# **889.** *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part VII.* Halogenodiphenyls.*

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The introduction of even a single fluorine substituent into one of the *ortho*-positions of diphenyl results in a detectable blue shift and reduction in intensity of the conjugation band. In the series of 2 : 2′-dihalogenodiphenyls the blue shift and intensity reduction are progressively larger from fluorine to bromine; in 2 : 2′-di-iododiphenyl the spectrum does not show a conjugation band. In the same series, the absorption contributions due to unconjugated halogenobenzene chromophores appear with increasing distinctness as the conjugation band is inhibited, and progressively approach the expected intensity for an additive system of such absorbing units.

The ultraviolet absorption spectra of diphenyls containing fluorine substituents in the *meta*- and *para*-positions show them to be " perturbed " diphenyls, in which small changes in the conjugation band are accompanied by the appearance of low-intensity unresolved contributions from the phenyl chromophores. These minor spectroscopic effects are caused by non-steric, electronic interactions of the substituent groups with the diphenyl chromophore.

THE small covalent and van der Waals radii of fluorine make it of interest to determine whether the introduction of fluorine into one or both of the *ortho*-positions of diphenyl causes sufficient additional steric hindrance to coplanarity of the phenyl groups, relative to hydrogen, for the resultant loss of conjugation across the $C_{(1)}$–$C_{(1')}$ bond to be detectable by alterations in the ultraviolet absorption spectrum. The marked effects of four chlorine atoms in the *ortho*-positions were demonstrated by Pickett, Walter, and France [1] at a time

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* Part VI, *J.*, 1956, 2286.

[1] Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296.

when the importance of coplanarity for the complete development of the intense conjugation band at *ca.* 250 mμ in diphenyl was only just being recognized. These authors showed that either chlorine atoms or methyl groups in these four positions were sufficient to cause the spectra of the derivatives to revert, more or less completely, to the additive contributions to be expected for two substituted phenyl chromophores. Williamson and Rodebush [2] found similar effects for 2 : 2′-dichlorodiphenyl and many other 2 : 2′-disubstituted diphenyls, which they related to loss of coplanarity due to steric interactions between the groups in the *ortho*-positions. The absorption spectrum of 2-iododiphenyl [3] shows similar alterations in the intensity and position of the conjugation band.

The effects of halogen in the *meta*- and *para*-positions of diphenyl, uncomplicated by steric effects, are exemplified by the spectra of appropriate compounds examined by Pickett, Walter, and France,[1] Williamson and Rodebush,[2] and Friedel and Orchin.[4]

The spectrum of 2 : 2′-difluorodiphenyl itself does not appear to have been discussed, at least in the present connection, although Bilbo and Wyman [5] compared benzidine with its 2 : 2′-difluoro-, 2 : 2′-dichloro-, 3 : 3′-dichloro-, and 2 : 2′ : 6 : 6′-tetrafluoro-derivatives and concluded that there was appreciable loss of conjugation in all the *ortho*-halogenated compounds, including the 2 : 2′-difluoro-derivative. The relative departures from coplanarity inferred from the spectra, notably from the positions of the band maxima, ran parallel with the relative reactivities of the same compounds to bromine water, in which a coplanar quinone imine intermediate with a $C_{(1)}$–$C_{(1')}$ bond of essentially double-bond character is thought to be concerned. However, the two *p*-amino-groups in benzidine may have some influence on the partial double-bond character of the $C_{(1)}$–$C_{(1')}$ collinear bond, and hence on the steric consequences of introducing *ortho*-substituents (cf.[6, 7, 8]).

The four 2 : 2′-dihalogenodiphenyls are of particular interest, since estimates of the angle (θ) between the planes of the benzene rings have been obtained by electron-diffraction.[9, 10] Littlejohn and Smith [11] have also computed values of θ which are most consistent with their dipole-moment measurements. These results are listed in Table 1, together with values for the $C_{ar}$–X bond lengths and van der Waals radii for the halogens. Estimates of θ in the crystalline state from *X*-ray diffraction studies on *ortho*-substituted diphenyls have been discussed earlier in this series.[12]

Apart from the surprisingly large value of θ found by Bastiansen for diphenyl itself, the most interesting feature of both the electron-diffraction and dipole results is that all four 2 : 2′-dihalogenodiphenyls have a "*cis*"-conformation, corresponding to halogen–halogen contacts, rather than a "*trans*"-conformation, with halogen–hydrogen contacts, that might have been expected from a simple consideration of electrostatic repulsion. (Mason and Kreevoy [13] have considered F–F and Cl–Cl interactions in a theoretical study of barriers to internal rotation about single bonds and find the Coulombic interaction to be only *ca.* 10% of the total repulsion energy, of which about half is due to ordinary van der Waals repulsions.) Although in the crystalline state the two nuclei of diphenyl itself appear to be coplanar, Pauling [14] drew attention to the possibility of steric interactions between the hydrogens in the four *ortho*-positions. Previous electron-diffraction work by Karle and Brockway [15] tends to support Bastiansen's non-coplanar conformation for the

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[2] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.

