Magnetochemical Study of Sydnones

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Introduction

The problem of providing an adequate structural formula for sydnones has engaged the minds of chemists, since Earl and Mackney[1] obtained N-phenylsydnone by dehydration of N-nitroso-N-phenylglycine about twenty years ago. The bicylic structure proposed by the discoverers was considered to be unacceptable, and the hybrid structure derived from a number of contributing ionic forms suggested by Baker[2] seems to be consistent with the known properties of the compounds, i. e. general stability of aromatic type, dipole moment [3,4] and ultra-violet absorption spectra[2,5]. The non-localized electrons in the sydnone ring will bring about the large diamagnetic contribution, so that the exaltation of molar susceptibility may be expected against the calculated values for any of the contributing ionic forms, and its magnitude may be considered as a measure of its aromatic character. With the intention of ascertaining the aromatic character of sydnone ring, we examined the diamagnetic susceptibilities of some derivatives of sydnone.

Experimental

Materials.— They were prepared by the methods described in the references cited. N-phenylsydnone[1], recrystallized from boiling water and sublimed in vacuum. m. p. 132-3°C. (all of m. p. are not corrected.) N-*p*-tolylsydnone[2], sublimed in vacuum. m. p. 140-1°C. N-*p*-methoxyphenylsydnone[6], sublimed in vacuum. m. p. 123-4°C. N-*p*-chlorophenylsydnone[2], recrystallized from the mixture of benzene and light petroleum. m. p. 113°C. N-*m*-nitrophenylsydnone. The mixture of nitrosoglycine and acetic anhydride was warmed on a steam bath for six hours and concentrated under reduced pressure. The precipitated crystals were washed and recrystallized from ethanol. m. p. 137-8°C. Eade and Earl[6] obtained the same material by the reaction at room temperature for two months; the above procedure was in imitation of that for *p*-analogue given by Baker. N-*p*-nitrophenylsydnone[2], recrystallized from the mixture of benzene and light petroleum. m. p. 180-2°C. N-β-naphthylsydnone[6], recrystallized from ethanol and sublimed in vacuum. m. p. 157°C. N-benzylsydnone[2], recrystallized from the mixture of benzene and light petroleum. m. p. 67-9°C. N-phenyl-C-bromosydnone[2], recrystallized from ethanol repeatedly. m. p. 133-4°C. N-phenyl-C-iodosydnone[7], recrystallized from methanol. m. p. 157-8°C. N-phenyl-C-chloromercurysydnone[7], recrystallized from methanol. m. p. 196-8°C. bis(N-phenylsyd-

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[1] J C Earl and A. W. Mackney, *J. Chem Soc.*, **1935**, 899

[2] W Baker, W. D Ollis and V. D. Poole, ibid., **1949**, 307

[3] J. C. Earl, E. M. W. Leake and R. J. W. Le Fèvre ibid , **1948**, 2269

[4] R A. W. Hill and L. E. Sutton, ibid., **1949**, 746; **1953**, 1482

[5] J. C. Earl,R. J. W. Le Fèvre and I. R. Wilson, ibid., **1949**, S. 103.

[6] R. A. Eade and J. C. Earl, ibid., **1946**, 591.

[7] K. Nakahara and M. Ohta, *J. Chem Soc. Japan* (*Pure Chem. Sect.*), **77**, 1306 (1956).

nonyl-C-)mercury[7], precipitated crystals were washed with methanol and used without further purification.

Magnetic Measurement. — The susceptibility was measured using a Gouy balance as previously described[8].

Results and Discussion

The results are shown in Table I[9] for N-arylsydnones which have no substituent in the sydnone ring. If we assume that the effect of conjugation between aryl and sydnonyl groups on the molar susceptibility is small, we may approximate their susceptibilities by the sum of those of constitutional fragments of the molecule, namely aryl and sydnonyl groups. For example, from the molar susceptibility of N-phenylsydnone the value of benzene is subtracted and twice the amount of Pascal's constant for hydrogen is added; the remainder may be considered as the molar susceptibility of the unsubstituted sydnone $C_2H_2N_2O_2$. The evaluated values by the similar method from the data of the other seven compounds are also given in column four of Table I. The following values were used for the calculations, benzene 55.2[10], toluene 65.8[11], anisol 72.6[12], chlorobenzene 70.0[13], nitrobenzene 61.8[11] and naphthalene 92.2[14]. Including the value derived from the molar susceptibility of N-benzylsydnone in which the conjugation between two constitutional fragments does not exist, their agreements are satisfactorily good, and the assumption made in the above evaluations is supported by this fact. The mean value 38.7 will be used in the discussion hereafter.

