362. *Molecular Polarisability. The Anisotropies of Diphenylpolyenes.*

By R. Bramley and R. J. W. Le Fèvre.

The molar Kerr constants for the four molecules Ph·[CH⁚CH]$_n$·Ph with n = 1—4 are reported. Results are discussed on the assumption that exaltations of polarisability occur predominantly along the directions of $b_{\text{max.}}$; on such a basis, *a priori* estimates of $_{\text{m}}K$ may be made from the semi-axes known for isolated (non-conjugated) bonds. Exaltations of $b_{\text{max.}}$ appear as linear with the cube of the length of the " bisector axis " (which joins the mid-points of the bonds of the polyene chain); they may also be empirically connected with $\lambda_{\text{max.}}$ of the K-band by the equation:

$$10^{23}\Delta b_{\text{max.}} = 9{\cdot}762 \times 10^{-7}(\lambda_{\text{max.}} - 206)^3.$$

This paper continues a study of the polarisability ellipsoid of the C=C bond. Bramley, Le Fèvre, Le Fèvre, and Rao[1] reported semi-axes as $b_{\text{L}}^{\text{C=C}} = 0{\cdot}280$, $b_{\text{L}}^{\text{C=C}} = 0{\cdot}073$, and $b_{\text{V}}^{\text{C=C}} = 0{\cdot}077$ (all 10^{-23} c.c.). Although these were drawn from the particular case of 1,1-dichloroethylene, they appeared to be satisfactorily applicable to *isolated* C=C links in other molecular environments. They are not expected to be usable in conjugated systems. To explore the effects of conjugation, measurements have now been made on the first four members of the αω-diphenylpolyene series, Ph·[CH=CH]$_n$·Ph, where n = 1—4. Examination of homologues higher than these is prevented by low solubility.

Experimental

Solutes.—Stilbene, prepared from benzylmagnesium chloride and benzaldehyde, as in ref. 2, had m. p. 124—124·5°. 1,4-Diphenylbutadiene, obtained by a Perkin reaction, with decarboxylation, from redistilled cinnamaldehyde and phenylacetic acid, had m. p. 152·5—153·5° after four recrystallisations from 3 : 5 benzene–ethanol. 1,6-Diphenylhexatriene was difficult to purify when made from cinnamaldehyde through hydrocinnamoin;[3] Ismail and Schönberg's directions,[4] however, gave pale-yellow crystals, m. p. 200° (from benzene). 1,8-Diphenyloctatetraene was prepared from litharge, succinic anhydride, and cinnamaldehyde as reported by Kuhn and Winterstein.[3] Instead of cooling the reaction mixture to 40° K as suggested, it was allowed to cool to room temperature and the solid filtered off and washed with ethanol. The amount of the tetraene thus lost was less than 5% of the total yield (tested by extraction and washing processes on the filtrate). Two crystallisations from chloroform then gave golden-yellow leaflets, m. p. 232°.

Solvent.—Commercial " Benzol cryst." from local sources was shaken with successive amounts of concentrated sulphuric acid until the latter no longer acquired colour. It was then refluxed over aqueous sodium hydroxide for 8 hr., dried with phosphoric oxide, and distilled on to sodium wire, with which the purified solvent was stored until required.

Solutions were made up and handled as far as possible in a weak light, to reduce any likelihood of photo-isomerisation of the otherwise " all-*trans* " solutes.[5]

Apparatus, Procedures, Observations, etc.—Normal routines have been followed; they are described in references cited by Bramley *et al.*[1] Observations are listed under usual headings in Table 1; they lead to quantities listed in Table 2.

---

[1] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.
[2] " Organic Syntheses," **17**, p. 90.
[3] Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 89, 96.
[4] Ismail and Schönberg, *J.*, 1945, 200.
[5] Wyman, *Chem. Revs.*, 1955, **55**, 625.

TABLE 1. *Observations on αω-diphenylpolyenes in benzene * at 25°.*

trans-1,2-*Diphenylethylene in benzene.*

10^5w_2	529	1397	2282	2526	2713	3050	4540·5	5162
ε_{12}	2·2752	2·2783	2·2814	2·2830	2·2832	2·2846	2·2908	2·2933
d_{12}	0·87449	0·87573	0·87684	0·87732	0·87764	0·87801	0·88010	0·88107
$10^4\Delta n$	7	19	33	36	39	44	66	76
$10^7\Delta B$	0·016	0·051	0·076	0·084	0·088	0·103	0·168	0·190

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}404_5$, $\sum\Delta d/\sum w_2 = 0{\cdot}1395$, $\sum\Delta n/\sum w_2 = 0{\cdot}144_2$, $10^7\sum\Delta B/\sum w_2 = 3{\cdot}49_6$.

