931. *Molecular Polarisability: the Molar Kerr Constants of Five Sydnones.*

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It is found that, despite the mesoionic character of sydnones, the molar Kerr constants of five examples can be predicted with fair accuracy by using the methods, bond data, experience, etc., accumulated from previous work, especially that on, conjugated molecules.

UNTIL now, no electric birefringence measurements on mesoionic compounds[1] have been reported, and whether or not the anisotropic polarisabilities of such molecules can be predicted *a priori* from available bond and geometrical data is an unanswered question. Of interest therefore are details here presented for *N*-phenylsydnone[2] and four of its derivatives as solutes in benzene.

EXPERIMENTAL

3-Phenyl-, 3-*p*-bromophenyl-, 3-β-naphthyl-, and 3,4-diphenyl-syndone were specimens used in previous work,[3] having m. p. 134—135°, 137—138·5°, 158—159° (decomp.), and 182—184°, respectively (after recrystallisation of the first-named from acetic anhydride and vacuum-drying over soda-lime); 4-bromo-3-phenylsydnone, m. p. 122—123° (decomp.), initially purple, was obtained colourless by two crystallisations from absolute ethanol. Apparatus and methods were as described in refs. 4—6 (wherein definitions of symbols and explanations of calculations may be found; for convenience, the equations involved have recently[7] been summarised in this *Journal*). Measurements (at 25° throughout), results, etc., are listed under usual headings in Tables 1 and 2. Attempts to obtain reliable readings of the electric birefringence of nitron

TABLE 1.

Differences Δn and ΔB between refractive indexes and Kerr constants of benzene * and solutions containing weight fractions w_2 of sydnones.

			3-Phenylsydnone					
$10^6 w_2$ ...	1239	4162	4197	5840	6623	8382	8475	
$10^4 \Delta n$ ...	—	4·5	—	6·5	—	10·0	—	
$10^{10} \Delta B$...	150	514	525	722	783	938	1011	
			3-*p*-Bromophenylsydnone					
$10^6 w_2$ ...	1561	3349	3998	5104	5610	5949	8589	8959
$10^4 \Delta n$ ...	2·5	3·5	—	—	5·5	—	9·0	—
$10^{10} \Delta B$...	126	230	326	400	434	486	—	719
			3-β-Naphthylsydnone					
$10^6 w_2$ ...	287	301	617	628	709	766	997	1094
$10^{10} \Delta B$...	62	66	—	141	145	156	203	224
			3,4-Diphenylsydnone †					
$10^6 w_2$ ...	1020	1242						
$10^{10} \Delta B$...	45	63						
			4-Bromo-3-phenylsydnone					
$10^6 w_2$ ...	1220	1302	1596	1639	2069	2376	2531	
$10^{10} \Delta B$...	72	80	98	102	133	141	166	

* At 25°, if $w_2 = 0$, $n_D = 1·4973$, $B = 0·410 \times 10^{-7}$ (Na$_D$ light), $\varepsilon = 2·2725$, and $d = 0·87378$.
† Limited supplies of solute available.

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[1] Baker and Ollis, *Quart. Rev.*, 1957, **11**, 15.

[2] Earl and Mackney, *J.*, 1935, 899.

[3] Earl, Leake, and Le Fèvre, *J.*, 1948, 2269.

[4] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) *J.*, 1953, 4041; (*c*) *J.*, 1954, 1577; (*d*) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 3rd edn., 1959, Vol. I; (*e*) *J.*, 1956, 3549; (*f*) *J.*, 1955, 1641

[5] Le Fèvre, (*a*) "Dipole Moments," Methuen, London, 3rd edn., 1953; (*b*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (*c*) *Proc. Chem. Soc.*, 1958, 283; 1959, 363.

[6] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

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

(the high polarity of which has been demonstrated by Warren [8]) were defeated by the low solubility of this substance.

TABLE 2.

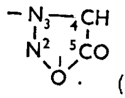
Calculation of molar Kerr constants, at infinite dilution, of five sydnones.

