

**679. Molecular Polarisability. The Molar Kerr Constants and Apparent Dipole Moments of Cyclopentadiene and Some of its Polymers.**

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The dipole moments and molar Kerr constants are recorded of cyclopentadiene and dicyclopentadiene as solutes in carbon tetrachloride, and of five polycyclopentadienes, having D.P.s (degrees of polymerisation) about 3, 4, 9, 22, and 31, as solutes in benzene. The polarities of the five polymers appear almost independent of the D.P. The anisotropic polarisabilities of the monomer and alternative dimers are calculated *a priori* and compared with experiment; the dimer studied is thus recognised as the *endo*-isomer. Empirical relations between D.P. and the density, dielectric constant, etc., measurements on benzene solutions are deduced and their applicabilities illustrated.

THE apparent polarities and anisotropic polarisabilities of cyclopentadiene and six of its oligomers as solutes in carbon tetrachloride or benzene have now been examined for reasons parallel to those given previously<sup>1</sup> in the cases of indene and the polyindenes.

#### EXPERIMENTAL

*Cyclopentadiene*.—Dicyclopentadiene (L. Light and Co.) was dried (MgSO<sub>4</sub>), filtered (under carbon dioxide), and distilled, b. p. 62°/14 mm. The dimer was then pyrolysed gently<sup>2,3</sup> (4—5 hr.) in an atmosphere of dry nitrogen, using a Friedrich-type condenser, and the distillate (cyclopentadiene, b. p. 42·5°/760 mm.,  $d_4^{25}$  0·7966,  $n_D^{25}$  1·4330) collected at solid-carbon dioxide temperature.

*Dicyclopentadiene*.—The pure monomer was allowed to dimerise spontaneously at room temperatures,<sup>4-6</sup> whereby colourless crystals, m. p. 31·5°, of the *endo*-dimer were slowly produced.

*Polycyclopentadienes I—V*.—Dicyclopentadiene was heated at 170—180° for 24 hr. in sealed tubes; <sup>5-7</sup> fractional vacuum-distillation then gave polymers I and II, b. p.s *ca.* 114°/12 mm. and 172°/12 mm. Polymers III—V were prepared by adding a 10% solution of anhydrous zinc chloride in chloroform at 25° to equal volumes of cyclopentadiene—chloroform mixtures (1 : 4 for III, 3 : 7 for IV, and 3 : 4 for V, v/v in each case). Addition was performed slowly, with constant stirring, under an atmosphere of nitrogen. With decrease of solvent ratio the reaction became more violent and the development of red colour more marked. After a further 24 hr. standing under nitrogen an excess of methanol was used to precipitate the crude polymers; these were taken up in benzene, fractionally reprecipitated by methanol, and the major fractions in each case, following ethanol washing, dried in a vacuum. They appeared as amorphous solids. Analyses of all samples of polymers I—V showed C and H contents within the limits 90—91 and 9·0—9·5% (Calc. 90·85 and 9·15%, respectively). Molecular weights, determined cryoscopically in benzene, recorded for different preparations were as follows (PCP = polycyclopentadiene; D.P. = degree of polymerisation indicated by the mean molecular weight):

PCP .....	I	II	III	IV	V
MW .....	198; 200	270; 260	607; 614; 576	1465; 1479	2031; 2093; 1950
D.P. ....	3	4	9·1	22·3	30·7

*Methods and Results*.—Details of apparatus, techniques, calculations, and symbols not defined below are in references given by Le Fèvre and Sundaram.<sup>1</sup> Cyclopentadiene and dicyclopentadiene were examined in carbon tetrachloride as solvent, and the polycyclopentadienes in benzene. Table 1 shows, for solutions each containing a weight-fraction  $w_2$  of solute, the differences  $\Delta n$ ,

<sup>1</sup> Le Fèvre and Sundaram, *J.*, 1964, 556.

<sup>2</sup> Moffett, *Org. Synth.*, 1952, **32**, 41.

<sup>3</sup> Khambata and Wassermann, *Nature*, 1936, **138**, 368.

