# 460. *The Dipole Moments of* N- *and* C-*Substituted Sydnones.*

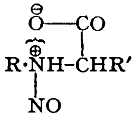
By J. C. EARL, ELEANOR M. W. LEAKE, and R. J. W. LE FÈVRE.

The dipole moments of seven selected sydnones have been determined in benzene solution at 25° by the refractivity method. The values obtained all lie within the range 5—7 D. The " sydnone " skeleton seems to contribute a component moment between 5 and 6 D. acting *approximately* along the R→N bond axis in each case. The measurements are discussed relatively to the possibilities of mesomerism in this and certain other series.

Data for *N*-nitrosophenylglycine and its benzyl ester are also included. The former does not appear to be a " zwitterion." Their two moments have magnitudes to be expected for an acid and its ester. No clear decision can, however, be made between the open-chain or a hydroxy-lactone formulation for nitrosophenylglycine.

DURING the past twelve years, Earl and his collaborators (*J.*, 1935, 899; 1946, 591) have prepared a range of " sydnones " by the treatment of variously substituted *N*-nitroso-*N*-alkyl- or -aryl-glycines with acetic anhydride. Neither the structures of these new substances (cf. Earl *et al.*, *loc. cit.*; *Nature*, 1946, **158**, 909; Baker and Ollis, *ibid.*, p. 703; Kenner and Mackay, *ibid.*, p. 909) nor the mechanisms underlying their formation are yet decided. Earl and Mackney (*loc. cit.*, 1935) have demonstrated that the apparent overall reaction is only the removal of the elements of water from nitroso-acids, whose formulations are themselves in doubt, since they may be free acids (I), zwitterions such as (II) or (III), or hydroxy-lactones of types shown by (IV). Earl and Mackney raised the possibility that (IV) or its acetyl derivative (V) might precede the isolable " sydnones," which were formulated tentatively as (VI) (*i.e.*, as lactones of 2-hydroxy-1-substituted-diaziridine-3-carboxylic acids).

$R\cdot N(NO)\cdot CHR'\cdot CO_2H$
(I.)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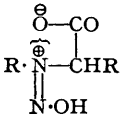
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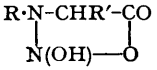
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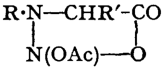
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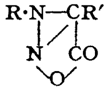

(VI.)

Two problems therefore exist : (*a*) Are the initial substances (I), (II), (III), (IV), or (V) ? (*b*) Are the sydnones adequately represented as (VI), and if not, what are preferable alternatives? In this paper we record attempts to investigate these questions by dipole-moment measurements. During the work we learned that, independently, similar projects were in hand by Dr. Sutton at Oxford and Professor Baker at Bristol. Preliminary results from the three groups have already appeared (*Nature*, 1947, **160**, 366, 367).

## EXPERIMENTAL.

The dielectric-constant measurements have been made with the simple 1 Mc. oscillator described by Le Fèvre and Calderbank (this vol., p. 1950), and the total molecular polarisations at infinite dilution evaluated by the equation ${}_{\infty}P_T = M[p_2(1 - \beta) + C\alpha\epsilon_2]$, where $M$ = molecular weight of solute, $p_2 = (\epsilon_2 - 1)/(\epsilon_2 + 2)d_2$, and $C = 3/d_2(\epsilon_2 + 2)^2$ (cf. *J.*, 1937, 1805). The suffix 2 refers to the solvent, benzene, for which we take $\epsilon_2 = 2{\cdot}2725$ and $d_4^{25^\circ} = 0{\cdot}87378$. Our determinations (all at 25°) have been made relatively to these figures. For the earlier experiments we were compelled to use a Sayce–Briscoe type cell of *ca.* 35 $\mu\mu$ F. air capacity in conjunction with the vernier of a 50—250 $\mu\mu$F. Sullivan variable air condenser. Observations so obtained are asterisked. Later, a cell of 93 $\mu\mu$F. air capacity was substituted and a revolution counter (reading to 0·01 turn, *i.e.*, *ca.* 0·007 $\mu\mu$F.) fitted to the driving shaft of the Sullivan condenser. Both accuracy and ease of reading were thus made greater.

