The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part III. The Ultra-violet Absorption Spectra of Some 2 : 2'-Bridged Compounds with* meta-*Substituents.*

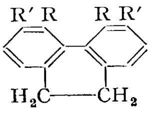
By G. H. BEAVEN, D. MURIEL HALL, MARY S. LESSLIE, E. E. TURNER, and
(in part) GWENDOLINE R. BIRD.

[Reprint Order No. 4472.]

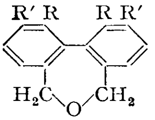
The ultra-violet absorption spectra of the 2 : 2'-bridged diphenyls (I, II, III; R = H, R' = OMe) indicate that the *mm'*-methoxyl groups reduce the conjugation across the 1 : 1'-bond by mesomeric interaction with the separate benzene rings to which they are attached. This finding supports the view, put forward in Part I (*J.*, 1952, 854), that in non-coplanar diphenyls of this type there is still appreciable conjugation which is reduced by the introduction of either *oo'*- or *mm'*-methoxyl groups; even in the *oo'*-case (because of the non-coplanar configuration of the diphenyl skeleton) the effect of these substituents is not primarily steric.

The spectrum of 2 : 2'-ditolyl has been redetermined and some new fine-structure observed. The spectrum indicates that this compound, in which there is some steric hindrance to free rotation, is still weakly conjugated; as in the other compounds examined, the conjugation is further diminished by the introduction of *mm'*-methoxyl groups.

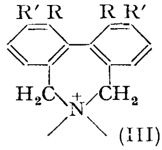
IN Part I (*J.*, 1952, 854) the configurations of molecules of the types (I), (II), and (III) were discussed. The changes in the ultra-violet absorption spectra of the rigidly bridged and non-coplanar compounds (R = R' = H) resulting from the introduction of methoxyl groups into the *ortho*-positions (R = OMe, R' = H) were considered, in the cases of compounds (II) and (III), to be due primarily to mesomeric interaction between the methoxyl groups and the separate benzene rings to which they are attached, with consequent reduction in the conjugation between the two rings. Only for the most nearly coplanar compound (I) (R = OMe, R' = H) are steric effects also likely to be appreciable. If this hypothesis is correct, and if the *o*-methoxyl groups in compounds (II) and (III) have, as we believe, no determinative steric effect, the introduction of methoxyl groups into the *mm'*-positions instead of the *oo'*-positions might be expected to have somewhat similar effects on the spectra of compounds (II) and (III).



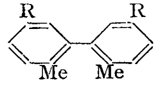
(I)



(II)



(III)



(IV)

For the synthesis of compounds (I), (II), and (III) (R = H, R' = OMe) it was necessary to obtain a considerable quantity of 5 : 5'-dimethoxydiphenic acid. This substance was made by Adams and Kornblum (*J. Amer. Chem. Soc.*, 1941, **63**, 188) by deaminating 4 : 4'-diamino-5 : 5'-dimethoxy-2 : 2'-ditolyl and oxidising the ditolyl, but the overall yield was not very good. The Vorländer diphenic acid synthesis from 2-amino-4-methoxybenzoic acid had been shown by Fieser (*J. Amer. Chem. Soc.*, 1929, **51**, 2471) to be unsatisfactory as a large-scale preparative method, and we found that attempted repetition of Ullmann and Dootson's reduction (*Ber.*, 1918, **51**, 9) of 4-methoxy-2-nitrobenzoic acid was accompanied by extensive decarboxylation. Moreover, the preparation of its precursor, 3-nitro-*p*-cresol,† by the diazo-method from 3-nitro-*p*-toluidine,† described by Ullmann and Dootson (*loc. cit.*) and by Nevile and Winther (*Ber.*, 1882, **15**, 2976), proved very unsatisfactory.

---

* Part II, *J.*, 1953, 2456.

† OH or NH_2 is numbered 1 (cf. *J.*, 1952, 5088, 5090, 5091) in these and similar compounds.

