Steric Effects of Methoxy-groups in 2,2'-Bridged Biphenyls. Part II.[1]

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Three *o,o'*-dimethoxy-bridged biphenyls, 5,7-dihydro-1,11-dimethoxydibenz[*c,e*]oxepin, 6,7-dihydro-1,11-dimethoxy-6,6-dimethyl-5*H*-dibenz[*c,e*]azepinium bromide (and iodide), and diethyl 6,7-dihydro-1,11-dimethoxy-5*H*-dibenzo[*a,c*]cycloheptene-6,6-dicarboxylate, have been prepared, each in both enantiomeric forms, starting from (+)- and (−)-6,6'-dimethoxydiphenic acid. Their optical stabilities have been determined and the anomalously large steric effect of the *o*-methoxy-groups is discussed. Their o.r.d. spectra have been measured and assignment of absolute configuration has been made; the great variation of the specific rotation of the dibenzocycloheptene with solvent (on the sodium D line) is seen as the effect of solvent on a Cotton effect situated below 220 nm.

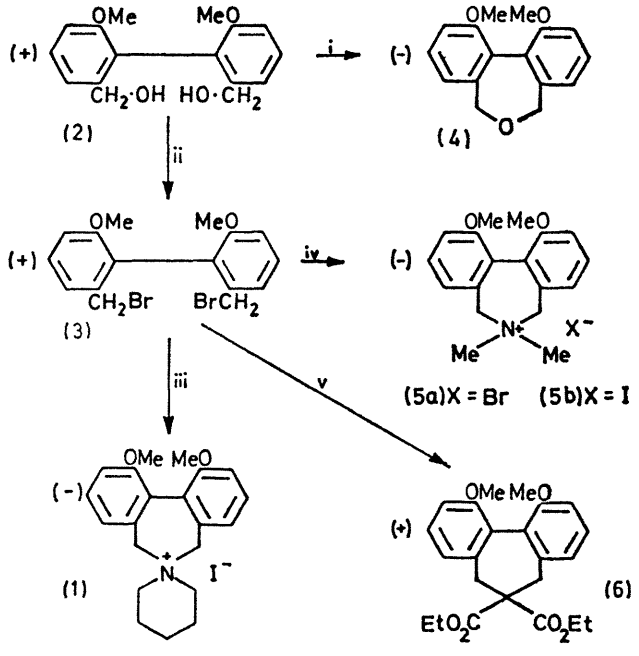
In view of the unexpectedly large steric effect of the methoxy-groups on the optical stability of the spiropiperidinium iodide (1), described in Part I,[1] a number of other bridged biphenyls with seven-membered bridging rings and methoxy-groups in the *ortho*-positions have been prepared in optically active forms and their racemisations studied. In each case the starting point was the optically active diol (2) or dibromide (3) made from resolved 6,6'-dimethoxydiphenic acid.[1] Further details are shown in Scheme 1 for one set of enantiomers.

Dehydration of (+)-diol (2) with 50% sulphuric acid, the method previously [2] used to dehydrate the racemic diol, gave (−)-oxepin (4).

(−)-Dimethyldibenzazepinium bromide (5a), obtained by adding dimethylamine to (+)-dibromide (3) in benzene, became hydrated on treatment with potassium hydroxide solution to remove dimethylamine hydrobromide, and recrystallisation from acetonitrile–ethyl acetate produced three distant crystalline forms of the one hydrate. The first recrystallisation gave a tight mass of needles which disappeared within two or three days and was replaced by large hexagonal prisms. The prisms were transparent in solution but became opaque within a few hours of filtration and later were found to have lost weight (1·7% loss). Subsequent recrystallisations of either type of crystal in more dilute solution usually produced the mass of needles, which changed more slowly (weeks instead of days) into the hexagonal prisms, or into long spines. Infrequently, the optically active bromide crystallised immediately in this form (spines) and, on one occasion, all three crystalline forms were obtained together from the same solution, although only the hexagonal prisms remained several weeks later. When heated, the optically active bromide, whatever the crystalline form, usually passed through two phases of melting and resolidification, the

[1] Part I, D. M. Hall and J. M. Insole, preceding paper.
[2] D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1951, 3072.

