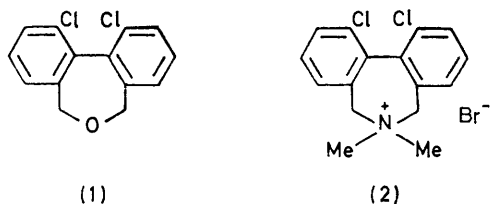


## Optical Stabilities of Some *oo'*-Bridged *oo'*-Dichlorobiphenyls

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Racemisation parameters have been determined for 1,11-dichloro-5,7-dihydrodibenz[*c,e*]oxepin (1) and 1,11-dichloro-6,7-dihydro-6,6-dimethyl-5*H*-dibenz[*c,e*]azepinium bromide (2). Their u.v. and c.d. spectra are discussed. Rotations of sodium 6,6'-dichlorodiphenate and 6,6'-dichloro-2,2'-bishydroxymethylbiphenyl are strongly temperature-dependent.

As part of an investigation of the effect of additional *ortho*-substituents on the optical stabilities of 2,2'-bridged biphenyls, we have determined racemisation parameters for the dichloro-compounds (1) and (2). Both compounds are readily available by standard



procedures<sup>1-5</sup> from resolved 6,6'-dichlorodiphenic acid<sup>6</sup> (17). The results (Table 1) show that, as expected, the

TABLE I  
Racemisation data

Compd.	<i>E</i>		$\log_{10} A / s^{-1}$	$\Delta G^\ddagger / kcal mol^{-1}$	$\Delta H^\ddagger / kcal mol^{-1} \text{ } ^\circ$	$\Delta S^\ddagger / cal mol^{-1} K^{-1} \text{ } ^\circ$
	kcal mol <sup>-1</sup>	kJ mol <sup>-1</sup>				
(1) <sup>b</sup>	34.8	146	13.3	34.1 at 185 °C	33.9	-0.5
(2) <sup>b</sup>	38.3	160	13.5	37.1 at 229.1 °C	37.3	+0.4

<sup>a</sup> Mean of values for each temperature at which rates were measured. <sup>b</sup> Solvent  $\beta$ -phenylethanol.

two *ortho*-chlorine atoms have a large steric effect, and confer considerable optical stability on both ring systems. The difference between the energies of activation for racemisation of compounds (2) and (1) may reasonably be attributed to the larger dihedral angle ( $\theta$ ) between the

two aromatic rings when the heteroatom in the bridging ring is N rather than O. For the compounds without additional *ortho*-substituents the dihedral angles, calculated<sup>7</sup> from normal bond lengths and angles, are 47° for the dihydrodibenzazepinium ion and 43° for the dihydrodibenzoxepin. Although the introduction of the chlorine atoms will probably increase the angle in both cases, the effect cannot be large, as the u.v. spectra (Table 2) show only a small reduction in conjugation in comparison with the unsubstituted compounds. A similar effect on *E* is observed<sup>8</sup> on going from the dihydrodimethyldibenzocycloheptenone (3) (*E* 39 kcal mol<sup>-1</sup>) to the dibenzocycloheptene (4) (*E* 36 kcal mol<sup>-1</sup>). Here the angles for the corresponding compounds without methyl groups are 52.4 and 50.6°, respectively.<sup>9</sup> In the dimethoxy-series (5) *E* likewise decreases<sup>10</sup> in the order X = <sup>+</sup>NMe<sub>2</sub> > X = O.

Apart from the dimethoxy-compound (5; X = O), the only other dihydrodibenzoxepin for which the energy barrier to racemisation has been determined<sup>9</sup> is the doubly bridged compound (6), of much lower optical stability than the other two. However, the energy barrier to inversion of conformation has been determined<sup>11-13</sup> by temperature-variable n.m.r. spectroscopy for a number of less highly substituted dihydrodibenzoxepins (7)–(10), and for compound (6). Whereas one *ortho*-substituent raises the energy barrier from *ca.* 9 to *ca.* 17 kcal mol<sup>-1</sup>, the second *ortho*-substituent raises it to *ca.* 28–35 kcal mol<sup>-1</sup>.