[3] Dunn and Iredale, *J.*, 1952, 1592.

[4] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley and Sons, Inc., New York, 1951, No. 183.

[5] Bilbo and Wyman, *J. Amer. Chem. Soc.*, 1953, **75**, 5312.

[6] Pickett, Groth, Duckworth, and Cuncliffe, *ibid.*, 1950, **72**, 44.

[7] Sherwood and Calvin, *ibid.*, 1942, **64**, 1350.

[8] Calvin, *J. Org. Chem.*, 1939, **4**, 256.

[9] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926.

[10] Bastiansen and Smedvik, *ibid.*, 1954, **8**, 1593.

[11] Littlejohn and Smith, (*a*) *J.*, 1953, 2456; (*b*) *J.*, 1954, 2552.

[12] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

[13] Mason and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808.

[14] Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1942, 2nd edn., p 220.

[15] Karle and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 1974.

vapour state, though Rousset and Pacault [16] concluded from light-scattering studies that in *cyclo*hexane solution the anisotropy of polarisibility of diphenyl was much greater than that of benzene, to an extent which suggested a highly conjugated and essentially planar conformation.

In considering the absolute magnitudes of θ estimated by electron diffraction, it must be remembered that these are equilibrium values. Torsional vibrations about the $C_{(1)}$–$C_{(1')}$ bond were indicated by the data, but the amplitudes of these vibrations were not evaluated, though procedures are becoming available.[17]

TABLE 1. 2 : 2′-*Dihalogenodiphenyls and related compounds.*

| Halogen | $C_{ar}$–Hal bond length (Å) [a] | van der Waals radius of halogen (Å) [b] | Angle between planes of benzene rings, θ | | | |
|---|---|---|---|---|---|---|
| | | | Electron diffraction [c] | Dipole moment [e] | Calc.[g] " *cis* " | Calc.[g] " *trans* " |
| (H) ............... | (1·04) | (1·20) [h] | 45 ± 10° | — | 42° [h] | |
| F .................. | 1·35 | 1·35 | 60 ± 5° [d] *cis* | 77° [f] | 55° | 49° |
| Cl .................. | 1·69 | 1·80 | 74 ± 5° *cis* | 81° [f] | 79° | 64° |
| Br ............... | 1·88 | 1·95 | 75 ± 5° *cis* | 85° | 83° | 67° |
| I .................. | 2·00 | 2·15 | 79 ± 5° *cis* | 84° | 91° | 72° |
| 2-Fluoro ......... | 1·35 | 1·35 | 49 ± 5° [d] | — | 49° | |
| 4 : 4′-Difluoro ... | — | — | 44 ± 5° [d] | — | (42°) | |

[a] Electron diffraction; Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46. [b] Pauling, ref. 14, p. 189. [c] Bastiansen.[9] [d] Bastiansen and Smedvik.[10] [e] Littlejohn and Smith.[11b] [f] Revised values based on bond lengths given in the second column; J. W. Smith, personal communication. [g] Values calculated by using data from *a* and *b* and $C_{(1)}$–$C_{(1')}$ 1·50 Å, C–$C_{ar}$ 1·40 Å. [h] For a van der Waals radius of 1·0 Å for hydrogen, θ for diphenyl is reduced to 23°.

Bastiansen calculated that the halogen–halogen distances corresponding to the observed values of θ were slightly less than twice the appropriate van der Waals radii for all the 2 : 2′-dihalogenodiphenyls except the difluoro-compound. The last column in Table 1 shows the values of θ calculated for conformations in which the *ortho* atoms are " touching," *i.e.*, the distance between the atomic nuclei is the sum of the van der Waals radii. Strictly, van der Waals radii apply to intermolecular contacts and not to approaches between atoms in the same molecule; however, a 2 : 2′-dihalogenodiphenyl could presumably take up (without strain) a conformation in which the halogen distance is *greater* than twice the van der Waals radius so that it seems justifiable to regard the contact between the two halogen atoms as of the intermolecular rather than of the intramolecular type. Other " interference radii " have been used by some workers but the choice is to a certain extent dependent on the physical property and the type of molecule under consideration (cf. Kofod, Kumar, and Sutton; [18] Braude and Sondheimer [19]); in the absence of unequivocal data on which to base adjustments to the covalent bond radii it seems preferable to use van der Waals radii to study steric interference in the 2 : 2′-dihalogenodiphenyls.

Calculations of θ for compounds of this type have a rather different significance from those for *ortho*-bridged diphenyls. In the latter the configuration of the diphenyl skeleton is fixed within fairly narrow limits by the bridging ring, and considerable distortion is required to change θ by more than a few degrees. Also the data required for the calculations are normal covalent radii, not van der Waals radii, and are thus subject to less ambiguity. In the non-bridged compounds, however, the " touching " conformation (for which θ has been calculated here) is only one of many possible conformations; even if it should, in fact, correspond to a preferred conformation there will be other conformations (with different values of θ) of only slightly higher energy.

