593. *Molecular Polarisability. The Molar Kerr Constants and Conformations of Eight Polyaryls as Solutes.*

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The molar Kerr constants of *o*-, *m*-, and *p*-terphenyl, 1,3,5-triphenylbenzene, 1,1′- and 2,2′-binaphthyl, and 1,3,5-tri-α- and -tri-β-naphthylbenzene are recorded for infinite dilution in benzene at 25°. They can be reconciled with "equivalent" conformations, specified by angles ϕ through which the planes of the substituents need to be rotated, about the aryl–aryl junction lines, out of the plane of the substituted ring. Sets of ϕ's then appear for the above solutes as (+55°, +55°), (+20°, ±20°), (+20°, ∓20°), (+38°, +38°, +38°), (48°), (*ca.* 0°), (+26, +26°, +26°), and (+20°, +20°, +20°), respectively. Where they have been made, previous assessments of ϕ by other methods do not agree among themselves or with the present values.

THE marked anisotropy of polarisability of benzene [1a] and naphthalene [1b] suggested that information on the conformations of molecules such as the phenyl- and naphthyl-benzenes, the binaphthyls, etc., as solutes should be deducible from the Kerr effects, refractivities, and dielectric polarisations of their solutions. We here record appropriate observations for the eight hydrocarbons named in Tables 1—3.

EXPERIMENTAL

Solutes.—The terphenyls (*o*-, m. p. 56—57°; *m*-, m. p. 86—87°; *p*-, m. p. 211—212°) were gifts from Dr. J. A. Cade (A.E.R.E., Harwell) who had purified them by Sangster and Irvine's method.[2] 2,2′-Binaphthyl was purchased from the Aldrich Chemical Co. Inc., U.S.A.; after crystallisation from benzene its m. p. was 188°. The remaining compounds have been prepared by following the directions of Vorländer, Fischer, and Wille [3] for 1,3,5-triphenylbenzene (m. p. 171°, from benzene), of Clapp and Morton [4] for 1,3,5-tri-α-naphthylbenzene (m. p. 191°, from 1 : 1 ether–carbon tetrachloride) and the tri-β-isomer (m. p. 234—235°, from toluene), and of Bennett and Turner [5] for 1,1′-binaphthyl (m. p. 153—154°, from benzene).

Solvents, Methods, etc.—Standard techniques, previously described,[1a, 1c, 1d] have been used. Symbols for observed quantities and equations required in calculations are defined and explained in refs. 1 and 6; they have recently been summarised in this *Journal*.[7]

Results.—Observations are listed under the usual headings in Table 1; values deduced therefrom follow in Tables 2 and 3.

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[1] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041; 1954, 1577; (*b*) 1955, 1641; (*c*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*d*) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 3rd edn., Vol. I, p. 2459.

[2] Sangster and Irvine, *J. Chem. Phys.*, 1956, **24**, 670.

[3] Vorländer, Fischer, and Wille, *Ber.*, 1929, **62**, 2836.

[4] Clapp and Morton, *J. Amer. Chem. Soc.*, 1936, **58**, 2172.

[5] Bennett and Turner, *J.*, 1914, **105**, 1057.

[6] Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chapter 2; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[7] Le Fèvre and Sundaram, *J.*, 1962, 1494.

TABLE 1.

Incremental values of Δn, Δn^2, Δd, $\Delta\varepsilon$, and ΔB for solutions in benzene * at 25°.

Solute: o-*Terphenyl*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
2230	23	69	400	83	14
3041	32	96	541	113	20
4538	50	150	808	167	29
5178	57	171	916	189	33

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}108$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}324$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1778$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}368$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}641 \times 10^{-7}$.

Solute: p-*Terphenyl*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
342	5	15	61	15	11
581	8	25	104	24	18
676	9	28	118	32	21
748	10	31	131	33	22
805	11	34	144	37	25
968	13	40	173	45	28

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}136$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}420$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1774$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}452$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}03 \times 10^{-7}$.

Solute: 1,1′-*Binaphthyl*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
211	4	12	42	11	6
320	6	18	64	16	9
499	9	26	106	25	15
561	10	29	113	28	17
645	11	32	137	32	19
798	14	41	160	40	24

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}178$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}521$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2050$; $\Sigma\Delta\varepsilon/\Sigma w_3 = 0{\cdot}501$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}97 \times 10^{-7}$.

