159. *Cyclic Meso-ionic Compounds. Part II. The Electric Dipole Moments of Some Sydnones.*

By R. A. W. Hill and L. E. Sutton.

The electric dipole moments of *N*-phenyl-, *N*-*p*-tolyl-, *N*-*p*-chlorophenyl-, *C*-chloro-*N*-phenyl, *C*-bromo-*N*-phenyl-, *N*-phenyl-*C*-methyl-, *N*-*cyclo*hexyl-, and *N*-benzyl-sydnones, measured in benzene solution at 25°, are reported.

By making likely assumptions about bond moments and the changes caused by substituent groups, it has been possible to elucidate the geometry of the compounds. Furthermore, the moment of Earl's bicyclic structure has been estimated and compared with the observed value.

It is concluded that this structure is inadequate to explain either the magnitude of the moment or the geometry of the sydnone ring; and that there is resonance between a number of polar structures. Those with a positive formal charge on the fully-substituted nitrogen atom and a negative one on the carbonyl oxygen are believed to predominate. A comparison with molecular-orbital calculations by Mr. C. H. Longuet-Higgins is made.

There is evidence for inter-ring resonance in the *N*-arylsydnones; but the resulting moments are small compared with the total moments.

The organo-chemical problem of formulating the sydnones has been stated in a letter by Baker and Ollis (*Nature*, 1946, **158**, 703) and in Part I of this series (this vol., p. 307). Some of the objections to Earl's original dicyclic structure, and the possibility of ionic alternatives, were pointed out independently to the present authors by Dr. J. A. Barltrop (Oxford) with whom work on the subject was planned. Publication of the letter mentioned above led to a joint programme being undertaken at Bristol and Oxford, concerning which a preliminary note has already appeared (*Nature*, 1947, **160**, 366).

Earl and Le Fèvre informed us that they had been engaged on a similar series of measurements (see *Nature*, 1947, **160**, 366; also *J.*, 1948, 2269) and have kindly allowed us to quote their results.

EXPERIMENTAL.

Preparation and Purification of Materials.—*Benzene.* " AnalaR " Benzene was purified by crystallising three times, rejecting about a quarter each time, and dried by standing over phosphoric anhydride. Immediately before use it was distilled over more phosphoric anhydride in an all-glass apparatus, from which moisture was excluded by a small pressure of dry air. The dielectric cell and the bottle in which solutions were made up were also kept dry in this way. The melting point of the solvent depended slightly on the original sample, but it always lay between 5·35° and 5·4°. The specific volume was constant to $\pm 0{\cdot}00025$ unit. No attempt was made to purify the solvent so as to obtain greater consistency of specific volume : the value for the solvent in each run was obtained from the mean curve of specific volume against weight fraction (see below) and is given in the appropriate table (p. 748).

Sydnones. Dr. J. A. Barltrop gave us samples of *N*-phenyl- and *N*-*P*-tolyl-sydnone. The other sydnones were provided by Prof. Wilson Baker and Messrs. W. D. Ollis and V. D. Poole (Bristol), who also sent a sample of *N*-phenylsydnone (see below and this vol., p. 307).

Physical Measurements.—Electric dipole moments were determined by measuring the dielectric constants, specific volumes and refractive indices of benzene solutions at 25°.

Dielectric constants were determined with a heterodyne-beat capacity meter, in principle the same as that described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668) but considerably improved in detail. A cathode-ray tube detector replaced the loudspeaker; and a new switch, compact, yet having low and very reproducible capacities, was installed. The apparatus was calibrated with benzene, purified as above, which was taken to have the dielectric constant 2·2727 at 25° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **123** *A*, 683).

Specific volumes were determined with a 10-ml. Sprengel–Ostwald pyknometer. They were not corrected for air buoyancy since this causes a negligible error in the moment which depends mainly on the differences between solvent and solutions, and because the solvent was not purified to so high a degree as to make absolute values very important.

Refractive indices. A Jamin interferometer * with divided cell was used to measure the difference in refractive index between solution and pure solvent, which was taken to have a standard refractive index of 1·50238.