first phase (182—184 °C) involving dehydration (and observed only as softening if heating was slow), the second (256—258 °C), melting of the anhydrous bromide; racemisation rapidly followed this second melting, and final melting occurred at the m.p. (*ca.* 330 °C) of the racemate. Sometimes, however, the second



SCHEME 1 Reagents: i, 50% H_2SO_4; ii, PBr_3–C_6H_6; iii, $C_5H_{11}N$; iv, Me_2NH; v, $CH_2(CO_2Et)_2$–NaOEt

melting was not observed, and as the bromide was molten for only a minute or two after the first melting, hardly long enough for substantial racemisation to occur, it appears that racemisation was occurring in the solid state below 256 °C. The racemic bromide remained unhydrated and existed in only one crystalline form.

(—)-Dimethyldibenzazepinium iodide (5b) lost iodine on exposure to the air, although the racemic iodide, with a very different crystalline form, was stable. The (—)-iodide showed a normal melting behaviour, but when kept just above the m.p. (169—170°) for 10—15 min resolidified spontaneously and remelted at the m.p. (328 °C) of the racemic iodide.

The specific rotation of (+)-dibenzocycloheptene (6), obtained from (+)-dibromide (3) by reaction with diethyl malonate in the presence of sodium ethoxide, depended to an unusual degree upon the nature of the solvent (Table 1). The magnitude of specific rotation does not bear any simple relationship to either dielectric constant or refractive index of the solvent; the highest rotations were observed in simple aliphatic solvents (methanol, acetone), and the lowest in homocyclic aromatic solvents (benzene, toluene). A heterocyclic aromatic solvent (pyridine) did not have such a profound effect on the rotation.

In methanol, the o.r.d. spectrum of (+)-(6) (Figure) shows two positive Cotton effects, one, at 249 nm, associated with the inherently dissymmetric biphenyl chromophore, and another of lower rotational strength at *ca.* 280 nm. The second Cotton effect appears, also at *ca.* 280 nm, with benzene as solvent, but the strong absorption of benzene prevents further measurement below 280

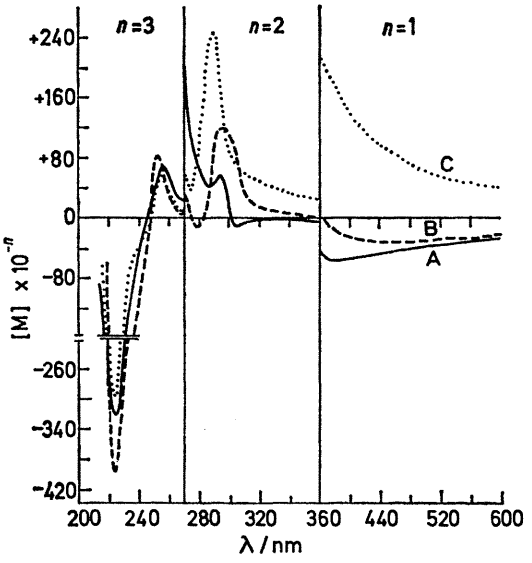
TABLE 1

Specific rotations [a] of (+)-diethyl 6,7-dihydro-1,11-dimethoxy-5*H*-dibenzo[*a*,*c*]cycloheptene-6,6-dicarboxylate (6) in various solvents

Solvent	*c*	$[\alpha]_D$ (°)
Acetone	1·03	+89 [b]
Methanol	1·01	+83 [b]
NN-Dimethylformamide	1·00	+79 [c]
Cyclohexanone	1·08	+78 [c]
Carbon tetrachloride	1·02	+59 [b]
Dioxan	1·01	+52 [d]
Pyridine	2·10	+51 [b]
Cyclohexene	1·00	+40 [c]
2-Phenylethanol	2·01	+26 [c]
Benzene	2·12	+9·6 [b]
Toluene	2·07	+7·4 [b]

[a] l = 1. [b] At 17 °C. [c] At 20 °C. [d] At 23 °C.

nm. The o.r.d. spectrum of (+)-(6) (other enantiomer actually used) in dioxan (*cf.* Table 1) shows only minor differences from its spectrum in methanol, but there is a slight overall negative shift which is even more noticeable in benzene; $[M]_{280}$ (methanol) is +9530°, $[M]_{280}$ (dioxan), +7260°, and $[M]_{280}$ (benzene), +1810°,