Solute: 1,3,5-*Tri-α-naphthylbenzene*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
641	—	—	147	—	24
742	14	42	—	44	—
838	16	48	—	52	—
948	17	51	—	56	—
1136	—	—	265	—	32
1733	—	—	420	—	40
2142	—	—	515	—	46
2390	—	—	570	—	—

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}186$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}558$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2384$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}601$; $10^7\Delta B = 4{\cdot}26w_2 - 69{\cdot}5w_2^2$.

Solute: m-*Terphenyl*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
548	7	22	97	21	11
729	9	27	127	29	15
994	12	36	178	39	19
1235	16	49	210	48	25
1405	18	55	253	52	30
1694	21	63	297	64	34

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}126$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}381$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1759$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}383$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}03 \times 10^{-7}$.

Solute: 1,3,5-*Triphenylbenzene; solvent: carbon tetrachloride* †

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
238	8	23	−150	24	9
341	12	35	−206	34	13
517	18	52	−344	50	20
802	28	82	−541	72	26
952	33	96	−585	84	35
1049	37	108	−663	94	37
1196	42	122	−754	106	43

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}349$; $\Sigma\Delta n^2/\Sigma w_2 = 1{\cdot}01_7$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}6365$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}911$; $10^7\Delta B = 3{\cdot}78w_2 - 17{\cdot}6w_2^2$.

Solute: 2,2′-*Binaphthyl*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
303	6	18	—	—	—
310	6	18	62	16	22
524	10	30	—	—	—
546	10	30	103	29	39
752	14	42	158	40	54
842	—	—	177	46	59
955	—	—	207	51	68

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}189$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}567$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2076$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}535$; $\Sigma\Delta B/\Sigma w_2 = 7{\cdot}11 \times 10^{-7}$.

Solute: 1,3,5-*Tri-β-naphthylbenzene*

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
623	13	39	160	40	44
838	18	54	219	52	58
1122	24	72	286	71	79
1458	31	93	380	93	99
1943	42	126	487	121	130

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}214$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}642$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2560$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}630$; $\Sigma\Delta B/\Sigma w_2 = 6{\cdot}85 \times 10^{-7}$.

* For $w_2 = 0$, $n_1 = 1{\cdot}4973$ (Na light), $d_1 = 0{\cdot}87378$, $\varepsilon_1 = 2{\cdot}2725$, $B_1 = 0{\cdot}410 \times 10^{-7}$ (Na light), at 25°. † For $w_2 = 0$, $n_1 = 1{\cdot}4575$ (Na light), $d = 1{\cdot}58454$, $\varepsilon_1 = 2{\cdot}2270$, $B_1 = 0{\cdot}070 \times 10^{-7}$ (Na light), at 25°.

TABLE 2.

Total polarisations at infinite dilution, molecular refractions, and dipole moments calculated from Table 1.

Solute	M_2	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$	${}_\infty P_2$ (c.c.)	R_D (obs.) (c.c.)
o-Terphenyl	230·3	0·368	0·2035	0·324	78·5	75·7
m-Terphenyl......................	,,	0·383	0·2013	0·381	79·3	78·4
p-Terphenyl	,,	0·452	0·2030	0·420	82·1	79·9
1,3,5-Triphenylbenzene * ...	306·4	0·911	−0·4017	$1{\cdot}01_7$	108·2	108·6
1,1′-Binaphthyl	254·3	0·501	0·2346	0·521	90·3	90·5
2,2′-Binaphthyl	,,	0·535	0·2376	0·567	91·7	92·5
1,3,5-Tri-α-naphthylbenzene	456·6	0·601	0·2728	0·558	164·8	160·0
1,3,5-Tri-*β*-naphthylbenzene	,,	0·630	0·2930	0·642	164·1	164·1

* Solvent: carbon tetrachloride; in other cases, benzene.

TABLE 3.

Molar Kerr constants at infinite dilution and exaltations from molar refractions calculated from Tables 1 and 2.

