P bond energy in HCP (MINDO)
5. E_σ-E_π =24 Kcal/mole: from the C-P bond energy in $MePH_2$ (CNDO) and the C≡P bond energy in HCP (MINDO)

TABLE 11

Compound	heat of atomization, Kcal/mole CNDO	MINDO	EXP.	C-P bond length, Å.	C-P bond Nominal bond order	C-P Bond bond energy by CNDO method, Kcal/mole
CH_3PH_2	527.36	526.692	---	1.863	1.0	73.0
CH_2PH	399.63	---	---	(1.677 calc.)	2.0	116.7
CP	160.47	---	159.1±2.3[1]	1.562	2.5	160.5
HCP	279.86	295.193	---	1.5421	3.0	172.0

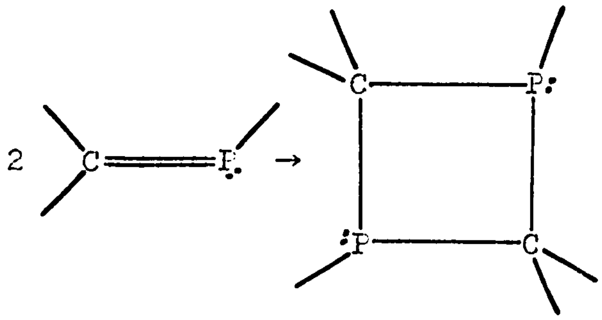
1. G. Hertzberg, Spectra of Diatomic Molecules, New York (1955)

For comparison with experimental values of (single) carbon to phosphorus bond energies, two reported values are given below.

Me_3P	65.3 Kcal./mole[42]
$\emptyset_3P$	71.0 Kcal./mole[48]

The calculated C-P single bond energy may then be as much as about 8 Kcal./mole too high. Qualitatively, it is evident that a π bond can form between carbon and phosphorus, but it is much weaker than a σ bond.

From the calculated double bond energy and the reported value of the single bond energy, a prediction may be made for the energy of head to tail dimerization of a double bonded species.



E = -26±20 Kcal. per mole of dimer

C-P = 65 Kcal./mole
C=P = 116.7 Kcal./mole

Note: if the CNDO C-P bond energy is used here, ΔE = -58.6 Kcal./mole. This is probably too large, as it leads to a value of $(E_\sigma - E_\pi)$ of 29.3 Kcal./mole, larger than the other estimates of this quantity.

42. Calc. from heat of combustion, L.H. Long and J.F. Sackman, Trans. Faraday Soc., 53, 1606-11 and standard heat of formation.
48. C.T. Mortimer, Pure Appl. Chem. 2, 71-6 (1961)

The dimerization is predicted to be exothermic. In the absence of an overriding entropy effect caused by very stringent demands on conformation, the dimerization should proceed readily. Thus it should be no surprise that such a compound as CH_2=PH has not as yet been isolated. I would predict that such a compound would be impossible to prepare except perhaps in a dilute glassy matrix at low-temperature. Note that the Woodward-Hoffmann rules do not apply to this dimerization due to the presence of d orbitals.

There is now sufficient data to use the modified Dewar thermocycle described earlier. It is only necessary to assume that the force constant for the phosphorus to carbon double bond is the average of that of the singly and triply bound species, a reasonable assumption considering the linear bond order-force constant relation discovered for all other bonds investigated. The required parameters for the thermocycle are given in Table 12.

The C-P single bond energy used here will be the CNDO value for methyl phosphine. This is in order to avoid making extra assumptions as to the "correct" single bond length and energy. The trimethylphosphine C-P bond energy value must certainly contain sizeable and opposing contributions from P-H hyperconjugation and H-H repulsion.

TABLE 12

Parameters for the thermocycle method applied to C=P bonds

r' = 1.863 Å. C-P in CH_3PH_2, exp.

r'' = 1.677 Å. C=P in CH_2PH, CNDO calculation

r''' = 1.5421 Å. C≡P in HCP, exp.

k' = 2.882 mdyne/Å. C-P in CH_3PH_2, exp.

k'' = 5.853 mdyne/Å. C=P in CH_2PH, from linear k-p relation

k''' = 8.824 mdyne/Å. C≡P in HCP, exp.

D' = 73.0 Kcal/mole = 3.1654 e.v. C-P in CH_3PH_2, CNDO calc.

D'' = 116.7 Kcal/mole = 5.0653 e.v. C=P in CH_2PH, CNDO calc.

(11,11) sp^2 = 10.49 e.v. average of (I-A) values for carbon and phosphorus, ref. 24

d Orbitals are not explicitly included, but are not needed if the PPP calculation that uses the value of the resonance integral produced does not explicitly include d orbitals either. Their presence is compensated for.

The straight line passing through the two experimental points of the bond order-force constant relation (figure 13) gratifyingly passes near the origin. The calculated force constant for the case of zero bond order is -0.089.

The results for the thermocycle are summarized in table 13 and plotted in figure 14.