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[16] Rousset and Pacault, *Compt. rend.*, 1954, **238**, 1705.

[17] Karle, *J. Chem. Phys.*, 1954, **22**, 1246, and earlier papers; Bartell, Brockway, and Schwendeman, *ibid.*, 1955, **23**, 1854.

[18] Kofod, Kumar, and Sutton, *J.*, 1951, 1790.

[19] Braude and Sondheimer, *J.*, 1955, 3754.

The overlaps between the *ortho*-atoms for the 2 : 2′-dihalogenodiphenyls are conventionally depicted in Fig. 1, van der Waals radii and a $C_{(1)}$–$C_{(1')}$ bond length of 1·50 Å (Bastiansen,[9] electron diffraction; corresponding to *ca.* 10% double-bond character) being used, and showing both "*cis*" (halogen-halogen) and "*trans*" (halogen–hydrogen) overlaps.

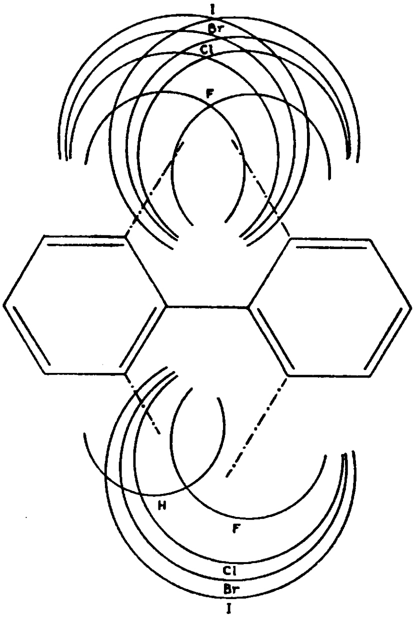

FIG. 1. *Plane projection scale diagram of* 2 : 2′-*substituent overlaps in diphenyl, van der Waals radii being used.*
*Top*: Halogen–halogen ("*cis*") overlaps.
*Bottom*: Hydrogen–halogen ("*trans*") overlaps.

Excellent spectra of the monohalogenobenzenes are available,[20] though in *iso*octane solution, and not extending below 220 mμ. Results for ethanolic solution,[21] which do not include iodobenzene, show the expected small differences in wavelengths and intensity. The available data for the *o*-halogenotoluenes [22] are older and also refer to hydrocarbon solvents. The results show, however, small long-wave shifts and intensity changes due to

TABLE 2. *Ultraviolet absorption spectra of fluorodiphenyls.*

| | Conjugation band | | | | Long-wave band | | | |
|---|---|---|---|---|---|---|---|---|
| Diphenyl | $\lambda_{min.}$ | $\varepsilon_{min.}$ | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ | $\lambda_{max.}$ | $\varepsilon_{max.}$ |
| Diphenyl ........................ | 222 | 4300 | 249 | 17,300 | — | — | — | — |
| 2-Fluoro- ........................ | 219·5 | 5500 | 241·5 | 16,500 | — | — | (281)<br>(274) | (1600)<br>(3000) |
| 2 : 2′-Difluoro- .................. | 216 | 7100 | 233·5 | 13,800 | 259 | 3000 | 268 | 3400 |
| 2-Fluoro-4 : 4′-dimethyl- ...... | 223·5 | 6000 | 248·5 | 20,000 | — | — | (278·5)<br>(276) | (5000)<br>(5500) |
| 2 : 2′-Difluoro-4 : 4′-dimethyl- | 221 | 8700 | 240 | 18,500 | 266·5 | 4900 | 271 | 5150 |
| 3 : 3′-Difluoro- .................. | 222 | 4800 | 247 | 15,500 | — | — | (279·5)<br>(275·5) | (5000)<br>(5700) |
| 4-Fluoro- ........................ | 221·5 | 4300 | 247·5 | 16,900 | — | — | (273)<br>(262·5) | (4000)<br>(8800) |
| 4 : 4′-Difluoro- .................. | 220 | 3600 | 245 | 15,000 | — | — | (271·5)<br>(263·5) | (4000)<br>(7000) |
| 4 : 4′-Difluoro-3 : 3′-dimethyl- | 225·5 | 4700 | 247 | 14,000 | — | — | (277·5)<br>(265·5) | (2900)<br>(6000) |

Wavelengths in mμ; figures in parentheses refer to inflections; solvent 96% ethanol.

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[20] American Petroleum Institute, Research Project No. 44, Ultraviolet Spectral Data, Serial nos. 296, 300, 304, 308.

[21] Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5252.