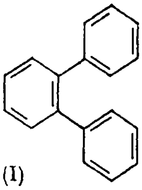
Solute	γ	δ	$10^{12}\ {}_{\infty}({}_{\mathrm{m}}K_2)$	R_D (calc.) (c.c.) *	$10^{23}\Delta b$
o-Terphenyl	0·072	1·56	36·6	74·4	0·155
m-Terphenyl	0·084	4·95	95·3	,,	0·476
p-Terphenyl	0·091	7·39	137·1	,,	0·654
1,3,5-Triphenylbenzene †	0·239	54·0	125·5	98·5	1·201
1,1′-Binaphthyl	0·119	7·24	145·6	86·7	0·452
2,2′-Binaphthyl	0·126	17·34	340·5	,,	0·690
1,3,5-Tri-α-naphthylbenzene	0·125	10·4	369·6	153·1	0·820
1,3,5-Tri-β-naphthylbenzene	0·143	16·71	585·4	,,	1·308

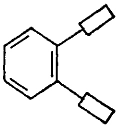
* From R_D of benzene (26·18 c.c.) and R_D of naphthalene (44·37 c.c.), together with bond-refraction data [8] for the C–H and C–C links. † Solvent: carbon tetrachloride; in other cases, benzene.

DISCUSSION

The molar Kerr constants, ${}_{\infty}(\mathrm{m}K_2)$, listed in Table 3, may be compared with those calculated for various conformations of the solutes concerned. Since with each of the eight molecules $1{\cdot}05R_D$ exceeds ${}_{\infty}P_2$ we initially regard them as non-polar (effects of this assumption are mentioned later). All C–C–C angles are taken to be 120°. From the principal polarisabilities of benzene [9] ($b_1 = b_2 = 1{\cdot}12_0$, $b_3 = 0{\cdot}736$), or naphthalene [1b] ($b_1 = 2{\cdot}15$, $b_2 = 1{\cdot}76$, $b_3 = 1{\cdot}03$), and the corresponding magnitudes for the C–H and C–C bonds [1c] ($b^{\mathrm{C-H}}_{1,2,\mathrm{or}\,3} = 0{\cdot}064$, $b^{\mathrm{C-C}}_{\mathrm{L}} = 0{\cdot}099$, $b^{\mathrm{C-C}}_{T\,\mathrm{or}\,V} = 0{\cdot}027$), the principal polarisabilities of the hydrocarbons in question are deduced for specified arrangements of aryl groups attached to the nuclei of benzene or naphthalene. (Throughout this paper all polarisabilities are quoted as 10^{-23} c.c. units.) In every instance the molecular refractions indicate an exaltation of polarisability; this is applied in the plane containing the aryl–aryl bonds (along which conjugative displacements are presumed to occur; cf. ref 1*c*, p. 301). From the molecular b_i's for a given structure, the related ${}_{\mathrm{m}}K$(calc.) follows by equation (b) of ref. 1*b*. The solutes will now be discussed separately.

o-*Terphenyl*.—Two extreme conformations are shown as (I) and (II); intermediate forms are defined by angles ϕ measured by looking from the *para*-position of a peripheral phenyl group towards the central ring and considering the rotation out of the central plane about the aryl–aryl bond as axis; clockwise rotations are given as $+\phi$, anti-clockwise as $-\phi$. Table 4 shows calculations for various pairs of ϕ's.


(I)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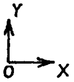

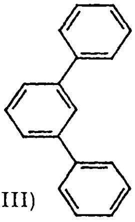
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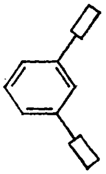
(IV)

The prediction in nearest accord with observation is obtained when both ϕ's are +55°; for this conformation b_1 is parallel to OX, b_2 is *ca.* 33° to OY, and 57° to OZ, and b_3 lies at *ca.* 122° to OY and 33° to OZ. Leybold models disfavour the alternatives with $+\phi$ and $-\phi$ by indicating H · · · H overlap; such an objection does not apply, of course, to *m*- and *p*-terphenyl.

m-*Terphenyl*.—Calculations for forms (III), (IV), and intermediate conformations are summarised in Table 5. The observed ${}_{\infty}({}_{\mathrm{m}}K_2)$ is $94{\cdot}3 \times 10^{-12}$; the ${}_{\infty}K$'s calculated for ϕ's of ±20° are 96—93 × 10^{-12}. A decision between the alternatives is not strictly warranted by the present results, although rotations of the phenyl substituents in the same

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[8] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.
[9] Aroney and Le Fèvre, *J.*, 1960, 3600.