We finally based our synthesis on 3-methoxy-*o*-toluidine hydrochloride, which could be made in large quantities by the sequence : *p*-cresol ⟶ *p*-tolyl carbonate ⟶ di(nitro-*p*-tolyl) carbonate ⟶ 3-nitro-*p*-cresol ⟶ 4-methoxy-2-nitrotoluene ⟶ 3-methoxy-*o*-toluidine hydrochloride. Replacement of the amino-group by iodine by the diazo-method gave 2-iodo-4-methoxytoluene as a liquid, though Willgerodt and Schloss (*Ber.*, 1911, **44**, 1708), who obtained it as one of the two products of iodinating methyl *p*-tolyl ether with iodine monochloride, described it as melting at 75°. In our hands this iodination leads to not less than 80% of 3-iodo-4-methoxytoluene, m. p. 30—31°, the rest being the liquid 2-iodo-compound. An Ullmann (copper bronze) reaction converted the 2-iodo-compound into 5 : 5′-dimethoxy-2 : 2′-ditolyl, from which 5 : 5′-dimethoxydiphenic acid was obtained by oxidation.

Reduction of the methyl ester of the diphenic acid gave 2 : 2′-bishydroxymethyl-5 : 5′-dimethoxydiphenyl, which passed readily into 2 : 7-dihydro-3′ : 2″-dimethoxy-3 : 4-5 : 6-dibenzoxepin in presence of 50% sulphuric acid and into 2 : 2′-bisbromomethyl-5 : 5′-dimethoxydiphenyl on treatment with phosphorus tribromide. This dibromo-compound was converted into 9 : 10-dihydro-3 : 6-dimethoxyphenanthrene by use of phenyl-lithium and into 2 : 7-dihydro-3′ : 2″-dimethoxy-3 : 4-5 : 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide by the action of piperidine. It was incidentally observed that alcoholic solutions of 9 : 10-dihydro-3 : 6-dimethoxyphenanthrene underwent oxidation in sunlight and deposited crystals of 3 : 6-dimethoxyphenanthraquinone.

The absorption spectrum of the *mm*′-dimethoxyoxepin (Fig. 1) is similar to that of the *oo*′-dimethoxyoxepin, showing some reduction in intensity of the conjugation band ($\lambda_{\text{max.}}$ 2550 Å, ε 11,000) compared with the parent, unsubstituted, oxepin ($\lambda_{\text{max.}}$ 2500 Å, ε 16,500), and the appearance of long-wave absorption. The reduction in intensity is, however, less than that observed in the *ortho*-compound ($\lambda_{\text{max.}}$ 2530 Å, ε 8650) and the long-wave band is of lower intensity ($\lambda_{\text{max.}}$ 2860 Å, ε 5600, compared with $\lambda_{\text{max.}}$ 2935 Å, ε 9950). The very intense short-wave absorption has here been observed as a band with $\lambda_{\text{max.}}$ 2220 Å (ε 51,000), well separated from the conjugation band, which, however, it obviously overlaps.

Ultra-violet absorption spectra.

(Wave-lengths in parentheses denote unresolved inflections.)

					Conjugation band				Benzenoid band	
Compound	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	$\varepsilon_{\text{min.}}$	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	$\varepsilon_{\text{min.}}$	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$
(I; R = H, R′ = OMe)	*ca.* 2150	*ca.* 40,000	2470	5550	2690 2610	12,000 11,500	2815 —	2800 —	3217 3115 (2965) (2850)	8200 7600 4800 3000
(II; R = H, R′ = OMe)	2220	51,000	2460	9450	2550	11,000	2710	3200	(2960) 2860	4800 5600
(III; R = H, R′ = OMe)	2260	54,500	2500	9900	2570	10,500	2770	3650	(2970) 2845	3000 4200
(II; R = H, R′ = $CH_2{\cdot}OH$)	2150	44,000	2340	6450	2540	14,500	—	—	—	—
(IV; R = H)	—	—	—	—	(*ca.* 2270)	6,800	2605	770	2708 2635	600 800
(IV; R = OMe)	—	—	—	—	—	—	2530	860	2869 2787	5550 5700

The absorption spectrum of the azepinium bromide (Fig. 1) is likewise very similar to that of the *oo*′-compound. The conjugation band ($\lambda_{\text{max.}}$ 2570 Å, ε 10,500) is of similar intensity, but is displaced to longer wave-length compared with the unsubstituted compound, whereas the *ortho*-compound shows a short-wave shift. Moreover, in the *meta*-compound the long-wave band is considerably less intense than in the *ortho*-compound ($\lambda_{\text{max.}}$ 2845 Å, ε 4200, compared with $\lambda_{\text{max.}}$ 2975 Å, ε 10,500). Here again an intense short-wave band ($\lambda_{\text{max.}}$ 2260 Å, ε 54,500) has been observed.