FIGURE 13

FORCE CONSTANT–BOND LENGTH RELATION FOR C–P BONDS

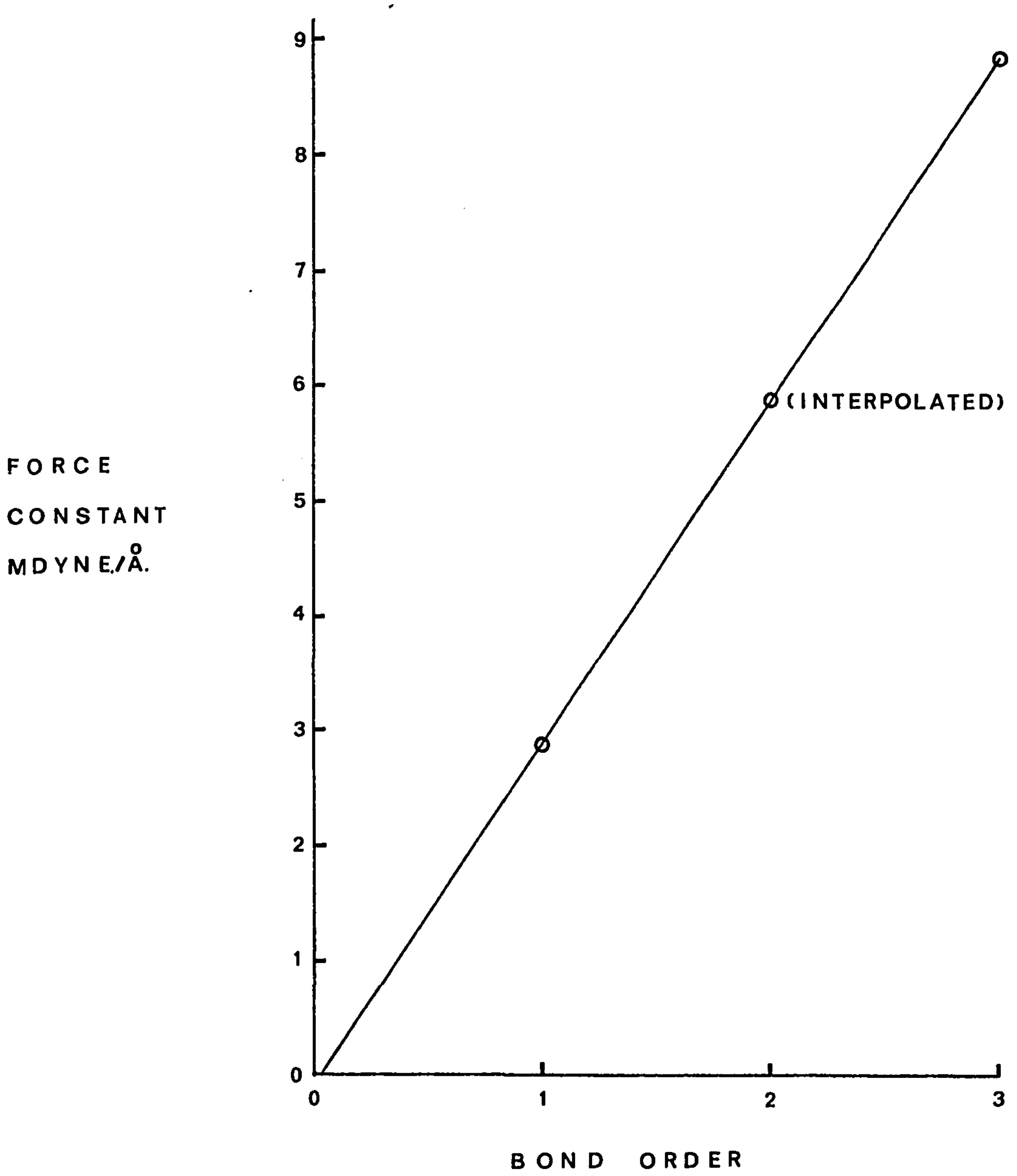


TABLE 13

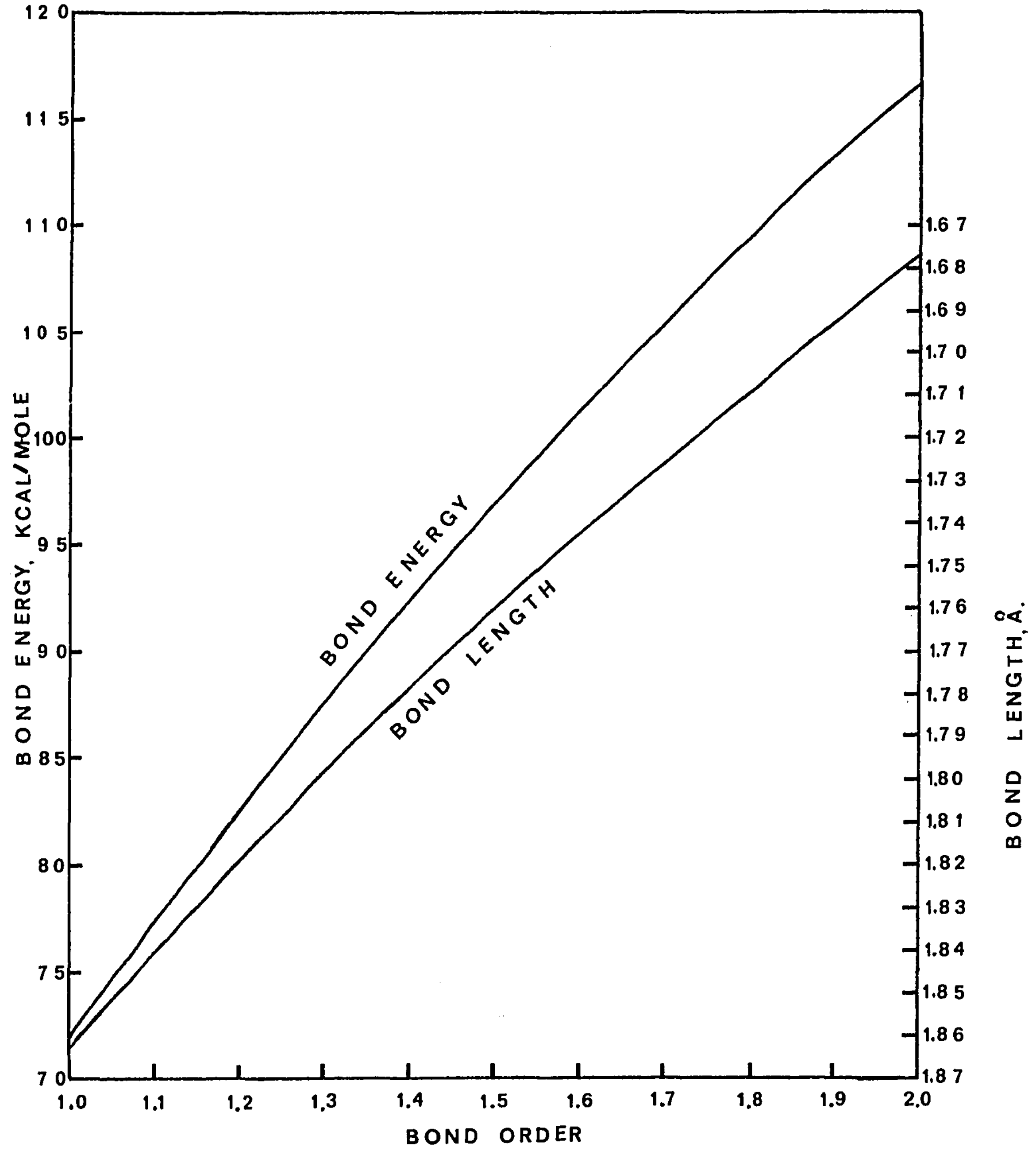
Thermocycle results for C-P double bonds

Bond energy e.v.	Bond energy Kcal/mole	Bond length Å.	Force constant mdyne/Å.	Total bond order	Beta e.v.
5.065	116.70	1.677	5.853	2.0	-2.126
5.035	116.12	1.68	5.794	1.980	-2.105
4.935	113.81	1.69	5.603	1.916	-2.035
4.834	111.48	1.70	5.416	1.853	-1.967
4.731	109.12	1.71	5.233	1.791	-1.901
4.628	106.74	1.72	5.054	1.731	-1.835
4.524	104.34	1.73	4.878	1.672	-1.772
4.420	101.93	1.74	4.706	1.614	-1.709
4.315	99.51	1.75	4.538	1.557	-1.648
4.209	97.08	1.76	4.374	1.502	-1.588
4.104	94.65	1.77	4.213	1.448	-1.530
3.998	92.21	1.78	4.056	1.395	-1.473
3.892	89.77	1.79	3.902	1.343	-1.417
3.786	87.33	1.80	3.752	1.292	-1.363
3.681	84.89	1.81	3.605	1.243	-1.309
3.575	82.46	1.82	3.461	1.195	-1.257
3.470	80.03	1.83	3.321	1.148	-1.206
3.365	77.60	1.84	3.184	1.101	-1.156
3.260	75.195	1.85	3.051	1.056	-1.108
3.156	72.79	1.86	2.920	1.012	-1.060
3.125	72.07	1.863	2.882	1.0	-1.046

Note that these results apply only to sp^2 hybridized carbon and phosphorus; not sp^3.

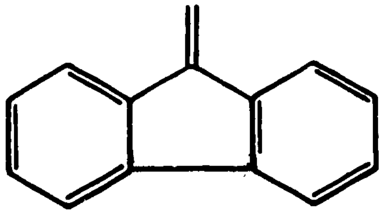
FIGURE 14

BOND ENERGY AND BOND LENGTH AS A FUNCTION OF BOND ORDER FOR P–C BONDS



CALCULATIONS INCLUDING THE FLUORENYLIDENE GROUP

The simplest model for the π structure of a fluorenylidenephosphine is the Huckel calculation on dibenzofulvene, which has been published.[49]



dibenzofulvene

The bond order between the central ring carbon and the cross conjugated exocyclic carbon is 0.829223. This parameter does not change much on going to more sophisticated models, perhaps due to the similar electronegativities of carbon and phosphorus.

CNDO calculations on the molecule fluorenylidenemethylphosphine, using bond distances and angles based on the known values for bifluorenylidene and values used earlier for $CH_2{=}P{-}CH_3$ yielded for the carbon to phosphorus bond a 2p-3p π bond order of .7294 and a 2p-3d π bond order of .4893.