TABLE 4.

Semi-axes, anisotropy terms, and molar Kerr constants, calculated for (I), (II), and intermediate forms.

Angles ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{\rm m}K$
0°, 0°	3·381	3·234	2·003	20·42	85·9
90, 90	3·074 *	2·616 *	2·773	1·93	8·12
+40, +40	3·302	3·134	2·182	—	54·8
+40, −40	3·302	2·994	2·321	—	37·8
+45, +45	3·285	3·108	2·225	11·50	48·4
+45, −45	3·285	2·945	2·388	7·31	30·7
+50, +50	3·269	3·079	2·270	—	42·2
+50, −50	3·269	2·894	2·455	—	24·9
+55, +55	3·252	3·048	2·318	8·60	36·2
+55, −55	3·253	2·846	2·519	4·82	20·3
+60, +60	3·237	3·013	2·368	7·25	30·5

* No exaltation included, as conjugation deemed unlikely in the orthogonal conformation.

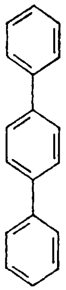
TABLE 5.

Semi-axes, anisotropy terms, etc., calculated for *m*-terphenyl.

Angles ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{\rm m}K$
0°, 0°	3·313	3·623	2·003	26·36	110·8
90, 90	2·616 *	3·074 *	2·773	1·93	8·12
+20, +20	3·245$_5$	3·613	2·080$_5$	22·82	95·96
+20, −20	3·245$_5$	3·600$_5$	2·093	22·15	93·15
+45, +45	3·024	3·650	2·265	17·15	72·12
+45, −45	3·024	3·527	2·388	11·62	48·86

* See footnote to Table 4.

sense appear slightly more favoured than rotations in the opposite sense. In the +20°,+20° model, b_1 is parallel to OX, b_2 at 6° to OY, and 84° to OZ, and b_3 at 96° to OY and 6° to OZ; when the ϕ's are +20° and −20° the structure has a plane of symmetry, so that b_1, b_2, and b_3 are along OX, OY, and OZ, respectively.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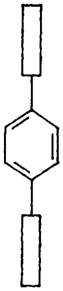
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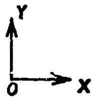

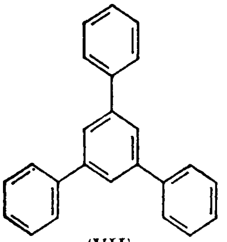
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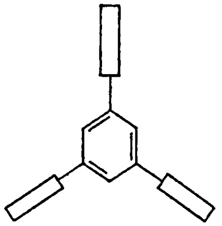
(VIII)

p-*Terphenyl*.—The $_\infty({}_{\rm m}K_2)$ by experiment is 137·1 × 10^{-12}; computations, as for the previous two isomers, are in Table 6. The conformation in which the end rings are coplanar (ϕ's +20°, +20°) produces an $_\infty K$ calc. in somewhat better agreement with the observed value than does the alternative (ϕ's +20°, +20°) in which the end rings are

TABLE 6.

Semi-axes, anisotropy terms, etc., calculated for *p*-terphenyl.

Angles ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{\rm m}K$
0° 0°	3·956	3·158	2·003	34·38	144·6
90, 90	3·302 *	2·388 *	2·773	7·51	31·6
+20, +20	3·956	3·068	2·093	30·96	130·2
+20, −20	3·956	3·127	2·034	33·13	139·3

* See footnote to Table 4.

disposed propeller-wise about the central ring; in the latter the principal axes are parallel to OX, OY, and OZ, but in the former b_1 is parallel to OY, b_2 is *ca.* 13° to OX and 77° to OZ, while b_3 is *ca.* 103° and 13° to OZ.