Thus in both the oxepin and the azepinium bromide the *mm*′-methoxyl groups cause some reduction in conjugation across the 1 : 1′-bond and correspondingly the appearance of long-wave selective absorption arising from the unconjugated benzenoid partial chromophores, although in these compounds the methoxyl groups cannot have any steric effect on the configuration of the diphenyl skeleton.

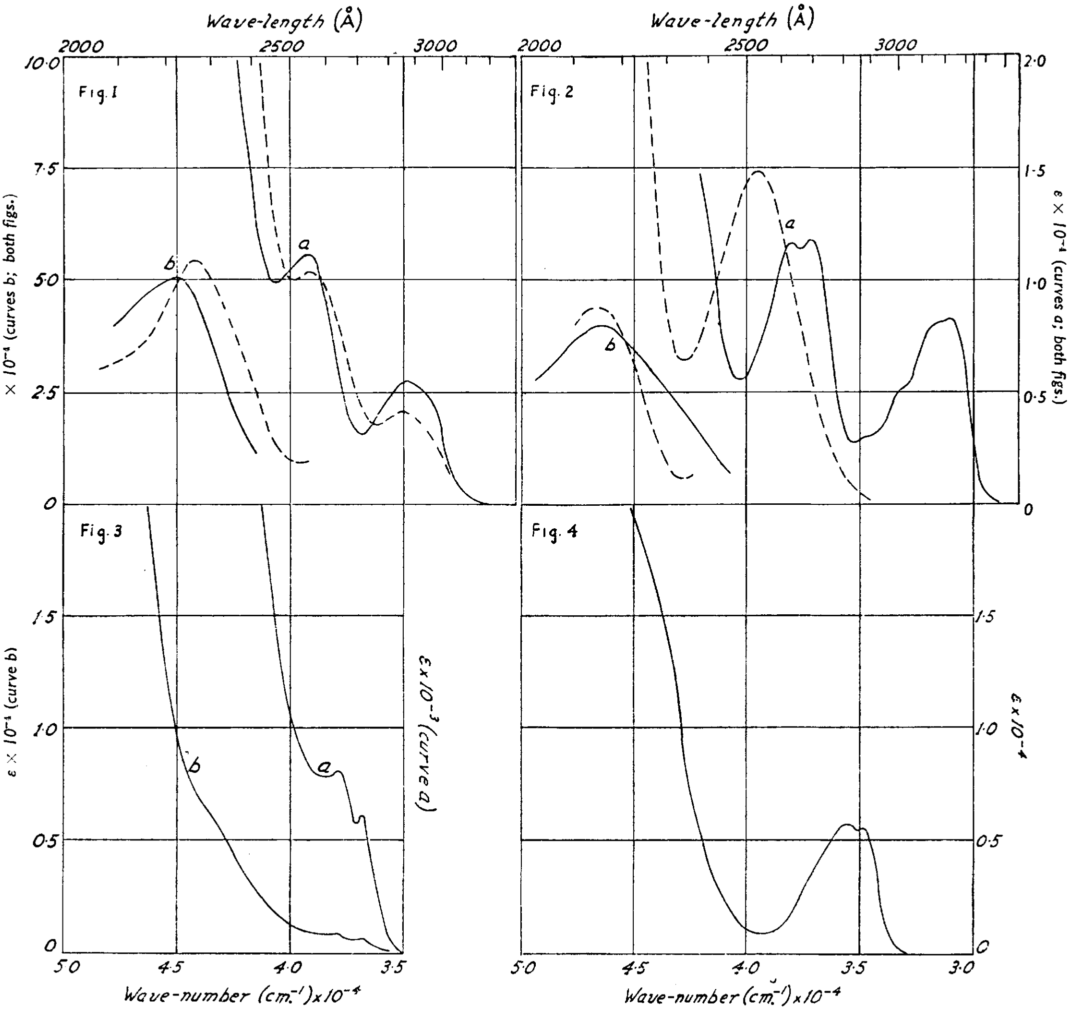


FIG. 1. ——— 2 : *7-Dihydro-3′* : *2″-dimethoxy-3* : 4-5 : *6-dibenzoxepin* (II; R = H, R′ = OMe).
– – – – 2 : *7-Dihydro-3′* : *2″-dimethoxy-3* : 4-5 : *6-dibenazapinium*-1-spiro-1‴-*piperidinium bromide* (III; R = H, R′ = OMe).
FIG. 2. ——— 9 : *10-Dihydro-3* : *6-dimethoxyphenanthrene* (I; R = H, R′ = OMe).
– – – – 2 : *7-Dihydro-3′* : *2″-bishydroxymethyl-3* : 4-5 : *6-dibenzoxepin* (II; R = H, R′ = CH_2·OH).
FIG. 3. 2 : *2′-Ditolyl* (IV; R = H).
FIG. 4. 5 : *5′-Dimethoxy-2* : *2′-ditolyl* (IV; R = OMe).

It was suggested in Part I that in 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene some distortion of the molecule occurs in order to accommodate the methoxyl groups and that this distortion may take the form of out-of-plane bending of the methoxyl groups, rather than an increased departure from coplanarity of the phenyl rings. The methoxyl groups would thus be expected to have a smaller effect in reducing conjugation across the 1 : 1′-bond than they do in the corresponding oxepin and azepinium bromide. If this hypothesis is correct, we should expect 9 : 10-dihydro-3 : 6-dimethoxyphenanthrene (where no such distortion is required) to show at least as much reduction in conjugation as the *ortho*-compound, rather than the somewhat lessened reduction in conjugation exhibited in the *meta*-series of oxepin and azepinium compounds. The absorption spectrum of 9 : 10-dihydro-3 : 6-dimethoxyphenanthrene (Fig. 2) does in fact show a small short-wave shift and slightly reduced intensity in the conjugation band compared with the *ortho*-compound. It also shows the remarkable feature of the splitting of the conjugation band into two separate maxima ($\lambda_{max.}$ 2690 Å, 2610 Å; ε 12,000, 11,500; for the *o*-compound $\lambda_{max.