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PART I

THE PHOTODEUTERATION OF OPTICALLY ACTIVE BIPHENYLS. THE POSSIBLE INTERMEDIACY OF A VIBRATIONALLY "HOT" MOLECULE

PART II

AN ORD STUDY OF THE CONFORMATION OF OPTICALLY ACTIVE BIPHENYLS IN SOLUTION

by

Arthur L. Blackwood

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment
of the requirements for the degree of
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July 12, 1977
date

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The City University of New York

Abstract

I. THE PHOTODEUTERATION OF OPTICALLY ACTIVE BIPHENYLS. THE POSSIBLE INTERMEDIACY OF A VIBRATIONALLY "HOT" MOLECULE

II. AN O. R. D. STUDY OF THE CONFORMATION OF OPTICALLY ACTIVE BIPHENYLS IN SOLUTION

by

Arthur L. Blackwood

Adviser: Professor Joseph J. Dannenberg

I. Photoracemization and photodeuteration of optically active biphenyls with 2537 Å light occur in the excited rather than from a "hot" ground state. Both of these processes are independent of sulfuric acid concentration. However, normal acid quenching of fluorescence is observed and, at the same time, a fluorescent protonated species, whose intensity of fluorescence varies directly with the acid concentration, is also observed. Therefore, two distinct excited state intermediates are involved. Photoracemization and photodeuteration are believed to occur from a higher excited state singlet while fluorescence occurs from the lowest excited state singlet.

II. Substituted biphenyls, including those that are resolvable, generally exist in two distinct conformations in the range of torsional angles of 0^o

to 180°. This is demonstrated by, a) a large reversible temperature dependence of the specific rotation of optically active biphenyls; b) by the temperature dependence of the N.M.R. chemical shift of the methyl protons of 2,2'-dimethyl-6,6'-dinitrobiphenyl, and c) by the observation of apparent splittings in the far infrared (torsional) frequencies of biphenyls with unsymmetrical torsional potential energy curves.

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The very first thank you goes to my thesis advisor Dr. Joseph J. Dannenberg for affording me the kind of research freedom which I consider the ideal environment for producing my best. My gratitude also goes to the members of my thesis committee, Dr. Robert Odum and Dr. Angelo Santoro, for their wisdom. Special thanks to Dr. Santoro's bright spirit and words of encouragement at those moments when it seemed that the vicissitudes of my extra-curricular duties might simply sweep me away. The reliability of Margie Sweier and of Otto Safferling for "coming through" during my many "rushes", thus saving me much valuable time, is also greatly appreciated.

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PART I

The Photodeuteration of Optically Active Biphenyls. The Possible Intermediacy of a Vibrationally "Hot" Molecule

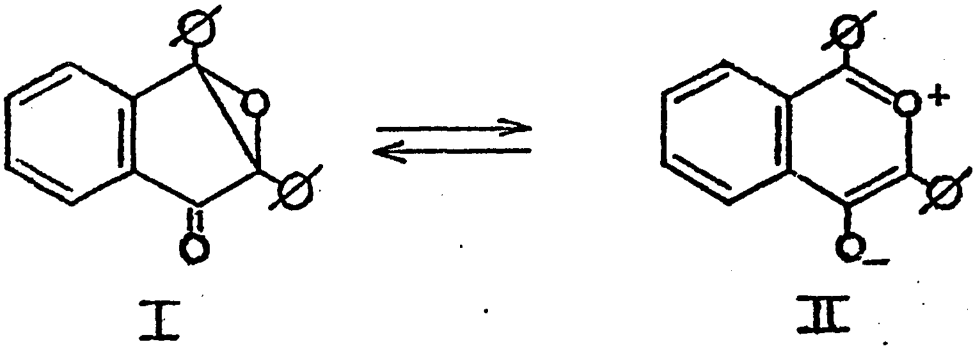
INTRODUCTION

The intermediacy of vibrationally excited ("hot") ground state molecules in gas phase photochemistry has long been accepted[1]. However, the lifetime of such vibrationally excited ground state molecules in condensed phase (i.e., liquid or solid) is generally thought to be too short to allow for a similar intermediacy in solution photochemistry[2]. The major reason for this opinion is attributed to intimate contact of the excited molecules with solvent molecules, making possible numerous deactivating collisions within a very short time.

Giving strong support to this belief was the work of Weber and Teale[3] in which the fluorescence quantum yields of twenty-six compounds were measured in dilute solutions and most were found to be independent of excitation wavelength throughout the experimentally accessible ranges. It was demonstrated that those compounds not exhibiting constancy of quantum yield were mixtures, either due to impurities or association (e.g., dimerization, hydrogen bonding, tautomerism, inter- or intra-molecular energy transfer, molecular bond dissociation, etc.). Furthermore, these investigators derived an apparent theoretically sound mathematical expression relating the relative lifetimes, τ and τ', for molecules in the same electronically excited state, but zero and higher than zero vibrational levels, respectively. By substituting the experimentally determined numbers into the equation, they showed that the lifetimes of the vibrationally excited molecules could not be greater than 10^{-10} second and that wavelength dependence would be observed only when the quantum yield of fluorescence was reduced, due to competitive processes, to a value of 0.05 or less.

Consequently, the rate constants of vibrational deactivation in solution are of the same order of magnitude, or greater, than those of diffusion (approximately, between 10^{-10} and 10^{-4} second, depending on solvent[4]). Thus, any true bimolecular reaction involving "hot" molecules seems unlikely since they must be present in low concentrations.

It is, therefore, not surprising that any claim of the intermediacy of "hot" molecules in solution be looked upon with great skepticism. This was the fate of the work done by Ullman and Henderson[5] who found it necessary to propose the intermediacy of a vibrationally excited ground state in order to explain the observed effect of triplet energy transfer agents on the reversible valence tautomerization of 2,3-diphenylindenone oxide (I) to cyclopentadienone oxide (II) in benzene solution.



On closer examination, however, one might expect that unimolecular reactions of "hot" molecules and/or "bimolecular" reactions, where the "hot" molecule is created after the two reactants have already diffused together, might remain as possiblities.

Electrophillic reactions of electronically excited substituted benzenes have been extensively studies by Havinga, et. al.[6] We were particularly attracted to the detailed photodeuteration studies of substituted benzenes done by De Bie and Havinga,[7] not only because of the unusual substitution patterns obtained, but mainly because of one of several hypotheses postulated by the authors in an attempt to rationalize the experimental results. Namely, the species involved in these reactions might be ". . . a vibrationally excited ground state (sigma)[a] complex . . . that will cool down very rapidly . . .".

The substitution patterns obtained by De Bie and Havinga could not be explained by the localization energies, calculated using M. O. Theory, of either ground state or first excited singlet state[b] (i.e., calculated Δ E's for the Wheland-type intermediates). The agreement was better with the calculated electron density of the first excited state singlet of compounds with electron donating groups on the ring, but could not explain the observed increased activation of the meta position when a

[a] *The authors did not use the word "sigma". It is interjected here for emphasis.*

[b] The experimental evidence suggested that these reactions occurred in or started from a singlet excited state.[7]

deactivating group such as nitro was on the ring. Therefore, these results seem to indicate that the reactions are not purely one of an excited state or of a normal ground state.

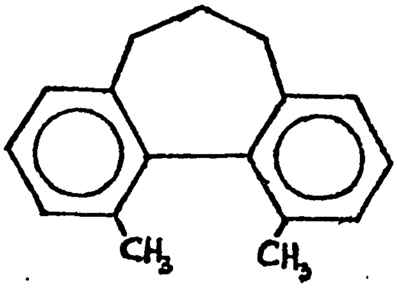
If, as De Bie and Havinga suggested, the reactant is attracted to the electron rich sites of the excited state singlet, then substitution involves a perturbation on the molecular orbital of the internally converting molecule.

One way of testing this hypothesis is to use optically active biaryls as substrates for photosubstitution since the vibrational energy liberated in the substitution/internal conversion process should be available to the torsional vibrational mode of the biaryl, which should lead to racemization.

Westheimer and Mayer[8a, b] and also Hill[8c] have shown that optically active biphenyls racemize thermally via several vibrational modes, the most important ones involving bending and stretching of the interannular bond and of the ortho substituents.

Therefore, if a "hot" ground state molecule is involved, differences in the rates of racemization should occur between molecules racemizing in an inert medium as opposed to the same molecules racemizing in photosubstitution medium, in this case photo-deuteration medium.

The photoracemization of a biphenyl had already been reported by K. Mislow and A. J. Gordon.[9] These investigators induced the racemization of the bridged biphenyl (III) by the room temperature photoirradiation (mercury resonance lamp) of 0.1 to 0.2% ether solutions under nitrogen atmosphere.[a] They found the inversion of (III) to proceed cleanly, that is, without the formation of side products (infrared, vapor phase chromatography) and that mass recovery was quantitative. The results were interpreted in terms of internal conversion of the initial electronically excited state to a "hot" ground state molecule. This, then, seems like the first clear-cut example of a unimolecular reaction involving a "hot" ground-state molecule in solution.



III

We hoped to test Havinga's hypothesis of the possible intermediacy of a "hot" ground state sigma complex in solution. This would be an example of a bimolecular reaction involving a "hot" ground state molecule in solution. Our approach to the problem consists in polarimetrically monitoring the rates of photoracemization of optically active biphenyls in solution, under two differing conditions: a) inert medium and, b) photo-deuteration medium, similar to the one used by De Bie

---

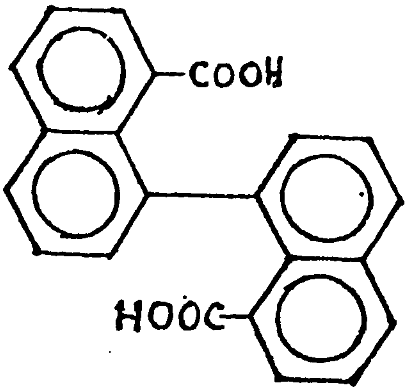
[a] The thermal activation energy for racemization of (III) is 39 Kcal/mole.[9]

and Havinga, to see if any difference in the rates of racemization between the two media is detected. Any difference in rates could be attributed to a perturbation of the excited molecule, thus, to the possible formation of a "hot" sigma complex.

Of course, it would have to be shown that the selected compounds are thermally stable under the given set of experimental conditions, that no photoproduct is formed, and that the mechanism for photoracemization did not involve the formation of benzvalene or other similar type intermediates.[10]

RESULTS

Our first attempt was to obtain a commercially available biaryl which could be resolved. The only such compound that we could find was 1,1'-dinaphthyl-8,8'-dicarboxylic acid (IV)[11]. Direct kinetic data could not be obtained with this compound because it was too optically labile, thermally,[12] and also gave evidence of reacting photochemically,[a]



IV

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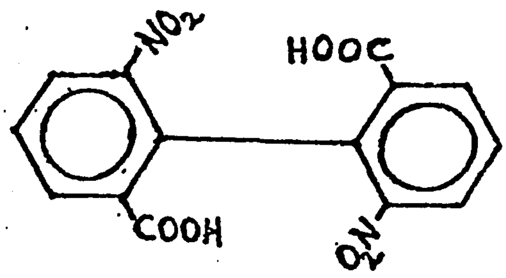
[a] This compound is suspected to decarboxylate photochemically with the full spectrum of a medium pressure arc (quartz), as judged by an apparent build-up of pressure in the sample tubes. This was not investigated.

Finally, we opted to synthesize 6, 6'-dinitrodphenic acid (V),[13] not only because of its very high thermal stability,[a] but, in addition, the nitro and carboxyl functional groups of this compound could be converted into other functional groups, using modern synthetic techniques.[14] (See scheme I for the reaction sequence). Furthermore, these compounds had already been synthesized and thoroughly characterized by Ingersoll and Little,[13] and, especially, by K. Mislow and co-workers.[14]



V

Interest in the other functional groups, such as $-NH_2$, $-N\overset{O}{\overset{\|}{C}}R$, $-COOR$, $-CH_2X$ (where X is either halogen or $-OH$) and $-CH_3$, is due to the fact that they differ in their effective Van der Waals radii, hence in their

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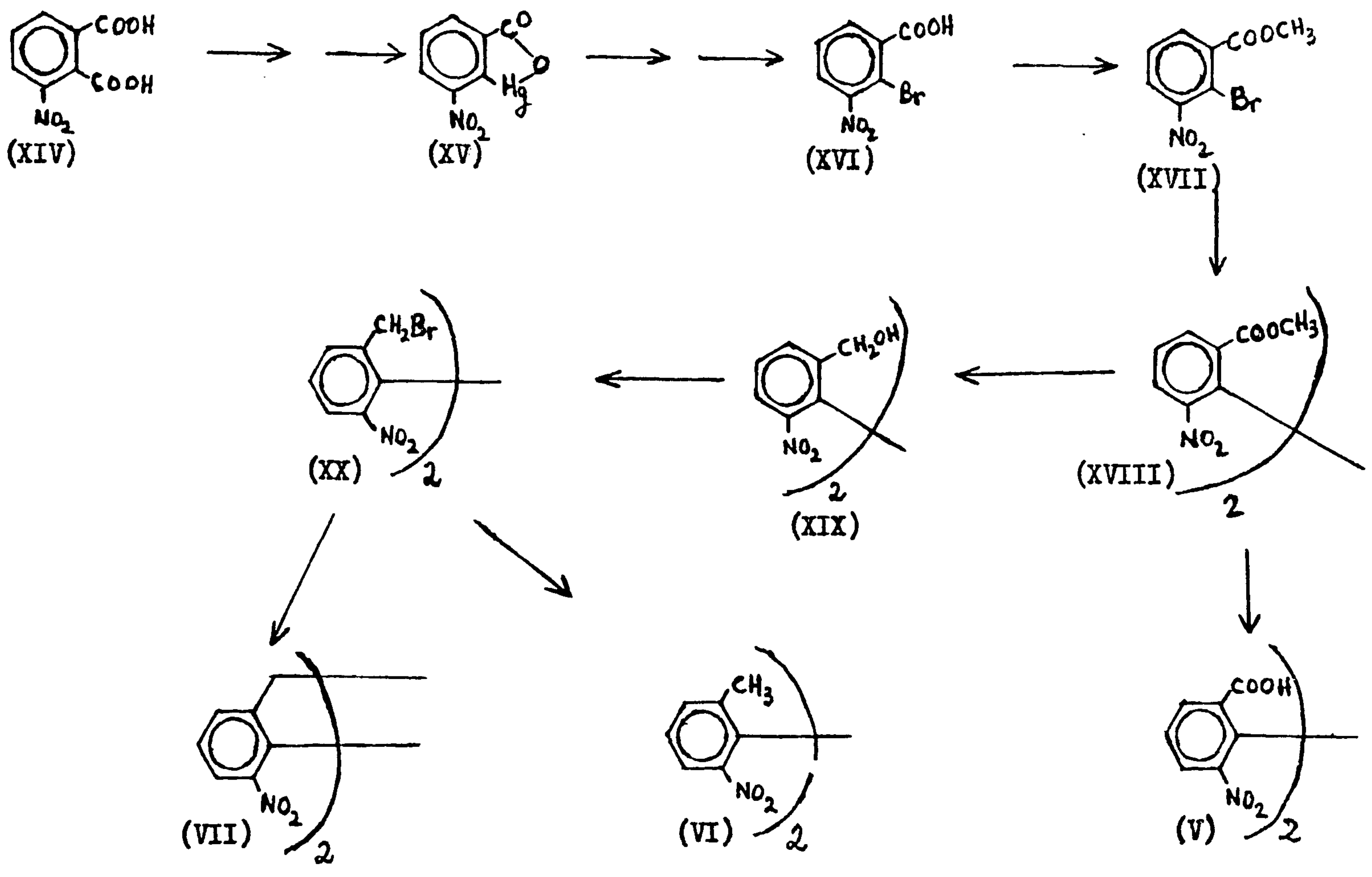
[a] Recrystallization from boiling water causes no loss of optical purity.[13]

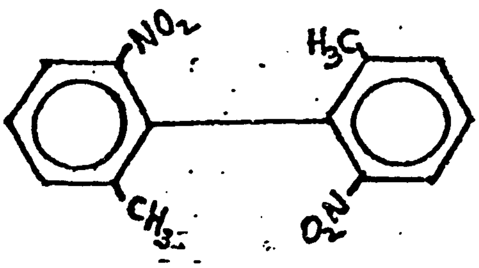


Scheme I . Synthesis of (V), (VI), and (VII). See experimental section for details.

energies of activation for racemization. A greater selectivity on the experimentally observed rates of racemization would have been afforded. Unfortunately, because of possible thermal reaction with the medium,[a] or photochemical reaction or decomposition,[15] most of these functional groups were not used and we were limited to $-NO_2$ $-COOH$, and $-CH_3$.

All compounds were irradiated under two sets of conditions: a) inert medium, consisting of the solvent methanol, and b) photo-substitution medium which consisted of glacial acetic acid-d_4, containing 0.2 molar sulfuric acid-d_2. See experimental section for details.

Irradiation of (+)-2,2'-dimethyl-6,6'-dinitrobiphenyl (VI) in



VI

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[a] For example, the $-CH_2OH$ group would react in the presence of sulfuric acid with the solvent, glacial acetic acid, to form an ester.

methanol solution at 50°C yielded a photoproduct.[a] Optical readings of solutions with initial low net positive rotation not only decreased with time, but upon extended irradiation (139 hours) with a mercury resonance lamp, the sign of the readings were inverted with reasonably high final absolute magnitude.[b] On the other hand, the same compound irradiated in acid medium appeared to racemize normally.[c] These results are in general agreement with those of Zimmerman and Crumrine.[16]

---

[a] We suspect that the nitro group of the excited molecule abstracts a proton, intra-molecularly, from the methyl group of the adjacent ring, by anology with other examples in the literature (see reference 1, p. 480).

[b] A solution with initial reading of +0.083 degrees had a final reading of -0.162, after irradiating for the specified length of time.

[c] No appreciable racemization occurs in any of these compounds with a medium pressure lamp, using Pyrex filter, after one week of continuous irradiation.

Similar irradiations of (+) or (-)-6,6'-dinitrodiphenic acid (V) at 25°C and also at 50°C gave the results shown in tables 1, 2 and 3. It can be seen from these tables that the rates of racemization in methanol are always greater than in glacial acetic acid. A t-test analysis, direct difference method, [17] of the data in tables 1 and 2 showed that the differences in rates of racemization were significant at the 2% level.

Table 3 shows that the rates of racemization increase in both solvents, for compound (V) at 50°C and that, within experimental error, the magnitudes of the rates are equal. The temperature dependence of the rates, although small, are significant. The rate approximately doubled in acetic acid and increased approximately 50% in methanol.

Thermal aromatic substitutions are known to sometimes show kinetic isotopic effects.[18] Also, steric isotope effects on the thermal racemization of optically active biphenyls have been reported.[19] Therefore, it behooved us to investigate the possibility of an isotope effect on the rates of racemization of these compounds. To this end, samples were prepared in identical fashion as those for photodeuteration, except that non-deuterated solvent and sulfuric acid were used. The results are shown in table 4. This table can be directly compared with table 3 since the run numbers correspond to concurrent experiments,

Table I

Photoracemization of 6,6'-dinitrodiphenic acid, (V), in methanol at 25°C.

Run no.	Observed rate x 10^{21} (% racemization/quantum)	Φ (molecules/quantum)
1	1.51 ± 0.10	0.000822 ± 0.000019
2	1.32 ± 0.09	0.000718 ± 0.000010
3	1.86 ± 0.11	0.00101 ± 0.00002
4	1.58 ± 0.13	0.000860 ± 0.000071
5	1.83 ± 0.12	0.000996 ± 0.000006
Average	1.62 ± 0.11	0.000881 ± 0.000025

Table 2

Photoracemization and deuteration of 6,6'-dinitrodiphenic acid, (V), in glacial acetic acid-d_4 containing 0.2 mole sulfuric acid-d_2, at 25°C

	RACEMIZATION		DEUTERATION	
Run no.	Observed rate x 10^{21} (% racemization/quantum)	Φ (molecules/quantum)	Observed rate x 10^{21} (% deuteration/quantum)	Φ (deuterium/quantum)
1	1.12±0.04	0.000609±0.000019	2.06±0.51	0.00112±0.00028
2	1.11±0.02	0.000604±0.000004	2.12±0.14	0.00115±0.00008
3	1.65±0.21	0.000898±0.000011	3.02±0.17	0.00164±0.00009
4	1.35±0.04	0.000734±0.000009	2.43±0.04	0.00132±0.00002
5	1.48±0.05	0.000805±0.000005	2.79±0.09	0.00152±0.00005
Average	1.34±0.07	0.000730±0.000010	2.48±0.19	0.00135±0.00010

Table 3

Photoracemization and deuteration of 6,6'-dinitrodiphenic acid, (V), at 50°C

	RACEMIZATION		DEUTERATION	
Run no.	Observed rate x 10^{21} (% racemization/quantum)	Φ (molecules/quantum)	Observed rate x 10^{21} (% deuteration/quantum)	Φ (deuterium/quantum)
		Methanol		
1	2.95±0.16	0.00161±0.0009	-	-
2	2.16±0.08	0.00117±0.00004	-	-
Average	2.56±0.12	0.00139±0.00007	-	-
	Glacial acetic acid-d_4 containing 0.2 mole sulfuric acid-d_2			
1	2.81±0.10	0.00153±0.00005	3.62±0.34	0.0018±0.0002
2	2.31±0.45	0.00117±0.00023	3.50±0.11	0.0019±0.0001
Average	2.56±0.28	0.00135±0.00014	3.56±0.23	0.0019±0.0002

Table 4

Photoracemization of 6,6'-dinitrodiphenic acid, (V), in acetic acid-d_0 containing 0.2 mole sulfuric acid-d_0, at 25°C

Run no.	Observed rate x 10^{21} (% racemization/quantum)	Φ (molecules/quantum)
1	1.13±0.02	0.000615±0.000012
2	1.07±0.04	0.000582±0.000004
3	1.10±0.02	0.000598±0.000012
4	1.37±0.08	0.000745±0.000045
5	1.42±0.04	0.000770±0.000005
Average	1.22±0.04	0.000662±0.000016

the only exception being run 3.[a] Because of the erratic nature of the individual results, the apparent higher average rate of racemization in deuterated medium is not satistically significant.

Our preliminary results[b] had indicated that photoracemization was enhanced in substitution medium (i.e., acetic acid containing 0.2 molar sulfuric acid) although later definitive results show the opposite to be true.

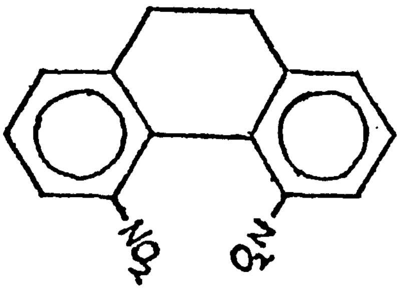
We investigated the photodeuteration-photoracemization of bridged biphenyl (VII) as a control experiment because non-bridged biphenyls that were protonated at the C_1-C_1' positions might have lower torsional

---

[a] These are included for statistical reasons. The counterparts of these two experiments were accidentally ruined before the analyses could be executed.

[b] We reported in 1970 that the rate of racemization was faster in acid than in methanol.[20] At that time there had been some scatter in the experimental data due to difficulties with the degassing of the acetic acid solutions (see experimental section for details). Least square values had been reported. Elimination of this problem has given the present results.

barriers. See figure 1. Also, because Zimmerman and Crumrine[16] observed the formation of a large proportion of benzvalene intermediates during their investigation of the photochemical racemization of 2,2'-diethyl-6,6'-dimethylbiphenyl; compound (VII) would also aid in ruling out the possibility of benzvalene formation, since by analogy with bridged biphenyl (III), it should not rearrange.



VII

The results from the photochemical racemization of (VII) are shown in table 5. It can be seen that the relative rates of racemization of this compound in the two solvents (i.e., lower rate in acid medium) are similar to those of compound (V).

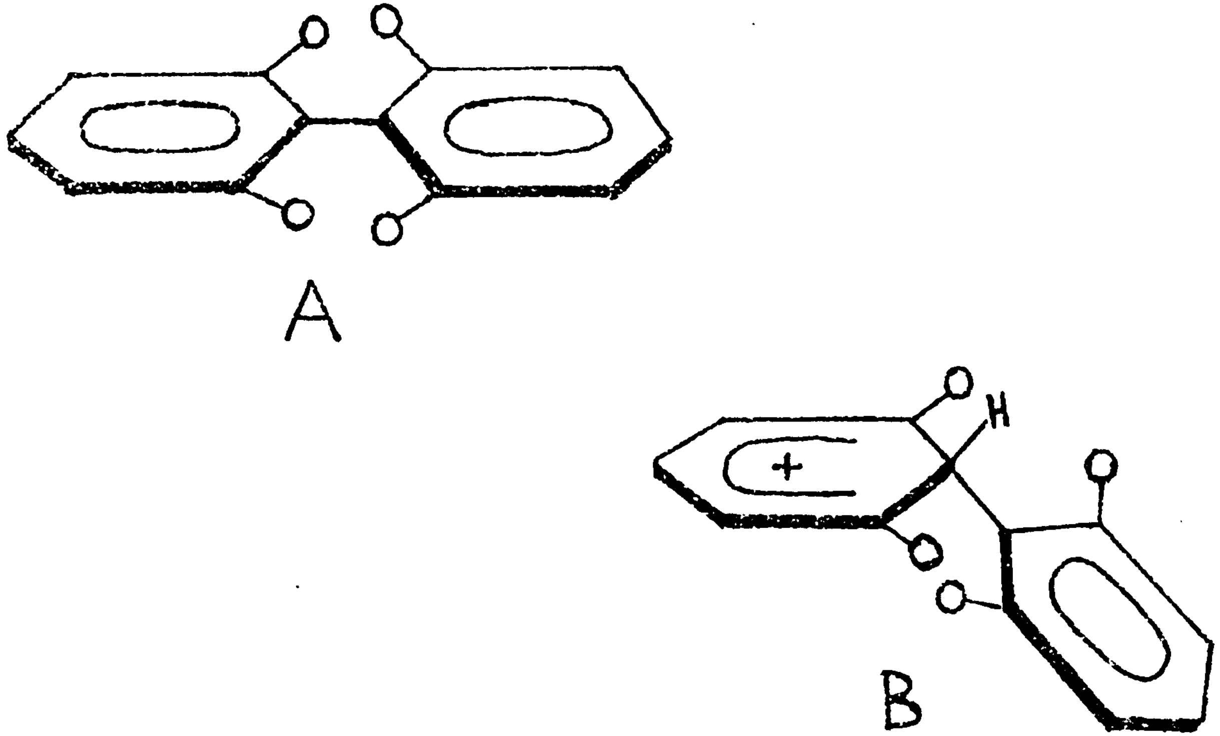


Figure 1. Transitions states to racemization of sterically hindered biphenyls: (A) unprotonated; (B) protonated at carbon 1.

Table 5

Photoracemization of (-)-9,10-dihydro-4,5-dinitrophenanthrene (VII) at 25°C

Solvent	Observed rate x 10^{21} (% racemization/quantum)	Φ (molecules/quantum)
Methanol	65.9±1.4	0.139±0.003
AcOD-d_4+0.2M D_2SO_4	34.9±0.7	0.0736±0.0016

The deuterium incorporation of this compound could not be monitored by N.M.R. because the sample concentration was very low (ca 0.003 milligram per milliliter). The solvent to compound peak ratio increased proportionately. At the instrument amplification necessary to detect the compound (Fourier transform, 1024 accumulations) the solvent acid peak was so broad that the aromatic peaks of the substrate appeared on its tail. Fold-over was also a problem.

Mass spectroscopy was also ineffective in detecting a trend in deuterium incorporation of compound (VII). In this case, the inability to detect a trend could be due to low deuterium incorporation since the maximum irradiation time was only 2.0 hours. Scrambling of the isotope is also a possibility.

The irradiated samples of compounds (V) and (VII) were recovered and very carefully inspected by U.V., O.R.D.,[a] and I.R. (KBr pellet)[b]

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[a] O.R.D., in spite of its ability to detect very small quantities of material is not an ideal analytical tool because it can only detect optically active compounds. Some, or even all, of rearranged pro-

spectroscopy. In addition, compound (V) was inspected by N.M.R. and T.L.C. No new T.L.C. spots or new absorption peaks, indicating skeletal rearrangements, were detected. This proves that the observed changes in optical rotation are due solely to inversion.

Since deuteration of the electronic ground state (dark reaction) of biphenyls does not occur,[7,21] but deuterium <u>is</u> incorporated by photochemical activation, it became of interest to see what influence, if any, the presence of acid would have on the excited state. Also, because Havinga and coworkers[22] observed that the efficiency of fluorescence quenching of substrate was dependent upon the concentration of substituting species, it became of interest to determine the quenching efficiency of sulfuric acid on the compounds here studies. The results are shown in figures 2 through 8.

ducts, if any, could be optically inactive.
Vapor phase chromatography could not be used in the case of compound (V) because of the high melting point. Its use was impractical in the case of (VII) because of concentration and quantity of material available.

[b] Several samples were combined, where necessary.