Present and Previous Conclusions concerning Terphenyls.—None of the above conformations, for which $_{\rm m}K$(calc) and $_{\rm m}K$(obs) are close, is advanced as unique (as though only a single solute species existed in each case), but rather as an " equivalent " conformation to describe a state of vibration in which the substituent phenyl groups are probably twisting about an unknown $\phi_{\rm equil.}$. Nevertheless it seems clear that in no instance is a fully planar structure the equilibrium form, and from steric causes it is reasonable that $\phi_{\rm equiv.}$ for *o*-terphenyl should exceed the corresponding values for the *meta*- and *para*-isomers.

Previous workers, using different methods, have not reached consistent conclusions. Mukerji and Singh[10] (Raman spectra) viewed *p*-terphenyl as planar. Hoffmann and Kinell[11] (nuclear magnetic resonance spectra) suggested that the two substituent groups in *o*-terphenyl are perpendicular to the central ring. Ultraviolet spectra[12-15] appear generally to have supported non-planarity of the solute; Suzuki[15] deduced ϕ's for *o*- and *p*-terphenyl of 43° and 10°, respectively. From infrared spectra, Hidalgo and Bellanato[16] thought a planar structure of *p*-terphenyl was evident; Dale[14] concluded that *o*- and *p*-terphenyl were not flat in solution, and Stewart and Hellmann[17] stated the same for *o*- and *m*-terphenyl. Bothorel,[18] from Rayleigh light-scattering studies of solutions, reported a 62° twist of the phenyl groups throughout all three terphenyls. Electron diffraction[19,20] by *o*-terphenyl agreed with the outer rings' being rotated through ~45° in the same direction.

1,3,5-*Triphenylbenzene.*—Conformations intermediate between (VII) and (VIII), each requiring three angles ϕ (defined as above) for their specification, are considered. Table 7 deals with a selection of cases in which the phenyl groups are rotated by various angles. When the ϕ's are equal in magnitude and sign, the principal molecular axes are obviously located with $b_1 = b_2$ in the YOX plane and with b_3 parallel to OZ; when the ϕ's are non-uniform, b_1 and b_2 differ slightly and b_3 deviates somewhat from OZ (*e.g.*, in the three instances listed last in Table 7 the direction cosines for b_3 with OZ are 0·9869, 0·9840, and 0·9679, respectively). Ref. 20 (M 252) cites two structures, one[21] in which all three ϕ's are 46° ± 5°, and another[22] in which they are +34°, −27°, and +24°; the former leads to an $_{\rm m}K$ which is lower, and the latter to an $_{\rm m}K$ which is higher, than the observed $_\infty(_{\rm m}K_2)$, which is $125{\cdot}5 \times 10^{-12}$. Were a single conformation sought for this hydrocarbon as a solute, then the form having uniform ϕ's of 38° would be suitable; twists of the order 25°, originally mooted by Lonsdale,[23] seem too small since they would produce $_{\rm m}K$'s which exceed 165×10^{-12}. Table 7 includes examples showing that twisting one phenyl by $-\phi°$, and the other two by $+\phi°$, *raises* the predicted $_{\rm m}K$; such calculations illustrate the facts that many " equivalent " conformations could be devised and that these might describe either states of oscillation or mixtures of individual species. However, H–H repulsions appear to us to favour forms with uniform ϕ's, and it is of interest that by

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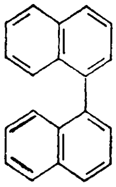
TABLE 7.

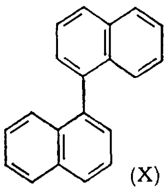
Semi-axes, anisotropy terms, etc., calculated for 1,3,5-triphenylbenzene with various ϕ's.

