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Richard L. Taber

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OF
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TABER

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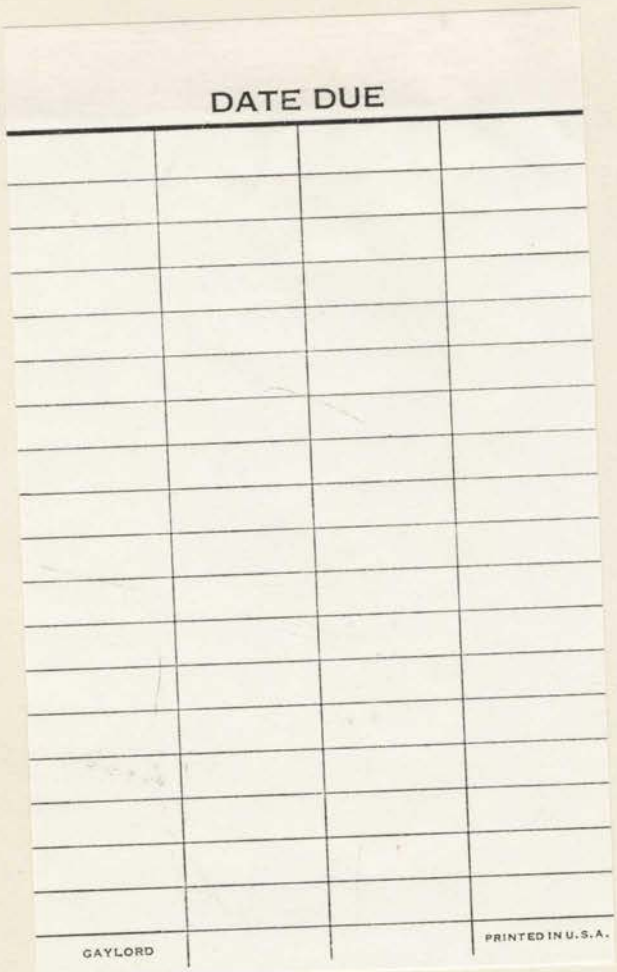

AN INVESTIGATION OF STERIC INHIBITION OF RESONANCE IN LIQUID SCINTILLATORS

By

Richard L. Taber

A Dissertation

in Partial Fulfillment of the

Requirements for the Degree of

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The writer wishes to express his gratitude to Professor Guido H. Daub for suggesting the original problem and for advice and encouragement during the course of the work. He is especially grateful for the many helpful suggestions given him by Dr. F. Newton Hayes and to Dr. Donald G. Ott of the Biomedical Research Group, Los Alamos Scientific Laboratory, for his much needed assistance.

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DEDICATION

This dissertation is respectfully and lovingly dedicated to my wife, Mary Alice Taber.

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INTRODUCTION

It is well known that the replacement of two or more of the ortho hydrogen atoms in the two benzene rings of biphenyl by larger atoms or groups hinders the rotation about the 1,1'-carbon single bond in the biphenyl system. If the groups are so large that they are unable to pass each other upon rotation of the 1,1'-bond, then the two benzene rings are forced to assume a non-planar configuration.

Among the steric effects most studied by electronic spectra are those involving a single bond attached to a conjugated system, such as the 1,1'-bond in biphenyl. If resonance interaction does cause the single bond to demonstrate some double bond character, this will affect the spectrum of the molecule involved. If only electronic energy is considered, the covalent bond order of a carbon to carbon bond with some double bond character will be at a maximum when the atoms or groups attached to the carbon atoms lie in the same plane. This planar structure allows for maximum overlap of the p-orbitals across the bond. In a molecule such as biphenyl, any additional resonance energy the

molecule has above that of the two isolated benzene rings depends upon some double bond character between the rings.

It has been demonstrated, however, that fairly large deviations from coplanarity will not completely inhibit resonance interaction between the rings. As can be seen in Figure 1, even when the rings are twisted far from coplanarity, considerable overlap of the p-orbitals can occur.

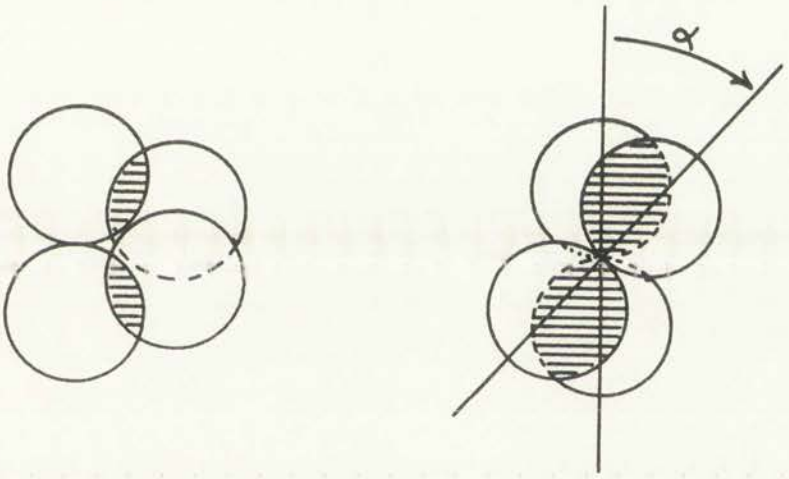

Figure 1. The overlap between p-orbitals when a double bond (2 pπ) is twisted by an angle α.[1]

(1) Lloyd L. Ingraham, "Steric Effects in Organic Chemistry," M. S. Newman, editor, John Wiley and Sons, Inc., New York, N. Y., 1956.

In the case of biphenyl itself, there is conflicting evidence as to whether or not the molecule has a planar configuration. X-ray crystal analysis of biphenyl has shown the molecule to have a completely planar configuration.[2]

However, electron diffraction investigations have suggested that in the gaseous state, biphenyl has a non-planar configuration in which the planes of the two benzene rings are at an angle of approximately 45° to one another.[3] In another study of the twisting of the 1,1'-biphenyl bond, the angles of deviation from coplanarity for 3,3'-dichloro-benzidine, 3,3'-dibromobiphenyl, and 3,3'5,5'-tetrabromo-biphenyl in the gaseous state have been found to be 45° $\pm$ 10°, 52° $\pm$ 10°, and 54° $\pm$ 5°, respectively.[4]

As was mentioned, biphenyl in the crystalline state is considered to be planar, and in this state exhibits an ultraviolet absorption maximum at 275 mμ. However, the ultraviolet absorption spectrum for biphenyl in solution (heptane) exhibits a maximum at 248 mμ. Suzuki[5] suggests

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(2) J. Dhar, Indian J. Phys., 7, 43 (1932).

(3) O. Bastiansen, Acta Chem. Scand., 3, 408 (1949).

(4) O. Bastiansen, Acta Chem. Scand., 4, 926 (1950).

(5) Hiroshi Suzuki, Bull. Chem. Soc. Japan, 27, 597 (1954).

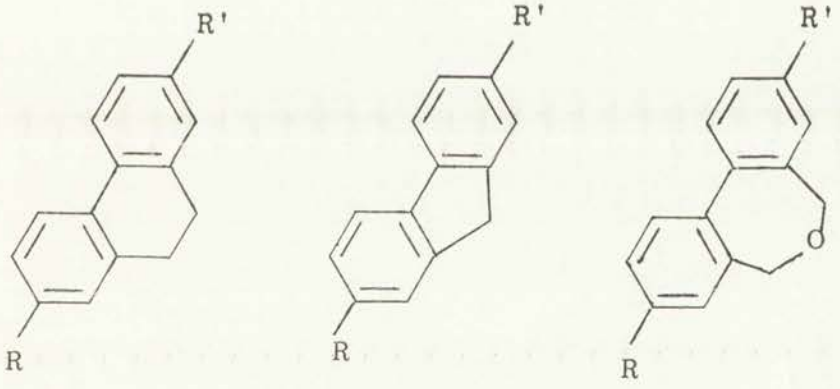
that biphenyl is non-planar in the liquid or gaseous state while in the crystalline state it is maintained in the co-planar configuration by the lattice forces which overcome the steric interference between the ortho hydrogen atoms. This angle of deviation from coplanarity has been estimated to be 50° as calculated by Suzuki using the molecular orbital method.[5] The agreement between the value obtained by Suzuki (50°) and the average value found by Bastiansen[3,4] for the non-ortho-substituted biphenyls (50° ± 5°) is surprisingly good, although the former refers to the molecule in solution while the latter refers to the molecule in the gaseous state.

When the biphenyl molecule is planar, the distance between the two nearest ortho-hydrogen atoms attached to different benzene rings is about 1.8 Å, which is much shorter than the usual van der Waals distance of 2.0 Å.[5] Therefore, there should be some steric interference between them.

The ultraviolet absorption spectrum of biphenyl is quite different from that of benzene and has an intense characteristic band at about 248 mμ. This band is believed to be due to the conjugation between the two benzene rings, which according to classical theory requires that the molecule of biphenyl be planar or nearly planar. It is most

interesting to note that the spectrum of a biphenyl derivative having the four ortho positions substituted, such as in bimesityl, fails to exhibit the characteristic biphenyl band. This spectrum is essentially that of mesitylene. This is explained by the postulate that conjugation cannot occur between the two highly hindered benzene rings because the two rings cannot become coplanar due to steric interference of the four ortho substituents.

In recent investigations of p-terphenyl and p-quaterphenyl derivatives as liquid scintillation solutes,[6,7] compounds of the types 4, 5, and 6 have been studied.



1, R = R' = H. 2, R = R' = H. 3, R = R' = H.

4, R = R' = C_6H_5. 5, R = R' = C_6H_5. 6, R = R' = C_6H_5.

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(6) M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, J. Am. Chem. Soc., 81, 4583 (1959).

(7) S. P. Birkeland, G. H. Daub, F. N. Hayes, and D. G. Ott, J. Org. Chem., 26, 2662 (1961).

An interesting fact is evidenced by constructing molecular models of 9,10-dihydrophenanthrene (1) (Figure 2) and the corresponding 5,7-dihydrodibenz[c,e]oxepin (3) (Figure 3). It is apparent from these models that the $-CH_2-CH_2-$ bridge of the dihydro compound (1) causes the bridged benzene rings to be twisted only slightly with respect to one another.

The degree of deviation from coplanarity of the molecular configuration of 9,10-dihydrophenanthrene (1) has been determined by Suzuki[5] to be 31.5° from calculations using the molecular orbital method. According to Beaven, the angle of twist in 1, as determined from molecular models, is only about 20°. The two rings in biphenyl, then, are not twisted to a great extent from a common plane by a two-carbon-atom bridge across the ortho positions. Fluorene (2), in which the 2,2'-positions are bridged by a single methylene group, is best regarded as a strained planar structure,[8] although the two-fold axes of the benzene rings are not collinear.[9] However, the ultraviolet absorption spectra of 1 and 2 are similar, with the exception that in the latter

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(8) G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, J. Chem. Soc., 854 (1952).

(9) J. Weisburger, E. K. Weisburger, and F. E. Ray, J. Am. Chem. Soc., 72, 4250 (1950).

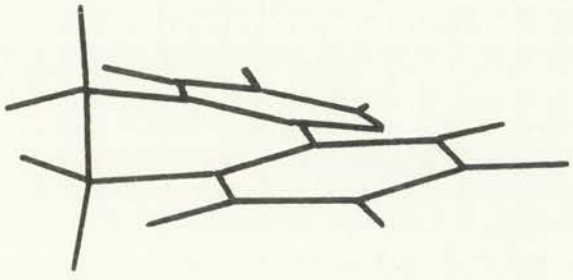

Figure 2. 9,10-Dihydrophenanthrene (1).

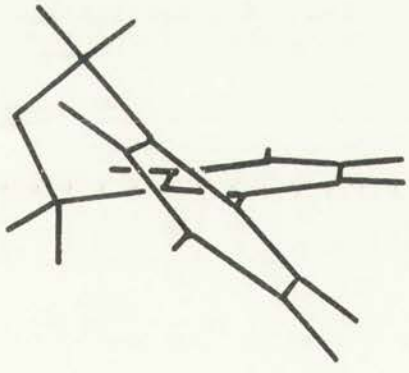

Figure 3. 5,7-Dihydrodibenz[c,e]oxepin (3).

compound fairly intense fine structures appear.[10] This peak at higher wavelengths in fluorene (2) is quite strong, while in 9,10-dihydrophenanthrene (1) there is a definitely resolved maximum at a longer wavelength (λ_{max} 299 mμ, ϵ_{max} 4750) but of low intensity. Jones ascribes this band to the bathochromic effect of the 9,10-methylene group acting simply as an alkyl substituent.[11] This explanation has been criticized by Braude,[12] who suggests that the relatively high intensity of the long-wave band is an indication of interaction between the phenyl groups through the $-CH_2-CH_2-$ linkage, so that this band has its origin in the same way as the long-wave band in fluorene (2) (λ_{max} 300 mμ, ϵ_{max} 10,000). Its lower intensity is attributed to a lower degree of interaction through two methylene groups rather than one such group.

The fact that the phenyl-phenyl conjugation bands for 1 and 2 (264 mμ and 261 mμ) are found at higher wavelengths than that for biphenyl (248 mμ) indicates that appreciable p-orbital overlap between the benzene rings in 1 and 2 can occur. As a matter of fact, if one accepts the use of

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(10) R. N. Jones, J. Am. Chem. Soc., 67, 2127 (1945).

(11) R. N. Jones, J. Am. Chem. Soc., 63, 1658 (1941).

(12) E. A. Braude, J. Chem. Soc., 1902 (1949).

ultraviolet absorption spectra as a criterion of coplanarity, then more p-orbital overlap can occur in 1 and 2 than in biphenyl. An analogous situation exists in the p-terphenyl and p-quaterphenyl systems, where 2,7-diphenyl-9,10-dihydrophenanthrene (4) and 2,7-diphenylfluorene (5) exhibit similar spectral properties as p-quaterphenyl. The corresponding 2-phenyl derivatives of 1 and 2 exhibit similar spectral properties as p-terphenyl.[6,7]

On the other hand, the $-CH_2-O-CH_2-$ bridge of 5,7-dihydrodibenz[c,e]oxepin (3) causes the bridged benzene rings to be twisted to a much greater extent than in 9,10-dihydrophenanthrene (1). Estimates from molecular models indicate that the bridged benzene rings are twisted at an angle of about 50° to one another. Suzuki estimates that the angle of deviation from coplanarity is 47° for 3.[5] Therefore, the p-orbital overlap between the directly bonded carbon atoms of the bridged benzene rings in 3 should be decreased from that in a coplanar structure and resonance interaction between the two rings should be inhibited.

However, the ultraviolet absorption spectrum for 3 indicates that approximately the same amount of resonance interaction can occur between the two benzene rings of the oxepin as between the rings in biphenyl (Figure 4), since the maximum for 3 is 250 mμ and the maximum for biphenyl is

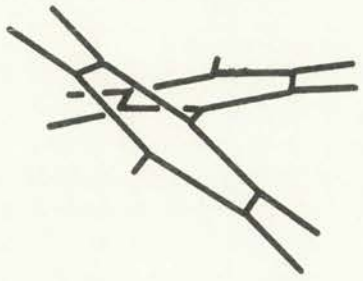


Figure 4. Biphenyl.

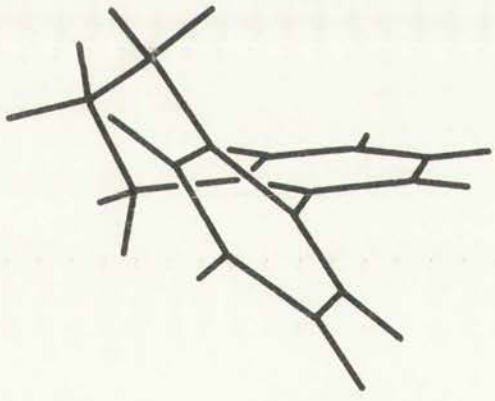
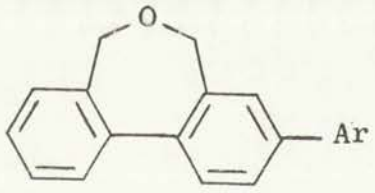


Figure 5. 5,7-Dihydrodibenzo[a,c]cycloheptadiene.

248 mμ. It is also interesting to note that the ultraviolet absorption maximum for 3,9-diphenyl-5,7-dihydrodibenz[c,e]-oxepin (6) (298 mμ) is similar to that found for the unbridged p-quaterphenyl (296 mμ).[13] It should also be noted that the scintillation data indicate that p-quaterphenyl and the oxepin 6 may have a similar amount of p-orbital overlap between the two bridged benzene rings. This observation is also true for 3-(4-biphenylyl)-5,7-dihydrodibenz[c,e]-oxepin (7a), which is an excellent liquid scintillation solute, and for 3-phenyl-5,7-dihydrodibenz[c,e]oxepin (7b), which has a relative pulse-height similar to that of p-terphenyl.[13]



7a, Ar = 4-$C_6H_5C_6H_4$

7b, Ar = C_6H_5

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(13) S. P. Birkeland, G. H. Daub, F. N. Hayes, and D. G. Ott, Z. fur Physik, 159, 516 (1960).

The evidence indicates, then, that the $-CH_2-O-CH_2-$ bridge across the ortho-positions does not appreciably prevent resonance interaction from occurring between the two phenyl rings. If one accepts Braude's[12] explanation of the fine line structures at longer wavelengths in the ultraviolet absorption spectrum of the 9,10-dihydrophenanthrene (1) and fluorene (2), then one might also expect such structures to be found at longer wavelengths in the spectrum for 3, and such is not the case.

It should be mentioned at this point that the values calculated for the angle of deviation from coplanarity by Suzuki (31.5° for 1, 47° for 3, and 50° for biphenyl) do not necessarily refer to the rigid configurations of the molecules but to the average configurations. The models of the molecules would more accurately represent the most probable configuration for the molecules.

Twisting the phenyl rings attached to the single bond in biphenyl away from planarity may, therefore, affect the spectrum in any of three ways: (1) No change in the wavelength of the maximum but a decrease in the absorption intensity. This effect is caused by relatively small twists. (2) Absorption maximum shifts to shorter wavelengths in addition to decreased absorption intensity. (3) The spectrum is similar to the sum of the spectra of the component

parts of the molecule on either end of the twisted bond. This type of spectrum is the result of a large amount of twisting. Table 1 lists in order of decreasing wavelengths (and increasing twist) a number of 2,2'-disubstituted biphenyls.

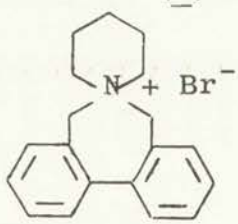
The ultraviolet absorption spectra for biphenyl, p-terphenyl, and p-quaterphenyl exhibit maxima at 248 mμ, 276 mμ, and 296 mμ, respectively, thus showing a shift toward longer wavelengths as additional linear benzene rings are included. It has been shown that compounds 1, 2, and 3 bear a strong resemblance to biphenyl in their spectral properties, and that the p-quaterphenyl derivatives 4, 5, and 6 are similar to p-quaterphenyl. In both sets of examples it is noted that the oxepins, fluorenes, and the 9,10-dihydrophenanthrenes all exhibit maxima at wavelengths longer than their non-ortho-substituted analogs, thus indicating that a larger amount of p-orbital overlap is occurring in these systems.

It is interesting to note the high relative pulse-height values of 1.15, 1.14, and 0.97[7] for the p-quaterphenyl derivatives 4, 5, and 6, respectively. It must be pointed out, however, that the maximum value of 0.97 does not indicate the true peak relative pulse-height value for 2,7-diphenylfluorene (5), as the peak had not yet been reached at maximum solubility.

TABLE 1. CONJUGATION BAND MAXIMA FOR SOME 2,2'-DISUBSTITUTED BIPHENYLS

Compound	Solvent	λ_{max} (mμ)	ϵ_{max}	Reference
Biphenyl	(crystal)	275		5
9,10-Dihydrophenanthrene	hexane	264	18,000	5
Fluorene	95% ethanol	261	19,000	14
5,7-Dihydrodibenz[c,e]-oxepin	hexane	250	16,500	8
(+)-6,6-Dicarbethoxy-5,7-dihydrodibenzo[a,c]cyclo-heptadiene	95% ethanol	249	16,980	15
Biphenyl	heptane	248	19,000	5
2,7-Dihydro-3,4,5,6-di-benzazepinium-1-spiro-1'''-piperidinium bromide*	water	248	15,000	16
5,7-Dihydrodibenzo[c,e]-selenepin	95% ethanol	247	6,250	16
5,7-Dihydrodibenzo[c,e]-thiepin	95% ethanol	245	10,000	16
2,2'-Dimethylbiphenyl	95% ethanol	228	6,800	17

*2,7-Dihydro-3,4,5,6-dibenzazepinium-1-spiro-1'''-piperidinium bromide (8).



(14) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.
(15) D. C. Iffland and H. Siegel, J. Am. Chem. Soc., 80, 1947 (1958).
(16) W. E. Truce and D. D. Emrick, J. Am. Chem. Soc., 78, 6130 (1956).
(17) G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner, and G. R. Bird, J. Chem. Soc., 131 (1954).

It would be better, for the purposes of comparison of similar compounds, to plot all relative pulse-heights on a basis of millimoles of solute per liter, rather than RPH versus concentration in grams of solute per liter, as better comparisons of scintillation ability could be made. It should also be better to make comparisons between different compounds at lower concentrations.

Figure 6, in which the relative pulse-heights for the three p-quaterphenyl derivatives 4, 5, and 6 are plotted against concentration in millimoles of solute per liter, shows that at lower concentrations a valid comparison of the three compounds can be made. At higher concentrations, a sound comparison of scintillation ability cannot be made, because of solubility problems and differences in self-quenching. A comparison of the relative pulse-heights for the three compounds 4, 5, and 6 at a concentration of 3.15 millimoles of solute per liter, which is the maximum solubility of 5 in toluene, shows values of 0.97 for 5, 0.90 for 4, and 0.84 for 6. Thus within the limits of its solubility, 2,7-diphenylfluorene (5) is the best liquid scintillation solute of the three.

Iffland and Siegel[15] have reported the successful preparation of an optically active biphenyl with a 2,2'- three-carbon-atom bridge, (+)-6,6-dicarbethoxy-5,7-dihydrodibenzo-[a,c]cycloheptadiene (9).

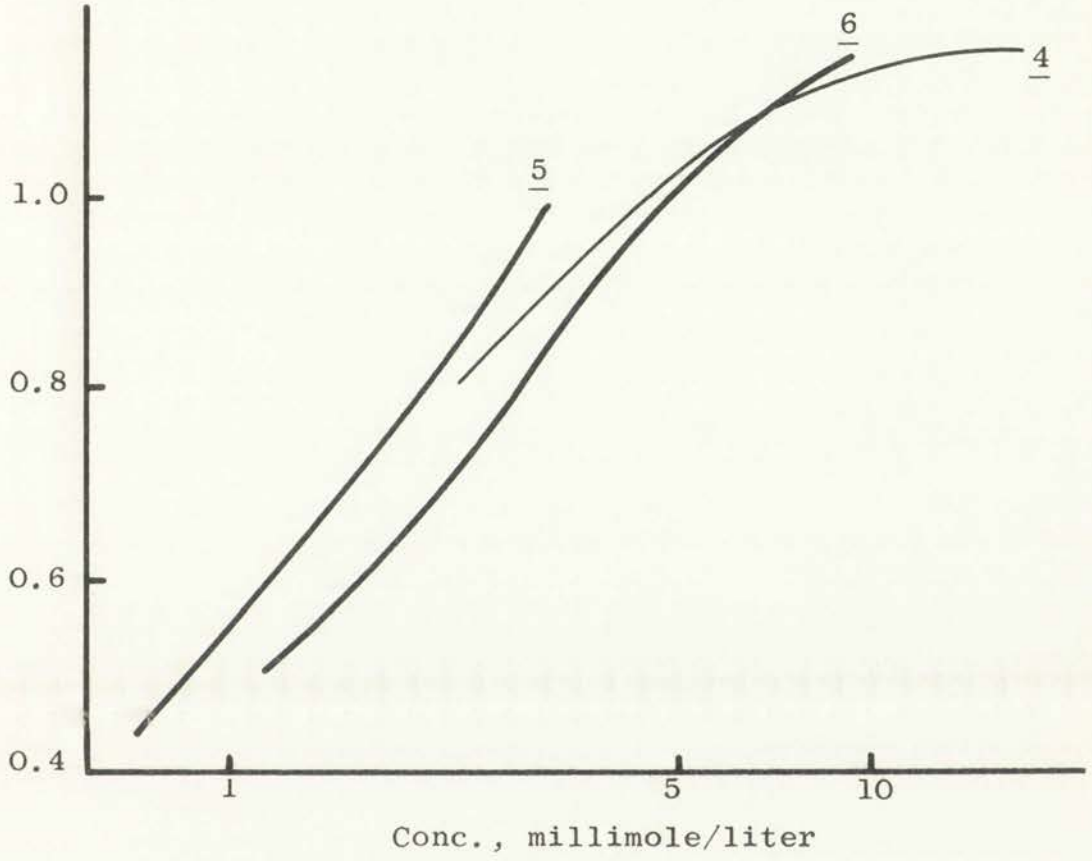
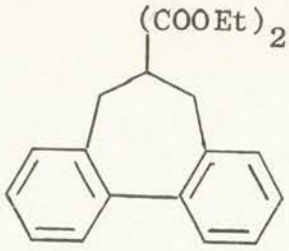


Figure 6. Relative pulse-height curves for 2,7-diphenyl-9,10-dihydrophenanthrene (4), 2,7-diphenylfluorene (5), and 3,9-diphenyl-5,7-dihydrodibenz[c,e]-oxepin (6) as primary solutes.



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While the diester 9, in cyclohexane solution, loses half of its activity in 80 minutes, the compound is optically stable in the crystalline state. No significant loss of optical activity was observed after about 200 hours in the solid state. Thus, the forces holding the molecule in the crystal lattice must reinforce the steric forces resulting from the seven-membered-ring bridge and the repulsive forces of the 1,11-hydrogen atoms. The relatively short half-life period in solution indicates that the energy barrier for attaining a planar transition state is not too great.

The observed optical activity of 9 is unquestionably a result of the steric requirement of the three-carbon-atom bridge maintaining the benzene rings in a non-coplanar configuration. In addition, it should be pointed out that the diester 9, which has a three-carbon-atom bridge across the ortho positions of biphenyl, exhibits an intense (ϵ_{max} 16,980) absorption band at 249 mμ. This phenomenon, when compared with the conjugation band for biphenyl (λ_{max} 248 mμ,

ϵ_{max} 19,000), indicates that the benzene rings in both biphenyl and the diester 9 are twisted out of the plane to approximately an angle of 50° to one another (Figures 4 and 5, p. 8). This similarity lends strong support to the observation made by Suzuki;[5] that is, perfect planarity is not necessarily a requirement for conjugation across the 1,1'-biphenyl bond.

It has been suggested by Ahmed and Hall[18] that in the few cases where reasonably valid comparisons can be made, the bridged biphenyls (with six- or seven-membered rings) are optically less stable than unbridged compounds with similar blocking groups. Presumably, this is because the molecules of the bridged compound are held in a position which is already part of the way toward the transition state for racemization.

The steric effects which have such a marked influence on the electronic spectra of substituted biphenyls are of the same type as those responsible for the occurrence of optical asymmetry in hindered biphenyls. Electronic spectra are, however, a much more sensitive index of restricted rotation than optical resolvability for two reasons. First, the existence of isolable optical isomers with half-lives of the

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(18) S. H. Ahmed and D. M. Hall, J. Chem. Soc., 3383 (1959).

order of hours or days requires energy barriers of ca. 15 kcal./mole or more, so as to prevent rapid racemization by thermal excitation. On the other hand, the smallest significant wavelength displacements of about 50 Å correspond to energy increments of only about 1 or 2 kcal./mole in the ultraviolet region. Secondly, optical resolvability is a function of the molecular ground state alone, and the spectral properties are conditioned by both the ground state and the excited electronic levels. The excited levels are particularly subject to steric effects. It can be seen, then, that a much higher degree of steric overlap is needed to produce optical resolvability than spectral phenomena. Mono- and di-o-substituted biphenyls are resolvable only if the groups are very large, while only one o-methyl substituent brings about a large change in the spectrum.

An investigation of the ultraviolet absorption spectrum for 2,2'-dimethylbiphenyl shows that the conjugation band is further shifted to a shorter wavelength, ca. 228 mμ, as an unresolved inflection, heavily overlapped by the much more intense band system at ca. 200 mμ. The angle of deviation from coplanarity of 70.5° for 2,2'-dimethylbiphenyl (Figure 7) as determined by Suzuki[5] indicates that there should be appreciable steric inhibition of resonance by the ortho methyl groups. Direct comparison of 2,2'-dialkyl biphenyls with

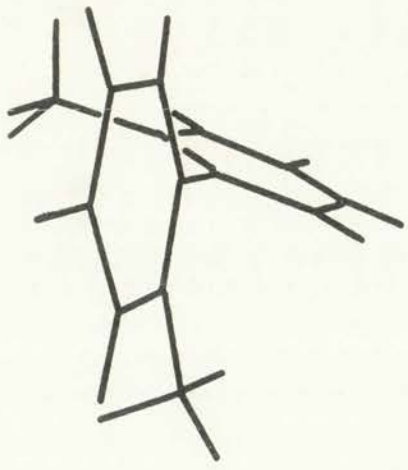


Figure 7. 2,2'-Dimethylbiphenyl.

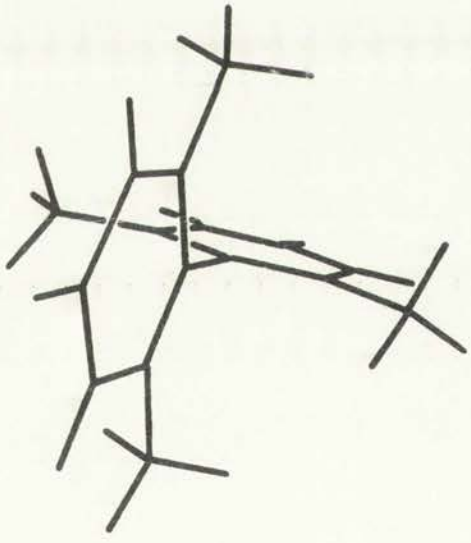
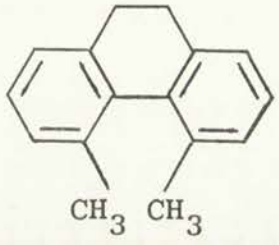


Figure 8. 2,2',6,6'-Tetramethylbiphenyl.

non-alkylated hindered biphenyls may not be perfectly valid. Even though such alkyl groups as methyl substituents probably exhibit only small inductive and resonance interaction with benzene rings of the biphenyl system, their over-all effect, as deduced from ultraviolet absorption spectra, are not necessarily completely negligible. This is probably confirmed by the rather similar maxima of 264 mμ and 261 mμ for 9,10-dihydrophenanthrene (1) and 9,10-dihydro-4,5-dimethylphenanthrene (10), respectively.

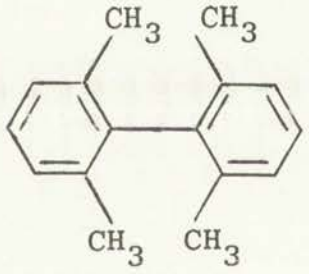


10

It might be expected that the ortho hindering methyl substituents of 10 should probably cause a somewhat larger shift to shorter wavelengths than that of only 3 mμ. Using the 4,4'-dimethylbiphenyls as a very rough basis, perhaps values as large as ca. 8 mμ should be subtracted from the absorption maxima of 2,2'-bridged biphenyls having 6,6'-methyl groups, in order to correct them for purposes of comparison to the bridged biphenyls.[16]

The effect of a single methyl group substituted either

in the 3- or 4-position of biphenyl is small. The greater increase in intensity of the conjugation band caused by a 4-methyl group is presumably due to hyperconjugation participating in the over-all conjugation through the 1,1'-bond. As is shown in Table 2, however, a single methyl group in the 2-position causes a marked reduction in intensity and a hypsochromic shift of the conjugation band. As seen from Table 2, the increase of methyl substitution in the ortho positions causes sharp decreases both in intensity and in wavelength of the conjugation band, until one reaches 2,2',6,6'-tetramethylbiphenyl (11) (Figure 8, p. 20),



11

whose ultraviolet absorption spectrum shows no conjugation band, as it is completely overlapped by the short-wave band system. It would be interesting to observe the scintillation and ultraviolet absorption properties of a similarly substituted tetramethyl-p-quaterphenyl. The ultraviolet

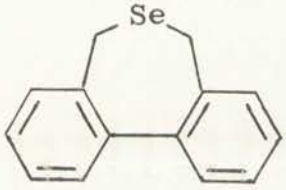
TABLE 2. CONJUGATION BAND MAXIMA FOR SOME METHYLATED BIPHENYLS[19]

Compound	λ_{max} (mμ)	ϵ_{max}
Biphenyl	248	19,000
4,4'-Dimethylbiphenyl	254.5	21,000
4-Methylbiphenyl	251.5	19,000
3,3'-Dimethylbiphenyl	250.5	16,100
3-Methylbiphenyl	249	16,300
2-Methylbiphenyl	236.5	10,250
2,6-Dimethylbiphenyl	(231)	5,600
2,2',6-Trimethylbiphenyl	(230)	4,000
2,2'4,4'-Tetramethylbiphenyl	(230)	9,600
2,2'-Dimethylbiphenyl	(228)	6,800
2,2',6,6'-Tetramethylbiphenyl	no conjugation band	

(19) G. H. Beaven and E. A. Johnson, Spectrochimica Acta, 14, 67 (1959).

absorption maximum and scintillation properties would be expected to be similar to that of 3,5-dimethylbiphenyl.

