# Conformations of 1-Formyl-, 1-Acetyl-, and 1-Benzoyl-2-methylnaphthalenes

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Dipole moments (D) and Kerr constants (e.s.u. mol$^{-1}$ × $10^{12}$) at 25 °C are reported for 1-formyl- (2·96, +485), 1-acetyl- (2·71, −314), and 1-benzoyl-2-methylnaphthalene (2·97, −531) as solutes in carbon tetrachloride. Analysis of results yields information concerning the preferred conformations of these molecules.

POLARISABILITY studies[1-5] of the conformations of aromatic aldehydes and ketones have been extended to 1-formyl- (I), 1-acetyl- (II), and 1-benzoyl-2-methylnaphthalene (III). Steric hindrance in these molecules would be expected to be intermediate between that occurring in the corresponding 9-anthryl[1,2] and 1-naphthyl[3,4] carbonyl compounds, whose conformations as solutes are already known. Experimental dipole moments and molar Kerr constants for the three 2-methylnaphthalene derivatives are reported and analysed below.

## EXPERIMENTAL

*Materials.*—Literature methods were used to prepare 1-formyl-2-methylnaphthalene,[6] m.p. 51·5—52°, 1-acetyl-2-methylnaphthalene,[7] b.p. 118—121° at 0·35 mmHg, $n_D^{20}$ 1·6056, and 1-benzoyl-2-methylnaphthalene,[8] m.p. 70°.

*Apparatus.*—Dielectric constants were determined with apparatus as in refs. 9 and 10; associated procedures giving

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

[2] P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1969, 227.

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[4] C. L. Cheng, R. J. W. Le Fèvre, G. L. D. Ritchie, P. H. Gore, and M. Yusuf, *J. Chem. Soc.* (*B*), 1971, 1579.

[5] C. L. Cheng, G. L. D. Ritchie, P. H. Gore, and M. Jehangir, *J.C.S. Perkin II*, 1972, 1432.

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[8] K. Dziewoński and E. Ritt, *Bull. Internat. Acad. Polon. Sci, Sér. A.*, 181, 1927.

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

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polarisations are standard.[11a] Kerr effects at 589 nm were recorded photometrically.[12]

## RESULTS

These are listed in the usual form in Table 1.* The symbols are those previously explained.[9, 11, 13]

## DISCUSSION

*Dipole Moments.*—The observed dipole moments (Table 1) are explicable in terms of steric and mesomeric effects occurring in these molecules.

For (I) the moment (2·96 D) is, not surprisingly, between those recorded for 1-formylnaphthalene (2·87 D)[14] and 9-formylanthracene (3·00 D).[1] Also the value for (I) is very similar to the moment of benzaldehyde (2·98 D), whose line of action is believed to make an angle of approximately 20° with the axis of the C=O bond.[15] We therefore adopt this direction for the moment of (I). However the moment of (II) (2·71 D) is significantly less than that of 1-acetylnaphthalene (2·89 D)[3] and almost the same as that of 9-acetylanthracene (2·72 D)[1] in which severe steric inhibition of resonance is known to occur. The result for (III) (2·97 D) is, once again, intermediate between those of the analogous 1-naphthyl and 9-anthryl compounds (1-benzoylnaphthalene, 3·01 D;[4] 9-benzoylanthracene, 2·89 D[2]). Because of crowding in both (II) and (III) conjugation of the carbonyl group is likely to be substantially reduced, so that it seems reasonable to assume that in these two molecules the moment acts along the C=O bond.