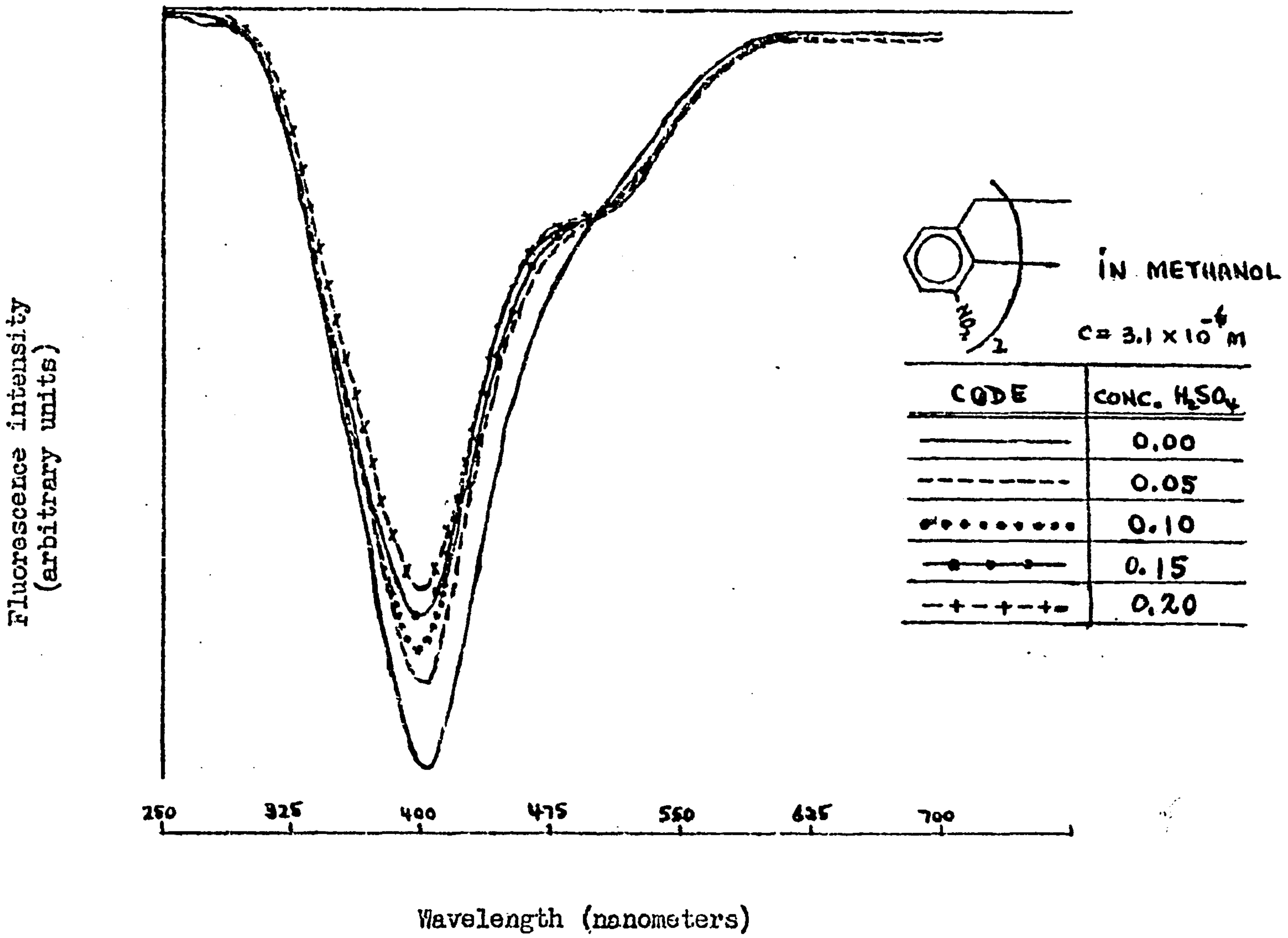


Figure 2. Effect of sulfuric acid concentration on the fluorescence spectrum of 9,10-dihydro-4,5-dinitrophenanthrene (VII) in methanol. c= 3.1×10^{-6}M.

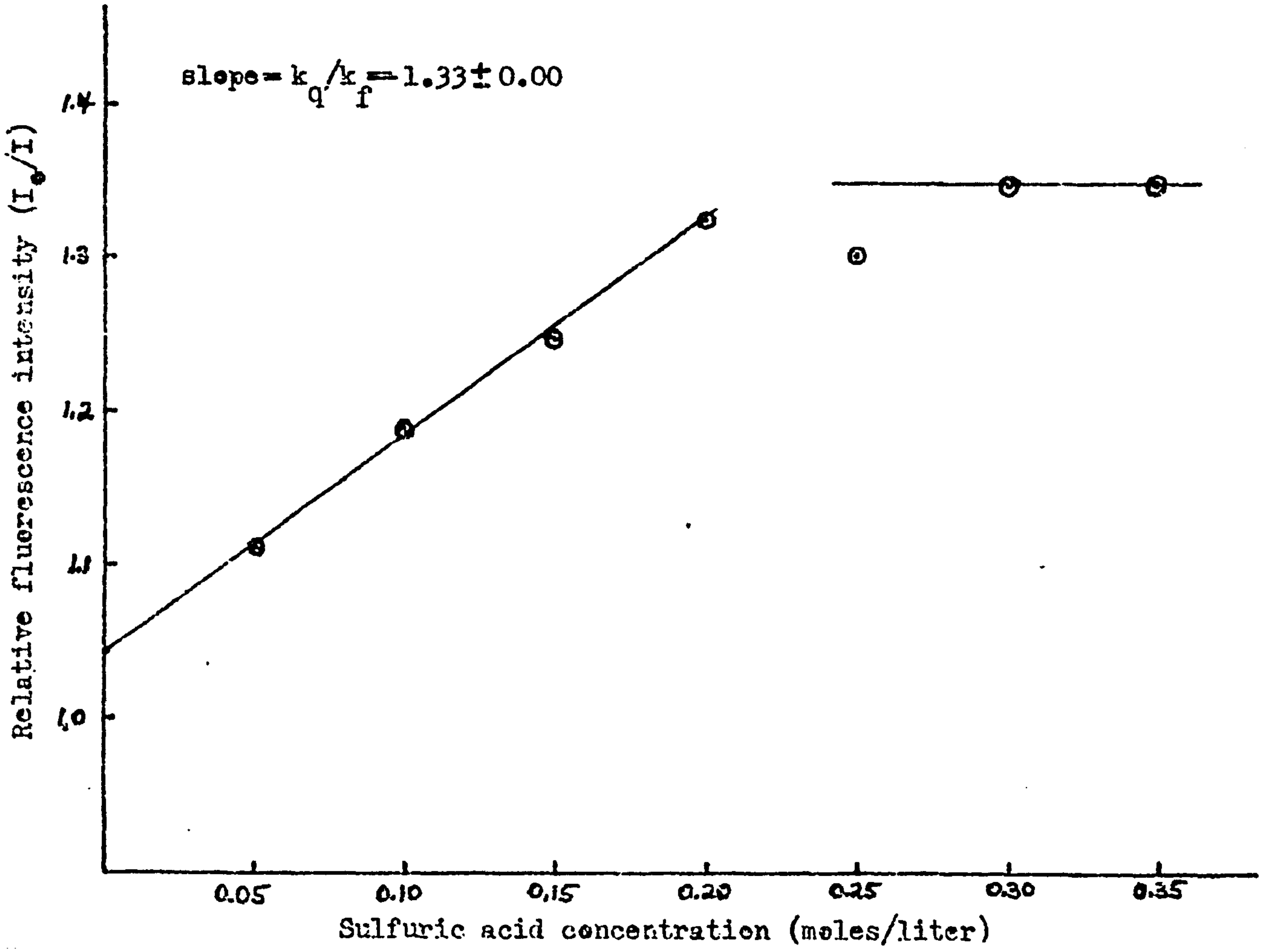


Figure 3. Fluorescence quenching of 9,10-dihydro-4,5-dinitrophenanthrene, (VII) in methanol. c= 3.1 x 10^{-6}M.

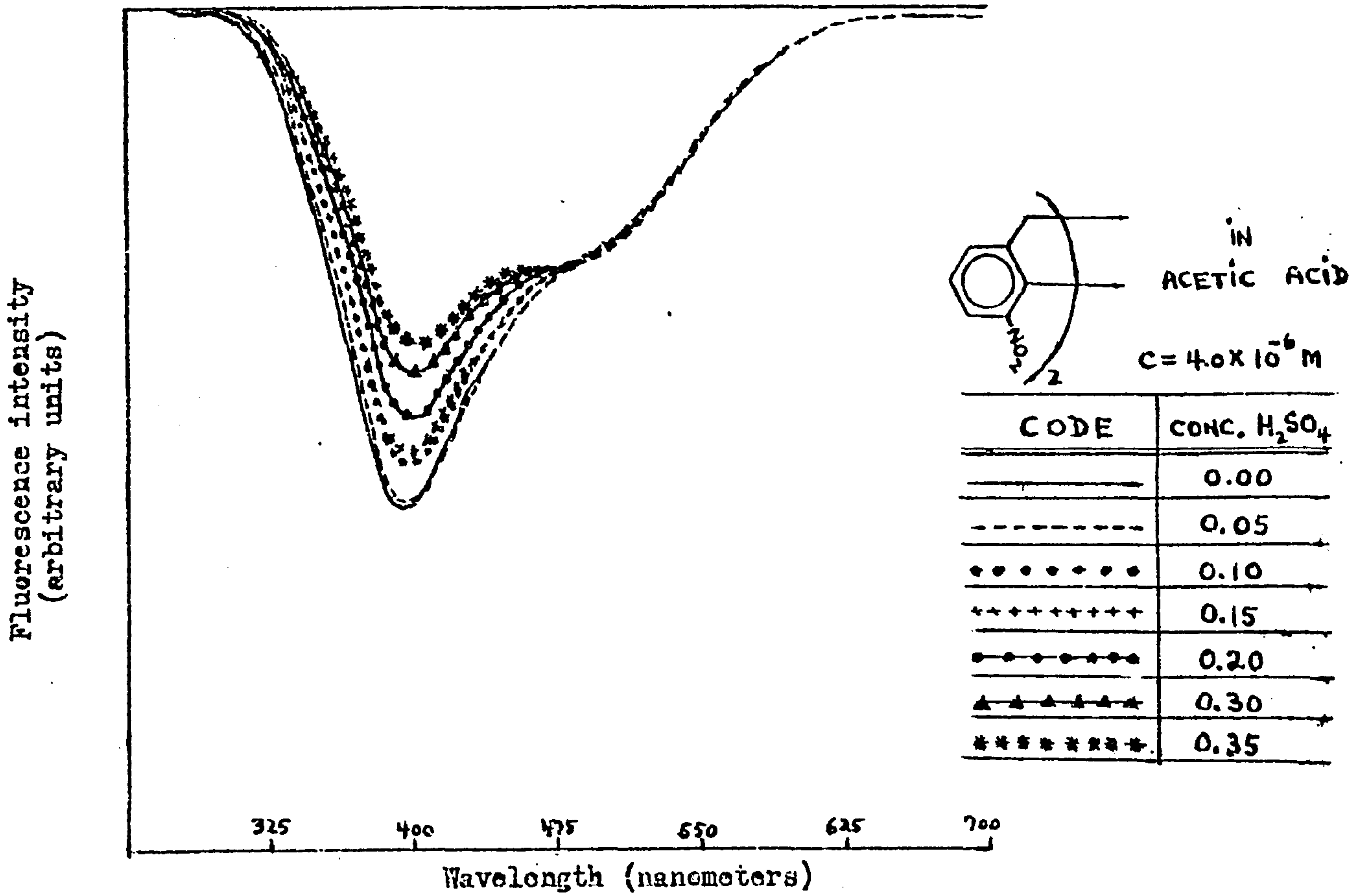


Figure 4. Effect of sulfuric acid concentration on the fluorescence spectrum of 9,10-dinydro-4,5-dinitrophenanthrene, (VII), in glacial acetic acid. 4.0 x 10^{-6}M.

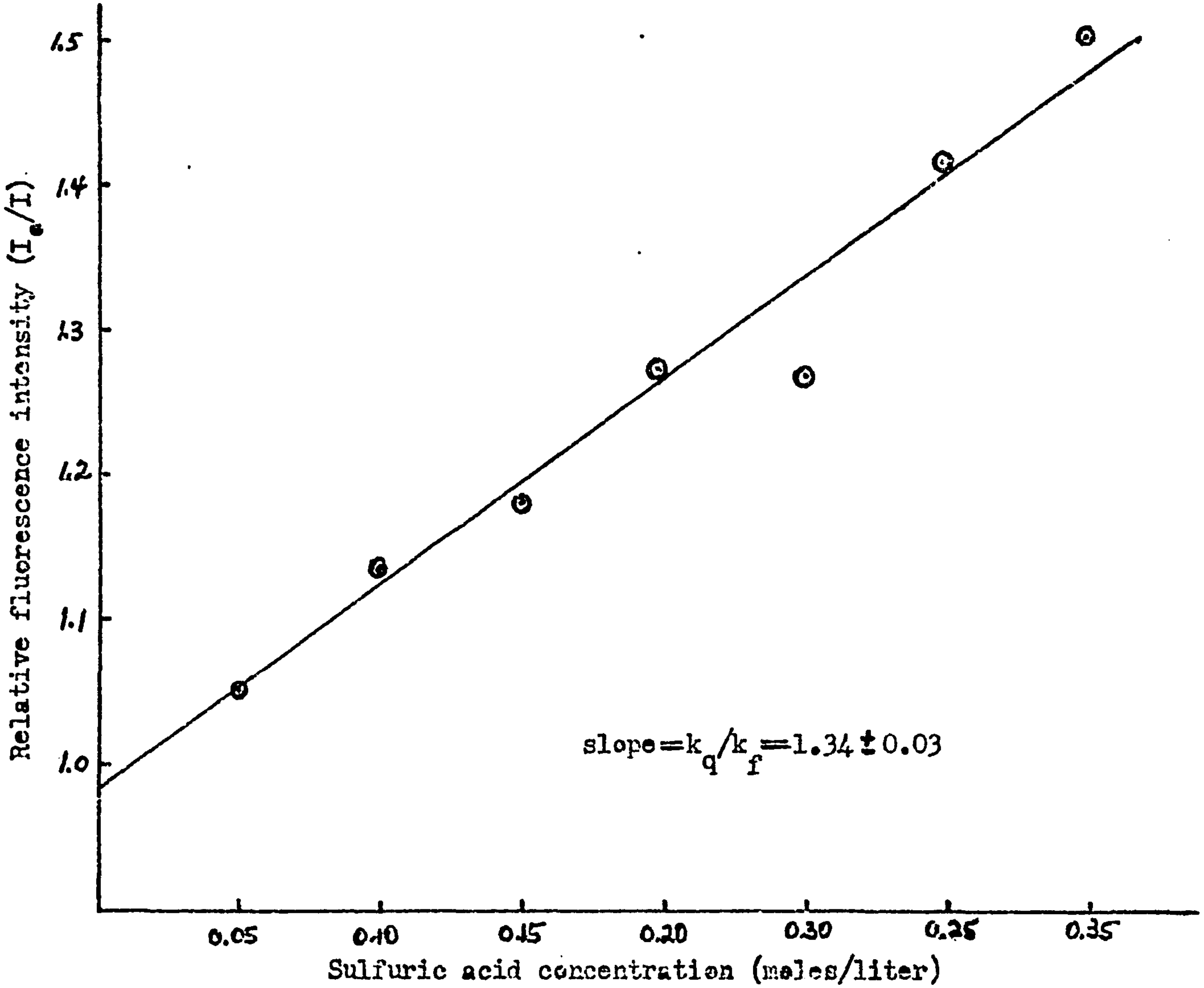


Figure 5. Fluorescence quenching of 9, 10-dihydro-4, 5-dinitrophenanthrene (VII) in glacial acetic acid. c= 4.0 x 10^{-6}M.

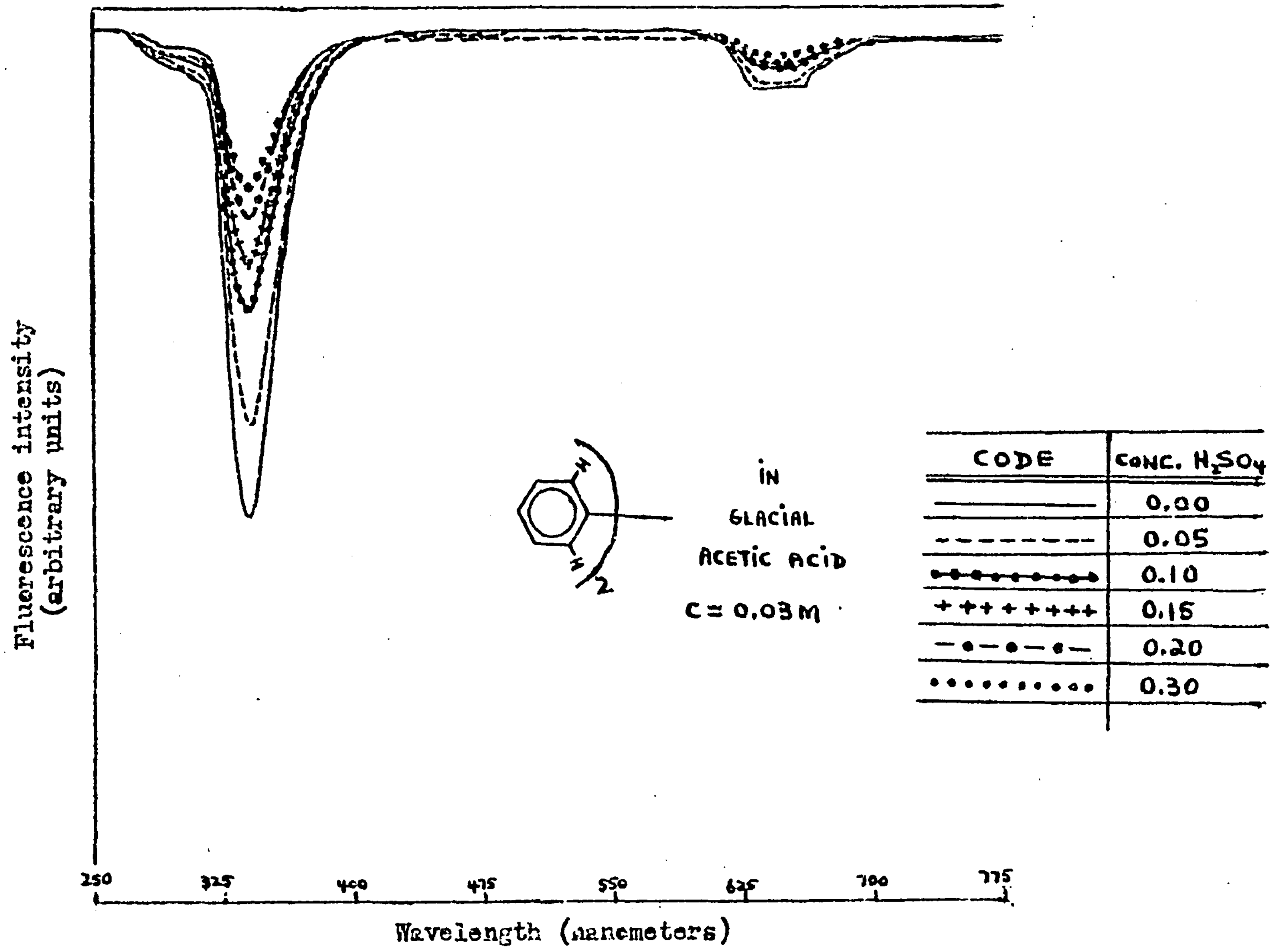


Figure 6. Effect of sulfuric acid concentration of the fluorescence spectrum of biphenyl (IX) in glacial acetic acid. c= 0.03M.

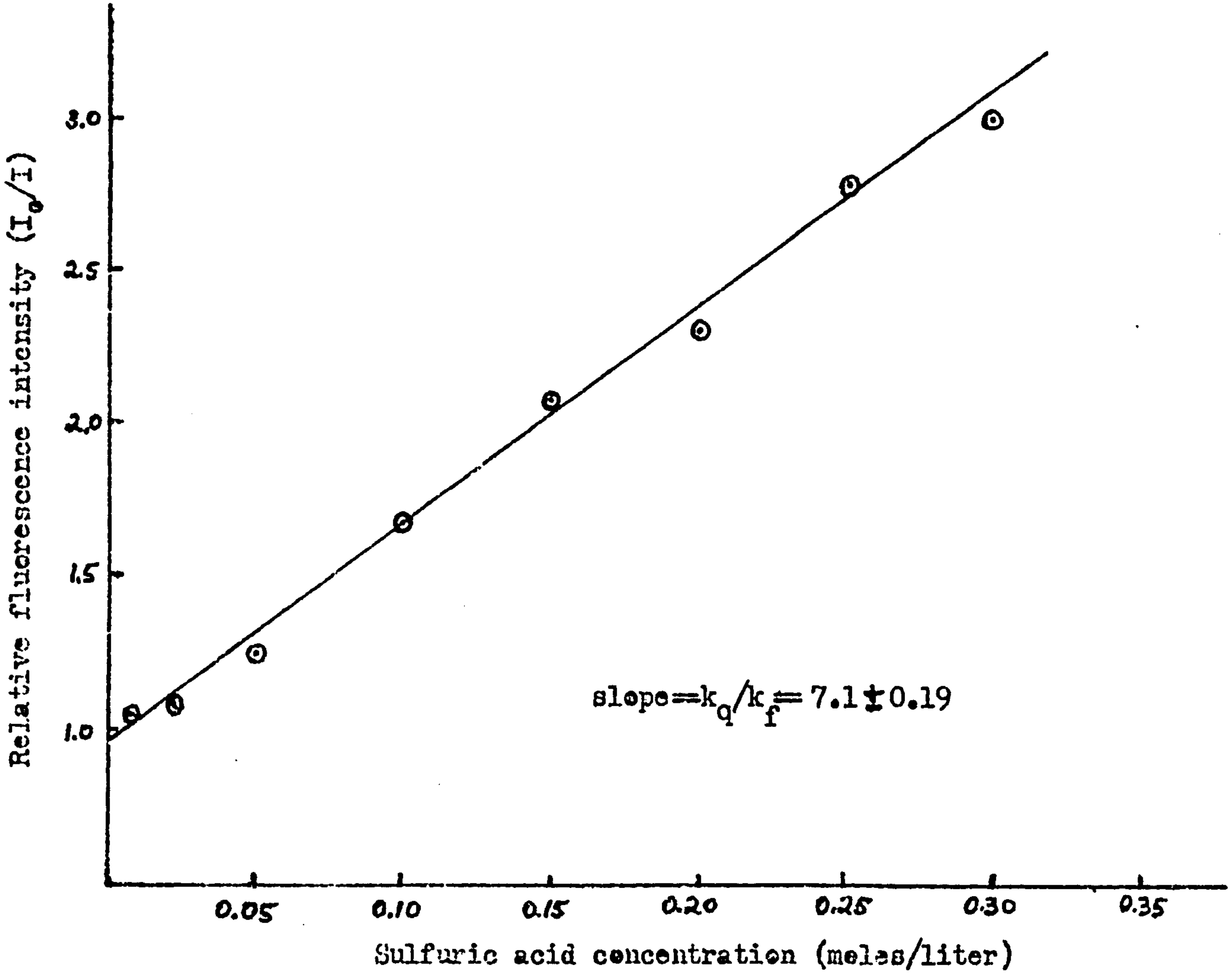


Figure 7. Fluorescence quenching of biphenyl, (IX), in glacial acetic acid. c= 0.03M.

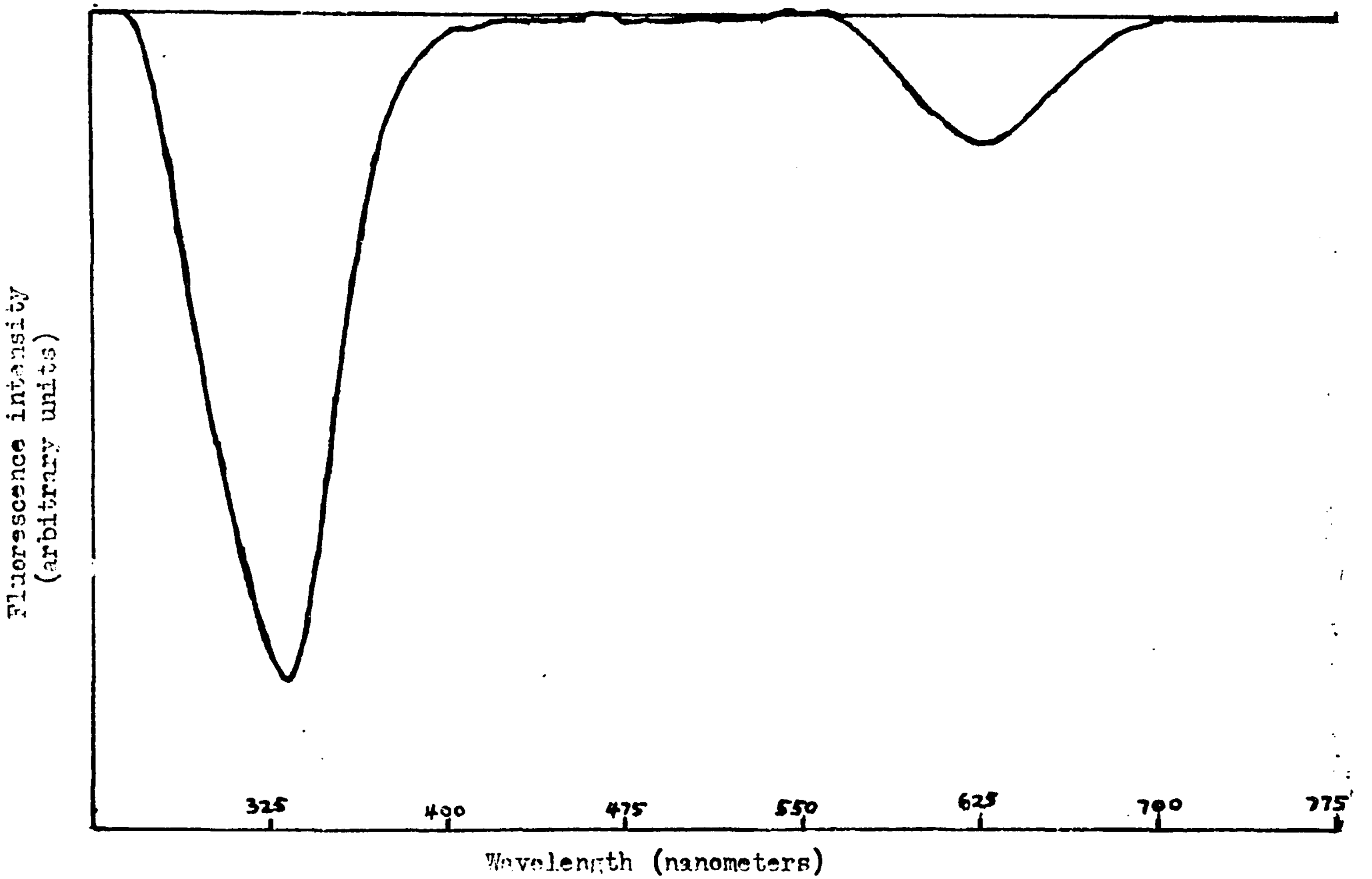


Figure 8. Fluorescence spectrum of biphenyl, (IX) in methanol solution.
c= 2.0 x 10^{-5}M.

The fluorescence of (V) was too weak, even in methanol, to allow the acid quenching to be determined with any reasonable degree of accuracy. Fluorescence of this compound in glacial acetic acid was practically absent (i.e., at least ten-fold less than in methanol). As an approximation, the acid fluorescence quenching of unsubstituted biphenyl (IX) was done instead. Also, acid quenching of (IX) in methanol was negligeable and could not be reliably separated from instrumental fluctuations. The spectrum in methanol is reproduced here simply for comparison purposes. Observe the large difference in substrate concentration between figures 6 and 8. Both were recorded with identical instrument settings. This indicates a very high efficiency of quenching in acetic acid.

Because of the appearance of a second band in the fluorescence spectrum of compound (VII) in the presence of acid, it seemed advisable to supplement the fluorescence studies with an inspection of the acid dependence of the ultraviolet spectrum. The results are shown in figures 9 through 14.

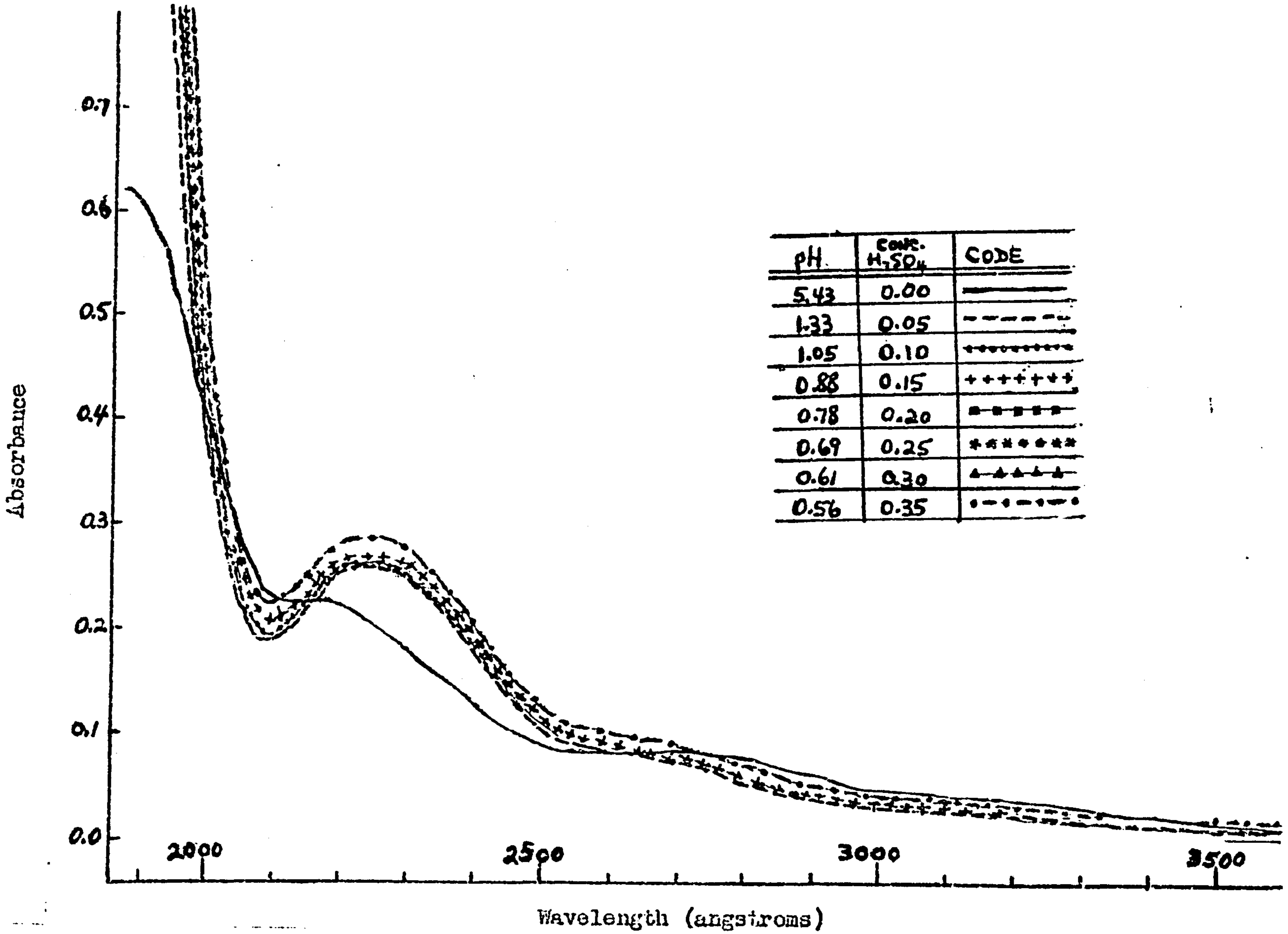


Figure 9. Effect of sulfuric acid concentration on the ultraviolet spectrum of 6, 6'-dinitrodiphenic acid (V) in distilled water. c= 1.0 x 10^{-5}M.

