Molar Kerr Constants of Six *N*-Aryl-4-Pyridones as Solutes in Benzene or Dioxan

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Abstract

The molar Kerr constants of six *N*-aryl-4-pyridones as solutes in benzene or dioxan have been determined.

Batts and Madeley[1] have recorded the dipole moments of a number of 1-aryl-4-pyridones and concluded that in these structures the rings are probably collinear.

Table 1. **Polarizations, molar Kerr constants, refractions and dipole moments of solutes of types**
$$RC_6H_4N(CH)_4C{=}O$$
Units: $_\infty P_2$ and R_D in cm^3; μ in D; $_\infty(_mK_2)$ in e.s.u. mol^{-1}

R	Solvent	$\alpha\varepsilon_1$[A]	β[A]	γ[A]	δ[A]	$_\infty P_2$	R_D[B]	μ[C]	$10^{12} \times {}_\infty(_mK_2)$[D]
H	benzene	28·34	0·289₅		483·5	954·0	(49·77)	6·6₄	6073
H	dioxan	30·87	0·139	0·127	3241	914·1	53·6	6·4₇	6420
o-Me	benzene	29·09	0·233	—	448·8	1062	(54·82)	7·0₀	6101
o-Me	dioxan	35·13	0·142	0·139	3023	1119	60·1	7·1₈	6471
p-Me	benzene	28·15	0·228	—	570·4	1029	(57·44)	6·8₈	7809
p-Me	dioxan	33·11	0·120	0·154	3664	1058	63·2	6·9₆	7853
o-Cl	benzene	28·41	0·311₅	—	467·7	1147	(57·38)	7·2₉	7071
o-Cl	dioxan	33·06	0·270	0·129	2865	1164	58·4	7·3₄	6809
p-Cl	benzene	13·83	0·323	—	310·6	582·4	(56·98)	5·0₅	4736
p-Cl	dioxan	17·27	0·248	0·143	2183	630·7	61·7	5·2₆	5196
p-Br	benzene	12·40	0·406	—	277·3	634·0	(63·60)	5·2₆	5142
p-Br	dioxan	16·64	0·288	0·125	2119	738·1	69·1	5·7₀	6137

[A] Coefficients derived from the observed incremental dielectric constants, densities, refractive indices and Kerr constants of solutions, containing weight fractions w_2 of solute, respectively by the relations $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$, $\beta = \Sigma\Delta d/d_1\Sigma w_2$, $\gamma = \Sigma\Delta n/n_1\Sigma w_2$ and $\delta = \Sigma\Delta B/B_1\Sigma w_2$.
[B] Values in parentheses by Batts and Madeley,[1] using ethanol as solvent.
[C] Calculated assuming distortion polarizations of $1\cdot05R_D$.
[D] At 25° and sodium light.

In the hope that molecular polarizabilities would provide[2,3] further evidence, the measurements summarized in Table 1 have been made, using standard methods,

[1] Batts, B. D., and Madeley, A. J., *Aust. J. Chem.*, 1972, **25**, 2605.
[2] Le Fèvre, R. J. W., *Advan. Phys. Org. Chem.*, 1965, **3**, 1.
[3] Le Fèvre, R. J. W., *Rev. Pure Appl. Chem.*, 1970, **20**, 67.

apparatus, techniques, etc.[2-6] The solutes were specimens originally prepared for another study.[1] They dissolved slightly in benzene and more so in dioxan. In general, to keep the electric birefringences—which were very high—within the ranges suitable for photometric registration,[4,5] concentrations employed in measuring incremental Kerr effects have never exceeded 0·1%. Insolubility in carbon tetrachloride or cyclohexane prevented a search for solute–solvent associations by procedures described before.[7,8]

Discussion

The dielectric polarizations now noted are compatible with those previously reported.[1] Except when R is H, apparent moments in dioxan slightly exceed corresponding values in benzene; however, solvent effects are not marked. From bond refractivities and related data for benzene, toluene, chlorobenzene and bromo-benzene, due to Vogel et al.,[9,10] molar refractions of 50·1, 55·0, 55·1, and 57·9 cm^3 are calculable respectively for the cases where the pyridone nitrogen is attached to C_6H_5, C_6H_4Me, C_6H_4Cl and C_6H_4Br. Comparisons with observations in Table 1 therefore suggest that polarizability exaltations occur in these arylpyridones. As the magnitudes and anisotropies of such extra polarizabilities are not reliably predictable in advance, no attempts have been made to relate molar Kerr constants with speci-fiable structures or conformations (cf.[4b]).