}$ 2720 Å, ε 13,500), a phenomenon which, to our knowledge, has not previously been recorded for the conjugation bands proper of substituted diphenyls; in the present case this splitting cannot be due to overlapping by the absorption bands of the benzenoid partial chromophores, as these are well separated at longer wave-length. The long-wave band is also slightly reduced in intensity compared with the *ortho*-compound ($\lambda_{max.}$ 3217 Å, ε 8200, compared with $\lambda_{max.}$ 3045 Å, ε 9300) but this reduction is much less than that observed in the 7-membered ring compounds. Thus the absorption spectrum of (I; R = H, R′ = OMe) does not provide much additional support for the hypothesis of out-of-plane bending of the methoxyl groups in the related *ortho*-compound but is still consistent with the indications from the corresponding oxepin and azepinium bromide that the *mm*′-methoxyl groups interact with the separate benzene rings in such a manner as to reduce the conjugation between the latter.

Attempts to obtain salts of the azepinium ion (III; R = H, R′ = OMe) in enantiomorphous forms were unsuccessful. Crystallisation of the (+)-camphorsulphonate from acetonitrile gave no indication of resolution. Fractional crystallisation of the (+)-α-bromocamphor-π-sulphonate from benzene appeared more promising as there seemed to be appreciable differences in the solubilities of various crops; over 30 were examined but it was difficult to follow the course of any separation polarimetrically owing to solvation of many of the fractions, and no real evidence of resolution was obtained.

Attempts were also made to resolve a suitably substituted oxepin. 2 : 2′-5 : 5′-Tetramethoxycarbonyldiphenyl was reduced with lithium aluminium hydride, and the resulting 2 : 2′-5 : 5′-tetrakishydroxymethyldiphenyl converted into 2 : 7-dihydro-3′ : 2″-bishydroxymethyl-3 : 4-5 : 6-dibenzoxepin (II; R = H, R′ = CH_2·OH). The dimenthoxyacetate did not crystallise and, although a crystalline di(hydrogen phthalate) was prepared, we failed to obtain satisfactory alkaloidal salts from it.

Non-resolution is, of course, no proof of the absence of enantiomorphism and we still consider that these compounds have dissymmetric molecules. So far, this has only been demonstrated for the not unequivocal cases of compounds with *ortho*-substituents (cf. Part I, *loc. cit.*; Wittig and Zimmermann, *Ber.*, 1953, **86**, 629).