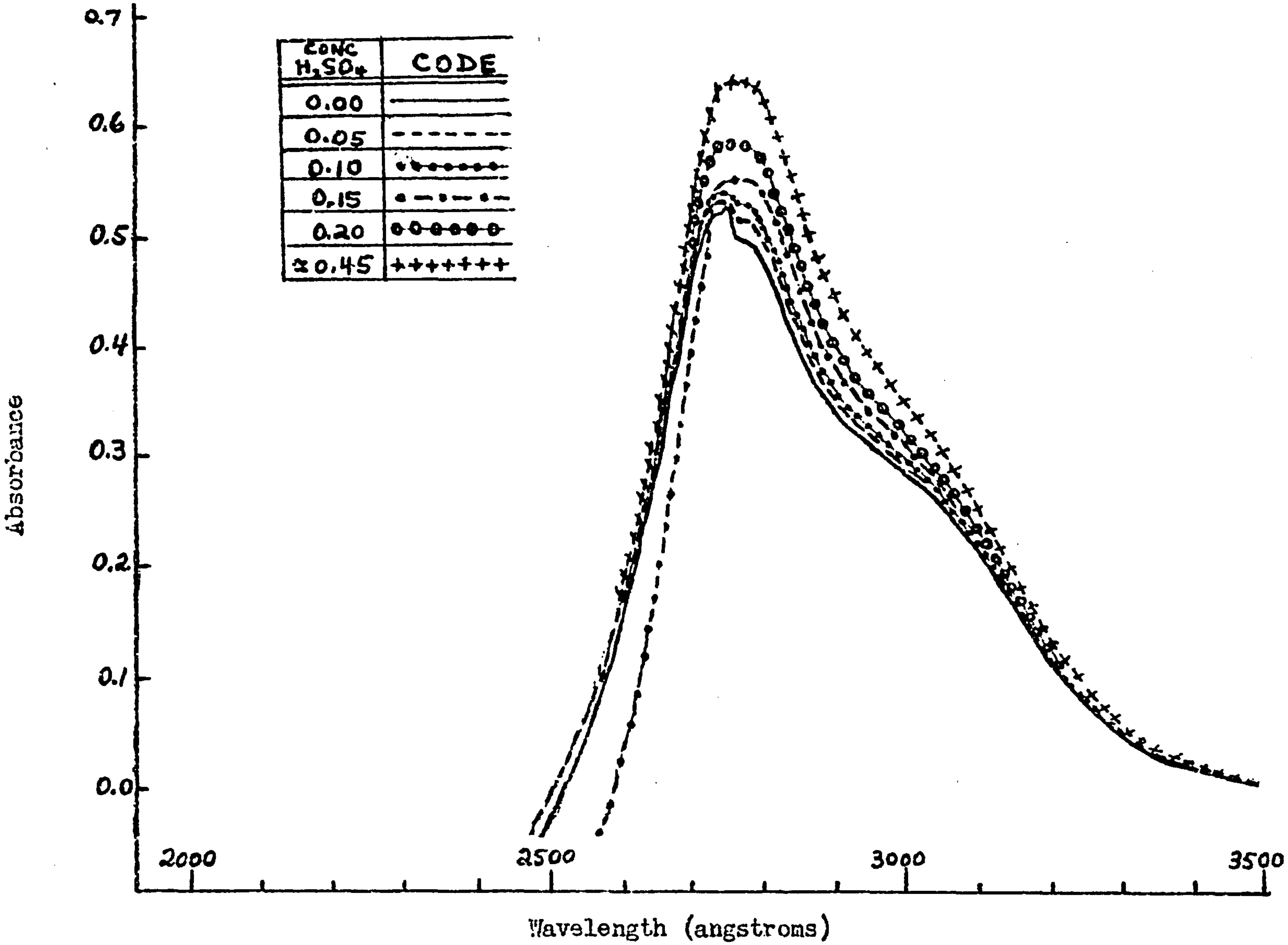


Figure 10. Effect of sulfuric acid concentration on the ultraviolet spectrum of 6, 6'-dinitrodiphenic acid (V) in glacial acetic acid. c= 5.0 x 10^{-5}M.

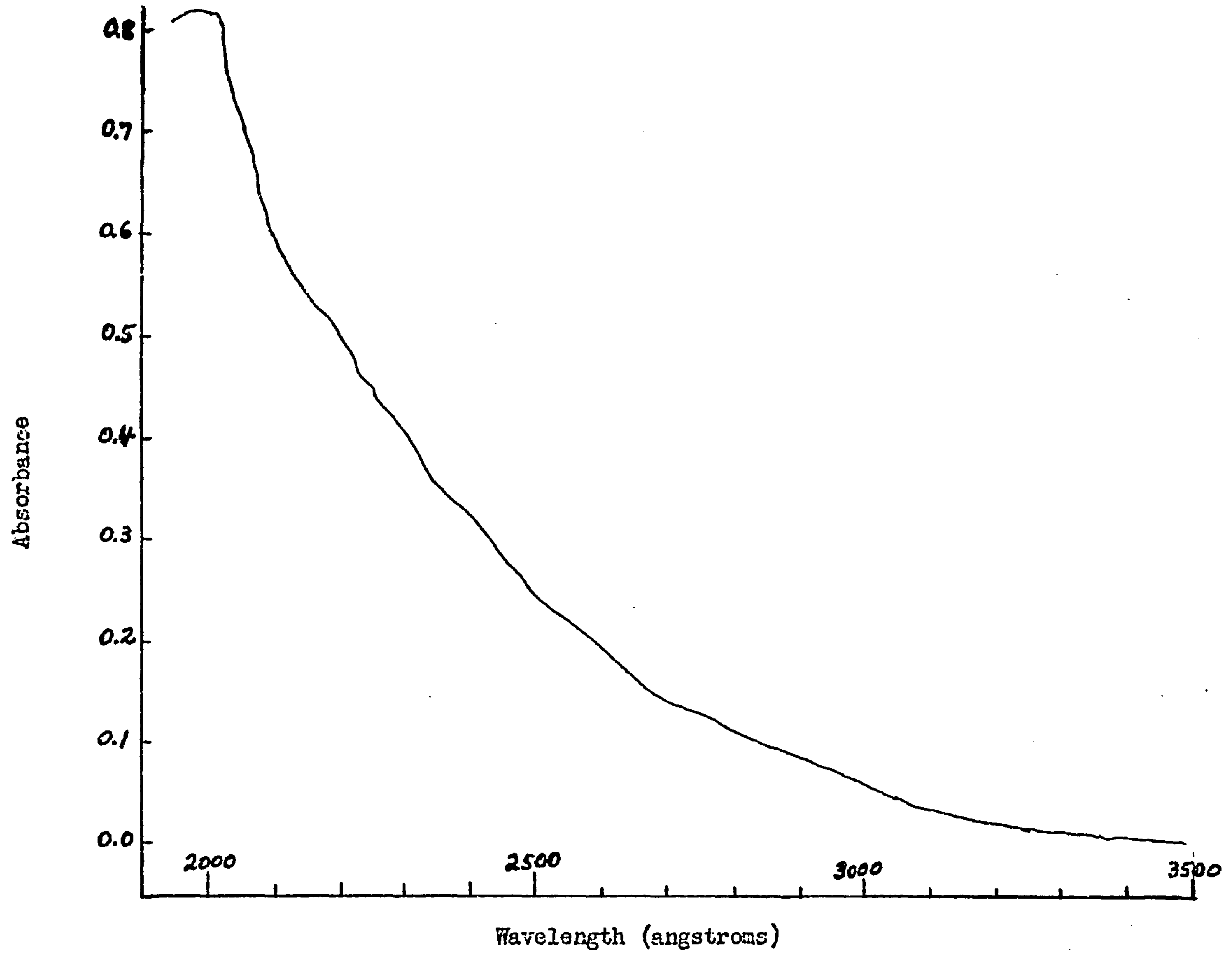


Figure 11. Ultraviolet spectrum of 9,10-dihydro-4,5-dinitrophenanthrene (VII) in methanol. c= 1.2 x 10^{-7}M.

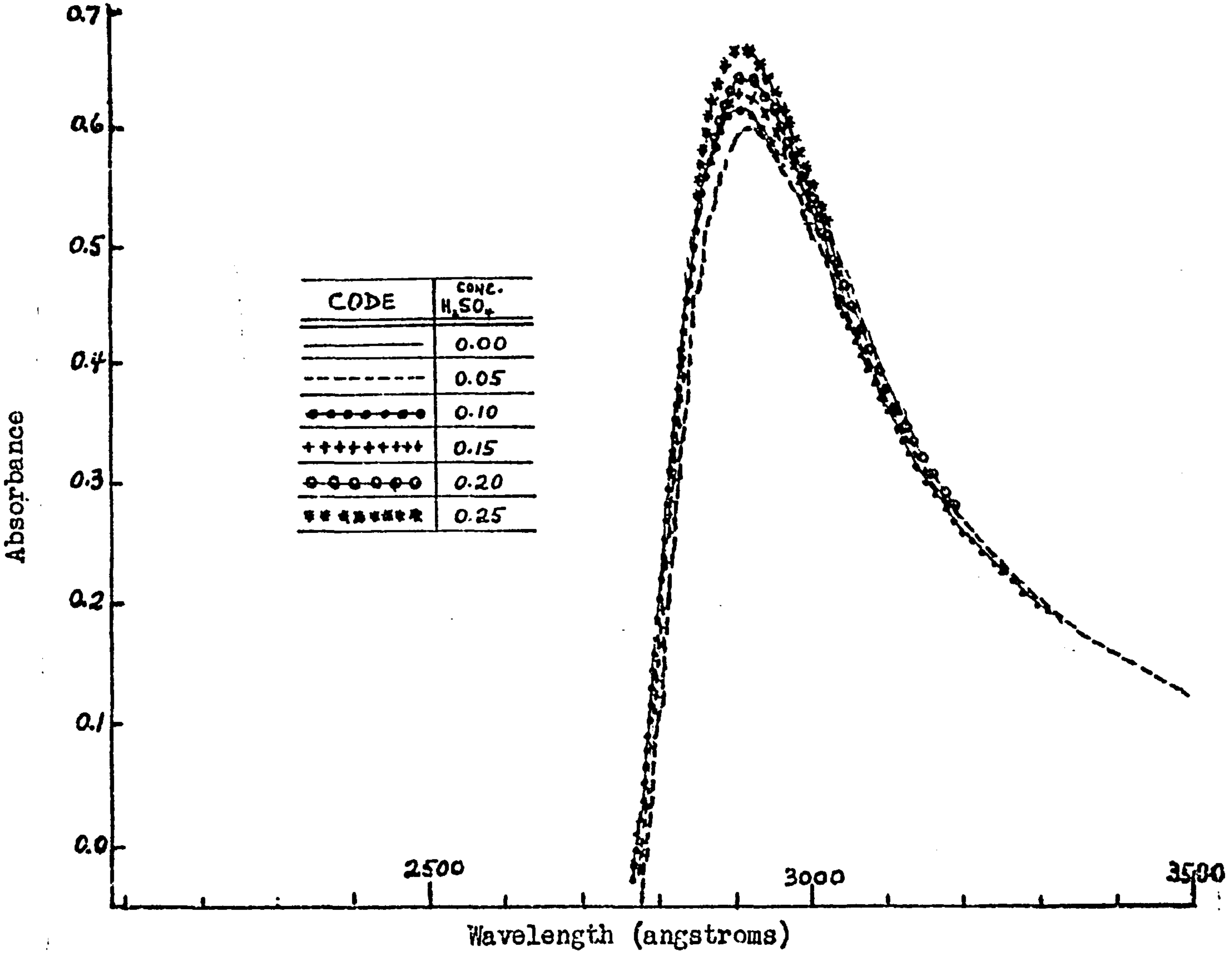


Figure 12. Effect of sulfuric acid concentration on the ultraviolet spectrum of 9,10-dihydro-4,5-dinitrophenanthrene (VII) in glacial acetic acid. c= 2.3 x 10^{-6}M.

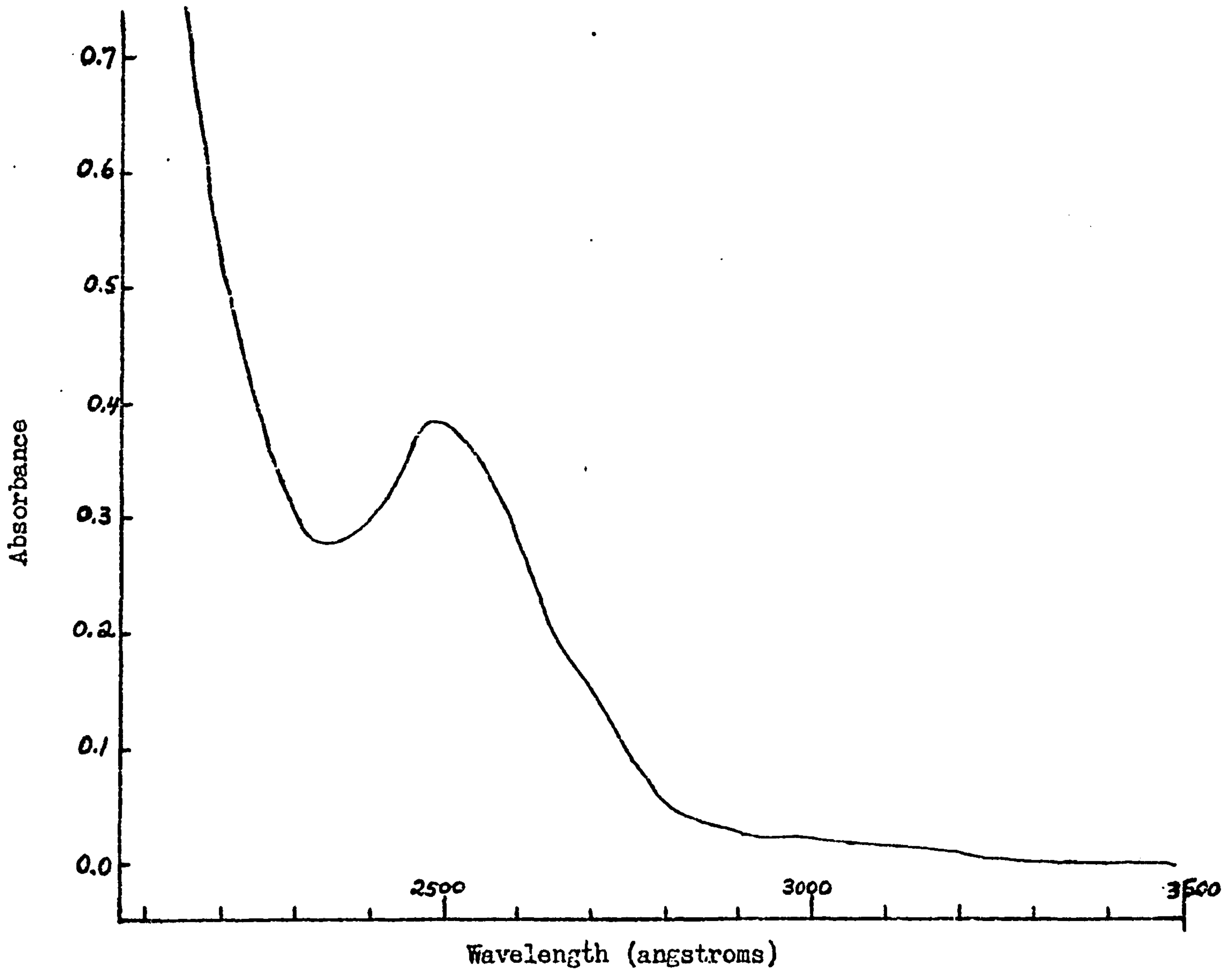


Figure 13. Ultraviolet spectrum of biphenyl (IX) in methanol. c= 1.0 x 10^{-5}M.

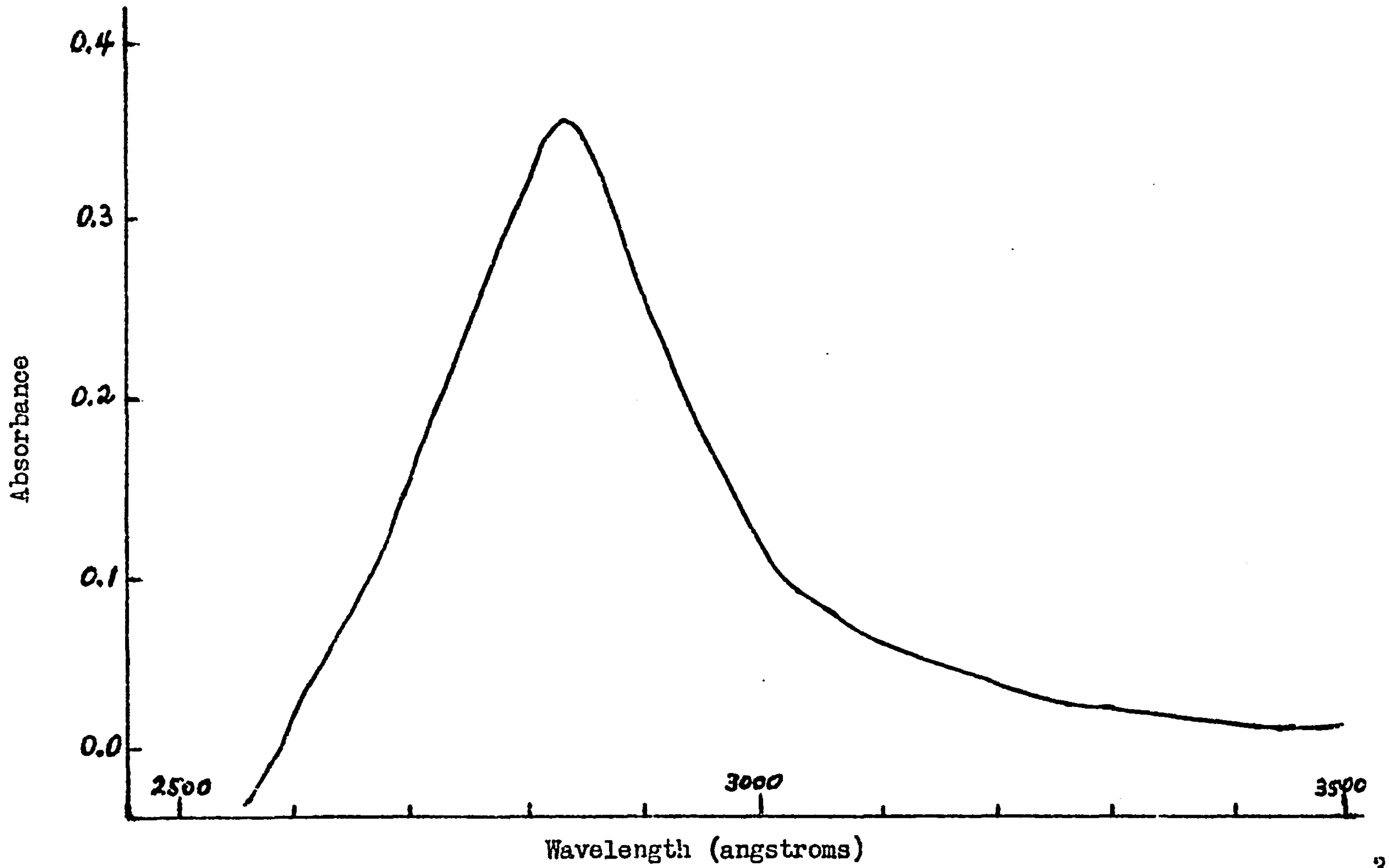


Figure 14. Ultraviolet spectrum of biphenyl (IX) in glacial acetic acid. c= 1.5 x 10^{-3}M.

There was no significant effect, upon addition of acid, on the U.V. spectrum of (IX) in either methanol or acetic acid. Compound (VII) having only end absorption maximum in the U.V., did not show acid dependence in methanol.

The apparent absence of instrument response in the U.V. spectra between approximately 2500 Å and 2000 Å, in the case of acetic acid solutions, is probably due to large absorption by solvent in the reference cell (made possible by the very small difference in specific volumes between reference and sample cells).

Figures 9, 10 and 12 show an increase in intensity at the absorption maximum as the sulfuric acid concentration is increased. Since two functional groups are involved (i.e., carboxyl and nitro) it was desirable to determine which functional group was responsible for the observed increase in intensity. To this end, the U.V. spectrum of nitrobenzene (X) and of benzoic acid (XI) in distilled water were inspected as a function of sulfuric acid concentration. These results are shown in figures 15, 16 and 17. While, in distilled water, nitrobenzene does not seem to

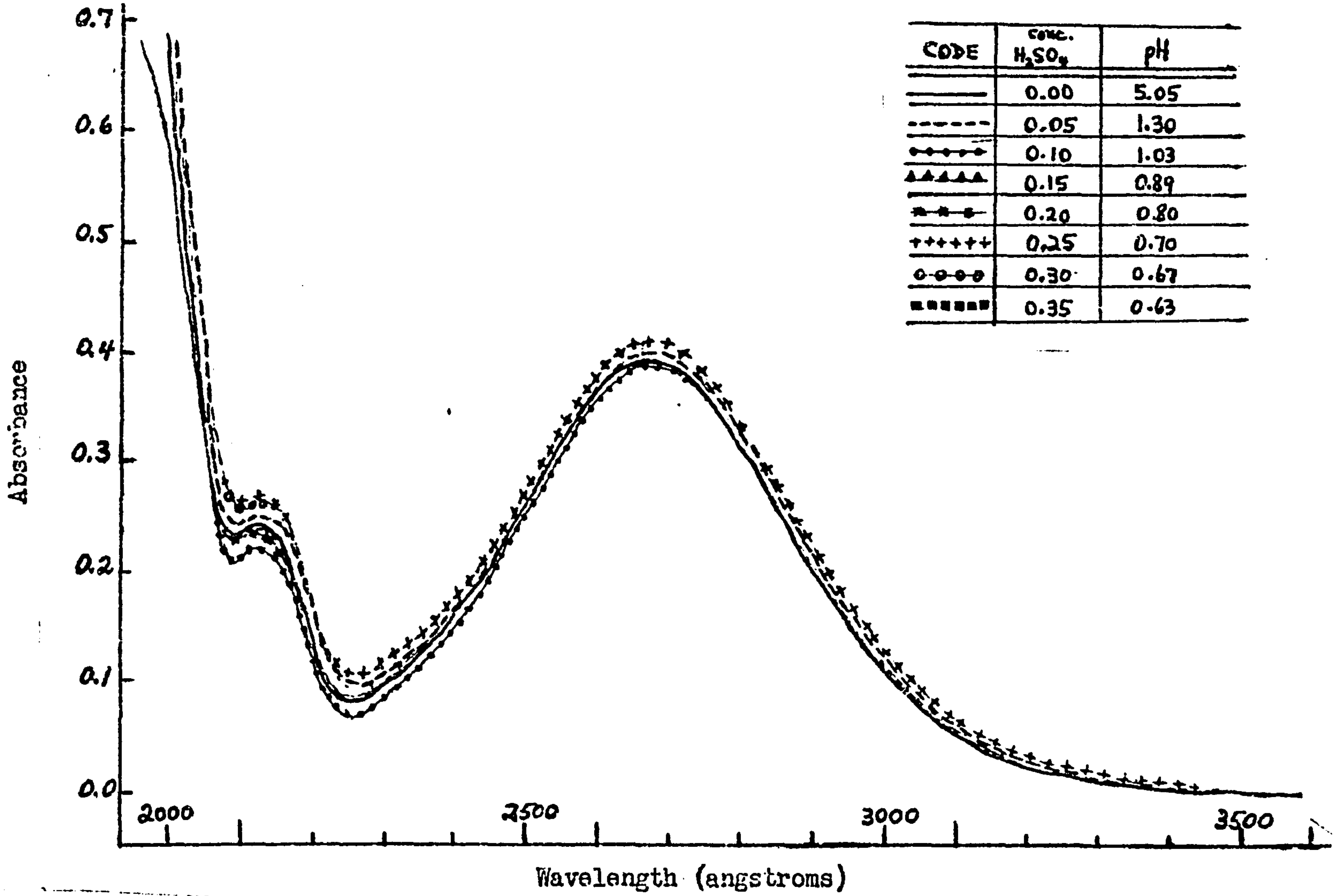


Figure 15. Effect of sulfuric acid concentration on the ultraviolet spectrum of nitrobenzene (X) in distilled water. c= 5 x 10^{-5}M.

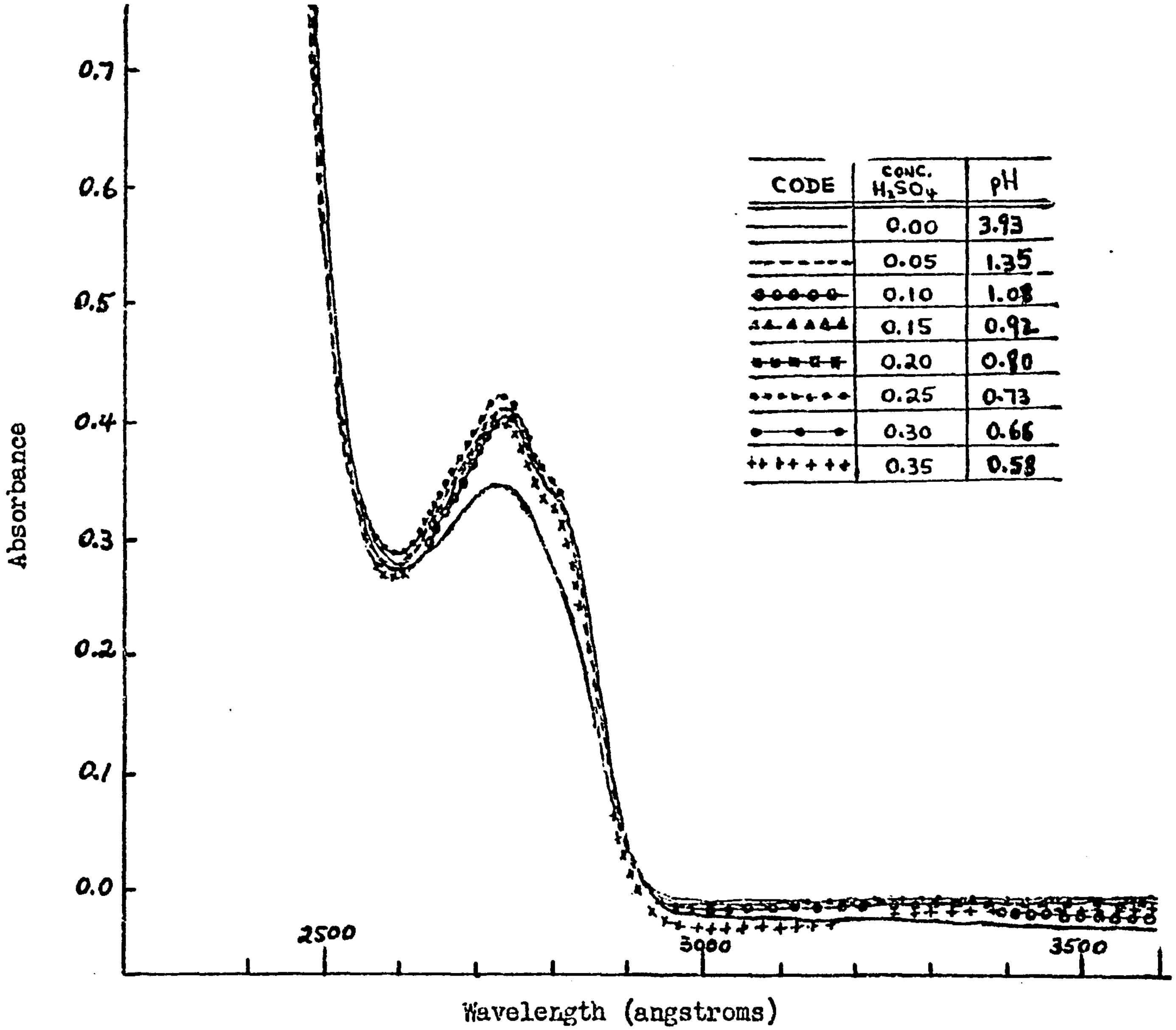


Figure 16. Effect of sulfuric acid concentration on the ultraviolet spectrum of benzoic acid (XI) in distilled water. c= 4.3 x 10^{-4}M.

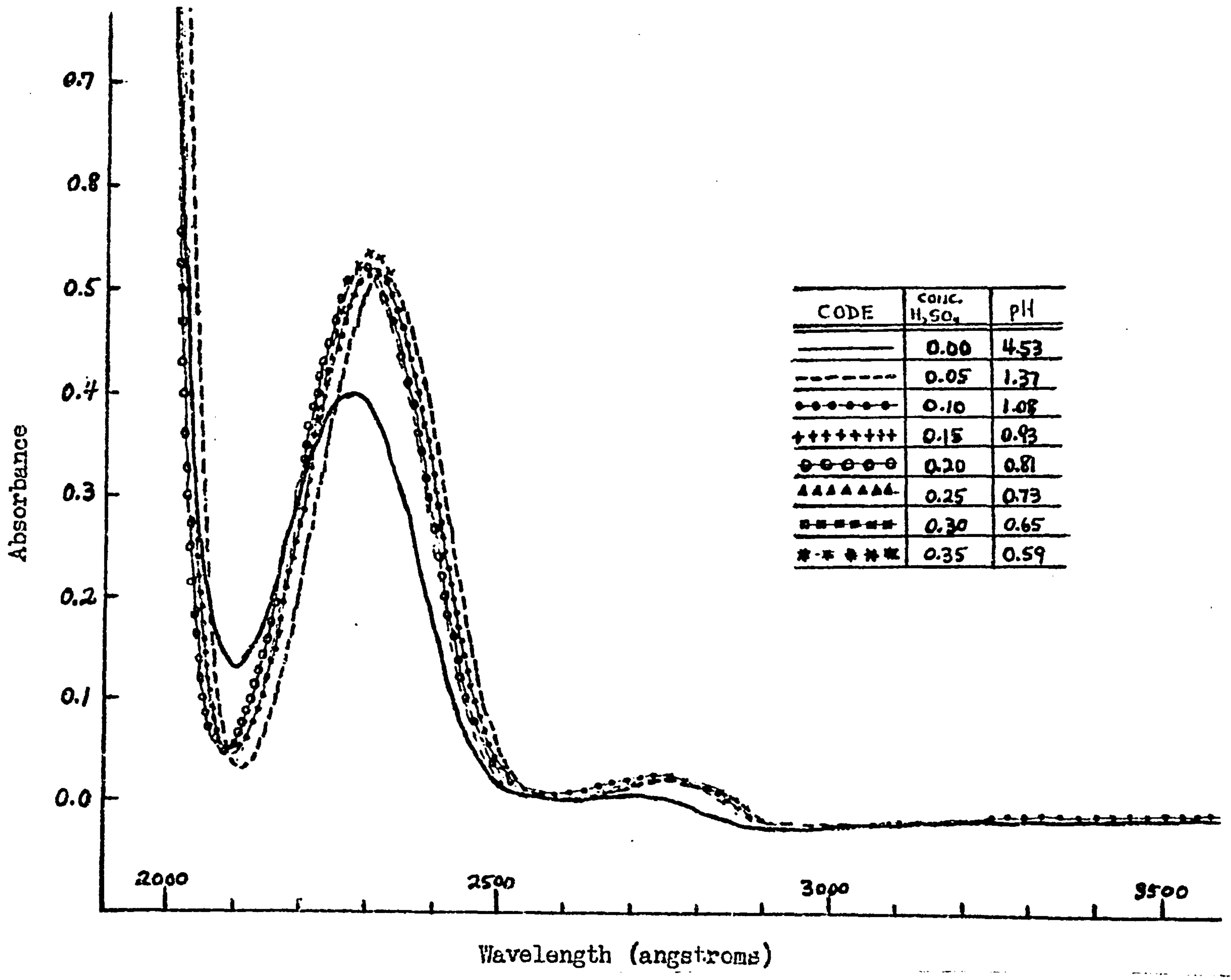


Figure 17. Effect of sulfuric acid concentration on the ultraviolet spectrum of benzoic acid (XI) in distilled water. c= 4.3 x 10^{-5}M.

show an increase in intensity as the sulfuric acid concentration is increased (figure 15), benzoic acid (figures 16 and 17) does show such an increase. As a matter of fact, the effect of acid on the U.V. spectrum of this latter compound in distilled water identically parallels the behavior of 6,6'-dinitrodiphenic acid (V). (See figure 9).