The solutes used were : *N*-nitrosophenylglycine, m. p. 101·5° (decomp.) (Earl and Mackney, *loc. cit.*, give m. p. 102—103°; *N*-nitrosophenylglycine benzyl ester, m. p. 55·5—56·5° (unpublished observation by Mr. J. Delmenico); *N*-phenylsydnone, m. p. 133—134° (Earl and Mackney give 134—134·5°); *N*-*p*-bromophenylsydnone, m. p. 138—139° (Eade and Earl, this vol., p. 2307, give 137·5—138·5°); *N*-phenyl-*C*-methylsydnone, m. p. 98—99° (Earl and Mackney give 98—99°); *C*-bromo-*N*-phenylsydnone, m. p. 133—134° (decomp.) (Kenner and Mackay, *loc. cit.*, give 134°); *NC*-diphenylsydnone, m. p. 184—185° (Eade and Earl give 184—185°); *N*-benzylsydnone, m. p. 66·5—67·5° (Baker, Sutton, *et al.*, *locc. cit.*, give 70°; Eade and Earl, 68—69°); *N*-$\beta$-naphthylsydnone, m. p. 161—162° (Eade and Earl give 159°, decomp.).

As solvent for the dielectric-constant and density measurements (Table I), A.R. benzene, dried over sodium wire, was fractionally crystallised, one-third rejected, and the melted residue stored over sodium. For the refractivities, however, the solubilities of the sydnones were found to be too low in benzene for accurate observations on the Abbé refractometer available. Solutions of *N*-phenyl- and *N*-$\beta$-naphthyl-sydnones in redistilled *cyclo*hexanone were therefore used at concentrations of 3—5%. The $[R_L]_D$ values for the remaining sydnones (Table III) were calculated from the results (Table II) so obtained.

Apart from the above points, experimental procedures have been those described by Le Fèvre (" Dipole Moments," Methuen, 2nd Edn., Chap. II). The symbols used in the following tables have their usual significance (cf., *e.g.*, *J.*, 1937, 1805).

In the discussion below reference is made to the effect of dissolved *N*-nitrosophenylglycine on the dielectric constant of water or alcohol. Our experiments on these points have been made using a small concentric cylindrical condenser, of about 2 $\mu\mu$F. air capacity, constructed similarly (except for size) to that illustrated in *Trans. Faraday Soc.*, 1938, **34**, 1128, Fig. 2. This was rigidly clamped by its earthed lead and immersed to constant depth in the solvent under examination; from it, a coaxial cable connection ran to the oscillator used above, and was attached in place of the lead to the thermostat, cell, etc.

The procedure was as follows : With conductivity water or absolute alcohol as dielectric, and the milliammeter indicating that the quartz crystal was only just resonating (the most sensitive setting), the vernier reading on the Sullivan condenser was noted. Small amounts of the solute were then stirred into solution without disturbing any of the components, and a new setting of the variable condenser found which would restore the original current. An increase of the measured capacity showed that $\epsilon_{\text{solution}}$ was less than $\epsilon_{\text{solvent}}$ and *vice versa*. The room temperature was steady at 28° throughout.

TABLE I.