Calculation of Moment.—In the following sections w_2 is the weight-fraction of the solute, ε_{12} the dielectric constant of the solutions, v_{12} its specific volume, and Δn the difference of refractive index between solution and solvent; ${}_{\mathrm{T}}P_2$ is the total molar polarisation of the solute, equal to ${}_{\mathrm{T}}p_2$ times M_2, and ${}_{\mathrm{E}}P_2$ the corresponding molar electron polarisation. For finding total polarisations at infinite dilution Hedestrand's procedure (*Z. physikal. Chem.*, 1929, *B*, **2**, 428) was used with the refinements, suggested by Halverstadt and Kumler (*J. Amer. Chem. Soc.*, 1942, **64**, 2988). When the plot of apparent molar polarisation against weight-fraction is not linear, as was the case with *N*-phenylsydnone, this is a much more precise way of extrapolating to infinite dilution.

Dielectric constants and specific volumes were plotted against weight fractions of solute and the straight lines.

$$\varepsilon_{12} = a + \alpha w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$v_{12} = b + \beta w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

fitted by the method of least squares. From the slopes α and β and the intercepts a and b, which were taken to be the solvent parameters ε_1 and v_1, the total specific polarisation of the solute could be calculated from the equation

$${}_{\mathrm{T}}p_2 = 3\alpha v_1/(\varepsilon_1 + 2)^2 + (v_1 + \beta)(\varepsilon_1 - 1)/(\varepsilon_1 + 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The electron polarisation was calculated as follows. The interferometer reading ΔR, proportional to the difference of refractive index, was plotted against w_2, and a straight line $\Delta R = c + \gamma w_2$ fitted as before. The refractive index of any solution could then be calculated by interpolation from the formula

$$n_{12} = n_1 + \gamma k w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k is the calibration constant and $n_1 = 1{\cdot}50238$.

Since it is unnecessary to extrapolate to infinite dilution, the electron polarisation was obtained by choosing a weight-fraction, conveniently 0·01, and calculating n_{12} and v_{12} from (2) and (4) and then ${}_{\mathrm{E}}p_{12}$ from

$${}_{\mathrm{E}}p_{12} = v_{12}(n_{12}^2 - 1)/(n_{12}^2 + 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Finally

$${}_{\mathrm{E}}p_2 = ({}_{\mathrm{E}}p_{12} - 0{\cdot}99\,{}_{\mathrm{E}}p_1)/0{\cdot}01 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$${}_{\mathrm{E}}p_1 = b(n_1 - 1)/(n_1^2 + 2)$$

At 25° the dipole moment μ equals

$$0{\cdot}2212\sqrt{M_2({}_{\mathrm{T}}p_2 - {}_{\mathrm{E}}p_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where M_2 is the molecular weight of the solute. Since the total polarisations are so large, we have not attempted to make an allowance for atom polarisation.

Precision of the Measurements.—*Dielectric constant.* When the moment is low ($<1{\cdot}0$ D.) the average scatter of points about the e_1–w plot is not greater than 0·0002 unit of dielectric constant. When it is large, however, the average scatter may be 0·0015.

Specific volume. The average scatter about the v_{12}–w_2 plot is never greater than 0·0001 unit of specific volume.

Refractive index. The average scatter about the Δn–w_2 plot is not greater than 0·00003 unit of refractive index.

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* Designed by Dr. H. G. Kuhn, of the Clarendon Laboratory, Oxford.

The results are given in the following tables, and are then summarised and compared with those of Earl, Leake, and Le Fèvre (E., L., LeF.).

$w_2 \times 10^6$.	ε_{12}.	v_{12}.	$\Delta n \times 10^5$.	$w_2 \times 10^6$.	ε_{12}.	v_{12}.	$\Delta n \times 10^5$.

N-Phenylsydnone.

2257	2·3376	—	29	8672	2·5194	1·1417	107
3006	—	1·1441	—	*4541	2·4046	1·1432	55
4470	2·4026	—	55	*7655	2·4945	1·1419	94
5648	2·4373	1·1432	67				

* Sample from Bristol.