Table 2. Calculated and observed polarizability tensor components in collinear
forms of p-$RC_6H_4N(CH)_4C=O$

$10^{24} \times$ polarizabilities in cm^3

Group	Section (A)[A]			Section (B)[B]	
R	b_1	b_2	b_3	b_1	(b_2+b_3)
H	23·8	19·4	14·0	28/29	31/32
Me	26·7	20·7	15·6	33/34	37/38
Cl	27·4	20·8	14·8	34	35
Br	29·4	21·3	15·5	37	41

[A] Directions: b_1 along p-R–C, C–N, and C=O bonds; b_3, perpendicular to C_6 and NC_5 rings.
[B] Alternative estimates drawn from data in benzene and dioxan.

It is relevant that the molar Kerr constants now found are considerably greater than those computed for uniaxial and flat hexagonal models in which the anisotropic polarizabilities of the C_6H_5, p-C_6H_4Me, p-C_6H_4Cl, and p-C_6H_4Br groups are as given by Le Fèvre and Radom,[11] and Le Fèvre and Rao,[12] and those of the C–H,

[4] Le Fèvre, C. G., and Le Fèvre, R. J. W., in 'Physical Methods of Chemistry' (Eds. A. Weissberger and B. W. Rossiter) Vol. 1, Part 3C, (a) p. 399; (b) p. 440; (c) p. 439 (John Wiley: New York 1972).
[5] Le Fèvre, R. J. W., and Solomons, S. C., Aust. J. Chem., 1968, 21, 1703.
[6] Le Fèvre, R. J. W., and Millar, D. J., Chem. Ind. (London), 1971, 399.
[7] Le Fèvre, R. J. W., Radford, D. V., Ritchie, G. L. D., and Stiles, P. J., J. Chem. Soc. B, 1968, 148.
[8] Hopkins, P. A., Le Fèvre, R. J. W., Radom, L., and Ritchie, G. L. D., J. Chem. Soc. B, 1971, 574.
[9] Vogel, A. I., J. Chem. Soc., 1948, 607, 654, 1833.
[10] Vogel, A. I., Cresswell, W. T., Jeffery, G. H., and Leicester, J., J. Chem. Soc., 1952, 514.
[11] Le Fèvre, R. J. W., and Radom, L., J. Chem. Soc., 1967, 1295.
[12] Le Fèvre, R. J. W., and Rao, B. P., J. Chem. Soc., 1958, 1465.

C=C, C–N and C=O bonds as quoted by Le Fèvre and Rao,[13] and Aroney and Le Fèvre.[14]

Table 2, section (A), lists the polarizability components so deduced for the phenyl and three p-substituted phenyl derivatives in which the resultant moments can be assumed to be acting in the b_1 directions of the molecular polarizability ellipsoids. Alternatively, with knowledge of observed polarities, refractions and molar Kerr constants, approximate estimates of b_1 and $(b_2 + b_3)$ can be extracted from the data in Table 1 (cf. [4c]). Results are in Table 2, section (B), and indicate that exaltations are predominantly operating along the lengths of these molecules—a circumstance consistent both with the structural conclusion already reached by Batts and Madeley,[1] and the principle that conjugative electronic displacements will occur more readily the more extended the conjugated chain supporting them (cf.[15]).

Acknowledgment

[13] Le Fèvre, C. G., Le Fèvre, R. J. W., and Rao, B. P., *J. Chem. Soc.*, 1959, 2340.
[14] Aroney, M. J., and Le Fèvre, R. J. W., *J. Chem. Soc.*, 1958, 3002.
[15] Le Fèvre, R. J. W., *Advan. Phys. Org. Chem.*, 1965, **3**, p. 64.