*Studies in Light Absorption. Part XIV.** *Steric Effects in* ortho-*Substituted Diphenyls.*

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The effects of *ortho*-substitution and *ortho*-bridging on the ultraviolet spectra of diphenyl and diphenyl derivatives are discussed and compared with steric effects observed in the acetophenone and styrene systems (Parts XI and XIII).

ortho-Substituted diphenyls show steric effects of type (2), signifying non-planar ground and excited states. *ortho*-Bridged diphenyls such as 9 : 10-dihydrophenanthrene and dihydrodibenzoxepin, on the other hand, show predominantly steric effects of type (1), signifying non-planar ground states but near-planar excited states. It is suggested that the difference arises from the restriction on twist imposed by the 2- and 3-atom *ortho*-bridges. For the two examples mentioned, the mean interplanar angles in the ground state calculated by the equation $\cos^2 \theta = \varepsilon/\varepsilon_0$ are *ca.* 20°, in good agreement with those indicated by models.

The introduction of *ortho*-substituents into short-bridged diphenyls increases the interplanar angle from about 20° to about 40°. In phenyldihydrothebaine, on the other hand, which contains a 5-membered *ortho*-bridge permitting a large twist, the interplanar angle deduced from the spectral data exceeds 60°.

THE study of diphenyl and its derivatives has not only provided one of the cornerstones of what may now be termed " classical " stereochemistry, but also led to the recognition of the influence of steric conformation on the characteristic spectral properties of conjugated systems. The initial suggestion that the pronounced effect of *o*-substituents on ultraviolet-light absorption may be due to steric hindrance to uniplanarity appears to have been made by Kistiakowsky to explain the observations of Pickett, Walter, and France on dimesityl and hexachlorodiphenyl (*J. Amer. Chem. Soc.*, 1936, **58**, 2296) and further extensive investigations have been carried out in this field during the last fifteen years by Rodebush, R. N. Jones, E. E. Turner, and others [for a summary, see Braude and Waight, " Progress in Stereochemistry " (Ed. W. Klyne), Chapter 4, Butterworths, London, 1954].

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* Part XI—XIII, preceding papers.

As a consequence, the diphenyl series represents the most fully documented example of the effects of *ortho*-substitution on the electronic spectra of a benzenoid system. Nevertheless, unanimity has not so far been reached even as to the detailed qualitative interpretation of many of the data and, indeed, the steric origin of some of the spectral phenomena has recently been questioned by Turner and his colleagues. The distinction between two different general types of steric effects and the semi-quantitative theory outlined in Part XI (*J.*, 1955, 3754) suggested a re-consideration of the evidence. This is the subject of the present paper.* In this connection, certain new data on mono-*o*-alkylated diphenyls are also reported.

ortho-*Substituted Diphenyls.*—Data for monosubstituted diphenyls are collected in Table 1. *o*-Alkyl substituents cause marked decreases in intensity as well as hypsochromic shifts, which are slightly larger with ethyl than with methyl, but do not differ appreciably for other primary and secondary alkyl groups. Similar decreases in ε are produced by *o*-hydroxyl and methoxyl substituents; in this case the observed hypsochromic shifts are quite small (Δλ *ca.* —50 Å) but, when it is remembered that such groups normally produce bathochromic shifts of the same order in conjugated systems (cf. Bowden, Braude, and Jones, Part III, *J.*, 1946, 948; Bowden and Braude, Part X, *J.*, 1952, 1068), the "theoretical" hypsochromic shifts (Δλ *ca.* —100 Å) are comparable with those observed with alkyl substituents. A strong hypsochromic shift is also observed in 2-iododiphenyl (Dunn and Iredale, *J.*, 1952, 1592); in this case the apparent effect on ε is small, but this is probably due to the overlap between absorption due to the diphenyl system and to the iodine atom in the 2200 Å region.