49. C. A. Coulson and A. Streitweiser, Jr., Dictionary of π-Electron Calculations, Oxford, 1965.

The energy level structure is, in part

0.209 e.v. ____ lowest unoccupied antibonding orbital (π^*)

-5.097 e.v. _⇅_ highest bonding orbital (π)

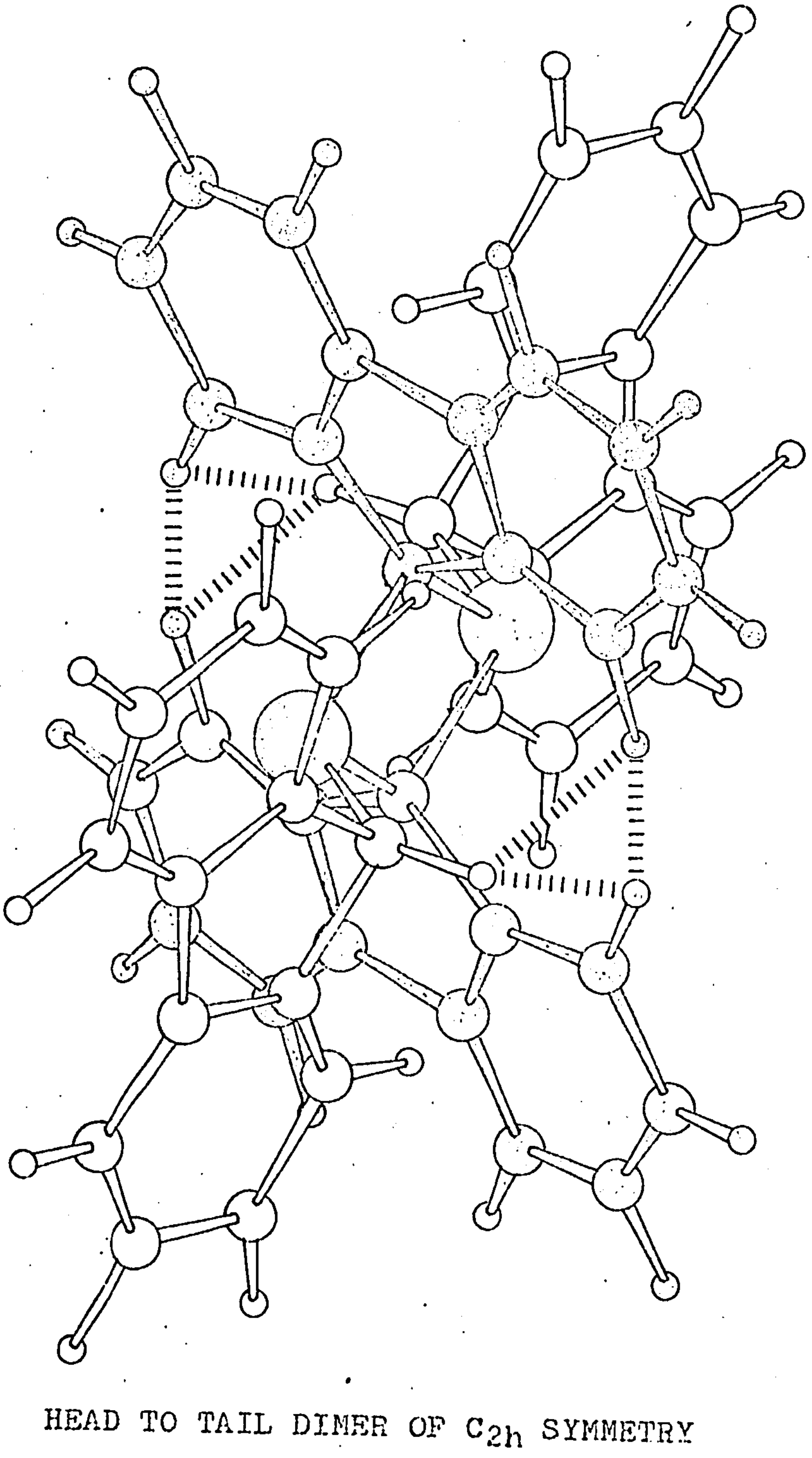
-5.215 e.v. _⇅_ (mostly) unshared pair on phosphorus

Qualitatively, the prediction can be made that there are two possible low energy transitions, an n-π^* and a π-π^*.

A Pople-Pariser-Parr calculation on the Fl=P grouping yielded a carbon to phosphorus π bond order of .831027 (p orbitals only). The thermocycle method predicts for this bond order a bond length of 1.7035 Å. and a bond energy of 110.7 Kcal/mole. Applying the thermocycle to the C-C bond orders in Fl=P and to the experimental bond lengths in fluorene (a model for the 9-fluorenyl group), together with the C-P single bond energy (CH_3PH_2 CNDO calculation) and the C=P double bond energy in Fl=P calculated above, gives the result that the dimerization of fluorenylidenefluorenylphosphine is exothermic, $\Delta H = -24.7$ Kcal per mole of dimer, not including steric hindrance. This result is similar to the result for CH_2PH, and can be generalized.

It is predicted that all compounds containing essentially unconjugated carbon to trivalent phosphorus double bonds will dimerize in the absence of extra steric repulsions in the dimer exceeding about 26 Kcal per mole.

FIGURE 15



HEAD TO TAIL DIMER OF C_{2h} SYMMETRY

○ = P

○ = C

○ = H

ııııııııı = CLOSE INTERACTION BETWEEN H'S

Dimerization of fluorenylidenefluorenylphosphine is inhibited sterically. The head to tail dimer, in the most favorable conformation is illustrated in figure 15. While the transformation of two carbon to phosphorus double bonds into four carbon to phosphorus single bonds is predicted to be slightly exothermic, in this particular molecule repulsive non-bonded interaction is predicted to be overriding.

The four membered ring is assumed to be square, with bond lengths of 1.87 Å. Other bond lengths and angles are adopted from fluorene and bisfluorenylidene.

There are a total of six close H-H interactions. The 1 and 8 hydrogens of the opposing fluorenylidene groups are 1.8 Å. apart, and each should be 1.9 Å. from a 9-fluorenyl hydrogen. In addition, the 1 and 8 hydrogens of the fluorenyl groups are 1.6 Å. away from the plane of the fluorenylidene groups, each coming close to three carbons, a total of twelve C-H interactions.

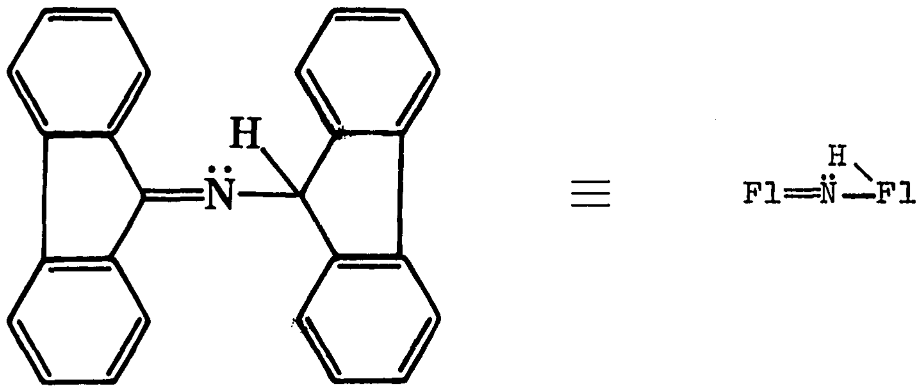
The effect of the carbon to hydrogen repulsions is difficult to estimate, but the hydrogen to hydrogen repulsion energy may be estimated from data due to Fieser and Fieser[50]. The total for the H-H interactions is 45.4 Kcal/mole, by itself sufficient to counter the (predicted) dimerization.

50. Fieser and Fieser, Advanced Organic Chemistry, New York 1961, p. 559

The entropy effect has been estimated by Hudson[19] as 25-30 e.v. for this type of compound. This amounts to 6-10 Kcal. at room temperature. The numbers are larger for solutions.

Head to head dimers, or higher order oligomers are even less favorable.

Another reported analog, first prepared by Ingold[51] is N-fluoren-9-ylidenefluorenyl-9-amine



It exists as pale yellow crystals, which are reported elsewhere[52] as becoming intensely green on melting at 174-5°, and decomposing at 180°. An intensely blue anion forms on treatment with alkali..

19. R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, New York, 1965, p.20
51. C. K. Ingold and C. L. Wilson, J. Chem. Soc., 1933, 1493
52. A. Schoenberg and E. Singer, Chem. Ber., 98, 812 (1965)

A third analog is fluoren-9-ylidene-9-fluorenyl methane, which is also yellow, and which also forms an anion (red).[53]

The final model to be discussed is thiofluorenone, isoelectronic with part of the molecule under consideration (the fluorenyl group's π structure is insulated since the 9-carbon is sp^3). J. Fabian and A. Mehlhorn[50] have performed Pople-Pariser-Parr and other types of calculations, including configuration interactions, which are in agreement with the observed visible absorption spectrum.[50] The spectrum consists of a medium intensity absorption at 430 mμ, and a weak absorption with a maximum at 650 mμ. The calculations serve to establish the origin of these bonds as π-π^* and n-π^*, respectively. The 430 mμ bond exhibits a shift to longer wavelengths and the 650 mμ bond exhibits a shift to shorter wavelengths, upon changing the solvent from cyclohexanol to ethanol, in agreement with the assignment.