The absorption spectrum of compound (II; R = H, R′ = CH_2·OH) is of some interest since the hydroxymethyl groups are only weakly auxochromic. The spectrum (Fig. 2) is practically identical with that of the parent unsubstituted oxepin (II; R = R′ = H) (cf. Part I, *loc. cit.*). These two compounds have $\lambda_{max.}$ 2540 Å (ε 14,500) and 2500 Å (ε 16,500), respectively, showing that the *mm*′-bishydroxymethyl groups have only a trivial effect on the location and intensity of the conjugation band of a non-coplanar diphenyl.

Because of the frequently cited steric effects of *oo*′-methyl groups on the coplanarity of diphenyl itself, as inferred from ultra-violet absorption spectra (O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906) and the availability of the related *mm*′-dimethoxy-derivative, the spectra of both ditolyl (IV; R = H) and 5 : 5′-dimethoxy-2 : 2′-ditolyl (IV; R = OMe) have been re-examined. The results for both compounds (Figs. 3 and 4) are in rather poor agreement with the earlier data (*idem, loc. cit.*; see also Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, 1951, No. 163), which were obtained by a photographic method of rather limited precision and not always suited to the detection of fine structure. On cursory inspection the spectrum of 2 : 2′-ditolyl suggests that it is a completely hindered diphenyl with no conjugation between the phenyl groups, and showing low-intensity absorption (with some fine structure not found in the earlier work) in the 2650—2850-Å region arising from the benzenoid partial chromophores. A comparison, however, with the spectra of alkylbenzenes, which may be summarised as having $\lambda_{max.}$ *ca.* 2500—2700 Å with much fine structure ($\varepsilon_{max.}$ *ca.* 300), $\lambda_{min.}$ *ca.* 2300 Å (ε *ca.* 30), $\lambda_{max.}$ below 2100 Å (ε *ca.* 10,000) (see, *e.g.*, American Petroleum Institute Research Project no. 44, Carnegie Institute of Technology, Catalog of Ultraviolet Spectral Data) shows that in 2 : 2′-ditolyl there is much more absorption on the short-wave side of the fine structure than would be expected for the additive absorption of two alkylbenzene chromophores, to the extent that the expected minimum is replaced by a steeply rising curve. Since this absorption occurs at much longer wave-lengths than the intense short-wave band of the alkylbenzene chromophore it is regarded as a vestigial conjugation band which, in comparison with diphenyl, is displaced to shorter wave-length with great reduction in intensity, owing to the higher energy of the excited state resulting from the reduction in resonance stabilisation associated with the 1 : 1′-conjugation (cf. Wheland, "The Theory of Resonance," John Wiley & Sons, Inc., New York, 1944, p. 161). The inflection at *ca.* 2300 Å also supports the suggestion that there is a weak conjugation band in this region which is overlapped by the intense benzenoid short-wave band, here located below 2150 Å with ε not less than 10,000 (per half molecule). The persistence of some conjugation in 2 : 2′-ditolyl is consistent with the view, advanced in Part I, that even in diphenyls which are appreciably non-coplanar significant conjugation is still present and can be detected spectroscopically. The spectrum of 5 : 5′-dimethoxy-2 : 2′-ditolyl (Fig. 4) indicates greatly reduced conjugation, as shown by a further short-wave displacement and intensity reduction of the conjugation band which is now completely merged into the long-wave side of the short-wave benzenoid band. The long-wave absorption band is therefore completely separate at *ca.* 2800 Å with some fine structure and $\varepsilon_{max.}$ *ca.* 5500; these values are consistent with the known absorption characteristics of the phenoxy-chromophore.