| 100 $w_1$. | $\epsilon^{t^\circ}$. | $d_4^{t^\circ}$. | $d\epsilon_2$. | $\beta d_2$. |
|---|---|---|---|---|
| 0·0000 | 2·2725 | 0·87378 | — | — |
| | | *N-Nitrosophenylglycine.* | | |
| 0·3745 | 2·2973 | 0·87486 | 6·62 | 0·288 |
| 0·4438 | 2·3012 | 0·87508 | 6·47 | 0·293 |
| 0·4546 | 2·3015 | — | 6·38 | — |
| 0·4797 | 2·3033 | 0·87515 | 6·42 | 0·286 |
| 0·5316 | — | 0·87528 | — | 0·282 |
| | | *N-Nitrosophenylglycine benzyl ester.* | | |
| 1·6890 | 2·3883 | 0·87756 | 6·86 | 0·224 |
| 2·2725 | 2·4282 | 0·87887 | 6·85 | 0·224 |
| 2·5780 | 2·4498 | 0·87959 | 6·87 | 0·225 |
| | | *N-Phenylsydnone.* | | |
| 0·3196 | 2·3691 * | 0·87485 | 30·23 | 0·335 |
| 0·4546 | 2·4017 | — | 28·42 | — |
| 0·5294 | 2·4360 * | 0·87551 | 30·88 | 0·327 |
| 0·5668 | 2·4322 | — | 28·18 | — |
| 0·5884 | 2·4424 | 0·87570 | 28·87 | 0·326 |
| 0·6023 | 2·4433 | 0·87571 | 28·36 | 0·324 |
| 0·6843 | 2·4658 | — | 28·25 | — |
| 0·7124 | 2·4754 * | 0·87612 | 28·48 | 0·329 |
| | | *N-Benzylsydnone.* | | |
| 1·1470 | 2·5389 * | 0·87720 | 23·23 | 0·298 |
| 1·7650 | 2·6823 * | 0·87910 | 23·22 | 0·301 |
| | | *N-p-Bromophenylsydnone.* | | |
| 0·4499 | 2·3270 | 0·87585 | 12·11 | 0·460 |
| 0·45365 | 2·3285 | 0·87586 | 12·34 | 0·459 |
| 0·6588 | 2·3530 | 0·87678 | 12·22 | 0·455 |
| 0·8263 | — | 0·87756 | — | 0·457 |
| 1·1169 | — | 0·87892 | — | 0·460 |
| | | *N-Phenyl-C-methylsydnone.* | | |
| 0·6812 | 2·4611 * | — | 27·70 | — |
| 1·0620 | 2·5645 * | 0·87697 | 27·50 | 0·300 |
| 1·5520 | 2·6902 * | 0·87836 | 26·91 | 0·295 |
| | | *C-Bromo-N-phenylsydnone.* | | |
| 0·2755 | 2·3256 * | 0·87504 | 19·3 | 0·457 |
| 0·4752 | 2·3696 * | 0·87590 | 20·4 | 0·446 |
| 0·8859 | 2·4391 * | 0·87774 | 18·8 | 0·447 |
| | | *NC-Diphenylsydnone.* | | |
| 0·2261 | 2·3190 * | 0·87434 | 20·57 | 0·248 |
| 0·3593 | 2·3458 * | 0·87473 | 20·40 | 0·264 |
| 0·4855 | 2·3681 * | 0·87512 | 19·69 | 0·276 |
| | | *N-β-Naphthylsydnone.* | | |
| 0·2500 | 2·3367 * | 0·87459 | 25·68 | 0·324 |
| 0·3163 | 2·3515 * | 0·87483 | 24·98 | 0·332 |
| 0·3643 | 2·3624 * | 0·87596 | 24·68 | 0·324 |

TABLE II.

*Molecular refractions.*

| 100 $w_1$. | $d_{4^\circ}^{25^\circ}$. | $n_D^{25^\circ}$. | $r_{12}$. | $[R_L]_D$. | 100 $w_1$. | $d_{4^\circ}^{25^\circ}$. | $n_D^{25^\circ}$. | $r_{12}$. | $[R_L]_D$. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *N-Nitrosophenylglycine benzyl ester in benzene.* | | | | | |
| 0·0000 | 0·8738 | 1·5095 | 0·3421 | — | 2·5788 | 0·8796 | 1·5120 | 0·3411 | 81·9 |
| 2·2725 | 0·8789 | 1·5116 | 0·3412 | 81·6 | | | | | |
| | | | | *N-Phenylsydnone in* cyclo*hexanone.* | | | | | |
| 0·0000 | 0·94110 | 1·4502 | 0·28567 | — | 4·866 | 0·95466 | 1·4569 | 0·28522 | 45·9 |
| | | | | *N-β-Naphthylsydnone in* cyclo*hexanone.* | | | | | |
| 0·0000 | 0·94111 | 1·4509 | 0·28599 | — | 3·568 | 0·95110 | 1·4570 | 0·28689 | 66·0 |

TABLE III.

