

### 689. *Molecular Polarisability. The Molar Kerr Constants and Conformations of cis- and trans-Decalins.*

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The longitudinal and transverse polarisabilities of the carbon-carbon and carbon-hydrogen bonds, as deduced previously,<sup>1</sup> have been used to calculate *a priori* the molar Kerr constants of *trans*-decalin and of the two alternative structures for its *cis*-isomer. The values obtained, when compared with the results of direct measurement, favour "two-chair" conformations for both decalins.

THE belief that *trans*- and *cis*-decalin are<sup>2</sup> (I) and (II) rather<sup>3</sup> than (I) and (III) respectively appears to be based on electron-diffraction studies<sup>2,4</sup> and calculations of energy differences;<sup>5</sup> only the former can be recognised as giving direct evidence. We



have therefore examined the Kerr effects of the two isomers and determined for each its molar Kerr constant. The results are compared with those computed for the three different geometrical arrangements by use of the known<sup>1</sup> polarisabilities of carbon-carbon and carbon-hydrogen bonds by the procedure previously described.<sup>1</sup>

#### EXPERIMENTAL

*cis- and trans-Decalin.*—Decalin ("redistilled" grade from British Drug Houses Ltd.) was fractionated;<sup>6</sup> the samples obtained finally had the following properties: *trans*-isomer, b. p. 68°/10 mm.,  $d_4^{15}$  0.8742,  $d_4^{20}$  0.8702,  $n_D^{20}$  1.4699; *cis*-isomer, b. p. 74°/10 mm.,  $d_4^{15}$  0.8981,  $d_4^{20}$  0.8938,  $n_D^{20}$  1.4809; these constants are in reasonable agreement with values in the literature.<sup>7-9</sup> The *trans*-form greatly predominated in the initial decalin.

*Apparatus and Technique.*—Electric double refractions were determined in solutions in carbon tetrachloride as described in refs. 1, 10, and 11, wherein are defined the various symbols used. A useful improvement in the closure of the cells has been to remove the brass ferrules (Fig. 2 of ref. 10) and to seal in their places standard B24 sockets. The smaller-diameter ends of the related cones were then ground and polarimeter cover glasses attached with Araldite type 101. Strains associated with the swelling of the rubber washers used previously are thereby avoided and two end-cones can be used with a number of cell bodies containing plates of different lengths and separations. Dielectric constants were measured in the circuit recently noted.<sup>12</sup> Tables 1 and 2 set out the observations and results.

<sup>1</sup> Le Fèvre and Le Fèvre, *J.*, 1956, 3549; *Rev. Pure Appl. Chem.*, 1955, 5, 261.

<sup>2</sup> Bastiansen and Hassel, *Tids. Kjemt.*, 1943, 3, 91; 1946, 6, 870; *Nature*, 1946, 157, 765.

<sup>3</sup> Cf. *Ann. Reports*, 1924, 21, 93; 1935, 32, 307; Hückel, *Annalen*, 1925, 441, 1; *Ber.*, 1925, 58, 1449; and many standard text books.

<sup>4</sup> Hassel and Viervoll, *Acta Chem. Scand.*, 1947, 1, 149.

<sup>5</sup> Barton, *J.*, 1948, 340; 1953, 1027; Turner, *J. Amer. Chem. Soc.*, 1952, 74, 2118; cf. Klyne,

"Progress in Stereochemistry," Butterworths, London, 1954, Ch. 2.

<sup>6</sup> Seyer and Walker, *J. Amer. Chem. Soc.*, 1938, 50, 2125.

<sup>7</sup> Beilstein's "Handbuch," V, 92, V\* 46, V\*\* 56; Selected Values of Properties of Hydrocarbons, Table 29a (Part 1), Amer. Petroleum Inst. Project 44, Carnegie Inst. of Tech., Pittsburgh, 1950.