Outside of the biphenyl moiety, the only functional group in 9,10-dihydro-4,5-dinitrophenanthrene (VII) that is potentially reactive thermally with acid is nitro. Since (VII) shows an increase in intensity (figure 12) of the absorption maximum in acetic acid solution as the sulfuric acid concentration is increased, but such an increase is not evident in the U.V. spectrum of nitrobenzene in distilled water, it was desirable to reinvestigate the acid dependence of the U.V. spectrum of this latter compound in acetic acid solutions. The results are shown in figure 18. Figure 18 shows that indeed an increase in intensity of the absorption maximum is observed.

Finally, since the rate of racemization seemed to decrease in the presence of acid, an attempt was made to monitor the quenching efficiency.

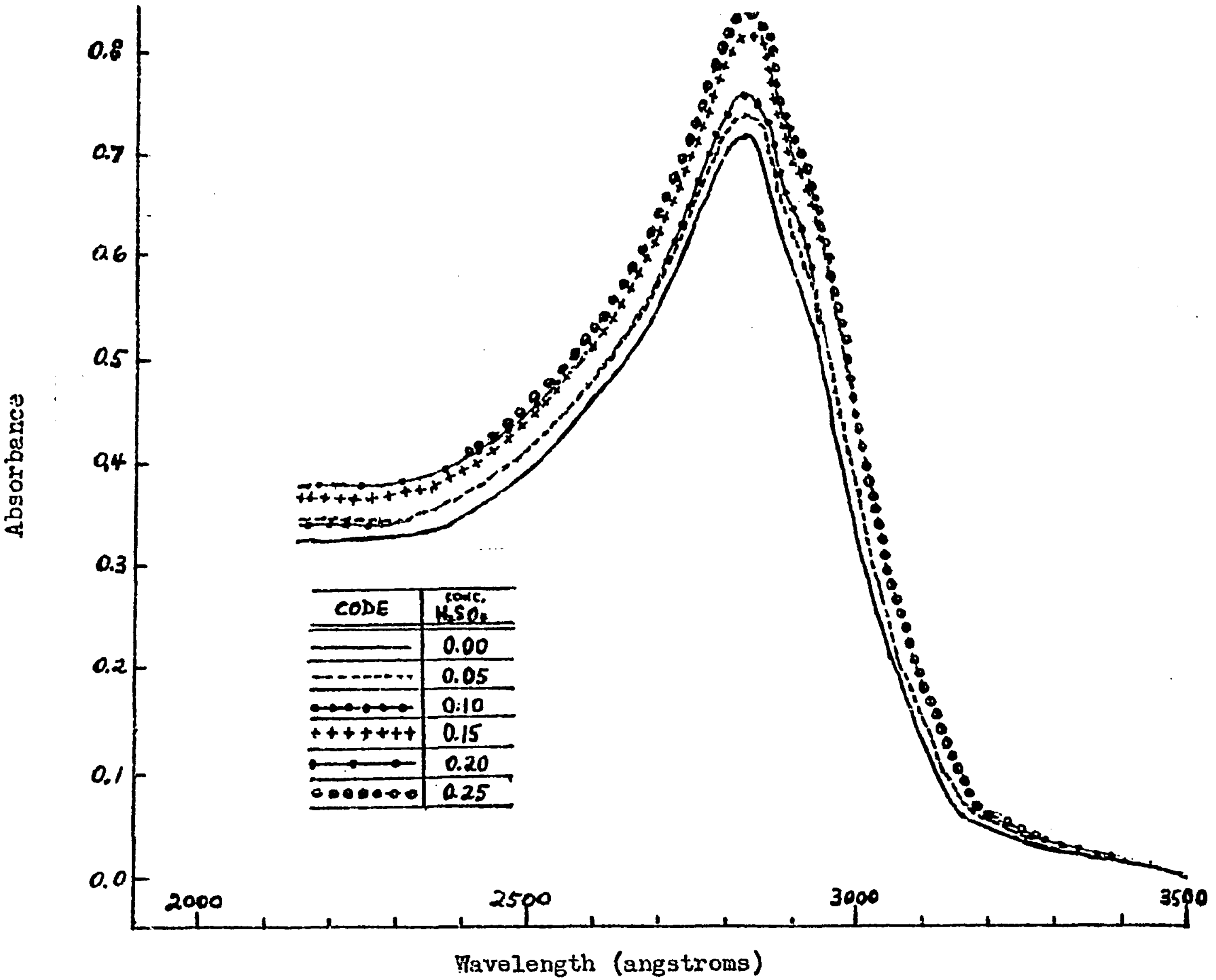


Figure 18. Effect of sulfuric acid concentration on the ultraviolet spectrum of nitrobenzene (X) in glacial acetic acid. c= 3.3×10^{-5}M.

Samples were prepared containing the usual fixed concentration of substrate, but the sulfuric acid concentration was varied from 0.00 to 0.25 molar (in one run, up to 0.30 molar) in increments of 0.05 molar. The results are shown in table 6.

Ignoring experimental scatter, the rates of racemization for each of the four runs in table 6 seem to be constant, essentially, for all samples within a given run, regardless of sulfuric acid concentration. Likewise, it can be seen from table 6 that, regardless of sulfuric acid concentration, the rates of deuterium incorporation are, for all practical purposes, constant for all samples of a given run. In other words, neither the rates of racemization or of deuteration show any increasing or decreasing tendencies when the sulfuric acid concentration is varied. The scatter in the data of table 6 is suspected to be due mainly to solvent loss during degassing. See experimental section for details.

Table 6

Effect of sulfuric acid concentration on the photoracemization and deuteration of 6,6'-dinitrodiphenic acid, (II), in glacial acetic acid.

(0.03 molar concentration)

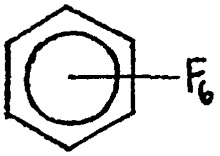
	RUN 1 (119.2 HRS)*	RUN 2 (155.2 HRS)*			RUN 3 (121.0 HRS.)*			RUN 4 (117.0 HRS.)*
SULFURIC ACID CONCENTRATION (moles/LITER)	% RACEMIZATION	% RACEMIZATION	% DEUTERATION	%D / % RAC	% RACEMIZATION	% DEUTERATION	%D / % RAC	% RACEMIZATION
0.00	5.14	7.14	13.4	1.88	5.37	8.75	1.63	3.95
0.05	4.58	6.01	11.3	1.88	4.37	8.13	1.86	4.13
0.10	5.06	6.48	9.81	1.51	5.14	9.56	1.86	4.00
0.15	4.64	5.04	**	--	5.16	9.60	1.86	4.29
0.20	4.33	6.25	10.8	1.73	4.79	8.38	1.75	4.18
0.25	4.66	5.87	10.7	1.82	5.50	9.35	1.70	4.32
0.30	—	—	—	—	5.51	10.3	1.87	—
Averages	4.74 ± 0.25	6.13 ± 0.50	11.2 ± 0.92	1.76 ± 0.12	5.12 ± 0.31	9.01 ± 0.65	1.79 ± 0.08	4.15 ± 0.12

* Lamp output was not monitored

** Sample tube accidentally destroyed

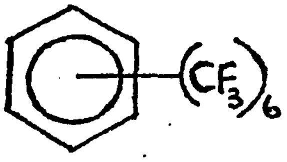
DISCUSSION

Benzvalene or other similar types of intermediates are known to decompose reversibly to yield, not one, but several isomers.[16,23] It is highly improbable that all isomers show identical spectroscopic behavior. In most cases where such isomerizations have been reported, at least one alkyl substituent was present on the ring. So far as we know, there are only two examples of such isomerizations in which only electron withdrawing groups were involved, namely,[23d,24]



XII

and



XIII

However, both of these compounds are per-substituted (i.e., very symmetrically substituted. Although the electron densities of the aromatic carbons are unquestionably decreased in these compounds, relative to unsubstituted benzene, there is no reason to expect the relative electron distributions to be any different, either in the ground state or in the excited state.

The evidence accumulated thus far in the literature indicates that the stability of the benzvalene type intermediates increases in direct proportion to the number of alkyl or electron donating substituents on the ring.[25] It is quite possible, in the case of unsymmetrically substituted benzenes (or biphenyls) where only electron withdrawing groups are present, that the associated benzvalene intermediates be so destablized that alternate mechanistic routes be more energetically favored. For similar reasons, it seems unlikely that bridged biphenyl (VII) would more readily yield a benzvalene intermediate than its analog compound (III). As mentioned earlier, (III) was found to photoracemize cleanly.[9]

It should be observed that based upon the known stability tendencies of substituted benzvalene intermediates, as noted above, the compounds studied by Zimmerman and Crumrine[16] (i.e., 2,2'-diethyl-6,6'-dimethylbiphenyl) is ideally suited for photochemical rearrangements. In these investigators own words, ". . . most of the benzvalene molecules formed proceed onward to rearrangement products rather than back to racemized reactant." There is no reason why we should expect benzvalene intermediates, once formed from the compounds here studied, to behave any differently. Therefore, in the case of the compounds studied by us, reversible formation of a benzvalene intermediate which reduces the internal rotational barrier, with subsequent reformation of the original compound only, does not seem to us a reasonable possibility.

Of great significance to the mechanism of racemization of the compounds here studied is the fact that our average quantum yields are of the same order of magnitude as those obtained by Zimmerman and Crumrine in acid media, conditions under which isomerizations via the benzvalene route were found to be completely suppressed. However, like the aformentioned investigators, we too observed a decrease in the rate of racemization in the presence of acid. In the case of compound (V) the average decrease in rate of racemization in the presence of acid was 17% while for compound (VII) it was 47%.

If, as reported by Zimmerman and Crumrine, most of the benzvalene intermediate rearranges, we should expect, in the case of compound (V) approximately a 17% isomeric product formation. This should have been easily detected, barring the formation of a very large number of isomers such that their individual concentrations were undetectable, again, unlikely. We could detect no isomers. It is reasonable, then, in our case, to assume that the acid is quenching the inversion, not an isomerization.

The fluorescence spectrum of compound (VII) as a function of sulfuric acid concentration (figures 2 and 4) reveals the following: a) there is a single peak in the absence of acid, b) the intensity of this peak decreases linearly with increase in sulfuric acid concentration, c) a second band appears in the presence of acid, and d) the intensity of the second band appears to be constant, or relatively insensitive to sulfuric acid concentration. These observations can be rationalized as follows: The decrease in intensity of the original band is due to normal quenching. The second band must be due to a protonated or acid associated species. The apparent invariance of the intensity of this band is due to compensation of the two overlapping peaks (i.e., increased protonated and, simultaneously, decreased unprotonated species).

It is well known that the acidity, or basicity, of excited aromatic compounds often differs considerably from that of the ground state. Fluorescence spectroscopy has been very useful in this respect. Fundamental to the use of fluorescence spectroscopy in determining or predicting the direction of the shift in acidity of excited acid-base pairs, relative to the ground state, is the premise that the direction of shift in acidity is dependent upon the relative excitation energies of protonated and unprotonated species, the so-called Förster cycle.[26] This will be made more clear by referring to figure 19. HA, in figure 19, refers to the proton donating species and A⁻ is its conjugate base. Electronically excited state species are asterisked. ΔE_i's are the pertinent energy differences between ground state and excited state species, and ΔG_i^0 is the free energy of dissociation of

$$HA \longrightarrow H^+ + A^-$$

or,

$$HA^* \longrightarrow H^+ + A^{*-}$$

It is presumed that if the protonated species absorbs at a higher frequency than the unprotonated species, then, in the excited state, the

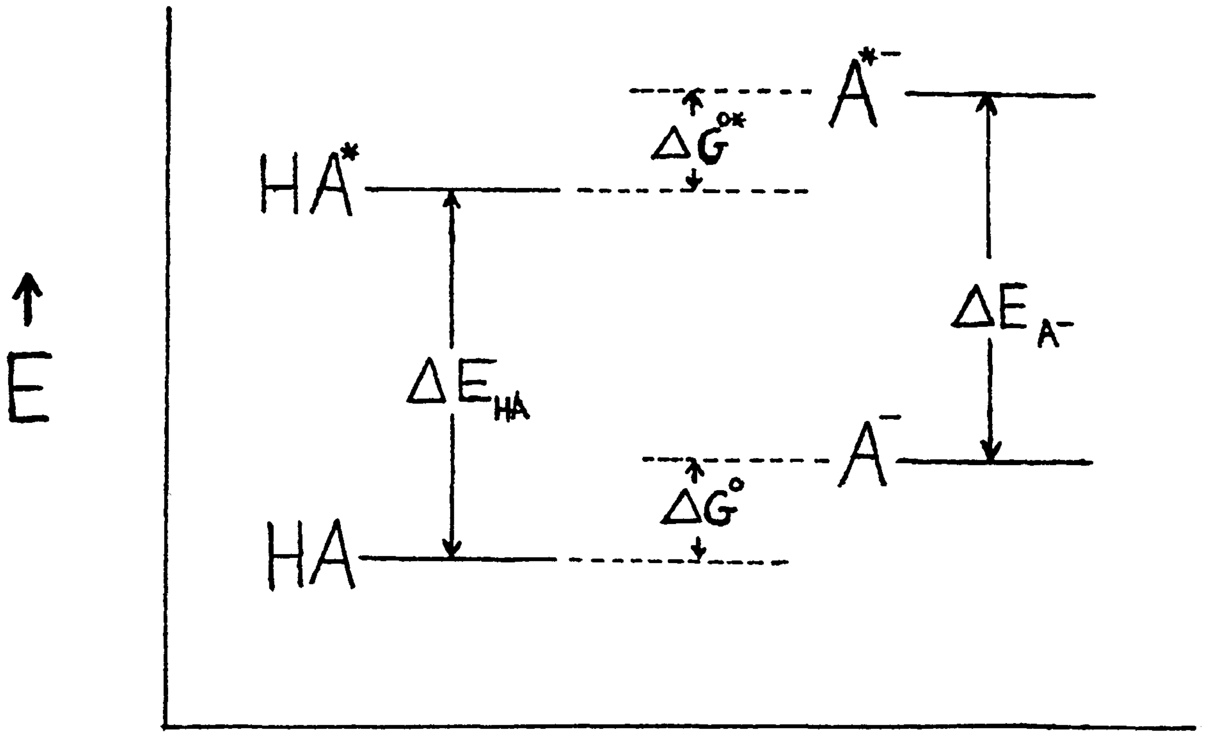


Figure 19. Förster cycle, demonstrating the relative energy levels (ΔE) of: Ground state proton donor (HA), ground state conjugate base (A^-), excited state donar (HA^*), and excited conjugate base (A^-). Also shown is the ground state free energy of dissociation (ΔG^0) and the corresponding excited state free energy of dissociation (ΔG^{0*}).

protonated species will find itself at a higher energy level than the unprotonated form (relative to the respective ground states) and will exhibit a greater tendency, in the excited state, to deprotonate. Namely, it will become a stronger acid in the excited state, relative to the ground state. The converse is also true. If the protonated species absorbs at a lower frequency than the unprotonated form, it (the protonated species) should become an even stranger base in the excited state and, therefore, will exhibit a greater tendency to become protonated.

The fluorescence spectrum of (VII) shown in figures 2 and 4, indicates that the protonated species fluoresce at a wavelength substantially greater than that of the unprotonated species. Since both species are in identical media, it is very likely that the protonated species also absorb at longer wavelength than the unprotonated form. Therefore, consistent with the aformentioned premise of the Förster cycle, the unprotonated species of (VII) should be a stronger base in the excited state. Therefore, it should show a greater tendency to be protonated in the excited state. For emphasis, we repeat that the fluorescence spectrum of (VII) suggests that the unprotonated species is a stronger base in the excited state than in the ground state.

The apparent increase in intensity of the U.V. absorption maxima of the compounds studied cannot be attributed to a protonated ground state species since only one absorption band is observed and, hence, there is no isobestic point. The observed increase in intensity is probably due to medium effects caused by the varying proportions of solvent and sulfuric acid. Such medium effects have been reported.[18]

Since we observe a decrease in fluorescence in the unprotonated species and a parallel increase in the protonated species, upon the increase in acid concentration, but the rate of photodeuteration is insensitive to acid concentration, it seems likely that the protonated species that is fluorescing is <u>not</u> an intermediate in the photodeuteration. Rather, it may be a species protonated on a substituent rather than on a ring carbon.

Since photodeuteration which must involve carbon deuteration or protonation, does not depend upon the acid concentration, it is likely that this process either involves a prior (to excitation) association of the reagents, or that the excited molecule can react only with nearest neighbor molecules before relaxing.

There is a disagreement between our substitution results and those reported by Havinga and coworkers.[22] While we found that the sulfuric acid concentration had no effect on the rate of substitution, they found a definite effect in that rather high concentrations of substituting agents were required in order to obtain a substantial quantum yield.

It seems reasonable to assume that in our case both racemization and deuteration are occurring from a vibrationally excited first singlet state. The specific rates of deactivation of these higher states are known to be greater (of the order of 10^{11} to 10^{13} per second)[27] than those of fluorescence (10^{7} to 10^{10} per second).[28] Consequently, the observed rates of deuteration and of substitution would have to be competitive with these processes.

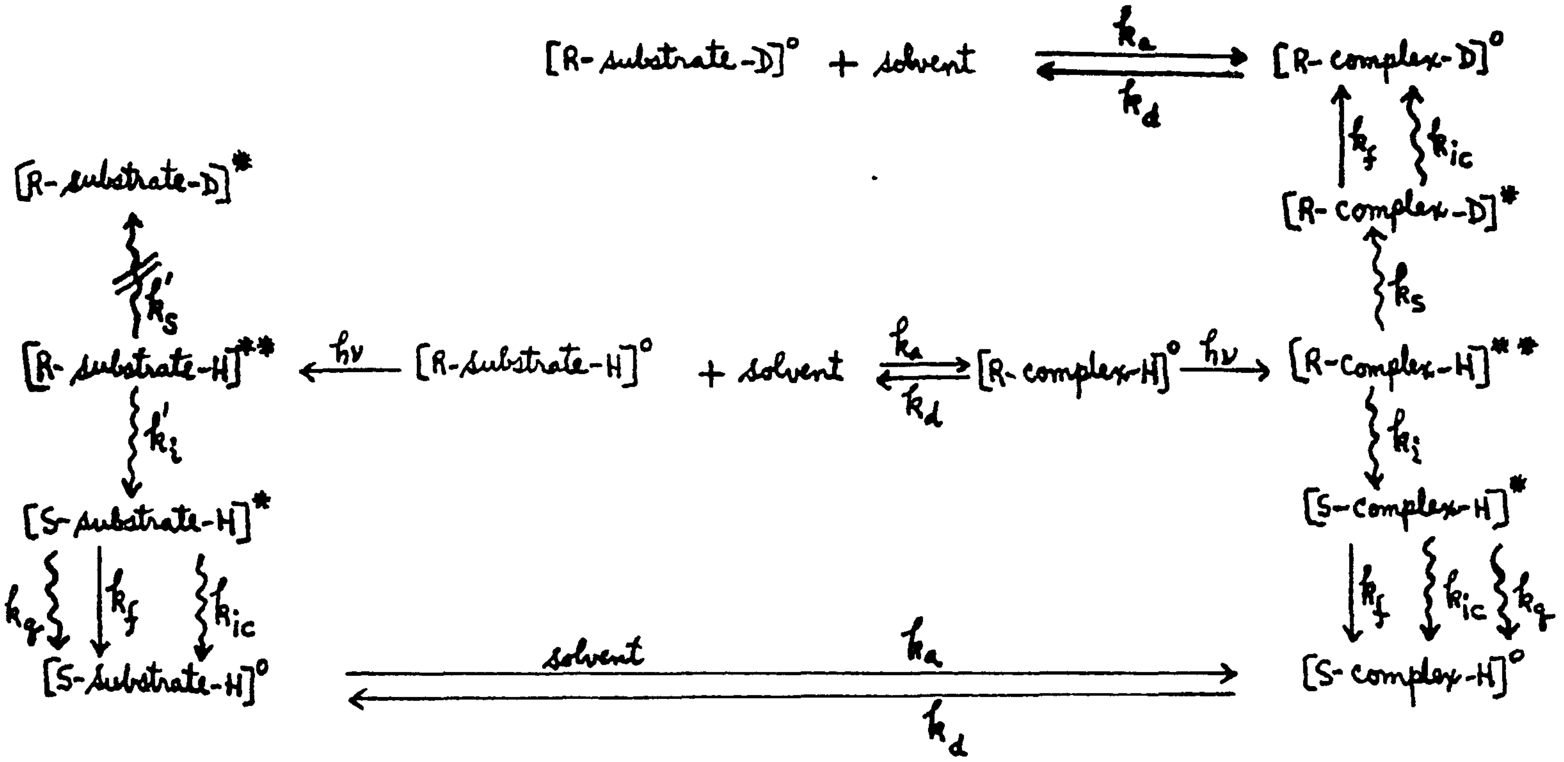
Protonation of the excited state yields only substituent protonation, as seen from the fluorescence spectra. Therefore, the carbon protonated species is probably of higher energy than either fluorescent species.

Meaningful rate constants cannot be calculated for the rates of racemization and deuteration because a knowledge of the concentration of higher excited-state species is not known. This concentration not only depends on the specific rate of photon absorption, but also on the specific rate for vibrational deactivation to the lowest excited singlet. Scheme II is consistent with the experimental data.

The symbols and subscripts of Scheme II have the following meaning:

R = chirality of original enantiomer
S = chirality of other enantiomer
k = rate constant
i.c. = internal conversion
a = association
d = dissociation
q = quenching
i = inversion
s = substitution
f = fluorescence

It is unfortunate that the effect of acid concentration on the photoracemization and photodeuteration of (VII) could not be done because of insufficient material. However, the parallelism in the relative rates of racemization of (VII) in the two solvents with that of compound (V) suggests that (VII) and (V) racemize via similar routes.



Scheme II. Mechanism of the photoracemization and photodeuteration of optically active biphenyls with 2537Å light. Only essential steps are shown so as to minimize the complexity of the chart which starts in the middle of the page. The subscripts have the following meaning:

*	first excited state singlet
**	higher than first excited state singlet
o	electronic ground state

H and D refer to hydrogen and deuterium, respectively. The meaning of the other symbols are given in the text.

EXPERIMENTAL

Analyses

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Satisfactory analyses were obtained on all compounds.

Spectra

Mass spectral analyses were performed by the analytical department of Hoffman-LaRoche, Inc., Nutley, N.J. We are indebted to Dr. Milan Uskokovic, of the organic chemistry department, for his cooperation. N.M.R. spectra were taken on either a Varian A60-A or a Varian S60-C spectrometer, continuous wave mode, or on Jeolco's PS-100, using Fourier transform (usually 1024 scans).

U.V. spectra were taken on a Cary 14 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter, using a 1 milliliter jacketed cell of 1 decimeter path length. Fluorescence spectra were recorded on Farrand Mark I spectrofluoremeter, using slit width of 10 millimicrons for both exciter and analyzer. Infrared spectra were taken on a Perkin-Elmer "Infracord" spectrometer.

Irradiation

Irradiations were carried out on a rotating test tube holder (known as a "merry-go-round")[29] using 3 milliliter samples of 0.03 molar solutions contained in sealed quartz tubes. All samples were degassed via three freeze-thaw cycles.

Methanol was used as the inert medium, while acetic acid-d_4, containing 0.2M D_2SO_4, was used as deuterating medium.[7]

Considerable difficulty was experienced with the acetic acid solutions. When these thawed, they had a tendency to do so with much spattering and, at times, the perifery of the solution would melt and the inner solid portion would jet up the sample tube, to the constricted area of said tube, smearing solvent and compound all along the sides.[a] This, of course introduced errors (namely, scattering) in our earlier data. See footnote b on page 18.

The error due to this effect was minimized, eliminated in most cases, by immersing the sample tubes all the way to the constricted area into the liquid nitrogen, to insure freezing of the smeared solvent, before further degassing. Also, before each sample tube was opened for analysis, it was first shaken to dissolve any solute that might have re-

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[a] The reason is believed to be due to the relatively high melting point of acetic acid which yields a very compact solid at liquid nitrogen temperatures. Less difficulties should be encountered with a higher temperature freezing bath. Unfortunately, liquid nitrogen was needed for the methanol solutions.

mained on the sides. No such difficulties were experienced with the methanol or aqueous (actinometer) solutions.

3130 Å light was obtained from a Hanovia 450 watt medium pressure mercury lamp, using a chemical filter prepared by dissolving 10.0 grams of reagent grade anhydrous sodium carbonate and 0.5 gram of reagent grade sodium dichromate with distilled water to a volume 1.0 liter.[30]

2537 Å light was obtained from a Hanovia SC-2537 mercury resonance lamp. No filter was used in this case because all samples were located at sufficient distance from the lamp to insure total decay of the 1849 Å output.[31] Both lamps were positioned at the center of the test tube holder.

All irradiations were done isothermally, using a distilled water bath thermostated to ±0.1°C by Neslab's T.E. 9 - PB.C. 2 heater-cooler unit.

The transparency of the water bath was checked periodically in order to insure constancy. With proper pre-cleaning care, it was found that the maximum decrease in transmittance did not exceed 2%.

Control samples, for both inert and deuteration media, were treated identically as the irradiated samples, except that they were held in the dark by wrapping the tubes in aluminum foil. No change in rotation, with time or temperature, was noted for the duration of the experiment.

Actinometry

Ferri-oxalate chemical actinometer was used.[32] Three milliliters were irradiated for approximately two minutes at the same temperature as the other samples. Three actinometer samples were irradiated for each racemization sample, at evenly spaced intervals.

Variation of the actinometer quantum yield with temperature was within experimental error.[32] Hence, no correction for temperature was necessary.

Absorbance of irradiated actinometry samples was checked on a Gilford 240 spectrophotometer, the same instrument as that used to prepare the calibration curve.

Materials

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid[33], (XV) — 211.0 grams (1.0 mole) of 3-nitrophthalic acid used to prepare the anhydromercuri derivative, using the method of reference [33], except that the mixture was first heated in an oil bath at 140°C for at least 14 hours. The temperature was then slowly increased to 170°C. This procedure seems to cut down the total hours of required heating to approximately forty-eight and greatly reduced the danger of bumping over. 281.0 grams (0.756 mole) obtained. 75.6% yield.

2-bromo-3-nitrobenzoic acid[34], (XVI) —286.0 grams (0.78 mole) of anhydro-2-hydroxymercuri-3-nitrobenzoic acid used to prepare the compound, by the method of P. J. Culhane[34], without any changes. 126.0 grams (0.513 mole) of recrystallized compound obtained. 59.3%

yield. M.p. 182° - 184°.

Methyl-2-bromo-3-nitro benzoate, (XVII) — 71.6 grams (0.291 mole) of the free acid prepared by the method of Ingersoll and Little[13], however, the volume of methanol was increased to one liter.

After refluxing and cooling, the solvent was removed on a rotary evaporator and the residue taken up in chloroform and washed with ice-cold saturated sodium carbonate solution, then with water to the neutral point. The solution was dried with anhydrous sodium sulfate. Stripping gave a 92% yield of the desired ester. M.p. 77° - 79°C.

d,l-methyl-6,6'-dinitro diphenate [13] (XVIII) — 52.0 grams (0.20 mole) of methyl-2-bromo-3-nitro benzoate melted in a 200 mls flask immersed in an oil bath at 145°C., maximum temperature. A portion of 27.5 grams (0.23 mole) of copper electrolytic dust added in small quantities with swirling, at thirty-second intervals, until the mixture solidified. The temperature was then raised very slowly to 170°C and the balance of the copper added in the same manner as before, again with constant swirling. After complete addition, the temperature of the bath was raised to 185° - 190°C and the mixture swirled for half an hour more. Benzene was added to the cooled mixture, and the compound extracted by refluxing for three to six hours. The extraction is repeated at least once. It is sometimes necessary to break up persistent lumps. A Soxhlet extractor can be used if the mixture is first powdered. Recrystallization from 95% ethanol gave greenish-yellow prisms in 90%

yield. M.p. 128° - 130°C.

d,l-6,6'-dinitro diphenic acid (d,l-V) — 36.0 grams (0.1 mole) of d,l-ester was hydrolyzed by the method of Ingersoll and Little[13] to give the free acid, after recrystallizing from glacial acetic acid, in 98.7% yield. M.p. 263° - 264.5°C.

d-(+)-6,6'-dinitro diphenic acid, (d-V)[13] — 29.95 grams (0.091 mole) of the d,l-acid was dissolved in 600 mls of a.c.s. grade acetone and treated with 11.94 grams (0.0987 mole) of d-(+)- α-methyl benzylamine. The mixture was stoppered and left standing in the dark overnight. The yellow crystals that formed were filtered, washed with acetone and air dried.[a] 22.21 grams (0.0489 mole) of salt obtained. M.p. 210° - 213°C.

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[a] The salt may not precipitate if the d,l-acid is not pure, or if the acetone contains water. In such a case, I) reducing the volume by approximately 30%, followed by addition of anhydrous ether to a point of slight turbidity, or II) cooling in an ice bath until the first sign of crystal formation, will, in most cases, yield the desired salt. In case II, purer crystals (optically) are obtained if, after crystallization is complete, the solid is allowed to sit in contact with the supernatant liquid, with mechanical stirring at room temperature for at least two hours. With very pure d,l-acid and dry solvent, crystallization is fast and can be assumed to be complete in three to five hours.

99% yield. $[\alpha]_D^{25}$ = +162.2 (c=1.00; methanol). The free acid was recovered by dissolving the salt in 200 mls of hot water, then adding 15 mls of concentrated hydrochloric acid. After allowing to stand for one hour, the mixture was cooled in an ice bath, filtered, washed with water and oven dried to give 14.6 grams (0.0440 mole). M.p. 227° - 229°C. $[\alpha]_D^{25}$ = +127.2 (c=1.00; methanol). 97% yield.