*Results calculated from mean α and β values.*

| Substance. | $\alpha\epsilon_2$. | $\beta d_2$. | $[R_L]_D$, c.c. | $P_1$, c.c. | $\mu$, D. |
|---|---|---|---|---|---|
| *N*-Nitrosophenylglycine | 6·47 | 0·287 | 53 | 260 | 3·18 |
| *N*-Nitrosophenylglycine benzyl ester | 6·86 | 0·224 | 81·7 | 417·3 | 4·06 |
| Sydnones : | | | | | |
| *N*-Phenyl- | 28·96 | 0·328 | 45·9 | 917 | 6·53 |
| *N*-*p*-bromophenyl- | 12·22 | 0·458 | 53·8 | 593 | 5·13 |
| * *N*-Phenyl-*C*-methyl- | 27·37 | 0·297 | 50·5 | 946 | 6·6 |
| * *C*-Bromo-*N*-phenyl- | 19·5 | 0·450 | 53·8 | 923 | 6·5 |
| * *NC*-Diphenyl- | 20·22 | 0·262 | 69·9 | 963 | 6·6 |
| * *N*-Benzyl- | 23·22 | 0·299 | 50·5 | 808 | 6·1 |
| * *N*-β-Naphthyl- | 25·1 | 0·326 | 66·0 | 1045 | 6·9 |

For comparison, we include data recently received (private communication) from Dr. Sutton, together with (in parentheses) the moments reported earlier by Baker, Ollis, Poole, Barltrop, Hill, and Sutton (*Nature*, 1947, *loc. cit.*) :

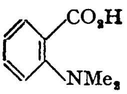
| | $\mu$, D. | | $\mu$, D. |
|---|---|---|---|
| *N*-Phenylsydnone | 6·47 (6·50) | *N*-Benzylsydnone | 6·28 |
| *N*-*p*-Tolylsydnone | 6·86 (6·93) | *C*-Bromo-*N*-phenylsydnone | 6·42 |
| *N*-*p*-Chlorophenylsydnone | 5·00 (5·04) | *N*-Phenyl-*C*-methylsydnone | 6·56 |
| *N*-*cyclo*Hexylsydnone | 6·70 (6·62) | *NC*-Diphenylsydnone | 6·62 |

*N*-Nitrosophenylglycine was thus found to *lower* the dielectric constants of both water and alcohol, but to a less degree than did aniline and acetanilide. With acetamide the diminution was slight but observable. We view this last fact as justifying our conclusions (see below), although observations were only made qualitatively. As a further check we examined successively specimens of chloroform, ether, chlorobenzene, acetone, and nitrobenzene, and plotted condenser readings against dielectric constants. From the resulting curve our settings for absolute alcohol and conductivity water corresponded to $\epsilon = 23{\cdot}8$ and 77·4, respectively, in good agreement with accepted modern values (Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125; Jones and Davies, *Phil. Mag.*, 1939, **28**, 307).

## DISCUSSION.

The measurements now reported indicate that *N*-nitrosophenylglycine lacks the polarity of the true zwitterions. The actual dipole moments of such molecules, although never yet *directly* measured, have been deduced from the alterations of dielectric constants of polar solvents which follow the addition of zwitterionic solute, the relevant observations being commonly expressed as the ratio $\Delta\varepsilon/\Delta c$ per mole. Thus the series $\overset{+}{N}H_3\cdot[CH_2]_n\cdot CO\overset{-}{O}$ has $\Delta\varepsilon/\Delta c = +26$, $+35$, $+52$, $+70$, $+73$, $+86$ per mole for $n = 1$ to 6 respectively (Wyman, *Chem. Reviews*, 1936, **19**, 213). It is relevant to note that phenylglycine itself shows $\Delta\varepsilon/\Delta c =$ *ca.* 30 per mole (Devoto, *Gazzetta*, 1934, **64**, 371). These figures refer to solutions in water. The contrast with similar data for substances soluble in both water and benzene is important. Thus aniline, $\mu = 1{\cdot}5$ D. in benzene, has $\Delta\varepsilon/\Delta c = -7{\cdot}6$ per mole in water, while for phenol, acetamide, *s*-dimethylurea, and dimethylanthranilic acid (VII) the corresponding data are 1·6 : − 6·6, 3·6 : − 0·8, 4·8 : + 3·0, 6·3 : 12—17 (Wyman, *loc. cit.*). The comparison of (VII) with *o*-benzbetaine (VIII; $\Delta\varepsilon/\Delta c = 19$ or 20, Devoto, *loc. cit.*; Edsall and Wyman, *J. Amer. Chem. Soc.*, 1935, **57**, 1964) suggests that (VII) is not fully dipolar.