TABLE 1. *Ultraviolet light absorption of mono-*o*-substituted diphenyls.*

Ph_2 derivative	$\lambda_{max.}$ (Å)	ε *	Ph_2 derivative	$\lambda_{max.}$ (Å)	ε *
Unsubstituted [1-5]	2490	17,000	2-OH [3]	2450	8000
2-Me [1, 3, 4]	2350	10,500		2850	4500
2-Et [1]	2330	10,500	2-OMe [4, 3]	2450	11,000
2-Pr^{n} [1]	2330	10,000		2850	5000
2-Pr^{i} [1]	2330	11,000	2-I [6]	2290	17,000
2-Bu^{n} [1]	2330	10,500		2500	5000

* There are considerable variations between the values recorded by different workers, or even by the same workers [3, 4] on different occasions. The data in the Table are taken from the first reference cited.

[1] Present work (in ethanol). [2] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018 (in ethanol). [3] Friedel, Orchin, and Reggel, *ibid.*, 1948, **70**, 199 (in *cyclo*hexane). [4] Friedel and Orchin, "Ultraviolet spectra of aromatic compounds," Wiley, New York, 1951 (in *cyclo*hexane). [5] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854 (in hexane). [6] Dunn and Iredale, *J.*, 1952, 1592 (in hexane).

TABLE 2. *Ultraviolet-light absorption of di-*o*-substituted diphenyls.*

	Diphenyl band		Phenyl or phenoxy-band			Diphenyl band		Phenoxy-band	
Ph_2 derivative	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	Ph_2 derivative	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Unsubstituted [1]	2490	17,000	—	—	2 : 2′-$(OMe)_2$ [4]	<2300	—	2770	6000
2 : 2′-Me_2 [2] ...	(2270) *	6,800	2635	800	3 : 3′-$(OMe)_2$ [4]	2500	12,000	2850	6000
3 : 3′-Me_2 [3] ...	2550	16,500	—	—	4 : 4′-$(OMe)_2$ [4]	2630	21,700	—	—
4 : 4′-Me_2 [3] ...	2600	20,000	—	—					
2 : 2′-$(OH)_2$ [3] ...	2420	10,000	2850	6000					
3 : 3′-$(OH)_2$ [3] ...	2550	12,000	2950	6000					
4 : 4′-$(OH)_2$ [3] ...	2650	22,400	—	—					

* Inflection.

[1] Present work (in ethanol). [2] Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131 (in ethanol). [3] Williamson and Rodebush, *loc. cit.* (in ethanol). [4] Williamson and Rodebush, *loc. cit.* (in hexane).

Data for disubstituted diphenyls are given in Table 2. It is apparent that the hypsochromic shifts produced by two *o*-methyl or *o*-methoxyl substituents are approximately twice as great as those due to one substituent, but the precise relations are rather blurred

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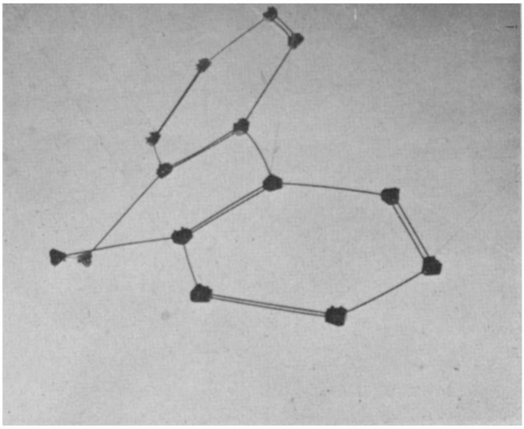
* For preliminary summaries, see Braude, *Chem. and Ind.*, 1951, 1002; *Experientia*, 1955, in the press; Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117).