1,4-*Diphenylbutadiene*

10^5w_2	986	1106	1155					
ε_{12}	2·2774	2·2780	2·2784					
d_{12}	0·87470	0·87475	0·87475					
10^5w_2	928	1097	1493·5	2274	3081	4057	4223	5846
$10^4\Delta n$	19	24	31	48	64	84	90	121
$10^7\Delta B$	0·090	0·103	0·130	0·213	0·278	0·368	0·392	0·535

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}502$, $\sum\Delta d/\sum w_2 = 0{\cdot}0881$, $\sum\Delta n/\sum w_2 = 0{\cdot}209_1$, $10^7\sum\Delta B/\sum w_2 = 9{\cdot}17$.

1,6-*Diphenylhexatriene*

10^5w_2	76·1	162·2	176·2	229·0
ε_{12}	2·2729	2·2740	2·2738	2·2743
d_{12}	—	0·87400	0·87402	0·87408
$10^4\Delta n$	2·5	3	5	6·5
$10^7\Delta B$	0·020	0·024	0·028	0·039

Whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}78$, $\sum\Delta d/\sum w_2 = 0{\cdot}134$, $\sum\Delta n/\sum w_2 = 0{\cdot}26_4$, $10^7\sum\Delta B/\sum w_2 = 16{\cdot}7$.

1,8-*Diphenyloctatetraene*

10^5w_2	68·5	69·1	75·7	78·8	79·2	94·5		
ε_{12}	2·2738	2·2742	2·2741	2·2741	2·2741	2·2742		
d_{12}	0·87409	0·87394	0·87407	0·87409	0·87401	0·87427		
10^5w_2	20·8	37·5	44·8	58·7	65·3	77·3	78·5	100·5
$10^4\Delta n$	1	2	2	3	3	4	4	5
$10^7\Delta B$	0·009	0·013	0·019	0·027	0·023	0·024	0·029	0·034

Whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}04$, $\sum\Delta d/\sum w_2 = 0{\cdot}384$, $\sum\Delta n/\sum w_2 = 0{\cdot}49_6$, $10^7\sum\Delta B/\sum w_2 = 36{\cdot}8$.

* For $w_2 = 0$, $\varepsilon_{12} = 2{\cdot}2725$, $d_{12} = 0{\cdot}87378$, $n_{12} = 1{\cdot}4973$, $B = 0{\cdot}410$.

TABLE 2. *Calculation of polarisations, molar Kerr constants, etc., for* Ph·[CH=CH]$_n$·Ph *in benzene at 25°.*

Solute	$\alpha\varepsilon_1$	β	γ	δ	${}_\infty P_2$ (c.c.)	$10^{12}\,{}_\infty({}_\mathrm{m}K_2)$
$n = 1$	0·405	$0{\cdot}159_6$	0·096	8·53	65·3	124
$n = 2$	0·502	$0{\cdot}100_8$	0·140	22·4	82·7	357
$n = 3$	0·777	$0{\cdot}153_2$	0·177	39·1	101·0	692
$n = 4$	2·04	$0{\cdot}439_7$	0·332	89·9	148·4	1740

DISCUSSION

Exaltations of Polarisabilities.—The molar Kerr constants for these polyenes increase more rapidly with n than would be expected from additivity; for the first three members they may be *roughly* expressed by $10^{12}{}_\mathrm{m}K = 41 + 79n^2$, which corresponds, when $n = 0$, 1, 2, or 3, to 41, 120, 357, or 752 respectively. Biphenyl with ${}_\infty({}_\mathrm{m}K_2) = 40{\cdot}5 \times 10^{-12}$ (ref. 6) can thus be brought into line with the present work, although the case of the octatetraene (${}_\mathrm{m}K$'s forecast and observed: 1305×10^{-12} and 1740×10^{-12}) appears unsatisfactory on this basis.