<sup>8</sup> Seyer and Barrow, *J. Amer. Chem. Soc.*, 1948, 70, 802.

<sup>9</sup> Mizuhara and Seyer, *ibid.*, 1953, 75, 3274.

<sup>10</sup> Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

<sup>11</sup> *Idem, ibid.*, 1954, 1577.

<sup>12</sup> Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

TABLE 1. Observations on solutions in carbon tetrachloride.

$10^6 w_2$	$\epsilon^{30}$	$d_4^{30}$	$n_D^{25}$	$\Delta B_D^{25}$	$10^6 w_2$	$\epsilon^{30}$	$d_4^{30}$	$n_D^{25}$	$\Delta B_D^{25}$	
0	2.2176	1.57480	1.4575	—						
							trans-Decalin			
		cis-Decalin			14,577	2.2157	1.55543	—	0.001	
4493	2.2174	1.56948	—	ca. 0	34,396	2.2127	1.53218	1.4582	0.002	
6962	2.2172	1.56642	—	-0.001	38,805	2.2124	1.52684	—	0.002	
14,080	2.2167	1.55798	1.4578	-0.001 <sub>5</sub>	52,470	—	—	—	0.002 <sub>5</sub>	
40,020	—	—	—	-0.003 <sub>5</sub>	83,778	2.2068	1.47471	1.4588	0.004	
43,045	2.2149	1.52521	1.4591	-0.003 <sub>5</sub>						
	whence $\Sigma \Delta \epsilon / \Sigma w_2 = -0.061_3$				whence $\Sigma \Delta \epsilon / \Sigma w_2 = -0.133$					
	$\Delta d = -1.225w_2 + 1.7w_2^2$				$\Delta d = -1.284w_2 + 1.1w_2^2$					
	$\Sigma \Delta n / \Sigma w_2 = 0.033_3$				$\Sigma \Delta n / \Sigma w_2 = 0.016_9$					
	$\Delta B = -0.115w_2 + 0.7w_2^2$				$\Delta B = 0.058_5 w_2 - 0.14w_2^2$					

TABLE 2. Calculation of  ${}_{\infty}P_2$  and  ${}_{\infty}(mK_2)$ .

	$\alpha \epsilon_1$	$\beta$	${}_{\infty}P_2$ (c.c.)	$\gamma$	$\delta$	${}_{\infty}(mK_2) \times 10^{12}$
cis-Decalin .....	-0.061	-0.778	44.1	0.023	-1.6 <sub>4</sub>	0.15
trans- ,, .....	-0.133	-0.815	44.0	0.012	0.83 <sub>6</sub>	2.8 <sub>0</sub>

## DISCUSSION

*Dielectric Polarizations.*—According to the M.I.T. Tables<sup>13</sup> *cis*-decalin has been examined in both benzene and carbon tetrachloride, but the *trans*-isomer in benzene only. The reference to Puchalik<sup>14</sup> is not available in Australia and the abstracts<sup>14</sup> merely state that  $\mu = 0$  without quoting the polarisations actually found. The entry for Seyer and Barrow<sup>15</sup> is incorrect in that their data are for the pure liquids, not for solutions in benzene, and a value by Fairbrother<sup>16</sup> is omitted. Present and past measurements are compared in Table 3. The dielectric constants and densities as functions of temperature, given in refs. 15—18, correspond to a slight increase of total polarisation with rise of temperature (*e.g.*, 0.4 c.c. from 25° to 142° according to Sutton *et al.*<sup>18</sup>; *ca.* 1 c.c. for the separate isomers between 20° and 100° according to Seyer and Barrow<sup>15</sup>); these facts, together with the very small dielectric loss noted for decalin by Whiffen<sup>19</sup> (*cf.* Heston and Smyth<sup>20</sup>), clearly indicate the non-polarity of both decalins.

TABLE 3. Total polarisations (c.c.) recorded for the decalins.