TABLE I

MOLAR SUSCEPTIBILITIES OF N-ARYLSYDNONES

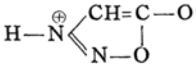
Substance	Suscept. (χ)	Molar Suscept. (χ_M) ArSy.*	Molar Suscept. (χ_M) HSy.*
N-Phenylsydnone	0.540	87.6	38.3
N-*p*-Tolylsydnone	0.556	98.0	38.1
N-*p*-Methoxyphenylsydnone	0.542	104.2	38.0
N-*p*-Chlorophenylsydnone	0.518	101.8	37.7
N-*m*-Nitrophenylsydnone	0.458	94.9	39.0
N-*p*-Nitrophenylsydnone	0.458	94.9	39.0
N-β-Naphthylsydnone	0.593	125.8	39.5
N-Benzylsydnone	0.568	100.1	40.2

* Sy is the abbreviation of sydnonyl group.

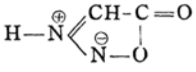
Generally the diamagnetic anisotropy of a molecule is expressed as

$$\Delta K=3(\chi_M-K_i)$$

where χ_M and K_i are the observed molar susceptibility for powdered specimen and its isotropic part respectively. The isotropic part of an ordinary aromatic compound is usually assumed to be equal to the principal molar susceptibility in the plane of a molecule, and approximated by the calculated value for its Kekulé form[15]. It seems to be acceptable that the isotropic part of molar susceptibility of meso-ionic compound can be approximated by the calculated value for the contributing ionic form; and the anisotropic part corresponds to the diamagnetic contribution of non-localized electrons in the meso-ionic ring. Although a regular pentagon was assigned by many chemists for the simplest model of sydnone ring, it must be noted that the application of the above formula is not restricted by the non-coplanarity of the ring[16]. In the case of aromatic compounds, the magnitude of the isotropic part does not depend on the forms in so far as we choose the Kekulé form for the purpose of evaluating it. But in the present case, the calculated values for the contributing ionic forms are not necessarily equal to each other, and it is incorrect to pick out one of them as the representative for which the isotropic part must be calculated. The following five forms (I—V) were considered by Baker[2] to make important contributions to the hybrid, and Hill and Sutton[4] suggested that there is a major contribution from form (I) and a lesser from (II) and (IV).



(I)



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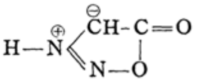
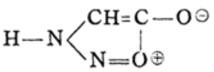


(III)



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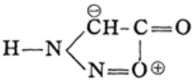
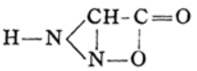


(V)



(VI)

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[8] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

[9] All susceptibility values in this paper are recorded in 10^{-6} c. g. s. units and the negative signs are omitted.

[10] B. C. Eggleston et al., *J. Chem. Soc.*, **1954**, 941.

[11] F. G. Baddar and S. Sugden, ibid., **1950**, 308.

[12] P. Rumpf snd M. Séguin, *Bull. soc. chim. France*, **1949**, D 366.

[13] C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

[14] H. Akamatu and Y. Matsunaga, This Bulletin, **29**, 800 (1956).

[15] H. Shiba and G. Hazato, ibid., **22**, 92 (1949)

[16] A. Pacault, *Bull. soc. chim. France*, **1949**, D 371.

Therefore, by means of Gray-Cruickshank's system⁽¹⁷⁾ we calculated the values for these forms as the isotropic part of molar susceptibility of unsubstituted sydnone. For example, the value for form (I) was calculated based on the model shown in Fig. 1 using the constants presented in Table II.

TABLE II

CALCULATION OF MOLAR SUSCEPTIBILITY OF IONIC FORM (I) OF SYDNONE

Atom (Charge)	Ionic Diamagnetism	Bond	Bond Depression
H (+0.04)	2.28	C—H	0.53
H (+0.29)	1.68	C=C	9.50
C (+0.02)	9.89	C—N	1.78
C (+0.26)	9.10	C—O	1.92
N (+0.08)	8.09	C—O	1.92
N (+0.65)	6.74	N—H	0.57
O (−0.21)	7.58	N=N	13.3*
O (−1.13)	9.82	N—O	2.06
Total Diamagnetism	55.18		31.58
Total Bond Depression	31.58		
Resultant Molar Suscept.	23.60		

* Estimated from the constant for azo group determined previously[18].