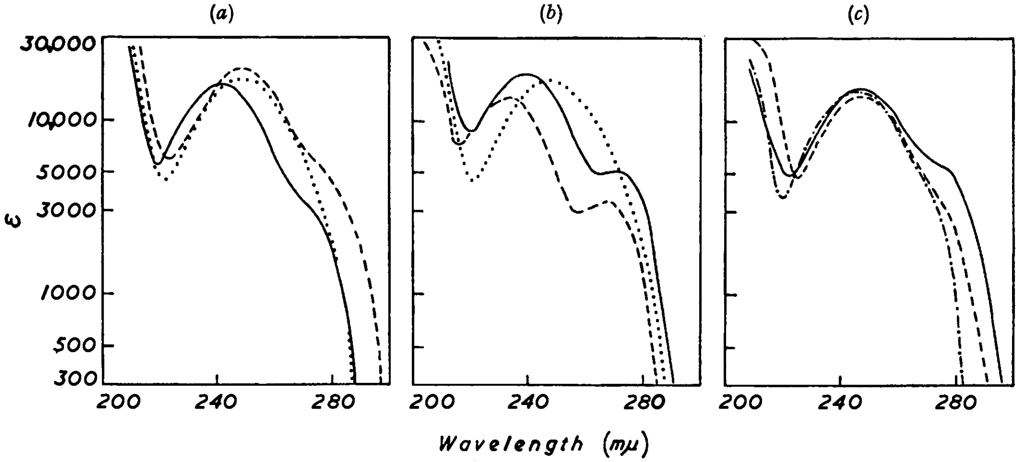
[22] Conrad-Billroth, *Z. phys. Chem.*, 1934, *B*, **25**, 139; Wolf and Herold, *ibid.*, 1931, *B*, **13**, 201.

the introduction of the alkyl group. The intensity change is small for *o*-fluorotoluene, but increases through the series to *ca.* 100% for the bromo- and chloro-derivatives. Taken as a whole the literature data are adequate for comparison with the spectra of the 2 : 2'-dihalogenodiphenyls.

It is convenient to consider the results for the fluorodiphenyls (Table 2), including the 2 : 2'-difluoro-derivative, before discussing the 2 : 2'-dihalogenodiphenyls as a separate group.

The spectrum of 2-fluorodiphenyl (Fig. 2*a*), compared with that of diphenyl, shows a small short-wave (blue) shift and slight reduction in intensity of the conjugation band, and also a distinct long-wave double inflection. In 2-fluoro-4 : 4'-dimethyldiphenyl the introduction of the methyl groups results in the conjugation band having nearly the same intensity as in 4 : 4'-dimethyldiphenyl ($\lambda_{max.}$ 253 mμ, $\varepsilon_{max.}$ 21,100),[23] but at shorter wave-length. The higher intensities of the long-wave inflections in 2-fluoro-4 : 4'-dimethyldiphenyl are obviously due to increased overlapping by the conjugation band. A further indication of the effect of the *p*-methyl groups is the shift of the minimum on the short-wave side of the conjugation band.

FIG. 2. *Ultraviolet absorption spectra of fluorodiphenyls.*



(*a*) —— 2-Fluorodiphenyl. — — — 2-Fluoro-4 : 4'-dimethyldiphenyl. . . . . . Diphenyl.
(*b*) —— 2 : 2'-Difluorodiphenyl. — — — 2 : 2'-Difluoro-4 : 4'-dimethyldiphenyl. . . . . . Diphenyl.
(*c*) —— 3 : 3'-Difluorodiphenyl. - - - - 4 : 4'-Difluoro-3 : 3'-dimethyldiphenyl. —·—·— 4 : 4'-Difluorodiphenyl. Solvent, 96% ethanol.

In 2 : 2'-difluorodiphenyl (Fig. 2*b*), the short-wave shift and reduction in intensity of the conjugation band are very marked, and the long-wave feature is a shallow but distinctly resolved maximum. The effects of introducing methyl groups into the two *para*-positions are qualitatively similar to those for 2-fluorodiphenyl, but the apparent compensation for the steric effect of two *o*-fluoro-substituents on the position and intensity of the conjugation band is less than in the 2-fluoro-compound.

It may be concluded that the steric effect of even one *o*-fluoro-substituent in diphenyl is sufficient to affect the conjugation band to an easily detectable extent.

The other four compounds listed in Table 2, containing fluorine in non-*ortho*-positions, all show small reductions in intensity and slight blue shifts of the conjugation band, compared with diphenyl (Fig. 2*c*), and all have faint long-wave inflections, which are most easily detectable by the moving-plate, logarithmic-cam photographic method. The observed intensities of these inflections are obviously determined very largely by the over-lapping conjugation bands in all four compounds.

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[23] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906; ref. 2.

The small short-wave shifts of the conjugation band suggest that the inductive and mesomeric effects of the fluorine substituents are giving rise to opposing blue and red shifts of nearly equal magnitude, as suggested by Cooper[24] (cf. Smith and Turton[25]) for fluorobenzene. The cancellation of blue-shifts and summation of red-shifts proposed by this author to explain the large red-shift in *p*-difluorobenzene does not seem to apply to the diphenyls with 4 : 4′-difluoro-substituents. The effects of these substituents are in striking contrast to those of chlorine, bromine, and iodine in the same positions, which give rise to progressively larger red shifts and intensity increases of the conjugation band[2, 4] analogous to the effects in the corresponding 1 : 4-dihalogenobenzenes. Friedel and Orchin's curve for 4 : 4′-dichlorodiphenyl shows some very faint long-wave fine structure in the 280—300 mμ region, with extinction coefficients in the 100—1000 range, which may be analogous to the fine structure in 4 : 4′-difluorodiphenyl. Apart from this, the 4 : 4′-difluoro-substituents are clearly exceptional, compared with the other halogens, in not producing an increase in intensity of the conjugation band, as well as in causing a small blue shift.