<sup>4</sup> Waring, Kern, and Blann, *J. Amer. Chem. Soc.*, 1941, **63**, 767.

<sup>5</sup> Standing and Rheiner, *Helv. Chim. Acta*, 1924, **7**, 23.

<sup>6</sup> Wilson and Wells, *Chem. Rev.*, 1944, **34**, 1.

<sup>7</sup> Standing and Bruson, *Annalen*, 1926, **447**, 97.

TABLE 1.

Values of  $\Delta n$ ,  $\Delta n^2$ ,  $\Delta d$ ,  $\Delta \epsilon$ , and  $\Delta B$  for solutions containing weight fractions  $w_2$  of solute at 25°.

*Cyclopentadiene in carbon tetrachloride*

$10^3 w_2$ ...	2213	3695	4254	5177	7913	8157	9742	10,452	10,645	12,056	13,995
$-10^4 \Delta n$ ...	—	2	—	—	4	4	5	5	—	6	7
$-10^4 \Delta n^2$ ...	—	6	—	—	11	11	14	14	—	17	20
$-10^5 \Delta d$ ...	—	—	6084	7301	—	11,303	12,859	—	—	—	17,339
$10^4 \Delta \epsilon$ ...	—	—	—	—	210	224	253	278	—	325	378
$10^{10} \Delta B$ ...	18	28	31	38	51	—	60	—	65	—	—

whence  $\Sigma \Delta n / \Sigma w_2 = -0.005$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = -0.014$ ;  $\Delta d = -1.5334w_2 + 2.1w_2^2$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 0.268$ ;  
 $10^7 \Delta B = 0.8322w_2 - 2.17w_2^2$ .

*Dicyclopentadiene in carbon tetrachloride*

$10^3 w_2$ ...	1599	3449	5068	6890	8209	9196	9295	9357	13,075	17,774	23,016
$10^4 \Delta n$ ...	15	34	50	69	79	91	—	92	—	—	—
$10^4 \Delta n^2$ ...	45	102	150	207	237	273	—	276	—	—	—
$-10^5 \Delta d$ ...	1568	3352	4882	6602	8158	8624	—	9224	—	—	—
$10^4 \Delta \epsilon$ ...	100	196	300	350	440	460	—	480	—	—	—
$10^{10} \Delta B$ ...	—	—	—	—	—	—	43	—	54	76	93

whence  $\Sigma \Delta n / \Sigma w_2 = 0.098$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = 0.295$ ;  $\Sigma \Delta d / \Sigma w_2 = -0.9690$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 0.531$ ;  
 $10^7 \Sigma \Delta B / \Sigma w_2 = 0.421$ .

	<i>PCP I in benzene</i>					<i>PCP II in benzene</i>					
$10^3 w_2$ ...	1241	1655	2105	2855	3109	1064	1511	2305	3106	3621	4442
$10^4 \Delta n$ ...	11	16	19	25	28	10	13	20	27	31	37
$10^4 \Delta n^2$ ...	33	47	56	75	84	29	38	59	80	93	110
$10^5 \Delta d$ ...	271	362	458	624	682	235	332	484	714	797	988
$10^4 \Delta \epsilon$ ...	58	82	113	139	155	50	77	106	127	160	186
$10^{10} \Delta B$ ...	1	1	2	2	3	—	—	0.9	—	1.1	1.4

whence  $\Sigma \Delta n / \Sigma w_2 = 0.090$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = 0.269$ ;  $\Sigma \Delta d / \Sigma w_2 = 0.2186$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 0.499$ ;  
 $10^7 \Sigma \Delta B / \Sigma w_2 = 0.082$ .

whence  $\Sigma \Delta n / \Sigma w_2 = 0.086$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = 0.255$ ;  
 $\Sigma \Delta d / \Sigma w_2 = 0.2212$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 0.440$ ;  
 $10^7 \Sigma \Delta B / \Sigma w_2 = 0.033$ .