$\varepsilon_{12} = 2{\cdot}2749 + 28{\cdot}49w_2$; $v_{12} = 1{\cdot}1453 - 0{\cdot}43w_2$; $n_{12} = n_1 + 0{\cdot}122w_2$; ${}_{\mathrm{E}}P_2 = 45{\cdot}4$; ${}_{\mathrm{T}}P_2 = 903{\cdot}5$; $\mu = 6{\cdot}48$ D.

N-*p*-Tolylsydnone.

2702	2·3537	1·1444	33	7610	2·5000	1·1425	—
6067	2·4565	1·1429	69	8776	2·5331	1·1421	99

$\varepsilon_{12} = 2{\cdot}2748 + 29{\cdot}58w_2$; $v_{12} = 1{\cdot}1454 - 0{\cdot}38w_2$; $n_{12} = n_1 + 0{\cdot}109w_2$; ${}_{\mathrm{E}}P_2 = 50{\cdot}7$; ${}_{\mathrm{T}}P_2 = 1021{\cdot}2$; $\mu = 6{\cdot}89$ D.

N-Benzylsydnone.

2513	2·3346	1·1441	26	6937	2·4443	1·1423	68
3910	2·3688	1·1436	39	9631	2·5085	1·1413	94

$\varepsilon_{12} = 2{\cdot}2733 + 24{\cdot}49w_2$; $v_{12} = 1{\cdot}1451 - 0{\cdot}40w_2$; $n_{12} = n_1 + 0{\cdot}096w_2$; ${}_{\mathrm{E}}P_2 = 48{\cdot}5$; ${}_{\mathrm{T}}P_2 = 851{\cdot}7$; $\mu = 6{\cdot}27$ D.

N-*p*-Chlorophenylsydnone.

2683	2·3108	1·1442	33	6663	2·3674	1·1423	81
4389	2·3343	1·1436	53	8894	2·3989	1·1413	108

$\varepsilon_{12} = 2{\cdot}2723 + 14{\cdot}23w_2$; $v_{12} = 1{\cdot}1455 - 0{\cdot}48w_2$; $n_{12} = n_1 + 0{\cdot}122w_2$; ${}_{\mathrm{E}}P_2 = 52{\cdot}1$; ${}_{\mathrm{T}}P_2 = 566{\cdot}2$; $\mu = 5{\cdot}01$ D.

C-Chloro-*N*-phenylsydnone.

1961	2·3170	1·1441	24	4501	—	1·1428	46
3313	2·3487	—	—	5694	2·4046	1·1421	56
4032	2·3658	1·1431	46				

$\varepsilon_{12} = 2{\cdot}2708 + 23{\cdot}51w_2$; $v_{12} = 1{\cdot}1451 - 0{\cdot}50w_2$; $n_{12} = n_1 + 0{\cdot}086w_2$; ${}_{\mathrm{E}}P_2 = 47{\cdot}2$; ${}_{\mathrm{T}}P_2 = 908{\cdot}2$; $\mu = 6{\cdot}49$ D.

C-Bromo-*N*-phenylsydnone.

6198	2·3882	1·1417	65	14440	2·5450	1·1340	142
9702	2·4582	1·1395	105	18748	2·6258	1·1344	187

$\varepsilon_{12} = 2{\cdot}2730 + 18{\cdot}85w_2$; $v_{12} = 1{\cdot}1452 - 0{\cdot}57_5w_2$; $n_{12} = n_1 + 0{\cdot}095w_2$; ${}_{\mathrm{E}}P_2 = 53{\cdot}8$; ${}_{\mathrm{T}}P_2 = 896{\cdot}8$; $\mu = 6{\cdot}42$ D.

N-Phenyl-*C*-methylsydnone.