Author(s)	Temp.	Unseparated mixture	<i>cis</i> -isomer	<i>trans</i> -isomer	Ref.
Lautsch .....	20°	42.3	—	—	17
Sutton, New, and Bentley ...	25°	43.7	—	—	18
Fairbrother .....	20°	43.8	43.7	44.3	16
Seyer and Barrow .....	20°	—	44.4	44.9	15
Present work * .....	30°	—	44.1	44.0	

All observations were on pure liquids over temperature ranges throughout which  $P$  did not diminish, except for that marked \*, which is for solution in carbon tetrachloride.

*Molar Kerr Constants.*—As shown in Table 1, the addition of *cis*-decalin lowers, while that of *trans*-decalin raises, the Kerr constant of carbon tetrachloride. The values obtained for  ${}_{\infty}(mK_2) \times 10^{12}$ , namely 0.15 and 2.8, indicate that the *cis*-isomer is more isotropically polarisable than is the *trans*.

<sup>13</sup> Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, 1948.

<sup>14</sup> Puchalik, *Acta Phys. Polon.*, 1933, **2**, 305; *cf. Brit. Abs.*, 1936, 408; *Chem. Zentr.*, 1935, **1**, 3914.

<sup>15</sup> Seyer and Barrow, *J. Amer. Chem. Soc.*, 1948, **70**, 802.

<sup>16</sup> Fairbrother, *Proc. Roy. Soc.*, 1933, *A*, **142**, 173.

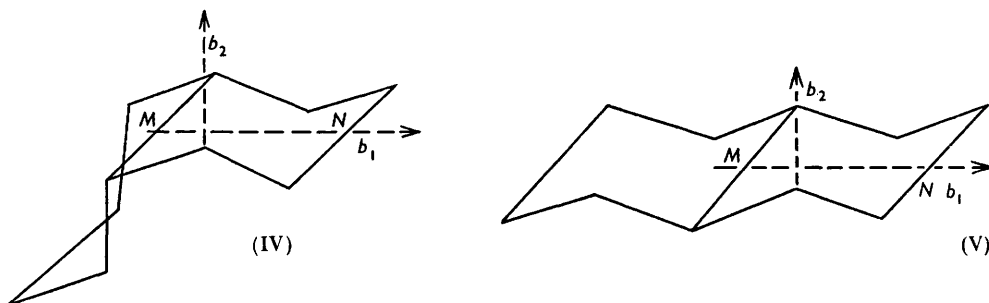
<sup>17</sup> Lautsch, *Z. phys. Chem.*, 1928, **1**, *B*, 118.

<sup>18</sup> Sutton, New, and Bentley, *J.*, 1933, 652.

<sup>19</sup> Whiffen, *Trans. Faraday Soc.*, 1950, **46**, 124.

<sup>20</sup> Heston and Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 99.

The birefringences are small and not far from the limits set by the apparatus. The molar Kerr constant was also determined of a liquid sample obtained by cutting B.D.H. "redistilled" decalin from 185–190° (this fraction formed the greater part of the initial



material; both from its physical constants and the weakness of its infrared absorption<sup>21</sup> at *ca.* 11.4  $\mu$  it appeared to be largely *trans*-decalin).  $B_D^{20}$  was  $0.103_5 \times 10^{-7}$  which, with  $d_4^{20} = 0.8722$ ,  $\epsilon_{20} = 2.166$ , and  $n_D^{20} = 1.4714$ , corresponds to  ${}_mK_{\text{liquid}} = 2.8_3 \times 10^{-12}$ ; agreement with the  ${}_{\infty}({}_mK_2)$  measured in carbon tetrachloride is good.