The optical stability of compound (2) is greater than that of any other dihydrodibenzazepinium salt so far

<sup>1</sup> G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1952, 854.

<sup>2</sup> G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner, and G. R. Bird, *J. Chem. Soc.*, 1954, 131.

<sup>3</sup> M. Siegel and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 473.

<sup>4</sup> F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 476.

<sup>5</sup> D. D. Fitts, M. Siegel, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 480.

<sup>6</sup> G. H. Christie, C. W. James, and J. Kenner, *J. Chem. Soc.*, 1923, **123**, 1948.

<sup>7</sup> D. M. Hall and F. Minhaj, *J. Chem. Soc.*, 1957, 4584.

<sup>8</sup> K. Mislow and A. J. Gordon, *J. Amer. Chem. Soc.*, 1963, **85**, 3521.

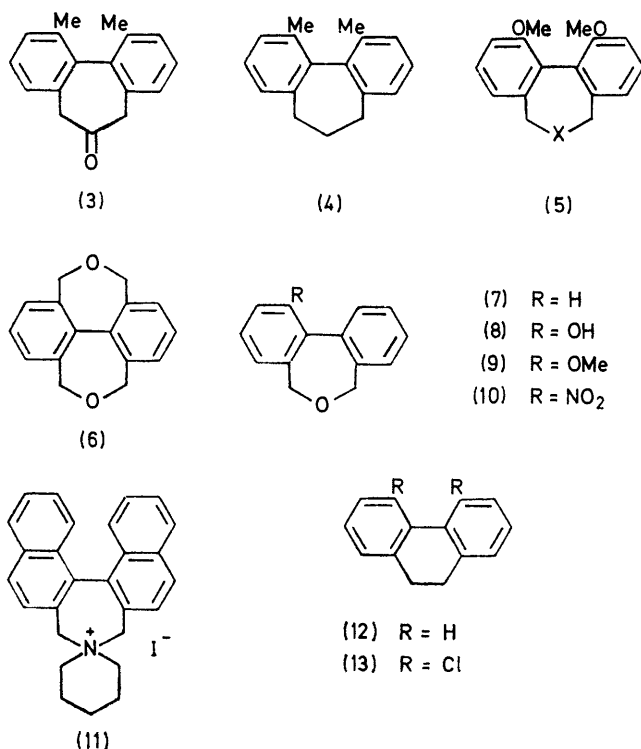
<sup>9</sup> K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

<sup>10</sup> J. M. Insole, *J.C.S. Perkin II*, 1972, 1164.

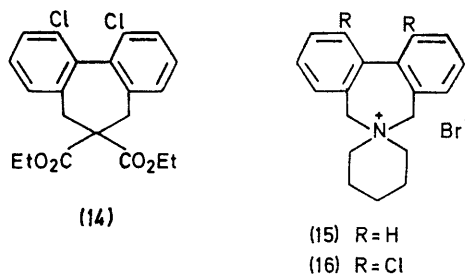
<sup>11</sup> R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

<sup>12</sup> M. Ōki, H. Iwamura, and T. Nishida, *Bull. Chem. Soc. Japan*, 1968, **41**, 656.

<sup>13</sup> M. Ōki, H. Iwamura, and N. Hayakawa, *Bull. Chem. Soc. Japan*, 1964, **37**, 1865; M. Ōki and H. Iwamura, *Tetrahedron*, 1968, **24**, 2377.



the conjugation band. A slight hypsochromic shift is observed in compounds (1) and (2) but not in (13), where intramolecular overcrowding could be expected to be greatest. This supports the view that moderately large *ortho*-substituents are accommodated by in-plane and out-of-plane bending of the substituent, rather than by appreciable distortion of the bridging ring which would increase the dihedral angle.