53. R. Kuhn, H. Fischer, F. Neugebauer and H. Fischer, Ann. 654, 64 (1962)
50. Fieser and Fieser, Advanced Organic Chemistry, New York, 1961. p. 559

The energy levels for the fluorenylidene-phosphorus structure should be very similar to those of the isoelectronic thiofluorenone, as the particular valence states of sulfur and phosphorus have similar properties. The following data are due to Hinze and Jaffe.[24]

TABLE 14

Electronic properties of phosphorus and sulfur

	$P(3)\ tr^2 tr\ tr\pi$	$S(2)\ tr^2 tr^2\ tr\pi$
$I_v\ \sigma$	15.59 e.v.	16.33 e.v.
$E_v\ \sigma$	3.74 e.v.	5.43 e.v.
$I_v-E_v=(11,11)\sigma$	11.85 e.v.	10.95 e.v.
$I_v\ \pi$	11.64 e.v.	12.70 e.v.
$E_v\ \pi$	1.80 e.v.	2.76 e.v.
$I_v-E_v=(11,11)\pi$	9.84 e.v.	9.94 e.v.

Further, both single and double bond energies for phosphorus and sulfur to carbon are similar (based on CNDO calculations for double bonded P compounds, and CS_2 for sulfur) the π bond energy for sulfur being a little larger.

24. Jurgen Hinze and H. H. Jaffe, J. Am. Chem. Soc., 84, 540 (1962).

From this and the previous data, it may be concluded that the integral β has similar values for C=P and C=S bonds. Thus from this we might expect that the energy levels, and hence the absorption spectra for isoelectronic phosphorus and sulfur compounds might be similar. An exception would be the intensity of an n-π^* transition, the greater polarizability of the phosphorus giving rise to a stronger absorption.

Fluorenylidenefluorenylphosphine in hexamethylphosphoramide solution gave rise to two peaks in the visible region, a medium intensity peak at 430 mμ and a strong peak at 645mμ, (thiofluorenone: 430 and 650 mμ).

SECTION 3

DISCUSSION OF EXPERIMENTAL WORK

The preceding discussion has suggested that a compound with the structure $R_2C=PR$ should be stable to autodissociation, but should also be very reactive, due to the weakness of the π bond. In particular:

1) Dimerization of a compound containing a carbon-phosphorus double bond is not forbidden by orbital symmetry, as is, for example, the concerted dimerization of ethylene. The Woodward-Hoffmann rules do not apply when d-orbitals are present.

If the ethylene concerted dimerization process is slightly asymetric, energy levels do not cross along the reaction profile, and the resulting cyclobutane is in the ground state. The reaction is still 'forbidden' by a large energy barrier.[55]

In the head to tail dimerization of $R_2C=PR$, d-orbitals are involved in bonding throughout the dimerization process. In particular, d-orbitals provide bonding in the energy level of the transition state that in their absence would be the lowest lying antibonding orbital.

55. R. Hoffmann and R. B. Woodward, Accounts of Chemical Research, 1, 19 (1968)

This has the effect of lowering the energy barrier in the reaction profile. Calculations performed on a range of systems containing d-orbitals indicate that there is little or no energy barrier present in this type of reaction.[56]

2) Dimerization of $R_2C=PR$ can be inhibited sterically. It will not occur if the R groups are bulky enough so that their repulsion makes dimerization unfavorable.

3) Stability of a compound containing a carbon-phosphorus bond can be conferred by conjugation, by analogy with 2p-2p π bonds.

4) Energy barriers to reaction of $R_2C=PR$ are lowered, since the d-orbitals of phosphorus are available for bonding to other molecules. Thus exothermic reactions of $R_2C=PR$ are facile. The σ bond-π bond energy differential becomes a driving force for reaction. A compound of the type $R_2C=PR$ is predicted to be highly reactive.

These considerations have shaped an approach to the synthesis of compounds containing carbon to trivalent phosphorus double bonds, and have also suggested the types of compound for which synthesis might be attempted. As the

56. Neil McKelvie, unpublished work

thesis work is restricted to compounds of the type $R_2C=PR$, all considerations reduce to questions about the nature of the R groups.

It was decided that the R groups should be aromatic carbocycles for the following reasons:

1) The bulkiness of aryl groups can provide the required steric inhibition of dimerization.

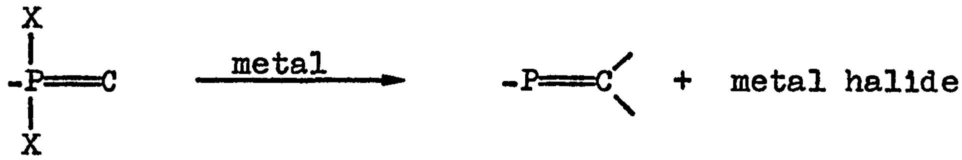
2) The conjugation of the aryl groups should increase the stability of the compound as a whole.

3) Starting materials are readily available for syntheses via simple reaction schemes.

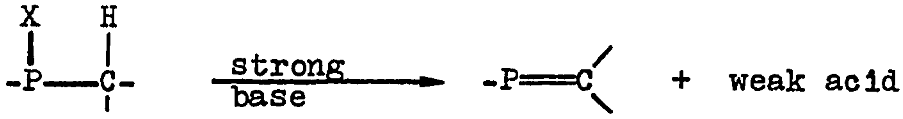
It was decided to design syntheses on conservative principles, with each reaction step being as simple and as unambiguous as possible. In particular, the final step of formation of the carbon-phosphorus π bond should be as free as possible from side-reactions, and the reaction products should not react further with one another.

With these considerations in mind, suggested synthetic schemes evolved around three similar possible steps leading to a carbon to trivalent phosphorus double bond:

1) Reduction of a di- P-halo ylid with a metal.



2) Dehydrohalogenation of a P-halo phosphine with a strong base.



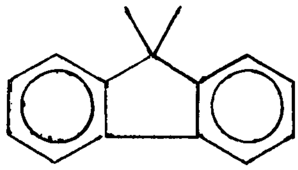
3) The reaction of a dilithio phosphine with a gem-dihalide.

Work along these lines with phenyl groups as the substituents on phosphorus and carbon was carried out but was largely unsuccessful. The species $\phi_2C{=}P\phi$ was not formed, except possibly as an unstable intermediate which disproportionated. This work will not be treated further in this thesis.

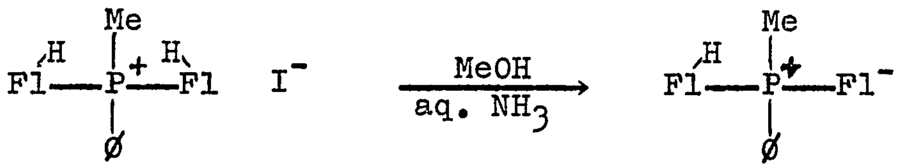
In an attempt to overcome this (assumed) disproportionation, and in order to try other variations on this same theme, it was decided to substitute fluorenyl and fluorenylidene groups for the phenyls. A fluorenylidene group must remain planar, and makes a molecule containing it more difficult to dimerize.