4057	2·3888	1·1438	46	11062	2·5780	1·1410	124
6904	2·4679	1·1427	75	17597	—	1·1386	195

$\varepsilon_{12} = 2{\cdot}2802 + 26{\cdot}97w_2$; $v_{12} = 1{\cdot}1453 - 0{\cdot}38_5w_2$; $n_{12} = n_1 + 0{\cdot}111w_2$; ${}_{\mathrm{E}}P_2 = 50{\cdot}9$; ${}_{\mathrm{T}}P_2 = 932{\cdot}2$; $\mu = 6{\cdot}57$ D.

N-*cyclo*Hexylsydnone.*

	First series.				Second series.		
2923	2·3564	1·1438	11	1547	2·3183	1·1450	4
6600	2·4655	1·1430	21	4923	2·4151	1·1441	15
10898	—	1·1420	32	6926	2·4729	1·1434	—

$\varepsilon_{12} = 2{\cdot}2725 + 29{\cdot}03w_2$; $v_{12} = 1{\cdot}1450 - 0{\cdot}26w_2$ (β and b are obtained by averaging the results of the first and the second series); $n_{12} = n_1 + 0{\cdot}029w_2$; ${}_{\mathrm{E}}P_2 = 46{\cdot}8$; ${}_{\mathrm{T}}P_2 = 964{\cdot}1$; $\mu = 6{\cdot}7$ D.

* The dielectric constants of the *N*-*cyclo*hexylsydnone solutions were observed to fall slowly with time, presumably as a result of some chemical change in the solute. They have therefore been extrapolated to the time of mixing. As a further precaution this sydnone was recrystallised (from benzene–*cyclo*hexane) immediately before use.

Electric Moments of Sydnones.

Ref. No.		H. & S.	E., L., LeF.	Ref. No.		H. & S.	E., L., Le F.
(1)	*N*-Phenyl-	6·48	6·53	(6)	*C*-Chloro-*N*-phenyl-	6·49	—
(2)	*N*-*p*-Tolyl-	6·89	—	(7)	*C*-Bromo-*N*-phenyl-	6·42	6·5
(3)	*N*-β-Naphthyl-	—	6·9	(8)	*N*-Phenyl-*C*-methyl-	6·57	6·6
(4)	*N*-*p*-Chlorophenyl-	5·01	—	(9)	*N*-*cyclo*Hexyl-	6·7	—
(5)	*N*-*p*-Bromophenyl-	—	5·13	(10)	*N*-Benzyl-	6·27	6·1 *

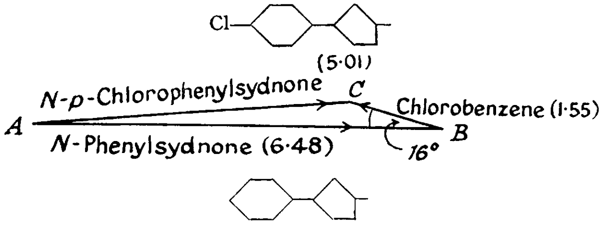
* Stated with some reserve because only a small quantity was available.

DISCUSSION.

Our results show immediately (*a*) that the moment of the sydnone grouping is large and (*b*) that it is directed with its negative pole away from the benzene ring in the *N*-arylsydnones. We shall first calculate the magnitude and direction of this moment and later discuss it in the light of the suggestion that these molecules are resonance hybrids of highly polar forms.

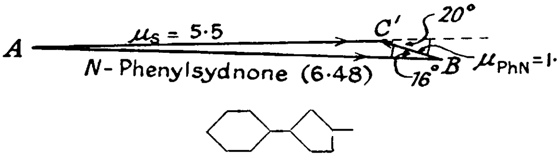
(A) *The Direction of the Moment and the Geometry of the Molecule.*—From the known moments of chlorobenzene (1·55 D.), toluene (0·4), and of the pairs of compounds differing only by *para*-substitution (*viz.*, 1 and 2; 1 and 4) it follows that the angle between the Cl–C_6H_4 bond (see, *e.g.*, *Ann. Reports*, 1935, **32**, 126) and the moment of *N*-phenylsydnone is approximately 16° : this is also the angle between the Ph–N bond and the moment (see Fig. 1).