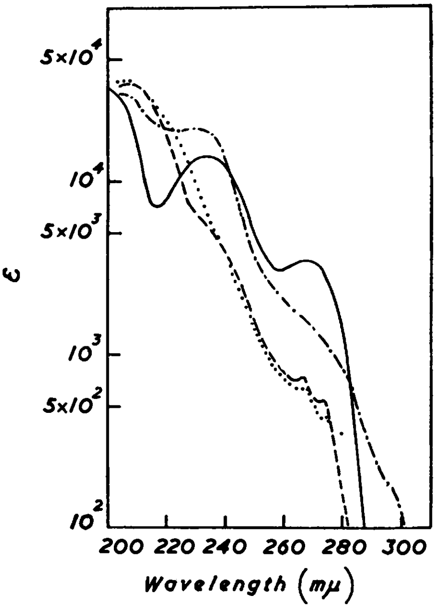

FIG. 3. *Ultraviolet absorption spectra of 2 : 2′-Dihalogenodiphenyls.*

———— Difluoro-.
— — — Dichloro-.
. . . . . Dibromo-.
—·—·— Di-iodo-.

Solvent, 96% ethanol.

It is of interest to note that in 4 : 4′-difluoro-3 : 3′-dimethyldiphenyl, although the spectrum shows the expected red shift due to the introduction of the methyl groups, the conjugation band is still further reduced in intensity, consistent with the effect of 3 : 3′-dimethyl substituents alone.[23] The overall effect on the diphenyl conjugation band of introducing a single fluorine into the 4-position is very slight, apart from the appearance of the long-wave inflections.

On the basis of the long-wave absorption features, these non-*ortho*-substituted diphenyls can all be regarded as " perturbed " diphenyls, in the sense that the term is used by Wentzel.[26] The effects of these substituent groups, including the reduced intensity of the conjugation band, can alternatively be accounted for on the basis of their electronic interaction with the benzene rings in such a manner as to reduce slightly the conjugation across the $C_{(1)}$–$C_{(1')}$ bond (cf. Part 1[12]). The two viewpoints are essentially identical, except that Wentzel, following Platt,[27] considers that the benzene-type transition, which gives rise to

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[24] Cooper, *J. Chem. Phys.*, 1954, **22**, 503.
[25] Smith and Turton, *J.*, 1951, 1701.
[26] Wentzel, *J. Chem. Phys.*, 1953, **21**, 403.
[27] Platt, *ibid.*, 1951, **19**, 101.

the long-wave inflections in " perturbed " diphenyls, must also be present, for theoretical reasons, in diphenyl itself but is obscured by the conjugation band.

For the fluorine-substituted diphenyls, the intensity changes alone do not differentiate the *ortho*-substituted from the other derivatives. The magnitudes of the wavelength shifts are clearly of greater importance but even here allowance must be made for the (bathochromic) effects of the methyl groups.

The spectra of the other 2 : 2′-dihalogenodiphenyls (Fig. 3 and Table 3) differ markedly from that of the 2 : 2′-difluoro-derivative. In the dichloro-derivative the conjugation band has suffered a further blue shift and reduction in intensity and takes the form of a broad inflection at *ca.* 230 mμ of about one-third the extinction coefficient of diphenyl itself, and even this is to some extent due to overlapping by more intense bands at much shorter wavelength. In 2 : 2′-dibromodiphenyl there is a very faint inflection at *ca.* 228 mμ; the total intensity in this region is about twice that of the dichloro-derivative, presumably because of a larger red shift of the intense short-wave bands. In 2 : 2′-di-iododiphenyl the spectrum is quite different, showing a broad but resolved band with a maximum at 230 mμ, well separated from the band at shorter wavelength, which is of rather lower intensity than in the other 2 : 2′-dihalogenodiphenyls. Comparison of this spectrum with those of iodobenzene and iodotoluene strongly suggested that the 230 mμ band can be identified as that of the iodophenyl chromophore, occurring at about the same wavelength but showing some vibrational fine structure in iodobenzene; its intensity (*ca.* 20,000) is also comparable with the expected value (*ca.* 27,000) for two