TABLE 1

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

| | $\alpha\epsilon_1$ | $-\beta$ | $\gamma' n_1^2$ | $_\infty P_2$/cm$^3$ | $R_D$/cm$^3$ | $\mu$/D * | $\gamma$ | $\delta$ | $10^{12}{}_\infty({}_mK_2)$ e.s.u. mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| (I) | $10·63 \pm 0·03$ | $0·369 \pm 0·003$ | $0·79 \pm 0·04$ | $234 \pm 1$ | $55 \pm 1$ | $2·96 \pm 0·01$ | $0·19 \pm 0·01$ | $323 \pm 4$ | $+485 \pm 6$ |
| (II) | $8·51 \pm 0·05$ | $0·437 \pm 0·004$ | $0·76 \pm 0·02$ | $214 \pm 1$ | $61 \pm 1$ | $2·71 \pm 0·01$ | $0·18 \pm 0·01$ | $-188 \pm 2$ | $-314 \pm 3$ |
| (III) | $7·82 \pm 0·02$ | $0·362 \pm 0·001$ | $0·84 \pm 0·04$ | $265 \pm 1$ | $81 \pm 1$ | $2·97 \pm 0·01$ | $0·20 \pm 0·01$ | $-239 \pm 3$ | $-531 \pm 7$ |

* Calculated assuming $_DP = 1·05 R_D$.

*Calculation of Molar Kerr Constants.*—Standard procedures[11b, c] were employed to predict molar Kerr constants † for conformations of (I)—(III). Bond and group polarisability tensor components used were as given in Table 3 of ref. 4. Valence angles around the carbonyl carbon atom were taken as 120°, although steric effects may be expected to cause deviations from regular values. Exaltations of polarisability [(I) 2·0 Å$^3$; (II) 3·4 Å$^3$; (III) 3·4 Å$^3$] were apportioned isotropically.

*1-Formyl-2-methylnaphthalene.*—Particular conformations of this molecule are defined by the dihedral angle $\theta$ between the planes of the C–CO–H and 1-naphthyl groups. The planar structure shown (I) in which the carbonyl group is directed towards the 2-methyl substituent has $\theta = 0$. Two competitive effects operate to determine the apparent value of $\theta$: (i) a coplanarity-favouring conjugative interaction which tends to minimize $\theta$; and (ii) various non-bonded repulsive interactions, due to crowding, which keep $\theta$ above a minimum.

Some calculated molar Kerr constants for (I) are shown in Table 2. The experimental Kerr constant (+485) is in agreement with those predicted for conformations having a dihedral angle of approximately 20 or 180°. Examination of a scale model shows clearly that the former ($\theta = 20°$) is favoured on steric grounds.

The uncertainty in this conformational result comes from two sources: errors in the experimental quantities; and errors in the computed Kerr constants, arising from imperfect additivity of group polarisabilities, and other factors. It is reasonable to estimate the overall uncertainty in $\theta$ as *ca.* ±5°.

TABLE 2

Calculated Kerr constants (e.s.u. mol$^{-1}$ × $10^{12}$) for conformations ($\theta$) of 1-formyl-2-methylnaphthalene

| $\theta$(°) | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|
| $_mK$ | +578 | +375 | +16 | −153 | −29 | +298 | +488 |

Finally we note that the conformation deduced above for 1-formyl-2-methylnaphthalene ($\theta = 20 \pm 5°$) is consistent with those previously reported for 1-formylnaphthalene ($\theta$ *ca.* 15°)[14] and 9-formylanthracene ($\theta$ *ca.* 25°).[1]

*1-Acetyl-2-methylnaphthalene.*—The procedure used to deduce the effective conformation of the acetyl compound is similar to that described above for the formyl derivative. Conformations are again defined by a dihedral angle $\theta$, the sterically-disfavoured uniplanar form shown (II) having $\theta = 0$.

The measured Kerr constant (−314) is consistent with those calculated (see Table 3) for structures having $\theta = 75$ or 100°, and a scale model shows that both are sterically permissible. It is therefore not possible to

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* Experimental data (incremental dielectric constants, *etc.*) are deposited as a Supplementary Publication SUP No. 20772 (5 pp.). For details of supplementary publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue 20. Items less than 10 pp. are supplied as full size copies.

† Kerr constants are quoted throughout as $10^{12}{}_mK$/e.s.u. mol$^{-1}$.

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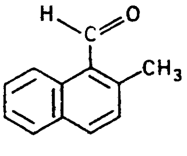
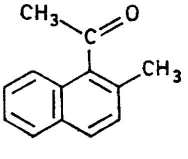
decide, on the present evidence, the most likely of these two conformations. In fact, a more realistic interpretation would be that the most probable conformations (corresponding to energy minima) have θ = 75 or 100°, and that the acetyl group librates through the approximate range 65° ⩽ θ ⩽ 110°.