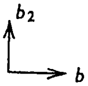
Angles ϕ	$b_1 = b_2$		b_3	$10^{35}\phi_1$	$10^{12}{}_{\mathrm{m}}K$
0°, 0°, 0°	$4{\cdot}885_5$		2·637	60·08	252·6
90, 90, 90	$3{\cdot}707_5$ *		3·792 *	$0{\cdot}08_5$	0·4
20, 20, 20	4·818		2·772	49·75	209·2
30, 30, 30	4·741		2·926	39·15	164·6
37, 37, 37	$4{\cdot}676_5$		3·055	31·25	131·4
38, 38, 38	$4{\cdot}666_5$		3·075	30·10	126·6
45, 45, 45	4·597		3·214	22·71	95·5
	b_1	b_2			
+34°, −27°, +24°	4·746	4·813	$2{\cdot}849_5$	44·30	186·3
−38, +38, +38	$4{\cdot}666_5$	$4{\cdot}742_5$	2·999	34·62	145·6
−45, +45, +45	4·597	4·697	$3{\cdot}114_5$	27·99	117·7
0, 90, 90	4·908 †	4·093	3·407	20·13	$84{\cdot}6_5$

* See footnote to Table 4. † Exaltation added only to the planar diphenyl portion.

assuming $b_1 = b_2$ and that ${}_{\mathrm{E}}P = 0{\cdot}96R_{\mathrm{D}}$, the experiment results (Tables 2 and 3) yield $b_1 = b_2 = 4{\cdot}66$ and $b_3 = 3{\cdot}08$; attention is thus again drawn (cf. Table 7) to ϕ's of +38°, +38°, +38° as specifying an acceptable " equivalent " structure.


(IX)


(X)



1,1′-*Binaphthyl*.—Extreme planar conformations appear as (IX) and (X) but, because the $C_{10}H_7$–$C_{10}H_7$ bond is in both parallel to a principal axial direction in each naphthyl unit, (IX) and (X) cannot be distinguished by their polarisability anistropy. Non-planar variants of (IX or X), generated by rotations of ϕ° about the internuclear link, need also to be considered, as Table 8 shows. The observed ${}_{\infty}({}_{\mathrm{m}}K_2)$ is 145·6 × 10^{-12}.

TABLE 8.

Semi-axes, anisotropy terms, etc., calculated for 1,1′-binaphthyls with various ϕ's.

Angle ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{\mathrm{m}}K$	Angle ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{\mathrm{m}}K$
0°	4·651 ‡	3·491	1·959	65·00	273·3	45°	3·871	3·943 ¶	2·287	31·24	131·4
0	4·425 §	3·717 §	1·959	57·48	241·7	48	$4{\cdot}280_5$ ‡	3·491	$2{\cdot}329_5$	34·34	144·4
0	4·199	3·943 ¶	1·959	53·60	225·4	48	$4{\cdot}054_5$ §	3·717 §	$2{\cdot}329_5$	29·80	125·3
90 *	3·079	3·491	3·079	2·02	8·5	48	$3{\cdot}828_5$	3·943 ¶	$2{\cdot}329_5$	28·90	121·5
45	4·323 ‡	3·491	2·287	37·36	157·1	70 †	3·914 ‡	3·491	2·696	13·63	57·32
45	4·097 §	3·717 §	2·287	32·48	136·6						

* Δb not included; were it spread equally over the 3 semi-axes, the ${}_{\mathrm{m}}K$ calc. would remain 8·5 × 10^{-12}. † Δb included as in footnote § or ¶ leads to lower values of ${}_{\mathrm{m}}K$ (calc.). ‡ Polarisability exaltation Δb added to b_1. § Δb divided equally over b_1 and b_2. ¶ Δb added to b_2.

Although it seems reasonable to regard the exaltation of polarisability as operating mainly along the 1,1′-bond (as in biphenyl[24]), in compiling Table 8 two other possible distributions have been included. Since a preliminary *X*-ray study [25] has suggested that a ϕ of 73° may occur in the crystal-held molecule, the calculation for the case when $\phi = 70°$ has also been carried through, yielding an ${}_{\mathrm{m}}K$ which is too small; the value for $\phi = 73°$ would be still smaller.

Both the details in Table 8 and Harris and Mellor's isolation [26] of optically active

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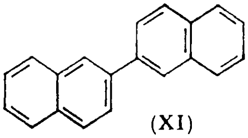
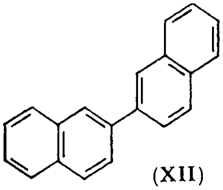
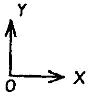
[24] Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666; cf. ref. 1*c*, p. 301.
[25] Brown, Trotter, and Robertson, *Proc. Chem. Soc.*, 1961, 115.
[26] Harris and Mellor, *Chem. and Ind.*, 1961, 1082.