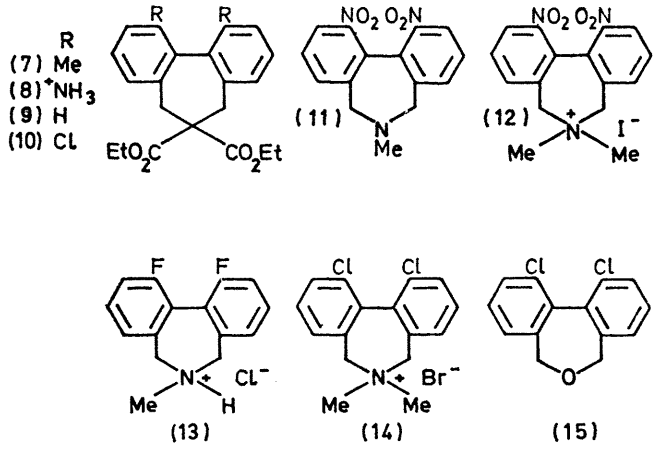


O.r.d. of A, (—)-(4); B, (—)-(5a); and C, (+)-(6) in methanol

whereas $[M]_{224}$ (methanol) is —298,000° and $[M]_{225}$ (dioxan), —323,000°. The effect of solvent therefore appears to be on the negative background rotation rather than on either of the two Cotton effects within instrumental range.

This background rotation, the tailing of a negative Cotton effect of great rotational strength at short wavelengths, dominates the visible region of (—)-(4) and of (—)-(5a), but not of (+)-(6). Although the sign

of rotation in the visible region of most bridged biphenyls with seven-membered bridging rings is determined by a background rotation,[3] two other dibenzocycloheptenes (7) and (8) [and possibly [3] the parent



compound (9) [4]], also show [3] the exceptional dispersion of (6) due, it has been suggested,[3] to the presence of the carboxy-groups. On the other hand, the 1,11-dichlorodibenzocycloheptene (10) has the more usual type of dispersion,[3] and the relationship between background rotation and the large variation of specific rotation with solvent, evident in the case of (+)-(6), is not shown by (+)-(7) which has almost identical specific rotations in dioxan ($[\alpha]_{589}$ +85°) and in benzene ($[\alpha]_D$ +88°).[3]

In the o.r.d. spectrum of (−)-oxepin (4) and (−)-azepinium bromide (5a) in methanol (Figure), a positive Cotton effect associated with the biphenyl conjugation band appears at 246 nm and at 248 nm, respective, and (−)-(5a), like (+)-(6), shows a positive Cotton effect of lower rotational strength at a longer wavelength (*ca.* 285 nm). In contrast, (−)-(4) has a negative Cotton effect at 299 nm. It has been shown [3] with the corresponding bridged 6,6′-dimethyl- and 6,6′-dichlorobiphenyls that a positive Cotton effect at *ca.* 245 nm is characteristic of the *R*-configuration; it thus appears that the compounds shown in Scheme 1 all have the *R*-configuration.

Racemisation Studies.—The racemisation of both azepinium bromide (5a) and iodide (5b) was studied in *NN*-dimethylformamide, the solvent used for the racemisation of the spiropiperidinium iodide (1).[1] The iodide (5b) racemised fractionally more slowly than the bromide (5a), and as the change in anion should have no effect on the racemisation process, this could be due to the introduction of a trace of water into the solution from the hydrated bromide.

The racemisation of oxepin (4) was studied in dimethylformamide, to allow comparison with the azepinium salts, and in 2-phenylethanol; racemisation occurred rather more quickly in dimethylformamide than in 2-phenylethanol.

