Molecular Polarisability. Conformations of 1- and 2-Benzoylnaphthalenes

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Dipole moments and molar Kerr constants ($\times 10^{12}$) at 25 °C are reported for 1-benzoylnaphthalene (3·01 D, -183) and 2-benzoylnaphthalene (3·14 D, $+317$) as solutes in carbon tetrachloride. Analysis of results yields information concerning the preferred conformations of these molecules.

STUDIES of the conformations of aromatic aldehydes and ketones [1-5] are extended to the 1- and 2-benzoylnaphthalenes. Experimental dipole moments and molar Kerr constants for these molecules as solutes in carbon tetrachloride are reported and analysed.

EXPERIMENTAL

Solutes.—The ketones were obtained in *ca.* 80% yield by Friedel–Crafts acylations using 1- or 2-naphthoyl chloride, aluminium chloride, and an excess of benzene. 1-Benzoylnaphthalene had m.p. 75 °C (lit.,[6] m.p. 76 °C), $\nu_{\text{max.}}$ ($CHCl_3$), 1646 cm^{-1} (C=O); 2-benzoylnaphthalene had m.p. 82° (lit.,[6] m.p. 82°), $\nu_{\text{max.}}$ ($CHCl_3$), 1643 cm^{-1} (C=O).

TABLE 1

Incremental * dielectric constants, densities, refractive indices, and Kerr effects for solutions in carbon tetrachloride at 25 °C

1-Benzoylnaphthalene

$10^5 w_2$	138	283	394	436	558	706
$10^4 \Delta\varepsilon$	117	237	331	362	462	585
$-10^5 \Delta d$	83	171	233	254	321	405
$10^4 \Delta n$	4	7	10	11	15	19
$-10^{11} \Delta B$	100	199	283	318	416	516

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 8{\cdot}33$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}584$,
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}262$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}765$,
$10^7\Delta B = -7{\cdot}11 w_2 - 36{\cdot}2 w_2^2$

2-Benzoylnaphthalene

$10^5 w_2$	190	282	389	515	726	847
$10^4 \Delta\varepsilon$	171	254	350	464	655	767
$-10^5 \Delta d$	116	153	210	273	389	450
$10^4 \Delta n$	5	7	10	14	19	22
$10^{11} \Delta B$	243	380	519	697	998	1163

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 9{\cdot}02$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}539$,
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}261$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}760$,
$10^7\Delta B = 13{\cdot}0 w_2 + 96{\cdot}9 w_2^2$

* When $w_2 = 0$, $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}58454$, $(n_1)_D = 1{\cdot}4575$, $10^7(B_1)_D = 0{\cdot}083$.

Apparatus.—Dielectric constants were determined with apparatus as in ref. 7; associated procedures giving polarisations have been standard.[8a] Kerr effects at 589 nm were recorded photometrically.[9]

Results.—These are listed in usual form in Tables 1 and 2. The symbols are those previously explained.[7,8,10]

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants

	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$
1-Benzoylnaphthalene	8·33	−0·368	0·765
2-Benzoylnaphthalene	9·02	−0·340	0·760

	$_\infty P_2$/cm^3	R_D/cm^3	μ *
1-Benzoylnaphthalene	262·9	74·4	3·01
2-Benzoylnaphthalene	278·7	73·1	3·14

	γ	δ	$10^{12}{}_\infty({}_mK_2)$
1-Benzoylnaphthalene	0·180	−85·7	−183
2-Benzoylnaphthalene	0·179	156	+317

* Calculated assuming $_DP = 1{\cdot}05\ R_D$

DISCUSSION

Dipole Moments.—Two factors cause differences between the dipole moments of 1- and 2-substituted naphthalenes: enhanced mesomeric interaction at the 1-position, and the relative absence of steric hindrance at the 2-position. The observed dipole moments of the chloronaphthalenes (1-, 1·45 D; 2-, 1·65 D) [11] and formylnaphthalenes (1-, 2·87 D; 2-, 3·14 D) [12] are explicable in these terms.

The dipole moment of 2-benzoylnaphthalene (3·14 D) is greater than that of 1-benzoylnaphthalene (3·01 D), and indicates stronger conjugative interaction in the former molecule.