TABLE 3. *Ultraviolet absorption spectra of* 2 : 2′-*dihalogenodiphenyls, halogenobenzenes, and* o-*halogenotoluenes.*

| | | Short-wave bands. | | | | Conjugation band | | Long-wave band |
|---|---|---|---|---|---|---|---|---|
| Compound | | | min. | max. | min. | max. | min. | max. |
| 2 : 2′-Difluorodiphenyl | λ | — | — | <200 | 216 | 233·5 | 259 | 268 |
| | ε | — | — | >35,000 | 7100 | 13,800 | 3000 | 3400 |
| 2 : 2′-Dichlorodiphenyl | λ | — | — | 208 | — | (230) | 264 | 273·5 |
| | ε | — | — | 36,000 | — | 6,600 | 700 | 540 |
| | λ | — | — | — | — | — | — | 266·5 |
| | ε | — | — | — | — | — | — | 735 |
| 2 : 2′-Dibromodiphenyl | λ | — | — | *ca.* 206 | — | (*ca.* 228) * | 265 | 274·5 |
| | ε | — | — | *ca.* 37,000 | — | 12,000 | 620 | 430 |
| | λ | — | — | — | — | — | — | 267·5 |
| | ε | — | — | — | — | — | — | 640 |
| 2 : 2′-Di-iododiphenyl | λ | *ca.* 204 | 222 | 230 | — | Absent | — | (*ca.* 280) |
| | ε | *ca.* 32,000 | 19,700 | — | — | — | — | 840 |
| | λ | — | — | 19,100 | — | — | — | (*ca.* 273) |
| | ε | — | — | — | — | — | — | 1200 |
| Fluorobenzene [20] ...... | λ | — | — | — | 222 | — | — | 260 fs |
| | ε | — | — | — | 6·7 | — | — | 1060 |
| *o*-Fluorotoluene [22]...... | λ | — | — | — | — | — | — | 268 fs |
| | ε | — | — | — | — | — | — | 910 |
| Chlorobenzene [20] ...... | λ | — | — | <219 | 235 | — | — | 265 fs |
| | ε | — | — | >5700 | 22·3 | — | — | 236 |
| *o*-Chlorotoluene [22] ... | λ | — | — | — | 237 | — | — | 266 fs |
| | ε | — | — | — | 37 | — | — | 390 |
| Bromobenzene [20] ...... | λ | — | — | (223) | 248 | — | — | 265 fs |
| | ε | — | — | 5940 | 101 | — | — | 204 |
| *o*-Bromotoluene [22] ... | λ | — | — | — | 250 | — | — | 267 fs |
| | ε | — | — | — | 130 | — | — | 420 |
| Iodobenzene [20] ......... | λ | — | *ca.* 215 | 228 fs | 244 | — | — | 258 fs |
| | ε | — | *ca.* 6900 | 13,300 | 534 | — | — | 693 |
| *o*-Iodotoluene [22] ...... | λ | — | — | — | 252 | — | — | 261 fs |
| | ε | — | — | — | 900 | — | — | 1130 |

* Very faint.

Wavelengths in mμ; figures in parentheses refer to inflections; fs denotes resolved fine structure, with figures given for principal maxima. Solvents : diphenyls, 96% ethanol; halogenobenzenes,[20] *iso*octane; *o*-halogenotoluenes,[22] hexane.

iodophenyl groups. The spectrum of 2 : 2′-di-iodiphenyl is therefore that of a severely hindered and markedly non-coplanar diphenyl, in which there is no evidence of conjugation and which is qualitatively, and to a large extent quantitatively, in agreement with the additive absorption of two independent iodophenyl chromophores.

The spectra of 2 : 2′-dichlorodiphenyl (cf. Friedel and Orchin [28]) and of 2 : 2′-dibromodiphenyl also exhibit resolved low-intensity long-wave fine structure. In the 2 : 2′-di-iodo-derivative the only long-wave features are two faint inflections. As in 2 : 2′-difluorodiphenyl, these long-wave features can be regarded as absorption contributions of the halogenobenzene partial chromophores, but with intensities determined to varying extents by overlapping conjugation band contributions.

Quantitative comparisons with the spectra of the *o*-halogenotoluenes are best made at the wavelengths corresponding to the principal long-wave maxima and the principal minima of these compounds. The ratios listed in Table 4 are the extinction coefficients of the diphenyls divided by *twice* the extinction coefficients of the corresponding *o*-halogenotoluenes, at these wavelengths. If the total absorption of the diphenyl were simply the additive contributions of two non-conjugated halogenophenyl chromophores, these ratios should be about unity. Table 4 shows that for the longer wavelength comparison ($\lambda_{max.}$ of *o*-halogenotoluene) the ratio is approximately unity for the dichloro-, dibromo-, and di-iodo-diphenyls, but nearly 2 for 2 : 2′-difluorodiphenyl, in which the conjugation band makes an appreciable contribution to the total absorption at this wavelength. At the shorter wavelength ($\lambda_{min.}$ of *o*-halogenotoluene) the ratio is very much greater than unity for all but the iodo-derivatives, indicating that the total absorption in this region still contains a contribution from a conjugation band, even in the case of 2 : 2-dibromodiphenyl.