	<i>PCP III in benzene</i>				<i>PCP IV in benzene</i>				<i>PCP V in benzene</i>				
$10^3 w_2$ ...	1845	2127	3123	3974	1001	1414	2179	3148	3529	2121	2918	3347	3990
$10^4 \Delta n$ ...	21	25	36	46	12	17	25	35	40	25	34	39	45
$10^4 \Delta n^2$ ...	62	74	107	137	35	50	74	105	119	74	101	116	134
$10^5 \Delta d$ ...	421	485	713	907	228	324	498	721	812	489	672	776	913
$10^4 \Delta \epsilon$ ...	85	96	146	185	43	60	93	135	153	90	127	140	170
$10^{10} \Delta B$ ...	—	—	—	—	-1	-2	-3	-4	-5	-3	-4	-6	-7

whence  $\Sigma \Delta n / \Sigma w_2 = 0.116$ ;  $\Sigma \Delta n^2 / \Sigma w_2 = 0.343$ ;  
 $\Sigma \Delta d / \Sigma w_2 = 0.2282$ ;  $\Sigma \Delta \epsilon / \Sigma w_2 = 0.463$ ;  
 $\Sigma \Delta B / \Sigma w_2 = 0$ .

whence  $\Sigma \Delta n / \Sigma w_2 = 0.114$ ;  
 $\Sigma \Delta n^2 / \Sigma w_2 = 0.340$ ;  
 $\Sigma \Delta d / \Sigma w_2 = 0.2292$ ;  
 $\Sigma \Delta \epsilon / \Sigma w_2 = 0.429$ ;  
 $10^7 \Sigma \Delta B / \Sigma w_2 = -0.133$ .

whence  $\Sigma \Delta n / \Sigma w_2 = 0.116$ ;  
 $\Sigma \Delta n^2 / \Sigma w_2 = 0.343$ ;  
 $\Sigma \Delta d / \Sigma w_2 = 0.2303$ ;  
 $\Sigma \Delta \epsilon / \Sigma w_2 = 0.426$ ;  
 $10^7 \Sigma \Delta B / \Sigma w_2 = -0.162$ .

TABLE 2.

Total polarisations, molar refractions, apparent dipole moments, and specific and molar Kerr constants deduced from Table 1.

	Monomer *	Dimer *	PCP I †	PCP II †	PCP III †	PCP IV †	PCP V †
$\alpha \epsilon_1$ .....	0.268	0.531	0.499	0.440	0.463	0.429	0.426
$\beta$ .....	-0.9677	-0.6115	0.2502	0.2532	0.2612	0.2623	0.2636
$\gamma' n_1^2$ .....	-0.014	0.295	0.269	0.255	0.343	0.340	0.343
$\gamma$ .....	-0.003	0.067	0.060	0.057	0.077	0.076	0.077
$\delta$ .....	11.89	6.02	0.200	0.080	0	-0.324	-0.395
$\infty P_2$ (c.c.) .....	0.3888	0.3510	0.3500	0.3379	0.3389	0.3322	0.3312
$\infty r_2$ (c.c.) .....	0.3359	0.3101	0.3030	0.2992	0.3130	0.3120	0.3123
$10^{14} \infty (K_2)$ ...	10.3	5.5	4.9	4.2	3.3	0.97	0.42
$M_2$ .....	66.1	132.2	198	264	599	1472	2025
$10^{12} \infty (M_2)$ ...	6.8	7.3	9.7	11.2	19.8	14.3	8.5
$T_P$ (c.c.) .....	25.7	46.4	69.3	89.2	203.0	489.0	670.6
$R_D$ (c.c.) .....	22.2	41.0	60.0	79.0	187.5	459.2	632.5
$\mu$ (D) ‡ .....	0.34	0.40	0.51	0.55	0.55	0.58	0.56

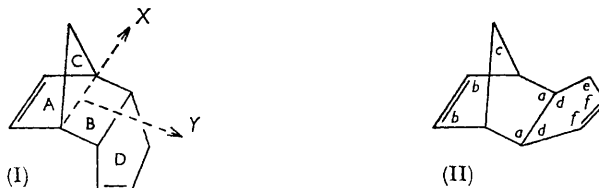
\* Solvent: carbon tetrachloride. † Solvent: benzene. ‡ Calculated assuming  $D^P = 1.05R_D$ .