1,1′-binaphthyl show a completely planar structure to be unacceptable. Comparing the found and calculated ${}_{m}K$'s provides an " equivalent " conformation for this solute in which ϕ is in the neighbourhood of 48°.

2,2′-*Binaphthyl.*—From models either of the flat extreme forms (XI) and (XII) appears unobjectionable. Table 9 contains the relevant data for both.


(XI)


(XII)



The ${}_{m}K$ by experiment is $340{\cdot}5 \times 10^{-12}$; accordingly—with $\phi = 0°$ in both cases—form (XI) appears more appropriate than (XII).

TABLE 9.

Semi-axes, anisotropy terms, etc., calculated for 2,2′-binaphthyls with various ϕ's.

Angle ϕ	b_1	b_2	b_3	$10^{35}\theta_1$	$10^{12}{}_{m}K$
			Form (XI)		
0° *	4·944	3·436	1·959	79·42	334
90 †	4·119	2·744	2·786	21·80	91·7
			Form (XII)		
0 ‡	4·766	3·614	1·959	70·98	298·5

* b_1 and b_2 almost parallel to OX and OY, respectively; Δb included in b_1. If Δb taken as operative along the C_{ar}–C_{ar} bond, b_1 and b_2 become 4·792 and 3·588, whence ${}_{m}K$ calc. is 303×10^{-12}. † Exaltation not included; cf. footnote to Table 4. Locations of semi-axes not defined as ${}_{m}K$ (calc.) is too small. ‡ b_1 and b_2 in the molecular plane with b_1 *ca.* 30° anti-clockwise from OX, Δb added to b_1.

1,3,5-*Tri-α-naphthylbenzene.*—The two possible planar structures, (XIII) and (XIV), have the same anisotropy of polarisability and therefore cannot be distinguished by the Kerr effect; for both, the calculated ${}_{m}K$ is 676×10^{-12}. Since the observed ${}_{m}K$ is only 370×10^{-12}, non-planar modifications of (XIII) or (XIV) are indicated; Table 10 shows that a suitable " equivalent " structure is achieved when the three naphthyl radicals are rotated each by about 26°. No data in the literature with which to compare this result appear to exist, although Magill and Ubbelohde [27] quote unpublished X-ray work by Parry as suggesting that the planes of the naphthalene groups are at " a large angle to the plane of the central benzene ring," and in their calculations they took this angle to be 45°.

TABLE 10.

Semi-axes, anisotropy terms, etc., calculated for 1,3,5-tri-α-naphthylbenzene with various ϕ's.

Angles ϕ	b_1 * = b_2 *		b_3	$10^{35}\phi_1$	$10^{12}{}_{m}K$
0°, 0°, 0°	7·200		3·522	$160{\cdot}7_7$	676·1
90, 90, 90	5·110 †		6·882 †	37·32	156·9
45, 45, 45	6·360		5·202	15·94	67·0
30, 30, 30	6·780		4·362	69·49	292·2
27, 27, 27	6·854		4·214	82·83	348·3
26, 26, 26	6·877		4·168	87·22	366·8
	b_1	b_2			
26, 26, −26	7·159	6·895	3·868	119·2	501·3

* Exaltation divided equally between b_1 and b_2. † See footnote to Table 4.

1,3,5-*Tri-β-naphthylbenzene.*—Here, unlike the tri-α-case, none of the principal axes

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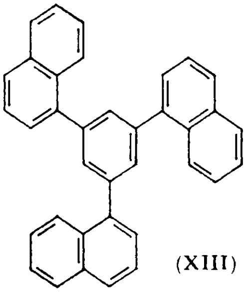
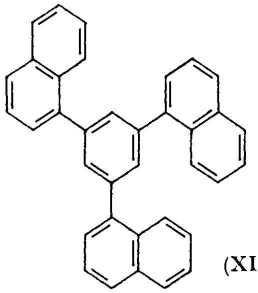
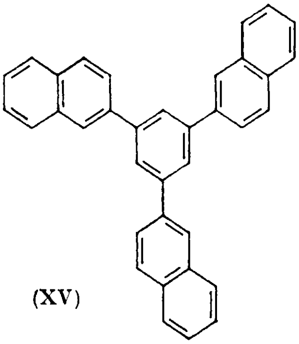
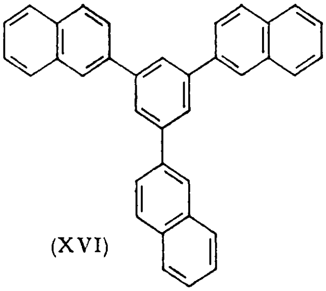
[27] Magill and Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 1811.