TABLE 4. *Comparison of molecular-extinction coefficients of* 2 : 2′-*dihalogenodiphenyls and corresponding* o-*halogenotoluenes at selected wavelengths.*

| Halogen | $\lambda_1$ [a] | $\varepsilon_{DP}/2\varepsilon_T$ [b] | $\lambda_2$ [c] | $\varepsilon_{DP}/2\varepsilon_T$ |
|---|---|---|---|---|
| (H) | 262 [d] | 17 | 231 [d] | 163 |
| F | 268 | 1·9 | 235 [e] | 98 [f] |
| Cl | 266 | 0·93 | 237 | 63 |
| Br | 267 | 0·76 | 250 | 5·5 |
| I | 261 | 0·87 | 252 | 1·7 |

[a] Wavelength of principal maximum of *o*-halogenotoluene, mμ; ethanol. [b] Molecular-extinction coefficients of 2 : 2′-dihalogenodiphenyl ($\varepsilon_{DP}$) and of corresponding *o*-halogenotoluene ($\varepsilon_T$), both at the indicated wavelength. [c] Wavelength of minimum of *o*-halogenotoluene, mμ; ethanol. [d] Toluene in ethanol (data from references given by Jones, *Chem. Rev.*, 1943, **32**, 1). [e] Estimated, short extrapolation. [f] From data for fluorobenzene.

The 2 : 2′-dihalogenodiphenyls thus form a series in which the spectroscopic indications of conjugation and of halogenophenyl partial chromophore absorption vary continuously from the slightly hindered difluoro-compound to the severely hindered di-iodo-compound.

In spite of the uncertainty attaching to the values of $\theta$ for non-bridged diphenyls, it is of interest to compare the spectra of such compounds with those of bridged diphenyls having similar angles between the benzene ring planes. For a compound with an *ortho* : *ortho*′ bridge of three carbon atoms $\theta$ is 49° and with a bridge of four carbon atoms $\theta$ is 59° (calculated values). In the latter case (*e.g.*, in dimethyl 4 : 5-6 : 7-dibenzo*cyclo*octa-4 : 6-diene-1 : 2-carboxylate [29]) the conjugation band ($\lambda_{max.}$ 236·5 mμ, $\varepsilon_{max.}$ *ca.* 13,000) shows a blue shift and a reduction in intensity comparable to that shown by 2 : 2′-difluorodiphenyl. The similarity between the value of $\theta$ for the bridged compound and that (electron diffraction or calculated) for 2 : 2′-difluorodiphenyl is striking. Equally striking is the correlation between the great reduction in conjugation, judged spectroscopically, and the large increase in $\theta$ in passing from the difluoro- to the dichloro-compound.

The 2 : 2′-dialkyldiphenyls are a simpler series of compounds in which to study the

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[28] Friedel and Orchin, ref. 4, No. 182.

[29] Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

spectroscopic effects of *ortho*-substitution in the diphenyl structure. However, the smallest alkyl group (methyl) is of comparable size to bromine (van der Waals radii 2·0 and 1·95 Å, respectively); whereas only with fluorine as an *ortho-ortho'* substituent is the value of $\theta$ (calculated for the " *cis* " " touching " conformation) small enough to be comparable with those calculated for the 2 : 2'-bridged diphenyls. The persistence of the conjugation band in 2 : 2'-difluorodiphenyl and in the bridged compounds and its almost complete repression in the 2 : 2'-dialkyldiphenyls [30] and in the other 2 : 2'-dihalogenodiphenyls therefore appear in both series of compounds to be consistent with the calculated $\theta$ values.

An interesting spectroscopic confirmation of the steric effects of 2 : 2'-difluoro- and 2 : 2'-dichloro-substituents in diphenyl comes from the study by Lewis and Kasha [31] of the phosphorescence spectra involving a triplet excited state with a central double bond (I and related resonance structures; each asterisk denoting an unpaired electron). Compared with diphenyl (wavenumber, $\bar{\nu}_p$, of highest frequency phosphorescence band, 22,800 cm.$^{-1}$) the halogenated derivatives show blue shifts of 1600 cm.$^{-1}$ (2 : 2'-difluoro) and 2200 cm.$^{-1}$ (2 : 2'-dichloro), due to steric inhibition of the resonance stabilization of the triplet excited state. From a comparison with the $\bar{\nu}_p$ value for 2 : 2' : 6 : 6'-tetrachlorodiphenyl, Lewis and Kasha concluded that the inhibtion was substantially complete with two *o*-chloro-substituents. The magnitudes of the blue shifts of $\bar{\nu}_p$ in the phosphorescence spectra are compared with the shifts ($\Delta\bar{\nu}$) of the conjugation band of the ordinary absorption spectra (singlet-singlet transitions) in Fig. 4.

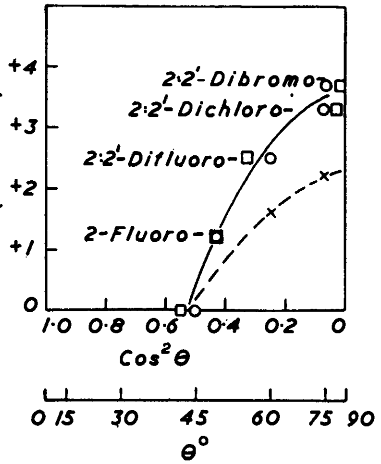
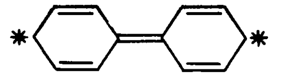
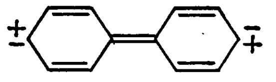


FIG. 4. *Frequency shift* ($+\Delta\bar{\nu}$) *of conjugation band maximum against* cos$^2\theta$ ($\theta$ = *angle between planes of benzene rings*).