by the fact that, particularly in di-*o*-tolyl, the displaced *K*-band overlaps with the short-wavelength absorption due to the separate phenyl rings (cf. Part X; Beaven *et al.*, *loc. cit.*). Although few data are available for mono-*m*- or -*p*-substituted diphenyls, those for *mm'*- and *pp'*-disubstituted derivatives show that in these positions, alkyl and methoxyl substituents exert normal variochromic effects of opposite sign, and it is therefore reasonable to regard the *ortho*-effects as steric in origin. (The effect of *m*-methoxyl groups on ε, which is somewhat exceptional, is discussed below.) Scale-projections employing double covalent radii, which represent a suitable measure of interference between non-bonded atoms (Part XI, *loc. cit.*), indicate appreciable overlap between an *ortho*-substituent such as Me or MeO and the *o'*-hydrogen atoms of the other phenyl ring in diphenyl. The fact that either one or two *ortho*-substituents, unless they are exceptionally large, do not confer measurable optical stability on the rotational enantiomorphs at room temperature (cf. Adams and Yuan, *Chem. Rev.*, 1933, **12**, 261) shows that the energy barrier to uniplanarity does not exceed *ca.* 15 kcal./mole in the ground state, but this sets no definite limit to the hindrance in the excited state. The hypsochromic shift from 2500 to 2350 Å due to one *o*-methyl substituent actually corresponds to an increase in transition energy of 7 kcal./mole, which is the amount by which the energy level of the electronic excited state has been raised relative to that of the ground state and it is obviously reasonable that the effect of two such substituents should be about twice as great. The fact that there are only second-order differences between the effects of methyl, ethyl, and other primary alkyl groups is in agreement with the observations made in the acetophenone series (Part XI, *loc. cit.*); all but the methylene group attached directly to the phenyl ring can adopt conformations such that they cause little or no additional interference.

If the steric origin of the spectral displacements in mono-*o*-substituted diphenyl is accepted, this system provides an excellent example of what we have termed steric effects of type (2), *i.e.*, those involving hypsochromic wavelength shifts as well as changes in intensity. This contrasts with the position with *o*-substituted acetophenones and styrenes (Parts XI and XIII) which exhibit steric effects of type (1), *i.e.*, decreases in intensity without unusual changes in wavelength. A behaviour intermediate between these two has been observed in *o*-substituted phenylpyrimidines (Russell, *J.*, 1954, 2951). The divergence in spectral behaviour is at first sight surprising, since the geometries of the relevant parts of these systems and the areas of steric overlap are quite similar. There is, however, an important difference between the diphenyl system on the one hand, and the acetophenone and styrene systems on the other, which can be appreciated by considering, for example, 2-methyldiphenyl: the two possible uniplanar conformations of this compound are identical and involve the same extent of steric hindrance, whereas the two uniplanar conformations of 2-methylacetophenone or 2-methylstyrene are not identical and one involves much less steric hindrance than the other. Hence the steric hindrance produced by an *o*-methyl substituent will be effectively much larger in the diphenyl than in the other two systems, and the probability of any *o*-substituted diphenyl molecule's occupying a near-planar vibrational state will be extremely low. Thus, the conditions pre-requisite for the display of steric effects of type (1) no longer exist.

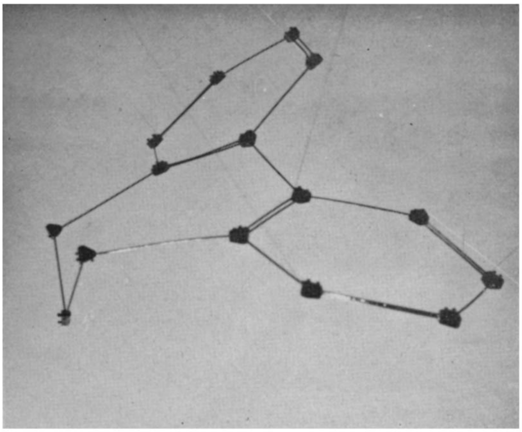
Secondly, the forces resisting in-plane bending will be considerably greater in the case of hydrogen atoms or methyl groups attached to a phenyl ring than when they are attached to a carbonyl or ethylenic group; this is reflected, for example, in the infrared C–H bending frequencies (cf. Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954). A third factor, which is related to the second, is that owing to the, albeit slight, repulsion between *o*-hydrogen atoms, the equilibrium interplanar angle in diphenyl itself may deviate more from 0° than in styrene or acetophenone, so that any additional hindrance to other *ortho*-substituents will be more effective. An interplanar angle as high as 45° has been reported (Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408) for gaseous diphenyl, though the two rings appear to be coplanar in the solid, crystalline state (Dhar, *Indian J. Phys.*, 1932, **7**, 43; *Proc. Nat. Inst. Sci. India*, 1949, **15**, 11); in solution the interplanar angle will presumably have an intermediate value. Unpublished calculations by Coulson and Longuet-Higgins indicate that the decrease in repulsion energy between the *o*-hydrogen atoms and the decrease in resonance energy resulting from non-planarity are practically

Fig. 1.