FIG. 1.



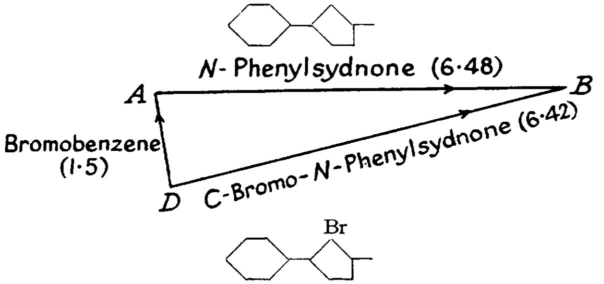
The *N*-phenylsydnone moment may be regarded as the resultant of a large moment in the plane of the sydnone ring, μ_s, and of a small one from the Ph–N bond. The latter is difficult to evaluate, but probably it is not more than 1·1 D.* We know, moreover, that it acts at 16° to the gross moment. By vector subtraction we find (*a*) that μ_s = 5·5 D. (see Fig. 2) and (*b*) that it is inclined to the Ph–N bond at about 20°.

FIG. 2.



Further, from the moments of *N*-phenyl-*C*-methyl-, -*C*-chloro-, or -*C*-bromo-compounds it is easy to calculate the angle between the C–X bond and the parent moment if we assume that the moment C–X is that of the compound Ph–X. The justification for doing this is that the substitution moments in 4-chloropyridine and in γ-picoline are 1·40 and 0·33 D., respectively,

FIG. 3.



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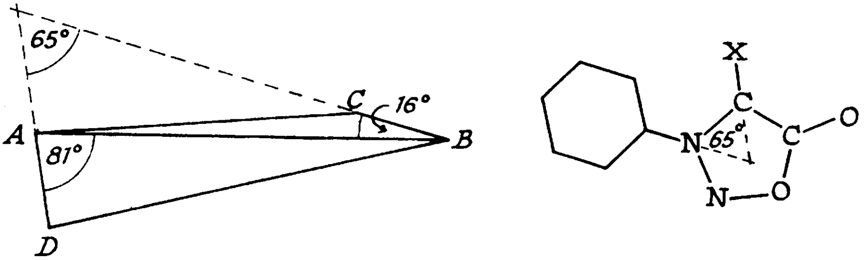
[*] The Ph–N moment in aniline, derived from the moments of this substance, of *p*-toluidine, and of toluene (cf. Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668) is only 0·6 D. This, however, may not be relevant, because the nitrogen atom in the sydnones is in a different state : it is likely (see below) to have a partial formal positive charge arising from π-bonding with the other atoms in the sydnone ring, and not to lend its electrons for π-bonding with the benzene ring. If we take Pauling's assessment of the electronegativity *x* of $>\overset{+}{N}<$ as 0·3 more than that of $>N-$, and take the normal H_3C–N moment as 0·86 (from trimethylamine), we find 1·16 D. as the maximum appropriate moment.

If the formal charge were less than $+e$, the moment would be correspondingly less, and 1·1 D. would be a likely maximum.

indicating that they are much the same in other aromatic systems as they are in benzene. The angles so obtained are: from the *C*-methyl compound, 79°; from the *C*-chloro-compound, 83°; from the *C*-bromo-compound, 81°. One of these results is illustrated by a vector diagram (Fig. 3). Remembering now that in this diagram *DA* is the direction of the C–X bond and that *CB* in Fig. 1 is that of the Ph–N bond, we can, by making *AB* of these two diagrams coincide, find the angle between these directions. We must not forget, however, that our measurements do not tell us the angle between the two planes *ABC* and *ABD*, which may have any value from 0° to 180°. Nevertheless, these extremes will give us limits between which the intervalency angle we seek should lie. Figs. 4 and 5 show that these limits are 65° and 97°.