(I)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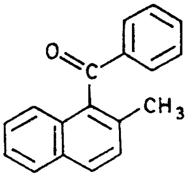

(III)

Polarisability studies of 9-acetylanthracene, which is sterically similar to 1-acetyl-2-methylnaphthalene yielded an effective conformational angle of 80°,[1] while for 1-acetylnaphthalene the corresponding angle was found to be 42°.[3]

TABLE 3

Calculated Kerr constants (e.s.u. $\text{mol}^{-1} \times 10^{12}$) for conformations (θ) of 1-acetyl-2-methylnaphthalene

| θ(°) | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|
| $_mK$ | +630 | +376 | −131 | −373 | −98 | +432 | +695 |

1-*Benzoyl*-2-*methylnaphthalene*.—Analysis of results for this molecule (III) closely parallels the treatment of 1-benzoylnaphthalene.[4] Conformations of (III) are specified by *two* dihedral angles (θ,ϕ). If the plane of the C–CO–C group is imagined to be fixed, the orientations of the planar phenyl and 2-methylnaphthyl groups relative to this reference plane are θ and ϕ, respectively. The (0,0) structure is the sterically-impossible uniplanar conformation shown (III), and the rotations θ,ϕ about the $C_{ar}$–C bonds are made in *anticlockwise* directions if the rotation axes are viewed from the aromatic carbon atom towards the carbonyl carbon atom.

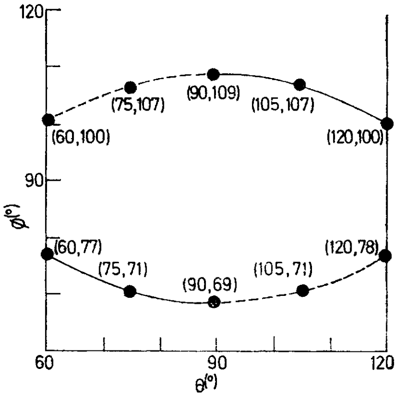
Some representative Kerr constants for conformations (θ,ϕ) of (III) are shown in Table 4. As with 1-benzoylnaphthalene and 9-benzoylanthracene the calculated values span a very wide range (+1053 to −673). Combinations (θ,ϕ) for which the predicted Kerr constant agrees with the experimental value (−531) are shown in the Figure.

TABLE 4

Calculated Kerr constants for conformations (θ,ϕ) of 1-benzoyl-2-methylnaphthalene

| θ(°)<br>ϕ(°) | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|
| 0 | +974 | +860 | +633 | +519 | +633 | +860 | +974 |
| 30 | +653 | +533 | +315 | +217 | +337 | +555 | +653 |
| 60 | +14 | −96 | −295 | −384 | −274 | −75 | +14 |
| 90 | −293 | −387 | −577 | −673 | −579 | −389 | −293 |
| 120 | +53 | −34 | −234 | −347 | −259 | −59 | +53 |
| 150 | +721 | +623 | +404 | +282 | +380 | +599 | +721 |
| 180 | +1053 | +938 | +709 | +594 | +709 | +938 | +1053 |

The most probable structure within the ranges (θ,ϕ) indicated cannot be decided with certainty. Once again, competing mesomeric and steric effects determine the most stable conformation. A scale model of (III) shows severe steric hindrance in many of the structures (shown by broken curves) in the Figure. Conformations in the approximate ranges (60,77) to (90,69) and (90,109) to (120,100) are sterically more favourable. Within these two regions intermediate forms such as (75,71) and (105,107) appear most likely, but a more definite conclusion is not justified.



Permissible combinations of θ and ϕ for 1-benzoyl-2-methylnaphthalene

We note that the ranges of possible structures for 1-benzoyl-2-methylnaphthalene are much smaller than those for 1-benzoylnaphthalene,[1] for which a (0,85) form was deduced as being most probable. In 9-benzoylanthracene [2] the additional *peri*-hydrogen atom considerably increases the steric hindrance, and polarisability data indicated that the (45,90) structure is preferred.

[3/433 *Received*, 26*th February*, 1973]