Qualitatively such facts are attributable to the considerable exaltations of polarisability which occur with highly conjugated molecules.[7] Molecular-refraction data for stilbene,[8] diphenylbutadiene,[9] and hexatriene [8] show $R_\mathrm{obs} - R_\mathrm{calc}$ to be *ca.* +6·45, +14·9, and

---

[6] Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666.

[7] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 125.

[8] Chilesotti, *Gazzetta*, 1900, **30**, I, 149.

[9] Smedley, *J.*, 1908, **93**, 376.

+24·2 c.c. (α-line); these indicate exaltations of *mean* molecular polarisability of about 0·25, 0·59, and 0·96 × 10^{-23} c.c.; for the octatetraene present measurements give an R_D near 124 c.c. (low solubility causes some uncertainty) so that, R_{calc} being 85·5 c.c., an exaltation of 1·52 × 10^{-23} c.c. follows: this seems reasonable. It is thus probable that to some extent the C=C bonds in these molecules have lost their identities, and the π-electrons become part of a delocalised system; nevertheless, in attempting an analysis of our results we must separate the exaltation of polarisability due to conjugation from the polarisability of an " isolated " C=C bond, although such an approach differs from that of most theoretical workers,[10–12] who treat the σ- and π-electrons independently. Admittedly the latter is the more obvious scheme, but unfortunately it is not experimentally possible.

For our purposes details of molecular geometry are assumed to be similar to those used by Zechmeister and Le Rosen[13] for the stereoisomers of diphenyloctatetraene; some recently available data[14,15] differ slightly from those of Zechmeister *et al.*,[13] but the discussion below is not significantly affected thereby. We take the diphenylpolyenes as planar, although in the crystal the aromatic rings may be a few degrees out of the plane of the polyene zig-zag.[14,15]

To begin a quantitative comparison of the experimental and calculated anisotropies it is first necessary to decide on a suitable direction for $b_{max.}$. Polarisability semiaxes of isolated bonds and of the phenyl group are adopted as follows:

	C–H	C–C	C=C	C_6H_5
$10^{23}b_L$	0·064	$0{\cdot}098_6$	0·280	1·05
$10^{23}b_T$	0·064	$0{\cdot}027_4$	0·073	1·05
$10^{23}b_V$	0·064	$0{\cdot}027_4$	0·077	0·669
Source	Methane[16]	Cyclohexane[17]	Vinylidene dichloride[1]	Benzene[18]

and inter-atomic distances in these polyenes accepted from ref. 13 as: carbon–carbon in the $[C_2H_2]_n$ chain, 1·33 Å and 1·46 Å alternately; carbon–phenyl-carbon, 1·44 Å, and C_{Ar}–C_{Ar} in each phenyl ring, 1·39 Å; the angles between the links of lengths 1·33 and 1·46 Å being 124·2° throughout.

If resonance is ignored and the above b's for the bonds are used with the geometry stated, the ${}_mK$'s to be expected may be calculated for three alternative dispositions of $b_{max.}$ ($=b_1$): (*a*) supposing that b_1 lies along the 4,4′-axis, (*b*) supposing b_1 to be parallel to the C–C bonds, or (*c*) supposing b_1 to be directed along a line joining the mid-points of the bonds of the polyene chain—the " bisector axis " in what follows. An attempt has also been made to calculate the position of $b_{max.}$ by expressing it in terms of an angle γ between its direction and that of the C–C bonds in the molecule. By differentiation we obtain $\tan 2\gamma = 0{\cdot}1928n/(0{\cdot}0712 - 0{\cdot}0041n)$ from which γ emerges as 35·2°, 40·2°, 42·5° and 42·8° for $n = 1$—4, and approaches 45·4° for $n = \infty$. However, since resonance affects both C–C and C=C bonds, such a solution is unrealistic.

The $10^{12}{}_mK$'s calculated for the three cases are given below; for comparison, the four ${}_mK$'s from experiment are shown in the right-hand column:

n	*a*	*b*	*c*	${}_mK$
1	43·9	43·4	44·7	124
2	58·5	57·1	61·5	357
3	73·8	72·4	81·6	692
4	97·0	89·6	105·2	1740

---

[10] Bolton, *Trans. Faraday Soc.*, 1954, **50**, 1261, 1265.
[11] Mueller, *J. Chem. Phys.*, 1954, **22**, 120.
[12] Davies, *Trans. Faraday Soc.*, 1952, **48**, 789.
[13] Zechmeister and Le Rosen, *J. Amer. Chem. Soc.*, 1942 **64**, 2757.
[14] Dreuth and Wiebenga, *Acta Cryst.*, 1955, **8**, 755.
[15] Sutton, *Chem. Soc. Special Publ.* No. 11, 1958.
[16] Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.
[17] Le Fèvre and Le Fèvre *J.*, 1956, 3549.
[18] *Idem*, *J.*, 1954, 1577.