Wyman (*ibid.*, 1934, **56**, 536; 1936, **58**, 1482) and Kuhn (*Z. physikal. Chem.*, 1935, **175**, *A*, 1) conclude from the rough proportionality between $\Delta\varepsilon/\Delta c$ and molar polarisation that $\mu_{\text{glycine}}$ is about 12 D., *i.e.*, close to the value to be expected on elementary theory.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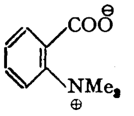
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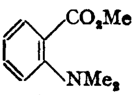

(IX.)

The examples (VII) and (VIII) are especially mentioned since in conjunction with (IX) they illustrate another test for a zwitterionic structure of nitrosophenylglycine.

The methyl ester (IX) isomeric with (VIII) has $\mu = 2{\cdot}05$ D. in benzene (Wyman, *loc. cit.*; Wyman and McMeekin, *J. Amer. Chem. Soc.*, 1933, **55**, 915) in common with other amino-acid esters. From nitrosophenylglycine to its benzyl ester, however, we find no diminution of moment, but instead an *increase* of 0·9 D.—a change in the expected direction for a normal acid–ester relationship (*e.g.*, $CH_3\cdot CO_2H$, 1·7; $CH_3\cdot CO_2Ph$, 1·9; $Ph\cdot CO_2H$, 1·0; $Ph\cdot CO_2\cdot CH_2Ph$, 1·9—2·1, cf. *Trans. Faraday Soc.*, 1934, Appendix) and quite contrary to that inferred for the amino-acid and ester pairs, and dimethylanthranilic acid and its methyl ester, cited above.

We conclude therefore that formulæ of the types (II) and (III) contribute negligibly to the real structure of *N*-nitrosophenylglycine and may be eliminated.

No decision between (I) and (IV) is possible on available evidence, since the moments now found for the acid and its benzyl ester both fall between the extreme values which may be forecast for various configurations of (I) or (IV) by the application of link moments (Eucken and Meyer, *Physikal. Z.*, 1929, **30**, 397) to reasonably assumable scale models.

Turning now to the sydnones themselves (Table III), it is seen that the ten examples, for which data are now provided, have moments between 5 and 7 D. If, throughout all sydnones, there is a fixed and recurrent " nucleus " of atoms, then likewise there should be a fixed and recurrent " nucleus " moment, which, compounded with appropriate substituent link moments, should enable the observed value for any member to be calculated from that for its unsubstituted parent. *Very roughly* this does seem to be the case for the *N*-phenylsydnones, since, taking $\mu C \rightarrow$ halogen as 1·55 D. and $\mu C \leftarrow Me$ as 0·4 D., angles of interaction, $\theta$, are calculable from Table III as follows :

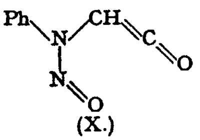
| Substance. | θ. | Angles between lines of action.* |
|---|---|---|
| *C*-Bromo-*N*-phenylsydnone | 98° | 98° |
| *N*-Phenyl-*C*-methylsydnone | 82 | 98 |
| *N*-*p*-Tolylsydnone | 13 | 167 |
| N-*p*-Chlorophenylsydnone | 164 | 164 |
| *N*-*p*-Bromophenylsydnone | 158 | 158 |

* Measured anticlockwise from the direction of action of the *N*-phenylsydnone moment.