An attempt was made to investigate the racemisation of the dibenzocycloheptene (6) in dimethylformamide. Runs at five temperatures over the range 161—196 °C were made, but at the higher temperatures some decomposition of solvent occurred. In addition, reaction (1) between the dibenzocycloheptene and a solvent decomposition product or the solvent itself could not be ruled out. A solution of (−)-(6) in dimethylformamide was heated until complete racemisation had occurred, and racemised product was recovered with m.p. 99 °C (pure racemate, 103—104 °C). Thermodynamic parameters were calculated from the five rate constants (Table 2), although their reliability must be suspect. As there was the possibility of a transesterification occurring with 2-phenylethanol, the racemisation was eventually studied in cyclohexanone in which it

$$-CO_2Et + HCO{\cdot}N(Me)_2 \rightleftharpoons -CO{\cdot}N(Me)_2 + HCO_2Et \quad (1)$$

occurred somewhat more rapidly than in dimethylformamide.

Thermodynamic parameters for the racemisation of all compounds are in Table 2. The accuracy of the values for the spiropiperidinium iodide (1) is less than that for the other compounds because the rate constants for (1) were determined on chemically impure material.[1] However, over the temperature range of the racemisation experiments, the iodide (1) and the dimethylazepinium salts (5a) and (5b) have almost identical optical stabilities, suggesting perhaps that the

TABLE 2

Racemisation data

	$t_{\frac{1}{2}}$/min	ΔE kcal mol^{-1}	log A/s^{-1}	$\Delta F^{\ddagger}$ [a] kcal mol^{-1}	$\Delta H^{\ddagger}$ [b] kcal mol^{-1}	$\Delta S^{\ddagger}$ [b] cal mol^{-1} K^{-1}	Solvent
(4)	110 at 100·7 °C	28·2	12·5	29·0	27·5	−3·8	Dimethylformamide
(4)	130 at 101·1 °C	29·9	13·4	29·0	29·1	+0·4	2-Phenylethanol
(1)	250 at 158 °C	34	13	34	33	−2·4	Dimethylformamide
(5a)	89 at 167·8 °C	36·0	13·9	34·0	35·1	+2·4	Dimethylformamide
(5b)	94 at 167·8 °C	35·6	13·7	34·1	34·7	+1·4	Dimethylformamide
(6)	106 at 183·2 °C	36·1	13·3	35·5	35·2	−0·6	Dimethylformamide
(6)	91 at 183·2 °C	34·1	12·4	35·3	33·2	−4·5	Cyclohexanone

[a] At highest temperature at which measurements were made. [b] Mean of values for each temperature at which rates were measured. 1 kcal = 4·186 kJ.

[3] K. Mislow, M. A. W. Glass, R. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455.

[4] D. C. Iffland and H. Siegel, *J. Amer. Chem. Soc.*, 1958, **80**, 1947.

results for (1) are not all that inaccurate, even though the E_{rac} for (5a) and (5b) are higher than that for (1); the higher values of E_{rac} for (5a) and (5b) are almost exactly counterbalanced by positive entropies of activation.

The results confirm that the 1,11-dimethoxyazepinium salts are more optically stable than the 1,11-dinitroazepine (11) (E_{rac} 30·0 kcal mol^{-1}; $\Delta S^{\ddagger}$ −8·3 cal mol^{-1} K^{-1}; $t_{\frac{1}{2}}$ at 145 °C, 156 min in benzene).[5] The anomalous steric effect of the methoxy-groups is obviously showing itself in the activation energy rather than in the entropy term, as the comparatively large entropy change for the dinitroazepine is tending to make it more, not less, optically stable than the dimethoxy-compounds. However, it is known that the valency state of the bridge nitrogen has an effect on optical stability. The dinitroazepinium iodide (12) is twice as optically stable as (11) at 145 °C ($t_{\frac{1}{2}}$ 4·75 h in acetone) [5] but, even so, is less optically stable than the dimethoxyazepinium salts. The racemisation of (12) was studied only at this one temperature and, in the absence of values for E_{rac} and $\Delta S^{\ddagger}$, it is impossible to make a more detailed comparison.

Racemisation parameters have been determined for two other *o,o'*-substituted dibenzazepinium salts, (13) (E_{rac} 27·8 kcal mol^{-1}; $\Delta S^{\ddagger}$ −2·9 cal mol^{-1} K^{-1}; $t_{\frac{1}{2}}$ at 91 °C, 119 min in aqueous hydrochloric acid) [5] and (14) (E_{rac} 38·3 kcal mol^{-1}; $\Delta S^{\ddagger}$ +0·4 cal mol K^{-1}; $t_{\frac{1}{2}}$ at 200 °C, 165 min in 2-phenylethanol).[6] Their $\Delta S^{\ddagger}$ values are closer to those of the dimethoxyazepinium salts and it becomes even more evident that E_{rac} for the dimethoxy-compounds is anomalously large considering that Cl is so much larger than either OMe or F.