ℓ-(-)-6,6'-dinitro diphenic acid[13] (ℓ-V) — The filtrate from the d-(+)-salt was stripped yielding a viscous liquid which was dissolved in approximately 200 mls of boiling water and treated with 15 mls of concentrated hydrochloric acid. After sitting one hour, the mixture was further cooled in an ice bath and filtered. The resulting solid was washed with water and dried. 15.54 grams (0.0468 mole) of free acid obtained was dissolved in 300 mls of a.c.s. grade acetone and treated with 5.68 grams (0.468 mole) of ℓ-(-)-α-methyl benzylamine, stoppered and left standing in the dark overnight. This latter treatment is necessary in order to obtain optically pure compound, otherwise, the optical purity is in the 90 plus percentile range. 19.64 grams (0.0433 mole) of salt obtained. M.p. 211° - 213°C. $[\alpha]_D^{25}$ = -162.0 (c=1.00; methanol). 92.5% yield. The free acid was recovered in the same manner as from the d-(+)-salt. 15.23 grams (0.458 mole) obtained. 98% yield. M. p. 227° - 229°C. $[\alpha]_D^{25}$ = -127.8 (c=1.00; methanol).

When the salt (of both atropisomers) is oven dried, or allowed to stand in the air for a few days, the initial rotation decreases to an absolute value of $[\alpha]_D^{25}$ = 141.6 (c=1.00; methanol). This is due to the loss of acetone of crystallization.[13] No further decrease occurs. Our results differ from that of the cited reference in so far as the maximum optical rotation of the salt is concerned.

(+) and (-)-methyl-6,6'-dinitro diphenate (d- and ℓ-XVIII)[14] — 13.9 grams (0.0419 mole) of the respective acids methylated using the same procedure as for the d,l-racemic acid. 98% yield. $[\alpha]_D^{25}$ = ±113.0 (c=1.00;ethyl acetate). M.p. 137° - 139°C.

(+) and (-)-6,6'-dinitro-2,2'-bis(hydroxymethyl) biphenyl, (ℓ- and d-XIX)[35] — 5.3 grams (0.0147 mole) of the respective dimethyl ester derivative, dissolved in anhydrous ether, was treated with an ethereal solution containing 7.8 grams (0.0588 mole) of anhydrous aluminum chloride, 1.6 grams (0.0423 mole) of lithium aluminum hydride (see reference 16 for details). Recrystallization of the crude product from benzene gave 2.10 grams (0.00691 mole) of desired compound. 52% yield. M.p. 136° - 138°C. $[\alpha]_D^{25}$ = ±65.4 (c=1.00; ethyl acetate).

(+) and (-)-6,6'-dinitro-2,2'-bis(bromomethyl) biphenyl (d- and ℓ-XX)[14] — 1.93 grams (0.0064 mole) of the respective bis(hydroxymethyl) derivate refluxed for forty minutes with 90 mls of 48% hydrobromic acid. The mixture cooled in an ice bath and filtered. The resulting solid was washed copiously with cold water and oven dried. 2.64 grams (0.00615 mole) of product obtained. 96% yield.

It was found that the conversion was virtually quantitative (I.R., N.M.R.) and that the suggested recrystallization did not improve the purity of the product, but rather drastically reduced the yield. Simply decolorizing was found to be satisfactory in most cases. Therefore, recrystallization was eliminated in subsequent runs. M.p. 165° - 167°C. $[\alpha]_D^{25}$ = ±8.45 (c=0.87; tetrahydro furan).

(+)-6,6'-dinitro-2,2'-dimethyl biphenyl (d- VI)[35] — 2.63 grams (0.00610 mole) of (+)-bis(bromomethyl) derivative and 1.27 gram (0.00955 mole) anhydrous aluminum chloride were dissolved in 7 mls of triglyme (dried as suggested in the reference). To this was added, slowly, a suspension of 1.0 gram (0.0265 mole) of sodium borohydride in 26 mls of triglyme (dried). After complete addition, the mixture was heated to 80°C for one hour, with mixing. 105 mls of 6N sulfuric acid was carefully added and the entire mixture allowed to stand overnight. The resulting crude product was filtered, washed with water and dried. 1.47 gram (0.0054 mole) obtained. 88.5% yield. M.p. 95° - 97°C. $[\alpha]_D^{25}$ = +26.6 (c=1.00; 95% ethanol).

0.8 gram of crude product was dissolved in a small volume of benzene and chromatographed as suggested in the literature.[35] 0.66 gram was recovered and this was recrystallized from hexane to give 0.43 gram of pure product. Yellow needles. M.p. 99° - 100°C. $[\alpha]_D^{25}$ = +28.0 (c=1.00; 95% ethanol).

(-)-6,6'-dinitro-2,2'-dimethyl biphenyl (ℓ-VI)[35] — 2.28 grams (0.00524 mole) of (-)-bis(bromomethyl) compound was treated with the proportionate quantities of reagents and solvent as in the (+)-isomer, above. 1.07 gram (0.00394 mole) of crude product obtained. 75.5% yield. M.p. 95° - 97°C. $[\alpha]_D^{25}$ = -27.3 (c=1.00; 95% ethanol). The entire sample was chromatographed, as with the d-isomer above, to give 0.9232 gram which was recrystallized from hexane. 0.7645 gram (0.00282 mole) of pure product resulted. 53.7% yield. M.p. 98.0° - 99.5°C. $[\alpha]_D^{25}$ = -27.4 (c=1.00; 95% ethanol). Notice that although the change in rotation was small, the increase in melting was significant.

(-)-9,10-dihydro-4,5-dinitrophenanthrene (ℓ-VII) — An attempt was made to synthesize this compound via the conventional routes. For example, following the method of Hall and Turner[36] or of Mislow and Hopps[37], (-)-6,6'-dinitro-2,2'-bis(bromomethyl) biphenyl, dissolved in benzene, or ether, was treated dropwise, under nitrogen, with an ethereal solution containing an equimolar amount of phenyl lithium. An immediate red color developed which persisted throughout the reaction. Upon addition of dilute hydrochloric acid, the red color disappeared. However, workup yielded only starting material, unchanged, according to I.R., N.M.R. and melting point.[a]

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[a] No effort was made to identify the red intermediate. However, it can be speculated that, due to the powerful electron withdrawing and coordinating abilities of the nitro group, the biphenyl becomes lithiated

Similar results were obtained using n-buthyl lithium. Likewise, magnesium metal (including activation by ethylene bromide and molecular iodine), lithium metal and metallic sodium, in the order given, were tried starting from dry ice-acetone to approximately 35°C (refluxing diethyl ether). An excess of phenyl or butyl lithium did not seem to help.

A successful synthesis, albeit in low yield, was achieved as follows:[b] 0.389 gram (0.00142 mole) of bis-(1, 5-cyclo-octadiene) nickel (0) was placed, under argon, in a 3-neck 100 mls flask equipped with a three-way stopcock and rubber serum stopper. A solution of 0.881 gram (0.00205 mole) of (-)-6, 6'-dinitro-2, 2'-bis(bromomethyl) biphenyl in 65 mls of dimethyl formamide (degassed by evacuating and filling with argon was added, all at once, at 25°C.

at a position ortho to the nitro group.[38] Possibly, with this compound, lithiation has a much lower activation energy than halogen-lithium exchange. The resultant highly conjugated carbanion apparently has a red color. Reprotonation would occur upon addition of dilute acid. This hypothesis can easily be tested with N.M.R., using deuterated acid.

[b] The crude product was kindly prepared by Dr. Richard D. Stauffer while a postdoctoral associate with Dr. Martin F. Semmelhack of Cornell University, Ithaca, New York.

After 18 hours at 25°C, the mixture, now green, was partitioned between 150 mls of dichloromethane and 100 mls of cold 1% aqueous hydrochloric acid. The organic layer was washed with five 100 mls portions of water, dried over anhydrous magnesium sulfate and concentrated by rotary evaporation (then at 0.01 Torr) to leave a yellow residue. 0.401 gram obtained which represents 83% of the theoretical yield for loss of two bromine atoms. Melting point and N.M.R. showed it to be a mixture.

The crude product was dissolved in 2:1 chloroform-methanol and purified by preparative T.L.C. on alumina (E. Merck, Darmstadt, Germany. F_{254}, Type T), activated by heating in an oven at 110°C for one hour. The results are shown in table 7.

Either a mixture of 1:1 carbon tetrachloride-benzene or 100% benzene can be used as developing solvent in conventional T.L.C. However, the desired solvent for preparative T.L.C. is benzene. The plates can be dried and re-developed if greater separation is desired. The sequence is the same in both solvent systems. Approximately 10% yield, based on crude mixture, of purified product is obtained. M.p. 108° - 110°C[a].

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[a] Because the compound racemizes as it melts, there is a slight uncertainty in the final reading. Because the racemic mixture has a higher

Table 7

Results from the thin layer chromatography of the crude product of (-)-9,10-dihydro-4,5-dinitrophenanthrene (VII) using benzene as developing solvent.

Compound I. D.	R_f values*	
	Preparative TLC	Regular TLC
(unidentified)	Very small	0.024
9,10-dihydro-4,5-dinitrophenanthrene	0.088	0.238
6,6'-dinitro-2,2'-bis(bromomethyl)biphenyl	0.230	0.471

*Averages of three runs

$[\alpha]_D^{25}$ = -458 (c=1.00; chloroform). The optical purity is not known. The N.M.R. and I.R. spectra are shown in figures 20 and 21, respectively.

The mass spectrum of (VII) did not show a molecular ion peak. The largest discernible mass corresponded to 238 (P - 32), apparently, due to loss of two oxygen atoms. The compound decomposes on the probe, as evidenced by ratio intensity changes with filament temperature. The base peak was not determined.

Due to the limited quantity of available material, an attempt was made to determine the thermal activation energy for racemization by the N.M.R. method.[39] Optically active compound is not required for this method. However, it was not possible to obtain consistently good peak resolution as the N.M.R. probe was heated. This is known to introduce large errors in the determined values.[39a]

melting point, repeated melting point determinations on the same sample yield varying results. Ultimately, the melting point of the racemic mixture is attained. The melting point of the racemic compound is 156° - 158°C.

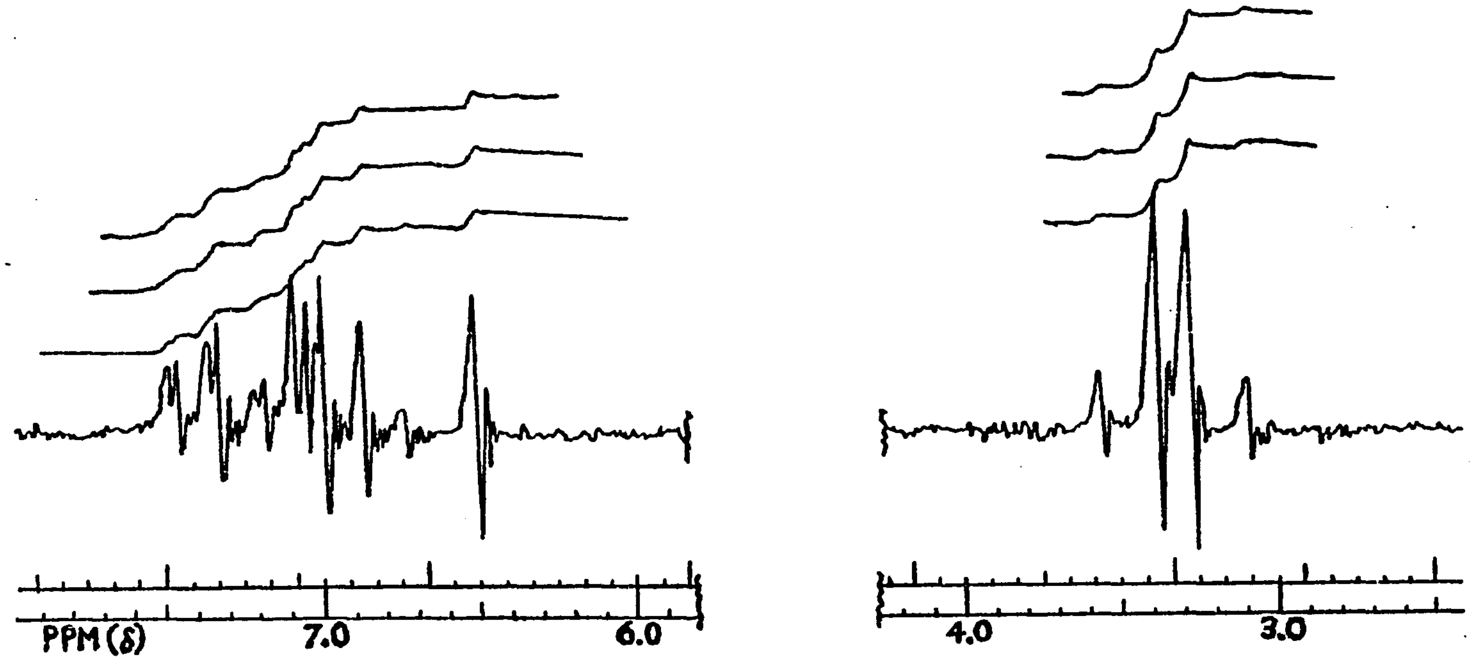

Figure 20. Varian S60-C N.M.R. spectrum of (±)-9,10-dihydro-4,5-dinitrophenanthrene, (IV), in CD_3CN. 500Hz sweep width, 50Hz offset, relative to TMS.

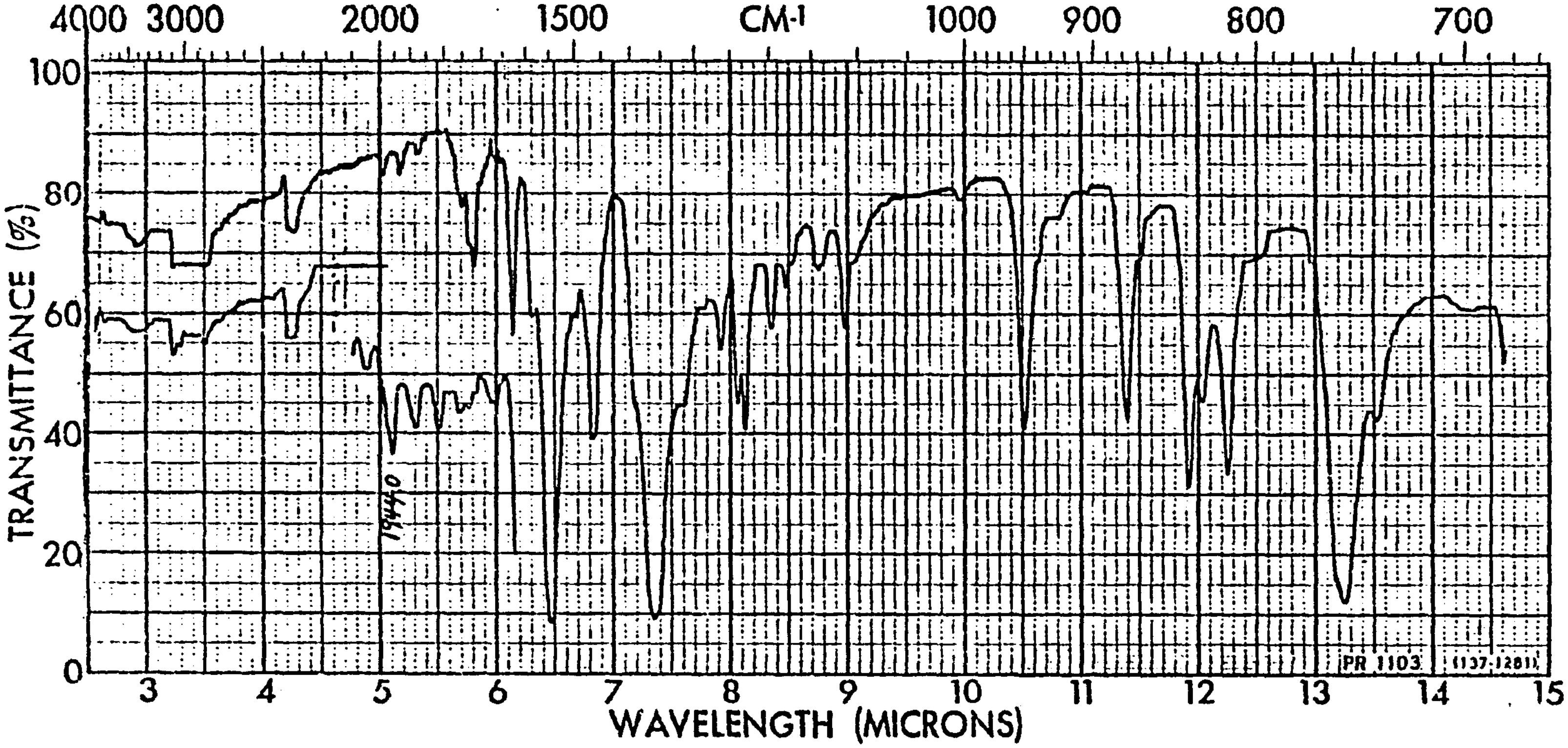

Figure 21. Infrared spectrum of (±)-9, 10-dihydro-4, 5-dinitrophenanthrene, (IV). Potassium bromide pellet.

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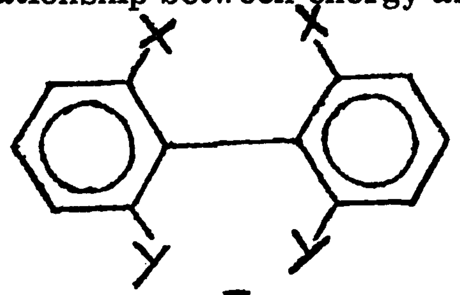
PART II

AN O.R.D. STUDY OF THE CONFORMATION OF OPTICALLY ACTIVE BIPHENYLS IN SOLUTION

INTRODUCTION

The preferred geometry of biphenyl varies considerably with experimental conditions. The dihedral angle between the rings has been variously reported to be 42°-45° (gas phase)[1], 0° (crystalline)[2] and 20° (solution)[3]. When the torsional angle, θ , is neither 0° or 90°, biphenyl exists in two enantiomeric conformations IIa and IIIa (see figure 1) with torsional angles θ and $180° - \theta$ that can interconvert by traversing a transition-state at either 0° or 90°.

If two conformations exist for optically active biphenyls such as II-be, the relationship between energy and torsional angle becomes more complicated than that for biphenyl itself (see figure 2).[4] The potential barriers at 0° and 180° no longer are of equal magnitude. In addition, the potential barriers that were at 90° and 270° are generally shifted somewhat from these angles. Notably, IIb-e are no longer enantiomers but diasteriomers of IIIb-e. Thus, IIb-e and IIIb-e differ in energy. Assuming the barrier near 90° to be small (e.i, accessible at moderate temperatures) IIb-e and IIIb-e will be in equillibrium with ther relative



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a: X=Y=H
b: X=CH_3; Y=NO_2
c: X=COOH; Y=NO_2
d: X=CH_2OH; Y=NO_2
e: X=CH_2Br; Y=NO_2

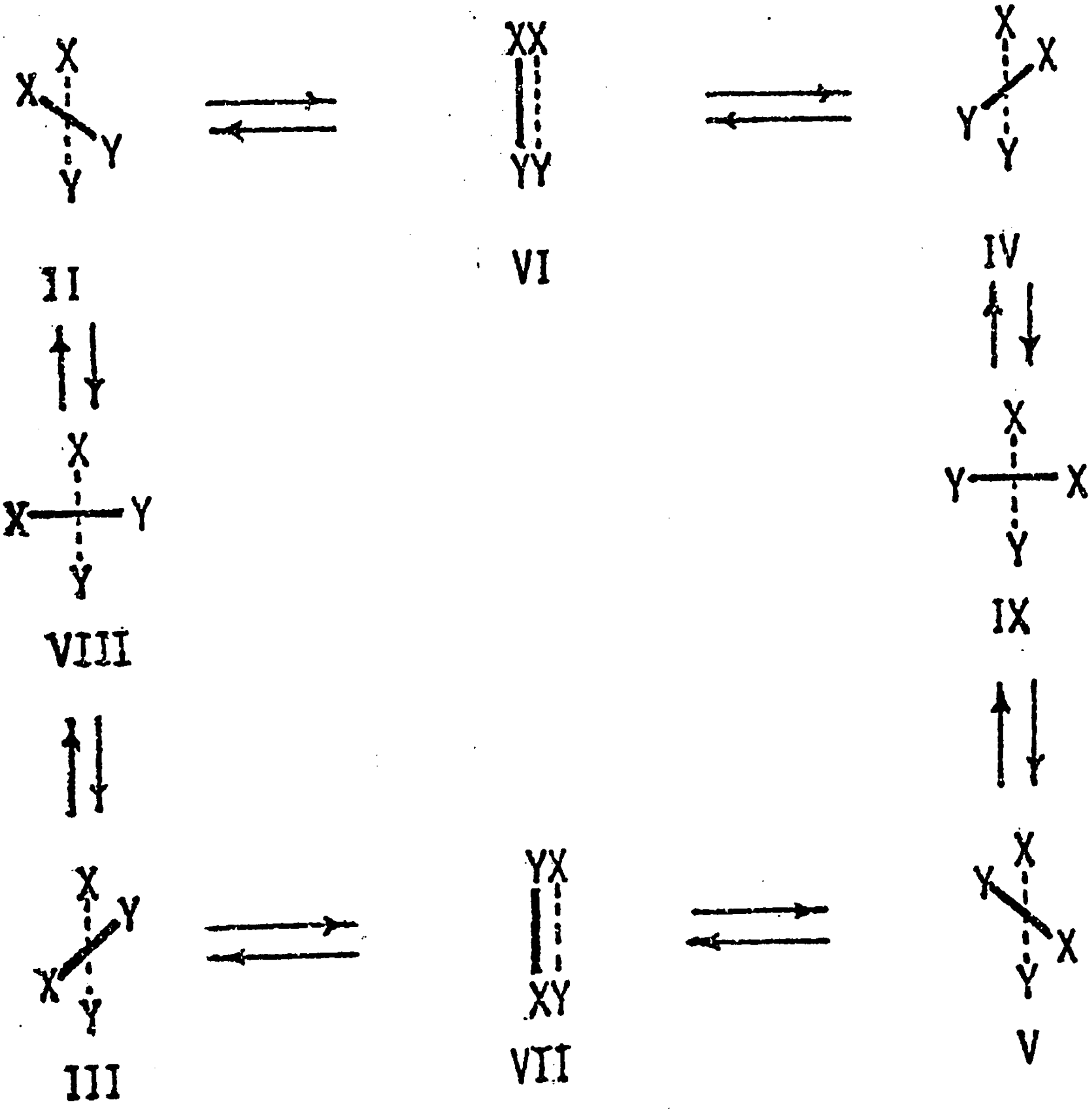

Figure 1. Possible conformations of substituted biphenyls.

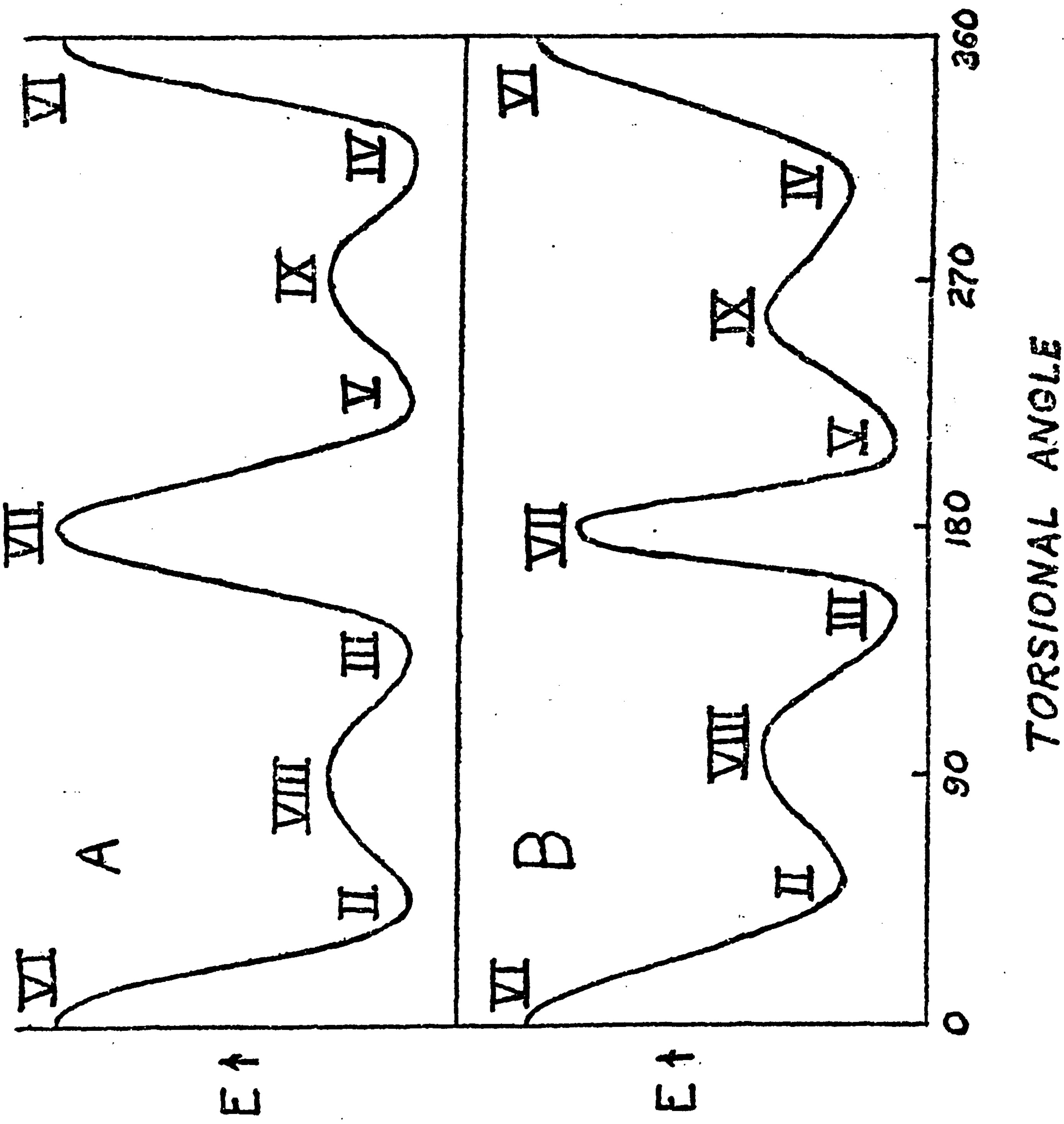

Figure 2. Energy vs. torsional angle for (a) biphenyl; (B) optically active biphenyls such as Ib or Ic. The values of the extrema are chosen for illustrative purposes only.

populations determinable from a Maxwell-Boltzmann distribution.

If we consider groups X and Y to be perturbations on Ia, we expect IIb-e and IIIb-e to have opposite chirality and molecular rotation. This has been predicted[5] from the theory of Kirkwood[6] for the transition near 260 nm. The sign of the rotation associated with the near 260 nm band has been shown, experimentally, to be due to the chirality of the phenyl-phenyl twist[7] rather than to other effects induced by this chirality.

Although substituted biphenyls of type I have long been known to have torsional angles different from 0°, 90° and 180° (0° is defined as X exlipsing X) in both the gas[8] and solution[5, 7] phases, no evidence for the existence of more than one conformation between $\vartheta = 0^{\circ}$ and 180° was ever presented.

All previous works, whether experimental or theoretical, have assumed, or implied, that these compounds exist, under invariant experimental conditions, in a single fixed torsional conformation[9] which is dictated by a balance between a desire to achieve maximum overlap of -orbitals (i.e., maximum inter-annular conjugation which leads to coplanarity of the two rings), steric crowding due to ortho substituents[10] (usually dominant), inter-annular bridging,[11] attractive London forces,[12] or hydrogen bonding.[13] It is also presumed that in non-bridged biphenyls, in a majority of cases, the two most important factors that determine the "equilibrium conformation" are conjugation and steric crowding. These two factors oppose each other and usually are not equal in magnitude. Throughout the rest of this thesis, we will give the label "equilibrium conformation" to the previously presumed single fixed conformation, as found in the literature.[5]

It would be desireable to identify the separate torsional frequencies of the postulated conformers and so prove our hypothesis. Although the far and near Raman and infrared spectra of unsubstituted biphenyl (Ia) have been extensively investigated, the torsional frequency of this compound is still uncertain. Only a few tentative assignments of the torsional frequency of biphenyl and of some of its derivates have been made. These assignments have all been associated with non-resolvable biaryls. Namely, biaryls in which there is, under standard conditions, relatively "free" rotation around the inter-annular bond.[a]

Thus, Zerbi and Sandroni[14] have assigned an experimental value of 70 cm^{-1} to unsubstituted biphenyl (Ia) in the solid phase, based upon neutron inelastic scattering. The 70 cm^{-1} assignment of Zerbi and Sandroni seemed to have been indirectly substantiated by infrared temper-

[a] There is always some resistance to free rotation. See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill Book Co., Inc., New York, 1962, p. 126.

ature studies on crystalline biphenyl done by Lecolier, Wyncke and Hadni.[15]

Lecolier, et. al. observed that the 70 cm^{-1} band of crystalline biphenyl resolved into a triplet (67 cm^{-1}, 76 cm^{-1} and 86 cm^{-1}) at temperatures between 80° and $15^{\circ}K$, the components of which were insentive to temperature. Hence, they ascribes these frequencies to internal molecular vibrations. Other peaks, such as the 90 cm^{-1} and the 118 cm^{-1}, which were more temperature sensitive, were ascribed to translational vibrations.

However, subsequently, Barrett and Steele[16] claimed to have made a definitive assignment of the 70 cm^{-1} band to a fundamental frequency of B_{1u} symmetry.[a] The torsional mode of unsubstituted biphenyl has A_u symmetry. Barrett and Steele arrived at their conclusions by comparing the experimental spectral differences, of both Raman and I. R.,

[a] The following symmetries apply to unsubstituted biphenyl: Planar ($\theta = 0^{\circ}$), D_{2h}; $0^{\circ} < \theta < 90^{\circ}$, D_2; $\theta = 90^{\circ}$, D_{2d}.[17]

The planar configuration is very unstable in optically active biphenyls, hence, it will not be considered. For compounds of type Ib-e, the symmetries are: $0^{\circ} < \theta < 90^{\circ}$, C_1; $\theta = 90^{\circ}$, C_s.

between liquid ($\vartheta = 45^{\circ}$) and crystalline ($\vartheta = 0^{\circ}$) biphenyl with the predicted changes, based upon the change in symmetry in going from liquid to solid or vice versa. Using the calculated torsional barriers for biphenyl obtained by Zerbi and Sandroni,[18] Barrett and Steele would prefer to predict a value of 60 cm^{-1} for the torsional frequency.[a]

H. Michelsen, et. al., using force field calculations and assuming the C_1-C_1' force constant to be invariant with angle of twist, obtained a theoretical torsional frequency of 242 cm^{-1} for the torsional frequency of 4, 4'-difluro-, 4, 4'-dicyano-, 4, 4'-dibromo-and 4, 4'-diiodobiphenyl (both for solid and solution). They tentatively assigned the experimental value of 246 cm^{-1} (obtained from the Raman spectrum of a carbon disulfide solution) to the torsional frequency of 4, 4'-diiodobiphenyl. H. Michelsen and collaborators also found that the torsional frequency did not vary with the dihedral angle.