It is therefore obvious that, as stated by Sutton *et al.* (*Nature, loc. cit.*), the moment of *N*-phenylsydnone can be viewed as operative in derived molecules and acting within 20° to the Ph–N bond, with its negative pole directed *away*, through the N atom, from the substituent. It will be noted also that from the *p*-bromo- to the *C*-bromo-member there is a θ difference of *ca.* 60°, and from the *p*-methyl- to the *C*-methyl-, one of *ca.* 70°. It may be significant that on a flattened model with N and C intervalency angles of 120° and 110°, respectively, the R–N and H–C directions intersect at 65°, while for a regular 5-ring (such as XIX, XX, etc.) the corresponding angle should be 72°. These calculations, although too sensitively affected by variations in the component values adopted to justify more than semi-quantitative conclusions, nevertheless indicate nothing *against* the idea that sydnones contain a common structural atomic arrangement. The case of quinoline (*J.*, 1935, 1470) may be cited as an extreme analogy since its moment can appear to act over a range of 50° in various alkylquinolines or over a range of 33° in the 5-, 6-, and 8-nitro-derivatives; yet the quinoline nucleus indubitably persists throughout.

The next point for remark is the general high order of moment now found for sydnones. Uncertainties of space formulation and absence of analogies make it difficult to forecast a series of " expected " values for the two unperturbed " Lewis " structures (VI) and (X) which have been included in earlier discussions (Earl and Mackney, *loc. cit.*; Earl, *Nature*, 1946, **158**, 909). For (X) we have already noted (*Nature, loc. cit.*) that the moments of *N*-nitroso-methyl- and -ethyl-anilines are 3·62 and 3·61 D., respectively (Cowley and Partington, *J.*, 1933, 1252), while that of keten is 1·45 D. (Hannay and Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 1357), so that the highest likely moment of a molecule containing these units without modification is 5·1 D. Regarding (VI), Sutton *et al.* (*loc. cit.*) comment that its moment should not be greater than that of a $\gamma$-lactone (4·12 D.; Marsden and Sutton, *J.*, 1936, 1383). The measured figure is, however, *ca.* 2·4 D. more.

In our preliminary note (*Nature, loc. cit.*) we interpreted the results then available as indicating mesomerism (Ingold, *Chem. Reviews*, 1934, **15**, No. 2; Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789; Zahn, *ibid.*, p. 804) between a number of dipolar extreme forms. Many of the stereochemically awkward " bridged " formulations proposed by earlier workers are now rewritten in this way. The various " endo "-compounds discovered by Busch and his collaborators (*J. pr. Chem.*, 1899, **60**, 187; 1903, **67**, 201, 216, 243, 257, 263; 1930, **124**, 301; *Ber.*, 1905, **38**, 4049) include some relevant examples, such as the " isodithiobiazolones " (XI) or (XII), the " thiotriazolines " (XIII) or (XIV), " nitron " (XV) or (XVI), etc. Schönberg (*J.*, 1938, 824), referring to the conceptions of Ingold (*J.*, 1933, 1120) and Sidgwick (*J.*, 1937, 694), suggested that the real states of Busch's compounds are resonance hybrids to which betaine forms such as (XVII) or (XVIII) contribute.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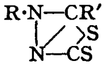
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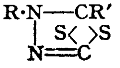
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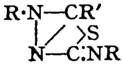
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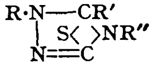
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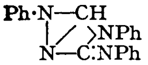
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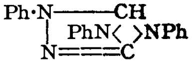
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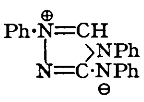
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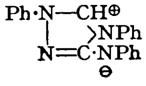
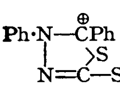
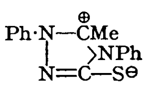

(XVIII.)

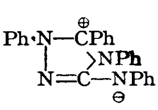
As mentioned on p. 2272, a fully formed zwitterion should have a moment of 20 or more D. units. Ingold's and Sidgwick's treatment, on the other hand, allows a lower moment than this to be observed experimentally; in fact, nitron shows $\mu = 7{\cdot}2$ D. (in benzene; Warren, *J.*, 1938, 1100). In the same way the unexpectedly high moments of a number of $\alpha$- and γ-pyrones (for some of which, incidentally, " bridged " structures were once current; see Collie, *J.*, 1904, **85**, 971; Homfray, *J.*, 1905, **87**, 1443) have been ascribed to contributions from several forms, certain being completely polar (Hunter and Partington, *J.*, 1933, 87; Le Fèvre and Le Fèvre, *J.*, 1937, 196, 1088). Jensen and Friediger (*Kgl. Danske Vidensk. Selsk.*, 1943, **20**, No. 20) have recently made a valuable and comprehensive dipole-moment study of resonance effects among heterocyclic systems, including nine of Busch's compounds, eight of which show high polarity, exemplified by the following :