(+)-6,6'-Dichlorodiphenic acid has the *R*-configuration<sup>3</sup> and the laevorotatory bridged compounds derived from it will therefore also be *R*. The c.d. spectra (Figures 1 and 2) of (-)-(*R*)-(1) and (-)-(*R*)-(2) in methanol are in accord with those of other bridged biphenyls with seven-membered bridging rings, including (14) and (16);<sup>15,16</sup> they show a strong positive Cotton effect at *ca.* 240 nm and also a much weaker positive Cotton effect at the long-wave end of the spectrum (288

investigated, except (11), for which *E* has not been determined (see Table 8 in ref. 14).\*

TABLE 2

Compound	Solvent	U.v. spectra		Conjugation band		Long-wave bands		Ref.
		Short-wave band $\lambda_{\max}^*$	$\epsilon_{\max}$	$\lambda_{\max}^*$	$\epsilon_{\max}$	$\lambda_{\max}^*$	$\epsilon_{\max}$	
9,10-Dihydrophenanthrenes								
(12)	96% EtOH			264	17,000	(289.5) 299.5	4200 4450	<i>a</i>
(13)	96% EtOH	215.5	29,400	264.5	11,100	(292)	2150	
5,7-Dihydrodibenz[ <i>c,e</i> ]oxepins								
(7)	96% EtOH	206.5	40,000	250.5	16,500	( <i>ca.</i> 277)	1600	<i>b</i>
(1)	96% EtOH	216	41,000	246	10,700	(273) (283)	1700 850	
6,7-Dihydro-5 <i>H</i> -dibenz[ <i>c,e</i> ]azepinium bromides								
(15)	H <sub>2</sub> O			248	15,000	(272) (281.5)	4750 2250	<i>a</i>
(16)	96% EtOH	219	43,000	247	10,000	277 (285)	3750 2350	<i>c</i>
(2)	96% EtOH	217.5	39,800	246	9400	276.5 (284) (293)	3500 2250 500	

\* In nm; values in parentheses indicate inflections.

<sup>a</sup> G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1952, 854. <sup>b</sup> G. H. Beaven and E. A. Johnson, *J. Chem. Soc.*, 1957, 651. <sup>c</sup> S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 1960, 4165.

The u.v. spectra of compounds (1) and (2) and of 4,5-dichloro-9,10-dihydrophenanthrene (13) are compared with those of the unsubstituted compounds in Table 2; the steric effect of the *ortho*-chlorine atoms in reducing conjugation is evident mainly in the reduced intensity of

nm in each case). Two negative maxima at 272 and *ca.* 282sh nm complete the fine structure in the long-wave region, revealing, in the case of the oxepin, a band which

<sup>14</sup> D. M. Hall, *Progr. Stereochem.*, 1969, 4, 1.

<sup>15</sup> E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, 1962, 84, 2823.

<sup>16</sup> K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, 85, 1342.

\* In this Table the dichloro-compound is printed without its Cl atoms.

is hidden in the u.v. spectrum. The intense short-wave band at *ca.* 224 nm is associated with a strong positive Cotton effect in both compounds.

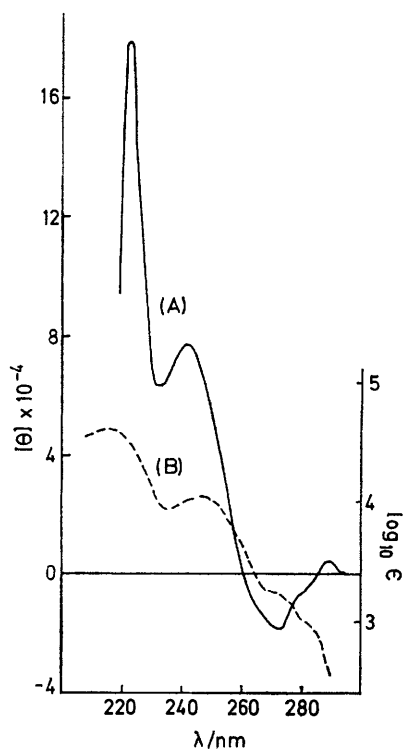


FIGURE 1 (A) C.d. spectrum in methanol and (B) u.v. spectrum in 96% ethanol of (—)(*R*)-1,11-dichloro-5,7-dihydrodibenz[*c,e*]oxepin (1)

