S 21. *Ultra-violet Absorption Spectra of* N-*Nitrosophenylglycine and its Benzyl Ester, and of Six Sydnones.*

By J. C. Earl, R. J. W. Le Fèvre, and I. R. Wilson.

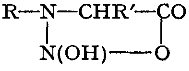
N-Nitroso-*N*-phenylglycine, its benzyl ester, and *N*-nitrosomethylaniline are found to have very similar ultra-violet absorptions between 2300 and 4000 A., suggesting that the acid has an open chain rather than a cyclic structure. Six sydnones examined resembled one another in all absorbing with the same order of intensity between the limits 3100 and 3400 A. These new observations are discussed *vis-à-vis* various recorded data for other substances; they are not at variance with the view (cf. *J.*, 1948, 2269) that sydnones form a class with an unusual mesomeric heterocyclic nucleus as a common feature throughout.

This paper records ultra-violet spectrographic evidence bearing upon two questions associated with the chemistry of the sydnones.

(a) *The Structure of* N-*Nitroso*-N-*phenylglycine*.—In a previous paper (*J.*, 1948, 2269) Earl, Leake, and Le Fèvre remarked that the *N*-nitroso-monosubstituted glycines (from which sydnones are produced by the dehydrating action of acetic anhydride) might have one of several structures some of which were "Zwitterionic". The dielectric evidence was against a structure of the latter type but did not assist in a choice between formulæ (I) and (II).

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

(I.)



(II.)

On the assumption that an *ester* of (I) would be unlikely to undergo internal addition to form a molecule of type (II), we have examined the ultra-violet spectrum in alcohol of *N*-nitroso-*N*-phenylglycine, in relation to that of its benzyl ester, and *N*-nitrosomethylaniline. Fig. 1 displays the results, the essential features of which are :

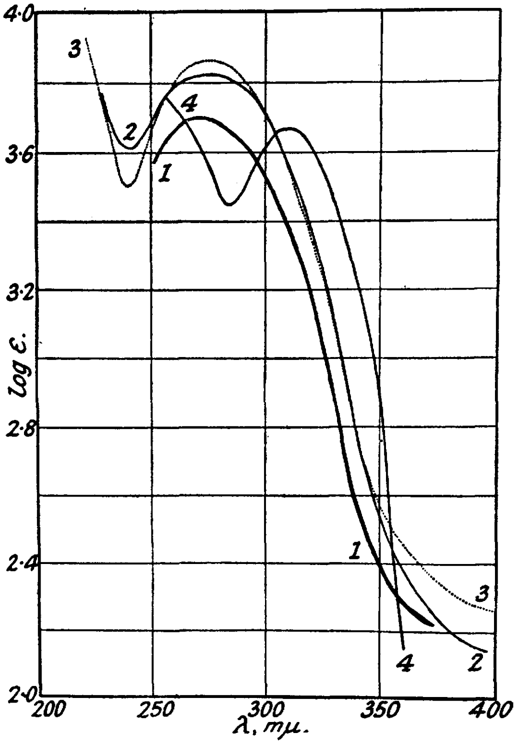
	$\lambda_{max.}$ (A.).	$\log_{10} \epsilon$.
N-Nitroso-*N*-phenylglycine	2700	3·70
,, ,, ,, benzyl ester	2750	3·83
N-Nitrosomethylaniline	2750	3·86
N-Phenylsydnone	3100	3·67

The fourth curve has been included to emphasise the difference between phenylsydnone (No. 4) and its precursor, nitrosophenylglycine (No. 1).

The similarities, not only of $\lambda_{max.}$ but also of general contour, among the first three spectra strongly suggest a near relationship for the molecules concerned. Of formulæ (I) and (II), the former accordingly seems preferable.

Our present results, by implication, also provide an argument, additional to that in the earlier paper quoted above, against a "Zwitterion" structure. In general, it appears that the spectra of an amine and its related ammonium salts differ in that certain characteristic absorptions appear at shorter wave-lengths with the latter than with the former [*e.g.* 350 A. between α-$C_{10}H_7$·NH_2 and (α-$C_{10}H_7$·NH_3)Cl (Rollett, *Sitzungsber. Akad. Wiss. Wien, Abt. IIb,* 1937, **146**, 425), 600 A. between anthranilic acid and its hydrochloride, or 300 A. between *o*-toluidine and its hydrochloride (Ramart-Lucas, *Bull. Soc. chim.*, 1936, **3**, 726)]. Other examples are to be found in Ph·NO and Ph·NO_2 (see later), and in comparisons between amines and amine oxides (French and Gens, *J. Amer. Chem. Soc.*, 1937, **59**, 2600).