Scale model of 9 : 10-*dihydrophenanthrene.*

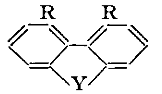
Fig. 2.



Scale model of 2 : 7-*dihydro*-3 : 4-5 : 6-*dibenzoxepin.*

balanced for interplanar angles of up to about 20°, so that there should be almost free rotation through an angle of this magnitude.* No electron-diffraction studies appear to have been carried out on styrene or acetophenone.

ortho-*Bridged Diphenyls.*—In fluorene (I; Y = CH_2, R = H), the two rings must be practically uniplanar in order to accommodate the methylene bridge. The fact that fluorene exhibits a " diphenyl-type " band slightly more intense than diphenyl itself (Table 3), supports the assumption that diphenyl is near-planar in solution; the small increase in ε is similar to that found in di-*p*-tolyl and may be ascribed to the normal substituent effect of the alkyl group, *i.e.*, fluorene shows the absorption of a planar, *oo'*-disubstituted diphenyl. In addition, fluorene has a band at longer wavelengths which has been ascribed to hyperconjugative interaction of the two rings through the methylene bridge (Part VIII, Braude, *J.*, 1949, 1902). Replacement of the CH_2 by a $CH_2{\cdot}CH_2$ bridge in 9 : 10-dihydrophenanthrene leads to a fall in ε of both bands. For the long-wavelength band, the decrease is to be expected, independently of steric effects, since hyperconjugative interaction will be diminished. For the " diphenyl-type " band, the decrease is to be expected since the ethane bridge will force the two benzene rings out of plane. Models show (Fig. 1) that, for the saturated carbon atoms to maintain their tetrahedral valency angle, the interplanar angle must be *ca.* 20° (cf. Beaven *et al.*, *loc. cit.*); this is in close agreement with the value of 18° obtained by applying the equation $\cos^2 \theta = \varepsilon/\varepsilon_0$, assuming that ε_0 will be the same as for fluorene, *i.e.*, $\varepsilon/\varepsilon_0 = 17{,}000/19{,}000 = 0{\cdot}89$.



(I)

TABLE 3. *Ultraviolet-light absorption of* ortho-*bridged diphenyls.*

Compound *	Diphenyl band $\lambda_{max.}$ (Å)	ε	$\varepsilon/\varepsilon_0$ †	θ°	Long-wavelength band $\lambda_{max.}$ (Å)	ε	Solvent
Fluorene [2]	2600	19,000	1·00	0	3000	10,000	E
9 : 10-Dihydrophenanthrene [1]	2640	17,000	0·90	18	2995	4,500	E
o : *o'*-Dimethyl derivative [3]	2600	16,000	0·84	24	—	—	E
o : *o'*-Dimethoxy-derivative [1]	2720	13,500	0·71	32	3045	9,300	E
2 : 7-Dihydrodibenzoxepin [1]	2500	16,500	0·87	21	—	—	H
o : *o'*-Dimethyl derivative [3]	2450	11,000	0·58	41	—	—	E
o : *o'*-Dimethoxy-derivative [1]	2530	8,700	0·46	47	2935	10,000	H
N-Acetylcolchinol methyl ether (II) [4]	2620	20,000	1·05	0	—	—	E
2 : 7-Dihydrodibenzazepinium bromide [1]	2480	15,000	0·79	27	2720	4,800	W
o : *o'*-Dimethoxy-derivative [1]	2375	11,500	0·61	39 ‡	2975	10,500	W
Phenyldihydrothebaine [5]	2810	5,600	0·29	57 §	—	—	?

* The designation *o* : *o'* refers to the positions of R in (I).

† The data refer variously to ethanol (E), hexane (H), or water (W) solutions. The comparisons are, nevertheless, justified, as measurements from one laboratory (ref. 1) show that ε is little solvent-dependent in this series.