It can be seen from the data given in Table 1 that the ultraviolet maxima for 5,7-dihydrodibenzo[c,e]selenepin (12) and 5,7-dihydrodibenzo[c,e]thiepin (13) are found at shorter wavelengths (247 mμ and 245 mμ, respectively) than for similar 7-membered-ring bridged biphenyls such as 6,6-dicarbethoxy-5,7-dihydrodibenzo[a,c]cycloheptadiene (9) and 5,7-dihydrodibenz[c,e]oxepin (3) (249 mμ and 250 mμ, respectively). This hypsochromic shift has been attributed to the increased



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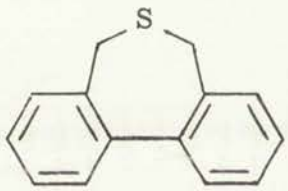


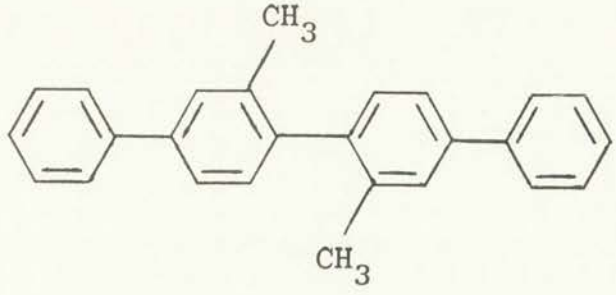
13

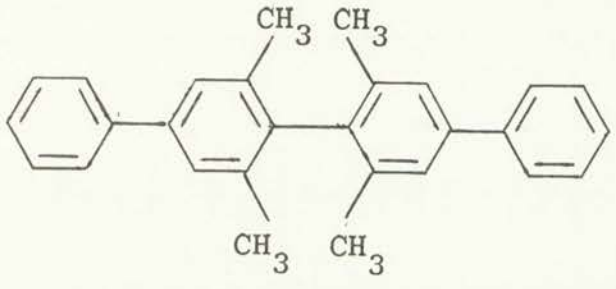
size of the hetero atom, which would cause the two bridged benzene rings to be twisted slightly more out of the plane than in 3 and 9.[16] It is also particularly interesting to note the very low values obtained for the extinction coefficients for the selenepin 12 and thiepin 13 (ϵ_{max} 6,250 and ϵ_{max} 10,000) compared with the relatively high values for 3 and 9 (ϵ_{max} 16,500 and ϵ_{max} 16,980).

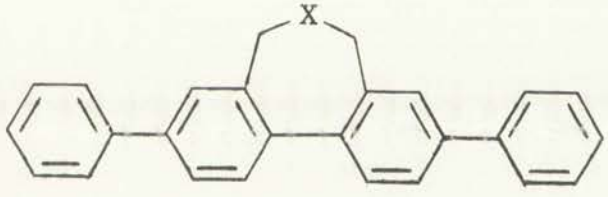
The ultraviolet absorption maximum and the extinction coefficient values for 2,7-dihydro-3,4,5,6-dibenzazepinium-1-spiro-1'''-piperidinium bromide (8), as seen from Table 1, are somewhat closer to those found for the oxepin 3 and the cycloheptadiene 9 than those for the corresponding thiepin 13 and selenepin 12. It would be interesting, therefore, to compare the scintillation and spectral properties of the corresponding azepine and oxepin derivatives of p-quaterphenyl.

It can be seen, then, from the spectral and optical studies on hindered biphenyls that conjugation does not necessarily require complete planarity. It would be actually more correct to speak of near-planarity rather than uniplanarity as a condition of effective conjugation.

It was proposed, then, to study the problem of the relationship between the angle of deviation from coplanarity and resonance interaction by investigating more fully the scintillation properties and the ultraviolet absorption spectra of some hindered p-quaterphenyl derivatives. The preparation of di- and tetramethyl-p-quaterphenyls and some seven-membered-ring bridged p-quaterphenyls, as illustrated below, would enable the investigator to make comparisons with the excellent liquid scintillation solutes 4, 5, and 6.







X = N-CH_3, S, Se, or $C(COOEt)_2$

THE SCINTILLATION PROCESS AND THE DETERMINATION OF PULSE-HEIGHTS

The scintillation process, in which incident radiation is converted to visible and near-ultraviolet photon energy, has been discussed by Barnett[20] and will not be discussed here.

It is important to the investigator of scintillation solutes to know the number of photons resulting from a certain deposition of energy in a scintillator, or more practically, the photon-emitting capabilities of the solute relative to a standard. Although the primary concern is with the number of photons emitted by the solute molecules, the distribution, or the emission spectrum, of the photons must also be considered as the photons being produced are not monoenergetic. A plot of the relative number of photons against wavelength, as shown in Figure 9, demonstrates that in order to obtain the total number of photons produced, a

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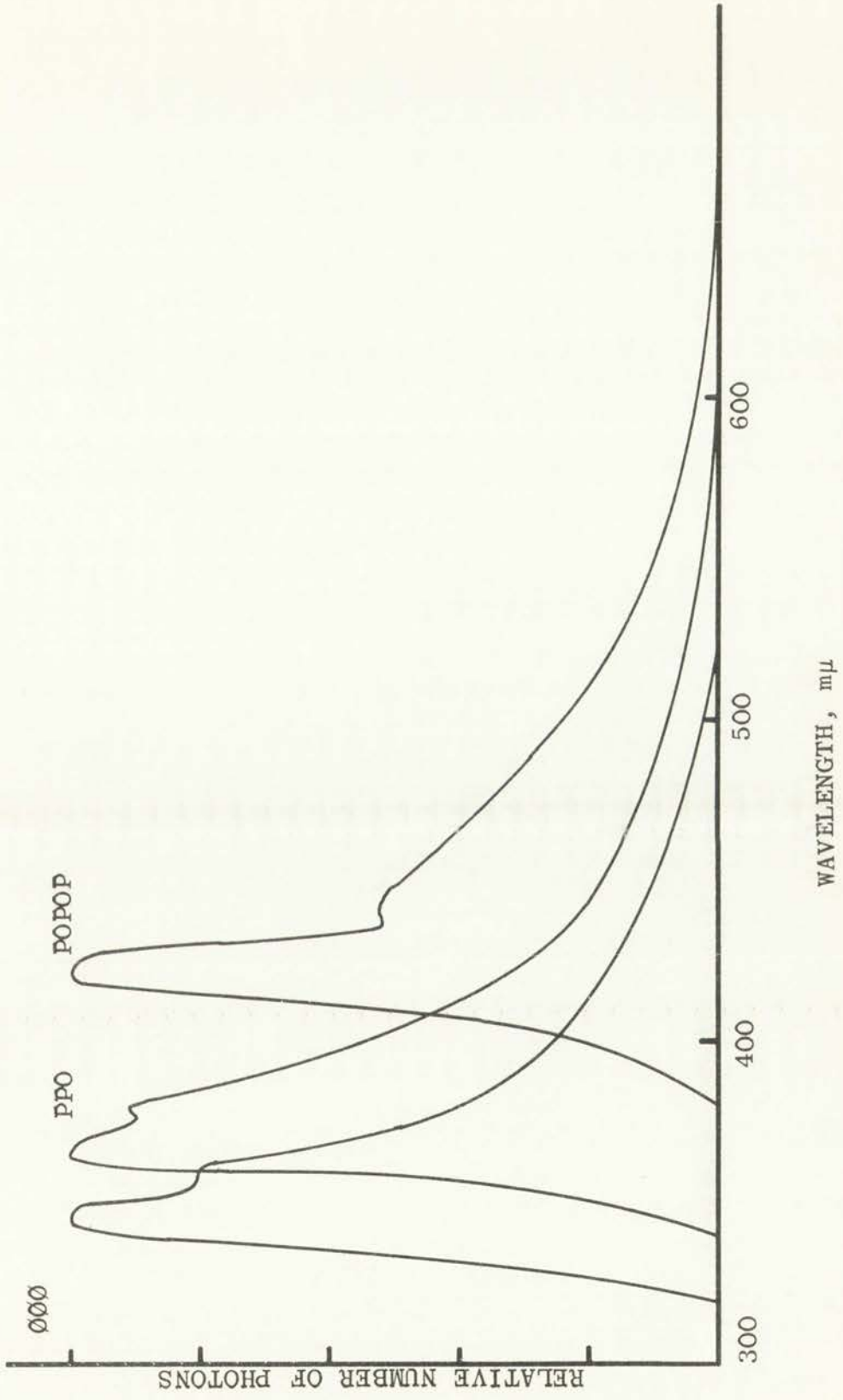
(20) M. D. Barnett, Doctoral Dissertation, University of New Mexico (1958).

Figure 9. Fluorescence curves for p-terphenyl, 2,5-diphenyl-oxazole (PPO), and 2,2'-p-phenylenebis-(5-phenyl-oxazole) (POPOP).


RELATIVE NUMBER OF PHOTONS
ØØØ
PPO
POPOP
300
400
500
600
WAVELENGTH, mμ

determination of the area under the curve must be effected.

Unfortunately, a simple determination of the spectrum of the photons emitted by the solute upon excitation by a radioactive source is not feasible. This is due to the fact that only about 3 per cent of the energy deposited by the source is available after energy degradation to raise the solute molecules to their first excited state. Thus, in order to be able to analyze the spectrum of the photons emitted by the scintillator in this manner, a very hot source would have to be employed. Irradiation of the solute by such a strong source would result in the decomposition of the solute molecules and would create a serious shielding problem.

However, the emission spectrum of a scintillation solute may be easily obtained by excitation with ultraviolet radiation, where all the deposited energy leads to light emission. Subsequently, spectral analysis is accomplished with a suitable spectrophotometer. Although the method of excitation is different in the determination of the fluorescence spectrum than in the determination of the light-emitting capabilities of a scintillator, the emission spectrum should be independent of the mode of excitation.

The emission spectra of many of the scintillation solutes employed do not match very well with the spectral

response curves for the photomultiplier tubes available. The spectral sensitivity response curve for the RCA 6903 photomultiplier tube is plotted in Figure 10. As can be

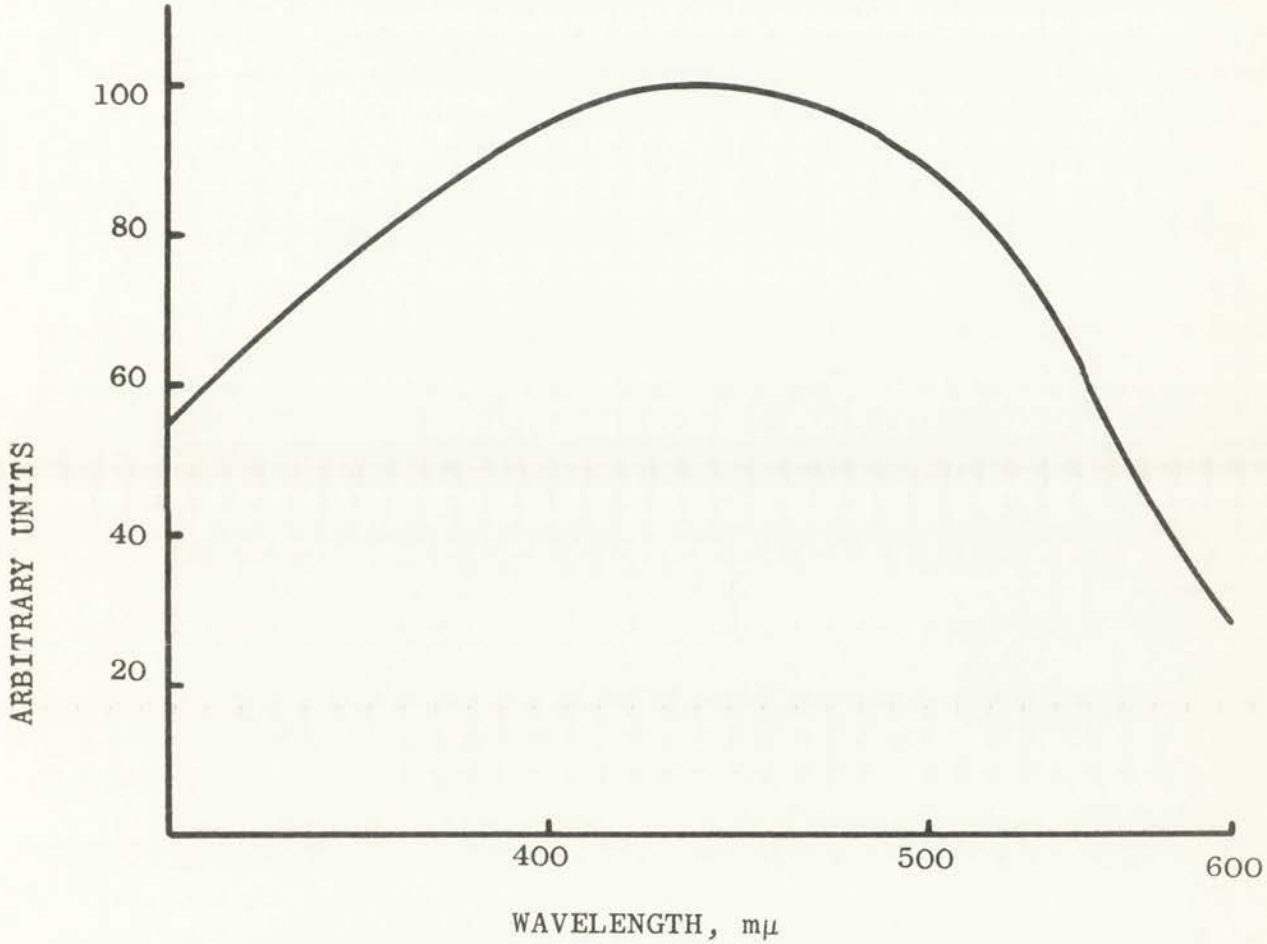


Figure 10. Spectral sensitivity characteristic of RCA Type 6903 photomultiplier tube, which has S-13 response.

seen from Figure 10, the range of maximum response for this particular tube is only about 100 mμ, although the practical range is somewhat greater. One of the reasons why discrepancies exist among scintillation testing data from various laboratories is that the spectral distribution of the emitted light influences the data obtained, depending upon the testing equipment used. The addition of a secondary solute, such as 2,2'-p-phenylenebis-(5-phenyloxazole) (POPOP), to the primary solute solution in a concentration of about 0.05 to 0.5 gram per liter will shift the spectrum of the emitted light to longer wavelengths. The emission spectrum is now that of POPOP, although the number of photons remain the same. As can be seen from Figure 9, the emission spectrum of POPOP has an excellent "matching factor" with the photomultiplier response curve in Figure 10.

A knowledge of the photon emission spectrum of the scintillator is also desirable, because solutes emitting at lower wavelengths are more subject to photon absorption by the solvent, the reflector, and the other photon transmitting media.

A special effort is made in our testing apparatus to make the number of photons emitted by the solute independent of the distribution of the emission spectrum by: (1) utilization of a quartz-faced RCA 6903 photomultiplier tube and a

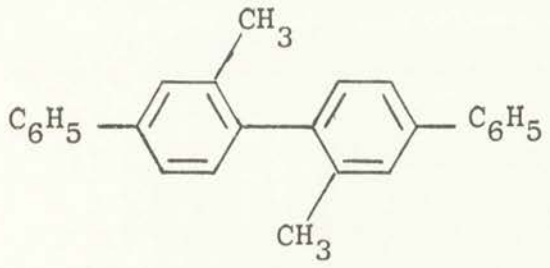
quartz beaker in order to minimize short wavelength absorption, and (2) employment of an evaporated aluminum reflector, which has essentially a flat response of reflectance versus wavelength.

The spectrum of light in a scintillator as seen by the photocathode is converted into photoelectrons. The number of electrons must first be multiplied many times and during this process a statistical distribution of electrons is obtained. At the anode circuitry, the electrons from a scintillation are converted to a peak voltage in a pulse. Utilization of a multichannel analyzer facilitates a rapid determination of the pulse-height distribution from the Ba^{137} internal conversion electron whose peak voltage is now proportional to the number of photons impinging on the photocathode.

Employment of a standard scintillation solute, such as PPO, and reporting Ba^{137} peak pulse-height voltages obtained from the solute being evaluated, and calculating this relative to PPO, give the ratio of the number of photons emitted by the solute in question to the number of photons emitted by the standard. Such a ratio of pulse-height voltages is used to compare the light-emitting capabilities of a scintillation solute and is referred to as the relative pulse-height of the solute.

SYNTHESIS OF THE COMPOUNDS

The aromatic hydrocarbons of initial interest in this study were the 2'',3'-substituted p-quaterphenyl derivatives 14 through 20. 2'',3'-Dimethyl-p-quaterphenyl (14) was



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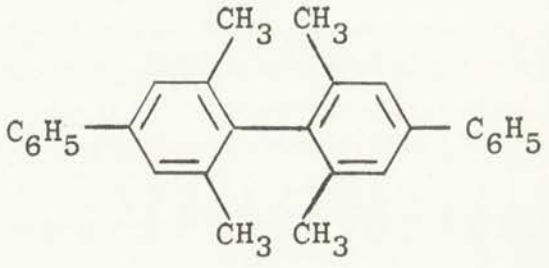

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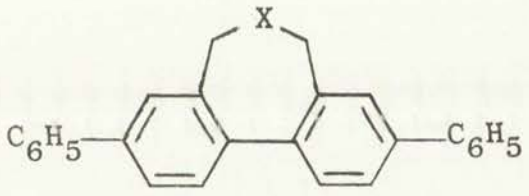


16 = N-CH_3

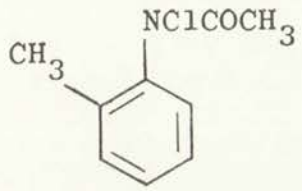
17 = S

18 = Se

19 = CH_2

20 = $C(COOEt)_2$

prepared via the Ullmann coupling of 4-iodo-3-methylbiphenyl (24). This was available in four steps from o-acetotoluidide, which was converted to N-chloro-o-acetotoluidide (21) in 85 per cent yield by reaction with potassium hypochlorite in the presence of potassium bicarbonate as previously described by Barnett.[6] A mixture of alcohol and water was used as the solvent, rather than water alone, and this modification made it possible to carry out larger preparations than those described by Barnett. The chloramide (21)



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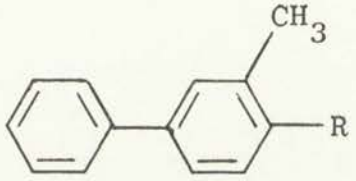

22, R = $NHCOCH_3$

23, R = $NH_2 \cdot HCl$

24, R = I

was allowed to react with benzene in the presence of aluminum chloride to give 4-acetamido-3-methylbiphenyl (22) in 54 per cent yield. Hydrolysis of the amide 22 with 20 per cent hydrochloric acid afforded 4-amino-3-methylbiphenyl hydrochloride (23) in 96 per cent yield. This was diazotized and

the diazonium salt allowed to react with potassium iodide. The resultant red oil was purified with difficulty by chromatography and crystallization from ethanol to give a 71 per cent yield of 4-iodo-3-methylbiphenyl (24).

The successful synthesis of 2'',3'-dimethyl-p-quaterphenyl (14) was accomplished by heating an intimate mixture of 4-iodo-3-methylbiphenyl (24) and activated copper bronze for 5 hours. Extraction of the organic material with hot benzene and chromatography through alumina, followed by crystallization from cyclohexane, gave a 45 per cent yield of 2'',3'-dimethyl-p-quaterphenyl (14). The hydrocarbon 14 was also successfully prepared from the iodo compound 24 by coupling of the Grignard reagent in the presence of cobaltous chloride according to the method outlined by Castro.[21] The Ullmann method is preferable, both in ease of isolation of the product and in yield, as the Grignard coupling afforded only 30 per cent of product as compared to 45 per cent from the Ullmann reaction.

The successful synthesis of the 7-membered-ring bridged compounds 16, 17, 18, and 20 was accomplished from 2'',3'-dimethyl-p-quaterphenyl (14) via 2'',3'-bis(bromomethyl)-p-quaterphenyl (25). The latter compound was prepared in

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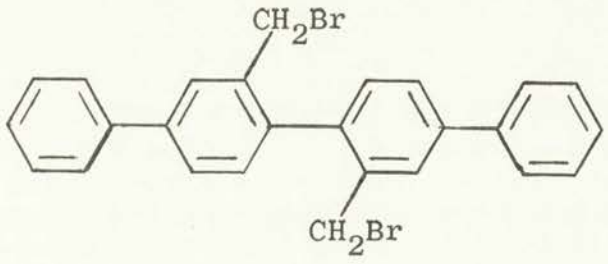
(21) C. E. Castro, L. J. Andrews, and R. M. Keefer, J. Am. Chem. Soc., 80, 2322 (1958).



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83 per cent yield by the reaction of N-bromosuccinimide with 2'',3'-dimethyl-p-quaterphenyl (14) in the presence of catalytic amounts of benzoyl peroxide.[22] Successful bromination was achieved only when very pure starting material was used.

6-Methyl-3,9-diphenyl-5,7-dihydrodibenz[c,e]azepine (16) was prepared in 69 per cent yield from the dibromide 25 by reaction with methyl amine in absolute benzene according to the method described by Wenner.[23]

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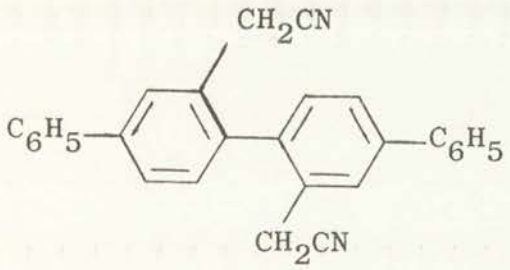
(22) W. Wenner, J. Org. Chem., 17, 523 (1952).

(23) W. Wenner, J. Org. Chem., 16, 1475 (1951).

The preparation of 3,9-diphenyl-5,7-dihydrodibenzo[c,e]-thiepin (17) was accomplished in 52 per cent yield by refluxing the dibromide 25 with sodium sulfide nonahydrate in a mixture of water, methanol, and dioxane.

3,9-Diphenyl-5,7-dihydrodibenzo[c,e]selenepin (18) was obtained in 51 per cent yield by the reaction of the dibromide 25 with potassium selenide in a manner as described by Truce and Emrick.[16]

Attempts to prepare 3,9-diphenyl-5,7-dihydrodibenzo[a,c]-cycloheptadiene (19) in significant amounts from the dibromide 25 were unsuccessful. 2'',3'-Bis(cyanomethyl)-p-quaterphenyl (26) was prepared in 75 per cent yield by



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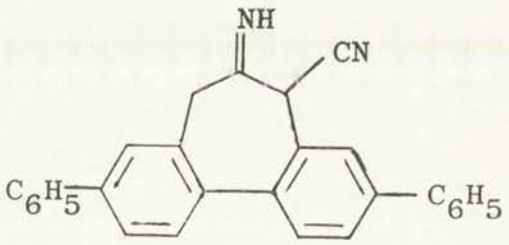

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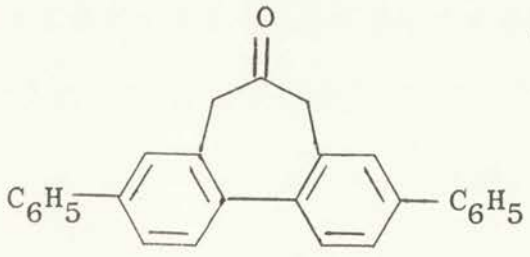

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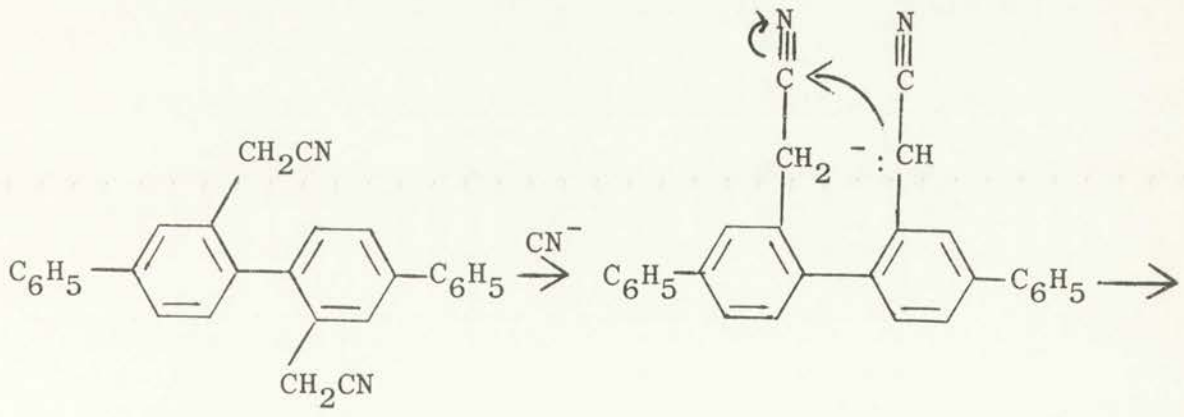
allowing the dibromide 25 to react with potassium cyanide in aqueous acetone. Repeated crystallizations from benzene failed to give a sharp melting point. Melting points of the products from various runs ranged from 220° to 269°, with the best melting point obtained having a range of 265° to 269°. The infrared absorption spectrum of the various products obtained indicated the presence of an imino group in addition to a nitrile, with the intensity of absorption for the imino group being greatest for the lower melting samples. It is believed that some cyclization to 5-cyano-6-imino-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (27) occurred during the course of the reaction. This cyclization could proceed by the mechanism as outlined below.



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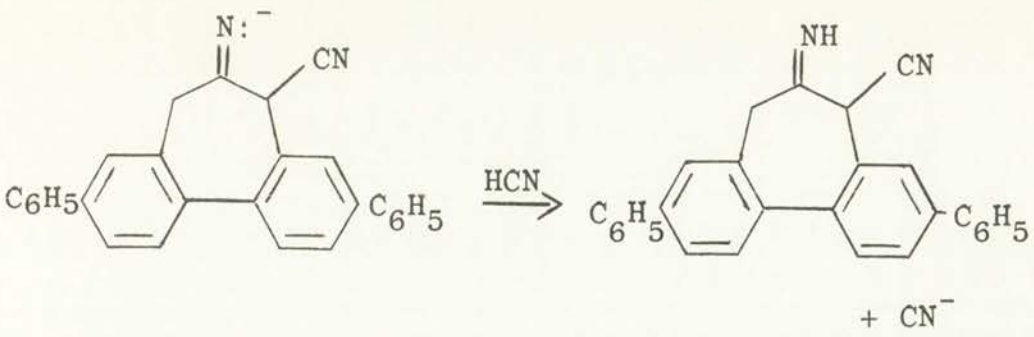

The various products from the reaction of potassium cyanide with the dibromide 25 were refluxed with sodium ethoxide in anhydrous dioxane and in each case gave the iminonitrile 27. After purification, the sample, m.p. 207° to 209°, had the correct analysis for the iminonitrile 27.

Hydrolysis of the iminonitrile 27 in 50 per cent sulfuric acid gave only a poor yield of a product which was believed to be at least in part 6-keto-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (28). Repeated crystallization of the sample gave a colorless compound, m.p. 246° to 249°, which failed to give the correct analysis for the ketone 28. Attempted hydrolysis of the iminonitrile 27 in 85 per cent phosphoric acid, according to the method as outlined by Mislow,[24] also failed to give the desired product. A Wolff-Kischner reduction of the impure ketone 28 gave only a trace of what is believed to be 3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (19), m.p. 181° to 184°. All of

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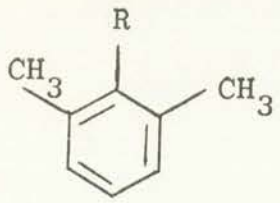
(24) K. Mislow, et. al., J. Am. Chem. Soc., 84, 1455 (1962).

the small amount of material available was used in the evaluation of the hydrocarbon 19 as a primary liquid scintillation solute, leaving an insufficient amount of compound for purification for analysis.

Due to the difficulty encountered in attempting to prepare the hydrocarbon 19, it was decided to attempt an alternate route to the 7-membered-ring carbon-atom bridge. Thus, 2'',3'-bis(bromomethyl)-p-quaterphenyl (25) was allowed to react with disodium ethyl malonate in absolute ethanol and anhydrous dioxane to give 6,6-dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20) in 85 per cent yield.

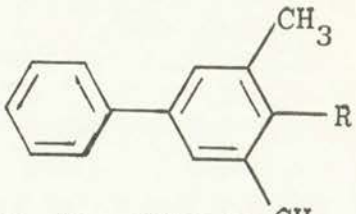
The preparation of 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) was accomplished by a route similar to the one employed in the synthesis of 2'',3'-dimethyl-p-quaterphenyl (14).

2,6-Dimethylacetanilide (29) was prepared in 87 per cent yield from 2,6-dimethylaniline. Treatment of the amide 29 with potassium hypochlorite in the presence of potassium bicarbonate in a similar manner as described for the preparation of 21 gave an 82 per cent yield of N-chloro-2,6-dimethylacetanilide (30). The chloramide 30 was then allowed to react with benzene in the presence of aluminum chloride to give 4-acetamido-3,5-dimethylbiphenyl (31) in 46 per cent yield. Hydrolysis of the amide 31 was accomplished in



29, R = $NHCOCH_3$

30, R = $NClCOCH_3$



31, R = $NHCOCH_3$

32, R = NH_2

33, R = I

72 per cent yield by refluxing with 100 per cent phosphoric acid[25] to give 4-amino-3,5-dimethylbiphenyl (32) as a viscous brown oil. The hydrochloride of 32 was diazotized, and the resulting diazonium salt was allowed to react with potassium iodide to give a 45 per cent yield of 4-iodo-3,5-dimethylbiphenyl (33). From this, 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) was prepared in 21 per cent yield by the coupling of the Grignard reagent of the iodide 33 in a manner similar to that employed in the preparation of 2'',3'-dimethyl-p-quaterphenyl (14).

The spectral and scintillation properties of the 2'',3'-substituted p-quaterphenyls indicated that it would be desirable to prepare the 2,2'-substituted p-quaterphenyl derivatives 34 and 35.

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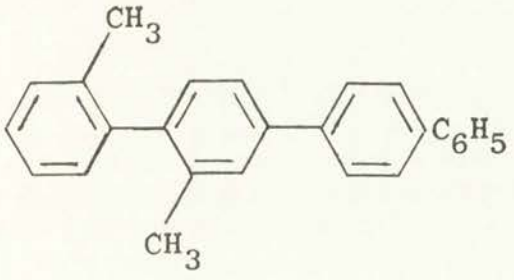
(25) Berger and Olivier, Recueil Des Travaux Chimiques Des Pays-Bas, 46, 600 (1927).