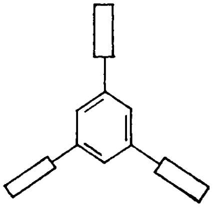

(XIII)


(XIV)

of a naphthyl group is collinear with its associated naphthyl–phenyl bond. Accordingly, the ${}_{\mathrm{m}}K$'s of the two planar extremes (XV) and (XVI) should theoretically be different, and rotations of +90° or −90° need to be considered with (XVII). Relevant calculations are in Table 11.


(XV)


(XVI)


(XVII)

Experiment (Table 3) gives ${}_{\infty}({}_{\mathrm{m}}K_2)$ as 585×10^{-12}, thereby counter-indicating all the fully planar and fully orthogonal extremes as appropriate single " equivalent " formulæ for this solute. Measurement and prediction can be reconciled satisfactorily if the β-naphthyl groups in either (XV) or (XVI) are rotated *ca.* 20° out-of-plane from the representations as printed; this angle is less than that found for the tri-α-isomer, as might be expected from simple steric considerations (although in general the ϕ's in this paper cannot be so explained except when the foreseeable hindrance is gross, as with *o*-terphenyl or 1,1′-binaphthyl; the finding[28] that in hexaphenylbenzene the C_6H_5 rings oscillate at ±10° about orthogonal dispositions is relevant in this connexion).

TABLE 11.

Semi-axes, anisotropy terms, etc., calculated for 1,3,5-tri-β-naphthylbenzenes with various ϕ's.

Angles ϕ	b_1 *	b_2 *	b_3	$10^{35}\theta_1$	$10^{12}{}_{\mathrm{m}}K$
Form (XV)					
0°, 0°, 0°	7·444	7·444	3·522	182·8	768·7
20, 20, 20	7·271	7·271	3·868	137·6	578·6
Form (XVI)					
0, 0, 0	7·782	7·106	3·522	186·9	786·0
20, 20, 20	7·605	6·939	3·866	141·82	596·4
Form (XVII)					
90, 90, 90	5·549 †	5·549 †	6·004	3·46	10·3
90, 90, −90	5·549 †	5·369 †	6·184	$6{\cdot}53_5$	27·5

* Including 0·5Δ*b* from Table 3. † See footnote to Table 4.

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[28] Almenningen, Bastiansen, and Skancke, *Acta Chem. Scand.*, 1958, **12**, 1215.

Effects of Non-vanishing Solute Moments.—The eight polyaryls have been considered above as non-polar because, as already stated, the measurements give by conventional treatment no grounds for assuming otherwise. However, were these hydrocarbons unusual in having distortion polarisations nearly equal to their R_D's, it may be significant that three of the four cases in Table 2 displaying an excess of $_\infty P_2$ over R_D happen to correspond to structures for which small moments might be expected. If we put $_DP = R_D$, the results would yield 0·37 D for *o*-terphenyl, 0·21 D for *m*-terphenyl, and 0·49 D for tri-α-naphthylbenzene, and appropriate non-zero θ_2 terms should enter the relevant preceding calculations of molar Kerr constants. By regarding the moments just quoted as maximum estimates, and making allowances for θ_2, we find the ϕ's required to produce the observed $_mK$'s need to be changed from 55° to 62° for *o*-terphenyl, from 20° to 22° for *m*-terphenyl, and from 26° to 27·5° for tri-α-naphthylbenzene. In conclusion, we submit that the ϕ's of this paper should not be judged against others reported for the crystalline or gaseous states; ours refer to solutes, the previous data for which [15,18] are sparse and discordant.

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