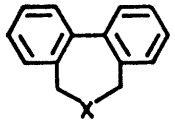
The 1,11-dimethoxyoxepin (4) is much less optically stable than the 1,11-dimethoxyazepinium salts (Table 2), a result in agreement with what is known about the corresponding 1,11-dichloro-compounds, the dichloro-oxepin (15) (E_{rac} 34·8 kcal mol^{-1}; $\Delta S^{\ddagger}$ −0·5 cal mol^{-1} K^{-1}; $t_{\frac{1}{2}}$ at 185 °C, 23·1 min in 2-phenylethanol) being the only other dibenz[*c,e*]oxepin to have had its optical stability investigated.[6] The dichloro-oxepin is very much more stable than (4), but the difference in E_{rac} between the dimethoxyazepinium salts and the dimethoxyoxepin is greater than that between the corresponding dichloro-compounds. It appears that the methoxy-groups are not exerting such an anomalously large steric effect in the oxepin as they exert in the azepinium salts, but it is not possible to decide from these results if they are only exerting their 'normal' steric effect in the oxepin.

The dibenzocycloheptene (6) is more optically stable than the azepinium salts (1) and (5) over the temperature range of the racemisation studies (Table 2), although it has the same activation energy as (5a) in dimethylformamide and an even lower E_{rac} in cyclohexanone; the greater optical stability is the result of a negative entropy change, as opposed to a positive entropy change for (5a). The racemisation of no other 6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene has been studied in detail, but it is of interest that the only bridged biphenyl with a seven-membered bridging ring and without additional *ortho*-substituents to be obtained optically active * is diethyl 6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene-6,6-dicarboxylate (9), which has a half-life of racemisation of 80 min at 32·5 °C.[4]

The order in optical stability of the 6,6'-dimethoxy-bridged biphenyls (4)—(6) parallels the order in size of the angle of torsion (the angle between the planes of the benzene rings) calculated for various unsubstituted bridged biphenyls (Table 3).[8] This connection

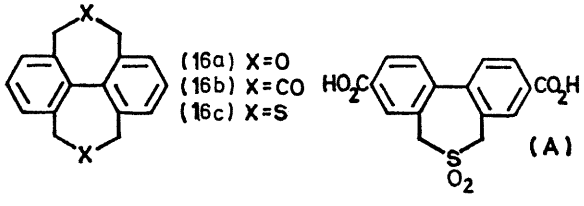
TABLE 3

Calculated values of the angle of torsion (θ) in 2,2'-bridged biphenyls [8]



X	O	NMe	$^{+}NMe_2$	CH_2	CO	S
θ	44·1	45·8	47	50·6	52·4	56·6
	43			49		

between angle of torsion and optical stability also holds for the two dichloro-compounds (14) and (15), and offers an explanation for the fact that the dinitroazepine (11) is more optically labile than its methiodide (12).



A similar relationship between optical stability and angle of torsion has been observed in doubly bridged biphenyls (16) where the order of increase in optical stability, in *o*-xylene, is dioxepin (16a) ($t_{\frac{1}{2}}$ at 23·3 °C, 11 min) < diketone (16b) ($t_{\frac{1}{2}}$ at 114·8°, 13 min.) < dithiepin (16c) ($t_{\frac{1}{2}}$ at 225·0 °C, 17 min).[9] Mislow and his co-workers discussed [9] this relationship in terms of a correspondence between angle of torsion and activation energy of racemisation [(16a), E_{rac} = 20·4 kcal mol^{-1}; (16b), E_{rac} = 31·2 kcal mol^{-1}; (16c), E_{rac} = 35·0 kcal mol^{-1}], but it appears with the dimethoxy-compounds that the influence of the angle of torsion

* Optically active solutions containing compound (A) have been obtained, but the optically active sulphone was not isolated.[7]

[5] S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 1958, 3043.