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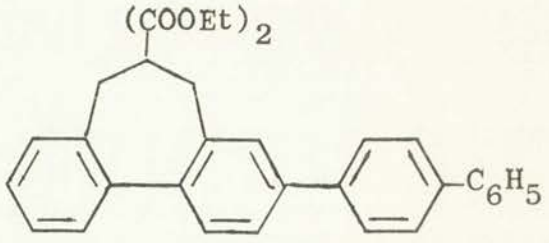

35

The route first employed to synthesize 2,2'-dimethyl-p-quaterphenyl (34) was only partially successful in that only small amounts of the hydrocarbon 34 were obtained. This route involved the preparation of 4-iodo-3-methyl-p-terphenyl (38), which was the key intermediate. The iodide 38 was prepared in three steps from 1-(4-biphenylyl)-3-methylcyclohexanol (36), which had been prepared in this laboratory from the Grignard reagent of 4-bromobiphenyl and 3-methylcyclohexanone.[26]

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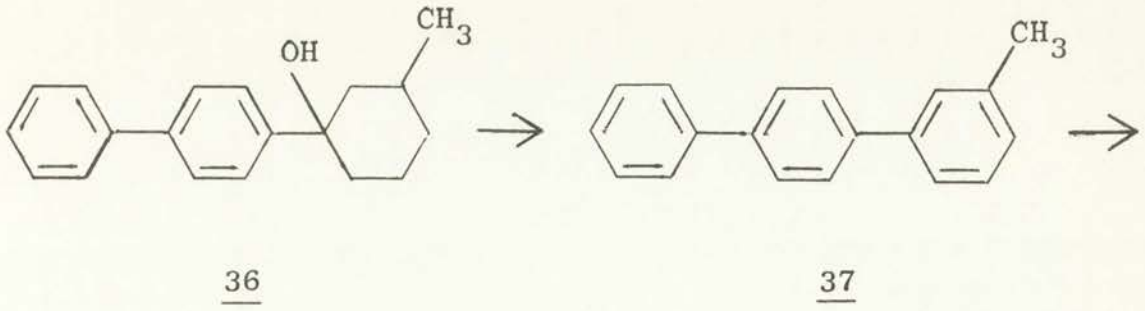
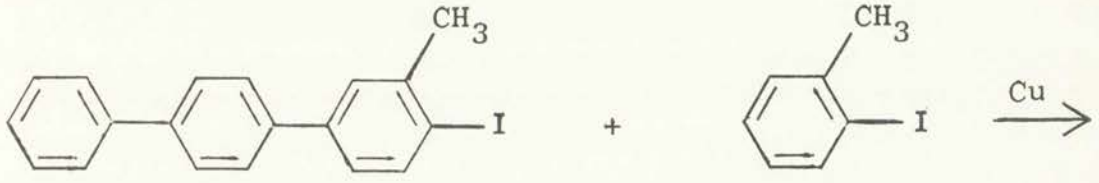
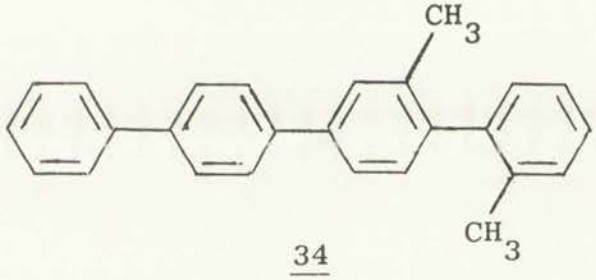
(26) G. H. Daub, Private Communication.



36 37



38 39



34

The dehydration and dehydrogenation of the alcohol 36 were accomplished in 75 per cent yield to afford 3-methyl-p-terphenyl (37). Iodination of the hydrocarbon by the procedure outlined by Wirth[27] gave 4-iodo-3-methyl-p-terphenyl (38)

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(27) H. O. Wirth, O. Konigstein, and W. Kein, Liebigs Ann. Chem., 634, 84-104 (1960).

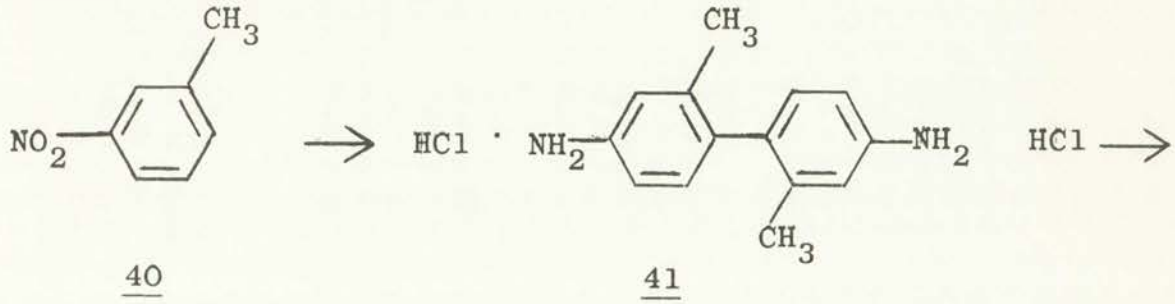
in 58 per cent yield. Attempts to prepare the Grignard or lithium derivatives of the iodo compound 38 were unsuccessful.

The synthesis of 2,2'-dimethyl-p-quaterphenyl (34) was accomplished via the mixed Ullmann coupling of the iodide 38 and o-iodotoluene (39). Isolation of the product by chromatography, evaporative distillation, and crystallization from cyclohexane gave a 15 per cent yield of the hydrocarbon 34. However, this method of preparation was unsuitable for the synthesis of the large quantities of 34 required for the preparation of additional 2,2'-derivatives of p-quaterphenyl.

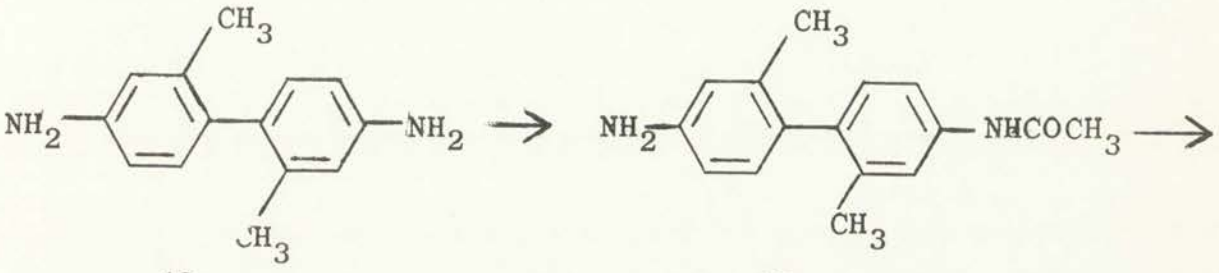
The alternate approach to 34 involved the preparation of the key intermediate, 4-iodo-2,2'-dimethylbiphenyl (46). 2,2'-Dimethylbenzidine dihydrochloride (41) was prepared from m-nitrotoluene (40) according to the procedure described by Wenner.[22]

Mono-acetylation of 2,2'-dimethylbenzidine (42) was accomplished by the slow addition of acetic anhydride to the diamine 42 dissolved in a minimum amount of ether. The key to the successful preparation was the precipitation of 4-acetamido-4'-amino-2,2'-dimethylbiphenyl (43) from the ether solution before appreciable diacetylation could occur. The attempted mono-acetylation of 42 according to the method

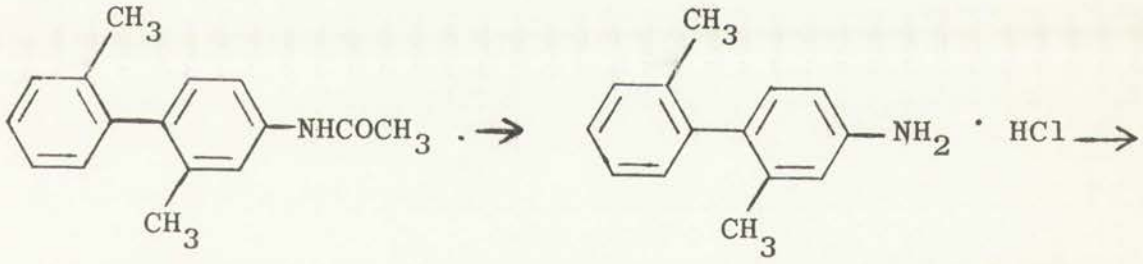
outlined by Kern, Seibel, and Wirth[28] failed to give a sufficient amount of the desired product.



40 41



42 43



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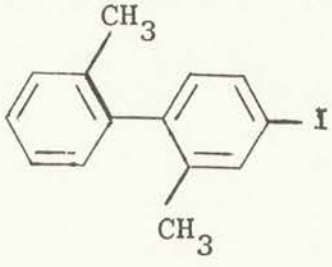

46

(28) W. Kern, M. Seibel, and H. O. Wirth, Makromolekulare Chem., 19, 186 (1959).

The monoamide 43 was diazotized and deaminated with 50 per cent hypophosphorous acid. Crystallization of the crude product from cyclohexane gave a 39 per cent yield of 4-acetamido-2,2'-dimethylbiphenyl (44). Hydrolysis of the amide 44 in 20 per cent hydrochloric acid afforded an 88 per cent yield of 4-amino-2,2'-dimethylbiphenyl hydrochloride (45), which was diazotized. The diazonium salt was allowed to react with potassium iodide, and the red oily product was purified by chromatography and distillation under reduced pressure to give a 69 per cent yield of 4-iodo-2,2'-dimethylbiphenyl (46).

The preparation of 4-phenylcyclohexanone (47) was accomplished in 81 per cent yield by the oxidation of trans-4-phenylcyclohexanol by N-bromoacetamide.[29] The 4-phenylcyclohexanone (47) was allowed to react with a cold solution of the lithium derivative of 4-iodo-2,2'-dimethylbiphenyl (46), and after hydrolysis 1-(2,2'-dimethyl-4-biphenylyl)-4-phenylcyclohexanol (48) was obtained. The unpurified alcohol 48 was dehydrated with 98 per cent formic acid to give 1-(2,2'-dimethyl-4-biphenylyl)-4-phenylcyclohexene (49) in 37 per cent yield from 46. The dehydrogenation of the alkene 49 was accomplished by heating an intimate mixture of 49 and

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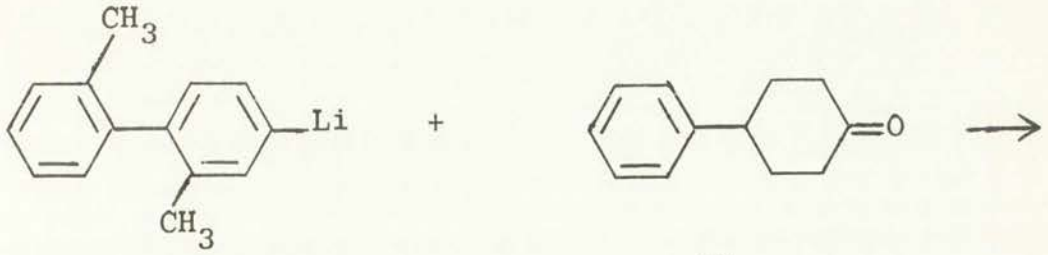
(29) G. H. Daub, Private Communication.



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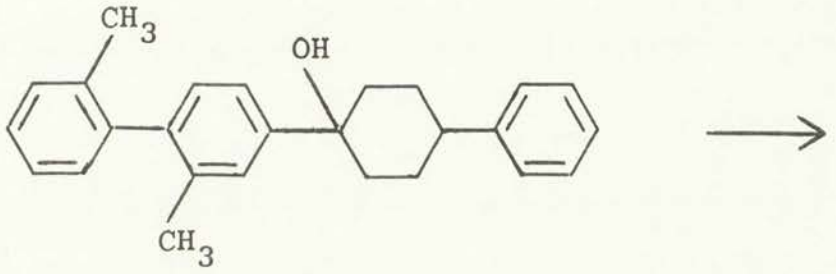

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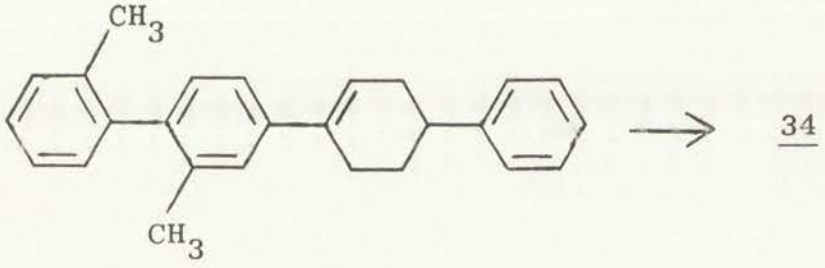
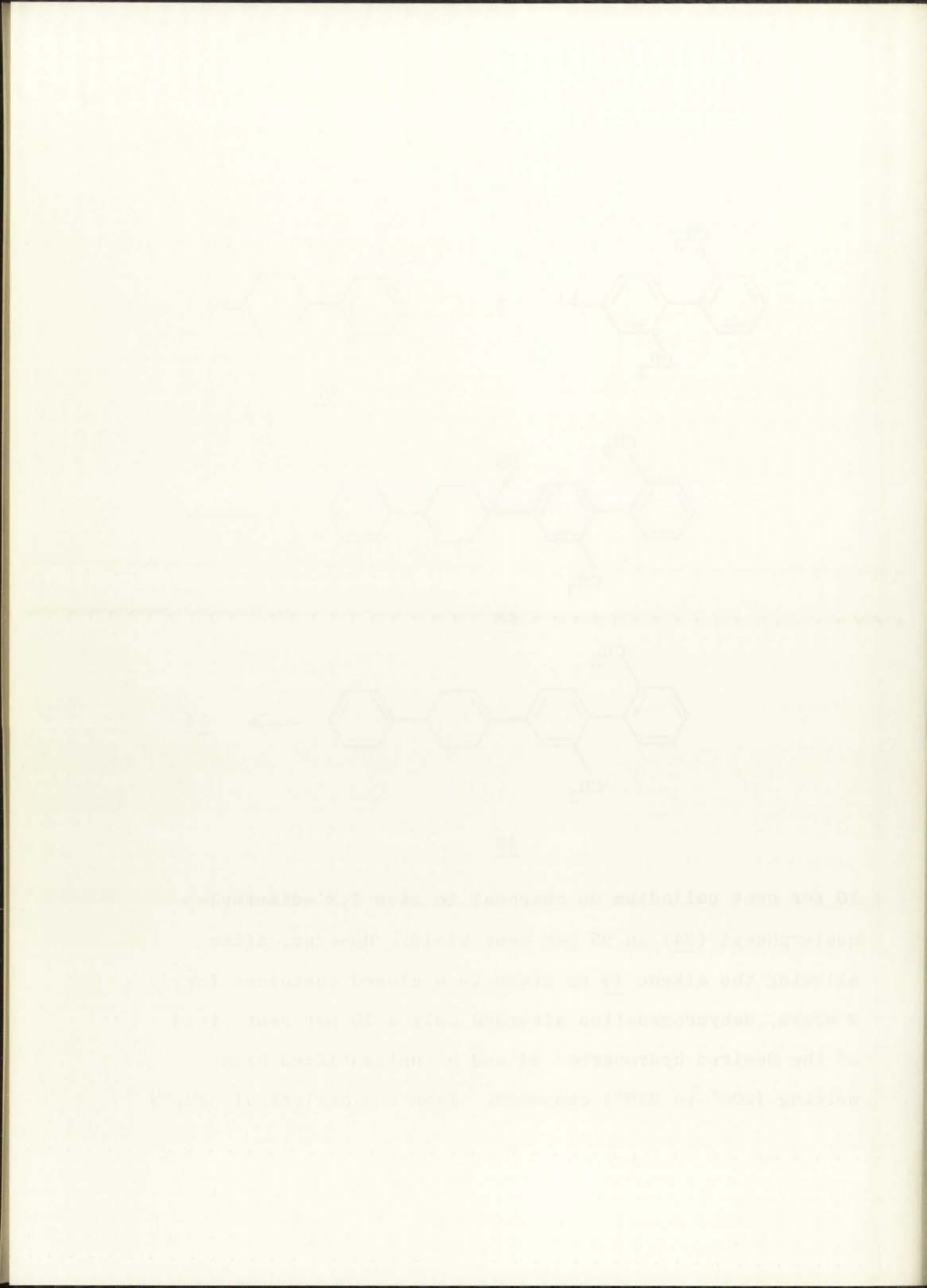
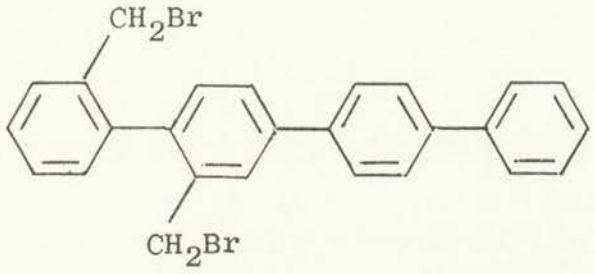


49

10 per cent palladium on charcoal to give 2,2'-dimethyl-p-quaterphenyl (34) in 95 per cent yield. However, after allowing the alkene 49 to stand in a closed container for 2 weeks, dehydrogenation afforded only a 20 per cent yield of the desired hydrocarbon 34 and an unidentified high-melting (200° to 250°) compound. Even the analytical sample



of the alkene 49 began to decompose after standing for two months. Four attempts to prepare 2,2'-bis(bromomethyl)-p-quaterphenyl (50) from the hydrocarbon 34 in the manner described for the preparation of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25) failed to give a pure product. Erratic results were obtained from the side chain bromination of

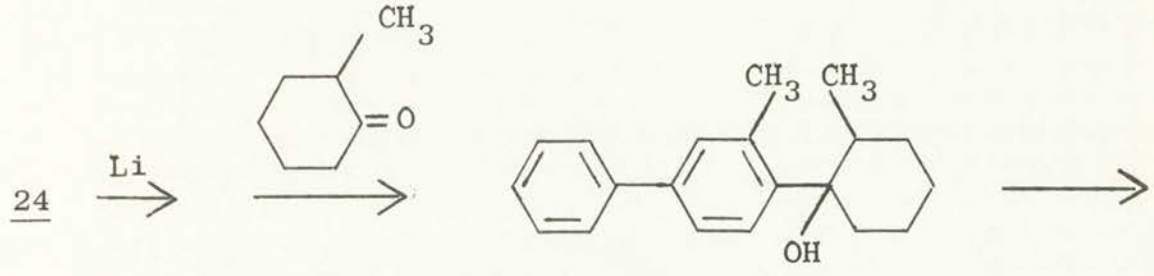


50

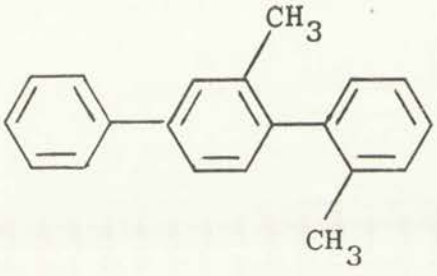
2'',3'-dimethyl-p-quarterphenyl (14) with N-bromosuccinimide and benzoyl peroxide, and the reaction failed to give a pure product in a reaction with 2,2'-dimethyl-p-quaterphenyl (34). Thus, the failure of the bromination of the hydrocarbon 34 to give the desired dibromide 50 rendered the 7-membered-ring bridged hydrocarbon, 3-(4-biphenylyl)-6,6-dicarbethoxy-5,7-dihydrodibenzo[a,c]cycloheptadiene (35), unavailable.

The availability of 4-iodo-3-methylbiphenyl (24) made it desirable to prepare 2,2'-dimethyl-p-terphenyl (52). A

reaction of the lithium derivative of the iodide 24 with o-methylcyclohexanone followed by hydrolysis afforded 1-(3-methyl-4-biphenylyl)-2-methylcyclohexanol (51). Dehydration



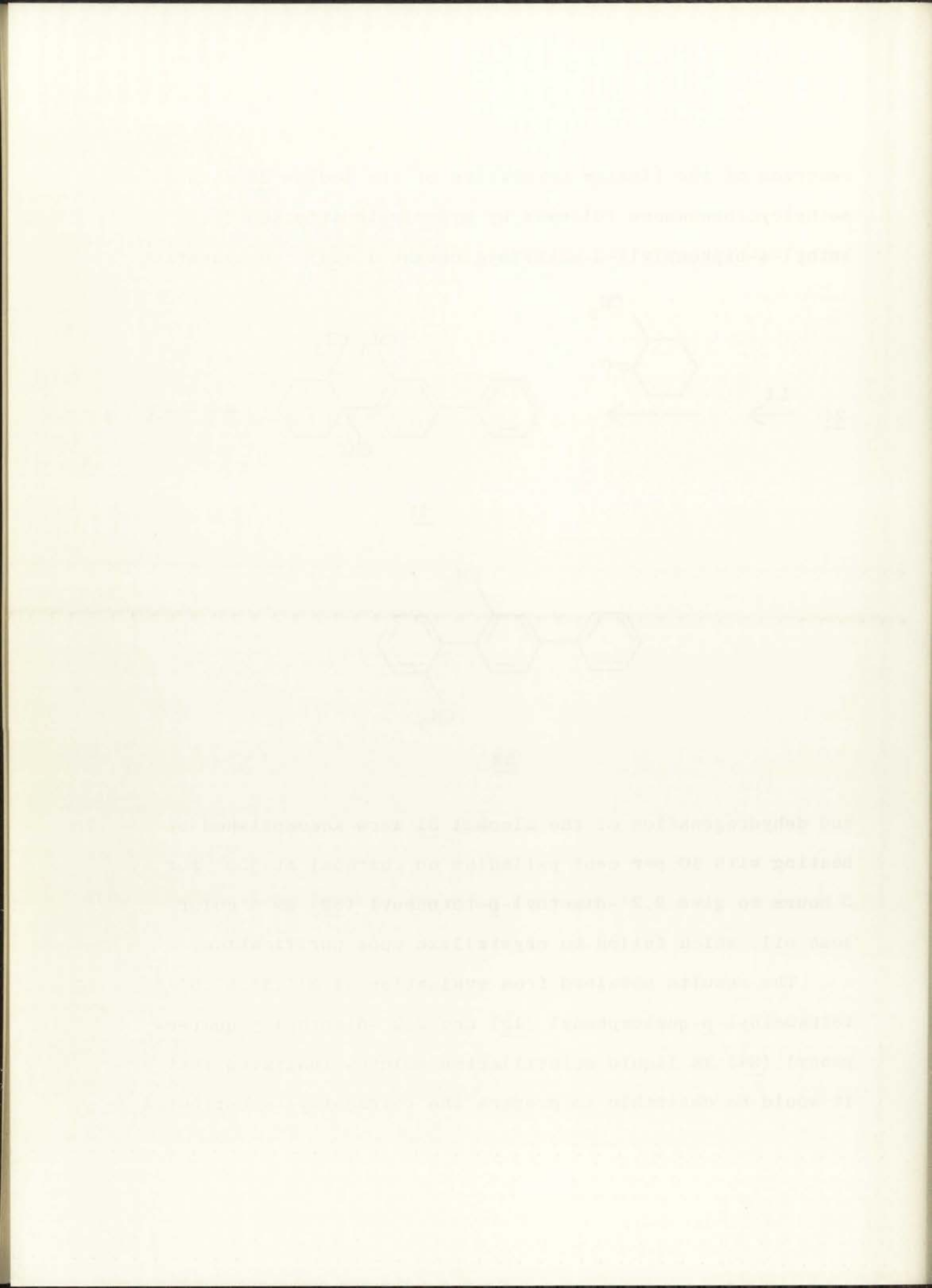
51



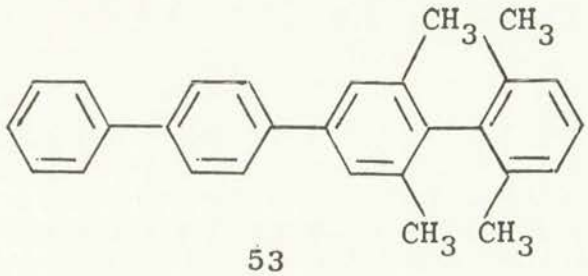
52

and dehydrogenation of the alcohol 51 were accomplished by heating with 10 per cent palladium on charcoal at 350° for 5 hours to give 2,2'-dimethyl-p-terphenyl (52) as a colorless oil, which failed to crystallize upon purification.

The results obtained from evaluation of 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) and 2,2'-dimethyl-p-quaterphenyl (34) as liquid scintillation solutes indicated that it would be desirable to prepare the tetramethyl-substituted



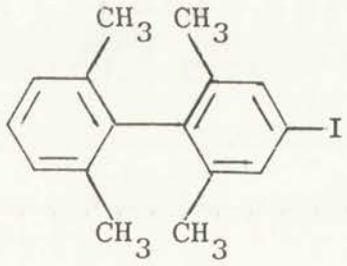
analog of 34, 2,2',6,6'-tetramethyl-p-quaterphenyl (53).



53

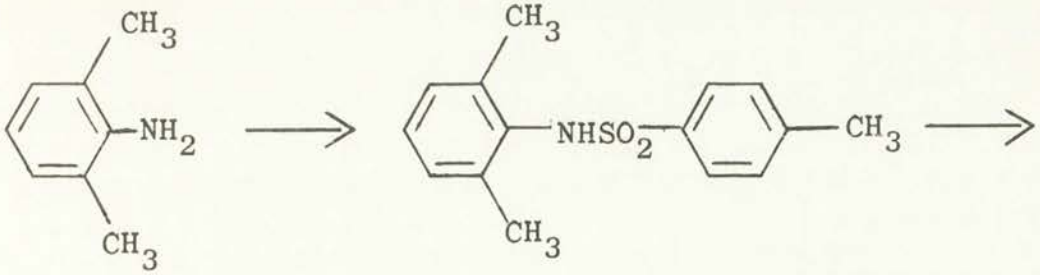
Although the total synthesis of this compound has not been accomplished, considerable progress has been made toward its preparation.

The key intermediate in the proposed synthesis of 53 is 4-iodo-2,2',6,6'-tetramethylbiphenyl (54). The first route



54

to the iodo compound 54 that was attempted involved the preparation of 4-iodo-2,6-dimethylnitrobenzene (58). 2,6-Dimethyl-1-(p-toluenesulfonamido)-benzene (55) was prepared in



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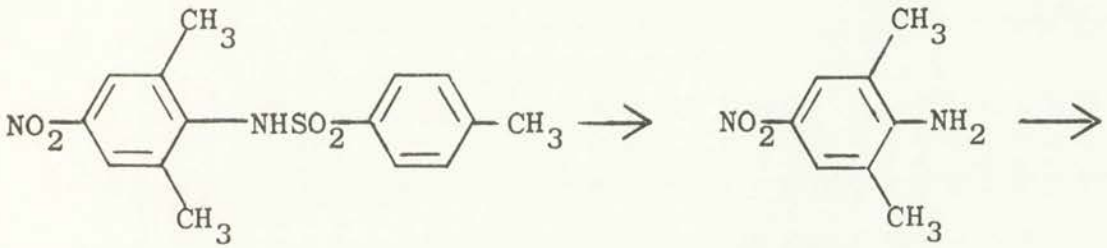
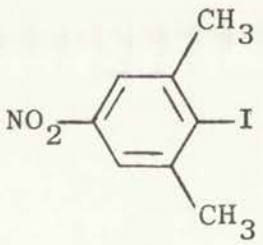
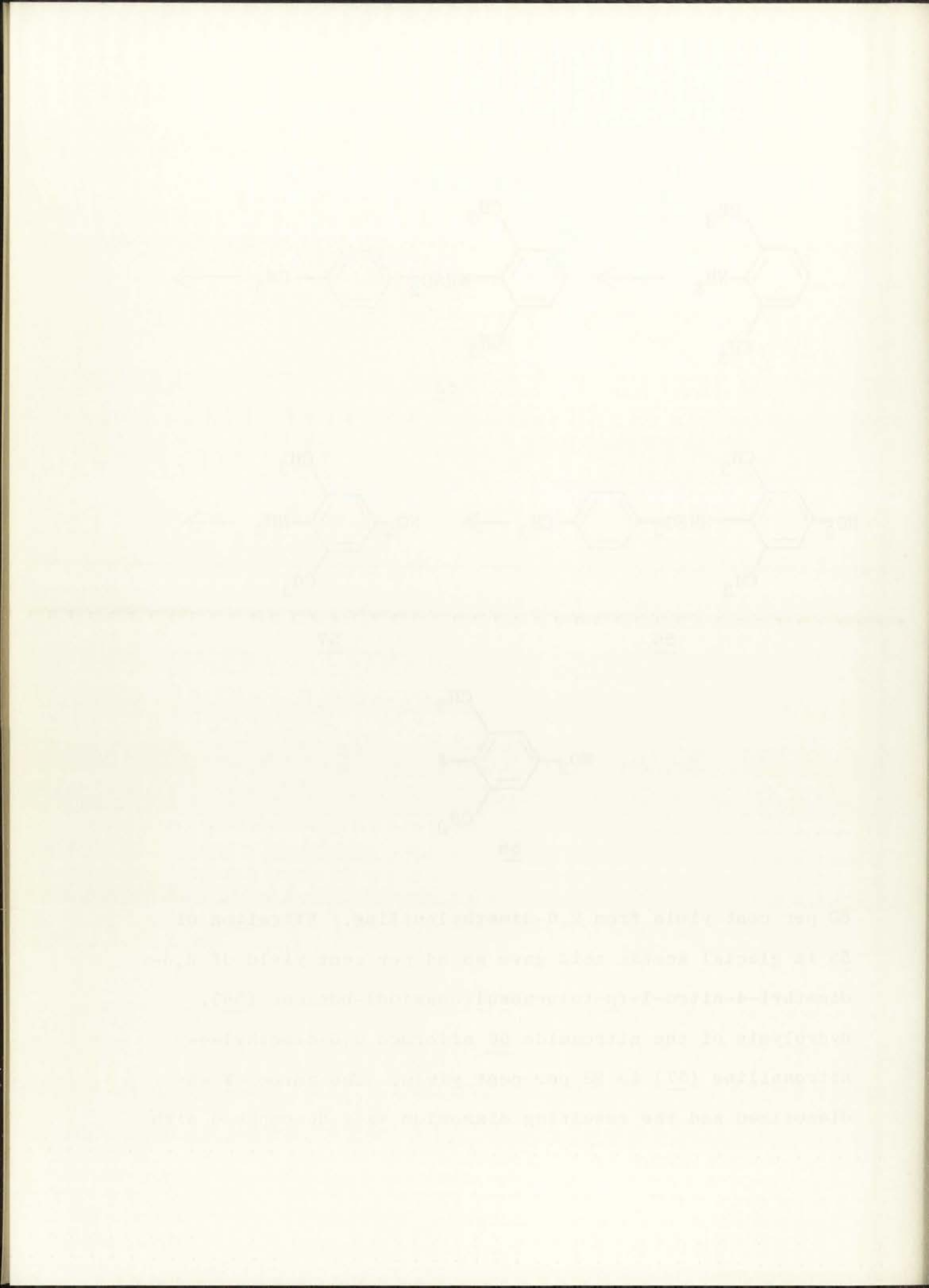


56 57

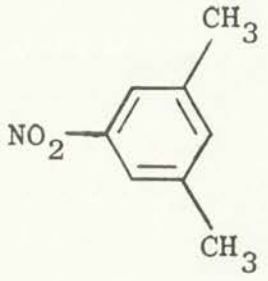


58

80 per cent yield from 2,6-dimethylaniline. Nitration of 55 in glacial acetic acid gave an 84 per cent yield of 2,6-dimethyl-4-nitro-1-(p-toluenesulfonamido)-benzene (56). Hydrolysis of the nitroamide 56 afforded 2,6-dimethyl-4-nitroaniline (57) in 98 per cent yield. The amine 57 was diazotized and the resulting diazonium salt decomposed with

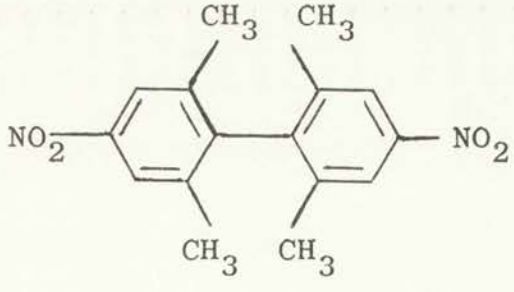


potassium iodide to give a 95 per cent yield of 4-iodo-2,6-dimethylnitrobenzene (58). The attempted Ullmann coupling of 58 resulted only in the elimination of iodine to give 5-nitro-m-xylene (59).



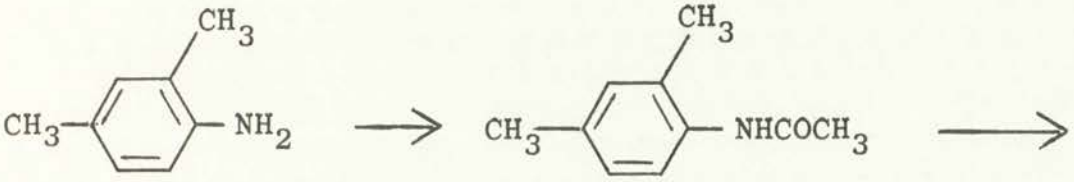
59

Since the Ullmann reaction failed to give the desired 2,2',6,6'-tetramethyl-4,4'-dinitrobiphenyl (60), it was decided to attempt an alternate route to the iodide 54.