$\Delta n^2$ ,  $\Delta d$ ,  $\Delta \epsilon$ , and  $\Delta B$  between the refractive indexes, the squares of the refractive indexes, the densities, the dielectric constants, and the Kerr effects, respectively, of the solutions and the solvent. All measurements were made at 25°. When  $w_2 = 0$ ,  $n$ ,  $d$ ,  $\epsilon$ , and  $B$  are, respectively, 1.4575, 1.5845, 2.2270, and  $0.070 \times 10^{-7}$  for carbon tetrachloride, and 1.4973, 0.8738, 2.2725, and  $0.410 \times 10^{-7}$  for benzene;  $n$  and  $B$  refer throughout to Na-light. Polarisation, dipole moments, etc., deduced from data in Table 1, are in Table 2.

## DISCUSSION

*Polarity and Molar Kerr Constant of Cyclopentadiene.*—Syrkin *et al.*<sup>8</sup> first reported the dipole moment of cyclopentadiene as 0.45 D in benzene as solvent. Hannay and Smyth,<sup>9</sup> for the gas at temperatures from 344.4 to 452.1°K, record 0.53 D as a mean value of 17 results ranging between 0.51 and 0.56 D. Microwave studies by Laurie<sup>10</sup> indicate 0.416 D. The moment now found in carbon tetrachloride (0.34 D) is lower than those from refs. 8–10, mainly because the  $R_D$  calculated from the  $\Delta n$ 's and  $\Delta d$ 's of Table 1 (22.2 c.c.) slightly exceeds that from the  $n_D$  and  $d_4^{25}$  of liquid cyclopentadiene (21.83 c.c.);<sup>11</sup> when 21.8 c.c. is taken as  ${}_D P$ , the  ${}_T P$  of 25.7 c.c. listed in Table 2 corresponds to  $\mu = 0.44$  D.

According to entry M 180 of ref. 12, cyclopentadiene is flat, with angles CH=CH=CH, CH=CH-CH<sub>2</sub>, and CH-CH<sub>2</sub>-CH of  $110 \pm 2^\circ$ ,  $109 \pm 3^\circ$ , and  $101 \pm 4^\circ$ , respectively. Using the anisotropic bond polarisabilities appropriate for the C=C, C-C, and C-H links,<sup>13</sup> together with values for the angles quoted of  $110^\circ$ ,  $109^\circ$ , and  $101^\circ$ , the semi-axes of the molecular polarisability ellipsoid should be  $b_1 = 1.034$  (measured along the direction of action of the resultant molecular moment, *i.e.*, the bisector of the angle CH-CH<sub>2</sub>-CH),  $b_2 = 0.817$ , and  $b_3 = 0.620$  (measured perpendicularly to the ring-plane).<sup>\*</sup> A calculated molar Kerr constant therefore follows as  $10.5 \times 10^{-12}$ , against the smaller observed  ${}_m K$  of  $6.8 \times 10^{-12}$ . This imperfect agreement may be in part due to incorrectness of the CCC angles chosen, but more probably arises from the over-simple view that the structure incorporates only single and double carbon-carbon bonds whereas, in fact (as inter-centre distances<sup>12</sup> of 1.46, 1.53, and 1.35 Å suggest), all five of these are more or less hybridised.



It is relevant that if the semi-axes of the unit (CH=CH), as deduced for benzene by Aroney, Le Fèvre, and Sundaram,<sup>14</sup> be applied in the present problem we have, for a regular pentagonal model,  $b_1 = b_2 = 0.996$ ,  $b_3 = 0.679$ , and  ${}_m K$  (calc.) =  $7.0 \times 10^{-12}$ .

*Polarity and Molar Kerr Constant of Dicyclopentadiene.*—Formulation of the *endo*- and *exo*-dicyclopentadienes as (I) and (II) has depended largely on chemical rather than physical arguments.<sup>15,16</sup> The dipole moment now reported for the dimer with m. p. 31.5° cannot differentiate between (I) and (II); either might show a  $\mu$  of *ca.* 0.4 D by analogy with other di-olefins.<sup>17</sup> The *a priori* calculation of the molar Kerr constants expected for (I) and (II) has, therefore, been attempted.