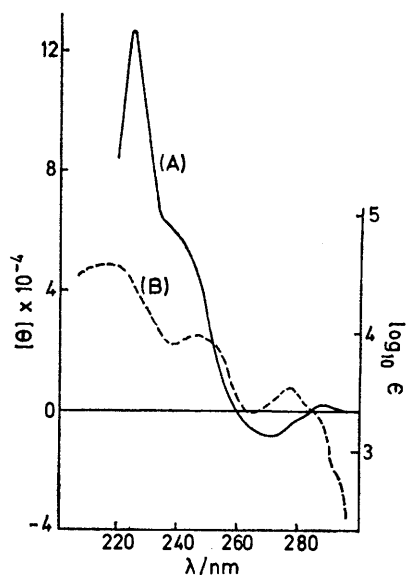


FIGURE 2 (A) C.d. spectrum in methanol and (B) u.v. spectrum in 96% ethanol of (—)(*R*)-1,11-dichloro-6,7-dihydro-6,6-dimethyl-5*H*-dibenz[*c,e*]azepinium bromide (2)

The rotations in the visible region of sodium 6,6'-dichlorodiphenate in water and the diol (18) in benzene

<sup>17</sup> W. F. Baitinger, P. von R. Schleyer, and K. Mislow, *J. Amer. Chem. Soc.*, 1965, **87**, 3168.

(Figure 3) are markedly temperature-dependent. The rotation of the acid (17) is also solvent-dependent.<sup>4</sup> Presumably both effects are associated with conformational changes in these unbridged biphenyls: hydrogen bonding in the acid in non-hydroxylic solvents and ion repulsion in the salt, together with changes in the degree of solvation, could well be responsible for the reversal of sign of rotation observed in going from acetone<sup>6</sup> to methanol<sup>4</sup> for the acid and on increase of temperature for the salt. The i.r. spectrum of the diol in carbon tetrachloride<sup>17</sup> shows the presence of OH...O bonding as

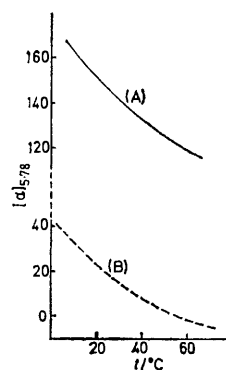


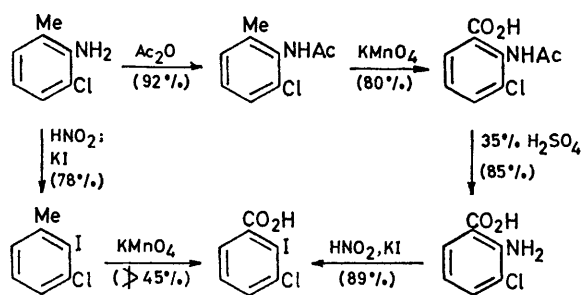
FIGURE 3 Effect of temperature on  $[\alpha]_{578}$  of (A) (*R*)-6,6'-dichloro-2,2'-bishydroxymethylbiphenyl (18) in benzene and (B) (*R*)-sodium 6,6'-dichlorodiphenate in water

