Conformations of Mesityl 1-Naphthyl Ketone and Mesityl 2-Naphthyl Ketone

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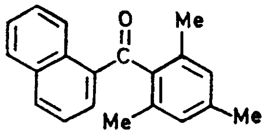
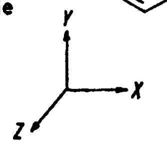
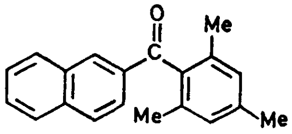
Dipole moments and molar Kerr constants ($\times 10^{12}$) at 25 °C are reported for mesityl 1-naphthyl ketone (2·85D, −132) and mesityl 2-naphthyl ketone (3·21D, +333) as solutes in carbon tetrachloride. Analysis of results yields information concerning the preferred conformations of these molecules.

CONSIDERATIONS of molecular polarity and polarisability recently were used to elucidate the preferred conformations of 1- and 2-benzoylnaphthalenes.[1] We have now examined the methyl-substituted derivatives mesityl 1-naphthyl ketone (I) and mesityl 2-naphthyl ketone (II), whose conformations have not previously been studied. Experimental dipole moments and molar Kerr constants for these molecules as solutes in carbon tetrachloride are reported and analysed below.



(I)





(II)

EXPERIMENTAL

Materials.—Mesityl 1-naphthyl ketone was obtained by the general method described for the benzoylation of mesitylene [2] as crystals, m.p. 158 °C (lit.,[3] 158—159 °C); $\nu_{max.}$ (KBr) at 1660 cm^{-1} (C=O); τ ($CDCl_3$) 0·80 (m, 1, 8-H), 1·8—2·9 (complex, 6, naphthyl-H), 3·14 (s, 2, *m*-H), 7·70 (s, 3, *p*-CH_3), and 7·90 (s, 6, *o*-CH_3). Mesityl 2-naphthyl ketone was prepared analogously as crystals, m.p. 97 °C (lit.,[4] 97—98 °C); $\nu_{max.}$ (KBr) 1665 cm^{-1} (C=O); τ ($CDCl_3$) 1·83 (s, 1, 1-H), 1·9—2·8 (complex, 6, naphthyl-H), 3·10 (s, 2, *m*-H), 7·66 (s, 3, *p*-CH_3), and 7·85 (s, 6, *o*-CH_3).

Apparatus.—Dielectric constants were determined with apparatus as in refs. 5 and 6; associated procedures giving polarisations have been standard.[7a] Kerr effects at 589 nm were recorded photometrically.[8]

Results.—These are listed in Table 1.† The symbols are those previously explained.[5,7,9]

DISCUSSION

Dipole Moments.—Reasons for differences between the dipole moments of 1- and 2-substituted naphthalenes have been given.[1] The value for mesityl 2-naphthyl ketone (3·21D) is larger than that found for mesityl 1-naphthyl ketone (2·85D), and suggests stronger conjugative interaction in the former molecule.

TABLE 1

Polarisations, refractions, dipole moments, and molar Kerr constants from solutions in carbon tetrachloride at 25 °C

	$\alpha\varepsilon_1$	β	$\gamma' n_1{}^2$	$_\infty P_2$ (cm^3)	R_D (cm^3)
Mesityl 1-naphthyl ketone	6·54	−0·414	0·775	260·8	90·3
Mesityl 2-naphthyl ketone	8·05	−0·427	0·772	305·4	90·8

	μ(D) *	γ	δ	$10^{12}{}_\infty(_mK_2)$
Mesityl 1-naphthyl ketone	2·85	0·183	−51·9	−132
Mesityl 2-naphthyl ketone	3·21	0·184	139	+333

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

Calculation of Molar Kerr Constants.—Standard procedures [7b,c,10] were employed to predict molar Kerr constants ‡ for conformations of these two molecules. Bond- and group-polarisability tensor components used were given in Table 3 of ref. 1, together with the following data for mesitylene:[11a] $b_1 = b_2 = 17{\cdot}14$, $b_3 = 12{\cdot}33$. Valence angles of 120° around the carbonyl carbon atom were assumed, and the exaltation of polarisability (1-, 3·0 Å^3; 2-, 3·5 Å^3) was apportioned equally in the *X*-, *Y*-, and *Z*-directions in (I) and (II). Particular conformations of (I) and (II) are completely specified by two dihedral angles, (θ, ϕ), defined as for the benzoylnaphthalenes,[1] except that θ now refers to the mesityl

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† Experimental data (incremental dielectric constants, densities, *etc.*) are deposited as a Supplementary Publication (SUP No. 20415, 2 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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

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group. The (0, 0) structures are the sterically-impossible uniplanar forms shown in (I) and (II). Rotations θ, φ about the C_{ar}–C bonds are made in *anticlockwise* directions if the rotation axis is viewed from the aromatic C-atom towards the carbonyl C-atom.

Mesityl 1-*Naphthyl Ketone*.—Expected molar Kerr constants for conformations (θ, φ) are summarised in Table 2. Because of the highly anisotropic polarisability and strong polarity of this molecule these calculated values, like those for the benzoylnaphthalenes,[1] span a very wide range (+972 to −650). The experimental molar Kerr constant is −132 (Table 1) and combinations (θ, φ) giving this result are shown in Figure 1, which is very similar to the corresponding curves found for 1-benzoylnaphthalene (Figure 1 of ref. 1).