60

An important compound in this second route was 4,4'-diamino-2,2',6,6'-tetramethylbiphenyl (64) which, it was hoped, could be mono-acetylated in a manner similar to that described for 4,4'-diamino-2,2'-dimethylbiphenyl (42). The



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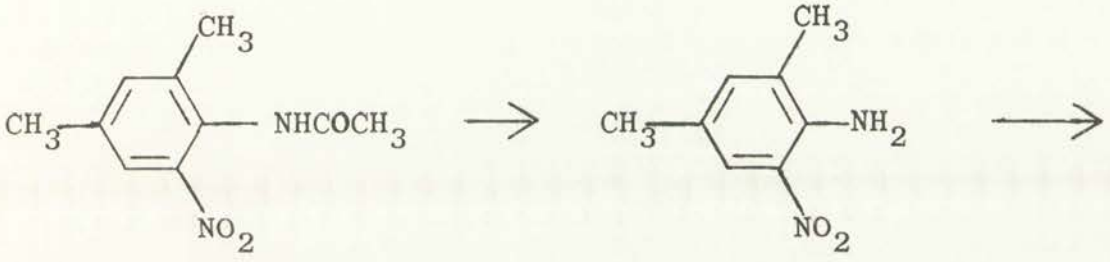
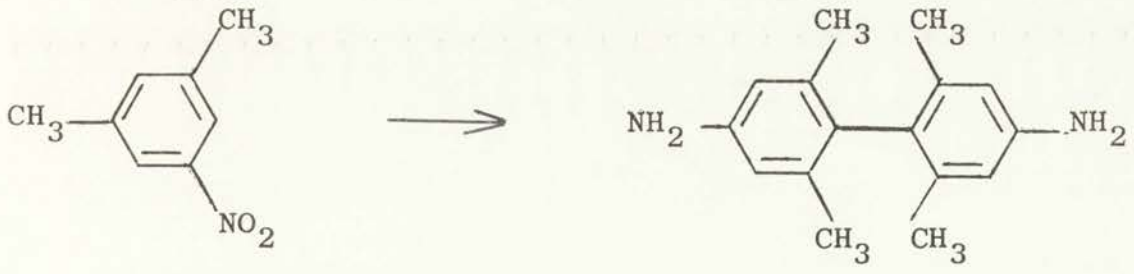
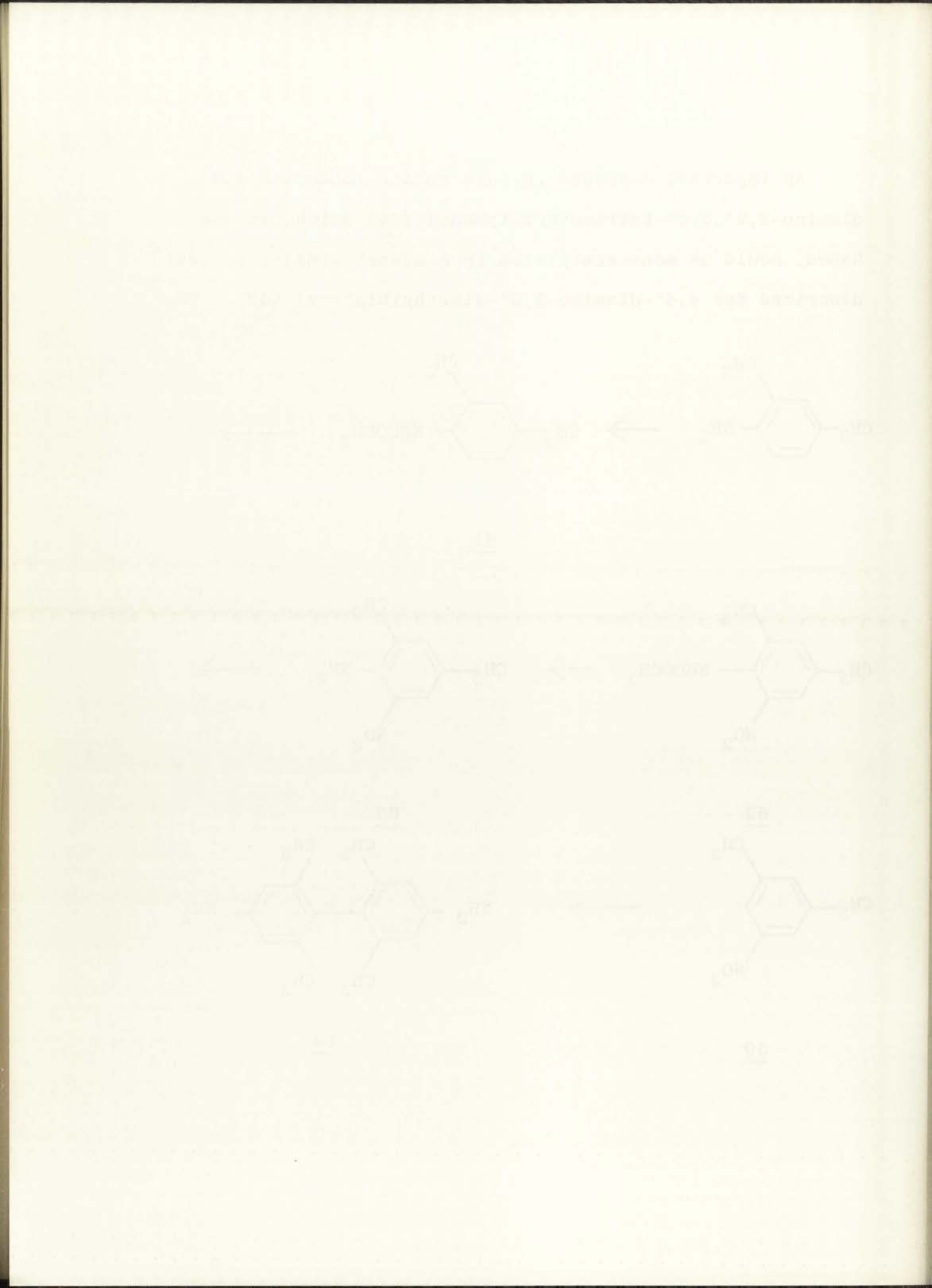


62 63



59 64



acetylation of 2,4-dimethylaniline was accomplished in 90 per cent yield to give 2,4-dimethylacetanilide (61). Nitration of the amide 61 afforded 2,4-dimethyl-6-nitroacetanilide (62) in 76 per cent yield. The hydrolysis of 62 to 2,4-dimethyl-6-nitroaniline (63) was accomplished in 77 per cent yield by refluxing in 20 per cent hydrochloric acid. Diazotization of the amine (63) and the decomposition of the diazonium salt in the presence of hypophosphorous acid gave an 85 per cent yield of 5-nitro-m-xylene (59). The preparation of 4,4'-diamino-2,2',6,6'-tetramethylbiphenyl (64) was accomplished from 59 according to the method outlined by Carlin.[30] Several attempts to mono-acetylate the diamine 64 failed to give the desired product, and additional material must be prepared in order to investigate this reaction further.

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(30) R. B. Carlin, J. Am. Chem. Soc., 67, 928 (1945).

EVALUATION OF THE COMPOUNDS

Solutions of the compounds prepared in this study were evaluated as primary liquid scintillation solutes and, in addition, the fluorescence and ultraviolet absorption spectra of the compounds were determined. The scintillation measurements[31] were carried out using a 10-channel pulse-height analyzer driven by the amplified output of an RCA 6903 quartz-face photomultiplier tube having average S-13 spectral characteristics. The solution to be tested was pipetted into a one milliliter quartz beaker, which was placed on the flat cathode of the vertically mounted photomultiplier tube. A few drops of mineral oil were used to ensure good optical coupling. The solutions were excited with monoenergetic Ba^{137} internal-conversion electrons from a Cs^{137} source mounted on the underside of the aluminum reflector that was used. The photomultiplier tube, solution, reflector, and source (Figure 11) were encased in a housing to exclude

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(31) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, Nucleonics, 13(12), 39 (1955).

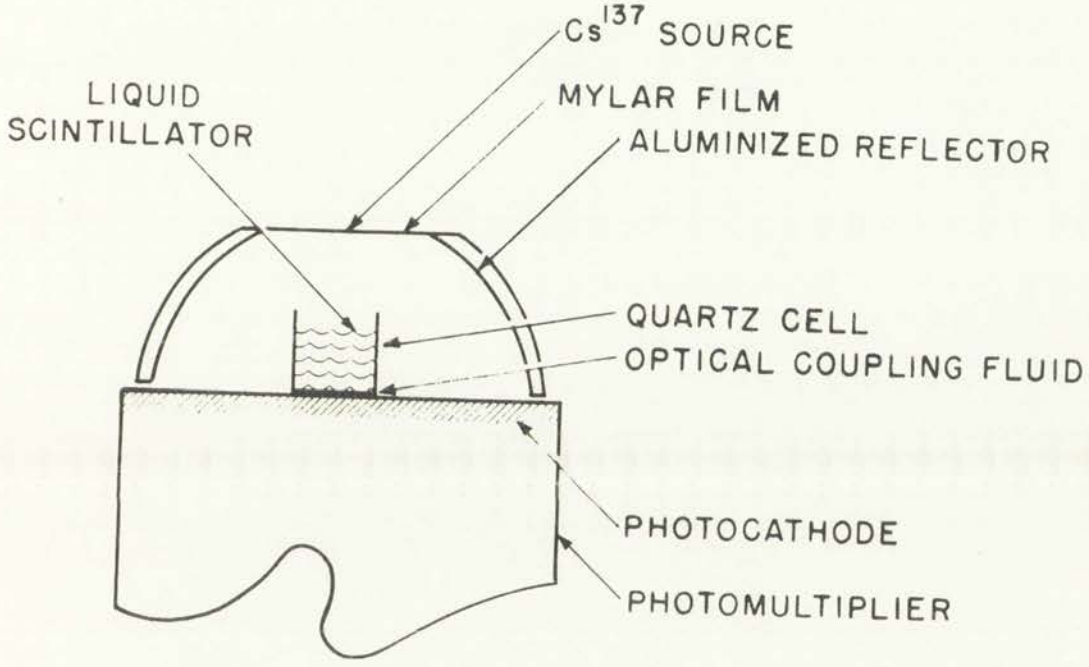

Figure 11. Arrangement for pulse-height measurement of liquid scintillators.

light. The solution was evaluated as a liquid scintillator by determining its pulse-height relative to that of a standard solution of 3 g./l. of 2,5-diphenyloxazole (PPO) in toluene. The results of these tests are given in Tables 5 through 13 (pp. 77 through 81) and are shown graphically in Figures 12, 13, and 14.

The ultraviolet-excited fluorescence spectra[32] were obtained by irradiation of toluene solutions (approximately 1 g./l.) contained in a triangular quartz cuvette and by analysis of the spectrum with an Aminco-Bowman spectrophotofluorometer. In order to obtain spectra involving the relative number of photons versus wavelength, the intensities at various wavelengths were tabulated, each was multiplied by a correction factor for that particular wavelength, and the data were plotted as shown in Figure 17 (p. 69) and Figures 20 through 26 (pp. 83 through 89).

The ultraviolet absorption spectra of the compounds in cyclohexane solution were determined using a Bausch and Lomb 505 recording spectrophotometer, and are plotted as log ϵ versus wavelength in Figures 27 through 33 (pp. 91 through 97).

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(32) D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, J. Am. Chem. Soc., 79, 5448 (1957).

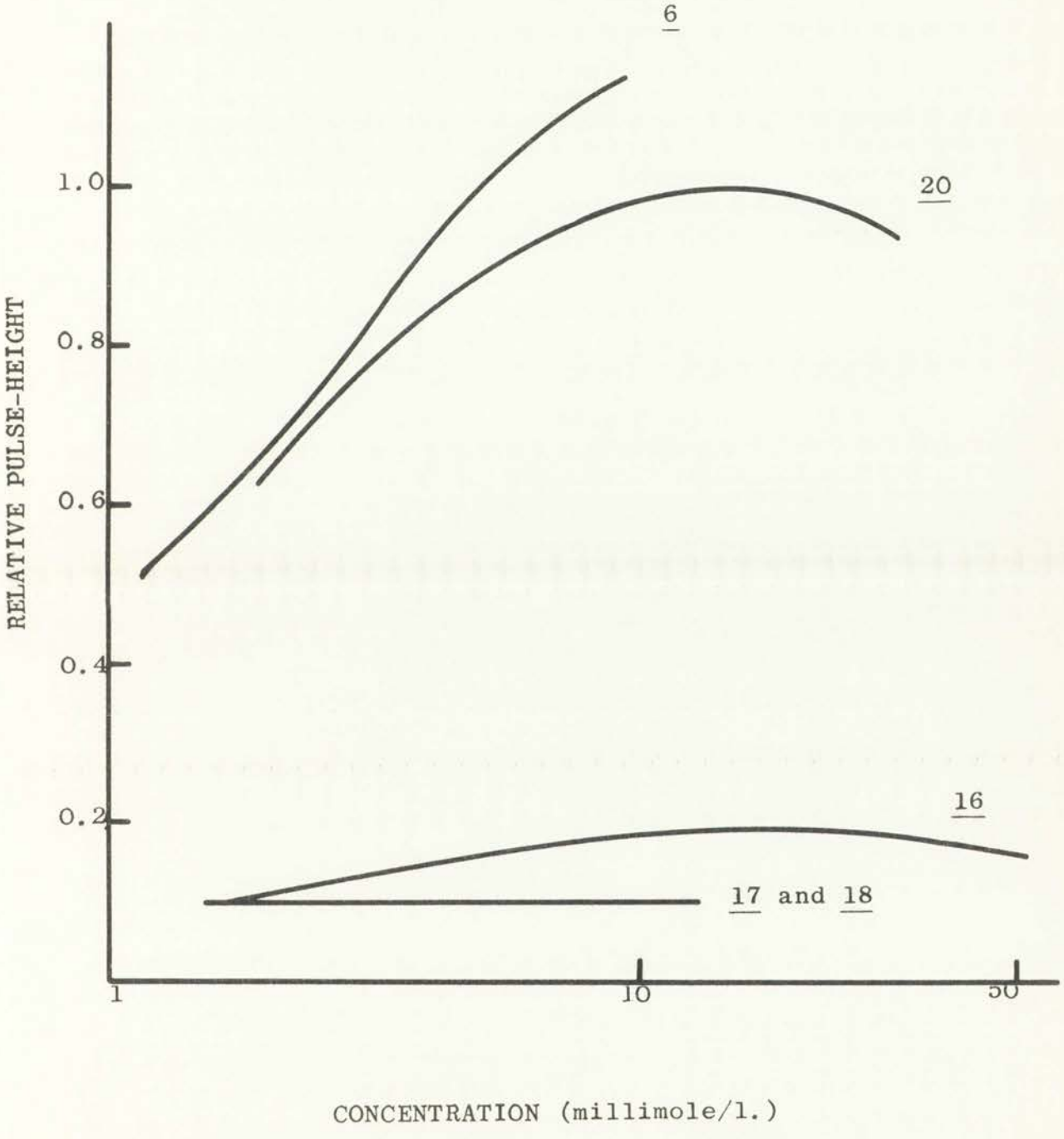
In addition to the results obtained from the testing of the compounds prepared in this work as primary scintillation solutes, it was also of interest to include for comparison purposes the pulse-height data for 2,7-diphenyl-9,10-dihydrophenanthrene (4), 2,7-diphenylfluorene (5), and 3,9-diphenyl-5,7-dihydrodibenz[c,e]oxepin (6).

As was mentioned in the introductory discussion of the angle of twist in biphenyl systems, the two phenyl rings in biphenyl itself are twisted out of the plane to an angle of about 50° to one another, and the angles for seven-membered-ring bridged biphenyls were found to be about 47° for 5,7-dihydrodibenz[c,e]oxepin (3), 55° for 6,6-dicarbethoxy-5,7-dihydrodibenzo[a,c]cycloheptadiene (9), and 49° for 2,7-dihydro-3,4,5,6-dibenzazepinium-1-spiro-1'''-piperidinium bromide (8). It would also be reasonable to assume that the angle of twist would be similar for 5,7-dihydrodibenzo[c,e]-thiepin (12) and 5,7-dihydrodibenzo[c,e]selenepin (13). If one assumes that the corresponding 2'',3'-substituted p-quaterphenyl analogs of the biphenyl derivatives (the oxepin 3, azepine 8, cycloheptadiene 9, selenepin 12, and thiepin 13) have a similar angle of twist about the 1',1''-bond of p-quaterphenyl, then the respective p-quaterphenyl derivatives (6, 16, 17, 18, and 20) should all exhibit similar scintillation properties to one another.

As seen in Figure 12, 3,9-diphenyl-5,7-dihydrodibenz[c,e]-oxepin (6) (maximum RPH = 1.14) and 6,6-dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20) (maximum RPH = 1.0) are excellent scintillators and show light-emitting properties similar to that of p-quaterphenyl. On the other hand, 3,9-diphenyl-5,7-dihydrodibenz[c,e]azepine (16) (maximum RPH = 0.19), 3,9-diphenyl-5,7-dihydrodibenzo[c,e]-selenepin (18) (maximum RPH $<$ 0.1), and 3,9-diphenyl-5,7-dibenzo[c,e]thiepin (17) (maximum RPH $<$ 0.1) are very poor liquid scintillation solutes.

These results may be rationalized either by the supposition that the angles of twist in 16, 17, and 18 are much greater than in 6 and 20, therefore greatly decreasing the p-orbital overlap across the 1',1''-bond, or more reasonably, that the scintillation is being quenched due to the presence of the respective hetero atom. The latter hypothesis was substantiated in the case of the azepine by an experiment in which a sample of an excellent scintillator, 2'',3'-dimethyl-p-quaterphenyl (14), was contaminated by the addition of a tertiary aliphatic amine. A 3×10^{-3} M solution of the dimethyl-p-quaterphenyl 14 had a relative pulse-height of 0.72, but with an equimolar concentration of triethyl amine present, the solution had a relative pulse-height of less than 0.1. It was found in a study of the role of solvents

Figure 12. Relative pulse-height curves for some 2'',3'-bridged p-quaterphenyls: 3,9-Diphenyl-5,7-dihydrodibenz[c,e]oxepin (6); 6-Methyl-3,9-diphenyl-5,7-dihydrodibenz[c,e]azepine (16); 3,9-Diphenyl-5,7-dihydrodibenzo[c,e]thiepin (17); 3,9-Diphenyl-5,7-dihydrodibenzo[c,e]-selenepin (18); and 6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cyclo-heptadiene (20).


6
20
16
17 and 18
1.0
0.8
0.6
0.4
0.2
RELATIVE PULSE-HEIGHT
1
10
50
CONCENTRATION (millimole/l.)

in liquid scintillators[33] that the addition of ketones, chloro- and bromobenzene, amines or thiophene to the scintillation solution caused an abrupt decrease in the relative pulse-height.

The limited pulse-height data obtained for the compound which is believed to be 3,9-diphenyl-5,7-dihydrodibenzo[a,c]-cycloheptadiene (19) indicate that this compound is similar to the diester 20 in its scintillation properties.

Figure 13 shows that 2'',3'-dimethyl-p-quaterphenyl (14) is a good liquid scintillation solute, but the p-quaterphenyl derivative with four ortho methyl groups, 2'',3',5',6''-tetramethyl-p-quaterphenyl (15), demonstrates scintillation properties more like those of a biphenyl rather than a quaterphenyl. This indicates that very little p-orbital overlap across the 1',1''-bond is possible in the tetramethyl derivative 15.

A comparison of the pulse-height data for 2'',3'-dimethyl-p-quaterphenyl (14) and 2,2'-dimethyl-p-quaterphenyl (34) (Figure 13) shows that the latter compound is a better scintillator (maximum RPH = 1.15) than the former (maximum RPH = 0.92). Assuming that the two methyl groups in each compound cause some hindrance to free rotation, one would expect that the 2,2'-dimethyl compound would be a better scintillator than the 2'',3'-dimethyl compound, since in the

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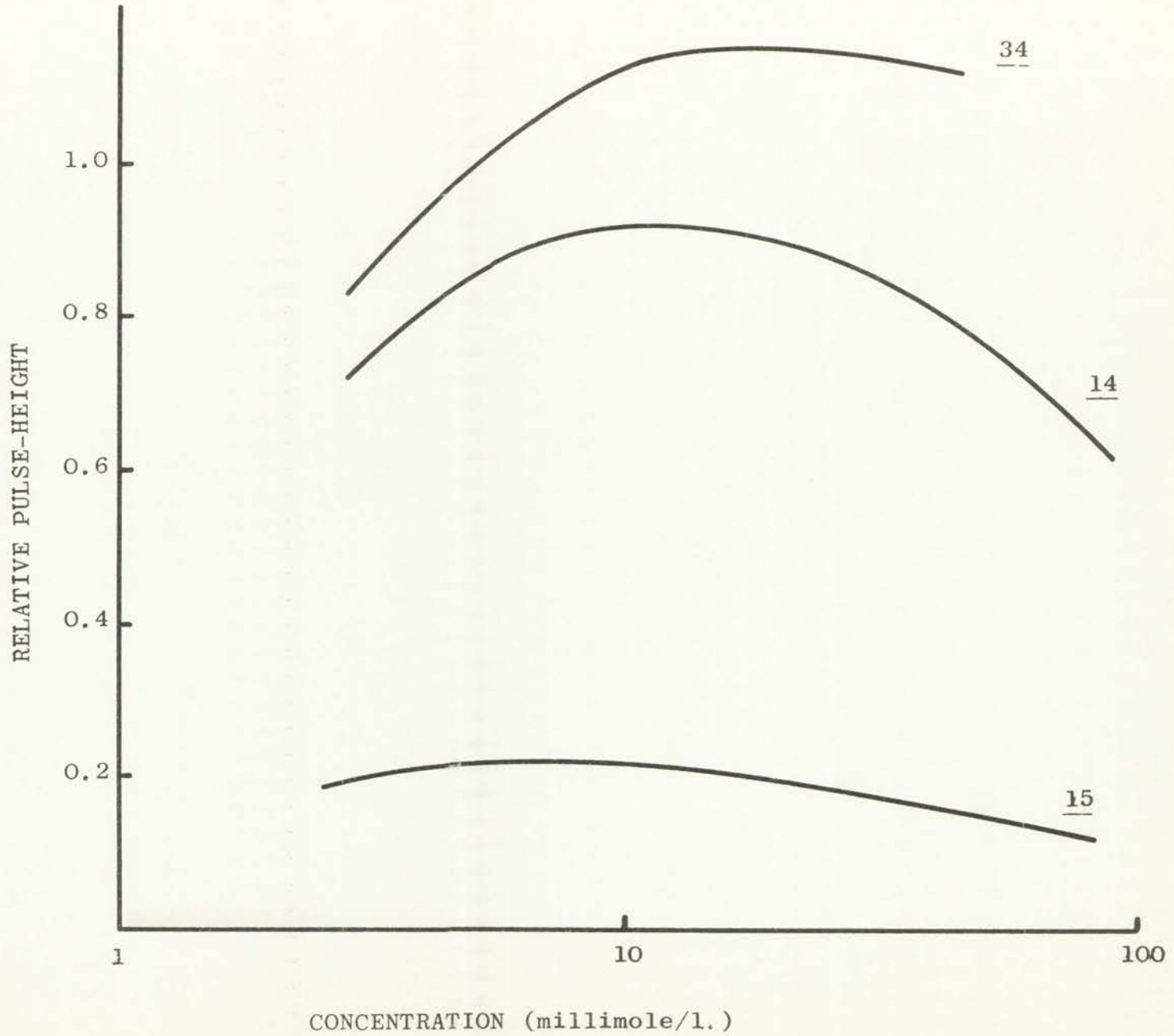
(33) F. N. Hayes, B. S. Rogers, and P. C. Sanders, Nucleonics, 13(1), 46 (1955).

Figure 13. Relative pulse-height curves of some polymethylated p-quaterphenyls: 2'',3'-Dimethyl-p-quaterphenyl (14); 2'',3',5',6''-Tetramethyl-p-quaterphenyl (15); and 2,2'-Dimethyl-p-quaterphenyl (34).


34
14
15
1.0
0.8
0.6
0.4
0.2
RELATIVE PULSE-HEIGHT
1
10
100
CONCENTRATION (millimole/l.)

former an unhindered p-terphenyl system is available, while in the latter only an unhindered biphenyl system is present.

In Figure 14, the compounds 4, 5, 6, 14, and 20 are plotted as RPH versus concentration in millimole/l. As can be seen from Table 3 and Figure 15, a comparison of the compounds at a fairly low concentration (3×10^{-3} M) shows that as the angle of twist increases the relative pulse-height decreases.

TABLE 3. THE RELATIVE PULSE-HEIGHTS FOR SOME 2'',3'-DISUBSTITUTED DERIVATIVES AT 3×10^{-3} M IN TOLUENE

2'',3'-p-Quaterphenyl Derivative	α	RPH	$\cos^2 \alpha$
$-CH_2-$ (5)	~ 0°*	0.96	1.00
$-CH_2CH_2-$ (4)	~ 31°**	0.89	0.735
$-CH_2OCH_2-$ (6)	~ 47°**	0.82	0.465
$-CH_2C(COOEt)_2CH_2-$ (20)	~ 55°*	0.77	0.330
$-CH_3$, CH_3- (14)	~ 70°**	0.72	0.117
2'',3',5',6''-Tetramethyl (15)	~ 90°*	0.19	0.00

*Estimates from molecular models.

**Estimates by Suzuki for analogous biphenyls.[5]

Figure 14. Relative pulse-height curves for some 2'',3'-disubstituted p-quaterphenyls: 2,7-Diphenyl-9,10-dihydrophenanthrene (4); 2,7-Diphenyl-fluorene (5); 3,9-Diphenyl-5,7-dihydrodibenz-[c,e]oxepin (6); 2'',3'-Dimethyl-p-quaterphenyl (14); and 6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20).

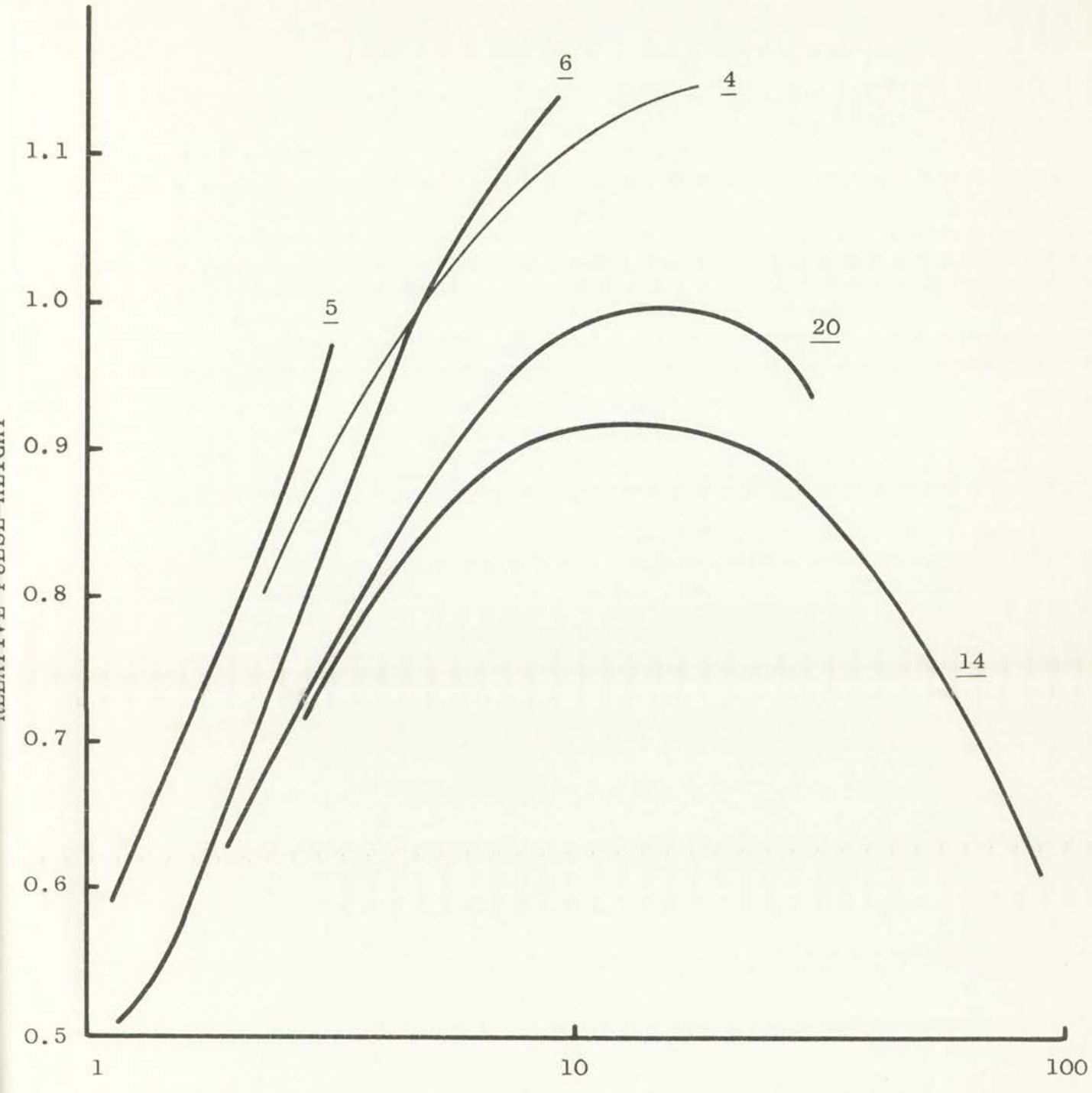
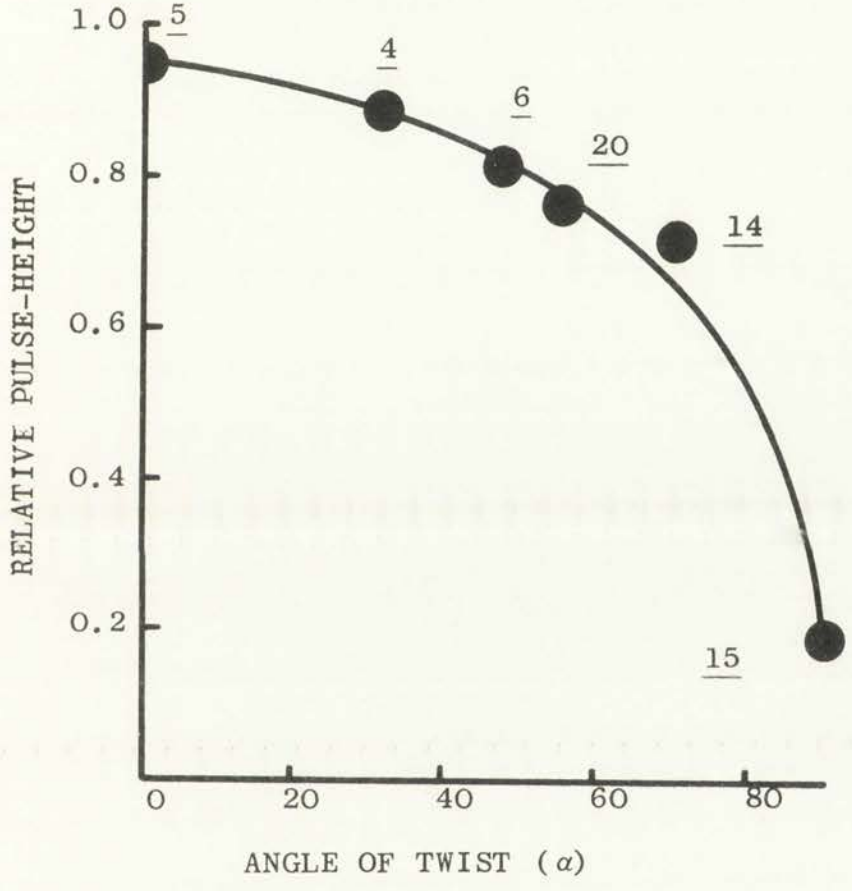

6
4
5
20
14
1.1
1.0
0.9
0.8
0.7
0.6
0.5
1
10
100
CONCENTRATION (millimole/l.)

Figure 15. Relative pulse-height versus angle of twist (α) for some 2'',3'-disubstituted p-quaterphenyls at 3 x 10^{-3} M: 2,7-Diphenyl-9,10-dihydrophenanthrene (4); 2,7-Diphenylfluorene (5); 3,9-Diphenyl-5,7-dihydrodibenz[c,e]oxepin (6); 2'',3'-Dimethyl-p-quaterphenyl (14); 2'',3',5',6''-Tetramethyl-p-quaterphenyl (15); and 6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20).


1.0
0.8
0.6
0.4
0.2
RELATIVE PULSE-HEIGHT
5
4
6
20
14
15
0
20
40
60
80
ANGLE OF TWIST (α)

The angles of twist, α, as given for the p-quaterphenyl derivatives listed in Table 3, are the values calculated by Suzuki[5] for the analogous biphenyl derivatives or, where such calculations have not been made, are estimated from molecular models. Figure 15, which is a plot of the relative pulse-height for each compound versus the angle of twist, shows that a surprisingly smooth curve is obtained and as α increases the RPH decreases.