[6] P. A. Browne and D. M. Hall, unpublished results, quoted in ref. 8.

[7] W. E. Truce and D. D. Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6130.

[8] D. M. Hall, 'Progress in Stereochemistry 4,' eds. B. J. Aylett and M. M. Harris, Butterworths, London, 1969, chap. 1, and references therein.

[9] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

on optical stability is not showing itself exclusively in the activation-energy term.

EXPERIMENTAL

The solvent for spectral determinations was methanol unless otherwise stated. U.v. maxima are given as λ in nm (ε); * denotes inflection. Racemisation rate constants are given as $10^4 k_t/s^{-1}$. For all $[\alpha]_D$, $l = 1$.

5,7-Dihydro-1,11-dimethoxydibenz[c,e]*oxepin* (4).—2,2′-Bishydroxymethyl-6,6′-dimethoxybiphenyl [1,2] (1·0 g) was heated (80 °C) with sulphuric acid (50%, 25 ml) for 5 min to give the oxepin, m.p. 135—137 °C (from ethanol) (lit.,[2] 136 °C); u.v. 247 (9290)*, 287 (9640)*, and 293 (10,000).

(+)-*5,7-Dihydro-1,11-dimethoxydibenz*[c,e]*oxepin* (4).—In the same way, (−)-diol [1] gave (+)-*oxepin* (0·60 g, 64%) as plates (from ethanol); m.p. 153—154 °C, $[\alpha]_D^{26.5}$ +129·4° (*c* 0·6490 in Me_2CO) (Found: C, 75·1; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·1; H, 6·4%).

(−)-*5,7-Dihydro-1,11-dimethoxydibenz*[c,e]*oxepin* (4).—Similarly, (−)-*oxepin*, m.p. 152—153 °C and $[\alpha]_D^{15}$ −128·4° (*c* 1·051 in Me_2CO), was obtained from (+)-diol [1] (Found: C, 75·2; H, 6·25%); o.r.d. $[M]_{589}$ −319°, $[M]_{380}$ −581°, $[M]_{321}$ −283°, $[M]_{305}$ −1120°, $[M]_{302}$ 0°, $[M]_{294}$ +5800°, $[M]_{288}$ +4100°, $[M]_{256}$ +67,600°, $[M]_{246}$ 0°, $[M]_{225}$ −323,000° (*c* 0·00530—0·0530).

Racemisation Rate Constants.—By use of both (+)- and (−)-(4), these were: in 2-phenylethanol, $k_{92·1}$ 0·317, $k_{97·0}$ 0·609, $k_{101·1}$ 0·889, $k_{104·9}$ 1·28, $k_{108·1}$ 1·86, $k_{111·3}$ 2·50, $k_{114·3}$ 3·75, and $k_{117·2}$ 4·77; in dimethylformamide, $k_{88·2}$ 0·253, $k_{94·7}$ 0·522, $k_{100·7}$ 1·05, $k_{108·8}$ 2·33, $k_{111·5}$ 3·02, and $k_{114·0}$ 3·64 s^{-1}.

6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz[c,e]*azepinium Bromide* (5a).—A solution of 2,2′-bisbromomethyl-6,6′-dimethoxybiphenyl [1] (1·0 g) in benzene (6 ml) was cooled in ice, and ice-cold dimethylamine (*ca.* 1 ml) was added. The product separated almost immediately as an oil, which rapidly crystallised. After some hours, the solution was decanted, the residue washed three times with fresh benzene, dissolved in water and the product reprecipitated with concentrated potassium hydroxide solution. The *azepinium bromide* was filtered off, washed with a little ice-cold water, and recrystallised from ethanol: cubes, m.p. 333 °C (decomp.), 76% yield (Found: C, 59·3; H, 6·15; Br, 21·9; N, 4·0. $C_{18}H_{22}BrNO_2$ requires C, 59·35; H, 6·1; Br, 21·9; N, 3·8%); u.v. 241·5 (11,800), 285 (7970)*, 300·5 (12,600).

6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz[c,e]*azepinium Iodide* (5b).—As cubes, m.p. 328 °C (decomp.), from ethanol (Found: C, 52·7; H, 5·4; I, 30·7; N, 3·4; O, 7·6. $C_{18}H_{22}INO_2$ requires C, 52·6; H, 5·4; I, 30·9; N, 3·4; O, 7·8%).