EXPERIMENTAL

Absorption spectra were determined in 96% ethanol, on the automatic-recording spectrophotometer designed and built by Holiday and Sutton (Sutton, *Trans. Soc. Inst. Technol.*, 1951, **3**, 157). This instrument gives records which are linear in optical density (*D*) *versus* wave number (ν), and Figs. 1—4 are direct tracings of such records, after application of suitable corrections for the instrument zero and absorption-cell inequalities. All important features of the spectra were also checked on a Unicam SP.500 spectrophotometer, and the wave-lengths of fine-structure maxima and inflections were determined by the moving-plate logarithmic-cam method (Holiday, *J. Sci. Instr.*, 1937, **14**, 166). The solutions used were adjusted to the same molar concentration ($0{\cdot}50 \times 10^{-4}$M) which allows the use of a simple factor for converting *D* into molecular extinction coefficient (ε), *viz.*, multiplying by 2×10^4 in the case of a 1-cm. absorption cell. In our experience, the slight extra labour entailed by working in this manner is more than off-set by the elimination of lengthy replotting which otherwise greatly detracts from the speed and convenience of the automatic-recording instrument. In the present case the use of a fixed concentration is feasible because the available range of *D* (0—1·2) may thus be made to cover a range of 0—24,000 for ε which is well suited to the compounds concerned. For measurements below 2400 Å, 0·20- and 0·10-cm. cells were mainly used, in order to cut down solvent absorption and to minimise stray light errors; these had been evaluated for both the spectrophotometers used.

4-*Methoxy*-2-*nitrotoluene*.—*p*-Tolyl carbonate (720 g.) was nitrated as described by Copisarow (*J.*, 1929, 251). The crude product was hydrolysed by boiling it for a few minutes with 10% sodium hydroxide solution and, after acidification and removal of 2-nitro-*p*-cresol (OH = 1) by steam-distillation, the crude 3-nitro-*p*-cresol was repeatedly extracted with boiling light petroleum (b. p. 80—100°). The yield of crystallised material was 1566 g. (64%) from 1920 g. of *p*-tolyl carbonate. Methylation with methyl sulphate in the presence of aqueous sodium hydroxide, followed by steam-distillation, gave 4-methoxy-2-nitrotoluene in 85% yield.

4-*Methoxy*-2-*nitrobenzoic Acid*.—This was obtained in 42% yield by the oxidation of 4-methoxy-2-nitrotoluene with aqueous potassium permanganate (40% excess). Addition of magnesium sulphate did not improve the yield.

2-*Amino*-4-*methoxybenzoic Acid*.—Reduction of the above nitro-acid (7·0 g.) with stannous chloride and hydrochloric acid gave 0·85 g. (14%) of the required amino-acid, together with

2·5 g. (57%) of *m*-anisidine (confirmed by mixed m. p. of the acetyl derivative with authentic acet-*m*-anisidide). Reduction of the nitro-acid with ferrous sulphate and ammonia also gave the amino-acid in 14% yield. 2-Amino-4-methoxybenzoic acid, after one crystallisation from aqueous alcohol, had m. p. 181° (decomp.); Ullmann and Dootson (*loc. cit.*) give m. p. 172° (decomp.).

3-*Methoxy*-o-*toluidine Hydrochloride.*—This was prepared by reduction of 4-methoxy-2-nitrotoluene with iron filings, water, and a little acetic acid. The mixture was boiled under reflux for 2 hr. and then extracted with hot alcohol. The filtered extract was freed from the bulk of alcohol by distillation and the residue poured into concentrated hydrochloric acid. The hydrochloride crystallised and was dried at 100° (yield 100%).

2-Iodo-4-methoxytoluene, b. p. 107—108°/3 mm., was obtained in 64% yield from the above hydrochloride.

Iodination of Methyl p-*Tolyl Ether.*—The ether (61 g., 1 mol.) was added gradually to a solution in glacial acetic acid of freshly prepared iodine monochloride. A vigorous reaction took place and was completed by boiling under reflux for ½ hour. The mixture was poured into water, and sulphur dioxide was passed in until the oily layer was pale yellow. The oil was separated, dried ($CaCl_2$), and distilled, giving (1) unchanged ether (22 g.), b. p. up to 102°/6 mm., (2) b. p. up to 120°/5 mm. (practically all at 112—114°) (50 g.), and (3) residual dark oil. When fraction (2) was cooled it set almost solid. Successive freezings and filtrations led to 39 g. of almost pure 3-iodo-4-methoxytoluene, which after being twice crystallised from absolute alcohol had m. p. 30—31°.

5 : 5′-Dimethoxy-2 : 2′-ditolyl was obtained in 64% yield by heating 2-iodo-4-methoxytoluene with copper bronze.