*Prediction of Molar Kerr Constants for Conformations (I), (II), or (III).*—The polarisability semi-axes expected for the two decalins can be calculated by use of the information given in ref. 1 for *cyclohexane* and the C–C and the C–H bond. Let the *b*'s for the isomers be disposed as indicated in (IV) and (V). Writing  $b_1^{cyH} = b_2^{cyH}$  and  $b_3^{cyH}$  for the appropriate polarisabilities of *cyclohexane*,  $b^{CH}$  for the semi-axis of the (isotropic) C–H link, and respectively  $b_L^{CC}$  and  $b_T^{CC}$  for the longitudinal and transverse polarisabilities of the C–C bond, and assuming all intercarbon angles to be tetrahedral, we have

(i) for *cis*-decalin :

$$\begin{aligned} b_1 &= b_1^{cyH} + 3b_T^{CC} + 2b_L^{CC} \cos^2 19^\circ 28' \cos^2 30^\circ + 2b_T^{CC} \sin^2 30^\circ \\ &\quad + 2b_T^{CC} \sin^2 19^\circ 28' \cos^2 30^\circ + 6b^{CH} \\ b_2 &= b_1^{cyH} + 2b_T^{CC} + b_L^{CC} \cos^2 19^\circ 28' (1 + 2 \cos^2 60^\circ) + b_T^{CC} \sin^2 19^\circ 28' \\ &\quad (1 + 2 \cos^2 60^\circ) + 2b_T^{CC} \sin^2 60^\circ + 6b^{CH} \\ b_3 &= b_3^{cyH} + 2b_L^{CC} + 3b_L^{CC} \sin^2 19^\circ 28' + 3b_T^{CC} \cos^2 19^\circ 28' + 6b^{CH} \end{aligned}$$

(ii) for *trans*-decalin :

$$\begin{aligned} b_1 &= 2b_1^{cyH} - b_T^{CC} - 6b^{CH} \\ b_2 &= 2b_1^{cyH} - b_L^{CC} \cos^2 19^\circ 28' - b_T^{CC} \sin^2 19^\circ 28' - 6b^{CH} \\ b_3 &= 2b_3^{cyH} - b_L^{CC} \sin^2 19^\circ 28' - b_T^{CC} \cos^2 19^\circ 28' - 6b^{CH} \end{aligned}$$

Insertion of the values<sup>1</sup> (all in units of  $10^{-23}$  c.c.)  $b_1^{cyH} = 1.117$ ,  $b_3^{cyH} = 0.975$ ,  $b_L^{CC} = 0.0986$ ,  $b_T^{CC} = 0.0274$ , and  $b^{CH} = 0.0635$ , gives

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
For <i>cis</i> -decalin .....	1.73 <sub>0</sub>	1.73 <sub>0</sub>	1.65 <sub>0</sub>
„ <i>trans</i> - „ .....	1.82 <sub>6</sub>	1.76 <sub>2</sub>	1.53 <sub>4</sub>

These correspond to molar Kerr constants of  $0.25 \times 10^{-12}$  and  $3.5 \times 10^{-12}$ , respectively. Considering the various assumptions made (geometry of the decalins, that  ${}_D P / {}_E P = 1.1$ , etc.) and the difficulty of measuring a small  ${}_{\infty}({}_mK_2)$  with accuracy, we regard the agreement between prediction and experiment as satisfactory, and as strengthening our earlier conclusions regarding the anisotropic polarisability of the aliphatic C–C single bond.<sup>1</sup>

Finally it is of interest to mention that application of similar calculations to the (now generally discarded) 2-boat structure (III) leads to  $10^{23}b_1 = 1.824$ ,  $10^{23}b_2 = 1.721$ , and  $10^{23}b_3 = 1.571$ , whence  ${}_mK$  should be  $2.43 \times 10^{-12}$ . This is definitely higher than the

<sup>21</sup> Seidman, *Analyt. Chem.*, 1951, **23**, 559.

$0.15 \times 10^{-12}$  observed, and thus further contradicts (III) as the correct formula for *cis*-decalin; the argument seems quantitatively not inferior to that <sup>5</sup> drawn from empirical or semi-empirical energy differences.

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