	3-Ph	3-*p*-C_6H_4Br	3-β-$C_{10}H_7$	4-Br-3-Ph	3,4-Ph_2
$\alpha\varepsilon_1$	$28{\cdot}9_6$ *	$12{\cdot}2_2$ *	25·1 *	19·5 *	$20{\cdot}2_2$ *
β	0·375 *	0·524 *	0·373 *	0·515 *	0·300
γ	0·076	0·072	0·118 *	0·071 *	0·069 *
δ	291·0	192·2	508·5	151·7	116·5
$M_2{}^1$	162·1	$241{\cdot}0_5$	212·2	$241{\cdot}0_5$	238·2
$_\infty P_2$ (c.c.)	—	—	—	—	—
R_D (c.c.)	45·9	53·8	66·0	53·8 †	69·9
μ (D)	$6{\cdot}5_3$	$5{\cdot}1_3$	6·9	6·5	6·6
$_\infty({}_mK_2) \times 10^{12}$	3407	3405	7979	2605	1939

* Calc. from measurements in ref. 3. † From Hill and Sutton.[9]

DISCUSSION

The molar Kerr constants of the five sydnones studied are large, those of the 3-phenyl and 3-*p*-bromophenyl members resembling that (3265×10^{-12}) for 4-nitrobiphenyl.[10] Interpretation in terms of anisotropic polarisabilities is begun by noting that refs. 3 and 9*a* together report directly determined molecular refractions R_D for nine sydnones. Subtraction of the appropriate group refractions, listed by Vogel,[11] for phenyl, bromine, etc., provides estimates of the contribution due to the sydnone nucleus (I). For the six cases containing a 3-phenyl or 3-*p*-bromophenyl group, R_{sydnone} lies between 20·0 and 21·9 c.c. (mean $20{\cdot}7_6$ c.c.); for 3-phenylsydnone, with $R_D = 45{\cdot}9$ c.c., R_{sydnone} appears as 20·5 c.c. These facts strengthen the idea, already suggested by the similarities of polarity [3, 9a] and spectra [12, 13] among members of this class, that the mesomeric state of the nucleus (I) is relatively insensitive to 3- or 4-substituents and may be viewed as roughly constant. Bond refractivities [14] summed for (I) *as shown* yield an R_D of 15·4 c.c., *i.e.*, mesomerism in the sydnone nucleus contributes an " exaltation " of polarisability to (I) corresponding to about 5·4 c.c. (*i.e.*, $20{\cdot}7_6$ — 15·4 c.c.).



(I)

TABLE 3.

Anisotropic bond and phenyl polarisabilities used in the calculations.

Bond	b_L	b_T	b_V	Ref.
C–H	0·064	0·064	0·064	4*a*
C–C	0·099	0·027	0·027	4*e*
C–N	0·057	0·069	0·069	16*a*
C–O	0·081	0·039	0·039	4*e*
C=O	0·230	0·140	0·046	17
Phenyl	1·056	1·056	0·672	16*b*
N–N	0·062	0·077	0·077	16*b* and 5*c*
N–O	$(0{\cdot}07_5)$	(0·10)	(0·10)	See text and 5*c*

We next compute the principal polarisabilities of the hypothetical skeleton (I), assuming that the single and the carbonyl link, and the phenyl group, have the anisotropies found for them from simpler structures (Table 3) or—for N–O and N–N—deduced from electronic polarisations [15] and empirical relations [5c] connecting b_L with intercentre distances or infrared stretching frequencies. Interbond angles are taken as 108°, which seems reasonable in view of the (*X*-ray) dimensions recently reported [18] for crystalline 3-*p*-bromophenylsydnone. Hill and Sutton [9b] conclude that in 3-phenylsydnone the Ph–N valency is

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[8] Warren, *J.*, 1938, 1100.

[9] Hill and Sutton, (*a*) *J.*, 1949, 746; (*b*) *J.*, 1953, 1482.

[10] Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666.

[11] Vogel, *J.*, 1948, 1833.

[12] Earl, Le Fèvre, and Wilson, *J.*, 1949, 103.

[13] Earl, Le Fèvre, Pulford, and Walsh, *J.*, 1951, 2207.

[14] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

[15] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

[16] Aroney and Le Fèvre, (*a*) *J.*, 1958, 3002; (*b*) 1960, 3600.

[17] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

[18] Bärnighausen, Jellinck, and Vos, *Proc. Chem. Soc.*, 1961, 120.