In all instances the ${}_mK$'s predicted are too small. Because basis (*c*) leads to the largest estimates, we select the " bisector axis " as the direction for b_1, and note that the calculated ellipsoids for (*c*) are specified as follow:

n	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	n	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
1	2·628	2·433	1·598	3	3·514	3·017	2·063
2	3·071	2·725	1·830	4	3·957	3·309	2·295

The " bisector axis " seems a reasonable line along which to measure $b_{\text{max.}}$ since it should correspond to the electromeric shifts, formulated as $C{=}\overset{\curvearrowright}{C}{-}C{=}\overset{\curvearrowright}{C}{-}C{=}\overset{\curvearrowright}{C}{-}$ and producing the mesomeric state.

To proceed further requires approximations and assumptions: (i) that the exaltations are entirely along b_1 with no corresponding changes in b_2 or b_3, (ii) that polarisability data for the bonds concerned remain constant throughout the homologous series, and (iii) that bond lengths and angles are also the same from molecule to molecule.

There are two ways of deducing $b_{\text{max.}}$ when b_2 and b_3 are known from calculations. From ${}_\infty({}_mK_2)$ may be derived $\phi = (b_1 + b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2$. Molar refractions give $A = b_1 + b_2 + b_3$. Thus:

$$b_{\text{max.}} = [(b_2 + b_3) \pm (2\phi + 6b_2b_3 - 3b_2^2 - 3b_3^2)^{0\cdot5}]/2$$

or

$$b_{\text{max.}} = A - (b_2 + b_3).$$

Results are as listed:

	From ϕ	From $0{\cdot}95R_{\text{D}}$	$10^{23}(\Delta b_{\text{max.}})$
for n = 1, $10^{23}b_{\text{max.}}$ =	3·41	3·38	0·78, 0·75
,, 2 ,, =	4·70	4·81	1·63, 1·74
,, 3 ,, =	6·24	6·33	2·73, 2·82
,, 4 ,, =	8·64	8·34	4·68, 4·39

Under $\Delta b_{\text{max.}}$ are given the exaltations, computed as $b_{\text{obs.}} - b_{\text{calc.}}$, drawn from ϕ or A respectively for each polyene. Values close to these (0·77, 1·77, 2·88, 4·58 × 10^{-23}) are also obtained if all the exaltations in R (6·45, 14·9, 24·2, 38·5 c.c.) are regarded as operating in the b_1 direction only.

Exaltation and Molecular Dimensions.—Davies[19] has used the simple molecular-orbital method of describing the π-electron behaviour of a conjugated system, the general case of a long all-*trans*-polyene being considered. His calculations for the π-electron polarisability of molecules containing from 1 to 20 double bonds, beginning with ethylene, lead to asymptotic expressions connecting this polarisability with the cube of the length over which the π-electrons are free to move. The π-polarisability becomes far more important than the σ-polarisability as the chain length increases, although the contribution of the latter is not less than 1% until the chain-length has reached 50 atoms.

Accordingly for the instances now under study we write:

$$b_{\text{max.}} = b_{1\,\text{calc.}} + kl^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where b_1 includes both the σ- and the isolated π-polarisabilities, k is a constant, and l is the distance between the 4- and the 4′-position projected on to the bisector axis. For the $\alpha\omega$-diphenylpolyenes, $l = (6{\cdot}25 + 2{\cdot}47n)$ Å. We thus have four pairs of equations, $\Delta b_{\text{max.}} = kl^3$, from which k emerges as follows (if l is in cm. and polarisabilities are $\times 10^{23}$ c.c.):

n	1	1	2	2	3	3	4	4
$\Delta b_{\text{max.}}$	0·78	0·75	1·63	1·74	2·73	2·82	4·68	4·39
l	8·72	8·72	11·19	11·19	13·66	13·66	16·13	16·13
10^2k	1·18	1·13	1·16	1·24	1·07	1·11	1·12	1·05

The mean k is 1·13 × 10^{-2}; by using it, exaltations in $b_{\text{max.}}$ are computed as 0·75, 1·58, 2·88, and 4·74 × 10^{-23} c.c. respectively.