‡ This value is probably too small, because it neglects the hypsochromic shift.

§ This value is a minimum, because any diphenyl absorption evidently overlaps with absorption due to the partial phenoxy-chromophores, and the latter has been neglected in calculating θ.

[1] Beaven *et al.*, *loc. cit.*, 1952. [2] Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634. [3] Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629. [4] Horowitz *et al.*, *ibid.*, 1950, **72**, 4331. [5] Small, Sargent, and Bralley, *J. Org. Chem.*, 1947, **12**, 839.

(The justification for equating ε_0 with the value for fluorene rather than that for diphenyl is that this makes an allowance for the normal, small increase in intensity due to the alkyl substituent; the importance of taking these effects into account has been demonstrated in other cases; cf. Part XI, *loc. cit.*)

The introduction of *o*-substituents into 9 : 10-dihydrophenanthrene (I; Y = $CH_2{\cdot}CH_2$, R = H) would be expected to increase further the angle between the benzene rings. The effects should be much less marked than in diphenyl, however, because they will be opposed by the ethane bridge and because the twist which already exists in 9 : 10-dihydrophenanthrene will facilitate the accommodation of *o*-substituents. In fact, the data for 9 : 10-dihydro-4 : 5-dimethyl- and -4 : 5-dimethoxy-phenanthrene (Table 3) show that, in contrast to diphenyl, *o*-substituents produce steric effects of type (1) (decrease in ε without hypsochromic shift) rather than of type (2). The " locking effect " of the ethane bridge

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* We are indebted to Professor C. A. Coulson, F.R.S., for communicating and allowing us to quote these results, first presented by him at a Conference held in Washington in September, 1951.

is evidently sufficient to enforce a near-planar conformation of the two rings in the excited state; and the interplanar angles of about 30° calculated for the ground state are considerably *less* than those deduced for the correspondingly *o*-substituted acetophenones and styrenes (Part XI and XIII), in which rotation is not structurally restricted.

In addition to the decrease in ε of the diphenyl-type band, 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene, but not the dimethyl derivative, shows an enhancement of the 3000 Å band. This enhancement ($\Delta\varepsilon = +6000$) may be ascribed to superposition of absorption due to the " phenoxy " chromophores $MeO{\cdot}C_6H_4$— and is almost exactly equal to the difference in ε between, for example, diphenyl and 3 : 3'-dimethoxydiphenyl in this wavelength region.

One condition for the display of steric effects of type (1) is that steric hindrance to planarity should not exceed *ca.* 3 kcal./mole (Part XI). It is gratifying to note that the height of the energy pass between the ground state and the coplanar state of 9 : 10-dihydrophenanthrene has recently been estimated as 1·4 kcal./mole (Howlett, *J.*, 1955, 1249).

We next consider 2 : 7-dihydro-3 : 4-5 : 6-dibenzoxepin derivatives (I; Y = $CH_2{\cdot}O{\cdot}CH_2$). The parent compound again exhibits a typical diphenyl-type band, but the intensity is slightly lower than in dihydrophenanthrene and the calculated interplanar angle (21°) is slightly larger. As in the case of dihydrophenanthrene (see above) this angle is in excellent agreement with that indicated by scale models (see Fig. 2), the valency angle at the oxygen atom being taken as *ca.* 110° as in other ethers (cf. Lander and Svirbely, *J. Amer. Chem. Soc.*, 1945, **67**, 322; Everard and Sutton, *J.*, 1949, 2312).

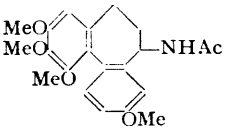
The introduction of two "*o*"-methoxy groups into dihydrodibenzoxepin again causes a decrease in ε of the " diphenyl-type " band and an increase in the interplanar angle to 47°. As in dimethoxydihydrophenanthrene, there is at the same time an increase in the absorption in the 3000 Å region, due to the two " phenoxy "-chromophores.