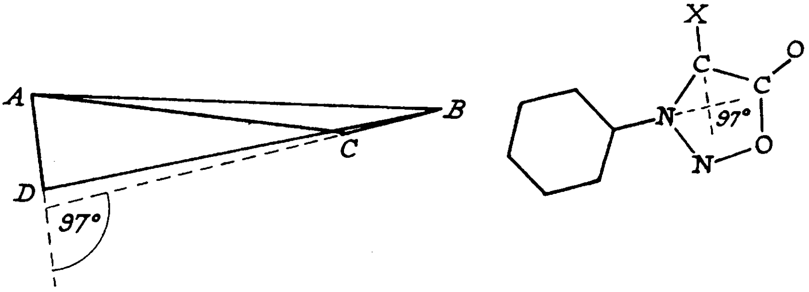
FIG. 4.



Vector diagram. *Molecular diagram.*

Interplanar angle 180°.

FIG. 5.



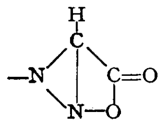
Vector diagram. *Molecular diagram.*

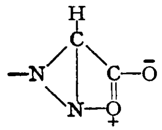
Interplanar angle 0°.

The predicted value for the simplest model based on the bond diagram assigned by organic chemists, *viz.*, a regular pentagon with the radiating valencies coplanar, is 72°. The observed angle is therefore compatible with this structure; but it is to be hoped that the rather wide range of uncertainty can eventually be reduced.

(B) *The Magnitude of the Sydnone Group Moment and Earl's Bicyclic Formula.*—We have already estimated (Fig. 2) that the sydnone group has a moment of about 5·5 D. Such a high value is incompatible with Earl's bicyclic formula (XXXIII), the moment of which we may calculate roughly by adding bond moments obtained by measurements on simple compounds.

(XXXIII.)





(XXXIV.)

Taking the following approximate values: $\mu_{C\text{-}H}$, 0·4($\overset{-}{C}$ — $\overset{+}{H}$); μ_{CN} (long and short), 0·5; μ_{NO}, 0·5; $\mu_{C\text{-}O}$, 0·8; $\mu_{C=O}$, 2·4 D., and assuming the ring to be a regular pentagon, we calculate the vector resultant to be 2·0 D. Some augmentation by resonance with a structure (XXXIV) might be expected, as in the case of the γ-lactones where the calculated moment is 3·4 D. and the observed one is 4·2 D. (see Marsden and Sutton, *J.*, 1936, 1383). The same amount of resonance in the sydnones would still give a total moment of only 2·8 D. We therefore conclude that the results cannot be satisfactorily explained by these bicyclic structures alone.

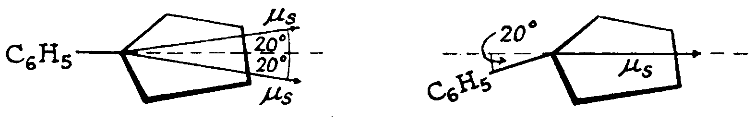
The Sydnone Group explained as a Resonance Hybrid.

(C) *Interpretation of the Direction of the Moment and of the Geometry of the Molecule.*—From Fig. 1, we saw that the moment of the *N*-phenylsydnone has its positive pole towards the phenyl group and its negative one towards the carbonyl group. As we shall show below, the direction of the moment of the sydnone ring itself is within 20° of the two-fold ring axis passing through the caudated nitrogen atom (N_1, Fig. 7). The calculated direction of the moment for structure (XXXIII) lies within these limits. Therefore the comparison of directions provides no evidence against the Earl structure. But if, as the magnitude indicates so strongly, the actual structure is a hybrid, the observed direction shows that the contributing structures are likely to have their formal positive charges on the caudated nitrogen atom and negative ones on the carbonyl oxygen.

These conclusions may be substantiated by an independent argument, as follows. Referring back to section (A), Fig. 2, we see that the sydnone group moment μ_s makes an angle of 20° with the Ph–N bond. We may visualise two extreme configurations (Fig. 6), *viz.*, α, in which the Ph–N bond and the sydnone ring are coplanar so that the 20° angle lies in their plane in either one of the directions shown; and β, in which it is 20° out of the sydnone ring plane, the angle now being contained in a plane perpendicular to this ring. The truth probably lies between these extremes.