Based upon solid phase fluorescence and phosphorescence spectra (n-hexane solution at 77°K) Lim and Li[20] assigned torsional frequencies to biphenyl-h_{10}(635 cm^{-1}); biphenyl-d_{10}(595 cm^{-1}); 3, 3'-difluro-

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[a] Semi empirical calculations have predicted a value of from 1.2 to 2.0 kilocalories for the barrier at approximately $\vartheta = 90^{\circ}$.[19]

biphenyl (515 cm^{-1}); 4, 4'-diflurobiphenyl (626 cm^{-1}). A long progression of overtones were present in each of the spectra.

The theoretical basis for the assignments by Lim and Li rests upon the assumption that a long progression of vibrational modes is to be expected when the geometry of a molecule is changed radically during an electronic transition (i.e., during a non-vertical or non-Frank-Condon electronic transition). The dihedral angle of the first excited singlet and triplet states of biphenyl, and even that of an ortho tetrasubstituted biphenyl, has been predicted to be planar or nearly planar.[21] As mentioned earlier, the dihedral angle of biphenyl in solution is approximately 20°. Therefore, there is a change in dihedral angle of approximately 20° in going from the ground state to the excited state, or vice versa[a] and the expectations of Lim and Li are justified.

The report by Friedman, Prasad and Kopelman[22] who studied the isotope dependent vibronic structure in the phosphorescence spectra of a mixed isotopic crystal containing biphenyl-h_{10} in biphenyl-d_{10} is in accord with the conclusion of Lim and Li.

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[a] The assumption here is that the dihedral angle of biphenyl in the solid solution is equal or close to that in the liquid phase. Since the intermolecular forces in solid n-hexane are undoubtedly weak (m.p. -95°C), the assumption is reasonable.

However, Barrett and Steele[16] are in disagreement with the assignments made by Lim and Li. They argue that "such a high (torsional) frequency would require an enormous torsion barrier."

Asymmetry in the potential energy curves of biphenyls is due mainly to unequal steric repulsions near the $\theta = 0^{o}$ and $\theta = 180^{o}$ barriers. Namely, it is due to asymmetric perturbation of the originally symmetric potential energy curve of unsubstituted biphenyl. However, while the barriers at 0^{o} and 180^{o} might differ greatly from compound to compound, the energy of the barrier at approximately 90^{o} changes to a much lesser degree. As a consequence, one side of the potential "wells" is affected much more than the other side and this introduces a greater degree of anharmonicity into the torsional modes.

The effect on the potential energy curves of changing the barriers at $\theta = 0^{o}$ and 180^{o} is illustrated qualitatively in figure 3. Figure 3 also suggests that the width of the "wells" might narrow as the barriers at 0^{o} and 180^{o} increase.

Although the harmonic oscillator approximation might be poor for assymetric surfaces such as those encountered here, it is useful to discuss its application to torsional frequencies. The frequency of such an oscillator is given by

$$\nu = \frac{n}{2\pi}\sqrt{\frac{V_o}{2I_r}} \qquad (1)$$

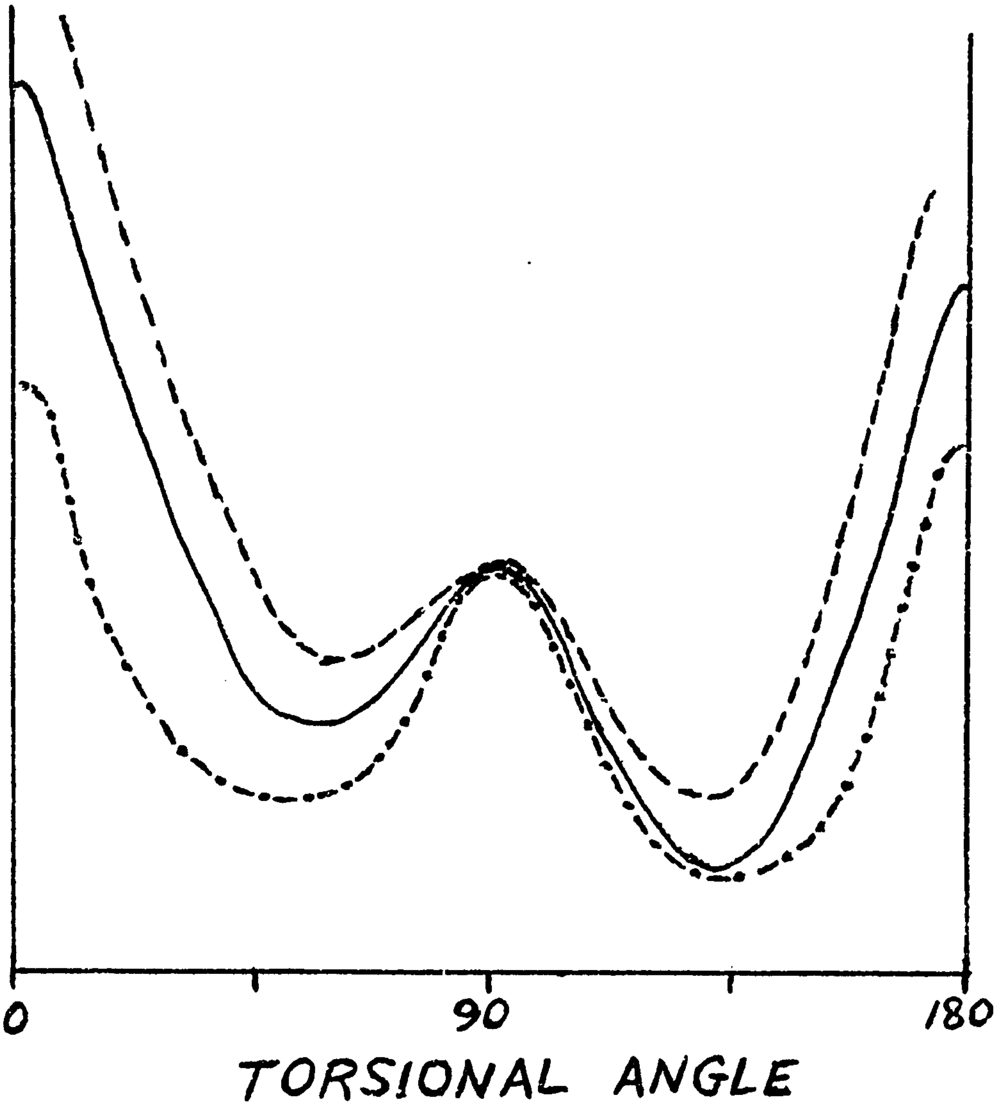


Figure 3. Variation of the potential energy curve (qualitative) of a substituted biphenyl as the potential barriers at $\theta = 0^\circ$ and $\theta = 180^\circ$ vary (i.e., as the size of the ortho groups vary). Arbitry energy units.

— — — — High potential barriers.

———— Intermediate potential barriers.

—·—·— Low potential barriers.

where n is a quantum level number, V_0 is the potential energy barrier and I_r is the appropriate reduced moment of inertia for torsional motion. The other symbols have their usual meanings. Equation (1) shows that as the potential energy barrier increases (at constant reduced moment of inertia) the torsional frequency also increases.

A consequence of the steric interactions at 0^0 and 180^0 is that, in a given set of isomers, ortho substitution should have a greater effect on the torsional frequency than para or meta substitution.

For a series of positional isomers having the same substituents, large substituents should have the greatest effect both on the torsional barrier and the reduced moment of inertia, I_r (see figure 4). Large groups in the ortho position increase the torsional barrier and, therefore, the torsional frequency. Moving such groups to the meta position virtually eliminates the steric repulsion, but has little or not effect on I_r. Moving the group from meta to the para position has little effect on the barrier, but lowers I_r and, therefore, increases the frequency. The expected order of torsional frequencies for biphenyls substituted with large groups is ortho > para > meta.

Dixon, Harris and Mazengo[23] have shown that the N.M.R. chemical shift of protons in an ortho methyl group of biaryls varies with the magnitude of the interannular dihedral angle. Consequently, a temperature dependence of the N.M.R. chemical shift of the ortho methyl protons in type I compounds is expected if our hypothesis is correct and would serve to reinforce our argument.

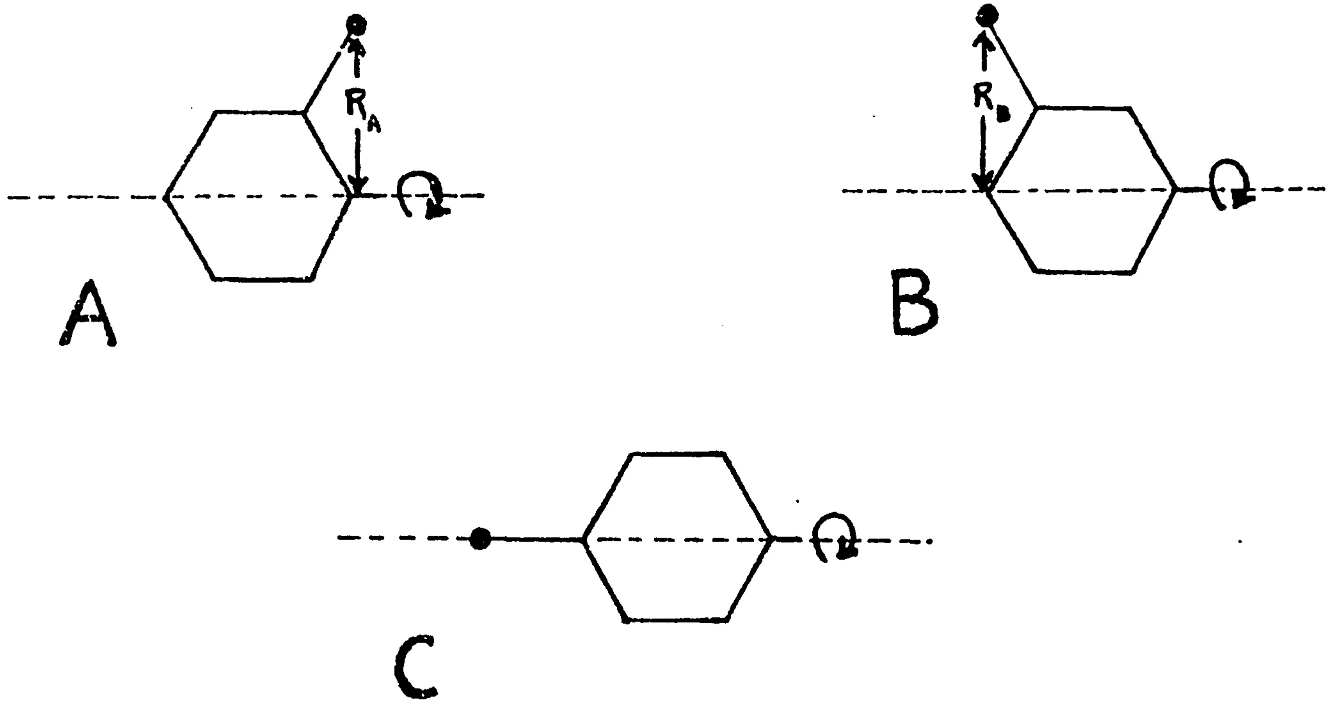
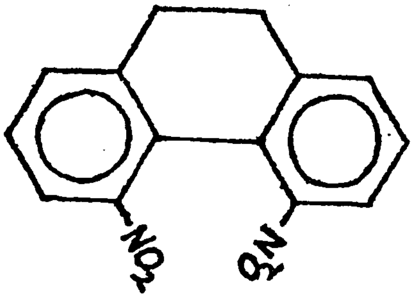


Figure 4. Rotational radii (R_i) of the ortho (A) and meta (B) isomers of a mono substituted biphenyl, relative to that of the para isomer (C). The dashed line (- - - - -) represents the torsional axis of rotation.

RESULTS

The O.R.D. spectra of compounds Ib through Ie, and also that of 9,10-dihydro-4,5-dinitrophenanthrene (X), were recorded at various temperatures. After the temperature was raised, the initial spectrum was remeasured. In each case, the initial spectrum was reproducible upon lowering of the temperature. This not only proved that the observed changes were reversible, but also that no racemization occurred in any of the compounds during the time lapse or duration of the experiment.[a, 24] The results are shown in figures 5 through 9.



X

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[a] The non-bridged biphenyls are known to be thermally stable to at least 75°. The optical stability of X was partially checked on a polarimeter. A thermostated sample at 30° lost none of its optical activity after four days. N.M.R. temperature study of the AB quartet due to the methylene protons indicated that compound X was optically stable at 45°. See experimental section, part I, of this thesis for details.

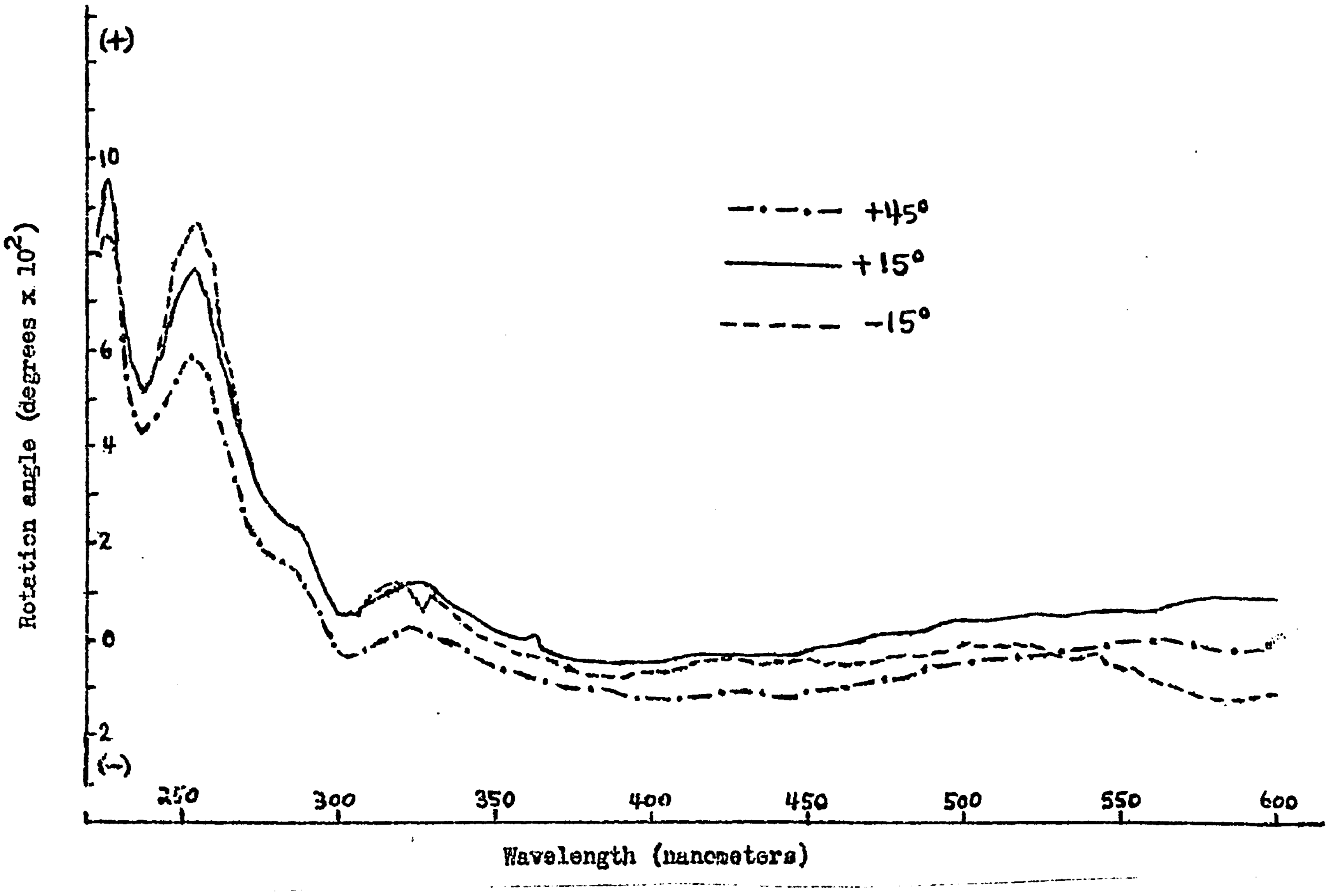

Figure 5. Temperature O.R.D. spectra of R-2, 2'-dimethyl-6, 6'-dinitrobiphenyl (Ib) in methanol. c=2.5 x 10^{-5}M.

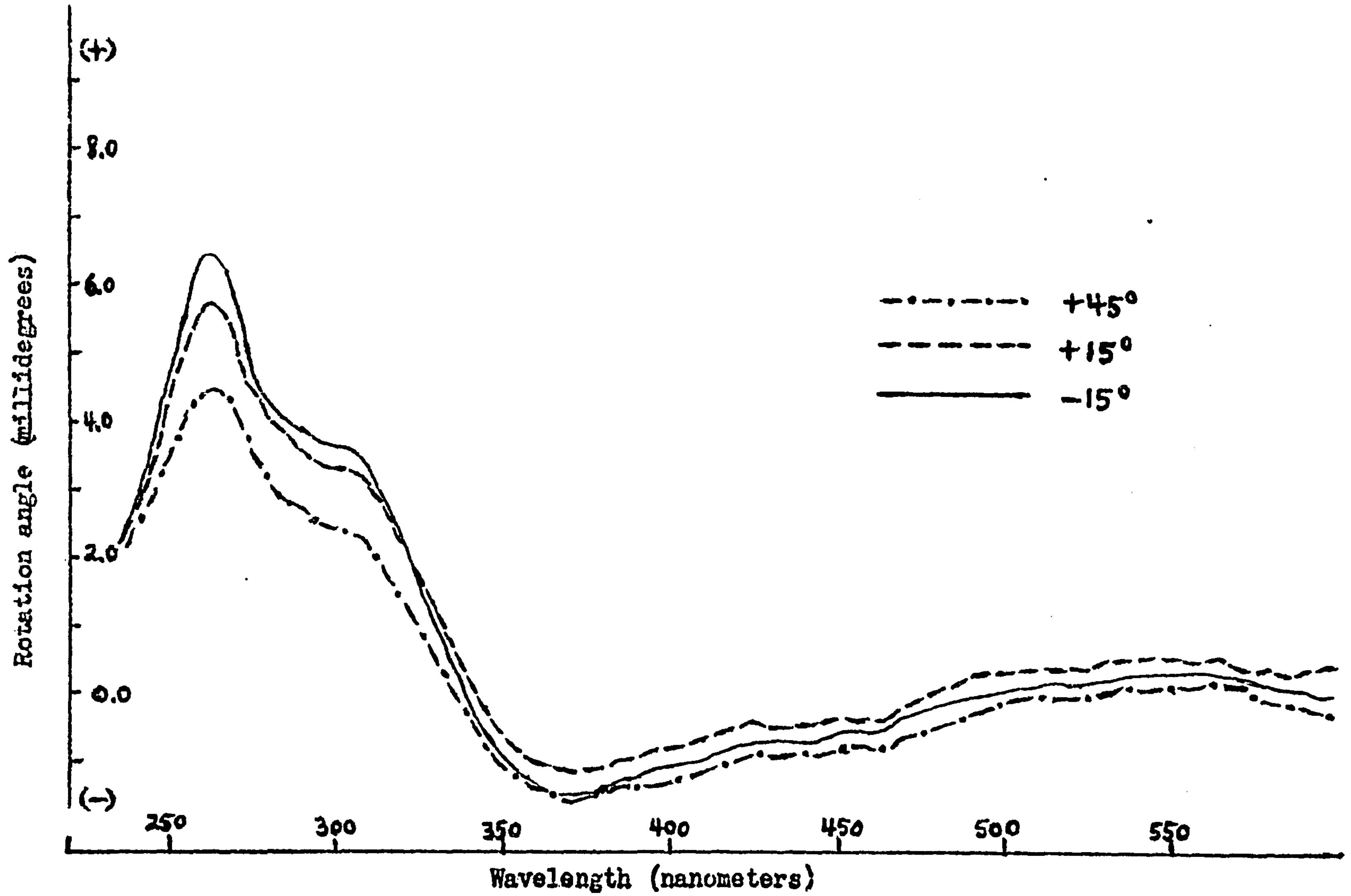

Figure 6. Temperature O.R.D. spectra of R-6, 6'-dinitro-2, 2'-diphenic acid (Ic) in methanol. c=3.0 x 10^{-4}M.

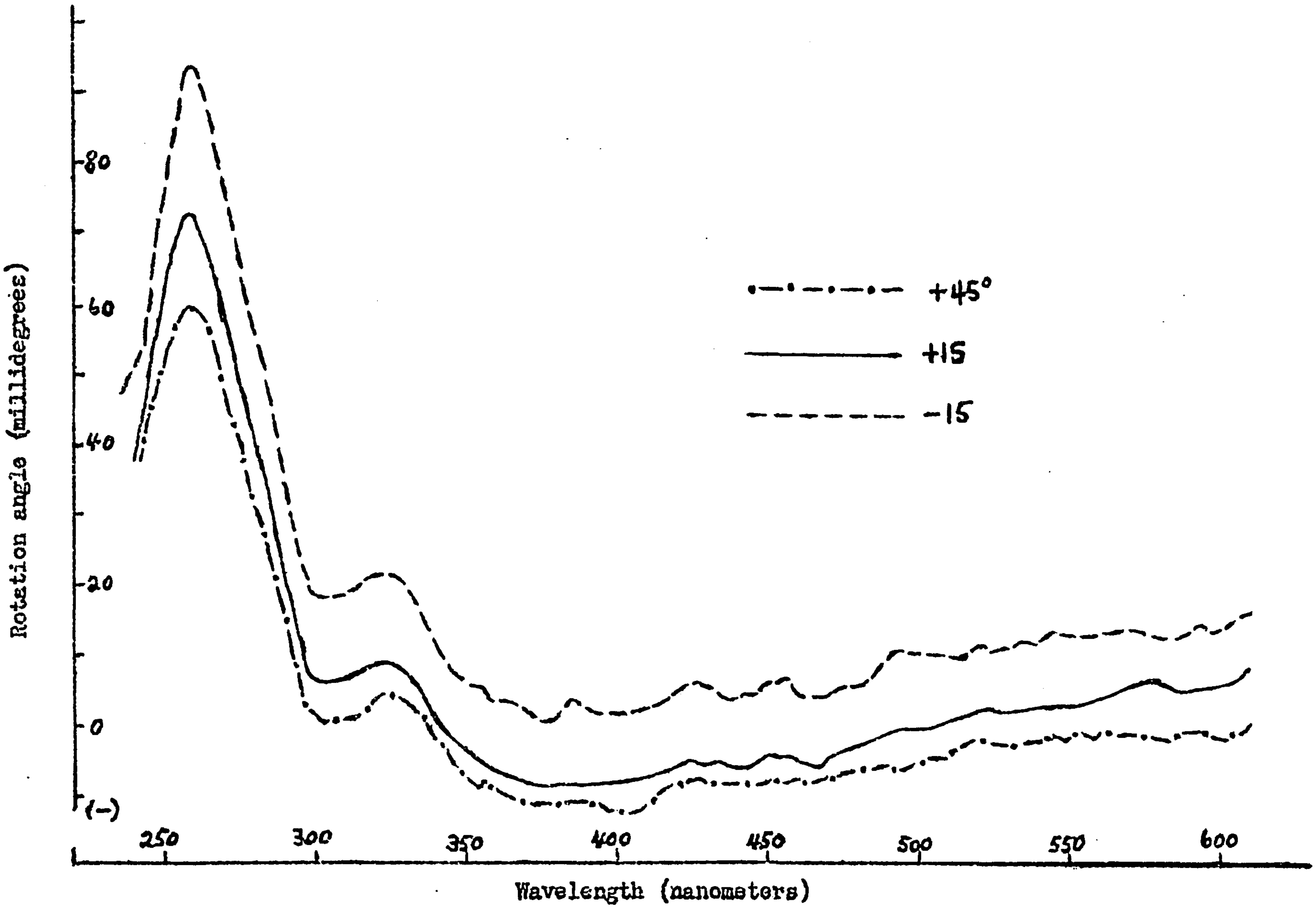

Figure 7. Temperature O.R.D. spectra of R-2,2'-bis-(hydroxymethyl)-6,6'-dinitrobiphenyl (Id) in methanol. c=3.0 x 10^{-4}M.

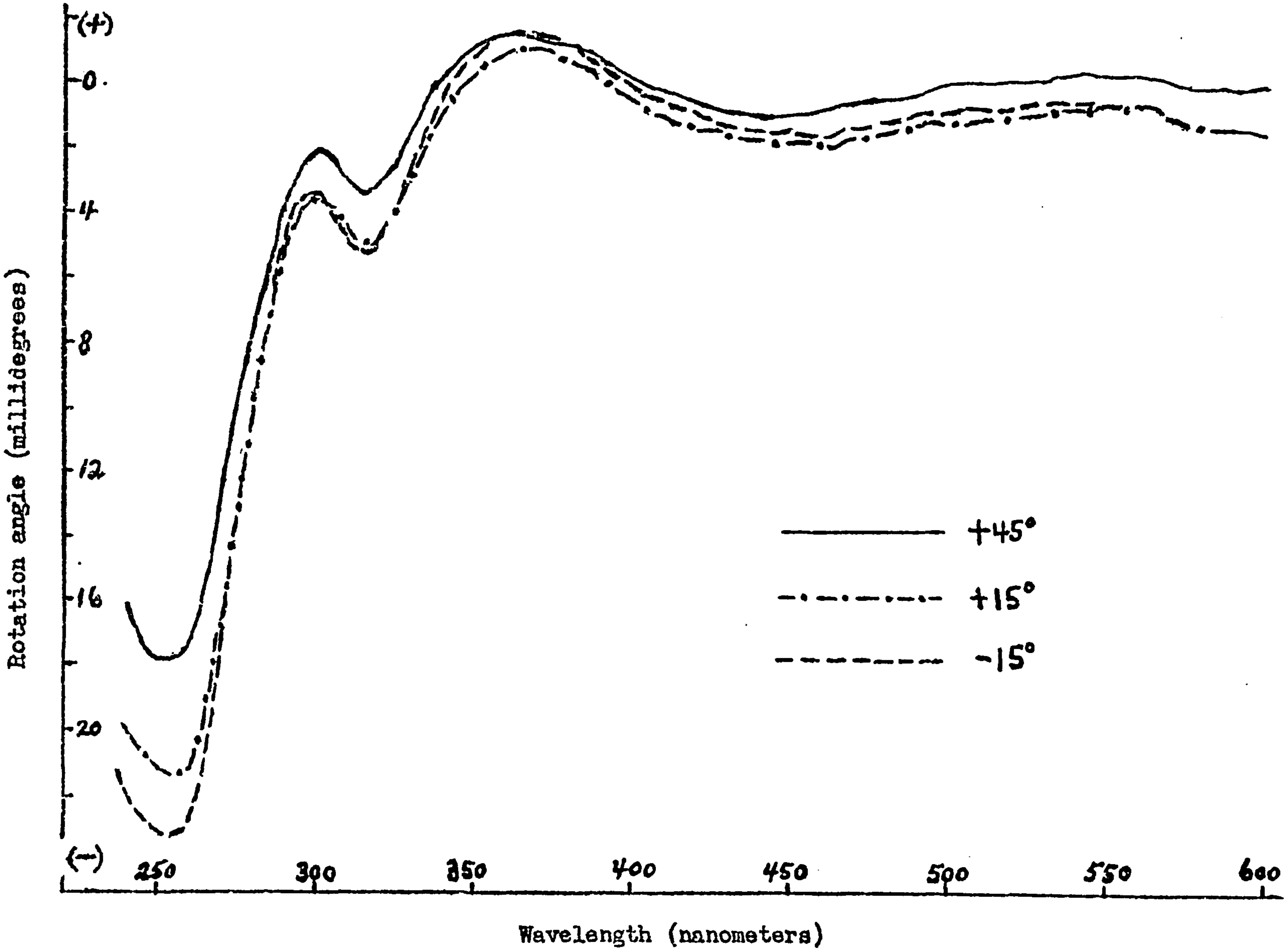

Figure 8. Temperature O.R.D. spectra of R-2,2'-bis-(bromomethyl)-6,6'-dinitrobiphenyl (Ie) in methanol. c=1.0 x 10^{-5}M.

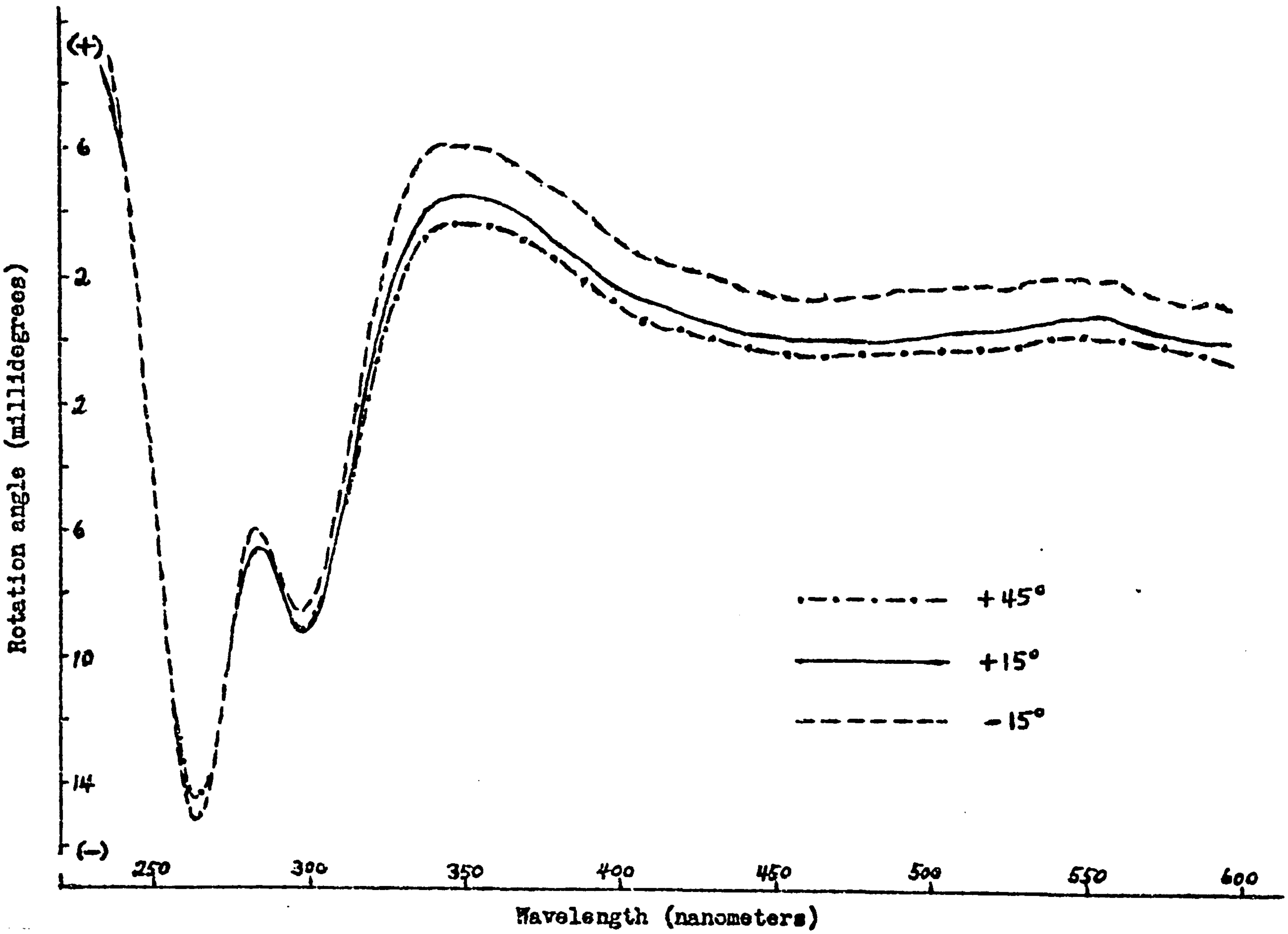

Figure 9. Temperature O.R.D. spectra of R-9, 10-dihydro-4, 5-dinitrophenanthrene (X) in methanol. $c=3 \times 10^{-6}$M.