Difluorenylphenylphosphine was prepared by reacting fluorenyl sodium with an excess of phenyl phosphinous dichloride in hexamethylphosphoramide at 0° C..

$$2\ FlH^- \quad + \quad ØPCl_2 \longrightarrow (FlH)_2ØP$$

note: Fl ≡ 

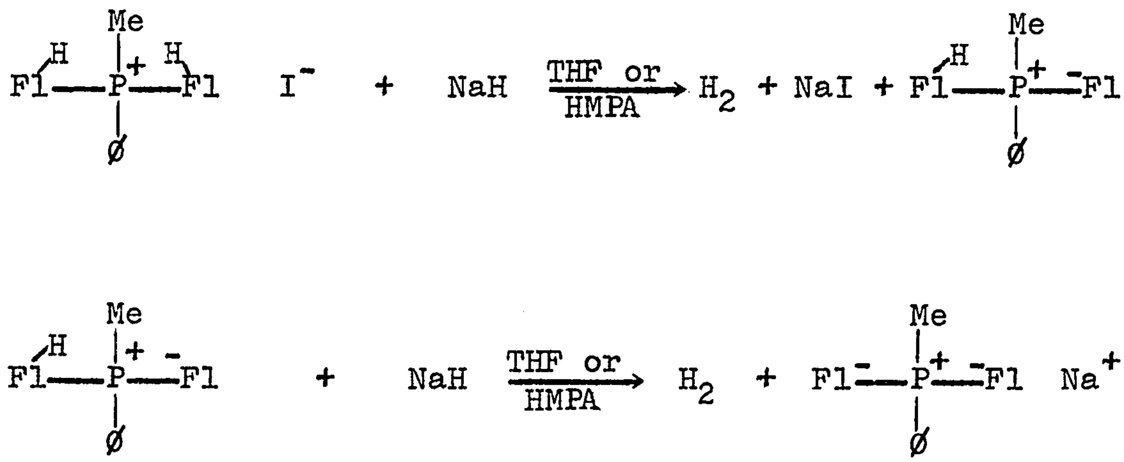
This was treated in tetrahydrofuran solution with methyl iodide to give difluorenylmethylphenylphosphonium iodide, which on treatment with dilute ammonia in water-methanol gave the yellow ylid, fluorenylidenefluorenylmethylphenylphosphorane.[57]



57. Fluorenylidenetriphenylphosphorane is produced by treatment of fluorenyltriphenylphosphonium iodide with ammonia. Louis A. Pinck and Guido E. Hilbert, J. Am. Chem. Soc., 69, 723 (1947)

Anion of fluorenylidenefluorenylmethylphenylphosphorane

When either the ylid or the phosphonium salt (fluorenylidenefluorenylmethylphenylphosphorane or difluorenylmethylphenylphosphonium iodide) is treated with an excess of sodium hydride in dimethylformamide, tetrahydrofuran or hexamethylphosphoramide, gas is evolved and the solution turns a pale green. It is proposed that a new species is formed, the anion of the ylid.



The infra-red spectrum of the tetrahydrofuran solution of the ylid-anion was measured on the Perkin-Elmer model 621, and comparison with a spectrum of the ylid taken under similar circumstances showed the spectra to be similar, but with sufficient differences to establish the separate identities of the species. The visible spectrum of the ylid-anion was found to contain extra peaks relative to the ylid.

TABLE 15

Ylid-anion in THF	Ylid in THF	Ylid in KBr	Assignments
1604 cm^{-1}	1614 cm^{-1}	1608 cm^{-1}	Ø, Fl
1577	1583	1583	Ø, Fl
1427	1433	1433) 1430)	Ø, on P
1377			
1326	1325	1323	
1308	1308	1308	Me on P
1290	1296) 1285)	1292) 1280)	Ø, Fl
1212	1213	1213	
1109	1115) 1103)	1114) 1104)	Ø, on P
999	998	1001) 998)	
991			
987			
747	749 737	753) 734)	Fl
697			
690	692	692	Ø

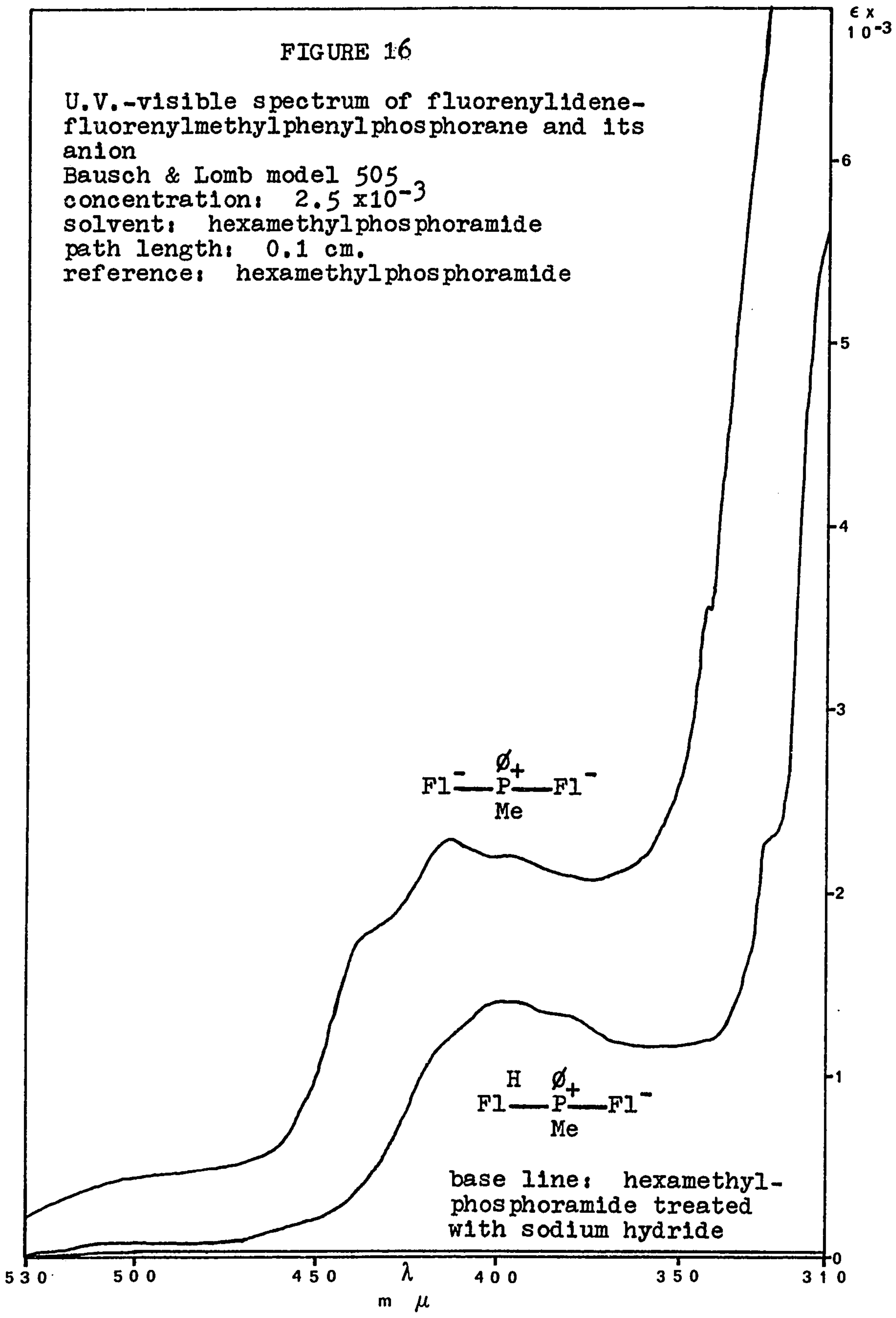


FIGURE 16

U.V.-visible spectrum of fluorenylidene-fluorenylmethylphenylphosphorane and its anion
Bausch & Lomb model 505
concentration: 2.5 x10^{-3}
solvent: hexamethylphosphoramide
path length: 0.1 cm.
reference: hexamethylphosphoramide

The ylid-anion solution on exposure to air turns red, and bifluorenylidene is produced, as detected by comparing its infra-red spectrum with that of a genuine sample. A phosphine oxide peak (1200 cm^{-1}, v.s.) also shows up.

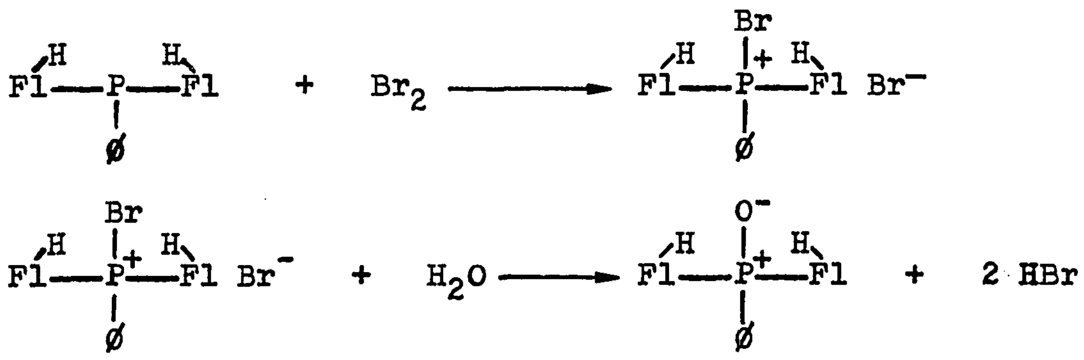
The ylid is not expected to react easily with ketones, towards which its analogue, fluorenylidenetriphenylphosphorane, has been reported to be inert.[58] The ylid-anion however, should have much weaker carbon to phosphorus double bonds, and should be expected to react more readily. Fluorenylidenefluorenylmethylphenylphosphorane did not undergo a Wittig reaction with fluorenone in dimethyl formamide, but remained inert. In the presence of sodium hydride, however, reaction commenced, and bifluorenylidene was formed.