well as OH... $\pi$  bonding (to the  $\pi$ -electrons of the ring to which the CH<sub>2</sub>OH group is attached). Intramolecular OH...O bonding has been shown<sup>17</sup> to be most favoured by a nearly perpendicular arrangement of the two rings but it is also possible for some *cis*-conformations; in *trans*-conformations however the OH...O distance will be too great. The situation in benzene is likely to be very similar to that in carbon tetrachloride: increase in temperature, by reducing the extent of hydrogen bonding, will permit changes in the dihedral angle which in unbridged biphenyls can lead to large changes in the o.r.d. curves,<sup>5,18</sup> here revealed by changes in the rotation in the visible region. The oxepin (1), of fixed conformation, and the dibromide (19), where neither hydrogen bonding nor ion-repulsion applies, show only slight dependence of rotation on temperature of the kind to be expected for normal expansion of the solution (*ca.* 0.05% change for a rise of 45 °C). However, the azepinium bromide (2) in chloroform is intermediate in behaviour; the fall in rotation for a rise of 45° is larger (0.135%) than that for the oxepin (in benzene) but much less than that for the diol. Since, like the oxepin, this compound has a fixed conformation, the most probable explanation is that of temperature-dependent changes in solvation at the positive nitrogen. (Chloroform and benzene have similar coefficients of expansion so the change of solvent is not significant.)

3-Chloro-2-iodobenzoic acid, required for the Ullmann

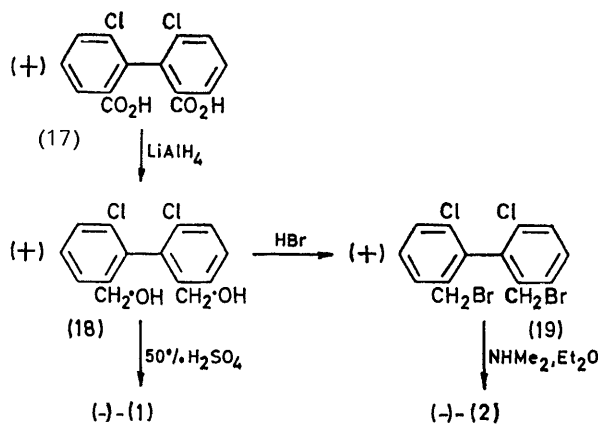
<sup>18</sup> K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455.

reaction on its ester,<sup>6</sup> was prepared from 2-amino-3-chlorotoluene in four stages (Scheme 1). The high yields



SCHEME 1

at each step made this route preferable to the two-step alternative involving the slow and unsatisfactory oxidation of 3-chloro-2-iodotoluene. Reduction of diazotised 3-chloroanthranilic acid with cuprammonium salts was explored as a shorter route to the diphenic acid. Yields were sensitive to the form of the cuprous reducing agent and the product was frequently contaminated with 2,3-dichlorobenzoic acid, in which case purification was difficult and wasteful. However the modification used by Atkinson *et al.*<sup>19</sup> for diphenic acid gave yields of 57–77% and both routes were therefore employed. The acid was resolved through the brucine salt<sup>3,6</sup> and the (+)-(R)-acid used as a source of (-)-(R)-(1) and (-)-(R)-(2) (Scheme 2).



SCHEME 2

## EXPERIMENTAL

U.v. spectra were determined for solutions in 96% ethanol on a Unicam SP 500 spectrophotometer, and c.d. spectra for solutions in methanol on a Roussel-Jouan Dichrographe.

**3-Chloroanthranilic Acid.**—2-Acetamido-3-chlorotoluene (74 g) and potassium permanganate (140 g) in water (2.5 l) were heated together on a water bath with stirring for 2 h. Normal work-up gave starting material (10 g) and 2-acetamido-3-chlorobenzoic acid (60 g, 80% based on compound

consumed), m.p. 207–208° (lit.,<sup>20</sup> 206.5–207°). This was heated with 35% sulphuric acid for 0.5 h; the solution was cooled and aqueous sodium hydroxide was added (to pH 4). 3-Chloroanthranilic acid had m.p. 193–194° (lit.,<sup>21</sup> 192°).