\* Polarisabilities are expressed as  $10^{-23}$  c.c. units.

<sup>8</sup> Syrkin and Shott L'vova, *Acta Physicochim. U.R.S.S.*, 1944, **19**, 379.

<sup>9</sup> Hannay and Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 244.

<sup>10</sup> Laurie, *J. Chem. Phys.*, 1956, **24**, 635.

<sup>11</sup> Auwers and Eisenlohr, *Ber.*, 1910, **43**, 821.

<sup>12</sup> Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ. No. 11*, 1958.

<sup>13</sup> Le Fèvre, *J. Proc. Roy. Soc. N.S.W.*, 1961, **95**, 1.

<sup>14</sup> Aroney, Le Fèvre, and Somasundaram (Sundaram), *J.*, 1960, 1812.

<sup>15</sup> Alder and Stein, *Annalen*, 1934, **514**, 1; *Ber.*, 1934, **67**, 613.

<sup>16</sup> Pirsch, *Ber.*, 1934, **67**, 101.

<sup>17</sup> Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, New York and London, 1955, p. 263.

In the absence from the literature of metrical structural information concerning (I) and (II), inter-valence and inter-plane angles have been measured on "Barton" models as follow:  $a = 104^\circ$ ,  $b = 109^\circ$ ,  $c = 92^\circ$ ,  $d = 105^\circ$ ,  $e = 106^\circ$ ,  $f = 112^\circ$ , between planes A and B  $112^\circ$ , between B and C  $121^\circ$ , between A and C  $127^\circ$ , and between B and D  $120^\circ$ ; in (I) the plane D is situated *trans*, and in (II) *cis*, to the methylene bridge which makes plane C. Three arbitrary axes  $OX$ ,  $OY$ , and  $OZ$  are placed in the models so that  $OX$  is parallel to the double bond in plane A,  $OY$  is in plane B and at  $90^\circ$  to  $OX$ , and  $OZ$  is perpendicular to  $OX$  and  $OY$ . The semi-axes of polarisability, and their locations within the  $OXYZ$  frame, computed (cf. ref. 18 for procedure) for (I) and (II) are in Table 3.

The anisotropy of (I) is less than that of (II) (cf. definition of  $\theta_1$  on p. 270 of ref. 19). The molar Kerr constants predictable from Table 3 depend upon the directions of action of the resultant dipole moment. If  $\mu = 0.4$  D acts parallel to  $b_3$  (*i.e.*, near to  $OZ$ ),  $10^{12}$  mK (calc.) is  $9.1_5$  for (I) and  $12.0_5$  for (II); if it acts parallel to  $b_1$  (*i.e.*, near to  $OX$ ), the corresponding values are  $12.7$  and  $29.4$ . Inspection of models suggests that the molecular resultant is likely to be nearer  $OZ$  in (I) and nearer  $OX$  in (II); as a consequence the mK for (I) should be less than for (II). The mK now observed ( $7.3 \times 10^{-12}$ ) is thus more consistent with the dicyclopentadiene of m. p.  $31.5^\circ$  being (I) than (II), in agreement with earlier conclusions drawn from other evidence.<sup>4-7,15</sup> As it is possible that  $\mu = 0.4$  D is a high assessment (owing to ignorance of the true distortion polarisation of this solute) it may be added that were  $\mu = 0$  D the mK's of (I) and (II) would be  $7.6 \times 10^{-12}$  and  $24.3 \times 10^{-12}$ , respectively, and the above inference would still be valid.

TABLE 3.

Semi-axes and locations of the molecular polarisability ellipsoids computed for (I) and (II).