In a discussion of the molecular orbital theory of organic chemistry, Dewar[34] emphasizes the point that mesomerism does not require perfect planarity of the conjugated system. In his study, the effect of conjugation between parts R and S on the total energy of a mesomeric system, RS, is discussed. The theorem states that the resonance energy of RS relative to (R + S), although greatest when the system is coplanar, varies as $\cos^2 \alpha$, where α is the angle through which S is twisted out of coplanarity with R. It is interesting to note from Figure 16 that a plot of the RPH at 3×10^{-3} M for the compounds listed in Table 3 versus the $\cos^2$ of the estimated angle of twist (α) gives essentially a straight line. The notable exception is 2'',3',5',6''-tetramethyl-p-quaterphenyl (15), which does not show the scintillation properties of a

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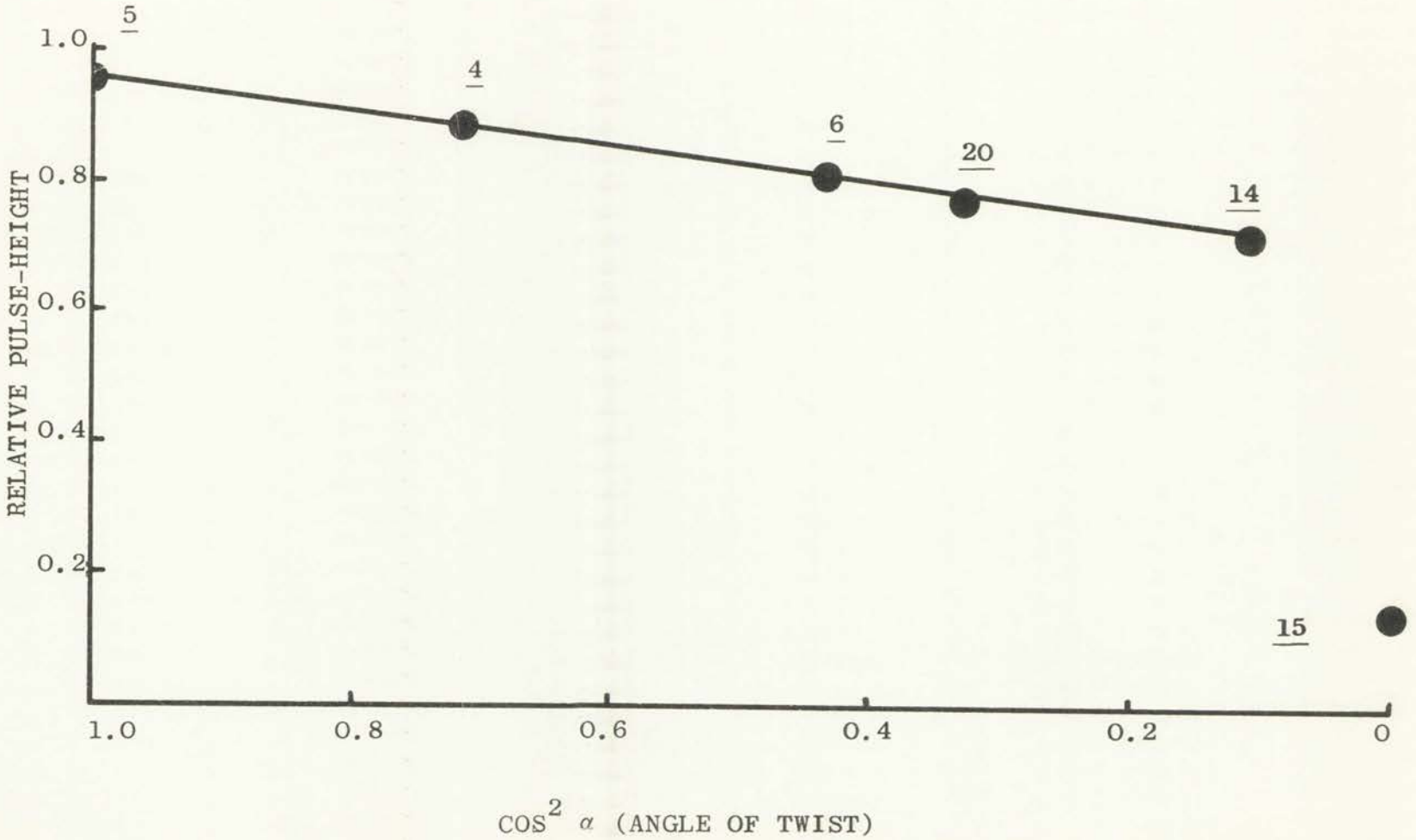
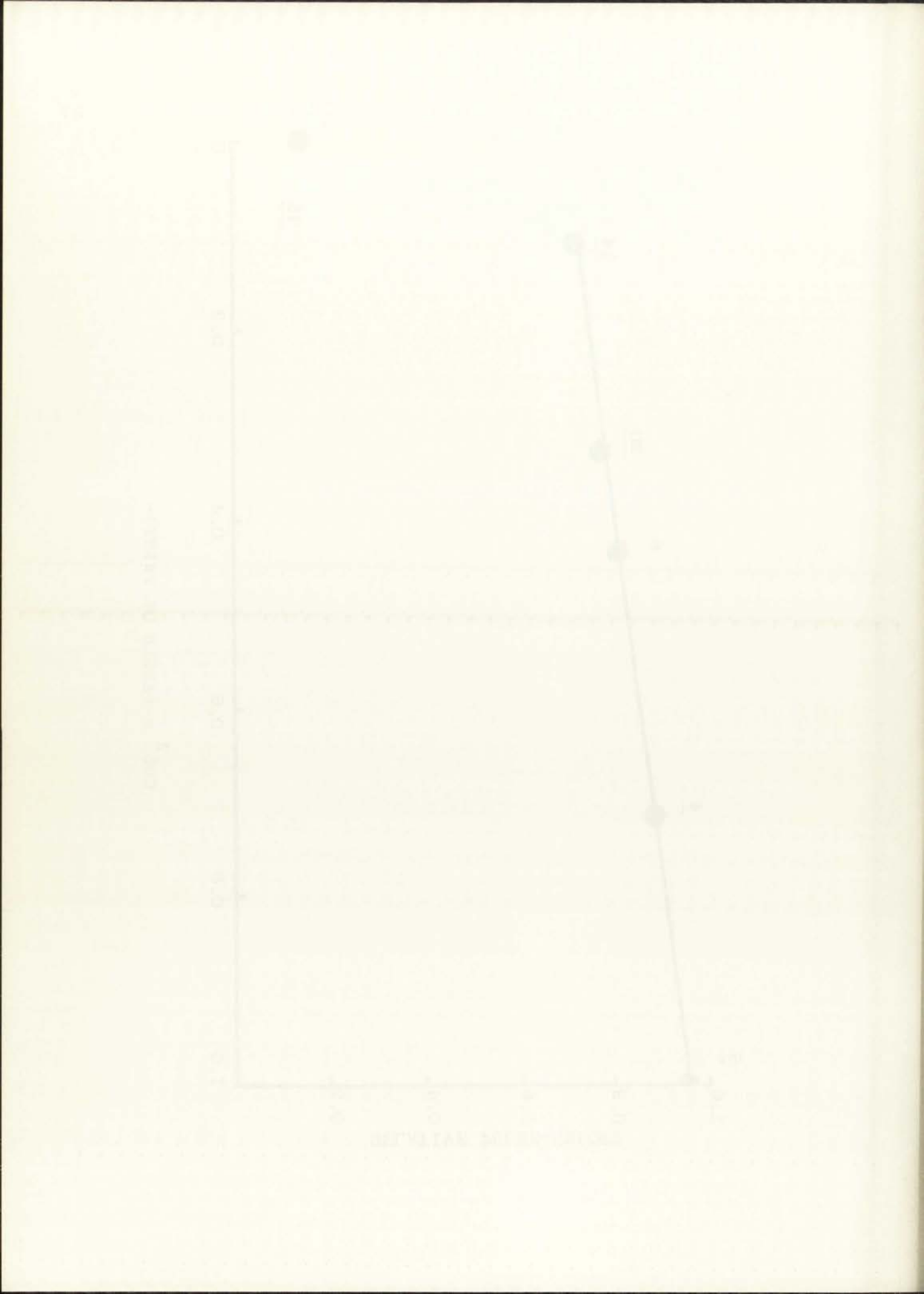
(34) M. J. S. Dewar, J. Am. Chem. Soc., 74, 3345 (1952).

Figure 16. Relative pulse-height at 3×10^{-3} M in toluene versus $\cos^2 \alpha$ (α (angle of twist) for some 2'',3'-substituted p-quaterphenyls: 2,7-Diphenyl-9,10-dihydrophenanthrene (4); 2,7-Diphenylfluorene (5); 3,9-Diphenyl-5,7-dihydrodibenz[c,e]oxepin (6); 2'',3'-Dimethyl-p-quaterphenyl (14); 2'',3',5',6''-Tetramethyl-p-quaterphenyl (15); and 6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20).

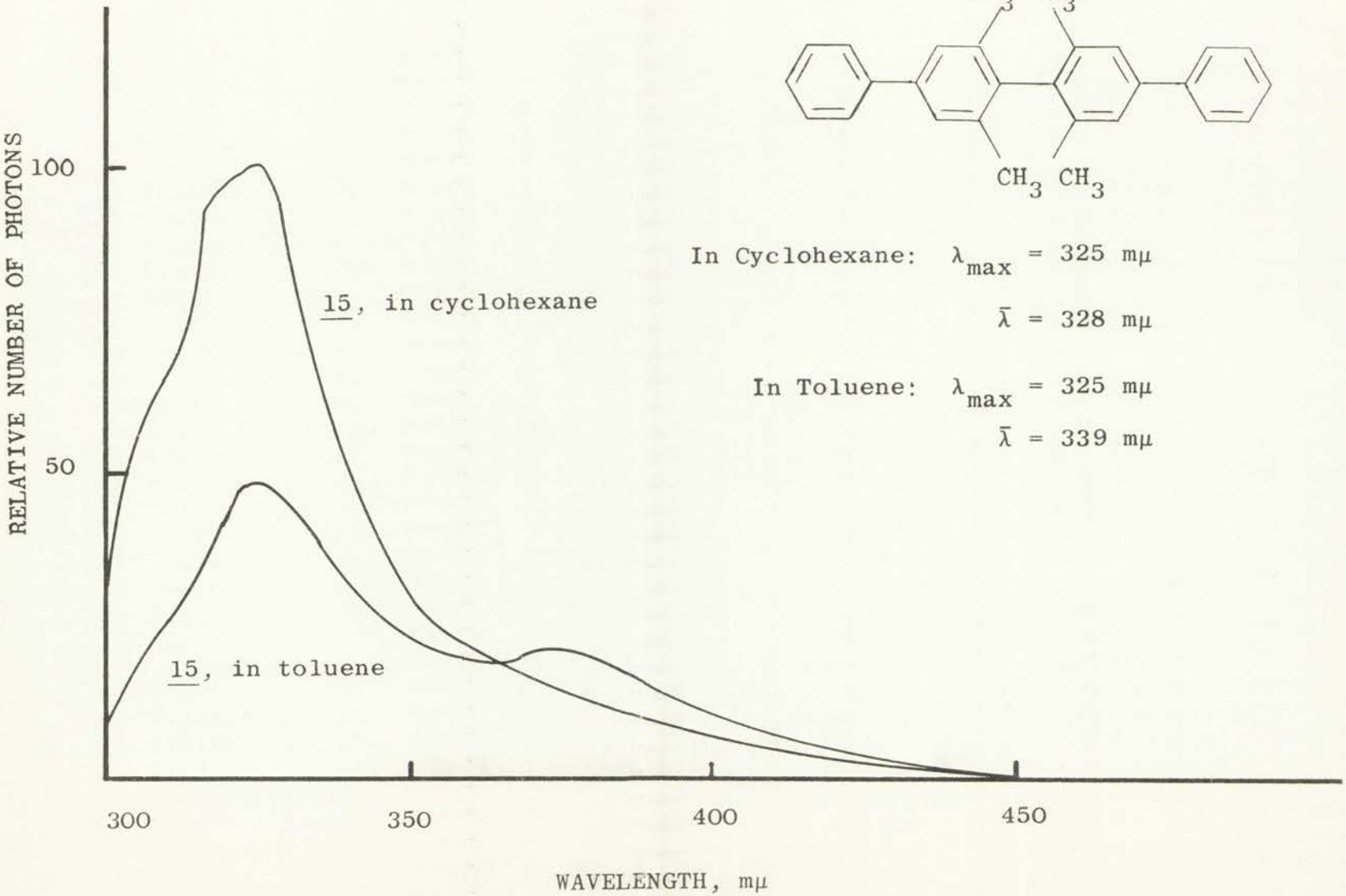

5
4
6
20
14
15
1.0
0.8
0.6
0.4
0.2
RELATIVE PULSE-HEIGHT
1.0
0.8
0.6
0.4
0.2
0
COS^2 α (ANGLE OF TWIST)



p-quaterphenyl system but of a biphenyl system. It appears, then, that although the biphenyl components of the p-quaterphenyl derivatives 4, 6, 14, and 20 are twisted out of the plane with one another, considerable resonance interaction across the 1',1''-bond is possible. The amount of resonance energy available to the p-quaterphenyl system from the 1',1''-interaction decreases as the $\cos^2$ of the angle of twist (α) and the scintillation ability of these compounds decreases in a like manner to the point at which there is no (or very little) p-orbital interaction across the 1',1''-bond, and the scintillation properties are now those of the isolated biphenyl components of the p-quaterphenyl system.

As was mentioned in the discussion of the determination of the light-emitting capabilities of a solute, the observed pulse-height of a compound depends in part upon the "matching factor" between the emission spectrum and the photomultiplier response curve (Figure 10, p. 30), as well as absorption by the solvent of light emitted at shorter wavelengths. Figure 17 shows that the fluorescence emission spectrum for 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) exhibits a maximum at 325 mμ, which is not within the range of maximum response for the photomultiplier employed (Figure 10). At 325 mμ, the photomultiplier response is about 68 per cent efficient, but all of the photons emitted by the solute 15 are not emitted at 325 mμ, as many are emitted at longer wavelengths, so that in

Figure 17. Corrected fluorescence spectra for 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) in cyclohexane and in toluene at 3×10^{-3} M.



In Cyclohexane: λ_{max} = 325 mμ

$\bar{\lambda}$ = 328 mμ

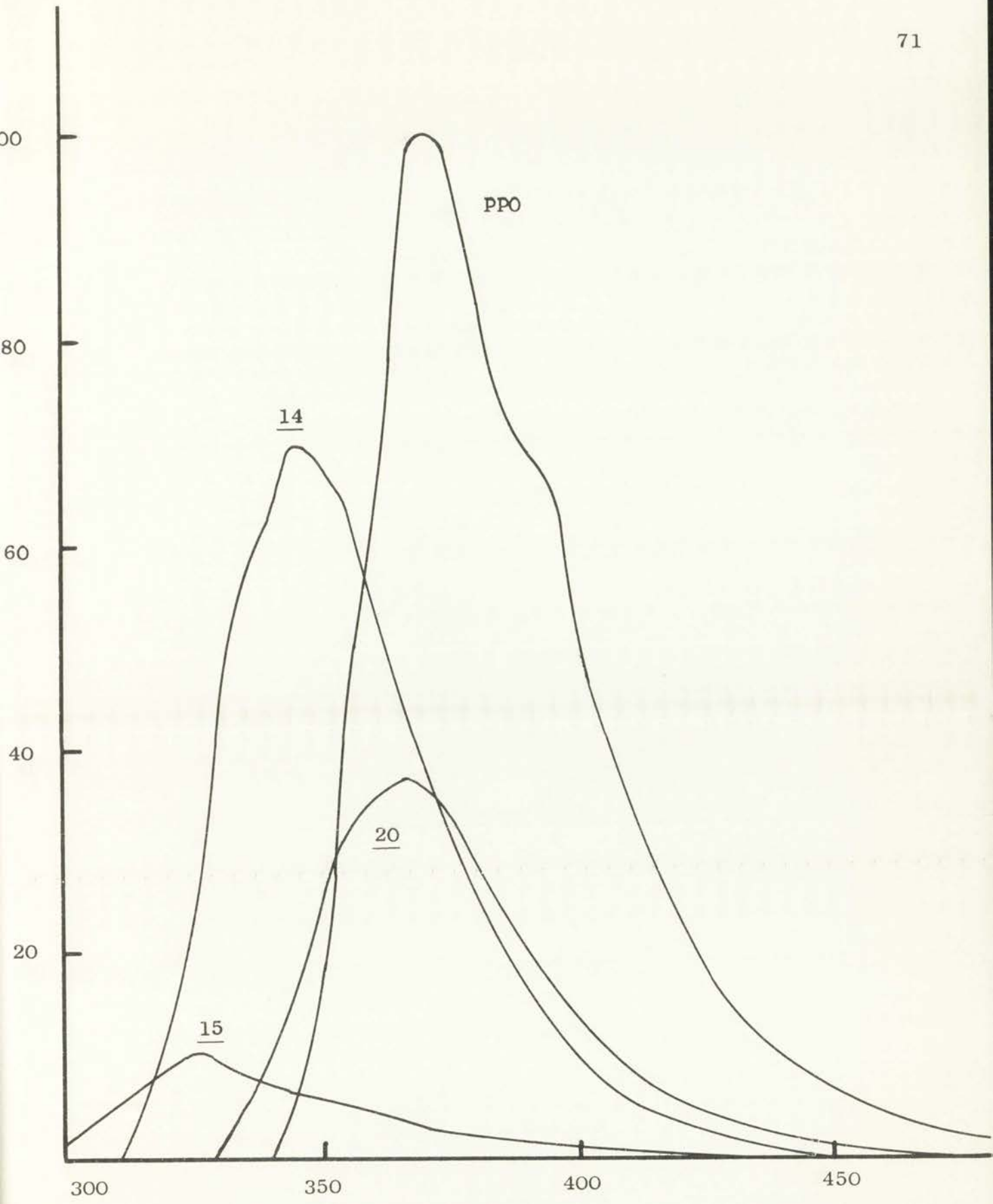
In Toluene: λ_{max} = 325 mμ

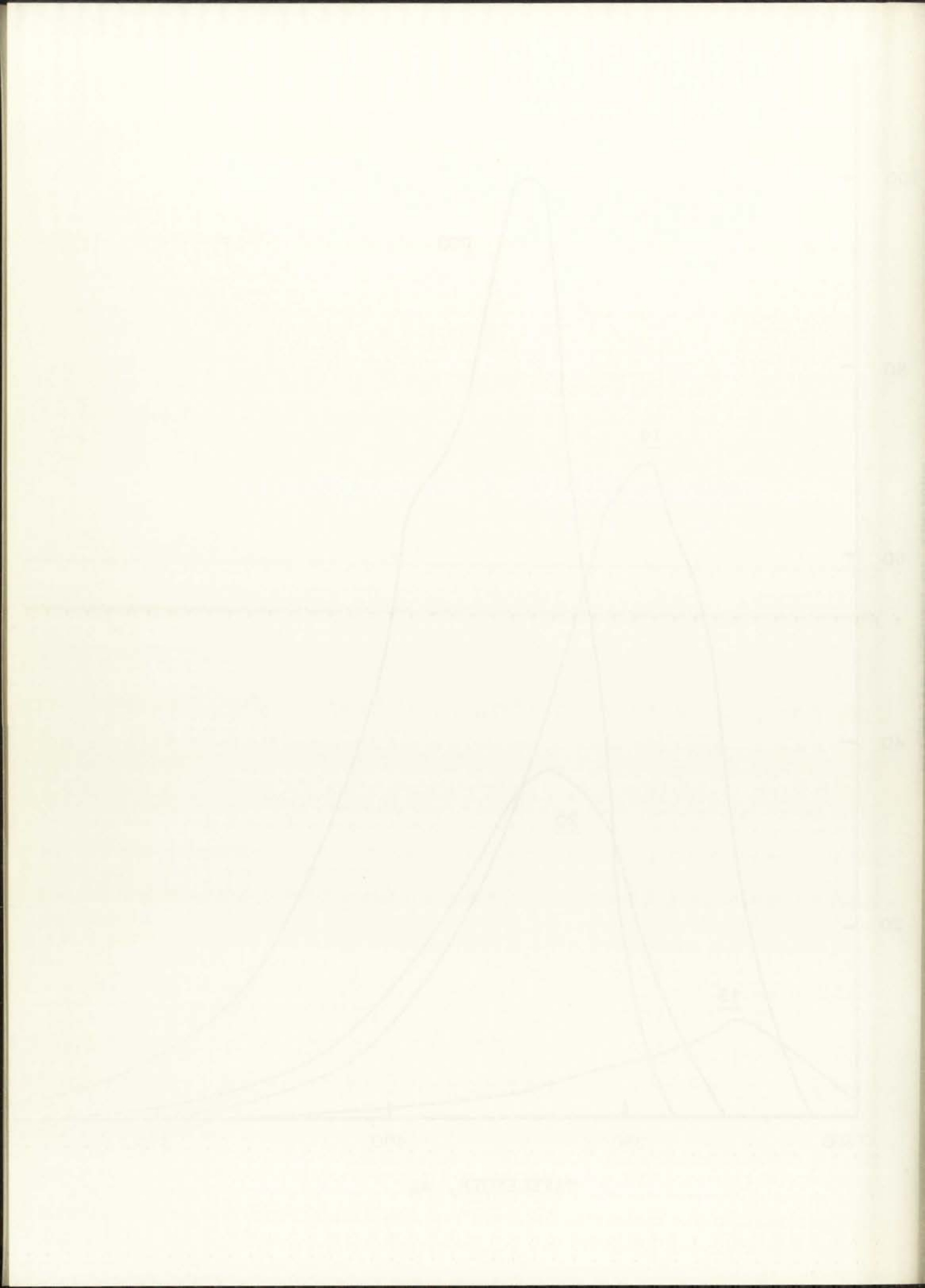
$\bar{\lambda}$ = 339 mμ

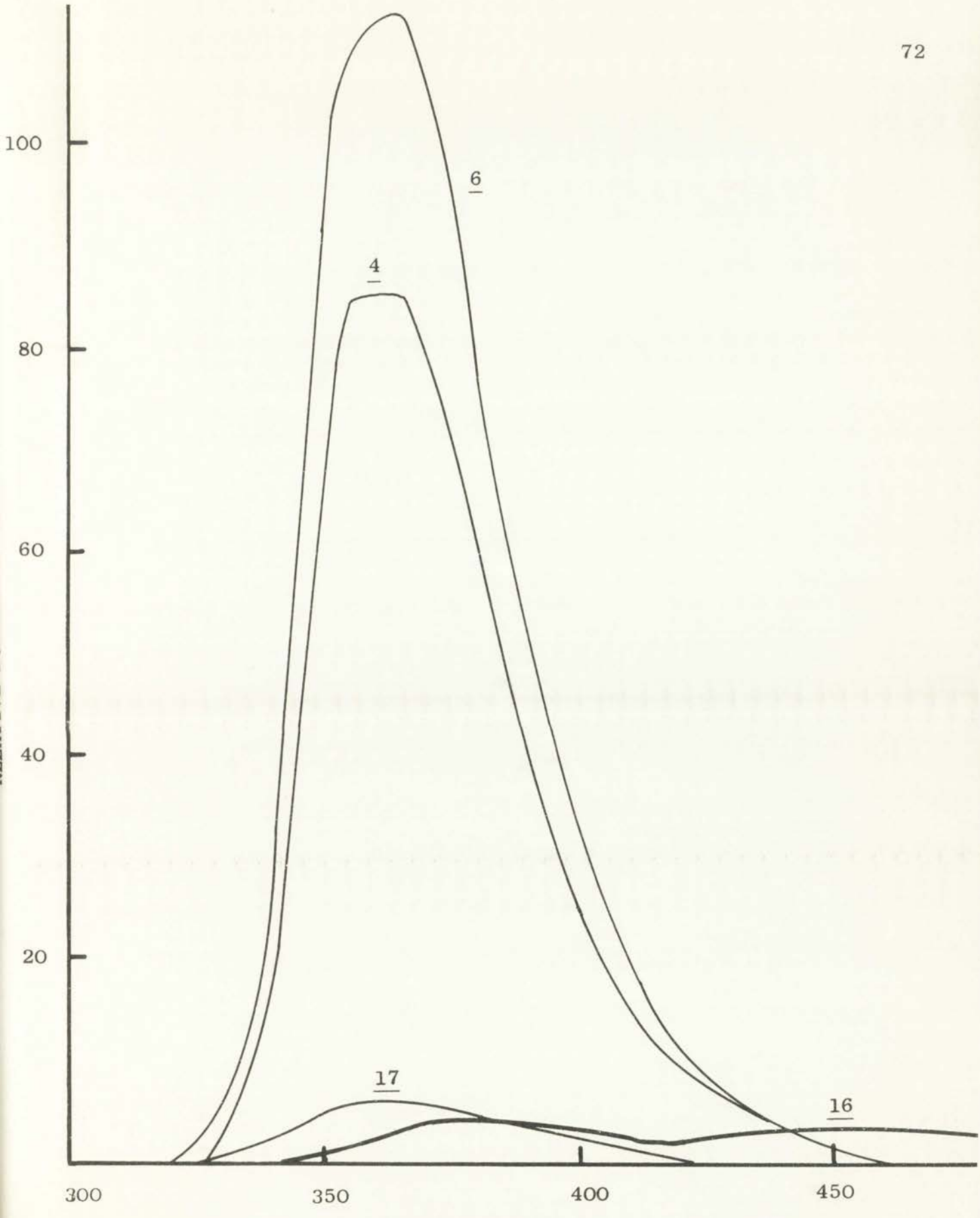
reality the efficiency of the photomultiplier should be better than 68 per cent for the hydrocarbon 15. Figure 17 also compares the light-emitting capabilities of 15 in cyclohexane and toluene. It can be seen that there is an appreciable amount of light absorbed by toluene when it is employed as the solvent. However, even though the light emitted by 15 is of shorter wavelength than that emitted by the standard, PPO, and is not as efficiently detected by the photomultiplier, an examination of the fluorescence spectra as plotted in Figure 18 shows that 15 is a poor light emitter compared to PPO. Figures 18 and 19 are plots of the corrected relative number of photons versus wavelength for the 9,10-dihydrophenanthrene 4, oxepin 6, dimethyl-p-quaterphenyl 14, tetramethyl-p-quaterphenyl 15, azepine 16, thiepin 17, and the cycloheptadiene 20 as compared to 3.0 g./l. of PPO as a standard. A comparison of these plots with scintillation data indicates that the compounds which are poor liquid scintillators are also poor light emitters when excited by ultraviolet radiation.

A tabulation of the ultraviolet absorption maxima for the compounds evaluated as primary scintillation solutes, as given in Table 4, shows that a definite hypsochromic shift of the maximum occurs as the angle of twist increases. The maxima for 2'',3'-dimethyl-p-quaterphenyl (14) and 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) are very close to the maxima

Figures 18 and 19. Corrected fluorescence spectra of some 2'',3'-substituted quaterphenyls at 3 x 10^{-3} M in toluene relative to 2,5-diphenyloxazole (PPO) at 3.0 g./l.: 2,7-Diphenyl-9,10-dihydrophenanthrene (4); 2,7-Diphenylfluorene (5); 3,9-Diphenyl-5,7-dihydrodibenz[c,e]oxepin (6); 2'',3'-Dimethyl-p-quaterphenyl (14); 2'',3',5',6''-Tetramethyl-p-quaterphenyl (15); 6-Methyl-3,9-diphenyl-5,7-dihydrodibenz[c,e]azepine (16); 3,9-Diphenyl-5,7-dihydrodibenz[c,e]thiepin (17); and 6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20).


00
80
60
40
20
PPO
14
20
15
300
350
400
450
WAVELENGTH, mμ




100
80
60
40
20
6
4
17
16
300
350
400
450
WAVELENGTH, mμ

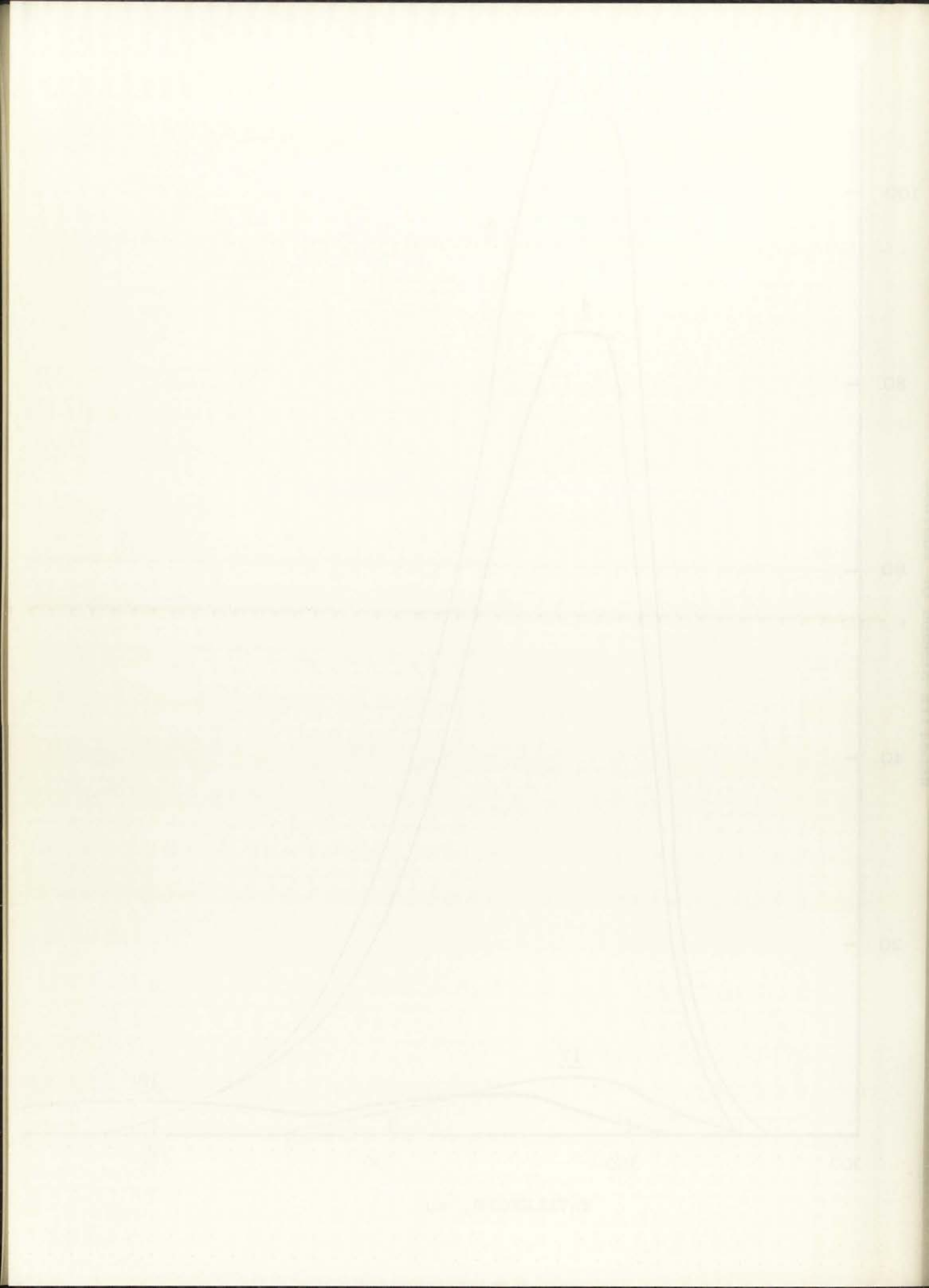


TABLE 4. ULTRAVIOLET ABSORPTION MAXIMA AND LOG ϵ VALUES FOR SOME 2'',3'-DISUBSTITUTED p-QUATERPHENYL DERIVATIVES

2'',3'-p-Quaterphenyl Derivative	Max (mμ)	Log ϵ	α
$-CH_2CH_2-$ (4)	323	4.60	31°
$-CH_2-$ (5)	310 323	4.72 4.76	strained planar
$-CH_2-O-CH_2-$ (6)	298	4.64	47°
$-CH_2C(COOEt)_2CH_2-$ (20)	296	4.65	55°
$-CH_2N(CH_3)CH_2-$ (16)	290	4.55	--
$-CH_2SeCH_2-$ (18)	288	4.55	--
$-CH_2SCH_2-$ (17)	286	4.51	--
$-CH_3$, CH_3- (14)	265	4.63	70°
2'',3',5',6''-Tetramethyl (15)	264	4.94	90°

exhibited by biphenyl systems. The value of 264 mμ for 15 should probably be corrected for the presence of two additional methyl groups for the purposes of comparison with the dimethyl compound 14. Truce and Emrick[16] have suggested that about 8 mμ should be subtracted for the addition of the two methyl groups. This would give a value of 256 mμ for the maximum of 15, which is close to the maximum of 3,5-dimethylbiphenyl (252 mμ).[19] It is also observed that the three compounds 16, 17, and 18, which are very poor scintillators, exhibit fairly low log ε values compared to the compounds which are good liquid scintillators. This indicates that the excitation energy is not being absorbed by the molecule, causing the compound to have fairly low emission intensities.

The scintillation data as tabulated in Table 12 for 2,2'-dimethyl-p-terphenyl (52) are of questionable value, as varying results were obtained from different samples. The hydrocarbon 52 was obtained as an oil, which rendered it difficult to obtain samples of constant purity.