(+)-*6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz*[c,e]*azepinium Bromide* (5a).—This was made from (−)-2,2′-bisbromomethyl-6,6′-dimethoxybiphenyl [1] (2·0 g) in the same way. After reprecipitation from aqueous solution with concentrated potassium hydroxide solution, the (+)-*azepinium bromide* was recrystallised from acetonitrile–ethyl acetate giving feathery needles, changing to transparent hexagonal prisms (1·80 g) under the solution during 2—3 days. After a few hours in the air the prisms became opaque (1·77 g). Recrystallisation gave needles gradually changing to hexagonal prisms or long spines; all crystals left in contact with the solution eventually gave the prisms. For all crystalline forms, first m.p. 182—184 °C (rapid heating); second m.p. 256—258 °C; third m.p. 330 °C (decomp.) (see Introduction section). The needles had $[\alpha]_D^{24}$ +46·6° † (*c* 1·470 in MeCN); the prisms had $[\alpha]_D^{13}$ +47·6° † (*c* 1·018 in MeCN) [Found for needles: C, 55·3; H, 6·3; Br, 20·4; N, 3·5. For (opaque) hexagonal prisms: Br, 20·3. For spines: Br, 20·4. $C_{18}H_{22}BrNO_2,1·5H_2O$ requires C, 55·25; H, 6·4; Br, 20·4; N, 3·6%].

(+)-*6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz*[c,e]*azepinium Iodide* (5b).—This was obtained, after three recrystallisations from acetone–ethyl acetate, as needles, m.p. 169—170° and $[\alpha]_D^{18}$ +42·7° (*c* 1·873 in MeCN) (Found: C, 52·4; H, 5·5; I, 30·7; N, 3·3%).

(−)-*6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz*[c,e]*azepinium Bromide* (5a).—Similarly, (+)-dibromide [1] gave (−)-*azepinium bromide* showing the same variation in crystalline form and the same melting behaviour as its enantiomer; $[\alpha]_D^{20}$ −47·1° (*c* 1·030 in MeCN) (Found: C, 55·3; H, 6·5; Br, 20·4; N, 3·6%); o.r.d. $[M]_{589}$ −281°, $[M]_{450}$ −355°, $[M]_{370}$ −95°, $[M]_{262}$ 0°, $[M]_{315}$ +149°, $[M]_{294}$ +11,900°, $[M]_{284}$ 0°, $[M]_{279}$ −1280°, $[M]_{275}$ 0°, $[M]_{253}$ +80,700°, $[M]_{248}$ 0°, $[M]_{245}$ −45,100°, $[M]_{224}$ −395,000° (*c* 0·00735—0·0735). (−)-*6,7-Dihydro-1,11-dimethoxy-6,6-dimethyl-5H-dibenz*[c,e]*azepinium iodide* (5b), m.p. 169—171 °C, had $[\alpha]_D^{20}$ −41·6° (*c* 1·982 in MeCN) (Found: C, 52·3; H, 5·75; N, 3·15%).

Racemisation Rate Constants.—With both (+)- and (−)-(5a) in dimethylformamide, $k_{151·6}$ 0·272, $k_{155·4}$ 0·382, $k_{160·6}$ 0·647, $k_{167·8}$ 1·30, $k_{172·7}$ 2·06, and $k_{176·3}$ 2·75 s^{-1}. With both (+)- and (−)-(5b) in dimethylformamide, $k_{151·6}$ 0·266, $k_{154·6}$ 0·347, $k_{160·0}$ 0·592, $k_{167·8}$ 1·23, $k_{172·7}$ 1·93, and $k_{175·6}$ 2·44 s^{-1}.