Model (I)	Direction cosines with			Model (II)	Direction cosines with		
	$OX$	$OY$	$OZ$		$OX$	$OY$	$OZ$
$b_1 = 1.756$	0.9979	0.0142	-0.0642	1.757	0.9980	0.0142	0.0617
$b_2 = 1.316$	-0.0448	0.8894	-0.4550	1.835	-0.0111	0.7933	0.6087
$b_3 = 1.622$	0.0480	0.4570	0.8882	1.102	-0.0625	0.6087	-0.7910

whence  $10^{30}\theta_1 = 1.81$  for (I) and  $5.78$  for (II).

*Polarities and Molar Kerr Constants of the Polycyclopentadienes.*—No dipole moments of polycyclopentadienes have previously been reported. Of interest is the fact that, in benzene, their apparent  $\mu$ 's are almost independent of their molecular weights. Accordingly, "Debye-Bueche" quotients<sup>20</sup> fall with the degree of polymerisation  $x$  whether the moment  $\mu_0$  of the repeating unit be taken as that of cyclopentene (*viz.*,  $0.97$  D, cf. ref. 21) or as the lower value of cyclohexene (*viz.*,  $0.6$  D, cf. ref. 17); moreover they are unusually small:

Polymer.....	I	II	III	IV	V
$\mu_{\text{apparent}}^2/x (0.97)^2$ .....	0.092	0.080	0.035	0.016	0.011
$\mu_{\text{apparent}}^2/x (0.6)^2$ .....	0.240	0.210	0.092	0.042	0.028

Such behaviour, in the light of ref. 20, suggests that these polymers are not flexible; it is in contrast with our observations recorded<sup>22</sup> for poly(vinyl chloride) and various other polyvinyls, but not with those made for the polyindenes.<sup>1</sup> The situation is understandable if, as supposed by Standing and Bruson,<sup>7</sup> dicyclopentadiene is first formed in the high-temperature polymerisation process, and the dimer reacts further in a series of steps, cyclopentadiene adding at the double bond in the bridged cyclohexene ring of the  $(n - 1)$ -mer. The polycyclopentadienes I and II now studied have molecular weights corresponding to

<sup>18</sup> Eckert and Le Fèvre, *J.*, 1962, 1081.

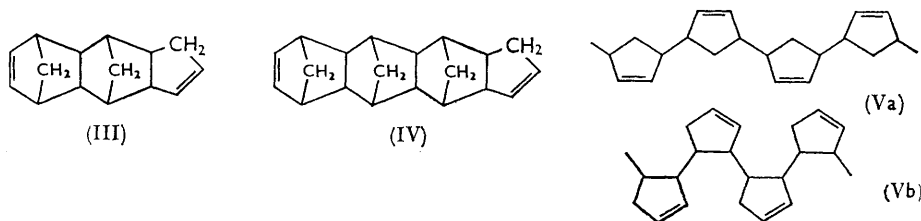
<sup>19</sup> Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem. (Australia)*, 1955, 5, 262.

<sup>20</sup> Debye and Bueche, *J. Chem. Phys.*, 1951, 19, 589.

<sup>21</sup> Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

<sup>22</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494, 4003; *J.*, 1963, 1880, 3188.

the trimer and the tetramer, respectively. They are probably mixtures of conformers (eight stereo-forms of the trimer are possible, although only two are known<sup>23,24</sup>). Table 2 shows the apparent moments of structures (III) and (IV) to be 0.51 and 0.55 D, so that assemblages of these types at the beginning of a macromolecular chain could contribute



an apparent moment of 0.5—0.6 D to all higher polymers produced by growth from them, whether such growth involves addition mechanisms characteristic of butadienoid or monoolefinic compounds.<sup>25</sup> The former mechanism merely interpolates non-polar units between the chain-ends, as in passing from (III) to (IV), and thus will not affect the resultant molecular moment so long as the relative dispositions of the two double bonds remain unchanged; the latter mechanism adds cyclopentene units to one or both double bonds to develop polycyclopentene chains, formulæ for which (cf. proposals by Wilson and Wells<sup>26</sup>) might be (Va) and (Vb). Scale models of such segments show (Va) to be less crowded than (Vb); in neither can adjacent rings be coplanar and in both there is space for partial rotations about the C—C bonds joining the rings. Chains built on these patterns are

TABLE 4.