**6,6'-Dichlorodiphenic Acid (17).**—(i) *By Ullmann reaction.*<sup>6</sup> 3-Chloroanthranilic acid and sodium nitrite were dissolved in *N*-sodium hydroxide and 10% hydrochloric acid was added gradually at <5°. The filtered diazo solution was added to an aqueous solution of potassium iodide at *ca.* 80°. Normal work-up gave 3-chloro-2-iodobenzoic acid, m.p. 141–143° (lit.,<sup>6</sup> 137–138°), and thence the methyl ester, m.p. 35–36°, b.p. 172° at 17 mmHg (lit.,<sup>6</sup> 182° at 28 mmHg). Copper bronze (32 g) was gradually added, with stirring, during 1 h to the ester (99 g) in a bath at 150°. The temperature was raised to 180° for 10 min and the mixture was then extracted with hot chlorobenzene. After filtration and concentration of the solution, dimethyl 6,6'-dichlorodiphenate, m.p. 157–159° (lit.,<sup>6</sup> 156°) crystallised (46.5 g, 90%); it was readily hydrolysed to the acid.

(ii) *By diazotisation and reduction.* A solution of diazotised 3-chloroanthranilic acid [from the acid (18.6 g)] was added gradually at 20° to a well stirred reducing solution prepared<sup>19</sup> from copper sulphate (37.8 g) in water (150 ml) and ammonia (*d* 0.88; 63 ml) to which a solution of hydroxylamine hydrochloride (10.65 g) in 6*N*-sodium hydroxide (25.5) and water (36 ml) was added just before use. The solution was then heated to boiling and iron(III) chloride (45 g) in water (66 ml) and concentrated hydrochloric acid (225 ml) was added. The precipitated acid was obtained *via* the sodium salt and crystallised from aqueous ethanol (charcoal), giving 6,6'-dichlorodiphenic acid (12.0 g, 77%), m.p. 291–292° (lit.,<sup>6</sup> 288°; lit.,<sup>3</sup> 289.5–291°). From an experiment in which a catalyst without ammonia was used, 2,3-dichlorobenzoic acid, m.p. 165.5–166.5° (lit.,<sup>22</sup> 160°), was isolated and characterised as the *benzylamine salt*,<sup>23</sup> m.p. 150–152° (Found: C, 56.5; H, 4.4; Cl, 23.7. C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub> requires C, 56.4; H, 4.4; Cl, 23.8%).

(+)- and (-)-6,6'-Dichlorodiphenic Acids.—The acid was resolved through the brucine salt.<sup>6</sup> The less soluble salt gave the (+)-(R)-acid, m.p. 263–265° (lit.,<sup>3</sup> 263–264.5°), [ $\alpha$ ]<sub>546</sub><sup>20</sup> +26.7° (*c* 0.776 in 0.1*N*-NaOH) (for rotations at other temperatures see Figure 3) (lit.,<sup>3</sup> [ $\alpha$ ]<sub>D</sub><sup>15</sup> +21.4°). The more soluble salt gave the (-)-(S)-acid, m.p. 267–270°, [ $\alpha$ ]<sub>546</sub><sup>21</sup> -20.0° (*c* 1.001 in 0.1*N*-NaOH).

**6,6'-Dichloro-2,2'-bis(hydroxymethyl)biphenyl (18).**—Dimethyl 6,6'-dichlorodiphenate was reduced with lithium aluminium hydride in ether, giving the diol, m.p. 119–120° (lit.,<sup>3</sup> 119–120°).

(+)-(R)-6,6'-Dichloro-2,2'-bis(hydroxymethyl)biphenyl.—This was obtained in 92% yield by direct reduction of the (+)-acid with lithium aluminium hydride; it had m.p. 104.5–106° (lit.,<sup>3</sup> 106–107°) and [ $\alpha$ ]<sub>546</sub><sup>21</sup> +17.6°, [ $\alpha$ ]<sub>578</sub><sup>21</sup> +15.4° (*c* 0.949 in benzene) (lit.,<sup>3</sup> [ $\alpha$ ]<sub>D</sub><sup>30</sup> +141°). Figure 3 shows rotations at other temperatures.