Diethyl 6,7-Dihydro-1,11-dimethoxy-5H-dibenzo[a,c]*cycloheptene-6,6-dicarboxylate* (6).—A solution of diethyl malonate (0·55 g) and sodium (0·16 g) in absolute ethanol (10 ml) was added dropwise to a stirred solution of 2,2′-bisbromomethyl-6,6′-dimethoxybiphenyl (1·0 g) in dioxan (3 ml). The mixture was heated under reflux for 1 h, cooled, and diluted with water. The solution was decanted from the product, a gum, which crystallised slowly during several days. Recrystallisation from ethanol gave the *dibenzocycloheptene* (0·83 g) as cubes, m.p. 103—104 °C (Found: C, 69·3; H, 6·6. $C_{23}H_{26}O_6$ requires C, 69·3; H, 6·6%); u.v. 248 (8430), 286 (8360)*, 291 (8730); u.v. (dioxan) 250 (8850), 286 (8950)*, 292 (9790); u.v. (benzene) 287 (9050)*, 293 (9880).

(−)-*Diethyl 6,7-Dihydro-1,11-dimethoxy-5H-dibenzo*[a,c]*cycloheptene-6,6-dicarboxylate* (6).—By the same method, (−)-dibromide gave (−)-*cycloheptene*, m.p. 83—84 °C and $[\alpha]_D^{18}$ −89·1° (*c* 1·100 in Me_2CO), as clusters of needles (83%) (Found: C, 69·4; H, 6·7%); o.r.d. (dioxan) $[M]_{589}$ −213°, $[M]_{350}$ −1990°, $[M]_{291}$ −25,700°, $[M]_{280}$ −7260°, $[M]_{274}$ −1140°, $[M]_{258}$ −44,500°, $[M]_{250}$ 0°, $[M]_{225}$ +323,000° (*c* 0·0640 −0·320).

(+)-*Diethyl 6,7-Dihydro-1,11-dimethoxy-5H-dibenzo*[a,c]*cycloheptene-6,6-dicarboxylate* (6).—Similarly, (+)-dibromide gave (+)-*cycloheptene*, m.p. 83—84 °C and $[\alpha]_D^{18}$ +89·9° (*c* 1·023 in Me_2CO) (Found: C, 69·4; H, 6·5%); o.r.d. $[M]_{589}$ +397°, $[M]_{350}$ +2610°, $[M]_{290}$ +24,300°, $[M]_{280}$ +9530°, $[M]_{275}$ +3640°, $[M]_{255}$ +51,800°, $[M]_{249}$ 0°, $[M]_{244}$ −298,000° (*c* 0·00695—0·0695); o.r.d. (benzene) $[M]_{589}$ +25°, $[M]_{350}$ +1390°, $[M]_{292}$ +23,300°, $[M]_{280}$ +1810° (*c* 0·0810—0·330).

† $[\alpha]$ from two preparations from different samples of (−)-dibromide.

Racemisation Rate Constants.—With both (+)- and (−)-(6): in cyclohexanone, $k_{168\cdot3}$ 0·359, $k_{172\cdot6}$ 0·514, $k_{177\cdot8}$ 0·800, $k_{183\cdot2}$ 1·27, $k_{189\cdot8}$ 2·13, and $k_{195\cdot3}$ 3·24 s^{-1}; in dimethylformamide, $k_{161\cdot1}$ 0·131, $k_{171\cdot1}$ 0·363, $k_{183\cdot2}$ 1·09, $k_{187\cdot2}$ 1·40, and $k_{196\cdot2}$ 2·84 s^{-1}.

Racemisation Experiments.—Equal volumes of a solution of the optically active compound were sealed under nitrogen in ten tubes, and the tubes were suspended in a thermostatted oil-bath (for the oxepin in dimethylformamide and in 2-phenylethanol, and for the dibenzocycloheptene in dimethylformamide), or in the vapour of a boiling liquid (for the dibenzocycloheptene in cyclohexanone, and for the azepinium salts in dimethylformamide). In each case the temperature remained constant to within ±0·2 °C. The tubes were removed at intervals, cooled, and opened. The rotations were measured at room temperature in a 1 dm microtube.

For each compound, a solution (with the appropriate solvent) was heated for sufficient time until the rotation decreased to zero. On each occasion racemic compound was recovered from the solution.

Spectroscopic Measurements.—U.v. spectra were determined on a Unicam SP 700 spectrophotometer; the positions and intensities of maxima and inflections were checked on a Unicam SP 500 spectrophotometer. O.r.d. measurements (in solutions at ambient temperatures) were made with a Fica Spectropol I spectropolarimeter.

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