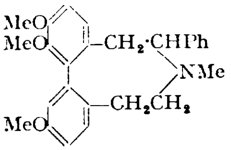
A different interpretation of the absorption of dihydrodibenzoxepin and its derivatives has been given by Turner, Beaven, and their colleagues (*loc. cit.*), to whom we owe many of the data just discussed, and, since this forms the central part of their theory of the spectral properties of substituted diphenyls, it will be considered in some detail. The starting point of their theory is the assumption, based on models of " Catalin " type (Beaven, personal communication ; cf. Settatree, Thomas, and Yardley, *Nature*, 1950, **166**, 59) that the interplanar angle between the benzene rings in dihydrodibenzoxepin is " about 50°." Since the absorption of the oxepin is very similar to that of dihydrophenanthrene, Beaven *et al.* conclude that this " would suggest that in the oxepin the phenyl groups are no less conjugated and hence no less coplanar than in diphenyl. Since, however, the oxepin cannot be coplanar, it follows that the diphenyl-type spectrum does not provide sure evidence for a coplanar configuration." Further, they considered that since, in their view, the benzene rings in dihydrodibenzoxepin are already at an angle of *ca.* 50°, the introduction of "*o*"-methoxyl groups should have no steric consequences. These arguments require the decrease in ε brought about by *o*-methoxyl groups to be explained by other than steric effects, and Beaven *et al.* provide such an explanation by postulating that the weakening of the diphenyl-type band and the appearance of longer-wavelength absorption is due " primarily to mesomeric interaction between the methoxyl groups and the separate rings to which they are attached, with consequent reduction in the conjugation between the two rings."· The fact that a smaller decrease in the ε of the diphenyl-type band is observed in 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene is considered to be due to out-of-plane bending of the methoxyl group so that their mesomeric interaction and the reduction in conjugation between the two rings is less effective. This interpretation appears to neglect the fact that the intensity of long-wavelength absorption is almost exactly the same in 2 : 7-dihydro-4 : 5-dimethoxydibenzoxepin and 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene. Moreover, the assumption of an angle of 50° between the phenyl rings in dihydrodibenzoxepin is questionable, and is not supported by " open " scale models, such as those shown in Fig. 2. The main difficulty with Turner's theory, however, appears to us to be that it does not account for the effects of *o*-methyl substituents. Methyl groups are known to have much weaker mesomeric effects than methoxyl groups and produce no marked long-wavelength absorption when attached to benzene rings; yet the data in Table 3 clearly show that they cause comparable reductions in the intensities of the diphenyl type bands in di-*o*-tolyl as well as in 9 : 10-dihydro-4 : 5-dimethylphenanthrene. These reductions can hardly be ascribed to electronic interactions between the methyl substituents and the separate benzene rings.

The effects of *o*-substituents on diphenyl-type absorption thus seem more plausibly explained as mainly due to steric rather than electronic interactions, and in a more recent paper, Hall, Ridgwell, and Turner (*J.*, 1954, 2498) appear to have accepted our theory of transitions between non-planar ground and near-planar excited states as providing an adequate interpretation of the spectral data of 1-phenylnaphthalene-2′-carboxylic acid derivatives. It still remains, however, to account for the above-mentioned effect of *m*-methoxyl substituents, which though smaller than those of *o*-substituents, are appreciable. Beaven *et al.* have interpreted these effects as mesomeric interactions similar to those involved in the case of *ortho*-substituents. An alternative view is that *meta*-substituents exert indirect steric effects by " buttressing " the *o*-hydrogen atoms against in-plane bending away from the diphenyl link. Convincing evidence for the existence of the " buttressing effect " has been provided by measurements on the ease of racemisation of *ortho*- and *meta*-substituted, optically active diphenyls (Chien and Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 1787; Rieger and Westheimer, *ibid.*, 1950, **72**, 19). The effect is not sufficient to impart optical stability to diphenyls containing no *ortho*-substituents, but, as was previously pointed out (Part XI), electronic spectra are a much more sensitive index of steric effects than is optical resolvability. No steric effects are observed in mono-*meta*-substituted acetophenones or styrenes (Part XI and XIII, *loc. cit.*) because the parent systems are " comfortably " planar and the effect of a single substituent will, in any case, be small. In the diphenyl system, on the other hand, there is slight interference even between the *o*-hydrogen atoms in the parent compound, which are therefore much more susceptible to the buttressing effect.