Difluorenylphenylphosphorane

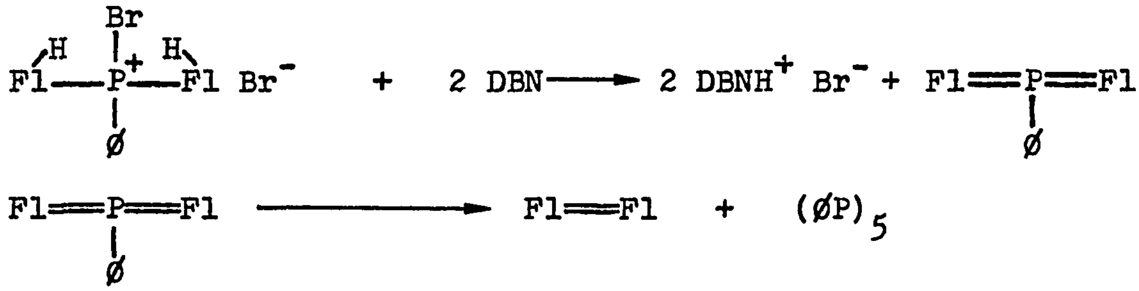
Difluorenylphenylphosphorane could be produced by a double dehydrohalogenation of a dihalide of difluorenylphenylphosphine, by analogy with the work of deKoe.[17,18]

Bromodifluorenylphenylphosphonium bromide was prepared by adding bromine to difluorenylphenylphosphine in benzene solution, and was found to be stable. On hydrolysis it gave a pure sample of the phosphine oxide.

58. A. W. Johnson, J. Org. Chem., 24, 282 (1959)



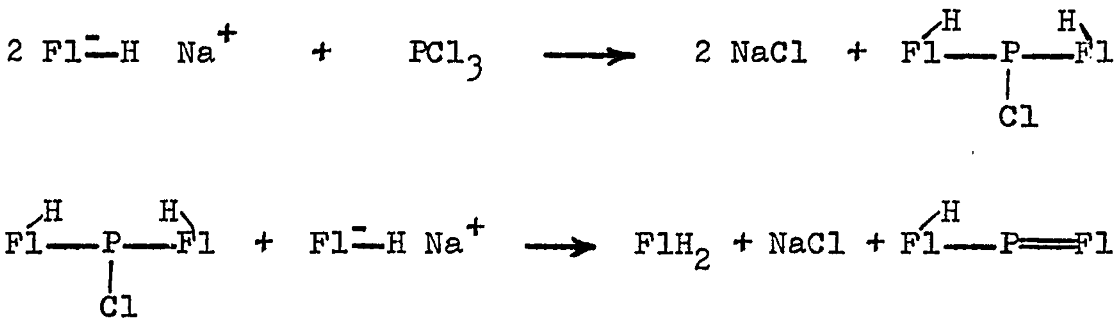
Treatment of the dibromide with DBN in hexamethylphosphoramide or acetonitrile gave a green solution which decomposed rapidly, yielding a red solution which contained bifluorenylidene, as determined by its infra-red spectrum. The reaction taking place may have been



Oxidation of the reaction mixture by exposure to air resulted in a complex mixture, in which was detected (i.r. and n.m.r.) DBN hydrobromide, difluorenylidene, fluorene, a phosphine oxide and other products that could not be identified. More work is needed here to establish the structure and reactivity of the green material. In particular, it is uncertain whether the green product decomposes by itself or by reaction with oxygen. P^{31} n.m.r. would certainly be a desirable tool here.

Fluorenylidenefluorenylphosphine

Working on the assumption that steric crowding would inhibit the formation of trifluorenylphosphine, sodium fluorenylide in hexamethylphosphoramide solution was added to phosphorus trichloride in the molar ratio of three to one.[59] The reactions that I hoped would occur are shown below.



The addition of the third mole of sodium fluorenylide was marked by the formation of an intensely green product extremely sensitive to air and moisture. A precipitate of sodium chloride was observed. The product reacts instantly with methyl iodide, methanol and iodine. If after addition of two moles of sodium fluorenylide, one mole of the base

59. A precedent exists: C. Eaborn and R. Shaw, (J. Chem. Soc., 1955, 1420) reported that sodium fluorenylide reacts with methyltrichlorosilane to give difluorenyldimethylsilane. However the yield was small, and no other products were characterized.

1,5-diazabicyclo [3.4.0] nonene-5 (DBN) was added, the same product was obtained, as evidenced by the U.V.-visible spectrum. Excess base produced no further change.

Evidently, two moles of sodium fluorenylide react with phosphorus trichloride to give chlorodifluorenylphosphine. The third mole of sodium fluorenylide, or the DBN, serves to remove a proton, yielding the green product.

No strongly acidic solution is formed on hydrolysis of the reaction mixture. If a phosphorus to chlorine linkage were present in the product, a mole of hydrochloric acid would have been produced, unless the product was itself an anion. Dilution of the hexamethylphosphoramide solution of the product with a large volume of benzene did not precipitate the green material, an indication of electrical neutrality.

Finally, the N.M.R. spectrum gave very sharp peaks, indicating that the product is not a free radical. The N.M.R. spectrum showed the 9-hydrogens of fluorene and a complicated series of absorptions in the region 6-8.5 delta, attributable to phenyl hydrogens. A lone 9-hydrogen of a fluorenyl group bound to doubly bonded phosphorus may also absorb in this region, as the probably more shielded 9-fluorenyl hydrogens of difluorenyl phenyl phosphine absorb at a mean delta of 6.21.

To summarize the conclusions that may be drawn so far, the green material is a neutral, highly reactive, non-radical species, composed of a phosphorus atom and two fluorenyl groups, less a hydrogen.

The visible spectrum shows absorption maxima at 430 mμ and 645 mμ, qualitatively resembling what is expected for the fluorenylidene-phosphorus chromophore, based on theoretical calculations on fluorenylidenemethylphosphine and the reported spectrum of 9-thiofluorenone, compounds that are isoelectronic with the chromophore.

The calculations predict small energies for transitions from the lone pair of electrons on phosphorus, and from the π bond between phosphorus and carbon to a low energy antibonding orbital. The spectrum of 9-thiofluorenone exhibits absorption maxima at 430 mμ and 650 mμ, assigned to π-π^* and n-π^* transitions, respectively. On the basis of this evidence, the most likely structure for the green material is that of fluorenylidenefluorenylphosphine (Fl(H)-P=Fl).