TABLE 2

Calculated molar Kerr constants for conformations (θ, φ) of mesityl 1-naphthyl ketone

φ \ θ:	0	45	90	135	180
0	+972	+698	+423	+698	+972
45	+388	+118	−113	+156	+388
90	−196	−423	−650	−423	−196
135	+388	+156	−113	+118	+388
180	+972	+698	+423	+698	+972

It is not possible to decide with certainty the most likely structure within this range of (θ, φ) for which there is agreement between calculated and observed Kerr constants. Two competitive effects operate to determine the interplanar angles θ and φ: repulsive interactions between non-bonded atoms, arising from crowding, and the tendency for maximum conjugation of both the mesityl and naphthyl groups with the carbonyl group. The actual molecular conformation represents the best compromise (*i.e.* energy minimisation) between the steric and conjugative effects. Relative resonance stabilisation energies (R.S.E.) can be evaluated using the relationship R.S.E. = $\alpha \cos^2 \theta + \beta \cos^2 \phi$, in which α and β measure the conjugative interaction of the mesityl and 1-naphthyl groups with the carbonyl group.[1] However only an approximate assessment of the steric effect can be made through examination of scale models, so that detailed calculations of R.S.E.'s are not reported here.

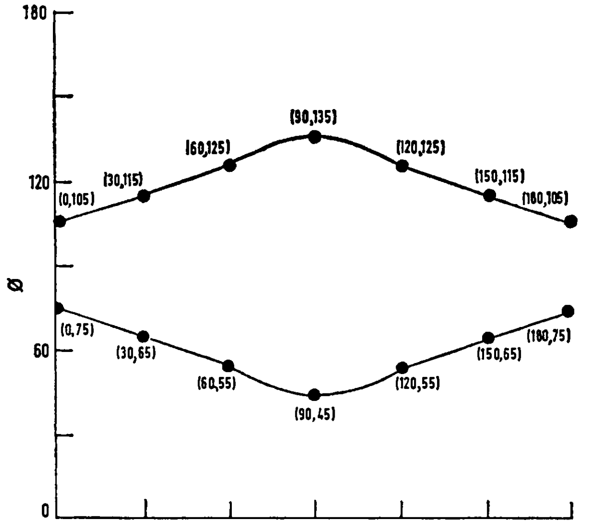

FIGURE 1

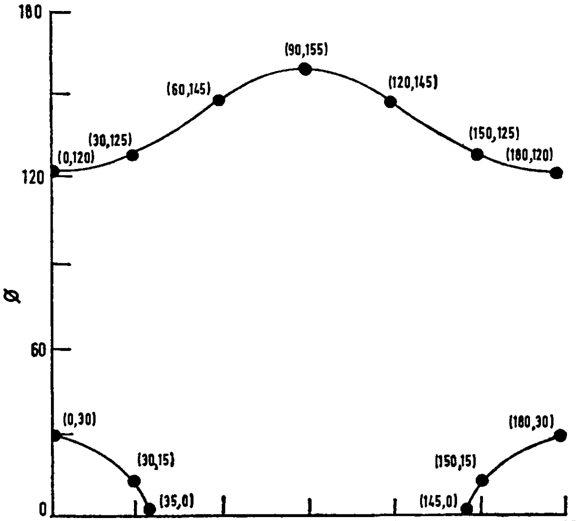

FIGURE 2

A scale model of mesityl 1-naphthyl ketone shows that structures having (θ, φ) in the approximate range (30, 65) to (90, 45) are favoured on steric grounds, and the (90, 45) form is the least hindered. However the conjugative effect favours the (30, 65) structure. It therefore seems possible that the conformation of mesityl 1-naphthyl ketone corresponds approximately to the intermediate (60, 55) combination. For 1-benzoylnaphthalene we concluded that the (0, 85) conformation is most likely. The corresponding (0, 75) structure of mesityl 1-naphthyl ketone, although favoured by the conjugative effect, is sterically impossible because of the bulky *o*-methyl groups. Finally we note that a (60, 60) structure was deduced for dimesityl ketone,[11b] which is sterically similar to mesityl 1-naphthyl ketone.

Mesityl 2-*Naphthyl Ketone*.—Calculated molar Kerr constants for conformations of this molecule are given in Table 3, and values of (θ, φ) corresponding to the observed result (+333) are graphed in Figure 2.

TABLE 3

Calculated molar Kerr constants for conformations (θ, φ) of mesityl 2-naphthyl ketone

φ \ θ:	0	45	90	135	180
0	+542	+203	−137	+203	+542
45	+181	−147	−473	−145	+181
90	−42	−344	−676	−373	−42
135	+651	+337	−23	+293	+651
180	+1206	+853	+498	+853	+1206

Concerning the upper curve, conformations in the approximate range (30, 125) to (150, 125) are sterically possible, with the (90, 155) structure being the least hindered. Structures in the right-hand section are somewhat less hindered than those in the left-hand portion, because the rings are anti-symmetrically rotated.[11b] Models having the combinations (θ, ϕ) indicated in the lower curves * in Figure 2 shows severe hindrance and many of these forms are sterically impossible.

Therefore it seems that the actual conformation of mesityl 2-naphthyl ketone has a value of (θ, ϕ) in the range (90, 155) to (150, 125). Although the (90, 155) structure is sterically favoured the (150, 125) form has the greatest conjugative stabilisation, so that once again an intermediate combination such as (120, 145) seems the most probable.

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* Comparison of Figures 1 and 2 in this paper with the corresponding graphs for the benzoylnaphthalenes (Figures 1 and 2 in ref. 1) shows a close similarity in the allowed combinations (θ, ϕ) for both the 1- and 2-substituted compounds. In ref. 1 the lower curves in Figure 2 were omitted; a re-examination of a scale model of 2-benzoylnaphthalene confirms that the (180, 118 = 0, 118) conformation is the most likely structure.