Calculation of Molar Kerr Constants.—Standard procedures [8b,c,13] are used to obtain theoretical molar Kerr constants [†] by addition of bond- and group-polarisability tensors. Anisotropic polarisabilities used in

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[†] Polarisabilities are quoted throughout in 10^{-24} cm^3 units (Å^3), and molar Kerr constants in 10^{-12} e.s.u.

[1] P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), (*a*) **1967**, 741; (*b*) 1969, 227; (*c*) 1969, 485.

[2] R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), **1968**, 775.

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[4] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), **1971**, 120.

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[6] G. Baddeley, *J. Chem. Soc.*, **1949**, S99.

[7] A. D. Buckingham, J. Y. H. Chau, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J. Chem. Soc.*, **1956**, 1405.

[8] R. J. W. Le Fèvre, (*a*) 'Dipole Moments,' Methuen, London, 3rd edn., 1953, ch. 2; (*b*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (*c*) *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

[9] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, **1963**, 4933.

[10] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, (*a*) **1953**, 4041; (*b*) **1954**, 1577; (*c*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*d*) Ch. XXXVI in 'Physical Methods of Organic Chemistry,' ed. Weissberger, Interscience, New York, 3rd edn., 1960, vol. 1, p. 2459.

[11] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1955**, 1641.

[12] R. J. W. Le Fèvre and A. Sundaram, *J. Chem. Soc.*, **1962**, 4756.

[13] J. M. Eckert and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1962**, 1081.

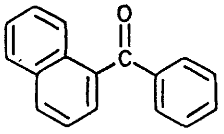
calculations are in Table 3. We have assumed valence angles of 120° around the carbonyl carbon atom. For both compounds the experimental molar refraction exceeds the value expected from tabulated bond and group values.[14] In calculating molar Kerr constants of benzoylnaphthalenes (I) and (II) we have apportioned the corresponding exaltations of polarisability (1-, 3·1 Å^3; 2-, 1·7 Å^3) equally in the X- and Y-directions as shown.

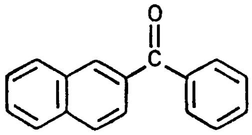
TABLE 3

Anisotropic polarisabilities of bonds and molecules

	b_L	b_T	b_V	Ref.
C–H	0·65	0·65	0·65	*a*
C–C	0·97	0·26	0·26	*a*
C=O	2·30	1·40	0·46	*b*
C_6H_6	11·15	11·15	7·44	*c*
$C_{10}H_8$	16·60	21·80	11·30	*c*

[a] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273. [b] C. G. Le Fèvre, R. J. W. Le Fèvre, and B. P. Rao, *J. Chem. Soc.*, 1959, 2340. [c] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.* (*B*), 1967, 1295.


(I)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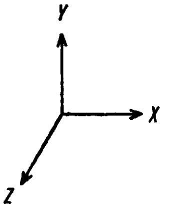

1-*Benzoylnaphthalene*.—Conformations of this molecule (I) are completely specified by two dihedral angles (θ, φ), defined in the following way. We imagine the C–CO–C group to be fixed in the XY-plane, so that the orientations of the planar phenyl and 1-naphthyl groups relative to this reference plane are θ and φ, respectively. The (0,0) structure is the sterically impossible uniplanar conformation shown (I), and the rotations θ, φ are made in anticlockwise directions with the C_{ar}–C bonds as axes.

Molar Kerr constants for conformations (θ, φ) have been computed in the usual way. Some representative values are in Table 4.

TABLE 4

Calculated molar Kerr constants for conformations (θ, φ) of 1-benzoylnaphthalene

φ \ θ	0	45	90	135	180
0	+1101	+863	+626	+863	+1101
45	+452	+218	+13	+247	+452
90	−197	−398	−599	−398	−197
135	+452	+247	+13	+218	+452
180	+1101	+863	+626	+863	+1101

We emphasise that for this highly anisotropic and strongly polar molecule the calculated values span an extremely wide range (+1100 to −600), so that the Kerr effect provides a particularly sensitive method for determining the actual structure.

The experimental molar Kerr constant of 1-benzoylnaphthalene is −183, and the combinations (θ, φ) having this calculated value are shown in Figure 1.