" 2 : 3-Diphenyl-2 : 5-endothio-1 : 3 : 4-thiodiazolin," $\mu$ = 8·8 D. in $C_6H_6$ or 9·1 D. in dioxan.



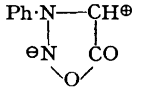
" 1 : 4-Diphenyl-5-methyl-3 : 5-endothio-1 : 2 : 4-triazolin," $\mu$ = 8·4 D. in $CHCl_3$.



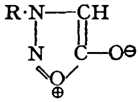
" 1 : 4 : 5-Triphenyl-3 : 5-endoanilo-1 : 2 : 4-triazoline," $\mu$ = 9·1 D. in $C_6H_6$ or 8·8 D. in dioxan.

These authors also explain their results by mesomerism between polar " amphoionen ", but mention as probable " das für die Konstitution dieser Verbindungen auch unpolare, biradikaloide Formeln von Bedeutung sind ".

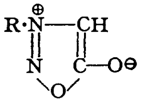
Arising out of the considerations noted above, we therefore imagine each sydnone to be a stable hybrid, containing a roughly regular 5-ring, to which (VI), (X), and several dipolar structures [*e.g.*, (XIX)—(XXII)] may contribute. Formula (XIX) is the activated form of



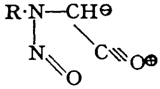
(XIX.)



(XX.)



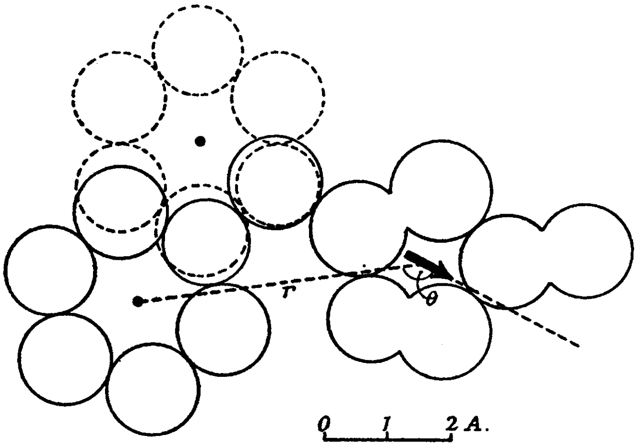
(XXI.)



(XXII.)

(VI) [without the charge signs (XIX) would correspond to the " biradikaloide " formulæ of Jensen and Friediger, *loc. cit.*]; (XX) has some analogies with the polarised α-pyrones (cf. Clayton, *J.*, 1908, **93**, 524) and, further, the nitroso-group is known to act as a " donor ", forming 5- or 6-rings, in the metallic derivatives of " cupferron " or the nitroso-naphthols; (XXII) is suggested because a 25% contribution of $\overset{\ominus}{\mathrm{C}}\mathrm{H_2}{-}\mathrm{C}{\equiv}\overset{\oplus}{\mathrm{O}}$ has to be assumed to explain the observed dipole moment of keten (Hannay and Smyth, *loc. cit.*) *vis à vis* that of an ordinary ketone. Neither (X) nor (XXII) can be eliminated on the ground that sydnones do not react chemically as nitroso-compounds, since some of the metal complexes just cited also fail in this respect; (XXI) corresponds to the formula given by Kenner and Mackay (*Nature*, *loc. cit.*) to the monobromination product of *N*-phenylsydnone. The directions of action of the high moments expected for each of the contributors will clearly differ sufficiently for their effects, in the real state, to be diminished by partial mutual cancellation. They are not undetectable, however, and from the conclusion drawn earlier (p. 2273) it is evident that forms with the substituted nitrogen bearing a positive charge (such as XXI) predominate.