5 : 5′-*Dimethoxydiphenic Acid.*—5 : 5′-Dimethoxy-2 : 2′-ditolyl (18 g.) was added to a boiling solution of potassium permanganate (48 g. in 2400 c.c. of water), containing 0·5 g. of manganous sulphate, and the mixture boiled under reflux with stirring. Further quantities of permanganate (12 g. each) were added after approx. 3 and 5 hr., the total time of heating being 7—8 hr. The acid was precipitated with sulphur dioxide, and, after purification through the sodium salt, had m. p. 228° (yield 55%). From each oxidation *ca.* 3 g. of dimethoxyditolyl were recovered. Esterification with methyl alcohol in the presence of sulphuric acid gave the *dimethyl ester* in 90% yield. It crystallised from methyl alcohol in long pointed prisms, m. p. 165—166° (Found : C, 65·1; H, 5·5. $C_{18}H_{18}O_6$ requires C, 65·45; H, 5·5%).

2 : 2′-*Bishydroxymethyl*-5 : 5′-*dimethoxydiphenyl.*—The above ester was reduced with lithium aluminium hydride in ethereal solution, the solid ester being washed into the reaction flask with ether. After 1 hour's boiling the product was decomposed with water and 2N-sulphuric acid, and the ethereal layer separated. (The diol readily underwent dehydration in the presence of more concentrated acid.) The ether was removed and the residual diol crystallised from benzene (yield, 92%). It crystallised in fine needles containing benzene of crystallisation which was readily lost on heating on a water-bath. The unsolvated 2 : 2′-*bishydroxymethyl*-5 : 5′-*dimethoxydiphenyl* had m. p. 107—108° (Found : C, 70·0; H, 6·7. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·6%).

2 : 7-*Dihydro*-3′ : 2″-*dimethoxy*-3 : 4-5 : 6-*dibenzoxepin.*—The diol was melted under boiling water, and an equal volume of 50% sulphuric acid added; the solid oxepin separated at once. It crystallised from alcohol in plates, m. p. 159—160° (Found : C, 74·6; H, 6·4. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%).

2 : 2′-*Bisbromomethyl*-5 : 5′-*dimethoxydiphenyl.*—The above diol (9 g.) was added gradually to phosphorus tribromide (54 g.) with ice-cooling. The mixture was left at room temperature for ½ hr., warmed to 30° for ¼ hr., cooled again, and poured on crushed ice. Solid dibromide separated and was ground with water and dried in a vacuum-desiccator over sodium hydroxide. After one crystallisation from light petroleum (b. p. 60—80°) it had m. p. 113—114° (24·5 g., 92%) (Found : C, 47·9; H, 4·2; Br, 40·3. $C_{16}H_{16}O_2Br_2$ requires C, 48·0; H, 4·0; Br, 39·9%).

9 : 10-*Dihydro*-3 : 6-*dimethoxyphenanthrene.*—2 : 2′-Bisbromomethyl-5 : 5′-dimethoxydiphenyl (20 g.), dissolved in ether (400 c.c.), was added to a warm ethereal solution of phenyllithium (from 1·0 g. of lithium and 10 g. of bromobenzene). Water and a little hydrochloric acid were added and the ethereal layer was separated, washed, and dried. The ether was removed and the remaining liquid distilled under reduced pressure. 9 : 10-*Dihydro*-3 : 6-*dimethoxyphenanthrene* was collected at *ca.* 205—215°/1 mm. and eventually solidified. It was crystallised from methyl alcohol (4·6 g., 38%) and then from light petroleum (b. p. 60—80°) and obtained as diamond-shaped plates, m. p. 80—81° (Found : C, 79·7; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). When an alcoholic solution of 9 : 10-dihydro-3 : 6-dimethoxyphenanthrene was left in sunlight it became yellow and deposited crystals of 3 : 6-dimethoxyphenanthra-

quinone, m. p. 235—236° (uncorr.) [Fieser, *loc. cit.*, records m. p. 235° (uncorr.), 241° (corr.)]. The oxidation occurred in a few hours in strong sunlight.