FIGURE 17

U.V.-visible spectrum of fluorenylidenefluorenylphosphine concentration about $2.5x10^{-3}$, assuming complete reaction; solvent: hexamethylphosphoramide; path length: 0.1 cm.; Bausch & Lomb model 505
reference: hexamethylphosphoramide

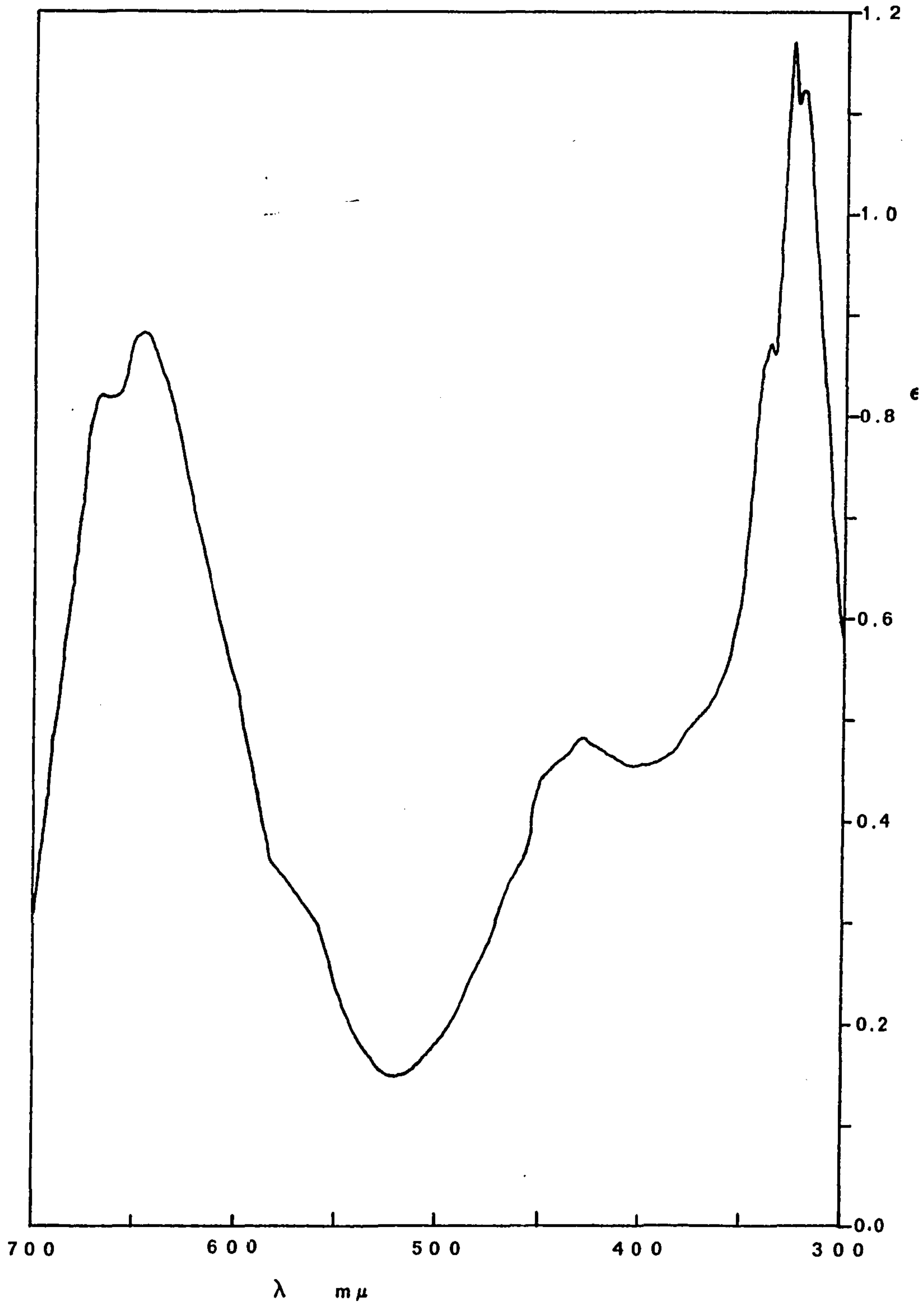


FIGURE 18

90 MHz proton N.M.R. spectrum of fluorenylidenefluorenylphosphine solvent: hexamethylphosphoramide; taken by Dr.L. Schwartz

SUMMARY AND CONCLUSIONS

Two ylids with contrasting properties were prepared from difluorenylmethylphenylphosphonium iodide. Treatment of the phosphonium salt with weak base afforded the ylid fluorenylidenefluorenylmethylphenylphosphorane. This ylid was reasonably stable towards air oxidation and did not undergo a Wittig reaction with fluorenone to produce difluorenylidene. These properties are to be expected by analogy to the known compound fluorenylidenetriphenylphosphorane.

Treatment of either the original phosphonium salt or the above-mentioned ylid with a strong base, sodium hydride, resulted in removal of a second proton, yielding a di-ylid, or ylid-anion. This anion has π bonds which are weaker than that of the mono-ylid, and undergoes facile reaction with fluorenone to produce difluorenylidene. It is air-sensitive.

The next system chosen for study was difluorenylidenephenylphosphorane. It was observed only as a green transient intermediate in the reaction of $(FlH)_2\phi PBr^+Br^-$ with DBN. While more work is required in this area (P^{31} n.m.r. in particular), it appears that difluorenylidenephenylphosphorane was formed and then decomposed, yielding difluorenylidene. This behavior may be contrasted with that of the previously discussed ylid-anion, which did not decompose in analogous manner in the absence of air.

The simplest explanation of this difference is that the negative charges of the fluorenylidene groups in the ylid-anion repel one another sufficiently to prevent their coming together. Also deterrent to the decomposition as written is the necessity of charge localization. The stronger p-d hybrid π bonds of difluorenylidenephenylphosphorane distribute charge more evenly, so that the merging of the fluorenylidene groups is not inhibited.

The final system to be studied was fluorenylidenefluorenylphosphine (Fl=P-(H)Fl), where it was hoped that every stumbling block encountered previously would be removed. Unimolecular decomposition pathways were unlikely (Fl=P-(H)Fl) $\longrightarrow$ Fl=Fl + PH), bimolecular reactions were inhibited by the difficulty of forming the dimer, and cleavage via base could be removed from consideration by methods of synthesis where fluorenyl anion was the strongest base present. Synthesis was accomplished by reaction of fluorenyl ion with phosphorus trichloride, followed by dehydrohalogenation with another mole of fluorenyl ion or with D.B.N.

$$2\ Fl^- + PCl_3 \longrightarrow \overset{H}{Fl}\!-\!\underset{Cl}{P}\!-\!\overset{H}{Fl} \xrightarrow[\text{or DBN}]{Fl^-} Fl{=}P\!-\!\overset{H}{Fl}$$

Proof of structure rests on its visible absorption spectrum, the stoichiometry of its formation, its electrical neutrality, the observation that it is formed by proton removal, and that its formation can proceed by a likely mechanism.

The conclusion of the theoretical work that a 2p-3p carbon-phosphorus π bond is a chemically stable entity is considered to have been confirmed.

SECTION 4

DETAILS OF EXPERIMENTS

Infra-red spectra were run on the Perkin-Elmer model 621 spectrophotometer, and also on models 137 and 237. Nuclear magnetic resonance spectra were run on the Varian A-60 and the Bruker HFX-90 spectrometers. Ultra-violet spectra were run on the Bausch and Lomb 505 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc., and Schwarzkopf Microanalytical Laboratory.

All starting materials were used as commercially available except as noted. All reactions were carried out under nitrogen.

Fluorene (Aldrich Chemical Company), m.p. 115°-116° was dried over Drierite for one week.

Hexamethylphosphoramide (Aldrich Chemical Company) was dried over sodium hydride for one week, and then distilled under vacuum.

Phenyl phosphonous dichloride (Aldrich Chemical Company) was distilled through a 2.5 x 60 cm. fractionating column packed with helices. At a reflux ratio of 10:1, the fraction boiling in the range 222.8°-223.2° (uncorrected) was collected and stored under nitrogen until used.

Difluorenylphenylphosphine:

A solution of 33.2 gms. (0.2 mole) fluorene in 200 ml. hexamethylphosphoramide was added dropwise with stirring to 10 gms. of a 55% dispersion of sodium hydride in petrolatum (0.2 mole sodium hydride) over a period of one-half hour, the flask contents being kept cool by an ice bath. After the addition was complete, hydrogen evolution diminished. The ice bath was removed and the reaction mixture, now very deep orange, was permitted to stand overnight.

The solution of sodium fluorenylide was transferred to a dropping funnel and added over a ten minute period to 40 ml. (0.3 moles, threefold excess) phenyl phosphonous dichloride at 0°. The mixture was then distilled under vacuum (0.2 mm. Hg.) to remove most of the solvent and excess dichlorophenylphosphine. The maximum bath temperature was 150°. The mixture was cooled, 500 ml. benzene was added, and refluxed for two hours. The mixture was filtered hot, and the yellow filtrate, on cooling overnight afforded white crystals of product, which were filtered off, washed with hexane and then dried under vacuum. Yield 22.3 gms., 51%. Mp. 225° dec. The product was purified by vacuum sublimation at 190° at 0.05 mm. Hg. for ten days. Mp. 208° dec. (uncorr.)