We have previously mentioned the possibility that mesomeric shifts may also occur in the aryl radicals of sydnones, thus allowing quadripolar forms further to affect the observable moments. The low value (Table III) for *N*-benzylsydnone (where conjugation with N is broken by interpolation of $>CH_2$) and the high moment of *N*-naphthylsydnone *could* partly be caused in this way. We now note, however, that electrostatically induced moments in the various nitrogen-held groups would qualitatively appear to operate in the same sense. Any substituent on the nitrogen atom will be more or less in line behind the point of action of the principal moment and hence (cf. Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919) the induced and principal moments will augment one another. With the benzyl derivative, the phenyl ring will obviously be some 70° (*i.e.*, 180° — 110°) out of line. Calculations on this suggestion must be somewhat uncertain since neither the *precise* position nor the value of the " nucleus " moment is known. Generally, however, the moments, $\mu_x$ and $\mu_y$, induced in a group whose polarisability is equivalent to $\alpha$ c.c. at $(r)(\theta°)$, by a primary dipole, $\mu$, situated at the pole and acting along the original line of a set of plane polar co-ordinates, are given by $\mu_x = \alpha\mu[(\varepsilon + 2)/3\varepsilon][(3\cos^2\theta - 1)/r^3]$ and $\mu_y = \alpha\mu[(\varepsilon + 2)/3\varepsilon][(3\sin\theta\cos\theta)/r^3]$, $\varepsilon$ being the dielectric constant of the intervening space ($\doteqdot 2{\cdot}4$), so that when the vectorial angle $\theta$ is *between* 55° and 125° $\mu_x$ and $\mu$ will not co-operate but oppose.



*Drawn using the following interatomic distances* (A.) : C–C, 1·54; CAr.–CAr., 1·46; N–N, 1·48; O–O, 1·48; C–O, 1·43; C–N, 1·47; C=O, 1·28, and N=O, 1·18 (*Pauling and Huggins,* Z. Krist., 1934, **87**, 205; *Schomaker and Stevenson,* J. Amer. Chem. Soc., 1941, **63**, 37).

If the " nucleus " moment (see p. 2273) is located as indicated in the figure, and the $C_6H_5$ polarisability is effectively at the centre of the Ar-ring, the scale drawing shows that $\theta$ in benzylsydnone is between 140° and 150° while that in phenylsydnone (broken lines) is approximately 180°. The radius vectors, $r$, are likewise *ca.* 4·6 and 4·0 A., respectively. In the two molecules $\mu_x$ should therefore augment $\mu$ in each case, but in the ratio 1 : 3. On the basis of the figure and Stuart and Volkmann's estimate ($1{\cdot}23 \times 10^{-23}$ c.c.; *Ann. Physik,* 1933, **18**, 121) of $\alpha$ for the plane of the benzene ring, $\mu_x$ for *N*-phenylsydnone appears to have an absolute value of $0{\cdot}235\mu$ unit (whence, from our measurements, $\mu$ is around 5·3 D.), while for the benzyl compound $\mu_x = 0{\cdot}42$ and $\mu_y = 0{\cdot}57$ D., so that the resultant induced moment is 0·7 D. acting in the general direction of the principal moment. Although the application of more refined calculations, *e.g.*, the method of Sugden and Groves (*J.*, 1937, 1992), would probably produce somewhat lower figures, nevertheless it is evident that induction effects *alone* may easily account for the relative moments observed for benzyl- and phenyl-sydnones.

By similar arguments, the resultants for *N*-β-naphthyl-, *N*-*cyclo*hexyl-, and *N*-phenylsydnones should diminish in the order named, *i.e.*, the order of the polarisabilities of naphthalene, *cyclo*hexane, and benzene for which $[R_L]_D = 44{\cdot}4$, 27·7, 26·1 c.c., respectively. This is the order found by experiment.

The authors are grateful to Mr. J. Delmenico for the preparation of various specimens including the hitherto undescribed benzyl ester of *N*-nitrosophenylglycine (selected since it is solid at ordinary temperatures), and to the Chemical Society for permission to retain certain apparatus previously purchased with grants from their Research Fund.

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