The relative rotations at the peaks or troughs, as the case may be, were calculated for transition nearest 260 nm. The largest observed rotation, at or near -15°C, was used as reference and assigned a relative value of unity (1.00). The results, corrected for temperature expansion (see experimental section for details) are shown in table 1. The wavelengths of the corresponding peaks or troughs are also given in table 1. It can be seen that, for the non-bridged compounds, the specific rotations at 45°C decreased by 25% (methyl), 24% (carboxyl), 36% (hydroxymethyl) and 15% (bromomethyl). By contrast, bridged biphenyl (X) in which the torsional motion is restricted because of the size of the dimethylene bridge, only a 9% decrease was observed.[a] This decrease is close to half of that of the smallest decrease observed among the non-bridged compounds.

Since intra- and, sometimes, inter-molecular hydrogen bonds are known to affect the conformation of some biphenyls in solution,[13] it was necessary to show that our results were not due to disruption and/or

[a] Due to the dimethylene bridge, the 90° barrier (VIII, figure 1) should not be accessible, effectively preventing equilibration of conformations analogous to II and III.

Table 1

Variation of O.R.D. intensity with temperature (methanol solution).

Compound	Temperature (°C)	max	relative rotation[a]
Ib	- 15.0	260	1.00 ± 0.02
	+ 14.5		.84
	+ 45.0		.75
Ic	-15.0	262	1.00
	+ 15.0		0.88
	+ 45.0		0.76
Id	- 14.0	255	1.00
	+ 14.0		.86
	+ 45.0		.64
Ie	- 15.0	255	1.00
	+ 15.0		.93
	+ 45.0		.85
X	- 15.0	263	1.00
	+ 14.8		0.94
	+ 45.0		0.91

a) Corrected for expansion. See experimental section for details.

formation of such bond. To this end, the O.R.D. temperature behavior of the methyl compound (Ib) was studied in n-octane. The nature of the functional groups and the expected torsional angles (i.e., large steric repulsion due to ortho substituents) of this compound are such that intra-molecular hydrogen bonding should not be possible. If present, it should be insignificantly small.

The temperature O.R.D. behavior of Ib in n-octane was essentially identical with that observed in methanol. The relative rotation of Ib in n-octane (254 nm) at +45° decreased to 0.76 of its -15°C value. Once again, the changes were found to be reversible. Unfortunately, the low solubility of the other biphenyls in n-octane precluded further studies in this solvent.

We examined the U. V. spectrum of the methyl compound (Ib) and also that of the carboxyl compound (Ic) at 0°, +10°, +20°, and +30°C. The observed changes in molar absorptivity at the absorption maximum of the near 260 nm band (corrected for solvent expansion) were modest. The wavelengths of interest are 262 nm (Ib) and 260 nm (Ic). These are the transitions that correspond with the O.R.D. data listed in table 1, that is, with the phenyl-phenyl twist or conjugation band. The U.V. temperature results, corrected for the thermal expansion, are given in table 2. There was no significant shift in the position of the near 260 nm absorption band of either compound studied. Thus, the observed changes in the O.R.D. spectra are not due to changes in the absorption spectra.

Table 2

Observed decrease in molar absorptivity with temperature of the near 260 nm band.

Compound	Temperature (°C)	max	% decrease[a]
Ib	0.0	260	-
	+ 10.0		0.6 ± 0.2
	+ 20.0		3.5
	+ 30.0		5.0
Ic	0.0	262	-
	+ 10.0		1.1 ± 0.3
	+ 20.0		2.3
	+ 30.0		3.2

a) Corrected for expansion.

An N.M.R. temperature study of the methyl proton resonance of 2,2'-dimethyl-6,6'-dinitrobiphenyl (Ib) was done between -48°C to +55°C. At least four scans were executed for each temperature reading. See experimental section for details. A sample spectrum is shown in figure 10 and the results are given in table 3. It is evident that there is a progressive upfield shift in the methyl proton resonance of Ib as the temperature is increased. This can be attributed to changes in the average magnetic environment of the protons which, in turn, reflect changes in conformation.

Finally, we recorded the crystal (Nujol mull) and solution far I.R. spectra of several substituted biphenyls, including those of optically active biphenyls Ib through Ie, the bridged biphenyl (X), and of biphenyl itself (Ia), between 250 cm^{-1} and 50 cm^{-1}.[a] A reproduction of the spectra in block form (significant peaks only) is shown in figure 11. A sample far I.R. spectrum, that of 3-methylbiphenyl (XII) in chloroform, is shown in figure 12.

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[a] No infrared absorption band has been observed for crystalline biphenyl between 50 cm^{-1} and 30 cm^{-1}, at low temperatures.[25]

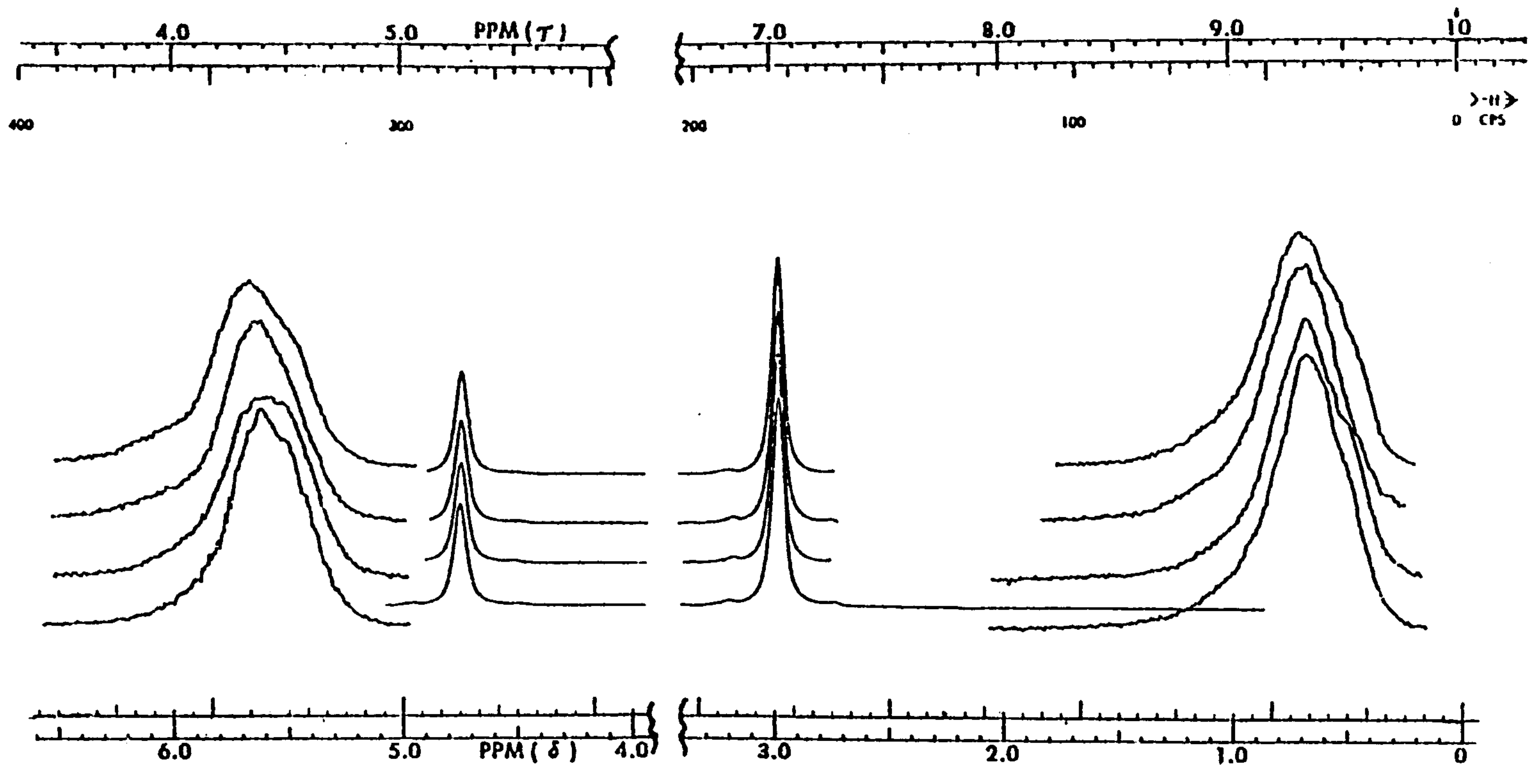

Figure 10. Sample spectrum (20^{o}C, four scans) in the determination of the relative methyl proton shift of 2,2'-dimethyl-6,6'-dinitrobiphenyl (Ib) in chlorobenzene (see table 3). The two center peaks are due to ethylene glycol (500 cps sweep width, 50 cps offset). The broad upfield peak is due to the methyl resonance of toluene (internal standard) while the broad downfield peak is due to the methyl resonance of Ib (50 cps sweep width, 94 cps offset). Varian A-60, 250 second sweep time.

Table 3

Variation of the methyl proton reasonances of 2,2'-dimethyl-6,6'-dinitrobiphenyl (Ib) with temperature.

Temperature (°C)[a]	Solvent	(Hz)[b]
55	chlorobenzene	27.0 ± 0.1
41	"	28.2
34	"	28.3
28	methylene chloride	23.7
2	"	24.5
-35	"	25.7
-48	"	26.0

a) Calibrated from ethylene glycol and methanol resonances.

b) Downfield from the methyl resonance of internal toluene.

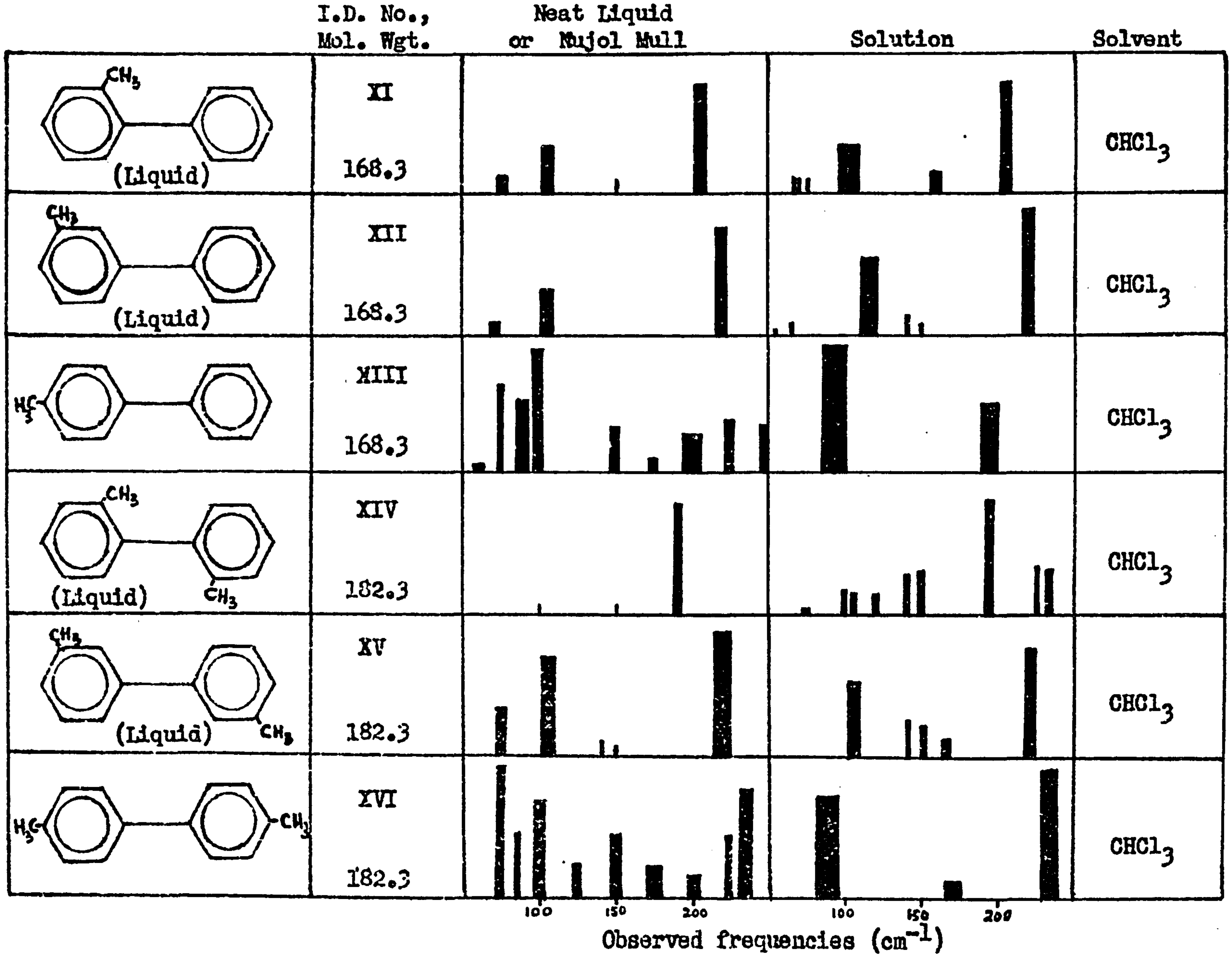

Figure 11. Block diagram representation of the far I.R. spectra (50 cm^{-1} to 250 cm^{-1}) of various biphenyls.

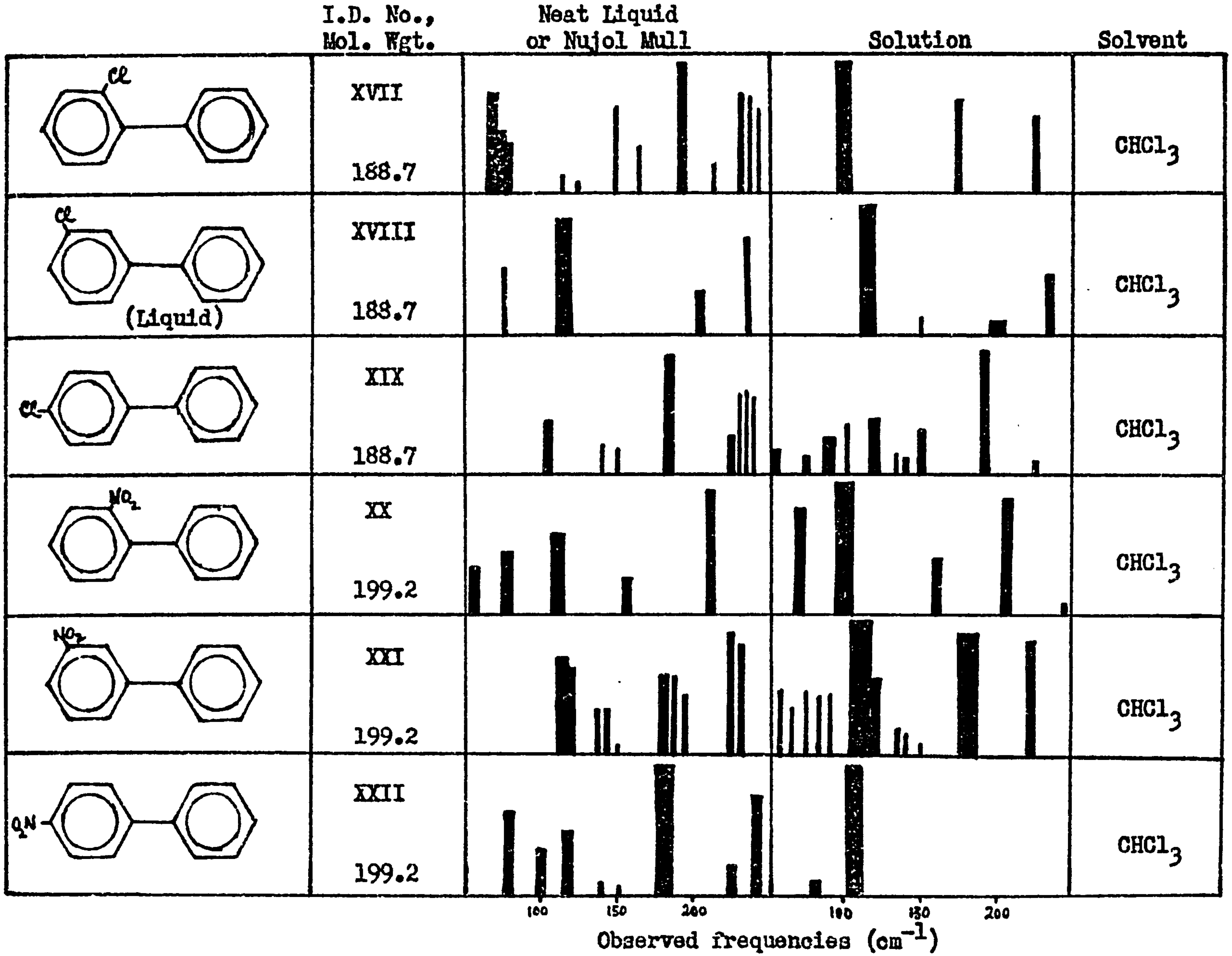

Figure 11. (Continued).

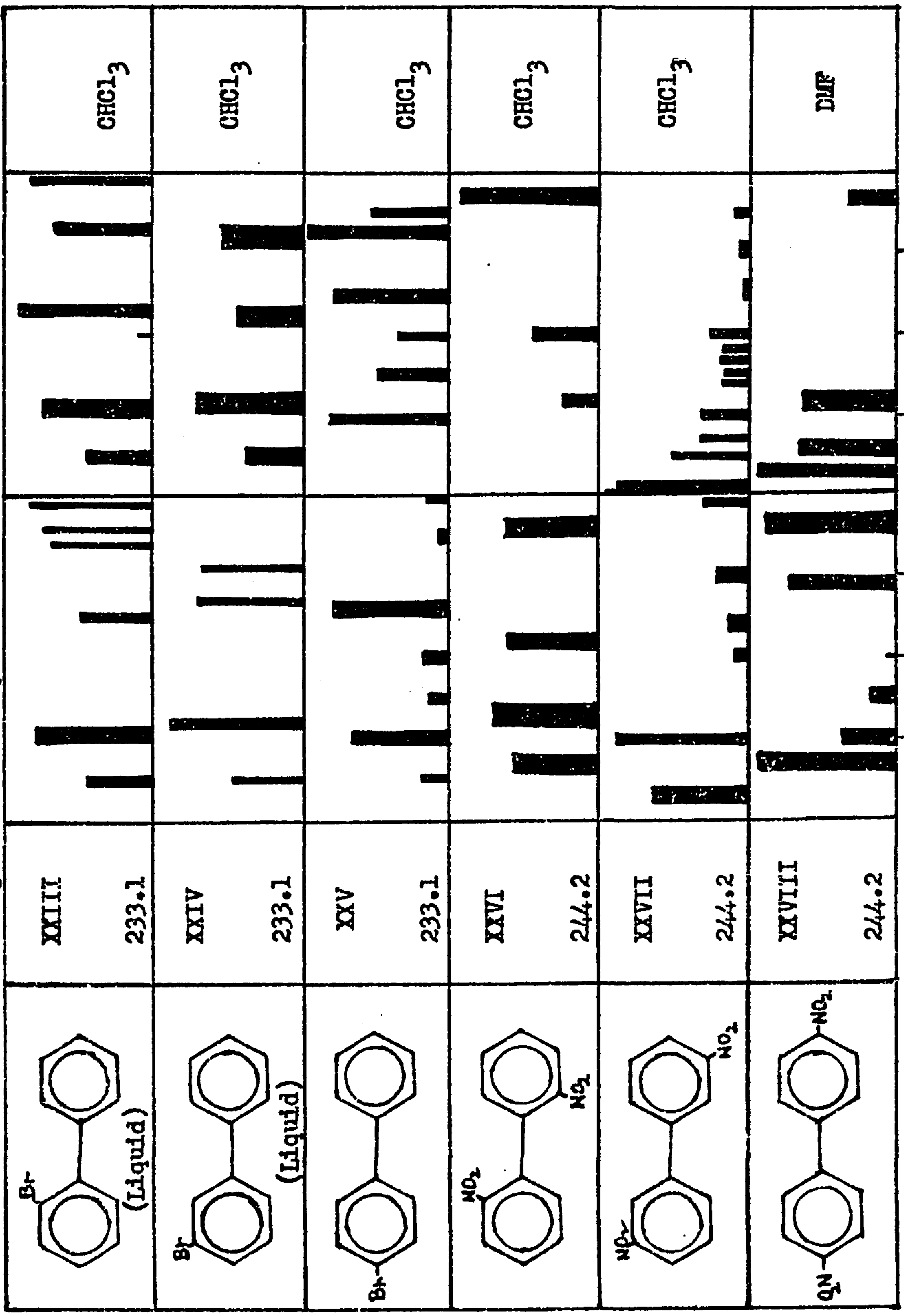

Figure 11. (Continued).

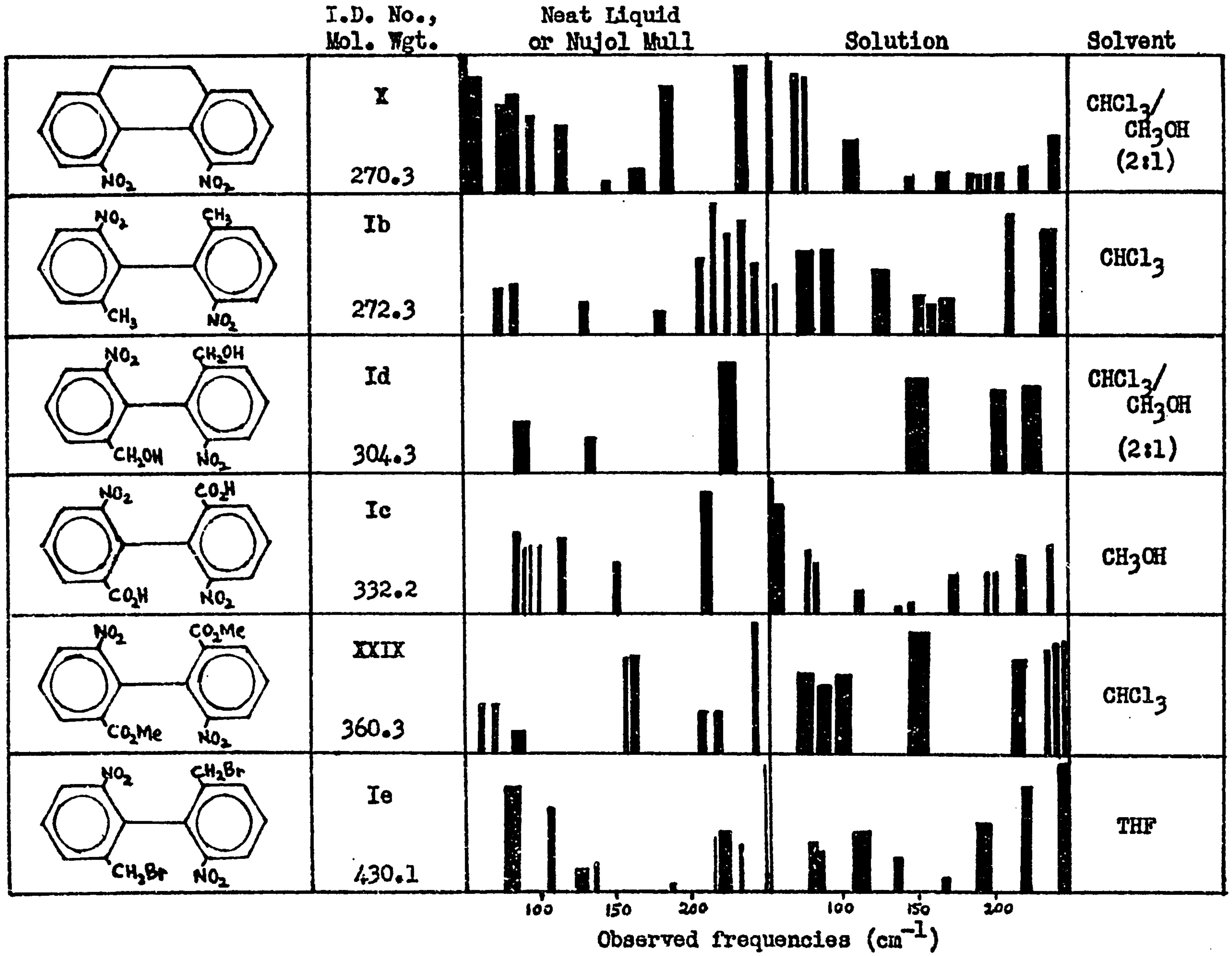

Figure 11. (Continued).

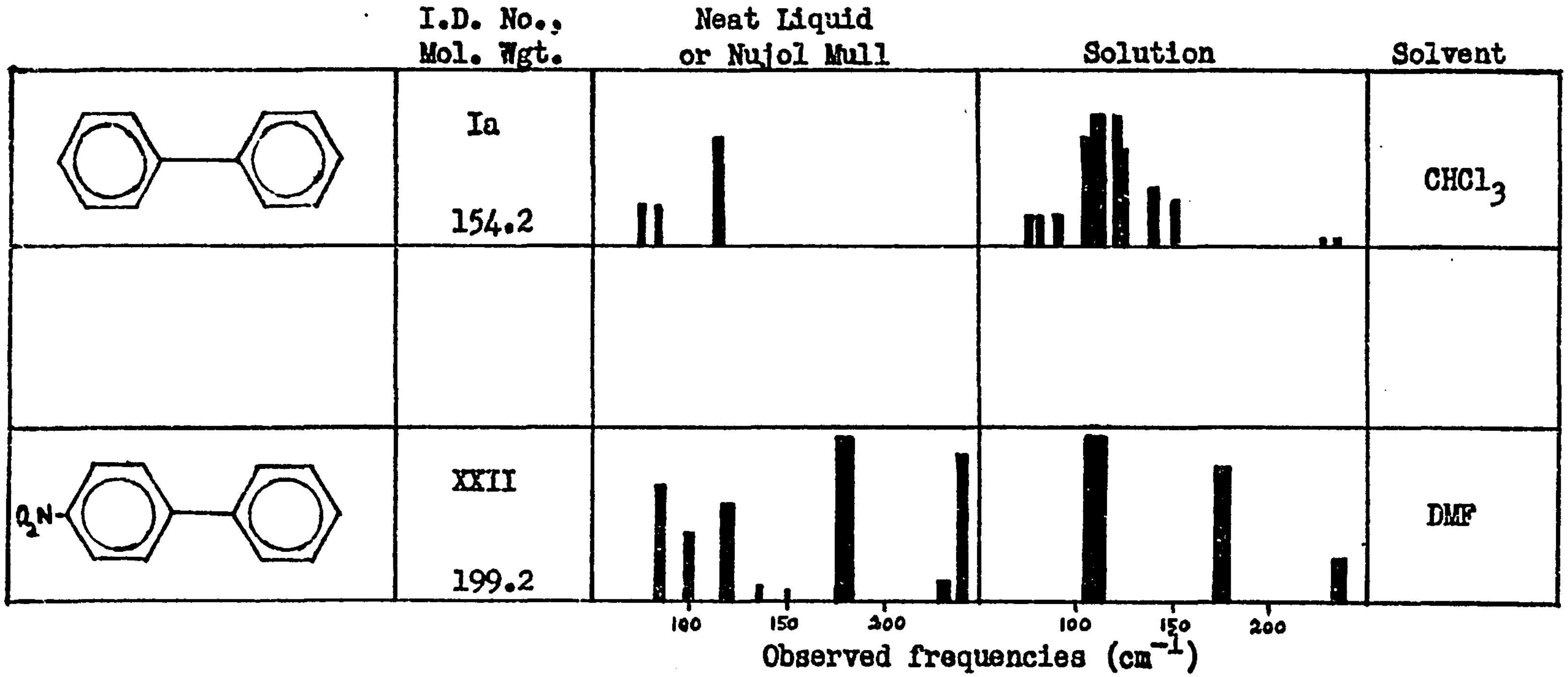

Figure 11. (Continued).