FIG. 1.



Curve No. 1 ... N-*Nitroso*-N-*phenylglycine.*
2 ... N-*Nitroso*-N-*phenylglycine benzyl ester.*
3 ... N-*Nitrosomethylaniline.*
4 ... N-*Phenylsydnone.*

This movement of $\lambda_{max.}$ to shorter wave-lengths as the nitrogen becomes a positive pole is thus seen to be often considerable. Yet *N*-nitroso-*N*-phenylglycine and its ester have maxima only 50 A. apart. On the whole, therefore, we submit that the spectroscopic indications are against a structure containing quaternary nitrogen.

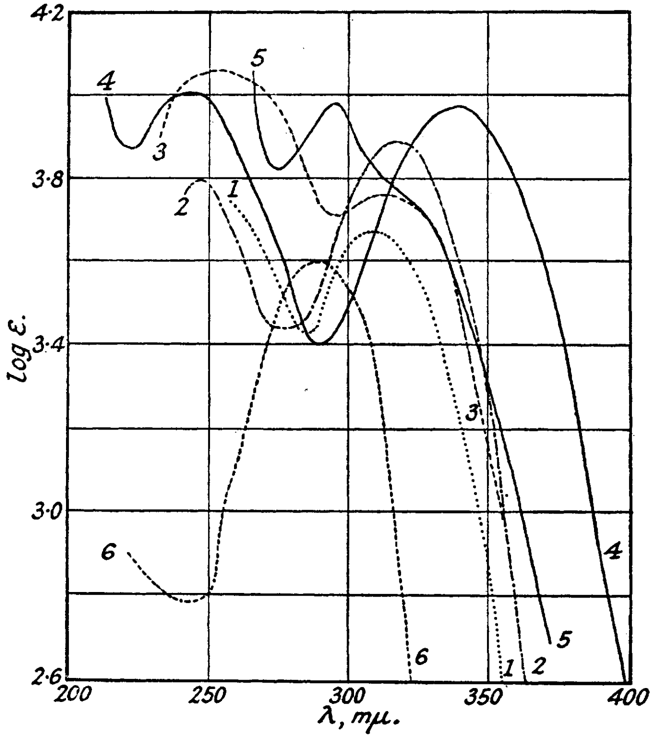
(b) *The Structure of the Sydnones.*—Earl, Leake and Le Fèvre (*loc. cit.*), reviewing the dipole-moment evidence, found nothing against the view that the sydnones possessed a common structural atomic arrangement. If this is correct the same qualitative spectral similarities as are found between members of other heterocyclic families should appear among the sydnones.

Fig. 2 and the following Table refer to solutions in ethyl alcohol :

Sydnone.	$\lambda_{max.}$	log ε.	$\lambda_{max.}$	log ε.
N-Phenyl-	3100	3·67	—	—
C-Bromo-*N*-phenyl-	3200	3·88	2450	3·8
N-*p*-Bromophenyl-	3150	3·74	2550	4·06
NC-Diphenyl-	3400	3·97	2450	4·01
N-β-Naphthyl-	(3150	3·8)	2950	3·98
N-Benzyl-	2900	3·61	(2600	3·1)

A preliminary examination of *N*-phenylsydnone was made during 1946 by F. B. Strauss who reported (private communication) "maxima at 3095 A. ($\varepsilon^{\text{molar}}_{\text{max.}}$ 5120) and 2350 A. ($\varepsilon^{\text{molar}}_{\text{max.}}$ 8540), minimum at 2870 A. ($\varepsilon^{\text{molar}}_{\text{min.}}$ 3870). There is an inflexion (phenyl absorption) at 2650 A. ($\varepsilon^{\text{molar}}$ 5530)". The solvent is not stated. Our extinction coefficients for $\lambda = 3100$ and 2875 A. are somewhat lower (log $\varepsilon = 3{\cdot}67$ against Strauss's 3·71, and 3·44 against 3·59), but it is clear that the two independent results are in general agreement.

FIG. 2.