2 : 7-*Dihydro*-3′ : 2′′-*dimethoxy*-3 : 4-5 : 6-*dibenzazepinium*-1-spiro-1′′′-*piperidinium Iodide*.—A benzene solution of piperidine (9·5 g., 2·2 mols.) was added gradually to 2 : 2′-bisbromomethyl-5 : 5′-dimethoxydiphenyl (20 g., 1 mol.) in benzene. A brisk reaction ensued and the quaternary bromide separated immediately. Water was added and the bromide dissolved very readily. The aqueous solution was washed with ether, and the iodide precipitated by the addition of potassium iodide solution. 2 : 7-*Dihydro*-3′ : 2′′-*dimethoxy*-3 : 4-5 : 6-*dibenzazepinium*-1-spiro-1′′′-*piperidinium iodide* (21·4 g., 94·5%) crystallised from water in needles, m. p. 274—275° (Found : C, 55·9; H, 5·9. $C_{21}H_{26}O_2NI$ requires C, 55·9; H, 5·8%). The *bromide* was prepared by shaking an aqueous solution of the iodide with silver bromide. After removal of the silver iodide the aqueous solution was evaporated to dryness; the bromide crystallised from ethanol in clusters of needles, m. p. 270—271° (Found : Br, 19·7. $C_{21}H_{26}O_2NBr$ requires Br, 19·8%).

2 : 7-*Dihydro*-3′ : 2′′-*dimethoxy*-3 : 4-5 : 6-*dibenzazepinium*-1-spiro-1′′′-*piperidinium* (+)-α-*bromocamphor*-π-*sulphonate* was prepared in aqueous ethanol from the above bromide and the filtered solution evaporated to dryness. The salt (28·5 g.) was crystallised from acetone–light petroleum but there was no indication of separation into diastereoisomerides. Recrystallisation from a large volume of benzene (3 l.) yielded two forms of crystals, stout rhombohedra and sheaves of fine needles, which were easily separated mechanically. The rhombohedral form had $[\alpha]_{5791}$ +52·5°, $[\alpha]_{5461}$ +62·5° (in EtOH) (Found : C, 58·7; H, 6·4. $C_{31}H_{40}O_6NBrS$ requires C, 58·7; H, 6·4%). The needles had $[\alpha]_{5791}$ +45·9°, $[\alpha]_{5461}$ +54·6° (in EtOH) (Found : C, 60·8; H, 6·7. $C_{31}H_{40}O_6NBrS,\frac{1}{2}C_6H_6$ requires C, 60·6; H, 6·4%). Subsequent recrystallisations from benzene confirmed the conclusion that variation in specific rotation could be explained by solvation.

2 : 2′ : 5 : 5′-*Tetramethoxycarbonyldiphenyl*.—3-Iodo-*p*-toluic acid (Klöppel, *Ber.*, 1893, **26**, 1733) was oxidised in 20-g. batches to iodoterephthalic acid by the method of Abbes (*ibid.*, p. 2951) and the dimethyl ester heated with copper bronze (Kenner and Witham, *J.*, 1913, **103**, 232). The reaction mixture was extracted with *o*-dichlorobenzene; the cooled solution deposited the tetra-ester as rhombs, m. p. 145—146°, which resolidified in a second form, m. p. 160—161°. Crystallisation from other solvents usually gave the low-melting form but on one occasion a benzene solution deposited plates, m. p. 158—161° (Kenner and Witham give m. p. 156°).

2 : 2′ : 5 : 5′-*Tetrakishydroxymethyldiphenyl*.—The above ester was reduced with a large excess of lithium aluminium hydride, a Soxhlet apparatus being used as the ester was sparingly soluble in ether. After the addition of water and acid, the ether was removed without separation and the insoluble product filtered. 2 : 2′ : 5 : 5′-*Tetrakishydroxymethyldiphenyl* crystallised from ethanol in needles, m. p. 202—203° (76%) (Found : C, 69·8; H, 6·9. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%).

2 : 7-*Dihydro*-3′ : 2′′-*bishydroxymethyl*-3 : 4-5 : 6-*dibenzoxepin* was obtained in almost quantitative yield by heating the above compound on a water-bath with an excess of 2N-sulphuric acid for 1 hr. The oxepin crystallised from alcohol in plates, m. p. 192° (decomp.) (Found : C, 74·9; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·25%). It was converted into the *di*(*hydrogen phthalate*), which crystallised from aqueous acetic acid in needles, m. p. 179—179·5° (Found : C, 69·1; H, 4·45. $C_{32}H_{24}O_9$ requires C, 69·6; H, 4·35%).

We thank Imperial Chemical Industries Limited for a grant, and Dr. E. R. Holiday for spectroscopic facilities.

Bedford College, University of London.
Medical Research Council Spectrographic Unit,
The London Hospital.

[*Received, July 9th,* 1953.]