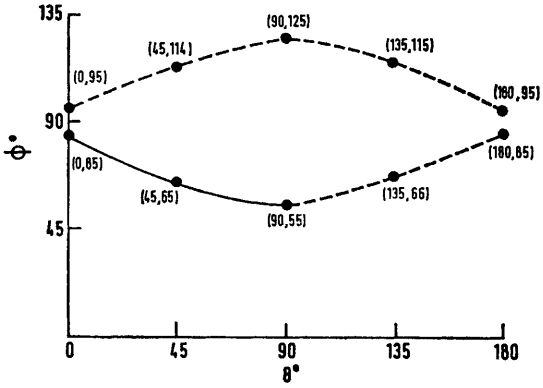

FIGURE 1 Permissible combinations of θ and φ for 1-benzoylnaphthalene

Examination of a scale model shows that conformations (θ, φ) indicated by the upper curve in Figure 1 are substantially more hindered than those in the lower curve. In addition, structures (0, 85)—(90, 55) are sterically more favourable than those in the range (90, 55)—(180, 85). We therefore restrict discussion to conformations corresponding to the left-hand portion of the lower curve, shown by an unbroken line.

In an attempt to deduce the most likely structure within this range we have calculated relative resonance stabilisation energies (R.S.E.) using the relationship (1).

$$\text{R.S.E.} = \alpha \cos^2 \theta + \beta \cos^2 \phi \qquad (1)$$

The parameters α and β measure the relative conjugative interaction of the phenyl and 1-naphthyl groups with the carbonyl group, and are taken as 1·00 and 1·11, respectively.[15] The results in Table 5 show that the structure (0, 85) has the maximum R.S.E. and we conclude that this is the preferred conformation of 1-benzoylnaphthalene.

TABLE 5

Relative resonance stabilisation energies for conformations of 1-benzoylnaphthalene (α = 1·00, β = 1·11)

θ	φ	$\alpha \cos^2\theta + \beta \cos^2\phi$
0	85	1·01
45	65	0·70
90	55	0·37

2-*Benzoylnaphthalene*.—The procedure for this molecule is very similar to that for 1-benzoylnaphthalene. Conformations are once again specified by dihedral

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[14] W. T. Cresswell, G. H. Jeffery, J. Leicester, and A. I. Vogel, *J. Chem. Soc.*, 1952, 514.

[15] C. A, Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188.

angles (θ, ϕ) defined as before. The (0, 0) structure is planar and as shown (II).

The range of calculated molar Kerr constants is indicated in Table 6, while combinations (θ, ϕ) giving the observed value (+317) are shown in Figure 2.

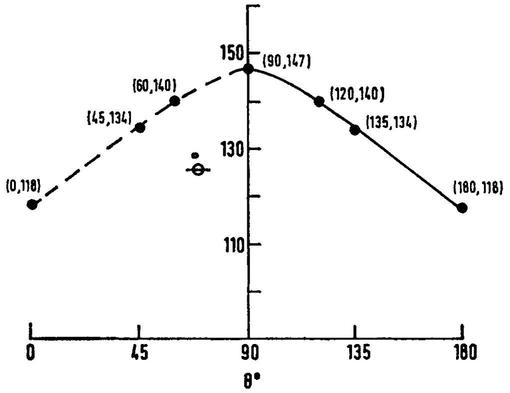

FIGURE 2 Permissible combinations of θ and ϕ for 2-benzoylnaphthalene

Configurations corresponding to the right-hand section of this curve are much less sterically hindered and are to be preferred. Relative resonance stabilisation energies have been calculated for these structures with[15] α = 1·00 and β = 1·02. From the results in Table 7 it can be inferred that the (180, 118) conformation of 2-benzoylnaphthalene is the most favourable structure.

TABLE 6

Calculated molar Kerr constants for conformations (θ, ϕ) of 2-benzoylnaphthalene

ϕ \ θ	0	45	90	135	180
0	+509	+254	−0·2	+254	+509
45	+167	−78	−323	−77	+167
90	−32	−253	−507	−286	−32
135	620	+391	+115	+344	+620
180	+1144	+879	+613	+879	+1144

TABLE 7

Relative resonance stabilisation energies for conformations of 2-benzoylnaphthalene (α = 1·00, β = 1·02)

θ	ϕ	$\alpha \cos^2\theta + \beta \cos^2\phi$
180	118	1·22
135	134	0·99
90	147	0·72

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