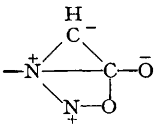
In α, we should say of the nitrogen atom to which the phenyl group is attached that it is quadrivalent, positive, and has its valencies coplanar like those of ethylenic carbon. Configuration β would require contributions from structures with tervalent, formally neutral, pyramidal nitrogen, to an increasing degree as the angle between the Ph–N bond and the ring increases. Our results show that this angle cannot be greater than 20°,[*] whereas if the nitrogen were wholly tervalent it should be *ca.* 53°. We may state confidently, therefore, that forms with planar nitrogen, probably having a formal positive charge, make important contributions to the hybrid.

FIG. 6.

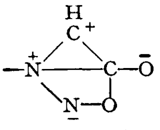


(α.) (β.)

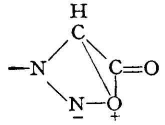
Of the dipolar and tetrapolar structures enumerated in the previous paper, those which satisfy the foregoing conditions are (IX), (X), (XI), (XII), (XV), (XVII), and (XVIII), with (XXI) and (XXII) as possibilities which, however, involve polarisation of the phenyl nucleus.



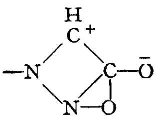
(XXXV.)



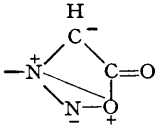
(XXXVI.)



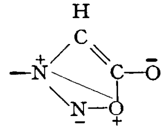
(XXXVII.)



(XXXVIII.)



(XXXIX.)



(XL.)

It must be added that there are polar bicyclic structures which also are satisfactory, *viz.*, (XXXV), (XXXVI), (XXXIX), and (XL). In the current language of resonance theory these would be

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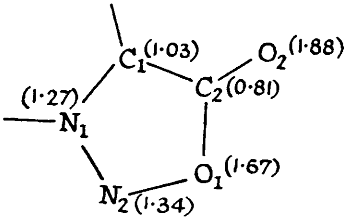
[*] This angle is sensitive to error in the moments, a change of 0·02 D. corresponding to 3°; and since the uncertainties in the moments of *N*-phenylsydnone, of its *p*-chloro-derivative, and of chlorobenzene are probably all of the order of 0·01 D., the angle is not known to better than ±5°.

described as first-excited structures; and if they are sufficiently numerous they are likely to be important as a group.

The large number of possible structures makes this discussion very complex; but it is satisfactory that the conclusions from the arguments based on the geometry and on the magnitude are in harmony; and it may be remarked that the structures deemed " satisfactory " by these criteria are usually those with positive charges on the less electronegative atoms and negative charges on the more electronegative ones, *i.e.*, those which on general energetic grounds are likely to be important.

(D) *The Magnitude of the Moment: Comparison with a Theoretical Value.*—A more quantitative theoretical treatment has been made by Mr. C. H. Longuet-Higgins, who has calculated the distribution of π-electrons by the molecular-orbital method. By his kind consent we show his conclusions in Fig. 7. The differences between the actual and the " initial " distribution of these electrons give the formal charges, which are therefore: on N_1 $+0{\cdot}73$, on N_2 $-0{\cdot}34$, on O_1 $+0{\cdot}33$, on O_2 $-0{\cdot}88$, on C_1 $-0{\cdot}03$, and on C_2 $+0{\cdot}19$.

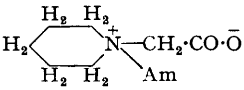
FIG. 7.