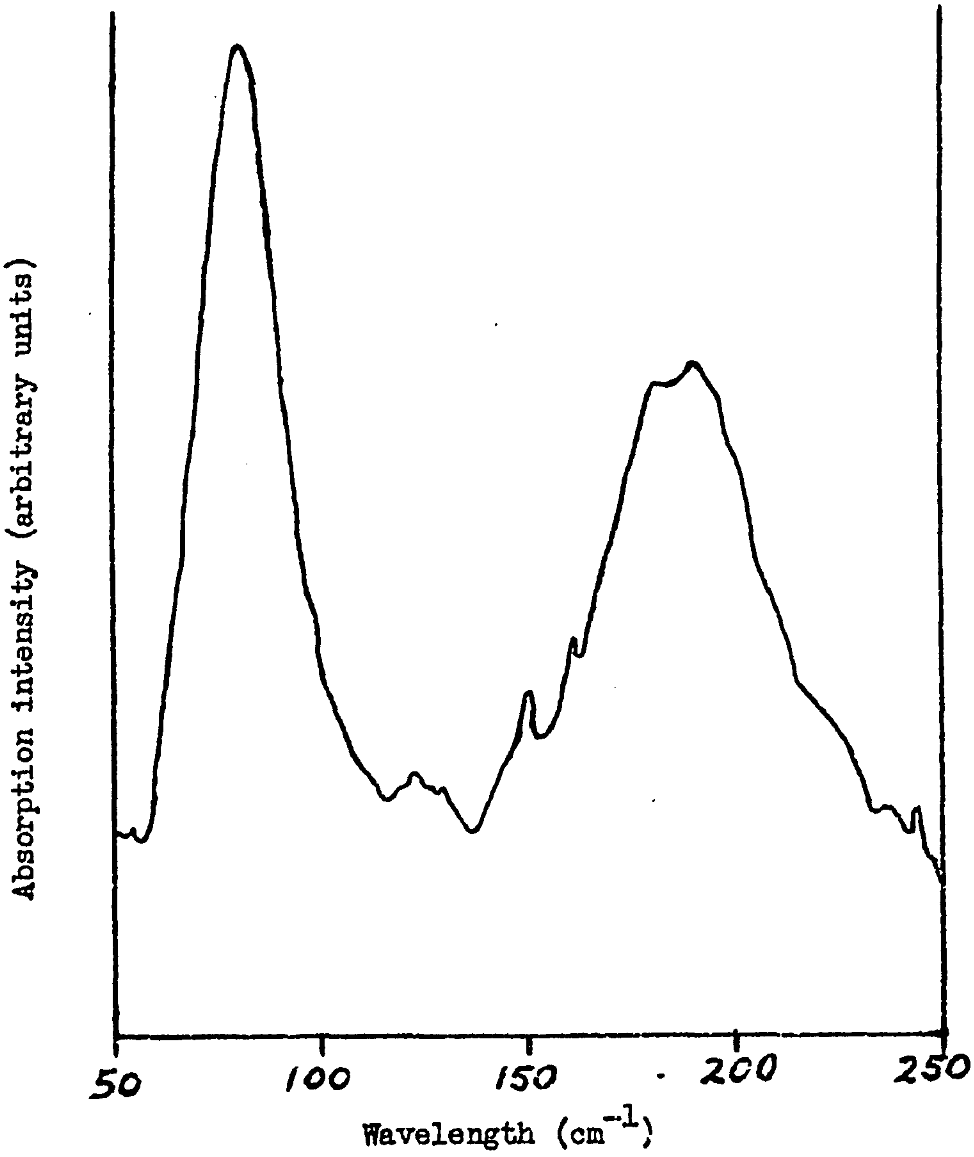

Figure 12. Far infrared spectrum (instrument smoothed) of 3-methylbiphenyl (XII) in chloroform. 128 scans.

With the exception of the last two spectra, the compounds in figure 11 are listed in order of increasing molecular weights. Isomers are listed in the order: ortho, meta, para. The last spectrum is a repeat of a previous compound, but in a different solvent.

DISCUSSION

Changes in the O.R.D. spectrum of a compound, as a consequence of a change in temperature, can be due to solvent expansion and contraction, or to changes in the molecular or specific rotation. In turn, an observed change in molecular or specific rotation can come about in several ways, the most obvious ones being: a) racemization; b) change in structure due to chemical reaction, including, molecular rearrangement; c) a change in the chirality of the molecule due to a change in conformation, and d) a larger temperature dependence of the extinction coefficient of left circularly polarized light, relative to that of right circularly polarized light, or vice versa.

In choice c), above, we could envision the possibility of the existence of a single conformer, the "equilibrium" or average dihedral angle of which was temperature dependent. Alternatively, we could envision the possibility of a dynamic equilibrium involving two or more conformers, shifting with temperature. Of these two possibilities, the latter is by far the most commonly encountered, for example, the equilibrium between the gauche and anti conformers of 2-bromobutane. The former is hardly known, except in the solid phase, and probably is non-existent in solution.

In order to justify the O.R.D. experimental results in terms of a single vibrating conformer, very anharmonic vibrations would have to be postulated. Figure 13 shows the potential energy "well" of a

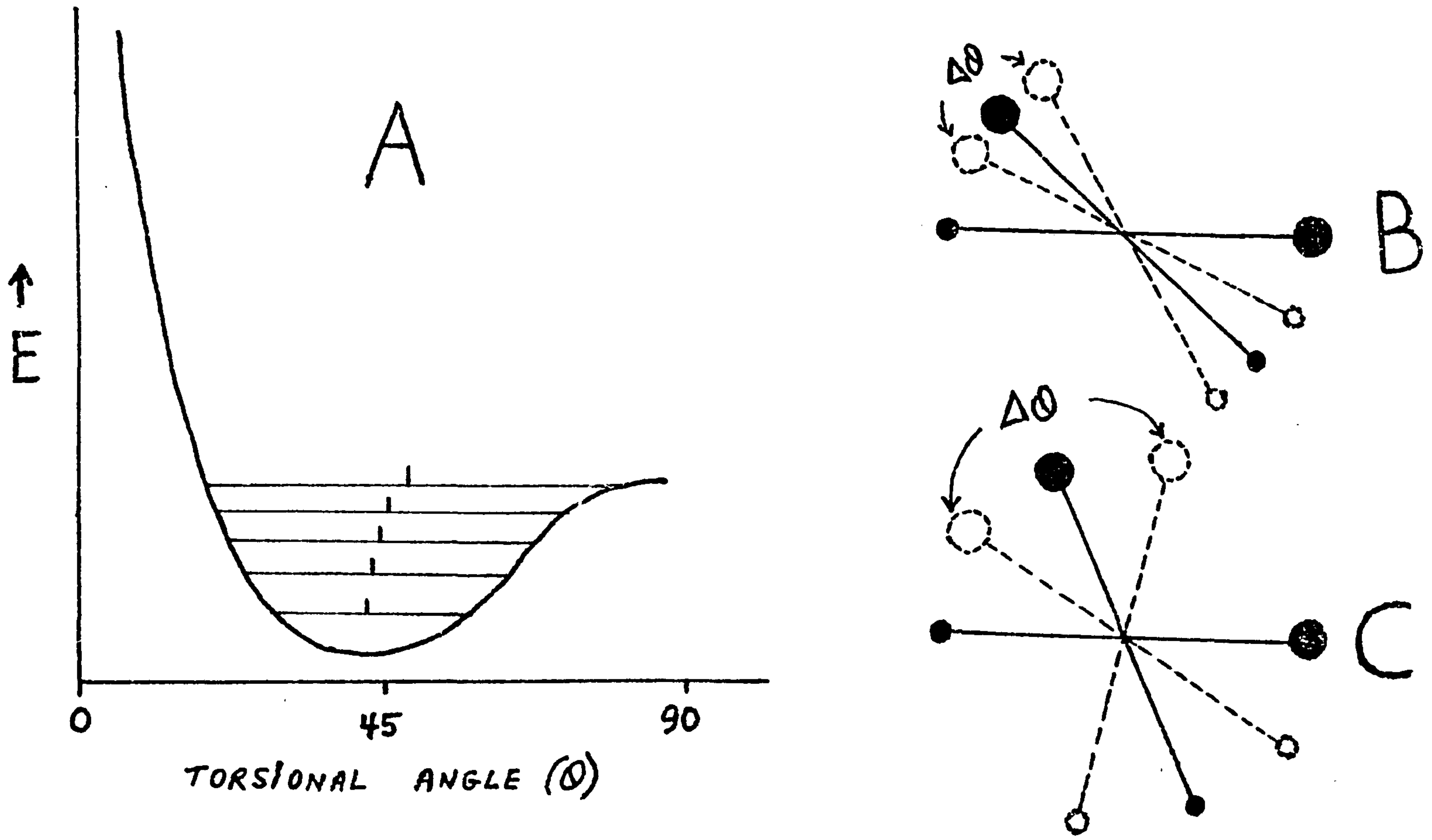

Figure 13. (A) Variation of the "equilibrium" torsional angle of biphenyls (indicated by vertical lines) with vibrational energy level (i.e., with vibrational amplitude) in the case of an asymmetric potential energy curve. Only one "well" is shown. (B) Low amplitude vibrations (broken lines) and related equilibrium conformation (solid line). (C) High amplitude vibrations and related equilibrium conformation. Notice the change in "equilibrium (or average) conformation" in going from B to C or vice versa.

anharmonic oscillator (somewhat exagerated in shape to illustrate the point). The "equilibrium" torsional angle is indicated for each energy level. Also shown is a pictorial representation of the vibrating system that pertains to the potential energy curve. It can be seen that if such a system is vibrationally excited, the "equilibrium" dihedral angle (represented by the mid-point of the respective vibrational levels) will increase with each successive excited level.

Mislow, et. al.[5] suggested that the angular dependence of the specific rotation of biphenyls of type Ib through Ie (R configuration) obeyed an equation of the type

$$[\alpha]_D = -K\sin 2\theta \qquad (2)$$

between $\theta = 45^o$ and $\theta = 135^o$. K is a constant. The other symbols have their usual, or conventional, meaning.

All of the optically active non-bridged biphenyls in this study are nitro substituted in the ortho position of each ring (i.e., $Y = N0_2$ in every case). One compound differs from the other only in X group. In other words, the potential energy function is constant for the Y - Y interaction, but varies for the X - X interaction according to the size of the groups involved.

Since $-N0_2$ has the smallest Van der Waals radius of all the groups involved,[26] it is reasonable that the bromomethyl compound (Ie) might have the most assymmetric potential energy curve (i.e., bromomethyl is the largest of the X groups) and should display the largest degree of assymmetric vibrations. Experimentally, the opposite is observed. Therefore, assymmetric vibrations exclusively cannot explain all of the experimental observations.

On the other hand, the postulation of a dynamic equilibrium between conformers easily explains the experimental observations. The smaller temperature effect in the case of the bromomethyl compound (Ie) is simply due to the greater instability of the cis conformer because of the greater repulsive energy. Furthermore, based upon this latter hypothesis, the predicted sequence for increasing temperature dependence should be $CH_2Br < CO_2H < CH_2OH < CH_3$. Table 1 shows that the only discrepancy is that of the hydroxymethyl group which is expected to have a larger Vander Waals radius than CH_3 because of the fact that oxygen is larger than hydrogen (1.40 Å versus 1.2 Å, respectively).[a] The discrepancy is believed to be due to the greater degree of hydrogen bonding afforded by the hydroxymethyl group with solvent molecules. We would like to emphasize that the reverse sequence is predicted for the assymmetric vibrations argument.

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[a] The paraffinic carbon-hydrogen bond (mono substituted) is listed as being 1.101 ± 0.003 Å, while the paraffinic carbon-oxygen bond (shortened by aromatic ring influences) is listed as 1.36 ± 0.01 Å.[27]

For purpose of illustration, let us assume a difference in energy between the two conformations, $\triangle G$, of 0.5 kilocalorie per mole and that the rotations of the two conformations are equal and opposite. Under these conditions, according to the Boltzmann distribution equation, the mole fraction of the higher energy species is 0.275 at - 15°C and 0.313 at +45°C. Thus, in raising the temperature from - 15°C to +45°C, the excess mole fraction of the lower energy conformer decreases by 17% from 0.450 to 0.374. The observed decreases in rotation (see table 1) upon raising the temperature from - 15°C to +45°C, are of the same order of magnitude. Of course, the actual compounds will differ from the model both in $\triangle G$ and because the specific rotation of the two conformers, while opposite in sign, will not be equal. A lower barrier than that of the model and/or a higher absolute specific rotation of the less stable conformer, will have the effect of a larger percent change in observed rotation for the same temperature change. Molecular orbital calculations on 2, 2'-difluorobiphenyl [19b] predict $\triangle E$ to be in a range similar to the model.

Although the N.M.R. temperature data (table 3) shows a definite increase in shielding as the temperature is increased, no definite conclusion can be drawn as to the nature of the perturbation causing the observed change in shielding. This will be made clear by referring to figure 14.

Figure 14 shows that complementary angles would have identical deshielding characteristics if due to asymmetrical ring current only.

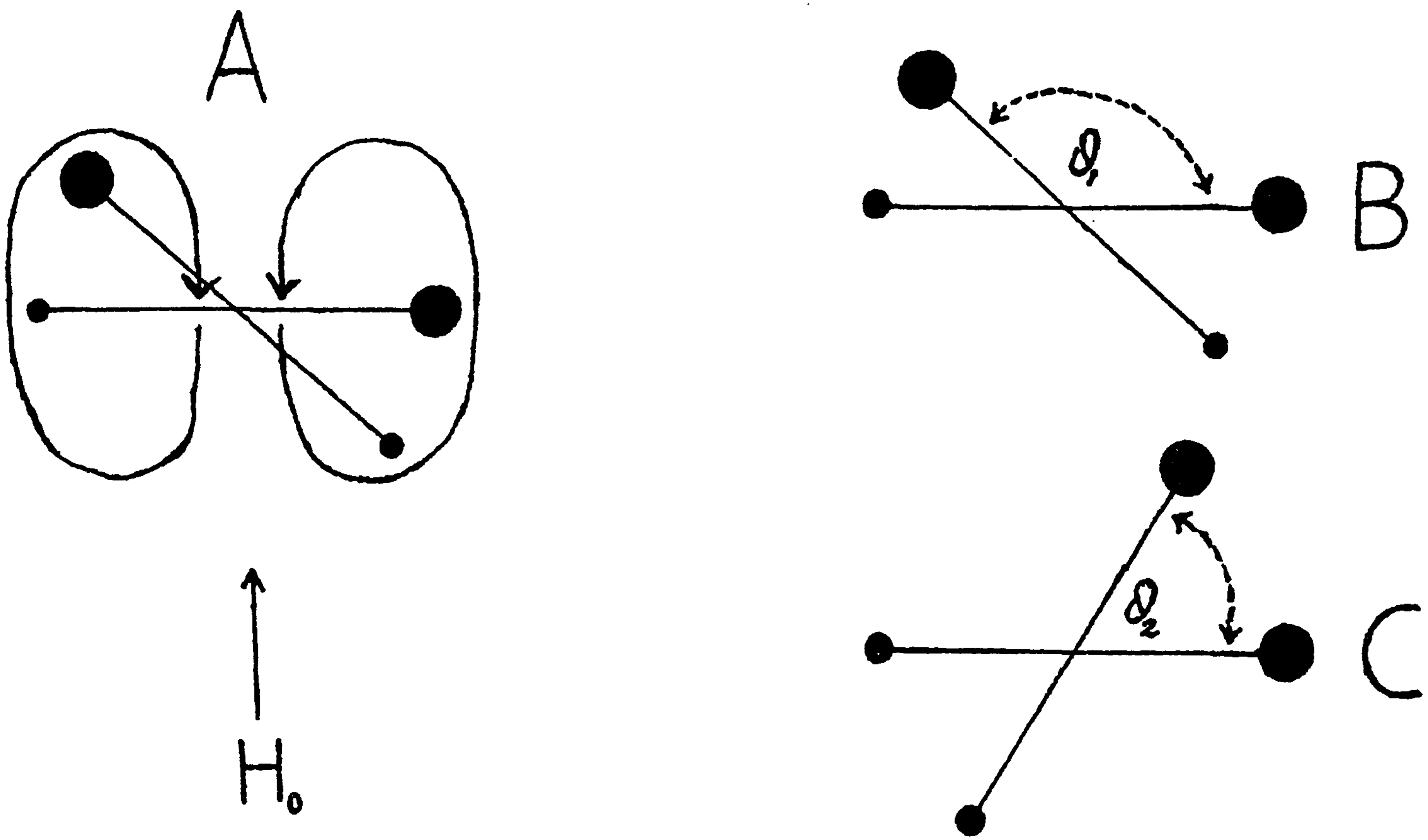

Figure 14. (A) Molecular magnetic lines induced by N.M.R. instrument's magnetic field (H_0). For simplicity, only one set of lines are shown.
(B) Low energy conformer with dihedral angle θ_1.
(C) High energy conformer with dihedral angle θ_2.
$\theta_2 > 180^0 - \theta_1$ because of the greater repulsion energe between large groups in C.

Therefore, if the torsional angles of the conformers are exactly complementary, or are close to being complementary (that is, the difference between ϑ_2 and $180^\circ - \vartheta_1$ is small) the observed N.M.R. temperature effect should be due to the magnetic properties of the near substituents or to the perturbations that these substituents induce in the ring current. The N.M.R. data do not allow us to distinguish between these two possibilities because the exact geometries involved, especially the conformation assumed by the substituents, are not known. Both ring current and magnetic environment, therefore, could cause the observed change in deshielding.

However, one thing is certain, a conformational change is demanded even in the case where the chemical shift difference is due to near neighbors. Therefore, it is likely that the experimentally observed changes in chemical shift are due to the average values resulting from a rapid interchange of conformational populations. The slowness, or inability of the N.M.R. time scale to resolve the peaks in such cases has been well documented and can be found in any standard N.M.R. textbook.

A complete and rigorous analysis of the infrared spectra of biphenyls requires a knowledge of the geometry or symmetry in both the crystal and solution (or liquid) of all conformers involved. In addition, the far I.R. spectra should at least be supplemented with the Raman spectra. From this and what was said in the introduction section concerning possible trends, it is obvious that a rigorous assignment of the torsional frequencies of twenty-five biphenyls is no small task. Therefore, we have opted for a more practical approach to the solution of the problem.

Our approach to the problem consists of inspecting the various spectra to see if any trends or patterns, consistent with the expectations outlined in the introductory section, are observed. We have concentrated our attention almost exclusively on the solution spectra because in this phase, providing we hold the solvent constant, any trend in the observed torsional frequencies will be due mainly to intramolecular properties or factors.

The crystal spectra of biphenyls are not only complicated by the sometimes unexpected molecular conformations of one or more compounds of a group of isomers,[28] but also by the possibility of the additional splitting of peaks due to crystal symmetry and lattice forces.[16,29] These are intermolecular effects. Hence, the observed torsional frequencies, in the case of crystals, may not be due entirely to inherent molecular structure or conformation.

The specific technique used in analyzing the spectra consisted in comparing a set of positional isomers (say, for example, the mono methylbiphenyls) among themselves, then with particular substitutional isomers (for example, all the para isomers or all the meta isomers) of other compounds.

Particular attention has been paid to any apparent splitting of a peak, or peaks, in the di-ortho substituted compounds. We are not able to make definitive assignments, but simply to suggest some possibilities. The following observations refer to solution spectra only, unless otherwise indicated.

Most of the non-resolvable biphenyls showed peaks around 90 cm^{-1} to 110 cm^{-1} and also around 190 cm^{-1} to 225 cm^{-1}. These two sets of peaks suggest a harmonic relationship. Thus, the lower frequency peak might be a fundamental.

Comparing the spectra of groups A compounds (i.e., the mono methyl compounds) among themselves, it can be seen that the spectra of the ortho and meta isomers XI and XII) are practically the same, the only significant difference being the slight shift to higher frequencies of the two strongest absorption peaks of XII. However, when we compare the spectrum of the para isomer (XIII) with that of XI or XII, we see that there is a shift towards lower frequencies of the suspected fundamental peak, near 100 cm^{-1}. Based upon differences in moments of inertia, we should expect a shift toward higher frequencies for the para isomer. The peak intensities also seem reversed.

It becomes apparent that there is a special, or abnormal, "para effect" when we compare the dimethyl compounds among themselves. Once again, there is an increase in frequency in going from the ortho isomer (XIV) to the meta isomer (XV).[a] The spectrum of the para

[a] It is assumed that, in the case of XIV, the peak at approximately 100

isomer (XVI) however, differs in that the lower frequency peak at approximately 100 cm^{-1} is shifted to even lower frequencies, as compared to its isomers XIV and XV.[b]

The trend in the frequencies clearly do not parallel the predictions that were based on a harmonic oscillator model (see page 84ff). This might be due to the fact that the energy wells clearly vary in shapes as well as depths upon changing the position of substitution (see figure 3). Another obvious possibility might be that our tentative assignments of the torsional frequencies are in error.

Spectral interpretations involving the other substituents could be complicated by inductive or mesomeric effects. Nevertheless, the same generalities are observed. Mono-chloro, mono-nitro and mono-bromo biphenyls show the same general tendencies as those mono-methyl and di-methyl biphenyl, if we concentrate on the peaks around 100 cm^{-1} to 110 cm^{-1}.

By comparing the spectra of the mono ortho-substituted compound of each group, a slight, but orderly shift toward lower frequencies is

cm^{-1} is split into a doublet.

[b] A large shift of the original 100 cm^{-1} peak, taking the para isomer frequency to 240 cm^{-1} seems unlikely.

observed as the mono ortho-substituent is charged from H to CH_3, Cl, $N0_2$ or Br, in the order given. This sequence parallels the masses of the substituents,[26] it does not parallel the Van der Waals radii as would be expected, based upon increasing torsional barriers. This is the expected trend, however, based upon reduced moments of inertia if the torsional barriers remain essentially constant.

Inspection of the mono meta-substituted compounds in a similar manner indicates that there is also a shift towards lower frequencies as the mass is increased. However, the decrease in going from mono meta-substituted hydrogen (i.e., unsubstituted biphenyl) to mono meta-bromo (XXIV) in only approximately 7 cm^{-1}.

The mono para-substituted compounds show the following sequence, in order of decreasing vibrational frequencies; $N0_2 > Cl > Br > CH_3$. This order parallels the electronegativities of the groups. The overall decrease in frequency in going from para mono-nitro to para mono-methyl is approximately 15 cm^{-1} (conversely, an increase in frequency with increase in electronegativity).

Since only two di para-substituted compounds were studies, a similar correlation cannot be postulated for these. However, it is very encouraging to see that the experimentally observed frequencies of these two compounds (approximately 110 cm^{-1} for the di para-nitro and approximately 90 cm^{-1} for the di para-methyl) are in accord with the observed trend of the mono para-substituted compounds.

The shift difference in the case of the di para-substituted compounds is 20 cm^{-1}. This difference is not far removed from that observed in the mono para-substituted analogs. For an additive effect, one would expect that the experimentally observed shift difference, in the case of the di para-substituted compounds, be twice the magnitude of that observed in the mono para-substituted compounds (i.e., $2\nu_1 - 2\nu_2 = 2\Delta\nu_{1-2}$). However, since the direction of the inductive or resonance effects in the di para-substituted compounds are opposing each other (as far as the two halves of the molecule is concerned) rather than reinforcing each other, perfect, or ideal, additivity should not be expected.

We will now attempt to locate, where applicable, a second peak in those compounds having unsymmetrical potential energy curves. As stated earlier (see page 84ff) the distinct postulated conformers should show, in at least some of the cases, distinct vibrational frequencies. Compounds having unsymmetrical potential energy curves are: di ortho-methyl (XIV), di ortho-nitro (XXVI) and the optically active biphenyls Ib-e.[a]

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[a] Bridged biphenyl (X) has a symmetrical potential energy curve. However, the angular dependence of the potential energy is different from that of non-bridged biphenyls.

A comparison of the spectrum of the di ortho-methyl compound (XIV) with that of the di ortho-nitro compound (XXVI) shows the following: a) The spectrum of the di ortho-nitro compound is relatively simple showing only three peaks located at approximately 110 cm^{-1}, 150 cm^{-1} and 237 cm^{-1}. b) The spectrum of the di ortho-nitro compound, showing significant peaks at approximately 100 cm^{-1}, 110 cm^{-1}, 144 cm^{-1}, 151 cm^{-1}, 194 cm^{-1}, 231 cm^{-1} and 236 cm^{-1}. However, if we group the peaks at 100 cm^{-1} and 110 cm^{-1}, 144 cm^{-1} and 151 cm^{-1}, 231 cm^{-1} and 236 cm^{-1} into doublets, it immediately becomes apparent that there is a correspondence between these doublets and the peaks in the spectrum of the di ortho-nitro compound. The centers of these doublets are shifted slightly downfield, relative to the corresponding peaks of the di ortho-nitro compound. This is consistent with the behavior observed in the mono-substituted analogs.

Optically active carboxylic acid (Ic) displays a similar pattern of doublets centered at approximately 75 cm^{-1}, 140 cm^{-1}, and 197 cm^{-1}. In the latter case, the doublet at 140 cm^{-1} is somewhat attenuated. These sets of doublets are shifted downfield, relative to the di ortho-methyl compound (XIV), consistent with the general observed trend toward lower frequencies as the size and mass of the ortho groups is increased.[a]

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[a] There is an 82% increase in mass in going from the di ortho-methyl compound (XIV) to (Ic).

An extension of the above observations could be made on the rest of the optically active biphenyls in an attempt to locate the torsional frequencies. However, such an extension would be highly speculative because of the complex nature of the spectra of these compounds. Of particular significance is the general trend of chiral biphenyls to show either apparent splitting of vibrational transitions, or significant broadening which may be due to unresolved splitting. This is what one would expect if two different potential wells exist, as predicted by the O.R.D. studies.

CONCLUSION

Substituted biphenyls, including those that are resolvable, generally exist in two distinct conformations in the range of torsional angles of 0^{o} to 180^{o}. This is demonstrated by, a) the reversible temperature dependence of the specific rotation of optically active biphenyls; b) by a similar temperature dependence upon the chemical shift of the methyl protons of 2,2'-dimethyl-6,6'-dinitrobiphenyl (Ib) and, c) by the observation of apparent splittings in the vibrational spectra of those compounds where the two wells should not be equivalent.

The far I.R. spectra of many substituted biphenyls are tabulated, unfortunately, no definite assignments can be made.

EXPERIMENTAL

General

Melting points were taken in capillary tubes either on a Hoover Uni-Melt oil bath apparatus or on Laboratory Devices' Mel-Temp air bath apparatus.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Mass spectral analyses were performed by the analytical department of Hoffman-LaRoche, Inc., Nutley, New Jersey. We are especially indebted to Dr. Milan Uskokovic of the organic synthesis department.

Spectra

O.R.D. spectra were taken on Jasco-Darrum's J-20 spectropolarimeter, using a 1.0 milliliter jacketed cell of 1.0 centimeter (0.10 decimeter) pathlength. Temperatures were controlled to $\pm 0.1^{o}C$. The coefficients of thermal expansion of methanol and n-hexane, for the experimental temperature range (-15^{o} to $+45^{o}$) in increments of 10^{o}, were determined by thermally equilibrating exactly 10 mls. of the respective solvents in a volumetric flask and determining the mass at each temperature. The same volumetric flasks were used throughout the entire temperature range and appropriate corrections for the thermal expansion of glass was also made. A plot of change in mass versus temperature gave a good straight line in each case. Essentially the same slope was obtained for both solvents. The calculated coefficient of expansion was found to be 0.1% per degree centigrade.

The N.M.R. temperature dependence studies were done on a Varian A-60A spectrometer, continuous wave mode. Chemical shift of the methyl protons of toluene was used as internal standard. Internal temperatures were calibrated with methanol (below $+20^{o}$) and ethylene glycol (above $+20^{o}$) resonances.[30]

Far I.R. spectra were taken on a Digilab, Model 296, interferometer spectrometer,[31] usually 128 scans. Appropriate Milar beam splitters were used to cover the range of interest. Solution spectra were taken in polyethylene cells of 1.0 millimeter pathlength. Solid spectra were Nujol mulls of appropriate thickness, between polyethylene plates. No judgment as to relative peak intensities of one spectrum with those of another spectrum can be made. Instrument print-out was adjusted, in each case, so that the most intense band would reflect (where possible) at least 80% of the Y axis.

U.V. spectra were recorded on a Cary 14 spectrophotometer, using matching cuvettes of 1.0 centimeter pathlength, 3 milliliters total volume. A thermostated methanol bath (apparatus described in part I of this thesis) was attached for the temperature studies. Temperatures were controlled to ± $0.1^{o}C$.

Materials

Unsubstituted biphenyl (Ia), mono p-methylbiphenyl (XIII), di m-methylbiphenyl (XV), di p-methylbiphenyl (XVI), mono p-chlorobiphenyl

(XIX), mono o-nitrobiphenyl (XX), mono m-nitrobiphenyl (XXI), di o-nitrobiphenyl (XXVI), and di p-nitrobiphenyl (XXVIII) were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.

Mono o-methylbiphenyl (XI), mono m-methylbiphenyl (XII), mono ortho-chlorobiphenyl (XVII), mono meta-chlorobiphenyl (XVIII), mono para-nitrobiphenyl (XXII), mono ortho-bromobiphenyl (XXIII) and mono meta-bromobiphenyl (XXIV) were purchased from K & K Laboratories, Inc., Plainview, New York.

Mono para-bromobiphenyl (XXV) was purchased from Chemical Procurement Laboratories, Inc., 18-17 130th Street, College Point, New York.

Most of the above compounds were used as obtained. A couple were recrystallized because of unsatisfactory melting points.

The following compounds were synthesized:

2, 2'dimethylbiphenyl (XIV)[32]

To 22.0 grams (0.35 mole) of activated copper powder, heated to approximately 260°C with a heating mantle, was added in small portions and at infrequent intervals, 25.0 grams (0.115 mole) of 2-iodotoluene. Heating was continued until reflux ceased (approximately 24 hours).

The solid was extracted with benzene (50 mls., hot), then with toluene (50 mls., hot). After stripping the solvent, the residue was distilled on a spinning-band column and the fraction boiling between

254°-256° was collected.[a] 5.1 grams (0.0282 mole) obtained. 49% yield. Literature b.p. 254°-256°. N.M.R. and I.R. were consistent with the structure.

3,3'-dinitrobiphenyls (XXVII)[33]

15.0 grams (0.0605 mole) of 1-iodo-3-nitrobenzene heated in a 250 mls. round bottom flask, equipped with a reflux condenser, to approximately 220°. 4.00 grams (0.0630 mole) of copper electrolytic dust added in small portions at intervals of at least one minute. After complete addition of copper, the mixture was heated three additional hours. The temperature was then reduced to 140° and heating was continued overnight.

The solid was extracted with hot benzene and recrystallized twice from toluene. Decolorizing with activated carbon was necessary. No attempt was made to maximize the yield. 1.10 gram (0.00451 mole) obtained. M. p. 201.0° -202.5°. Literature 202°. 14.9% yield.

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[a] A purple compound resulted from the distillation. It could be decolorized simply by dissolving in aged diethyl ether (peroxides? ?!) or by dissolving in fresh diethyl ether and washing with aqueous sodium bisulfite solution. The color reappeared when an attempt was made to redistill the liquid from a short all-glass column. Several decolorations with charcoal were then necessary. The pure product is light yellow, almost colorless.

(-)-9,10-dihydro-4,5-dinitrophenanthrene (X)[a]

See experimental section, Part I, this thesis, for details.

(-) and (+)-2,2'-dimethyl-6,6'-dinitrobiphenyl (Ib)[34]

See experimental section, Part I, this thesis, for details.

(-) and (+)-2,2'-bis(hydroxymethyl)-6,6'-dinitrobiphenyl (Id)[35]

See experimental section, Part I, this thesis, for details.

d, -6,6'-dinotrodiphenic acid (Ic)[36]

See experimental section, Part I, this thesis, for details.

d, -methyl-6,6'-dinitrodiphenate (XXIX)[36]

See experimental section, Part I, this thesis, for details.

(-) and (+)-2,2'-bis(bromomethyl)-6,6'-dinitrobiphenyl (Ie)[35]

See experimental section, Part I, this thesis, for details.

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[a] The crude product was kindly prepared by Dr. Richard D. Stauffer while a postdoctoral associate with Dr. Martin F. Semmelhack of Cornell University, Ithaca, New York.

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