The remaining *oo*′-bridged diphenyls in Table 3 may now be briefly considered. A three-carbon bridge, as in *N*-acetylcolchinol methyl ether (II), evidently causes no significant deviation to planarity, as has already been pointed out by Horning, Ullyot, and their co-workers (*J. Amer. Chem. Soc.*, 1950, **72**, 4331; cf. Rapoport, Allen, and Cisney, *ibid.*, 1955, **77**, 670). The dihydrodibenzazepinium bromide (as I; Y = $\mathrm{CH_2{\cdot}\overset{+}{N}Ph{\cdot}CH_2}$), like the other unsubstituted compounds, also shows a relatively small reduction in diphenyl absorption, from which an interplanar angle of 27°, in good agreement with that indicated by models, can be deduced. In this case, however, *o*-methoxyl substituents cause not only a further reduction in intensity of the diphenyl-band, but also a hypsochromic shift, similar to that found in 2 : 2′-dimethoxydiphenyl. It appears that the dihydrodibenzazepinium system is sufficiently flexible for the *o*-methoxyl substituents to cause appreciable non-planarity in the excited as well as in the ground state, thus resulting in steric effects of type (2).

(II)





(III)

In contrast to dihydrodibenzazepinium bromide, the arsenic analogue (as I; Y = $\mathrm{CH_2{\cdot}\overset{+}{As}Ph{\cdot}CH_2}$) exhibits no diphenyl-type band (Beeby, Mann, and Turner, *J.*, 1950, 1923), indicating that the large arsenic atom does not allow the two phenyl rings to approach a near-planar arrangement even at the expense of some valency-angle distortion. This is confirmed by scale models which show that the phenyl rings are almost at right angles to one another. On the other hand, some interaction between the phenyl rings appears to exist in the lower homologues (as I; Y = $\mathrm{\overset{+}{As}Ph}$ and $\mathrm{\overset{+}{Sb}Ph}$) (Campbell and Poller, *Chem. and Ind.*, 1953, 1126) but detailed interpretation of these data is difficult because of superposition between diphenyl-type absorption and absorption due to the Ph–As chromophore (cf. Bowden and Braude, Part X, *J.*, 1952, 1068).

Lastly, phenyldihydrothebaine (III) provides an example of a diphenyl containing a five membered *oo'*-bridge, as well as one *o*-hydroxyl substituent. Unlike a two- or three-membered bridge, a five-membered bridge, by itself, will tend to rotate the one phenyl ring by an appreciable angle with respect to the other, and can readily accommodate the additional repulsion caused by an *ortho*-substituent. As was pointed out by Robinson in his notable derivation of the structure of phenyldihydrothebaine (*Nature*, 1947, **60**, 815; *Proc. Roy. Soc.*, 1947, *B*, **135**, 14; Bentley and Robinson, *J.*, 1952, 947), the non-planarity of the diphenyl system in this compound is apparent both from its optical resolvability and from its ultraviolet absorption; the spectral data indicate that the interplanar angle is at least about 60°, and probably even larger (Table 3).

Experimental.—We are indebted to Drs. Goodman and Wise (cf. *J. Amer. Chem. Soc.*, 1950, **72**, 3076) for kindly providing the *o*-alkyldiphenyls.

After fractionation, 2-methyldiphenyl had b. p. 47°/0·03 mm., n_D^{21} 1·5908; 2-ethyldiphenyl had b. p. 57°/0·04 mm., n_D^{20} 1·5783; 2-*n*-propyldiphenyl had b. p. 68°/0·04 mm., n_D^{20} 1·5692; 2-*n*-butyldiphenyl had b. p. 62°/0·03 mm., n_D^{21} 1·5598; 2-*iso*propyldiphenyl had b. p. 65°/0·02 mm., n_D^{21} 1·5695. The spectra were determined on Hilger–Spekker and Beckman instruments. Some of the data are not in good agreement with those recorded in the American Petroleum Institute Collection (Nos. 94, 202, 248, 284, 285, and 286).

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