It is clear that this calculation is in good qualitative agreement with the conclusionspreviously reached; and that we could say that there is a major contribution from structure (IX) and lesser ones from (X) and (XII). The tetrapolar structure (XVII) probably contributes, and so may the excited structures (XXXIV), (XXXV), and (XXXIX). The ring being assumed to be, to a sufficient approximation, a regular pentagon, it is easy to calculate the magnitude and direction of the π-electron moment, using the above charges; and roughly to do the same, using the bond values already quoted, for the σ-bond moment. These are 12·2 D. and 1·3 D., making angles of $+10°$ and $-68°$ with the direction N_2–O_1 (Fig. 7)). From the latter, and from the total observed moment, if we know its direction as well as its magnitude, the " observed " π-electron dipole moment can be calculated. This direction cannot, as we have seen, be ascribed with certainty; but we can give probable limits relative to the ring framework and, using these, the magnitude of the required moment is found to be 4·6—5·4 D. It is, therefore, only about two-fifths of the calculated value. This discrepancy between calculated and observed values is of some general importance.

There are two points at issue: (*a*) Is the calculation of formal charges correct? (*b*) Can such a calculation give the effective π-electron dipole moment? Concerning (*a*), it seems generally agreed that the simple form of calculation will exaggerate the charges. Concerning (*b*), it seems possible that the field of the formal charges will polarise the σ-bonds and unshared electrons in such a way as to reduce the total moment, so that the effective π-electron moment is less than the calculated one. This latter possibility has previously been recognised (Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789) but not properly investigated.

Dr. J. A. Barltrop and the present authors have attempted a direct attack by extending and augmenting the work of Edsall and Wyman (*J. Amer. Chem. Soc.*, 1935, **57**, 1964) to obtain the moment of a betaine in benzene solution. This will be described more fully in separate communication, but the essential result is that the moment of (XLI), *viz.*, *N*-amylpiperidinium betainc, is about 6·0 D., which is about two-fifths of the value of 15 or 16 calculated simply from formal charges. The ratio is much the same as for the sydnones. This may indicate that the polarisation effect is the more important. (However, Edsall and Wyman, *loc. cit.*, postulate distortion of the molecule.)



(XLI.)

(E) *Resonance between Sydnone and Other Aromatic Rings: Induced Moments.*—In the course of the measurements on *N*-*cyclo*hexylsydnone, it was observed that the dielectric constant readings fell slowly with time (see p. 748). There were slight signs of this in the most concentrated solutions of *N*-benzylsydnone also; but no trouble was encountered with the *N*-arylsydnones. There is, therefore, an indication that the sydnone and the benzene ring are conjugated, which is supported by the dipole-moment evidence. The moment of the *N*-phenyl compound is 0·22 D. less than that of the *N*-*cyclo*hexyl compound, which would agree with there being small contributions from such structures as (XXII). However, Earl, Leake, and Le Fèvre (*J.*, 1948, 2269) believe that the difference can be explained by induction. They have pointed out that moments induced in the substituent on the nitrogen atom (1) will always augment the sydnone ring moment, so that the larger the polarisation of this group the larger the total moment is likely to be. They then observe that the order of moments, *N*-phenylsydnone 6·48 or 6·53 (1), *N*-*cyclo*hexylsydnone 6·70 (9), and *N*-β-naphthylsydnone 6·9 (3), is also the order of the molecular refractivities of benzene, *cyclo*hexane, and naphthalene, *viz.*, 26·2, 27·7, and 44·4.

Having these values in mind, however, it seems that the difference of moment between (1) and (9) is disproportionately large compared with that between (1) and (3), which suggests that polarisability alone does not account for the changes. It must be conceded that to explain the moment of (3) while retaining the hypothesis of a mesomeric moment we must suppose either that there is a large induced moment which swamps it, or that it is opposite to that in the *N*-phenylsydnone.

Earl *et al.* accounted for the moment of the *N*-benzylsydnone (6·1—6·27) by comparing it with *N*-phenylsydnone and taking account of the fact that the benzene ring is more remote from the polarising dipole in the former than in the latter. If we start from *N*-*cyclo*hexylsydnone, and allow 0·4 D. for the moment of the benzyl group (positive pole on the CH_2 group), we find that the moment of *N*-benzylsydnone should be 6·56 D. The difference between this and the observed value may be a measure of the difference of the induced moment in this compound and in the *N*-*cyclo*hexyl one.

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