○ Values of $\theta$ from electron diffraction.
□ Calculated values of $\theta$ for the " *cis* " conformation.
× Frequency shifts ($+\Delta\bar{\nu}_p$) of triplet-singlet phosphorescence band.



(I)



(II)

If the excited state of diphenyl is a dipolar (and more nearly coplanar) structure with a $C_{(1)}$–$C_{(1')}$ linkage of essentially complete double-bond character (*e.g.*, II; cf. Calvin,[8] Braude [32]) then the short-wave shift of the conjugation band in an *ortho*-halogenodiphenyl might arise from an increase in transition energy due mainly to a raising of the energy of the *excited* state, which will be more sensitive to *ortho*-steric effects than the ground state. On this basis a correlation might be expected between the steric requirements of the *ortho*-substituents, as indicated by the angles between the planes of the benzene rings in the

[30] Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131; Everitt. Hall. and Turner, *J.*, 1956, 2286.
[31] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[32] Braude, *Experentia*, 1955, **11**, 457.

ground state, and the short-wave shift, expressed on an energy scale (*i.e.*, $\Delta\bar{\nu}$). In fact, the electron-diffraction or calculated values of $\theta$ (Table 1) being used, plots of $\Delta\bar{\nu}$ (from Table 3) against $\cos^2\theta$ (cf. Dewar [33]) fall on a smooth curve (Fig. 4). The $\Delta\bar{\nu}_p$ values for the triplet states of 2 : 2′-difluoro- and 2 : 2′-dichloro-diphenyl also show a correlation with $\cos^2\theta$, though the smaller frequency shifts are at variance with the expectation that the triplet excited state is extremely sensitive to steric strain (Lewis and Kasha [31]). In view of the large effects of halogen substituents on the intensities and transition energies of aromatic chromophores the broad correlation between $\theta$ and $\Delta\bar{\nu}$ is perhaps as good as can be expected, and other series of substituted diphenyls may provide spectroscopic data more suitable for analysis along these lines.

The smallest blue shift, not complicated by methyl-group effects, observed in the present work is 1300 cm.$^{-1}$ (3·7 Kcal./mole) for 2-fluorodiphenyl; for the 2 : 2′-difluoro-compound $\Delta\bar{\nu}$ is 2700 cm.$^{-1}$ (7·7 Kcal./mole). For comparison, the blue shift in the triplet state of the 2 : 2′-difluoro-compound is $\Delta\bar{\nu}_p = 1600$ cm.$^{-1}$ (4·6 Kcal./mole). For the introduction of substituents into diphenyl itself, changes of this magnitude in the energy barrier to free rotation could not give rise to optical activity detectable by any known technique; among diphenyls with *o*-halogeno-substituents unstable optical activity first appears with a dibromo-derivative, in 2 : 2′-dibromodiphenyl-4 : 4′-dicarboxylic acid.[34] Nevertheless, it must be remembered that in a more hindered diphenyl (*i.e.*, one in which some small *ortho*-substituents are already present) the introduction of a single fluorine atom into the *ortho*-position is sometimes sufficient to produce observable (unstable) optical activity, not present in the parent compound (*e.g.*, 2′-fluoro-5′-methyl-6-nitrodiphenyl-2-carboxylic acid [35]). The appearance of (unstable) optical isomerism may on occasion, therefore, be just as sensitive a tool as ultraviolet absorption for the investigation of steric effects in diphenyls but is applicable to a different range of compounds. Optical resolvability (which implies considerable optical stability) is, however, a much less sensitive index of small steric effects (cf. Braude and Waight [36]).

## EXPERIMENTAL

2-Fluorodiphenyl (m. p. 72·5—73·5°), 2 : 2′-difluorodiphenyl (m. p. 118·5—119·5°), and 3 : 3′-difluorodiphenyl (m. p. 7·1—7·2°, b. p. 102°/2 mm.) were made by the standard method involving the thermal decomposition of a diazonium borofluoride.

The other fluoro-compounds were made available to us by Professor E. E. Turner, F.R.S., and the other 2 : 2′-dihalogenodiphenyls by Dr. J. W. Smith.

The spectra were measured on a Unicam SP. 500 spectrophotometer. Fine structure and inflections were detected photographically by the logarithmic-cam, moving-plate method.[37]

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[33] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3345.
[34] Searle and Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 2112.
[35] Stoughton and Adams, *ibid.*, 1932, **54**, 4426.
[36] Braude and Waight, " Progress in Stereochemistry," Vol. I (Ed. Klyne), Butterworths, London, 1954, p. 143.
[37] Holiday, *J. Sci. Instr.*, 1937, **14**, 166.