**2,2'-Bis(bromomethyl)-6,6'-dichlorobiphenyl (19).**—The diol (13 g) was heated under reflux with 48% hydrobromic acid (650 ml) for 2 h. The *dibromide* solidified on cooling and was crystallised from light petroleum (b.p. 60–80°); yield 14.1 g (75%), m.p. 99.5–100° (Found: C, 41.1; H, 2.5; Br, 39.05; Cl, 17.15. C<sub>14</sub>H<sub>10</sub>Br<sub>2</sub>Cl<sub>2</sub> requires C, 41.1; H, 2.5; Br, 39.1; Cl, 17.3%).

<sup>21</sup> P. W. Sadler and R. L. Warren, *J. Amer. Chem. Soc.*, 1956, **78**, 1251.

<sup>22</sup> T. Crauw, *Rec. Trav. chim.*, 1931, **50**, 753.

<sup>23</sup> Method of G. W. H. Cheeseman and R. C. Poller, *Analyst*, 1961, **86**, 256.

<sup>19</sup> E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball, and E. R. Read, *J. Amer. Chem. Soc.*, 1941, **63**, 730.

<sup>20</sup> E. Bamberger, *Annalen*, 1925, **443**, 192.

(+)-(R)-2,2'-Bisbromomethyl-6,6'-dichlorobiphenyl.— The (+)-diol was similarly converted into the (+)-dibromide. Heating for 4 rather than 2 h gave a cleaner product, m.p. 70–71°,  $[\alpha]_{546}^{20} + 93^\circ$ ,  $[\alpha]_{\text{D}}^{24} + 80^\circ$  (*c* 0.99 in  $\text{C}_6\text{H}_6$ ) (lit.,<sup>3</sup> 70–71°,  $[\alpha]_{\text{D}}^{29} + 77^\circ$ ).

4,5-Dichloro-9,10-dihydrophenanthrene (13).—2,2'-Bisbromomethyl-6,6'-dichlorobiphenyl (8.0 g) in dry ether was added to a freshly prepared ethereal solution of phenyllithium [from lithium (0.56 g) and bromobenzene (5.7 g)] and the mixture was heated under reflux for 4 h. The solid isolated was crystallised from light petroleum (b.p. 40–60°), and then ethanol, giving 4,5-dichloro-9,10-dihydrophenanthrene (1.1 g, 22%), m.p. 106.5–107.5° (Found: C, 67.65; H, 4.2; Cl, 28.35.  $\text{C}_{14}\text{H}_{10}\text{Cl}_2$  requires C, 67.5; H, 4.05; Cl, 28.5%).

1,11-Dichloro-5,7-dihydrodibenz[c,e]oxepin (1).—The diol (18) was warmed with 50% sulphuric acid until it formed a thick gum which solidified on cooling. The oxepin crystallised from ethanol in needles, m.p. 161–162° (Found: C, 63.3; H, 3.6; Cl, 26.65; O, 6.2.  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{O}$  requires C, 63.4; H, 3.8; Cl, 26.75; O, 6.0%).

(-)-(R)-1,11-Dichloro-5,7-dihydrodibenz[c,e]oxepin (1).—The (+)-diol was similarly converted into the (-)-oxepin, m.p. 143–144°,  $[\alpha]_{546}^{18} - 391^\circ$ ,  $[\alpha]_{578}^{18} - 344.5^\circ$  (*c* 0.770 in benzene) (Found: C, 63.3; H, 3.8; Cl, 26.7; O, 6.2%); c.d. data:  $[\theta]_{223} + 178,000^\circ$ ,  $[\theta]_{233} + 63,000^\circ$ ,  $[\theta]_{242} + 77,000^\circ$ ,  $[\theta]_{272} - 19,500^\circ$ ,  $[\theta]_{280} - 5600^\circ$ ,  $[\theta]_{288} + 3500^\circ$ .