The results of this investigation indicate that there is an appreciable amount of p-orbital overlap across the 1',1''-bond in p-quaterphenyl derivatives, even though the biphenyl portions of the molecule may be twisted as much as 70° out of the plane with one another. Indeed, it is indicated that the one- and two-carbon atom bridges across

the 2'',3'-positions of p-quaterphenyl force the molecule into a more planar configuration than in p-quaterphenyl itself. The three atom bridges, such as are found in the oxepin 6 and the diester 20, twist the rings out of the plane to a similar extent as in p-quaterphenyl. As a matter of fact, a linear relationship was shown to exist between $\cos^2 \alpha$ and the RPH for the fluorene (5), 9,10-dihydrophenanthrene (4), oxepin (6), cycloheptadiene (20), and the dimethyl derivative (14) at the equimolar concentration of 3×10^{-3} M.

Placing four methyl groups in the 2'',3',5',6''-positions so hinders rotation about the 1',1''-bond that the scintillation and ultraviolet absorption properties of the molecule are essentially those of the biphenyl components of the system.

The observation of the fact that 2,2'-dimethyl-p-quaterphenyl (34) is a better scintillator than 2'',3'-dimethyl-p-quaterphenyl (14) lends support to the observation by Birkeland[7] that 2,2'-substituted p-quaterphenyls are better scintillators than their 2'',3'-substituted analogs.

Finally, although the angles of twist for the azepine 16, the thiepin 17, and the selenepin 18 are believed to be comparable to the angles for the oxepin 6 and the diester 20, the former three compounds were found to be very poor primary liquid scintillation solutes, probably due to the presence of the hetero atom in the three-atom bridge.

EXPERIMENTAL

The experimental section is divided into four parts:

A. Tables 5 through 13, which list the pulse-height data for each of the compounds tested as primary solutes.

B. Figures 20 through 26, which are plots of corrected fluorescence spectra.

C. Figures 27 through 33, which are plots of ultraviolet absorption spectra.

D. Procedures used in the synthesis of the compounds.

A. Pulse-Height Data*

TABLE 5. 2'',3'-DIMETHYL-p-QUATERPHENYL (14)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
30.0	90.0	0.61
15.0	45.0	0.79
7.5	22.5	0.90
3.75	11.25	0.92
1.88	5.63	0.87
0.94	2.82	0.72

*In the following tables, the toluene solutions of solutes were measured relative to 3.0 g./l. of 2,5-diphenyloxazole (PPO) using a Ba^{137} electron source and an RCA 6903 quartz-faced photomultiplier tube. RPH = pulse-height relative to PPO. Saturated solutions are designated (sat.).

TABLE 6. 2'',3',5',6''-TETRAMETHYL-p-QUATERPHENYL (15)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
30.0	82.9	0.12
15.0	41.45	0.16
7.5	20.72	0.19
3.75	10.36	0.20
1.88	5.18	0.21
0.94	2.59	0.19

TABLE 7. 6,6-DICARBETHOXY-3,9-DIPHENYL-5,7-DIHYDRODIBENZO-[a,c]CYCLOHEPTADIENE (20)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
14.45 (sat.)	29.5	0.94
7.23	14.75	1.00
3.62	7.77	0.96
1.81	3.89	0.82
0.90	1.94	0.63

TABLE 8. 6-METHYL-3,9-DIPHENYL-5,7-DIHYDRODIBENZ[c,e]AZEPINE (16)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
19.2 (sat.)	53.2	0.16
9.6	26.6	0.19
4.8	13.3	0.19
2.4	6.65	0.17
1.2	3.33	0.15
0.6	1.67	0.10

TABLE 9. 3,9-DIPHENYL-5,7-DIHYDRODIBENZO[c,e]SELENEPIN (18)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
7.0 (sat.)	17.0	< 0.1
3.5	8.5	< 0.1
1.8	4.25	< 0.1
0.9	2.13	< 0.1

TABLE 10. 3,9-DIPHENYL-5,7-DIHYDRODIBENZO[c,e]THIEPIN (17)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
4.4 (sat.)	12.1	< 0.1
2.2	6.05	< 0.1
1.1	3.03	< 0.1
0.5	1.52	< 0.1

TABLE 11. 5-CYANO-6-IMINO-3,9-DIPHENYL-5,7-DIHYDRODIBENZO-[a,c]CYCLOHEPTADIENE (27)

Concentration (g./l.)	Concentration (millimole/l.)	RPH
17.5 (sat.)	45.6	< 0.1
8.75	22.8	< 0.1
4.38	11.4	< 0.1
2.19	5.7	< 0.1
1.09	2.9	< 0.1

TABLE 12. 2,2'-DIMETHYL-p-TERPHENYL (52)*

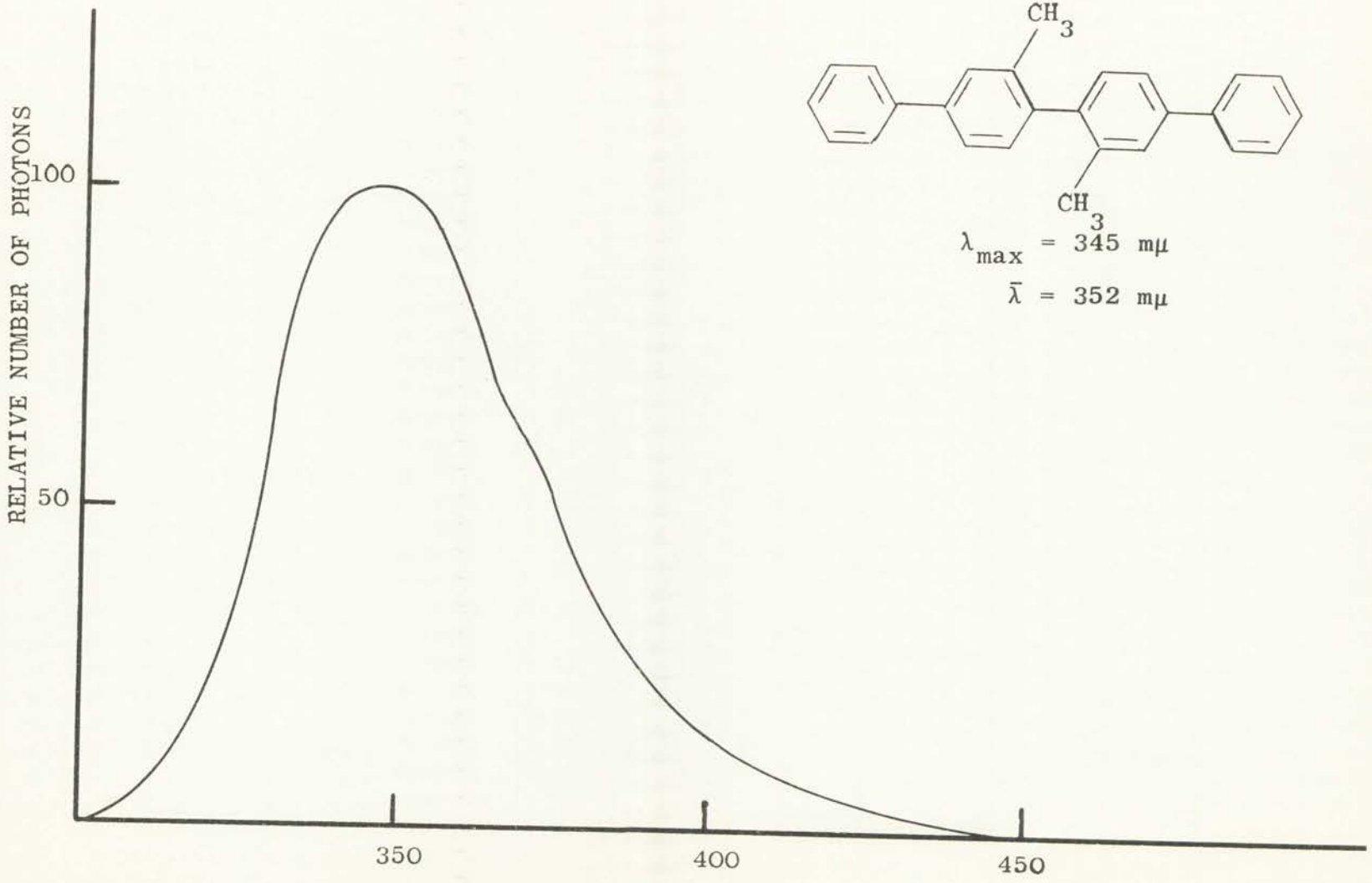
Concentration (g./l.)	Concentration (millimole/l.)	RPH
30.0	116.4	0.61
15.0	58.4	0.62
7.5	29.2	0.60
3.8	14.6	0.55
1.9	7.3	0.48
0.95	3.65	0.34

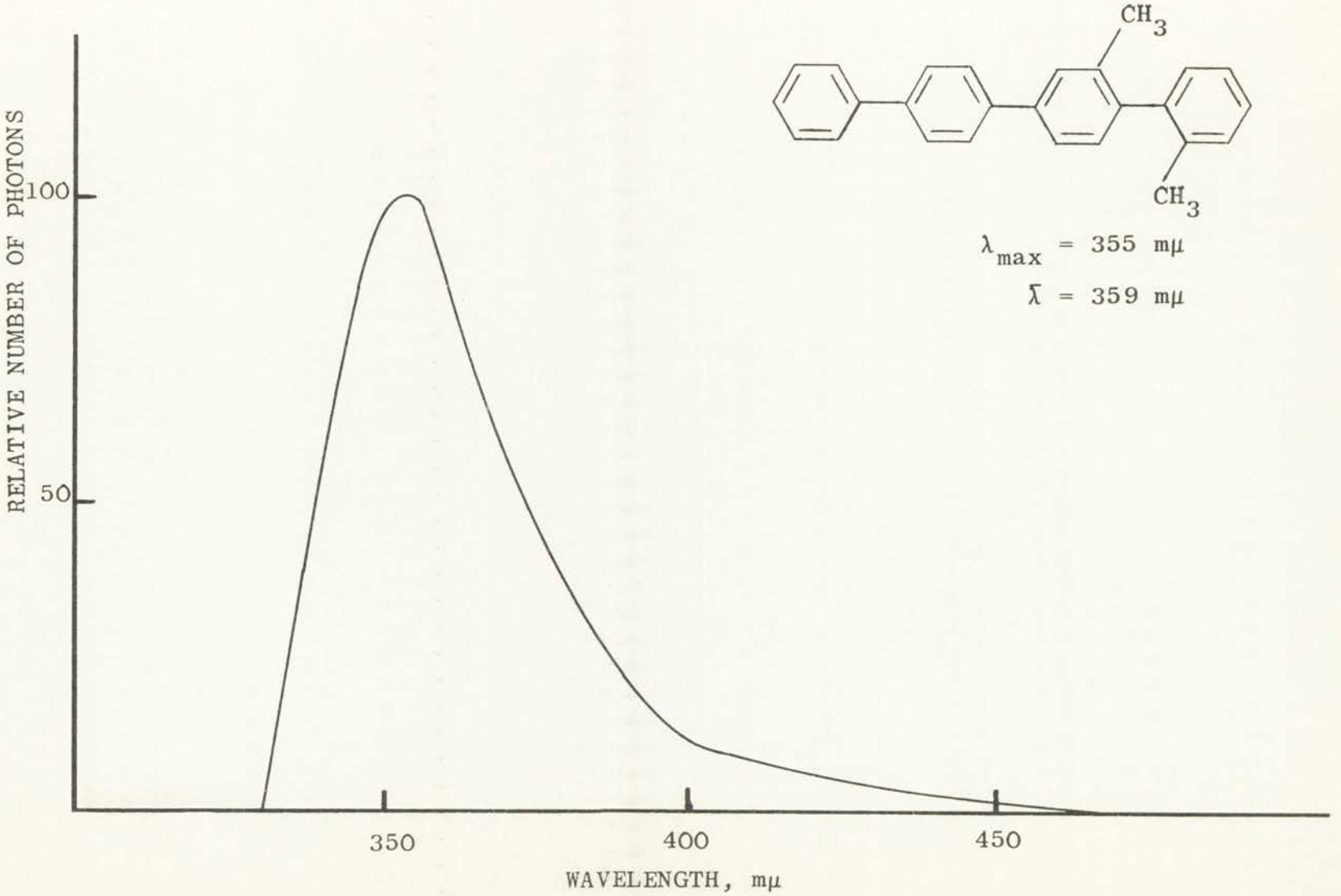
*The best RPH data obtained from various samples.

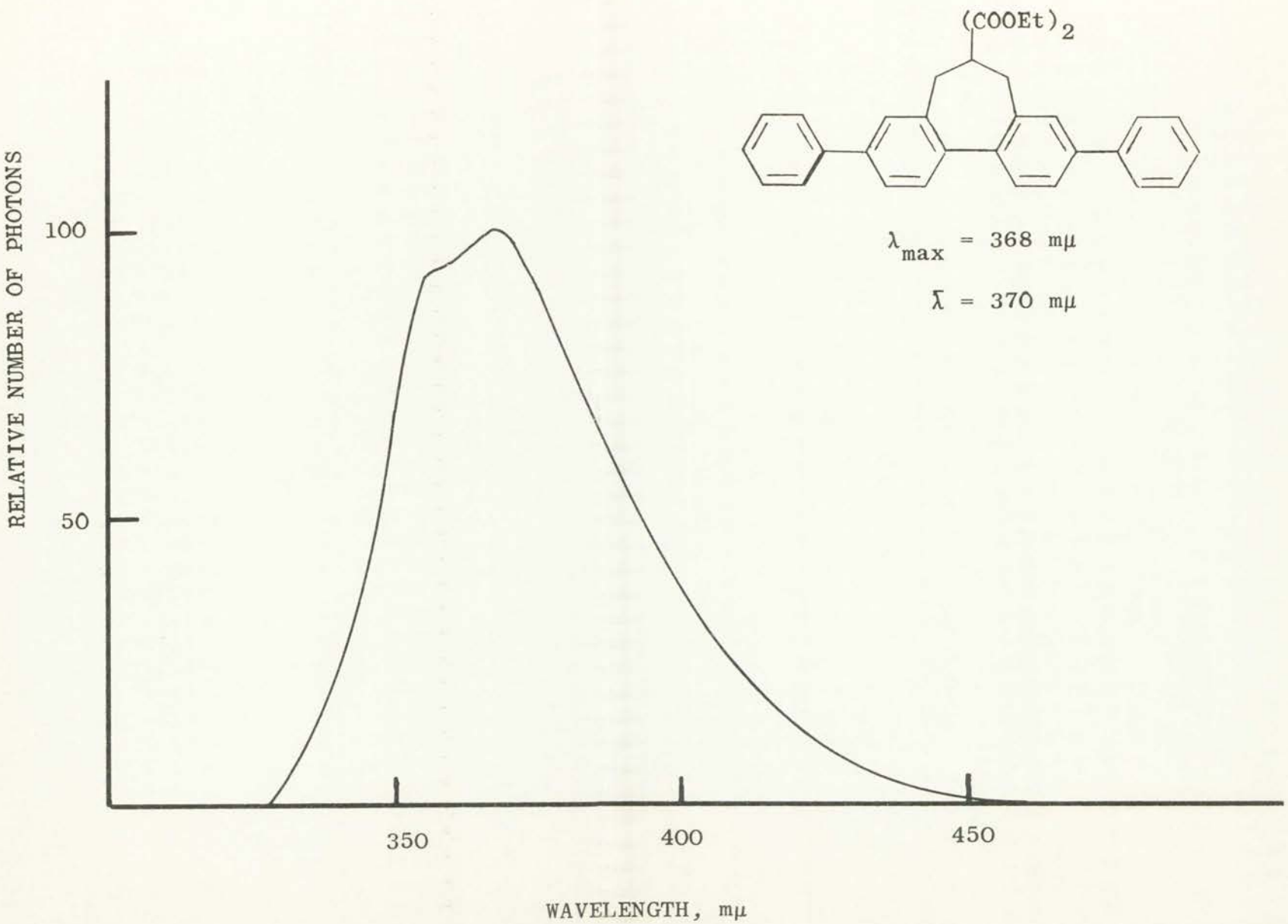
TABLE 13. 2,2'-DIMETHYL-p-QUATERPHENYL (34)

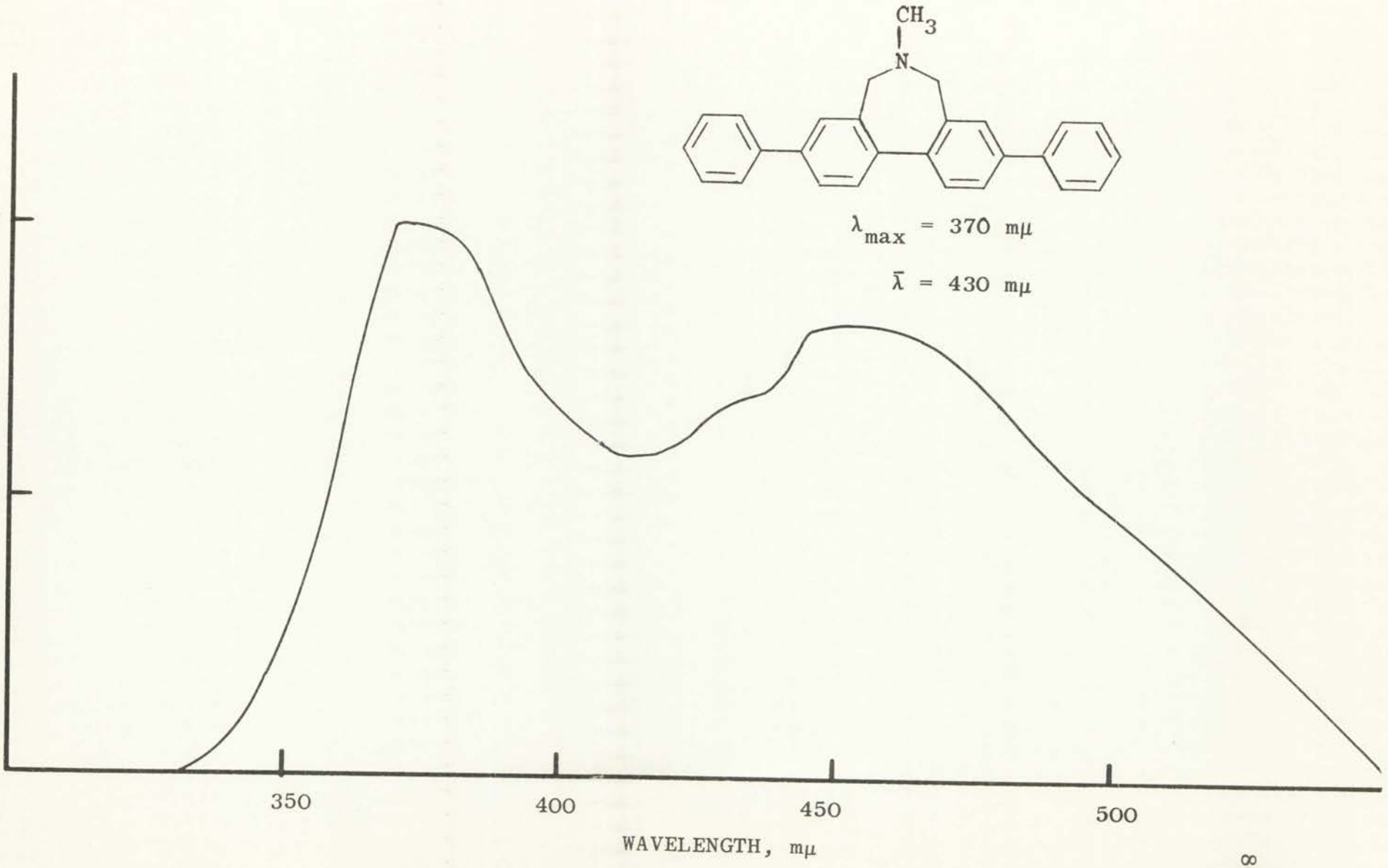
Concentration (g./l.)	Concentration (millimole/l.)	RPH
15.0	45.0	1.12
7.5	22.5	1.15
3.75	11.25	1.14
1.88	5.63	0.98
0.94	2.82	0.83

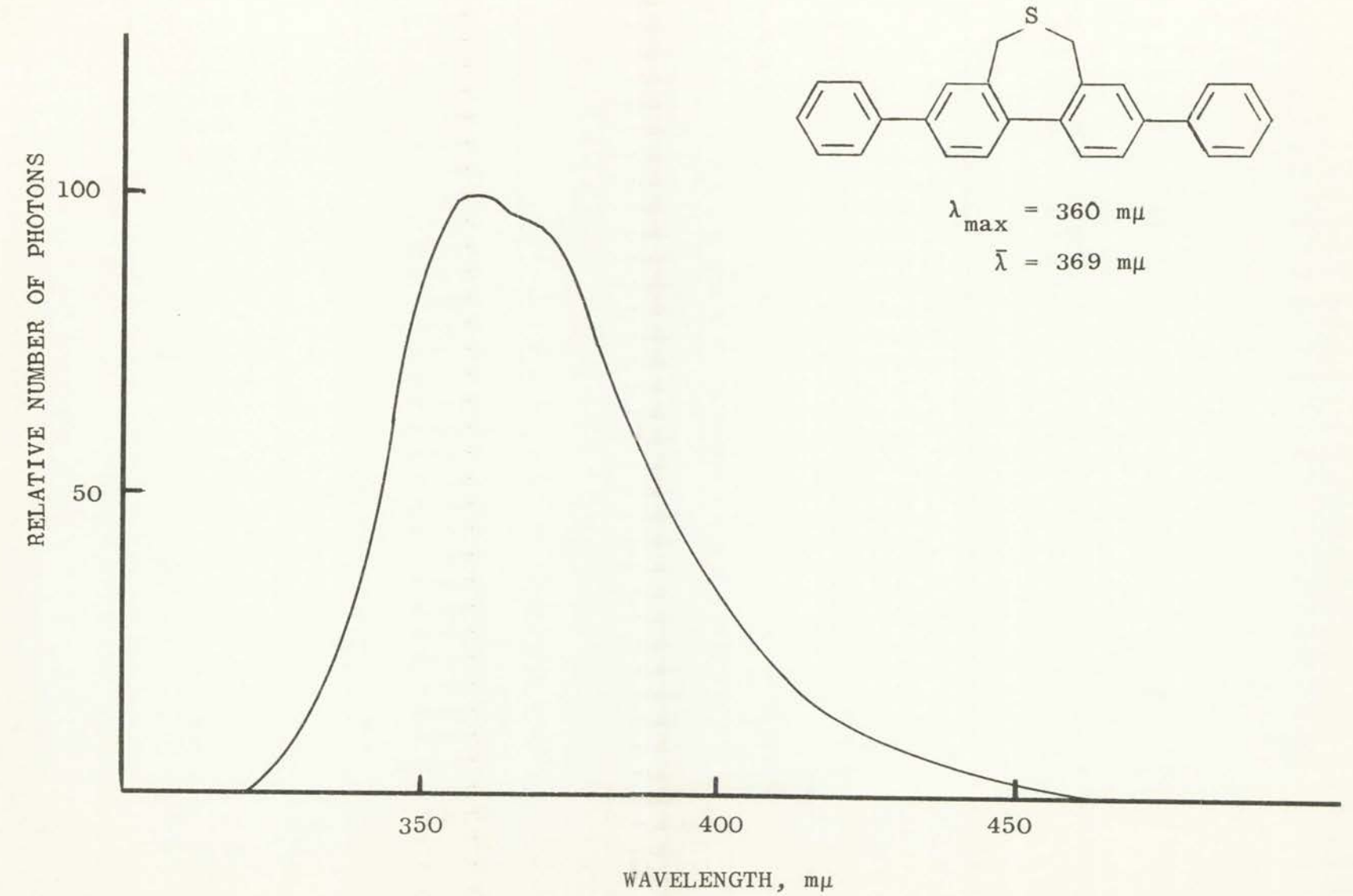
B. Figures 20 through 26. Corrected Fluorescence Spectra

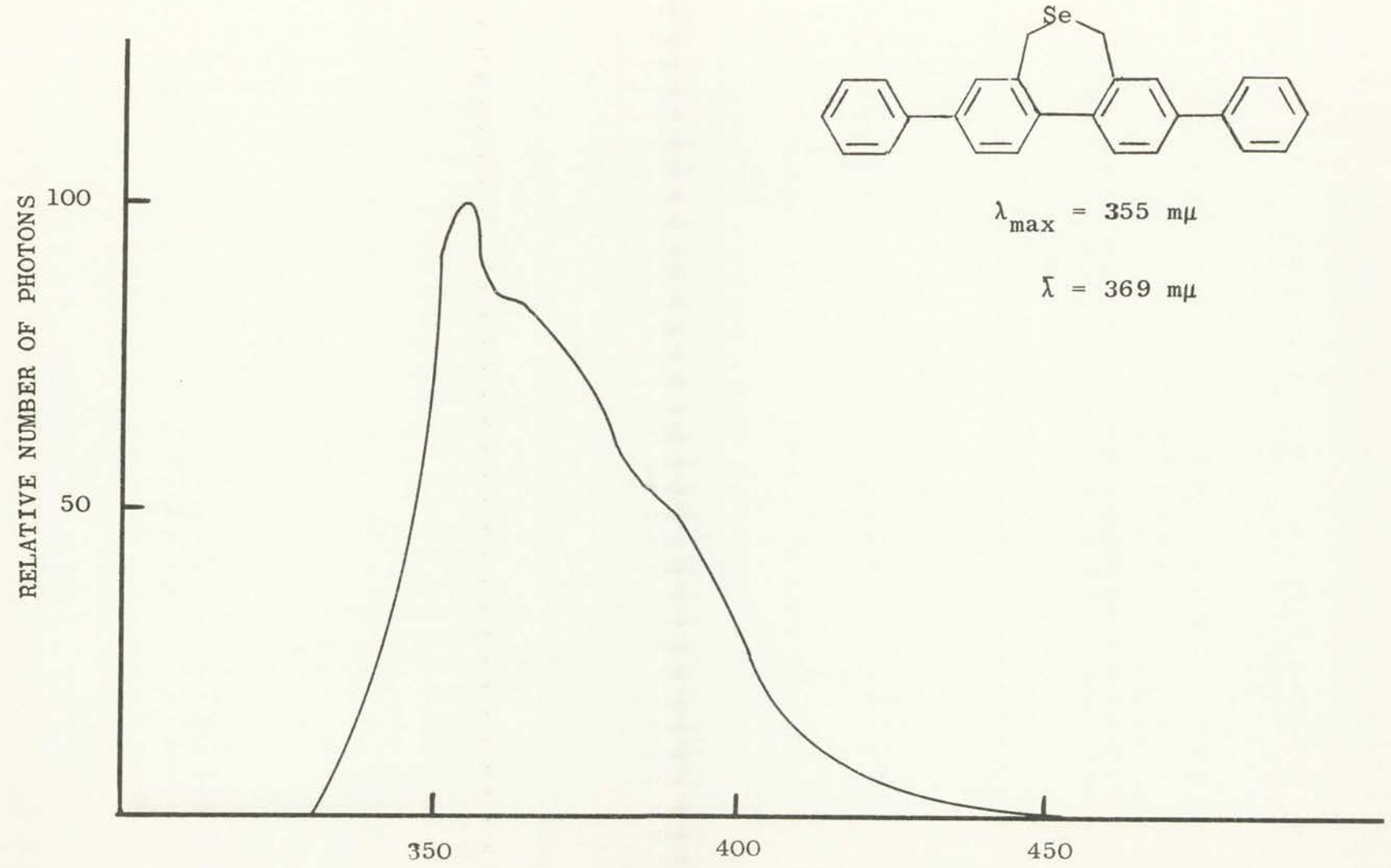

RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
WAVELENGTH, mμ
CH3
CH3
λmax = 345 mμ
λ̄ = 352 mμ

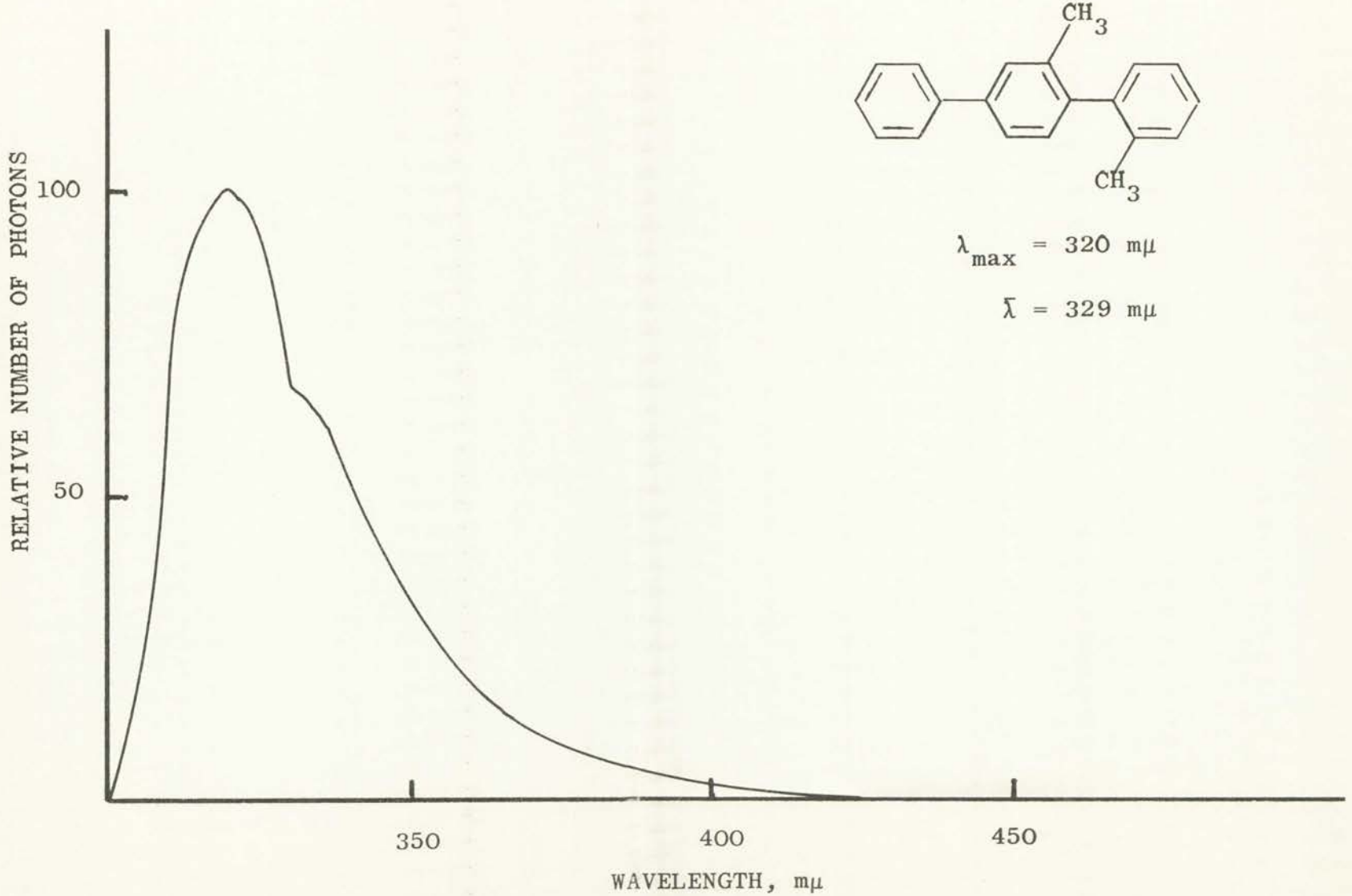

RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
WAVELENGTH, mμ
CH3
CH3
λmax = 355 mμ
λ̄ = 359 mμ


(COOEt)2
λmax = 368 mμ
λ̄ = 370 mμ
RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
WAVELENGTH, mμ


CH3
N
λmax = 370 mμ
λ̄ = 430 mμ
RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
500
WAVELENGTH, mμ


S
λ_{max} = 360 mμ
$\bar{\lambda}$ = 369 mμ
RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
WAVELENGTH, mμ