Calculated for $C_{32}H_{23}P$: C: 87.65%, H: 5.29%, P: 7.06%

Found: C: 87.20%, H: 5.03%, P: 8.02%

Found: C: 86.08%, H: 5.14%, P: 7.08%

Molecular weight of difluorenylphenylphosphine = 438.

Mass spectrum parent peak: m/e = 438

I.R. absorptions, cm^{-1} (KBr), (abbreviated)

3060, 2915, 1607, 1574, 1473, 1441, 1432, 1175, 1091, 1004, 998, 934, 782, 745, 730, 693, 502, 426, 407.

U.V. maxima, $m\mu$, (ϵ), (dioxane)

258, (56,000); 269, (48,000); 302, (15,000).

N.M.R. peaks, ppm.δ relative to T.M.S. (dimethyl sulfoxide)

6.21, doublet, J=15 cps.; 6.05- 8.3, complex.

A portion of the phosphine allowed to stand in air was partly oxidized to difluorenylphenylphosphine oxide, whose infra-red spectrum contained further peaks, particularly a strong absorption at 1200 cm^{-1}, attributed to P^{+}-O^{-}. This was absent from the infra-red spectrum of the phosphine. Also absent are the C=O peak of 9-fluorenone (1720), and the methylene peak of fluorene (1400).

Difluorenylmethylphenylphosphonium Iodide:

Difluorenylphenylphosphine (4.38 gm, 0.01 moles) were added to 200 ml. tetrahydrofuran which was then heated with

stirring until a clear solution was obtained. Methyl iodide, previously treated with mercury to remove iodine, was added (5.6 gm., 0.04 moles, a fourfold excess), and a precipitate soon formed. After ten minutes the source of heat was removed, and the reaction mixture was stirred over-night.
The solid was filtered off and dried under vacuum, yielding white crystals, weight 5.47 gm. (94.5%). The product was further purified by recrystalization from methanol.
Mp. 177° dec. (uncorr.), with evolution of methyl iodide.

Calculated for $C_{33}H_{27}PI$: C: 68.29%, H: 4.52%, P: 5.34%, I: 21.86%

Found: C: 67.92%, H: 4.75%, P: 5.41%, I: 21.77%

I.R., cm^{-1} (KBr), (abbreviated)
3045, 2900, 1602, 1583, 1447, 1443, 1435, 1298, 1106, 1005, 940, 911, 892, 763, 735, 710, 687, 517, 504, 427, 405.
U.V., mμ, (ϵ), (dioxane), (rapidly turns yellow)
250, (19,000); 258, (25,000); 270 (sh), (11,000); 455, (4,400).
in methanol: 240, (96,000); 268, (41,000).
N.M.R., ppm. δ, ($CDCl_3$)
1.77, doublet, J=12 cps.; 6.04, doublet, J=17 cps.; 6.8-8.2, complex.

Fluorenylidenefluorenylmethylphenylphosphorane:

Four gm. (0.069 moles), difluorenylmethylphenylphosphonium iodide, recrystalized from methanol, were added to 175 ml. methanol, and heated until a clear solution was obtained. 50 ml. aqueous 28% ammonia were then added slowly, precipitating a yellow solid. The mixture was cooled, and the solid filtered off and then dried, yielding 2.42 gm. (77.6%). Mp. 192.1-193.5° (uncorr.).

Calculated for $C_{33}H_{25}P$: C: 87.58%, H: 5.57%, P: 6.84%
Found: C: 87.33%, H: 5.93%, P: 6.48%

I.R., cm^{-1}, (KBr), (abbreviated)
3050, 2999, 2920, 1608, 1583, 1474, 1464, 1443, 1430, 1323, 1308, 1292, 1280, 1114, 1104, 1001, 998, 941, 907, 894, 872, 760, 753, 734, 704, 692, 514, 507, 469, 400.

U.V. $m\mu$, (ϵ), (dioxane)
225, (60,000); 250, (50,000); 324, (1,100); 382, (540).

N.M.R., ppm. δ, (deuterochloroform)
1.72, doublet, J=12 cps.; 6.9-8.3, complex.

Anion of fluorenylidenefluorenylmethylphenylphosphorane:

A 2.5 x 10^{-3} M. solution of fluorenylidenefluorenylphenylphosphorane and a 2.5 x 10^{-3} M. solution of difluorenylmethylphenylphosphonium iodide, both in hexamethylphosphoramide, were treated with an excess (greater than tenfold) of sodium hydride. After one hour, the solutions were decanted off and u.v.-visible spectra were taken and found to be identical. Five per cent solutions were used for infra-red spectra, the procedure for preparation otherwise being the same. The reactions were also carried out in dimethylformamide and tetrahydrofuran.

A sample of the ylid fluorenylidenefluorenylmethylphenylphosphorane (0.45 gm., 0.001 mole) was dissolved in 50 ml. dimethyl formamide and treated with an excess of sodium hydride (1.0 gm. 55% dispersion in petrolatum, 0.02 moles, a twenty-fold excess). Gas was evolved. After stirring for an hour, the reaction mixture was filtered, the filtrate dropping into a solution of fluorenone (0.18 gm., 0.001 moles) in 20 ml. dimethyl formamide. The reaction mixture turned red-brown. Water was added, and the gummy precipitate was filtered off and dissolved in hot ethanol. Red crystals formed on cooling, which were recrystalized from alcohol and dried under vacuum. Mp. 180-185°. The infra-red spectrum established it as bifluorenylidene (Lit.: 194-5°)[60] contaminated with fluorenone and a small amount of a phosphine oxide. Yield 0.24 gms. (73%).

60. Handbook of Chemistry and Physics, 50th Ed., The Chemical Rubber Co., Cleveland, 1969.

Bromodifluorenylphenylphosphonium bromide

Difluorenylphosphine (3.0 gms.) was dissolved in 500 ml. hot benzene, and bromine dissolved in benzene was added until the solution turned red from excess bromine. A yellow precipitate formed. The solution was cooled and stirred for one-half hour. The precipitate was filtered off, washed with hexane and then dried under vacuum. Yield 3 gms. The product decomposed upon melting at 153° with evolution of HBr, as detected with moist litmus paper and by its odor. The product of decomposition was red.

A portion of the bromide was hydrolyzed in water to give the pure phosphine oxide, previously identified in samples of difluorenylphenylphosphine. Mp. 305°-310°.

Analyzed for: $C_{32}H_{23}PO$. C: 84.60%; H: 5.10%; P: 6.82%; O: 3.52%

Found: C: 83.99%; H: 5.03%; P: 7.09%; O (by difference): 3.89%

Fluorenylidenefluorenylphosphine

A solution of sodium fluorenylide was prepared by adding a solution of 0.2 mole of fluorene in 250 ml. hexamethylphosphoramide to 0.2 mole of sodium hydride (petrolatum dispersion) at 0^{o}. This solution, after stirring overnight to complete the reaction, was diluted with tetrahydrofuran. It was then pumped via partial vacuum through a filter into a burette. The solution was standardized by hydrolysis of an aliquot, yielding a water solution of sodium hydroxide which was titrated with standardized sulfuric acid solution.

A portion of phosphorus trichloride was weighed out and standardized sodium fluorenylide solution was added. As the addition progressed, the reaction mixture became yellowish. A green color finally appeared, and was persistent and clearly visible at a molar ratio of phosphorus trichloride to sodium fluorenylide of 1:2.37. This was undoubtedly an overtitration, due to the difficulty of observing the green color in the presence of the yellow. To the reaction mixture was deliberately added an excess of sodium fluorenylide. It was then hydrolyzed and the sodium hydroxide now present was back-titrated with sulfuric acid to the point where the color of added phenolphthalein faded. The ratio of the number of moles of phosphorus trichloride to the number of moles of sodium fluorenylide less that accounted for by the back titration was 1:3.2. Repeated runs established the molar ratio as 1:3 ± 10%.

Solutions prepared for study were made from portions of the sodium fluorenylide solution that were individually standardized and weighed amounts of phosphorus trichloride.

In some runs benzene was used in place of tetrahydrofuran as a diluent for the sodium fluorenylide solution.

The green material did not precipitate out upon the addition of a large quantity of benzene, unlike sodium fluorenylide, which precipitated under comparable conditions.