Racemisation of the Oxepin (1).—A 0.6% solution of the oxepin in  $\beta$ -phenylethanol was prepared and sealed in

residue had an i.r. spectrum identical with that of the racemic oxepin.

1,11-Dichloro-6,7-dihydro-6,6-dimethyl-5H-dibenz[c,e]-azepinium Bromide (2).—Cooled solutions of 6,6'-dichloro-2,2'-bisbromomethylbiphenyl (20 g) and dimethylamine (11.6 ml) in dry ether were mixed, allowed to warm to room temperature, and left for 3 days. Water was added and the aqueous layer was separated and treated with concentrated potassium hydroxide solution to precipitate the quaternary bromide. This crystallised from water as the monohydrate (12 g, 63%), melting at 160–190° with loss of solvent (Found: C, 49.1; H, 4.6; Br, 30.2; Cl, 17.95; N, 3.7; O, 4.0.  $\text{C}_{16}\text{H}_{16}\text{BrCl}_2\text{N}_2\text{H}_2\text{O}$  requires C, 49.1; H, 4.6; Br, 20.4; Cl, 18.1; N, 3.6; O, 4.1%). The picrate had m.p. 222–223° (EtOH) (Found: C, 50.6; H, 3.8; Cl, 13.5; N, 10.7; O, 21.35.  $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_7$  requires C, 50.7; H, 3.5; Cl, 13.6; N, 10.75; O, 21.5%).

(-)-(R)-1,11-Dichloro-6,7-dihydro-6,6-dimethyl-5H-dibenz[c,e]azepinium Bromide (2).—This compound was similarly prepared from the (+)-dibromide and crystallised from methanol-ethyl acetate as the dihydrate,  $[\alpha]_{546}^{22} - 159^\circ$  (*c* 0.97 in  $\text{CHCl}_3$ ),  $[\alpha]_{546}^{18.5} - 300^\circ$ ,  $[\alpha]_{578}^{18.5} - 264^\circ$  (*c* 0.965 in  $\text{PhCH}_2\text{CH}_2\text{OH}$ ) (Found: Br, 19.3; Cl, 17.0; O, 7.4.  $\text{C}_{16}\text{H}_{16}\text{BrCl}_2\text{N}_2\text{H}_2\text{O}$  requires Br, 19.5; Cl, 17.3; O, 7.8%); c.d. data:  $[\theta]_{225} + 125,000^\circ$ ,  $[\theta]_{239} + 59,000^\circ$ ,  $[\theta]_{272} - 8800^\circ$ ,  $[\theta]_{282} - 3000^\circ\text{sh}$ ,  $[\theta]_{288} + 2000^\circ$ .

Racemisation of the Azepinium Bromide (2).—This was carried out as for the oxepin; a sample was similarly heated until the rotation was zero.

TABLE 3

Racemisation of (-)-(1) in  $\beta$ -phenylethanol

Temp. (°C)	$10^5 k/s^{-1}$	$t_{1/2}/\text{min}$
154.4	3.11	371
159.8	5.38	215
170.0	13.55	85.3
179.8	31.1	37.1
185.2	50.1	23.1

Whence  $E = 34.8 \text{ kcal mol}^{-1}$  (graphical and least squares).

10–14 Pyrex tubes under nitrogen. The tubes were suspended in a bath kept at constant temperature and removed at suitable intervals; they were rapidly cooled and opened, and the rotations were read at room temperature for samples in a semimicro tube. One sample was heated until the rotation was zero; the solvent was removed and the

TABLE 4

Racemisation of (-)-(2) in  $\beta$ -phenylethanol

Temp. (°C)	$10^5 k/s^{-1}$	$t_{1/2}/\text{min}$
188.8	2.69	429
199.9	7.01	165
211.3	19.15	60.3
220.7	39.25	29.4
229.1	77.1	15.0

Whence  $E = 38.3 \text{ kcal mol}^{-1}$  (graphical and least squares).

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