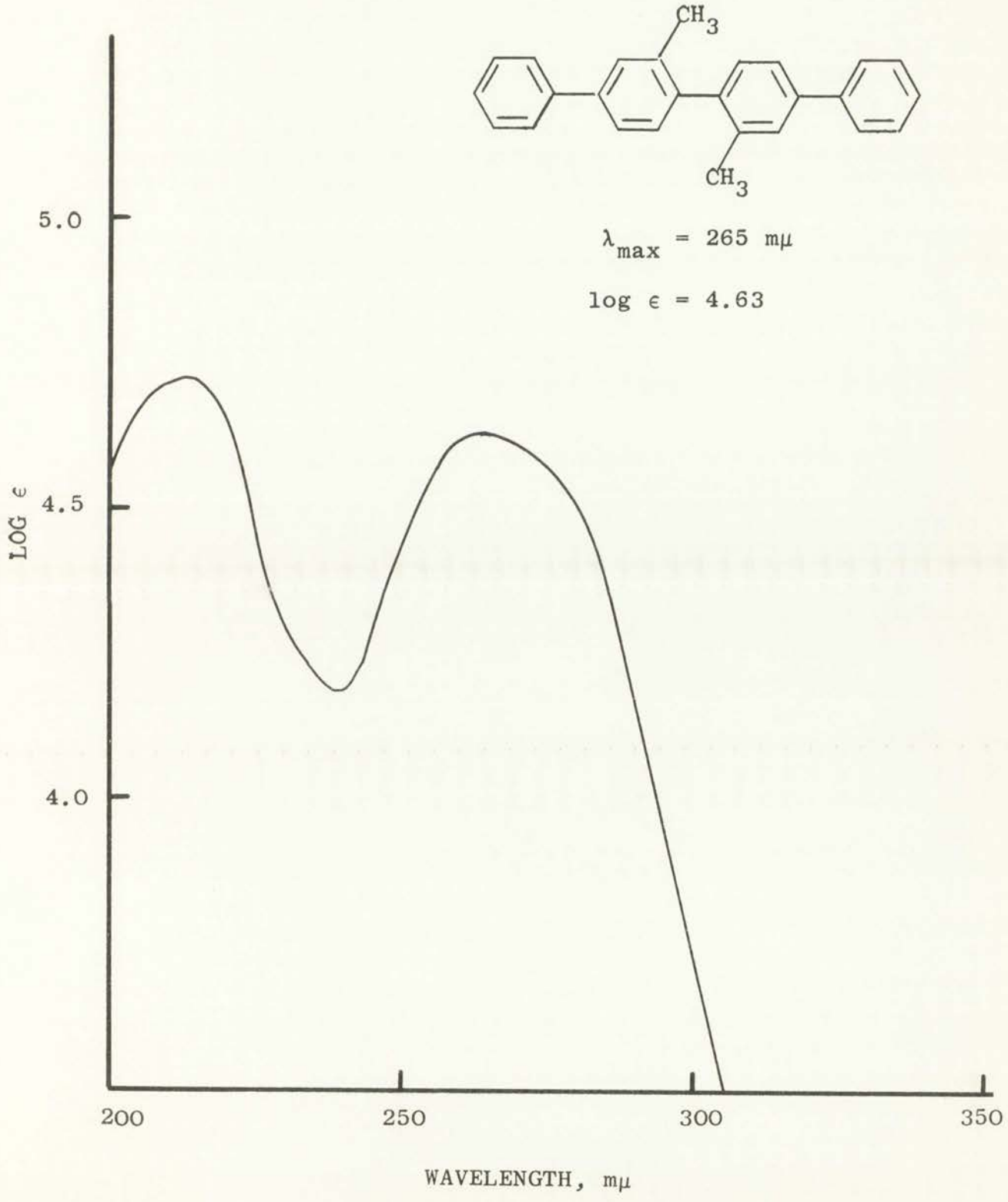

Se
λ_{max} = 355 mμ
$\bar{\lambda}$ = 369 mμ
RELATIVE NUMBER OF PHOTONS
100
50
350
400
450
WAVELENGTH, mμ

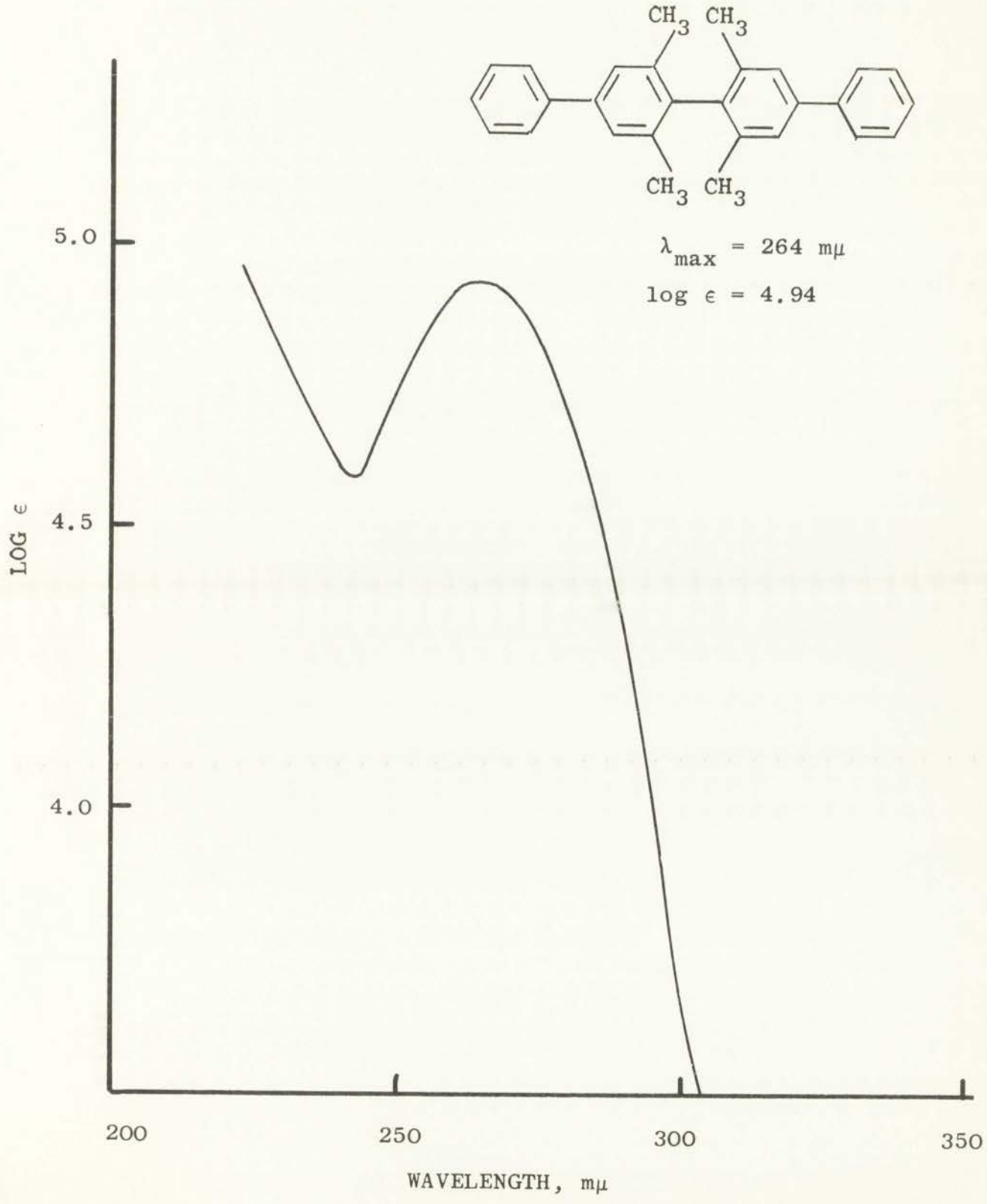


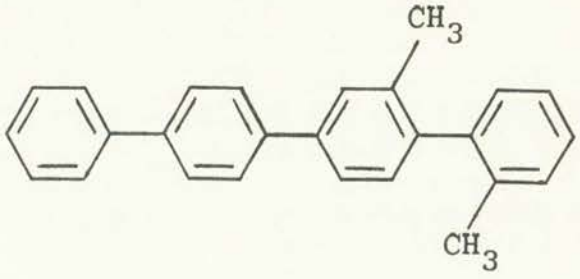
λ_{max} = 320 mμ

$\bar{\lambda}$ = 329 mμ

C. Figures 27 through 33. Ultraviolet Absorption Spectra

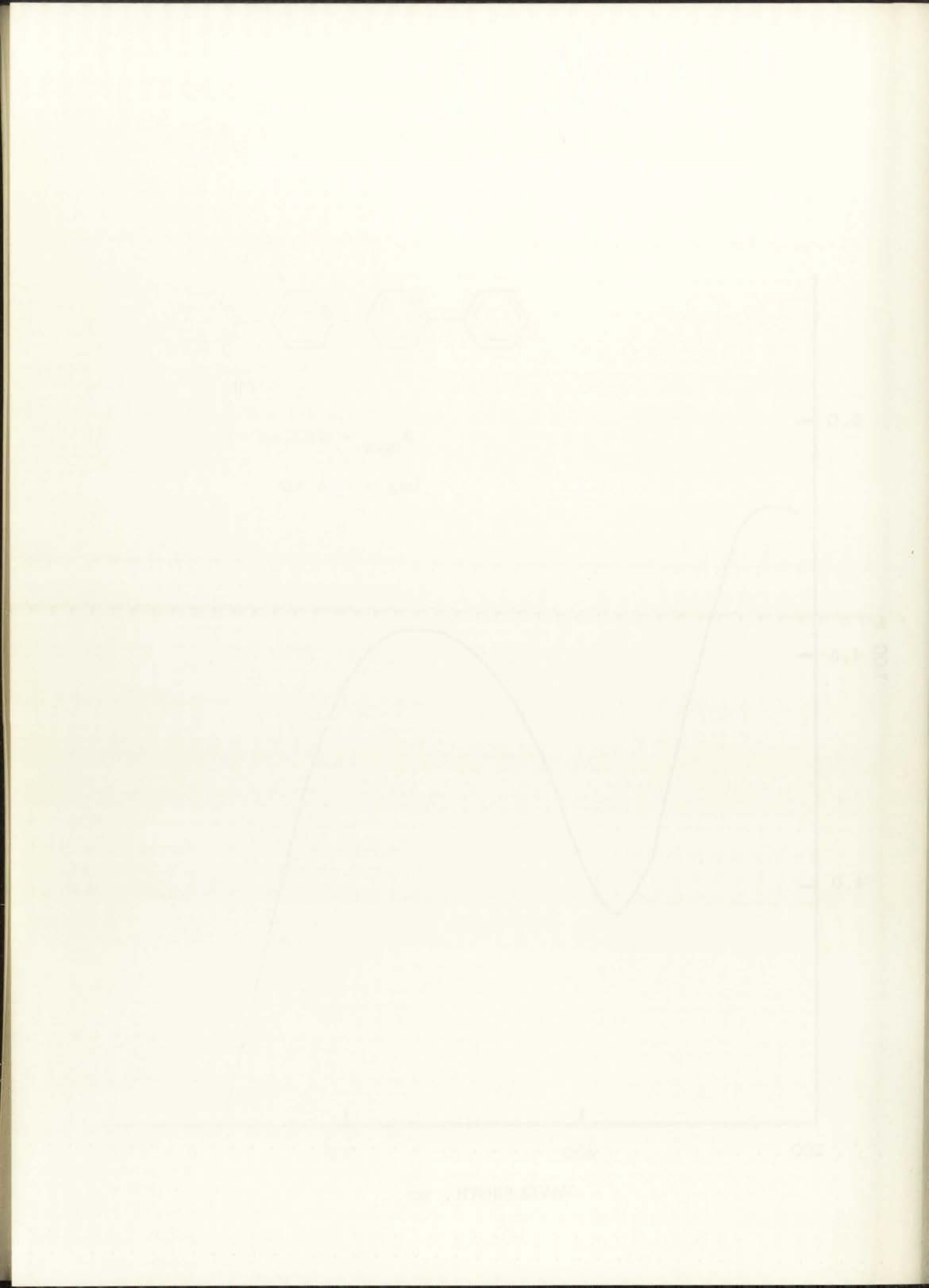

CH3
CH3
λmax = 265 mμ
log ε = 4.63
5.0
4.5
4.0
LOG ε
200
250
300
350
WAVELENGTH, mμ

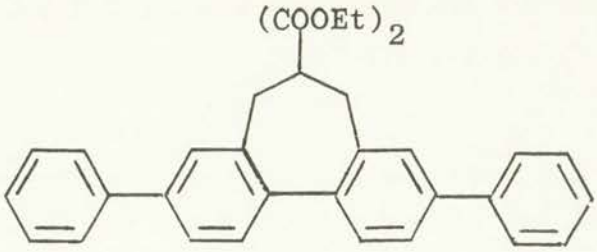

CH3 CH3
CH3 CH3
λmax = 264 mμ
log ε = 4.94
5.0
4.5
4.0
LOG ε
200
250
300
350
WAVELENGTH, mμ



λ_{max} = 285 mμ

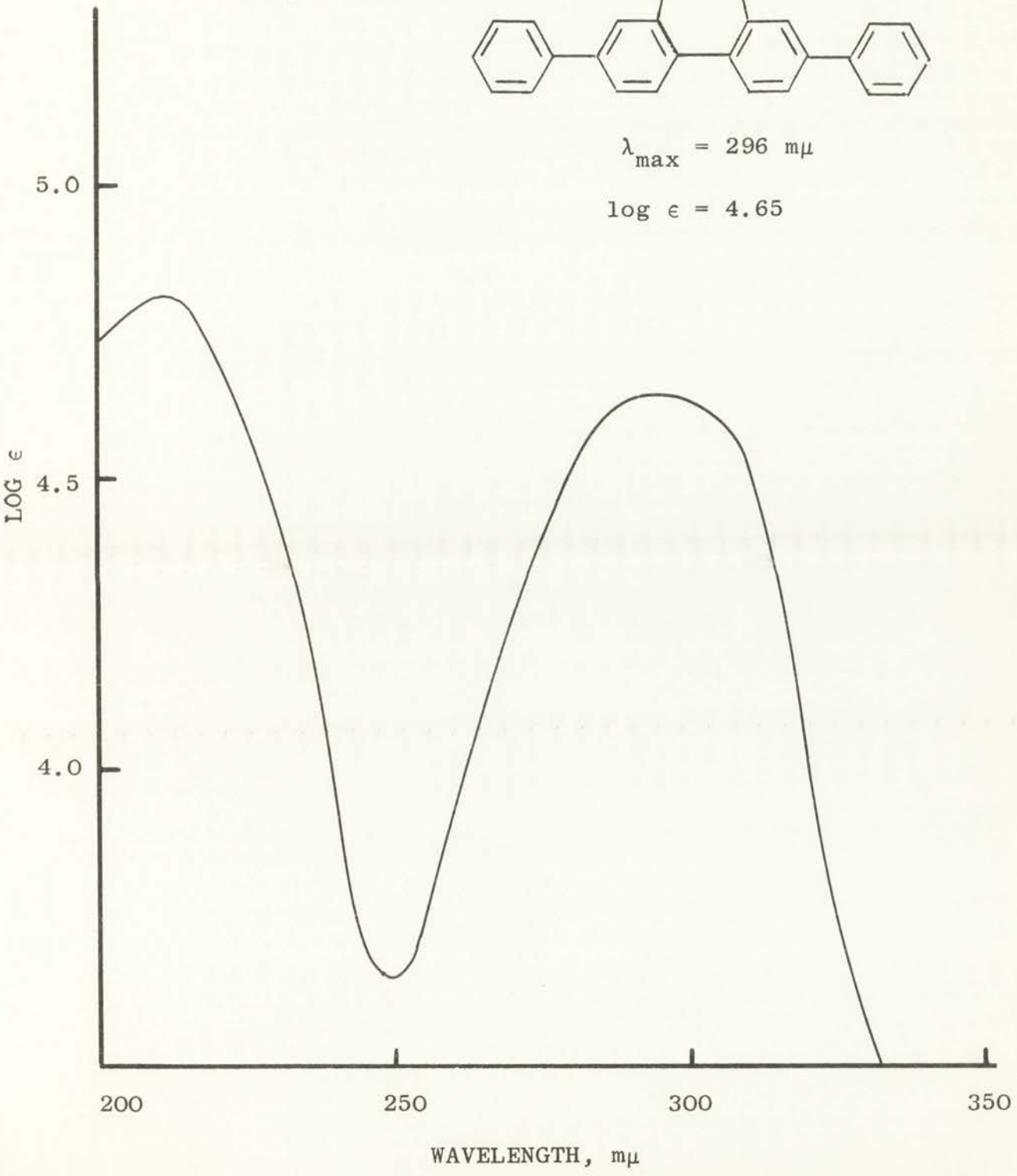
log ε = 4.56

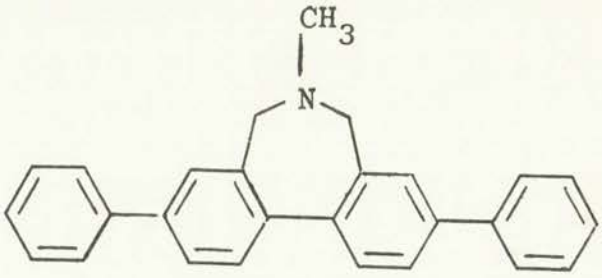




λ_{max} = 296 mμ

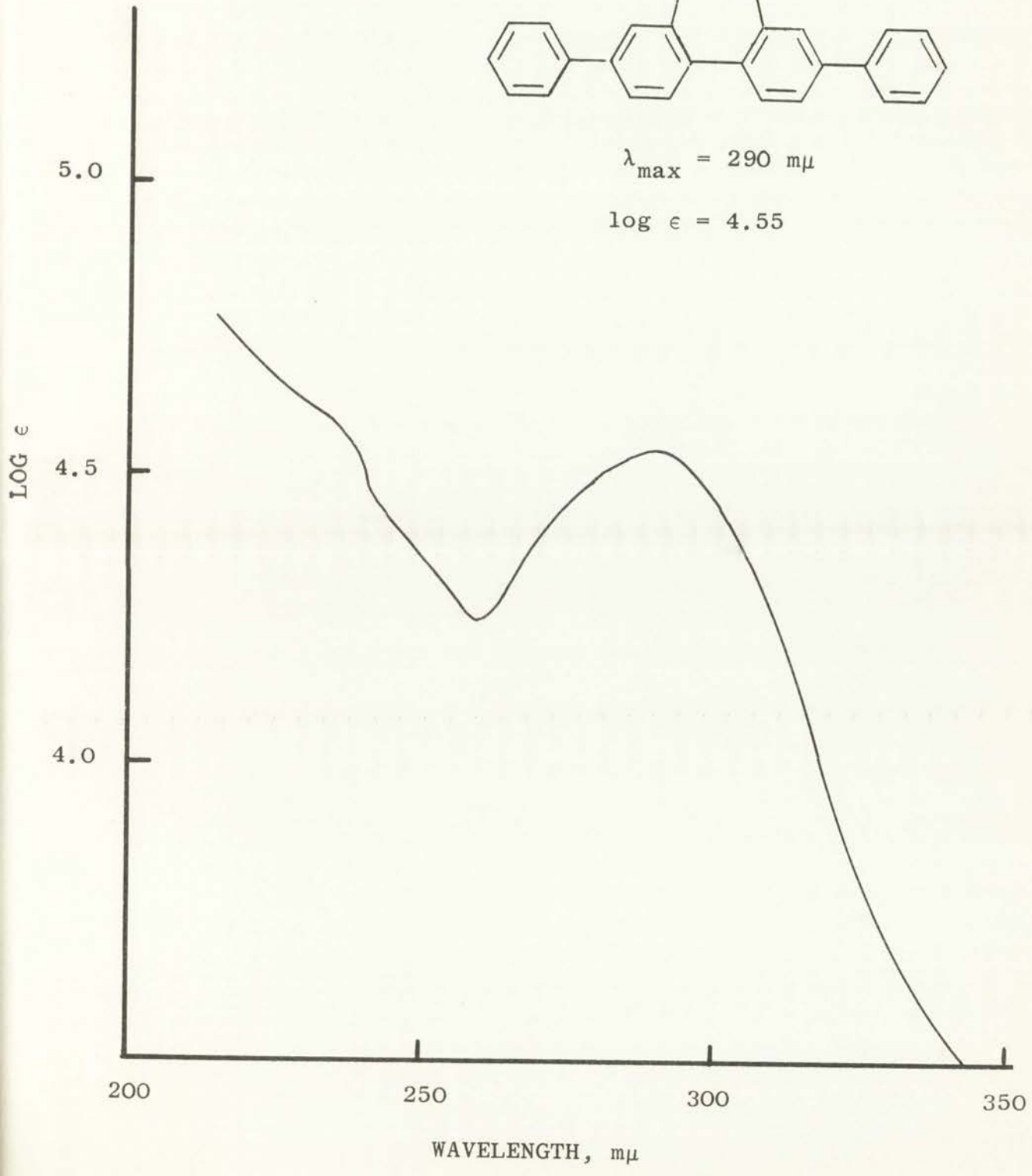
log ε = 4.65

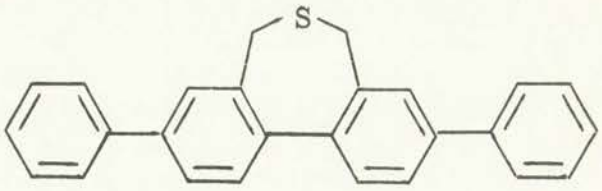




λ_{max} = 290 mμ

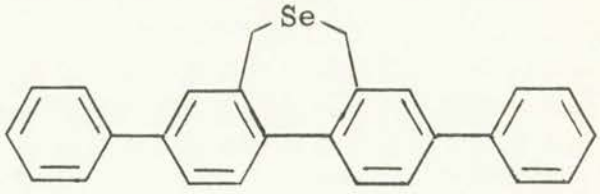
log ε = 4.55





λ_{max} = 286 mμ

log ε = 4.51



λ_{max} = 288 mμ

log ε = 4.55

D. Synthetic Experimental*

N-Chloro-o-acetotoluidide (21)--To a stirred solution of 183 g. (1.23 moles) of o-acetotoluidide (Eastman Kodak Co. 405) and 216 g. (2.16 moles) of potassium bicarbonate in 2 l. of ethanol and 8 l. of water cooled to 5° was added a solution of potassium hypochlorite prepared from 148.5 g. of "H. T. H.," 109 g. of potassium carbonate, and 29.1 g. of potassium hydroxide.[35] The temperature was not allowed to rise above 5° during the addition. After approximately three-fourths of the hypochlorite had been added, the mixture suddenly became milky in appearance. Stirring was continued for 1.0 hr. after addition was complete. The nearly colorless solid was filtered, washed with a small amount of ice-cold water, and dried overnight in a vacuum desiccator. The yield was 192 g. (85 per cent), m.p. 41 to 43°; reported[6] m.p. 44 to 45°. The material is sufficiently pure for the next step, and recrystallization is not recommended because of decomposition at elevated temperatures.

4-Acetamido-3-methylbiphenyl (22)--Treatment of 139 g. (0.757 mole) of N-chloro-o-acetotoluidide (21), m.p. 41 to

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*Melting points are uncorrected.

(35) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429.

43°, with anhydrous C.P. benzene and aluminum chloride in the manner described by M. Barnett[6] gave 92 g. (54 per cent) of tan 4-acetamido-3-methylbiphenyl (22), m.p. 165 to 167°; reported[6] m.p. 168 to 171°.

4-Amino-3-methylbiphenyl Hydrochloride (23)--One hundred and 50 g. (0.667 mole) of 4-acetamido-3-methylbiphenyl (22), m.p. 165 to 168°, and 3700 ml. of dilute (1:1) hydrochloric acid was refluxed with stirring for 24 hr., after which the mixture was cooled in ice, filtered, and washed with a small amount of ice-cold water. The solid hydrochloride was filtered and air-dried overnight to give 140 g. (96 per cent) of 4-amino-3-methylbiphenyl hydrochloride (23), m.p. 230 to 235°.

4-Iodo-3-methylbiphenyl (24)--A mixture of 290 g. (1.32 moles) of 4-amino-3-methylbiphenyl hydrochloride (23), 1550 ml. of water, and 580 ml. of concentrated hydrochloric acid was cooled to 0° and a solution of 91.8 g. (1.33 moles) of sodium nitrite in 625 ml. of water was added dropwise over a period of 1.0 hr. with the temperature being maintained at 0 to 2°. After stirring for 1.0 hr. at 0 to 2°, 3.0 g. of urea was added and stirring was continued for 15 min. The diazonium salt was decomposed by the dropwise addition of a solution of 766 g. (4.62 moles) of potassium iodide in 1 l.

of water. After stirring for 3.0 hr., the pasty mixture was warmed to expel nitrogen, and 25 g. of solid sodium bisulfite was added to reduce any free iodine. The mixture was extracted with benzene; the benzene layer was washed with 10 per cent sodium bisulfite and then with water. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed to afford 288 g. of a red oil. The product decomposed when distillation was attempted, but purification was accomplished by chromatographing a cyclohexane solution through an alumina column. Concentration of the eluates yielded 276 g. (71 per cent) of a pale yellow oil. A sample of the oil was crystallized from ethanol to give colorless crystals, m.p. 35 to 36.5°.

Anal. Calcd. for $C_{13}H_{11}I$: C, 53.08; H, 3.77. Found: C, 53.23; H, 3.76.

2'',3'-Dimethyl-p-quaterphenyl (14)--(a) Via the Ullmann Reaction. Seventy-seven g. (0.262 mole) of 4-iodo-3-methylbiphenyl (24) was warmed to 200° and three 5 g. portions of copper bronze (O. Hommel Co., Pittsburgh, Pa., 5347) were added with stirring. The temperature was slowly raised to 270° and then 85 g. of copper bronze was added over a period of 5.0 hr. The reaction mixture was allowed to cool and was extracted with large amounts of benzene. The benzene solution was filtered, the solvent removed, and the residue

dissolved in cyclohexane. The cyclohexane solution was chromatographed through an alumina column, the eluates were concentrated, and upon cooling 19.64 g. (45 per cent) of 2'',3'-dimethyl-p-quaterphenyl (14), m.p. 173 to 175°, was crystallized. Repeated crystallizations from cyclohexane gave colorless crystals, m.p. 176 to 176.5°; reported[28] m.p. 176°.

(b) Via the Grignard Reaction. About one-fourth of a solution of 71.0 g. (0.241 mole) of 3-methyl-4-iodobiphenyl (24) in 250 ml. of anhydrous ether was added to 32.0 g. (0.245 g.-atom) of magnesium turnings in 50 ml. of anhydrous ether under a stream of dry nitrogen. The reaction started immediately, and the remaining solution was added at such a rate as to maintain gentle refluxing. The reaction mixture was refluxed for 8.0 hr., at which time the magnesium had completely disappeared. A suspension of 31.4 g. (0.242 mole) of anhydrous cobaltous chloride in anhydrous ether was then added in portions over a period of 1.0 hr. The reaction mixture was refluxed for 3.0 hr., allowed to cool, and hydrolyzed with 10 per cent hydrochloric acid. The mixture was extracted with benzene, dried, and the solvent removed to yield a brown solid. Recrystallization of the residue from cyclohexane gave 12.26 g. (30 per cent) of 2'',3'-dimethyl-p-quaterphenyl (14), m.p. 173 to 175°; reported[28] m.p. 176°.

Maximum and log ϵ values for the ultraviolet absorption spectrum are: 265 mμ (4.63). The fluorescence spectrum of 14 was determined using an activating wavelength of 295 mμ and λ_{max} (fluorescence) was 345 mμ.

2'',3'-Bis(bromomethyl)-p-quaterphenyl (25)--The preparation of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25) was accomplished by the addition of 13.9 g. (0.0782 mole) of N-bromosuccinimide (Arapahoe Chemicals, Inc. 401) to 12.3 g. (0.0368 mole) of 2'',3'-dimethyl-p-quaterphenyl (14), m.p. 175 to 176°, and 0.13 g. of benzoyl peroxide dissolved in 250 ml. of anhydrous carbon tetrachloride. The mixture was gently refluxed with stirring for 1.0 hr. before the reaction began. After refluxing for 24 hr., the reaction mixture was allowed to cool, filtered, and the filtrate concentrated on a steam bath. The oily residue was crystallized from benzene to give 13.85 g. (83 per cent) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25) as a pale yellow solid, m.p. 164 to 167°. Repeated crystallizations from benzene gave colorless crystals, m.p. 172 to 173°; reported[7] m.p. 172 to 173°.

6-Methyl-3,9-diphenyl-5,7-dihydrodibenz[c,e]azepine (16)--A solution of 1.35 g. (0.003 mole) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25), m.p. 168 to 170°, in 40 ml. of anhydrous benzene was added dropwise to a stirred solution of 0.372 g. (0.012 mole) of methyl amine in 10 ml. of dry benzene. The

temperature was kept below 30° during the addition. Shortly after the beginning of the addition, methyl amine hydrobromide began to precipitate. Stirring was continued at 30° for 3.0 hr., and then the mixture was slowly warmed to 70° and kept at this temperature for 1.0 hr. The reaction mixture was then allowed to cool and stand overnight. The mixture was filtered, the precipitate washed with benzene, and the filtrate repeatedly extracted with water. The benzene layer was extracted with 10 per cent hydrochloric acid, and the acidic layers were made alkaline. The liberated base was extracted with ether and the solvent removed on a steam bath to yield 0.75 g. (69 per cent) of nearly colorless solid, m.p. 214 to 216°. Repeated crystallizations from benzene gave a colorless solid as an analytical sample, m.p. 215 to 216°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 290 mμ (4.55). The fluorescence spectrum of 16 was determined using an activating wavelength of 311 mμ and λ_{max} (fluorescence) was 370 mμ.

Anal. Calcd. for $C_{27}H_{23}N$: C, 89.71; H, 6.41. Found: C, 89.76; H, 6.27.

3,9-Diphenyl-5,7-dihydrodibenzo[c,e]thiepin (17)--A mixture of 75 ml. of methanol, 100 ml. of dioxane, 10 ml. of water, 1.67 g. (0.0037 mole) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25), m.p. 168-170°, and 2.76 g. (0.0115 mole)

of sodium sulfide nonahydrate was refluxed with vigorous stirring for 24 hr. The solvent was removed by distillation, the residue treated with ice-water, and the crude solid collected. The crude solid was crystallized from benzene to yield 0.7 g. (52 per cent) of 3,9-diphenyl-5,7-dihydrodibenzo[c,e]thiepin (17), m.p. 272 to 276°. Repeated crystallizations from ethanol gave an analytical sample, m.p. 273.5 to 274.5°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 286 mμ (4.51). The fluorescence spectrum of 17 was determined using an activating wavelength of 310 mμ and λ_{max} (fluorescence) was 360 mμ.

Anal. Calcd. for $C_{26}H_{20}S$: C, 85.68; H, 5.54. Found: C, 85.44; H, 5.61.

3,9-Diphenyl-5,7-dihydrodibenzo[c,e]selenepin (18)--A potassium selenide solution was prepared by passing hydrogen selenide gas* into a solution containing 0.88 g. of potassium hydroxide in 10 ml. of water until saturated. To this solution was then added an additional 0.88 g. of potassium hydroxide in 5 ml. of water. The resulting potassium selenide solution (ca. 15 ml., ca. 0.015 mole) was added to 300 ml. of

*Ferrous selenide (prepared by heating to redness an intimate mixture of equimolar quantities of powdered selenium and iron filings) was warmed with 25 per cent sulfuric acid, and the hydrogen selenide liberated was filtered through glass wool to remove entrained acid.

acetone and 1.75 g. (0.0038 mole) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25), and the resulting solution was refluxed with vigorous stirring for 24 hr., after which time about 275 ml. of the acetone was removed by distillation. About 100 g. of ice was added to the residue, and the precipitated solid was removed by filtration. The gummy precipitate was extracted with benzene, dried over magnesium sulfate, filtered, and the solution concentrated on a steam bath. Upon cooling, 0.81 g. (51 per cent) of 3,9-diphenyl-5,7-dihydrodibenzo[c,e]-selenepin (18), m.p. 267 to 268°, crystallized as a brown solid. An analytical sample purified by recrystallization from benzene was obtained as a colorless powder, m.p. 267 to 268°. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 288 mμ (4.55). The fluorescence spectrum of 18 was determined using an activating wavelength of 318 mμ and λ_{max} (fluorescence) was 355 mμ.

Anal. Calcd. for $C_{26}H_{20}Se$: C, 75.90; H, 4.90. Found: C, 75.70; H, 4.96.

2'',3'-Bis(cyanomethyl)-p-quaterphenyl (26)--A solution of 5.0 g. (0.011 mole) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25), m.p. 168 to 170°, and 2.7 g. (0.0414 mole) of potassium cyanide in 300 ml. of 70 per cent aqueous acetone was refluxed for 3.0 hr. About three-fourths of the solvent was removed by distillation, and the remaining mixture was

poured into water. The precipitate that formed was isolated by filtration and dried to give 3.16 g. of crude 2'',3'-bis(cyanomethyl)-p-quaterphenyl (26), m.p. 255 to 265°. Crystallization from benzene afforded 3.15 g. (75 per cent) of colorless solid, m.p. 265 to 269°. Repeated crystallization from benzene and ethyl acetate failed to improve the melting point. Other runs afforded products with melting points that ranged from 220° to 265°. It is believed that some cyclization to 5-cyano-6-imino-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (27) occurs during the course of the reaction. The product was not purified further and is sufficiently pure for the next step.