Apparent semi-axes of polarisability \* for polycyclopentadienes I—V.

Polymer	$\pm(b_1 - b_2)$	$b_1 + 2b_2$	$b_1$	$b_2$
I	0.239	6.778	2.418	2.180
II	0.242	8.924	3.136	2.894
III	0.378	21.178	7.312	6.933
IV	0.280	51.869	17.477	17.196
V	0.192	71.453	23.946	23.754

\* Calculated taking  $(b_1 - b_2)$  as positive.

TABLE 5.

Empirical connections between physical properties and logarithms of the degrees of polymerisation of polycyclopentadiene (PCP) preparations.

	$M_2$ of PCP	198	264	599	1472	2025
$\alpha\epsilon_1$	{ calc. as $0.539 - 0.082L$ .....	0.500	0.490	0.460	0.428	0.411
	{ obsd. ....	0.499	0.440	0.463	0.429	0.426
$\beta d_1$	{ calc. as $0.2147 + 0.0108L$ .....	0.2198	0.2212	0.2251	0.2293	0.2308
	{ obsd. ....	0.2186	0.2212	0.2282	0.2292	0.2303
$\delta B_1$	{ calc. as $0.20 - 0.247L$ .....	0.082	0.051	-0.037	-0.133	-0.167
	{ obsd. ....	0.082	0.033	0	-0.133	-0.162
$\infty P_2$	{ calc. as $0.3597 - 0.0204L$ .....	0.3500	0.3474	0.3401	0.3322	0.3294
	{ obsd. ....	0.3500	0.3379	0.3389	0.3322	0.3312
$\infty (sK_2)$	{ calc. as $6.7 - 4.4L$ .....	4.8	4.25	2.67	0.97	0.36
	{ obsd. ....	4.9	4.20	3.30	0.97	0.42

easily twisted into a variety of randomly coiled or helical conformations the resultant moments of which would be *ca.* zero; macromolecules composed of such chains united to a unit based, *e.g.*, on (III) or (IV) should, therefore, all show mainly the polarity due to the latter, irrespective of chain length.

<sup>23</sup> Alder, Stein, Reese, and Grassmann, *Annalen*, 1932, 496, 204.

<sup>24</sup> Alder and Stein, *Ber.*, 1934, 67, 373; *Angew. Chem.*, 1934, 47, 837.

<sup>25</sup> Farmer, *Ann. Reports*, 1932, 29, 105.

<sup>26</sup> Wilson and Wells, *Chem. Rev.*, 1944, 34, 1.

Because of the number and complexity of the models involved, *a priori* calculations of polarisability ellipsoids for (III) or (IV), with or without their possible side-chains, have not been attempted. If present measurements are analysed by the method used previously for other polymers,<sup>1,22</sup> apparent semi-axes emerge as in Table 4. (Ellipsoids of revolution are assumed; this assumption should become more valid the larger the polymer. Even if made for the monomer, the  ${}_mK$ ,  $\mu$ , and  $R_D$  given in Table 2 lead to  $b_1 = 1.00$ ,  $b_2 = b_3 = 0.74$ , compared with  $b_1 = 1.03$ ,  $b_2 = 0.82$ , and  $b_3 = 0.62$  deduced from bond data; the mean of  $b_2$  and  $b_3$  is 0.72). The anisotropies thus revealed are comparable with those of the polyindenes, and show signs of passing through a maximum around D.P.s of about 9.

*Physical Properties and Degrees of Polymerisation of the Polycyclopentadienes.*—As before<sup>1,22,27</sup> with other polymers, empirical equations involving  $L = \log (M_{\text{polymer}}/M_{\text{monomer}})$  can be fitted fairly satisfactorily to most of the measured quantities. Table 5 summarises the relations found; that they are straight-line functions of  $L$  is a further similarity between the polyindenes<sup>1</sup> and polycyclopentadienes.

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<sup>27</sup> Le Fèvre, Le Fèvre, and Parkins, *J.*, 1958, 1468; 1960, 1814.

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