Curve No. 1 ... N-*Phenylsydnone.*
2 ... C-*Bromo*-N-*phenylsydnone.*
3 ... N-p-*Bromophenylsydnone.*
4 ... NC-*Diphenylsydnone.*
5 ... N-β-*Naphthylsydnone.*
6 ... N-*Benzylsydnone.*

Fig. 2 therefore illustrates what we hoped to show, namely that the ultra-violet absorptions of different sydnones occur at roughly common wave-lengths and with the same order of intensities throughout. The variations from case to case are not greater than those found with other series, *e.g.* acridine and its amino- or hydroxy-derivatives (Craig and Short, *J.*, 1945, 419; Turnbull, *ibid.*, p. 441; Albert and Short, *ibid.*, p. 760), 1 : 2 : 3-benztriazoles (Macbeth and Price, *J.*, 1936, 111), or various *p*-benzoquinones (Braude, *J.*, 1945, 490). The marked change of $\lambda_{\text{max.}}$ from the three *N*-nitroso-compounds to *N*-phenylsydnone (2700—2750 A. to 3100 A.) is understandable if considered with the already well-established chemical fact (*e.g.* negative Liebermann test, Earl and Mackney, *J.*, 1935, 899) that in the "sydnone" arrangement the $-N{=}O$ group has lost its identity.

Our measurements may be regarded, in terms of Braude's review (*Ann. Reports*, 1945, **42**, 105), as cases of the type PhX where the phenyl group is in conjugation with other chromophores, so that the absorptions between 2450 and 2950 A. (log ε *ca.* 4) are "K bands", and those around 3200 A. (log ε slightly less than 4) the results of absorptions due to the "sydnone" structure superimposed on the expected "B bands" (for which log ε is commonly 2—3). We note that the "K" peak at 2550 A. (log $\varepsilon = 2{\cdot}4$; EtOH) for benzene appears at 2800 A. (log $\varepsilon = 3{\cdot}95$; EtOH) in nitrosobenzene, at 2850 A. (log $\varepsilon = 2{\cdot}3$; EtOH) in aniline, and at 2850 A. (log $\varepsilon = 3{\cdot}2$)

in phenylhydrazine (Braude, *loc. cit.*; Biquard and Grammaticakis, *Bull. Soc. chim.*, 1939, **6**, 1606). [Incidentally, comparison between the just quoted data for Ph·NO, and those for Ph·NO_2, 2520 A., log ε = 4 (hexane), provides a further example of the λ shift caused by a positive charge on an arylated nitrogen.] The *NC*-diphenyl- and benzyl-sydnones differ most from phenylsydnone where the longer wave absorption is concerned, but this could be anticipated *a priori* since (*a*) in general, as the number of phenyl substituents in a molecule is increased, absorption at all regions tends to move to longer wave-lengths, and (*b*) where conjugation is broken (*e.g.* by a CH_2 group), and the chromophores thereby become more isolated, such displacement is usually less (Braude, *loc. cit.*; Jones, *Chem. Reviews*, 1943, **32**, 1). The absorption at 2950 A. of naphthylsydnone is also not surprising, the corresponding absorption in the parent hydrocarbon being related to that in benzene in the same direction (C_6H_6, 2550 A.; $C_{10}H_8$, 2750 A.).

EXPERIMENTAL.

Materials.—*N*-Nitroso-*N*-methylaniline was prepared from purified methylaniline and redistilled immediately before use (cf. Beilstein, "Handbuch", **12**, 579). The various sydnones were those already specified by Earl, Leake, and Le Fèvre (*loc. cit.*).

Apparatus.—The majority of the measurements recorded in Figs. 1 and 2 were made initially with a Hilger Sector Photometer in conjunction with a quartz spectrograph, alcohol being the solvent throughout Later a Beckman (Model DU) photoelectric quartz spectrophotometer became available and several of the earlier curves were rechecked. The spectra of nitrosomethylaniline and *NC*-diphenylsydnone were studied only on the Beckmann instrument.

Some early studies of the spectra of *N*-nitroso-*N*-methylaniline were described by Dobbie and Tinkler (*J.*, 1905, **87**, 278) and Baly and Desch (*ibid.*, 1908, **93**, 1759). Their curves are rough but indicate absorptions covering that at 2750 A.

Acknowledgment is made to the Commonwealth Science Research Fund for financial assistance.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, July 10th*, 1948.]