nearly collinear with the main sydnone moment which acts within $\sim 5°$ of the plane of the sydnone ring; accepting this, we locate b_1 along the Ph–$N_{(3)}$ line and b_2 at 90° to b_1 in the said plane. Thus semiaxes * emerge for (I) as $b_1 = 0{\cdot}665$, $b_2 = 0{\cdot}645$, and $b_3 = 0{\cdot}491$. Attachment of a phenyl group to $N_{(3)}$ increases these to $b_1 = 1{\cdot}721$, $b_2 = 1{\cdot}701$, and $b_3 = 1{\cdot}163$. The sum $b_1 + b_2 + b_3$ is 4·585, to be compared with 4·549 deduced from Le Fèvre and Steel's bond electronic polarisations; [15] in view of the different sources of these two estimates their agreement is satisfactory. For 3-phenylsydnone, however, the value of $b_1 + b_2 + b_3$ deduced from $0{\cdot}95R_{\rm D}$ is 5·185, *i.e.*, 0·60 — 0·64 higher than the two totals just mentioned. Since the factor 0·95 is uncertain (cf. ref. 15) we can alternatively proceed by noting that Vogel's D-line bond refractions [14] lead to $R_{\rm D}$ for phenyl-(I) of 39·91 c.c., whereas the $R_{\rm D}$ observed for phenylsydnone is 45·9 c.c.; the deficiency corresponds to a polarisability of 0·712. These differences (0·60 — 0·712) are not wholly "exaltations" in the usual sense, partly because they must contain the equivalent of a missing bond. If we suppose that the transannular $N_{(2)}$–$C_{(4)}$ bond in Earl and Mackney's original formula (shown as IV in ref. 2) is in fact unlocalised, its polarisability may be added isotropically, so that semiaxes for 3-phenylsydnone appear as $b_1 = 1{\cdot}786$, $b_2 = 1{\cdot}766$, and $b_3 = 1{\cdot}228$, and the differences are reduced to 0·405—0·517. The last—in the light of results involving exaltations in conjugated systems described in refs. 4*c*, 10, 19, and 20—should mainly operate to augment b_1.

Accordingly we predict the actual molecular polarisability semiaxes for 3-phenylsydnone as $b_1 = 2{\cdot}191$—$2{\cdot}303$, $b_2 = 1{\cdot}766$, and $b_3 = 1{\cdot}228$, whence anisotropy and dipole terms (θ_1 and θ_2, respectively, see, *e.g.*, p. 270 of ref. 4*a*, or p. 2480 of ref. 4*d*) follow as $8{\cdot}3$—$10{\cdot}3 \times 10^{-35}$ and $777{\cdot}1$—$902{\cdot}5 \times 10^{-35}$, and $_{\rm m}K$ calc. is 3303—3838×10^{-12}, thus covering the observed value of 3407×10^{-12}. If instead of taking $\mu_{\rm resultant}$ as acting collinearly with b_1 we assume a divergence of 15° in the plane of the sydnone ring, the $_{\rm m}K$'s calc. become 3100—3574×10^{-12}; this range still includes the $_{\rm m}K$ from experiment.

The following argument suggests that b_1 is correctly taken as *ca.* 2·2: from the measured $_\infty({}_{\rm m}K_2)$ of 3407×10^{-12} (Table 3) the sum $\theta_1 + \theta_2$ is 810×10^{-35}; in view of the general smallness of anisotropy terms, θ_1 need not be stated precisely—let it be roughly 10×10^{-35} as for biphenyl,[10] with which phenylsydnone has some shape analogies; θ_2 is therefore *ca.* 800×10^{-35}, and (since $\mu_{\rm resultant} = 6{\cdot}53$ D) $2b_1 - b_2 - b_3$ becomes 1·428; $b_1 + b_2 + b_3$ (from Le Fèvre and Steel's data [15] plus the differences of 0·60—0·712 mentioned above) is 5·149—5·261; b_1 accordingly emerges as 2·19—2·23. The set of semiaxes finally suggested is $b_1 = 2{\cdot}19$, $b_2 = 1{\cdot}75$, and $b_3 = 1{\cdot}20$, since these correspond to $\theta_1 = 9 \times 10^{-35}$, $\theta_2 = 801 \times 10^{-35}$, $_{\rm m}K = 3406 \times 10^{-12}$, and to an electronic polarisation of 43·3 c.c. (*i.e.*, to $0{\cdot}943R_{\rm D}$); moreover, they permit calculation of the $_{\rm m}K$'s of other sydnones with reasonable success.

Removal of $b_{\rm i} = 0{\cdot}06$ (*i.e.*, the isotropic polarisability of C–H) from the b's for phenylsydnone and replacement by $b_{\rm L}^{\rm CBr} = 0{\cdot}63$, $b_{\rm T}^{\rm CBr} = 0{\cdot}25$, and $b_{\rm V}^{\rm CBr} = 0{\cdot}22$ (these being data extracted from bromobenzene [19]) lead to forecasts for 3-*p*-bromophenylsydnone of $b_1 = 2{\cdot}76$, $b_2 = 1{\cdot}94$, and $b_3 = 1{\cdot}36$, giving $_{\rm E}P$ calc. $= 50{\cdot}9_6$ c.c. (or $0{\cdot}947R_{\rm D}$), $\theta_1 = 18 \times 10^{-35}$, $\theta_2 = 767 \times 10^{-35}$, and $_{\rm m}K$ calc. $= 3301 \times 10^{-12}$.