5-Cyano-6-imino-3,9-diphenyl-5,7-dihydrodibenzo[a,c]-cycloheptadiene (27)--A solution of 2.5 g. (0.00652 mole) of 2'',3'-bis(cyanomethyl)-p-quaterphenyl (26), m.p. 265 to 269°, and 0.026 mole of sodium ethoxide in 120 ml. of a 1:1 mixture of absolute ethanol and anhydrous dioxane was refluxed for 12 hr. The reaction mixture was allowed to cool and was then poured into water. The precipitate was collected and crystallized from benzene to afford 1.83 g. (73 per cent) of 5-cyano-6-imino-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (27), m.p. 200 to 205°. Repeated crystallizations from benzene afforded an analytical sample, m.p. 207 to 209°.

Anal. Calcd. for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24. Found: C, 87.25; H, 5.18.

6,6-Dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]-cycloheptadiene (20)--To a solution of disodium malonate prepared by the addition of 0.48 g. (0.003 mole) of diethyl malonate in 25 ml. of anhydrous ether to a sodium ethoxide solution [prepared by a reaction of 0.138 g. (0.006 g.-atom) of sodium with 10 ml. of absolute ethanol] was added 1.19 g. (0.00264 mole) of 2'',3'-bis(bromomethyl)-p-quaterphenyl (25), m.p. 167 to 169°, in 75 ml. of anhydrous dioxane. After refluxing for 6 hr., the reaction mixture was filtered, extracted with benzene, and the solvent removed on a steam bath to give a colorless solid residue. Crystallization from a 25:75 mixture of benzene-cyclohexane gave 1.07 g. (85 per cent) of 6,6-dicarbethoxy-3,9-diphenyl-5,7-dihydrodibenzo[a,c]cycloheptadiene (20), m.p. 185 to 190°. An analytical sample, m.p. 189 to 190°, was prepared by recrystallization from a 25:75 mixture of benzene and cyclohexane. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 296 mμ (4.65). The fluorescence spectrum of 20 was determined using an activating wavelength of 310 mμ and λ_{max} (fluorescence) was 368 mμ.

Anal. Calcd. for $C_{33}H_{30}O_4$: C, 80.79; H, 6.16. Found: C, 80.76; H, 6.26.

2,6-Dimethylacetanilide (29)--To a stirred solution of 100 g. (0.825 mole) of freshly distilled 2,6-dimethylaniline (Eastman Kodak Co. 1736), 690 ml. of concentrated hydrochloric acid, and 1.7 l. of water was added 97.5 ml. of acetic anhydride. As soon as the acetic anhydride went into solution, 101 g. (1.24 moles) of sodium acetate in 400 ml. of water was added. The reaction mixture was allowed to stir for 1.0 hr. and then was allowed to cool to 5° and filtered. The crude product was recrystallized from benzene to yield 117 g. (87 per cent) of 2,6-dimethylacetanilide (29), m.p. 179 to 180°; reported[36] m.p. 176°.

N-Chloro-2,6-dimethylacetanilide (30)--To a stirred solution of 49 g. (0.301 mole) of 2,6-dimethylacetanilide (29), m.p. 179 to 180°, and 50 g. (0.498 mole) of potassium bicarbonate in 9 l. of water cooled to 5° was added a solution of potassium hypochlorite prepared from 31.2 g. of "H. T. H.," 23.9 g. of potassium carbonate, and 6.82 g. of potassium hydroxide.[35] The temperature was not allowed to rise above 5° during the addition. After all of the hypochlorite had been added, the mixture suddenly became milky in appearance.

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(36) S. M. McElvain, "The Characterization of Organic Compounds," The MacMillan Company, New York, N. Y., 1956.

Stirring was continued for 1.0 hr. after addition was complete. The nearly colorless solid was filtered, washed with a small amount of ice-cold water, and dried overnight in a vacuum desiccator. The yield was 49 g. (82 per cent), m.p. 110 to 112°; reported[37] m.p. 112 to 113°.

4-Acetamido-3,5-dimethylbiphenyl (31)--To a stirred, cold solution of 91 g. (0.461 mole) of N-chloro-2,6-dimethylacetanilide (30), m.p. 110 to 112°, in 1870 ml. of anhydrous C.P. benzene was added, in portions, 186 g. (1.39 moles) of anhydrous aluminum chloride. After stirring for 5 hr. at 7°, the reaction mixture was poured over ice. The benzene was removed by steam distillation and the resulting slurry filtered. Crystallization of the brown solid from ethanol (Norit) gave 50.5 g. (46 per cent) of 4-acetamido-3,5-dimethyldiphenyl (31) as a colorless solid, m.p. 203 to 204°; reported[38] m.p. 203 to 204°.

4-Amino-3,5-dimethylbiphenyl (32)--To 55 g. (0.230 mole) of 4-acetamido-3,5-dimethylbiphenyl (31), m.p. 200 to 202°, was added 150 ml. of 100 per cent phosphoric acid prepared

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(37) M. J. S. Dewar and J. M. W. Scott, J. Chem. Soc., 1845 (1955).

(38) D. H. Hey and E. R. Buckley Jackson, J. Chem. Soc., 645 (1934).

from 86 g. of phosphorus pentoxide and 200 g. of 85 per cent phosphoric acid.[25] The reaction mixture was stirred for 2.0 hr. at 200°, allowed to cool, neutralized with potassium hydroxide, extracted with benzene, and dried over magnesium sulfate. The solvent was removed on a steam bath to yield a brown oily residue which was dissolved in cyclohexane and the solution was chromatographed through an alumina column. Concentration of the eluates afforded 33 g. (72 per cent) of pale yellow oil; reported as a brown oil.[38] The product was sufficiently pure for the next step.

4-Iodo-3,5-dimethylbiphenyl (33)--A hot solution of 33 g. (0.168 mole) of 4-amino-3,5-dimethylbiphenyl (32) in 34.2 g. (0.349 mole) of sulfuric acid and 450 ml. of water was rapidly cooled to 0°, and a solution of 11.56 g. (0.169 mole) of sodium nitrite in 50 ml. of water was added over a period of 45 min. After stirring for 15 min., 2.0 g. of urea was added, and a solution of 74.6 g. (0.450 mole) of potassium iodide in 150 ml. of water was added dropwise over a period of 30 min. After stirring for 4.0 hr., the reaction mixture was warmed on a steam bath until the evolution of gases ceased. The reaction mixture was treated with sodium bisulfite, extracted with benzene, and the organic layer dried over magnesium sulfate. The benzene solution was chromatographed through an alumina column and the eluates

concentrated to afford a red oil. The viscous oil was distilled to give a colorless solid, b.p. 150 to 155° at 0.1 mm. Recrystallization from ethanol (Norit) gave 24.7 g. (45 per cent) of 4-iodo-3,5-dimethylbiphenyl (33) as colorless needles, m.p. 69 to 70°. Repeated crystallizations from ethanol gave an analytical sample, m.p. 69.5 to 70.5°.

Anal. Calcd. for $C_{14}H_{13}I$: C, 54.62; H, 4.25. Found: C, 54.55; H, 4.17.

2'',3',5',6''-Tetramethyl-p-quaterphenyl (15)--About one-fourth of a solution of 5.0 g. (0.016 mole) of 4-iodo-3,5-dimethylbiphenyl (33), m.p. 69 to 70°, in 25 ml. of anhydrous ether was added to 0.4 g. (0.0165 g.-atom) of magnesium turnings in 15 ml. of anhydrous ether under a stream of dry, oxygen-free nitrogen. The reaction started immediately upon warming, and the remaining solution was added rapidly enough to maintain gentle refluxing. After the addition was completed, the reaction mixture was refluxed for 4 hr., during which time the magnesium had completely reacted. A suspension of 2.3 g. (0.0175 mole) of anhydrous cobaltous chloride in anhydrous ether was then added in portions over a period of 15 min. The reaction mixture was then refluxed for 3 hr., allowed to cool, and hydrolyzed with 5 per cent hydrochloric acid. The mixture was extracted with benzene, dried over magnesium sulfate, filtered, and the solvent removed

on a steam bath to afford a brown solid residue. Recrystallization of the residue from ethanol (Norit) gave 0.61 g. (21 per cent) of 2'',3',5',6''-tetramethyl-p-quaterphenyl (15) as colorless needles, m.p. 175 to 176°. An analytical sample, m.p. 175.5 to 176°, was obtained by repeated crystallization from ethanol. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 264 mμ (4.94). The fluorescence spectrum of 15 was obtained using an activating wavelength of 280 mμ and λ_{max} (fluorescence) was 325 mμ.

Anal. Calcd. for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.87; H, 7.44.

3-Methyl-p-terphenyl (37)--The dehydration and dehydrogenation of 7.0 g. (0.0262 mole) of 1-(4-biphenylyl)-3-methylcyclohexanol (36)[26] were accomplished by heating an intimate mixture of the alcohol 36 and 0.7 g. of 10 per cent palladium on charcoal at 350° for 2.0 hr. The reaction mixture was extracted with benzene, filtered, and the benzene solution chromatographed through alumina. Concentration of the eluates afforded a dark brown residue. Recrystallization from ethanol (Norit) afforded 4.8 g. (75 per cent) of 3-methyl-p-terphenyl (37), m.p. 123 to 124°; reported[39] m.p. 125.5 to 126°.

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(39) H. Gilman and E. A. Weipert, J. Org. Chem., 22, 446 (1957).

4-Iodo-3-methyl-p-terphenyl (38)--A mixture of 1.65 g. (0.00676 mole) of 3-methyl-p-terphenyl (37), m.p. 123 to 124°, and 12 ml. of glacial acetic acid was warmed to 85°. Water was added dropwise with vigorous stirring until the solution became turbid. Five drops of concentrated sulfuric acid was then added, followed by the addition of 0.69 g. (0.00545 mole) of iodine, 0.27 g. (0.00158 mole) of iodic acid, and 0.6 ml. of carbon tetrachloride. The resultant solution was dark red in color, and stirring was continued until the solution became lighter in color and a solid precipitated. The reaction mixture was filtered, and the precipitate was dissolved in benzene. The benzene solution was washed with a 10 per cent solution of sodium bisulfite and then with water. The organic layer was dried over magnesium sulfate, filtered, and concentrated on a steam bath. Upon cooling, there was obtained 1.45 g. (58 per cent) of 4-iodo-3-methyl-p-terphenyl (38), m.p. 168 to 170°. An analytical sample, m.p. 170.2 to 170.8°, was prepared by repeated crystallization from cyclohexane.

Anal. Calcd. for $C_{19}H_{16}I$: C, 61.47; H, 4.34. Found: C, 61.73; H, 4.21.

2-Iodotoluene (39)--A mixture of 25 g. (0.234 mole) of o-toluidine, 250 ml. of water, and 90 ml. of concentrated hydrochloric acid was cooled to 0° and was diazotized by the

dropwise addition of 16.1 g. (0.234 mole) of sodium nitrite in 75 ml. of water. After stirring at 0° for 1.0 hr., a small amount of urea was added. The diazonium salt was decomposed by the dropwise addition of 116 g. (0.70 mole) of potassium iodide in 150 ml. of water. After stirring for 3.0 hr., the reaction mixture was warmed and the free iodine reduced by the addition of a 10 per cent solution of sodium bisulfite. The mixture was extracted with benzene, washed with dilute sodium hydroxide, followed by water, and the organic layer dried over potassium carbonate overnight. The solvent was removed on a steam bath, and the red oily residue was distilled to give 32 g. (63 per cent) of 2-iodotoluene (39) as a pale yellow oil, b.p. 95 to 98° at 20 mm.

2,2'-Dimethyl-p-quaterphenyl (34)--(a) Via the Mixed Ullmann Reaction. To a stirred mixture of 0.80 g. (0.00216 mole) of 4-iodo-3-methyl-p-terphenyl (38), m.p. 168 to 170°, and 1.41 g. (0.00649 mole) of 2-iodotoluene (3) was added 2.5 g. of activated copper bronze over a period of 1 hr. with the temperature being maintained at 220 to 230°. The reaction mixture was cooled and extracted with hot benzene. The benzene solution was filtered, the solvent removed on a steam bath, and the residue dissolved in cyclohexane. The cyclohexane solution was chromatographed through an alumina column. Concentration of the eluates afforded a colorless

solid and a colorless oil. The solid was evaporatively distilled at 150 to 160° at 0.05 mm., and crystallization from ethanol gave 108 mg. (15 per cent) of 2,2'-dimethyl-p-quaterphenyl (34), m.p. 162 to 164°. An analytical sample, m.p. 165.5 to 166.5°, was prepared by recrystallization from ethanol. Maximum and log ϵ values for the ultraviolet absorption spectrum are: 285 mμ (4.56). The fluorescence spectrum of 34 was obtained using an activating wavelength of 315 mμ and λ_{max} (fluorescence) was 355 mμ.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.49; H, 6.79.

(b) Dehydrogenation of 1-(2,2'-dimethyl-4-biphenylyl)-4-phenylcyclohexene (49). The dehydrogenation of 5.3 g. (0.0157 mole) of 1-(2,2'-dimethyl-4-biphenylyl)-4-phenylcyclohexene (49) (p. 119), m.p. 77 to 78°, was accomplished by heating an intimate mixture of 49 and 0.6 g. of 10 per cent palladium on charcoal at 380 to 400° for 6 hr. The reaction mixture was extracted with benzene, filtered, and the solvent removed on a steam bath. The colorless residue was recrystallized from cyclohexane to give 5.0 g. (95 per cent) of 2,2'-dimethyl-p-quaterphenyl (34), m.p. 162 to 164°. A mixed melting point with a sample prepared by the mixed Ullmann reaction melted at 163 to 165°.

4-Acetamido-4'-amino-2,2'-dimethylbiphenyl (43)--An ether solution of 4,4'-diamino-2,2'-dimethylbiphenyl (*m*-tolidine) was prepared by shaking 25.6 g. (0.09 mole) of the dihydrochloride 41,[22] 200 ml. of ether, and 45 ml. of 6 *N* sodium hydroxide in a separatory funnel until all solid material had dissolved. The layers were separated and the ether solution dried over anhydrous potassium carbonate. The ether solution thus prepared was placed in a 500-ml., three-necked, round-bottomed flask, and to the stirred solution was added dropwise a solution of 9.2 g. (0.09 mole) of acetic anhydride in 10 ml. of anhydrous ether. After approximately one-fourth of the anhydride had been added, the addition was stopped and the inside of the flask was scratched with a glass rod to induce crystallization of the monoamide 43. After the solution became cloudy with the separation of 43, the addition was resumed. The reaction mixture was stirred for an additional 2 hr., the crystalline product was collected by filtration, and the solid was washed with ether. The product was dried at room temperature under reduced pressure and amounted to 20.7 g. (90.5 per cent yield). The crude 4-acetamido-4'-amino-2,2'-dimethylbiphenyl (43) thus prepared contained some of the diamide; however, this did not interfere with the next step, and the crude monoamide was not purified further.

In a larger run, 285 g. of the dihydrochloride afforded 210 g. (83 per cent yield) of crude monoamide 43.

4-Acetamido-2,2'-dimethylbiphenyl (44)--To a cooled (0 to 5°) slurry of 5.08 g. (0.02 mole) of crude 4-acetamido-4'-amino-2,2'-dimethylbiphenyl (43) in 20 ml. of water and 5.2 ml. (0.06 mole) of concentrated hydrochloric acid was added slowly with stirring a solution of 1.38 g. (0.02 mole) of sodium nitrite in 5 ml. of water. After the addition of the sodium nitrite, the yellow diazonium salt solution was filtered to remove the insoluble diamide which contaminated the crude 43 used. To the filtered diazonium salt solution at 0° was added a small amount of sulfamic acid, and after the excess nitrous acid was thus destroyed, 31 ml. (0.3 mole) of 50 per cent hypophosphorous acid was added slowly. The reaction mixture was placed in a refrigerator at 0 to 5° for 2 days, after which time the precipitated solid was filtered. The gummy solid thus obtained was extracted with boiling cyclohexane, the hot cyclohexane solution was filtered, and was allowed to crystallize. There was thus obtained 1.87 g. (39 per cent yield) of almost colorless 4-acetamido-2,2'-dimethylbiphenyl (44), m.p. 96 to 98°, reported[28] m.p. 101 to 102°.

In a larger run, 210 g. of the monoamide 43 afforded 90 g. (45.5 per cent yield) of the amide 44, m.p. 96 to 98°.

4-Amino-2,2'-dimethylbiphenyl Hydrochloride (45)--The hydrolysis of 80 g. (0.335 mole) of 4-acetamido-2,2'-dimethylbiphenyl (44), m.p. 96 to 98°, was accomplished by refluxing in 1750 ml. of 20 per cent hydrochloric acid for 24 hr. The reaction mixture was cooled to 5°, filtered, and the precipitate air-dried to give 69 g. (88 per cent) of 4-amino-2,2'-dimethylbiphenyl hydrochloride (45), m.p. 225 to 234°.

4-Iodo-2,2'-dimethylbiphenyl (46)--A mixture of 77.0 g. (0.329 mole) of 4-amino-2,2'-dimethylbiphenyl hydrochloride (45), 425 ml. of water, and 150 ml. of concentrated hydrochloric acid was cooled to 0°, and a solution of 23.45 g. (0.340 mole) of sodium nitrite in 150 ml. of water was added dropwise over a period of 1.0 hr. with the temperature being maintained at 0 to 3°. After stirring for 30 min. at 0°, 2.0 g. of sulfamic acid was added. The diazonium salt was decomposed by the dropwise addition of 198 g. (1.19 moles) of potassium iodide in 250 ml. of water. After stirring for 1.0 hr. at 0°, the pasty mixture was warmed to expel nitrogen, and a small amount of solid sodium bisulfite was added to reduce traces of iodine. The mixture was extracted with cyclohexane, and the cyclohexane solution was washed with a 10 per cent solution of sodium bisulfite and then with water. The organic layer was dried over magnesium

sulfate, filtered, and chromatographed through an alumina column. The eluates were concentrated on a steam bath to yield a light red oil. Distillation of the oil gave 70.1 g. (69 per cent) of 4-iodo-2,2'-dimethylbiphenyl (46) as a colorless oil, b.p. 107 to 110° at 0.01 mm; reported[28] b.p. 105 to 107° at 0.05 mm.

4-Phenylcyclohexanone (47)--To a cold (0 to 5°) solution of 10.56 g. (0.06 mole) of trans-4-phenylcyclohexanol, m.p. 120 to 121°,[29] in 160 ml. of C.P. acetone and 40 ml. of water was added 16.56 g. (0.12 mole) of N-bromoacetamide (Arapahoe Chemicals, Inc., Cat. No. 390) in three portions over a period of 1.0 hr. The homogeneous solution was allowed to stand in an ice-bath for an additional 2.0 hr. and then at room temperature for 1.0 hr. The reaction mixture was poured into 600 ml. of water containing 20 g. of sodium sulfite. The colorless solid that precipitated was removed on a filter and dried to give 9.73 g. of 4-phenylcyclohexanone (47), m.p. 75 to 78°. Recrystallization from cyclohexane gave 8.45 g. (81 per cent) of 47, m.p. 78 to 79°; reported[40] m.p. 77 to 78°.

1-(2,2'-Dimethyl-4-biphenylyl)-4-phenylcyclohexene (49)--Approximately one-fourth of a solution of 43.4 g. (0.141 mole)

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(40) Herbert E. Ungnade, J. Org. Chem., 13, 361 (1948).

of 4-iodo-2,2'-dimethylbiphenyl (46) in 250 ml. of anhydrous ether was added to 1.96 g. (0.282 mole) of cut lithium wire in 100 ml. of dry ether under a stream of dry nitrogen. The reaction started immediately upon warming, and the remaining ether solution of 46 was added over a period of 1.0 hr. After refluxing for an additional 6.0 hr., the reaction was complete. The solution was cooled to 5°, and 24.5 g. (0.141 mole) of 4-phenylcyclohexanone (47), m.p. 78 to 79°, in 300 ml. of anhydrous ether was added dropwise over a period of 1.0 hr. The reaction mixture was allowed to stir for 1.0 hr. at 5° and then for 1.0 hr. under gentle refluxing. The mixture was poured over a mixture of 10 per cent sulfuric acid and ice and extracted with ether. The ether layer was dried, filtered, and the solvent removed to afford an oily residue. The oil and 90 ml. of 98 per cent formic acid were heated on a steam bath with occasional shaking for 30 min., after which time the formic acid was removed under reduced pressure. The residue was taken up in benzene, washed with water and 5 per cent sodium carbonate solution, and dried over magnesium sulfate. The solvent was removed on a steam bath to afford nearly colorless oil. Crystallization of the oil from ethyl acetate afforded 17.6 g. (37 per cent) of 1-(2,2'-dimethyl-4-biphenylyl)-4-phenylcyclohexene (49), m.p. 76 to 78° as a colorless solid. An analytical

sample, m.p. 78 to 79°, was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.74.

1-(3-Methyl-4-biphenylyl)-2-methylcyclohexanol (51)--A small amount of a solution of 10.6 g. (0.036 mole) of 4-iodo-3-methylbiphenyl (24), m.p. 32.5 to 33.5°, in 40 ml. of dry ether was added to 0.552 g. (0.0796 mole) of cut lithium wire in 30 ml. of dry ether under a stream of dry nitrogen. The reaction started upon warming, and the remaining solution of 24 was added over a period of 15 min. After refluxing for 4.5 hr., the reaction was complete, and after cooling to 5°, 4.07 g. (0.36 mole) of o-methylcyclohexanone in 40 ml. of dry ether was added dropwise over a period of 15 min. The mixture was stirred under gentle refluxing for 1.0 hr., cooled, and hydrolyzed by pouring into a mixture of 10 per cent sulfuric acid and ice. The mixture was extracted with ether, dried over magnesium sulfate, filtered, and the solvent removed. The oily residue did not crystallize and was converted directly to 2,2'-dimethyl-p-terphenyl (52).

2,2'-Dimethyl-p-terphenyl (52)--The dehydration and dehydrogenation of the unpurified 1-(3-methyl-4-biphenylyl)-2-methylcyclohexanol (51) were accomplished by heating an

intimate mixture of 51 and 0.5 g. of 10 per cent palladium on charcoal at 350° for 1.5 hr. The cooled residue was extracted with benzene, filtered, and the solvent removed to yield a viscous oil. The oil was dissolved in cyclohexane and chromatographed through an alumina column. Concentration of the eluates gave a colorless oily residue. Fractionation through a Vigreux column gave 2.6 g. (28 per cent) of 2,2'-dimethyl-p-terphenyl (52), b.p. 125 to 127° at 0.01 mm. An analytical sample was prepared by chromatographing several times through alumina and three distillations.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.69; H, 7.22.

2,6-Dimethyl-1-(p-toluenesulfonamido)-benzene (55)--To a stirred solution of 78.0 g. (0.65 mole) of 2,6-dimethylaniline (Aldrich Chemical Co., Inc.) in 250 ml. of anhydrous pyridine was added 135 g. (0.71 mole) of p-toluenesulfonyl chloride. The reaction mixture was refluxed for 2.0 hr., allowed to cool, and poured into 1 l. of 2 N hydrochloric acid. The resulting mixture was filtered and the precipitate dried to give 150 g. of a light tan solid, m.p. 125 to 130°. Recrystallization from ethanol gave 146 g. (80 per cent) of 2,6-dimethyl-1-(p-toluenesulfonamido)-benzene (55), m.p. 133 to 135°; reported[41] m.p. 136 to 137°.

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(41) B. M. Wepster, Rec. Trav. Chim., 73, 808 (1954).

2,6-Dimethyl-4-nitro-1-(p-toluenesulfonamido)-benzene (56)--To a solution of 375 g. (5.99 moles) of concentrated nitric acid in 3 l. of water was added 413 g. (1.5 moles) of 2,6-dimethyl-1-(p-toluenesulfonamido)-benzene (55), m.p. 133 to 135°, 3 l. of glacial acetic acid, and 10.5 g. (0.152 mole) of sodium nitrite. The reaction mixture was allowed to reflux for 1.0 hr., during which time a precipitate formed. The reaction mixture was then allowed to cool and was poured into 5 l. of water. After standing overnight, the mixture was filtered and the precipitate dried to give 410 g. of dark brown solid, m.p. 160 to 165°. Recrystallization from ethanol gave 402 g. (84 per cent) of 2,6-dimethyl-4-nitro-1-(p-toluenesulfonamido)-benzene (56), m.p. 163 to 165°; reported[41] m.p. 166 to 167°.

2,6-Dimethyl-4-nitroaniline (57)--The hydrolysis of 100 g. (0.32 mole) of 2,6-dimethyl-4-nitro-1-(p-toluenesulfonamido)-benzene (56), m.p. 163 to 165°, was accomplished by stirring a mixture of 56 and 300 ml. of 90 per cent sulfuric acid for 24 hr. at room temperature. The reaction mixture was poured into 2.5 l. of water and was neutralized with ammonium hydroxide. After cooling, the reaction mixture was filtered and the precipitate dried to afford a yellow solid. Recrystallization from 50 per cent aqueous ethanol gave 51 g. (98 per cent) of 2,6-dimethyl-4-nitroaniline (57), m.p. 161 to 162°; reported[41] m.p. 163.5 to 164.5°.

4-Iodo-2,6-dimethylnitrobenzene (58)--A hot solution of 95.1 g. (0.573 mole) of 2,6-dimethyl-4-nitroaniline (57), m.p. 161 to 162°, in 117 g. of concentrated sulfuric acid and 1550 ml. of water was rapidly cooled to 0°, and a solution of 40.6 g. (0.59 mole) of sodium nitrite in 200 ml. of water was added dropwise over a period of 1.0 hr. After stirring for an additional 45 min., the excess sodium nitrite was destroyed by the addition of a small amount of urea, and a solution of 282 g. (1.7 moles) of potassium iodide in 600 ml. of water was slowly added. Severe foaming occurred during the addition of the potassium iodide. After stirring for 2.0 hr., the reaction mixture was treated with a 10 per cent solution of sodium bisulfite and warmed on a steam bath. The reaction mixture was allowed to cool, and the precipitate that formed was removed by filtration. Crystallization from ethanol gave 150 g. (95 per cent) of 4-iodo-2,6-dimethylnitrobenzene (58), m.p. 127 to 129°. An analytical sample, m.p. 130 to 131°, was prepared by repeated crystallizations from ethanol.

Anal. Calcd. for $C_8H_8NO_2I$: C, 34.65; H, 2.91. Found: C, 34.68; H, 2.85.

Attempted Preparation of 2,2',6,6'-Tetramethyl-4,4'-dinitrobiphenyl (60)--An intimate mixture of 50 g. (0.18 mole) of 4-iodo-2,6-dimethylnitrobenzene (58) and 5 g. of copper

bronze was warmed to 240°. An additional 55 g. of copper bronze was added with stirring over a period of 3.0 hr., after which the reaction solidified into a hard mass and the stirrer broke. The hard lump was pulverized and repeatedly extracted with hot benzene. The benzene solution was filtered, chromatographed through alumina, and the solvent removed to afford a brown oily residue. Crystallization of the oil from ethanol gave 6.67 g. of a colorless solid, m.p. 72 to 74°. A mixed melting point with 5-nitro-m-xylene (59), m.p. 74 to 75°, did not depress. Additional runs of the Ullmann reaction with the iodide 58 at temperatures ranging from 200 to 290° resulted only in the elimination of iodine to give 5-nitro-m-xylene (59) in about 44 per cent yield, with no 2,2',6,6'-tetramethyl-4,4'-dinitrobiphenyl (60) being isolated.

2,4-Dimethylacetanilide (61)--To a stirred solution of 404 g. (3.33 moles) of 2,4-dimethylaniline (Eastman Kodak Co. 755), 2.77 l. of concentrated hydrochloric acid, and 6.9 l. of water, was added 394 ml. of acetic anhydride. As soon as the acetic anhydride went into solution, 424 g. (5.14 moles) of sodium acetate in 1600 ml. of water was added. The reaction mixture was stirred for 1.0 hr at 5° and was filtered to give 542 g. (90 per cent) of 2,4-dimethylacetanilide (61), m.p. 133 to 134°; reported[36] m.p. 133°.

2,4-Dimethyl-6-nitroacetanilide (62)--To 89.4 g. (0.55 mole) of 2,4-dimethylacetanilide (61), m.p. 132 to 133°, was added dropwise and with stirring 445 ml. of cold concentrated nitric acid (d = 1.4). The reaction mixture was kept cold during the addition, and after addition was complete stirring was continued for 1.5 hr. at 20°. The reaction mixture was poured into water and ice, filtered, and the precipitate dried to give a yellow solid, m.p. 162 to 170°. Recrystallization from ethanol gave 84 g. (76 per cent) of 2,4-dimethyl-6-nitroacetanilide (62), m.p. 175 to 178°; reported[42] m.p. 176.5°.

2,4-Dimethyl-6-nitroaniline (63)--The hydrolysis of 120 g. (0.0384 mole) of 2,4-dimethyl-6-nitroacetanilide (62), m.p. 174 to 176°, was accomplished by refluxing in 3.0 l. of 20 per cent hydrochloric acid for 24 hr. The reaction mixture was allowed to cool and was poured into 6 l. of water. The resulting slurry was filtered and the precipitate dried to give 80 g. of crude 2,4-dimethyl-6-nitroaniline (63), m.p. 62 to 70°. Recrystallization from 60 to 90° petroleum ether gave 73 g. (77 per cent) of 63, m.p. 69 to 71°; reported[42] m.p. 70 to 72°.

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(42) P. Karrer, H. Salomen, R. Kunz, and A. Seebach, Helv. Chim. Acta., 18, 1349 (1935).

5-Nitro-m-xylene (59)--A hot solution of 78.0 g. (0.47 mole) of 2,4-dimethyl-6-nitroaniline (63), m.p. 69 to 71°, 94 ml. of concentrated hydrochloric acid, and 190 ml. of water was rapidly cooled to -5°, and an additional 110 ml. of concentrated hydrochloric acid was added. Diazotization was accomplished by the dropwise addition of 32.4 g. (0.47 mole) of sodium nitrite in 85 ml. of water. Stirring was continued at -5° for 1.0 hr. after addition was complete. The excess nitrous acid was destroyed by the addition of a small amount of sulfamic acid. To the diazonium salt was added 244 ml. of 50 per cent hypophosphorous acid over a period of 1.0 hr. with the temperature being maintained at -5°. After the addition was complete, the reaction mixture was allowed to stand for 48 hr. at 0°. The mixture was filtered and the precipitate dried to give 64 g. of an orange precipitate, m.p. 64 to 72°. Recrystallization from ethanol gave 59.7 g. (85 per cent) of 5-nitro-m-xylene (59), m.p. 74 to 75°; reported[43] m.p. 75°.

4,4'-Diamino-2,2',6,6'-tetramethylbiphenyl (64)--To a stirred solution of 12.5 g. of zinc dust in a boiling solution of 5.0 g. (0.033 mole) of 5-nitro-m-xylene (59), m.p. 74

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(43) Heilbron's "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1934.

to 75°, in 20 ml. of ethanol was added dropwise a solution of 7.5 g. of sodium hydroxide in 25 ml. of water. The sodium hydroxide was added at such a rate that the solution boiled vigorously. Partial crystallization of the azo and hydrazo compounds occurred occasionally, and ethanol was added as required to bring these compounds into solution. After addition of the alkali was complete, the solution was still colored, and the solution was refluxed with frequent addition of 0.5 g. portions of zinc dust for 5 hr. The mixture was rapidly filtered through a large preheated Buchner funnel into a solution of 75 ml. of 30 per cent acetic acid and 0.25 g. of sodium bisulfite. The insoluble residue from the reaction mixture was extracted twice with 15 ml. portions of hot ethanol, and the extracts were filtered into the acetic acid solution. The mixture was cooled to 10° and the precipitate collected on a filter. The 3,3',5,5'-tetramethylhydrazobenzene was immediately added to 150 ml. of boiling 10 per cent hydrochloric acid through which nitrogen was being bubbled. Most of the solid material dissolved immediately, but a small amount remained undissolved even after refluxing for 5 hr. The nitrogen stream was discontinued, and the mixture was allowed to stand overnight. After removal of the insoluble material by filtration, the filtrate was stirred and boiled with Norit for 30 min. and filtered. The

colorless filtrate was allowed to cool and then was treated with 20 per cent sodium hydroxide until the solution became cloudy, and then with a saturated solution of sodium acetate until precipitation was complete. The pinkish solid which separated was extracted from the aqueous solution with three 75-ml. portions of ether. The ether solution was dried over Drierite, filtered, and the solvent removed on a steam bath. The residue was dissolved in 10 ml. of hot benzene, was treated with 20 ml. of petroleum ether (b.p. 60 to 90°), and the resulting solution allowed to cool. The fine, buff-colored crystals which precipitated were collected on a filter and dried to give 1.53 g. (41 per cent) of 4,4'-diamino-2,2',6,6'-tetramethylbiphenyl (64), m.p. 164 to 166°; reported[30] m.p. 167 to 168°. The solution was concentrated on a steam bath, and upon cooling there crystallized 0.42 g. (11 per cent) of 2,4'-diamino-2',4,6,6'-tetramethylbiphenyl, m.p. 137 to 139°; reported[30] m.p. 143°.