---

[19] Davies, *Trans. Faraday Soc.*, 1952, **48**, 789.

Exaltation and $\lambda_{\max.}$ of K-Band.—Braude[20] noted that the wavelengths of maximum absorption for the K-bands of conjugated hydrocarbons show a straight-line relation with the " chromophore lengths " in the molecules concerned; he chose as the axes for these lengths those of the dipolar excited states (4,4′-line). However, the use of such lengths in the extraction of k from $\Delta b_{\max.}$ produces inconstant values ($0{\cdot}8$, $1{\cdot}2$, $1{\cdot}0$, $1{\cdot}8 \times 10^{-2}$); for our purposes the bisector axis lengths appear superior. In conjunction with spectral data[21] ($\lambda_{\max.} = 295, 328, 349, 375$ mμ for diphenylpolyenes with $n = 1, 2, 3, 4$ respectively) and the appropriate bisector axis lengths l, we find $\lambda_{\max.} = 206 + 10{\cdot}5l$ (giving calc. $\lambda_{\max.} = 298, 324, 349, 375$ mμ). The exaltation of polarisability may therefore be rewritten as:

$$10^{23}\Delta b_{\max.} = 9{\cdot}762 \times 10^{-7}(\lambda_{\max.} - 206)^3 \quad . \; . \; . \; . \; . \; . \quad (2)$$

(when λ is inserted as mμ). Calculated values are:

for $n = 1$, $10^{23}\Delta b_{\max.} = 0{\cdot}69$ (obsd. 0·78, 0·75)
,, 2, ,, $= 1{\cdot}77$,, 1·63, 1·74
,, 3, ,, $= 2{\cdot}85$,, 2·73, 2·82
,, 4, ,, $= 4{\cdot}71$,, 4·68, 4·39

Calculation of ${}_{\mathrm{m}}K$'s from Bond Polarisabilities.—On the basis of the assumption that exaltation occurs predominantly with b_1 we now have, through equations (1) or (2), two routes by which molecular semi-axes should be predictable from known polarisabilities of isolated bonds applied appropriately to the geometry of the structures concerned. The following is the situation for the four polyenes of this paper:

n	1	2	3	4
$10^{23}b_1$ (No exaltn.)	2·63	3·07	3·51	3·96
$10^{23}b_1$ (eqn. 1)	3·38	4·65	6·39	8·70
$10^{23}b_1$ (eqn. 2)	3·32	4·84	6·36	8·67
$10^{23}b_2$ (No exaltn.)	2·43	$2{\cdot}72_5$	3·02	3·31
$10^{23}b_3$ (No exaltn.)	1·60	1·83	2·06	$2{\cdot}29_5$
$10^{12}{}_{\mathrm{m}}K$ (No exaltn.)	45	62	82	105
$10^{12}{}_{\mathrm{m}}K$ (eqn. 1)	119	311	775	1777
$10^{12}{}_{\mathrm{m}}K$ (eqn. 2)	111	358	764	1759
$10^{12}{}_{\mathrm{m}}K$ (observed)	124	357	692	1740

Consideration of the last four lines shows the very substantial improvement in the *a priori* computation of ${}_{\mathrm{m}}K$'s made possible by the means introduced above: in the two worst cases the ${}_{\mathrm{m}}K$'s predicted from $\lambda_{\max.}$ and link data are *ca.* 10% from those measured, while in the two best, disagreement is scarcely 1%.

Conclusion.—Present indications are therefore that the tensorial additivity of bond polarisabilities can be usefully retained for conjugated structures, provided it is accepted that exaltations of polarisability occur predominantly in those directions along which electromeric effects are expected by theory to be most easily transmitted; the polyenes thus provide further instances of the phenomena noted in refs. 18 and 22, and by Ingold on p. 137 of ref. 7.

This work was started during the tenure by R. B. of a Research Scholarship provided by Beetle-Elliott Pty. Ltd. of Sydney to whom grateful acknowledgment is made.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, August 5th,* 1959.]

---

[20] Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, 1955, p. 149.

[21] Braude, *Ann. Reports*, 1945, **42** 105.

[22] Le Fèvre and Rao, *J.*, 1958, 1465.