With 4-bromo-3-phenylsydnone there is little information regarding either the angle between the Ph–N and C–Br links or the direction of action of $\mu_{\rm resultant}$. From the remarks of Earl, Leake, and Le Fèvre [3] it seems that the two bonds in question may be mutually at roughly 90° (although 72° is required by a regular pentagonal sydnone nucleus); the resultant of two components, 6·53 D for 3-phenylsydnone and 1·60 for bromobenzene, should then act *ca.* 14° from the Ph–N line. Thus $b_1 = 2{\cdot}38$, $b_2 = 2{\cdot}32$, $b_3 = 1{\cdot}36$, $_{\rm E}P$ calc. $= 50{\cdot}9_6$ c.c. (or $0{\cdot}947R_{\rm D}$), $\theta_1 = 12 \times 10^{-35}$, $\theta_2 = 593 \times 10^{-35}$, and $_{\rm m}K$ calc. $= 2544 \times 10^{-12}$.

If in 3,4-diphenylsydnone we assume the 4-phenyl attachment to be as C–Br in the last

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* Throughout this paper polarisabilities b_1, b_2, etc., are quoted in 10^{-23} c.c. units.

[19] Le Fèvre and Rao, *J.*, 1958, 1465.

[20] Bramley and Le Fèvre, *J.*, 1960, 1820; 1962, 56.

case, and then proceed by replacing the semiaxes for C–H by those for phenyl, we obtain for a planar structure $b_1 = 3{\cdot}19$, $b_2 = 2{\cdot}75$, and $b_3 = 1{\cdot}81$, whence ${}_{\mathrm{m}}K$ calc. $= 4437 \times 10^{-12}$. This is more than twice that observed. If, however, the 4-phenyl group is disposed orthogonally the semiaxes expected are $b_1 = 2{\cdot}80$, $b_2 = 2{\cdot}75$, and $b_3 = 2{\cdot}20$, from which $\theta_1 = 4 \times 10^{-35}$, $\theta_2 = 379 \times 10^{-35}$, and ${}_{\mathrm{m}}K$ calc. $= 1581 \times 10^{-12}$, an estimate much nearer to the observed value. The sum $b_1 + b_2 + b_3$ for both conformations is 7·75, corresponding to an ${}_{\mathrm{E}}P$ of 65·2 c.c. (or $0{\cdot}933R_{\mathrm{D}}$).

For 3-β-naphthylsydnone we note that R_{D} for naphthalene [4f] is 44·37 c.c., which, less $R_{\mathrm{C-H}}$, is 42·7 c.c. Now $R_{\text{naphthylsydnone}} - R_{\text{naphthyl}}$ is 23·3 c.c., while $R_{\text{3-phenylsydnone}} - R_{\text{phenyl}}$ is 21·5 c.c., *i.e.*, the substitution of naphthyl for phenyl in 3-phenylsydnone involves a further increase of polarisability equivalent to $\Delta R = 1{\cdot}8$ c.c.; by analogy with the treatment above, b_1 calc. for 3-β-naphthylsydnone should be augmented by $\Delta b_1 = 0{\cdot}21$. Using data from ref. 4*f* we estimate b_1's for the β-naphthyl radical by subtracting the semiaxes for the C–Br bond in bromobenzene from those for β-bromonaphthalene and uniting the remainders appropriately to those left after similar subtractions of phenyl semiaxes from those of 3-phenylsydnone. For 3-β-naphthylsydnone we thus obtain $b_1 = 3{\cdot}32$, $b_2 = 2{\cdot}23_5$, $b_3 = 1{\cdot}50$; therefore $\theta_1 = 30 \times 10^{-35}$, $\theta_2 = 1816 \times 10^{-35}$, and ${}_{\mathrm{m}}K$ calc. $= 7763 \times 10^{-12}$. (The electronic polarisation computed from these b_i's is 59·33 c.c., or $0{\cdot}90R_{\mathrm{D}}$.)

Where four of the five sydnones are concerned, the question asked at the outset is answered by these comparisons:

Sydnone:	3-Ph	3-p-C_6H_4Br	4-Br-3-Ph	3-β-$C_{10}H_7$
$10^{12}{}_{\mathrm{m}}K$ calc. ……………	3406	3301	2544	7763
$10^{12}{}_{\mathrm{m}}K$ expt. ……………	3407	3405	2605	7979

Thus, by the use of methods and experience gained in previous work, especially that on conjugated compounds, molar Kerr constants can be predicted *a priori* which do not differ by more than 3% from those obtained by direct measurement. The fifth case provides indications that in 3,4-diphenylsydnone the 4-phenyl ring is held out of the plane occupied by that attached at $N_{(3)}$.

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