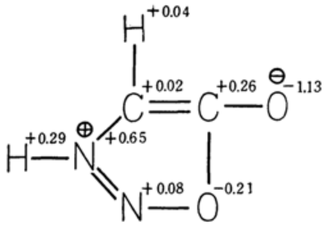

Fig. 1. Model of ionic form (I) of sydnone.

Table III illustrates the calculated values for the five forms, including also the value for bicyclic structure (VI) calculated using Pascal's constants, and the latter which must be compared directly with the experimental value appears to be unacceptable again from this standpoint. Fortunately the calculated values for (I—V) are so close to each other that we estimate the isotropic part of molar susceptibility of sydnone at the mean value 24.57. By the comparison between the value derived from the experimental data shown in Table I and the estimated one, we obtain 14.1 as the exaltation of molar susceptibility i. e. $\Delta K/3$ which must be due to the contribution of non-localized electrons in the sydnone ring. The estimated exaltation is nearly equal to those of furan 13.4 and pyrrole 14.4 and slightly less than that of thiophene 17.9 given by Pacault[19]. According to Dewar[20], an aromatic compound is defined as a cyclic compound with a large resonance energy. The relation between resonance energy and diamagnetic anisotropy is uncertain and not simple. It is not correct to affirm that the molecule which shows the larger diamagnetic anisotropy has always the larger resonance energy. As an example of the extremely conflicting cases, perylene shows the diamagnetic anisotropy less than twice as large as that of naphthalene, but its resonance energy is larger than twice the latter's[21]. As to sydnone, however, the nearly isoelectronic structure with furan and pyrrole results from a large fractional negative charge borne by the oxygen atom in carbonyl group, so it seems to be probable that sydnone ring has the aromatic character in the same order with furan and pyrrole rings.

TABLE III

CALCULATED MOLAR SUSCEPTIBILITIES OF IONIC AND BICYCLIC FORMS OF SYDNONE

Form	Molar Suscept. (χ_M or K_i)
Ionic (I)	23.60
Ionic (II)	24.69
Ionic (III)	24.74
Ionic (IV)	24.08
Ionic (V)	25.22
Bicyclic (VI)	25.46

Next we examined the molar susceptibilities of four derivatives of N-phenylsydnone in which the substituent is linked to the carbon atom of the sydnone ring, and compared them with the calculated values based on the constant for sydnone 38.7 derived from eight N-arylsydnone by the aid of the additivity rule. The results are presented in Table IV. Kadomtzeff[22] showed that the magnetic contribution of mercury depends markedly on the nature of the rest of the molecule and gave the values from 23.8 to 43.0 for the mercury in RHgX, and from 28.5 to 46.0 for the same atom in R_2Hg. We used in our cal-

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[17] F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31**, 1491 (1935).

[18] Y. Matsunaga, This Bulletin, **29**, 308 (1956).

[19] A. Pacault, *Rev. sci.*, **86**, 38 (1948).

[20] M. J. S. Dewar, " The Electronic Theory of Organic Chemistry ", Oxford Univ. Press, Oxford, (1949) p. 160.

[21] F. Klages, *Ber.*, **82**, 358 (1949).

[22] I. Kadomtzeff, *Bull. soc. chim. France*, **1949**, D 394.

culations the constants of mercury in the most similar compounds which have ever been measured, namely the derivatives of thiophene.

TABLE IV

MOLAR SUSCEPTIBILITIES OF DERIVATIVES OF N-PHENYLSYDNONE

Substance	Suscept. (χ)	Molar Suscept. (χ_M)		
		Obs.	Calcd.	Diff. (%)
N-Phenyl-C-bromosydnone	0.461	111.1	111.5	-0.3
N-Phenyl-C-iodosydnone	0.429	123.6	125.5	-1.4
N-Phenyl-C-chloromercury-sydnone	0.378	150.1	144.0*	$+4.3$
Bis (N-phenyl-sydnonyl-C-) mercury	0.383	200.3	198.5**	$+1.0$

* The constant of mercury 38.9 was used.

** The constant of mercury 28.5 was used.

The calculated molar susceptibilities agree well with the observed ones, except the case of N-phenyl-C-chloromercury-sydnone. At the present, we cannot decide conclusively between the incorrect estimation of the constant of mercury used in the calculation and the remarkable change of the contribution of non-localized electrons in a sydnone ring as the cause of this disagreement. The latter case was found by Hazato[23] in the derivatives of tropolone which some investigators regard as one type of meso-ionic compounds. However, the author is inclined to the former cause, as such a large influence of substituent on diamagnetism is not common in a number of aromatic compounds, besides such a disagreement is not found in the other three cases presented here.

Summary

The molar susceptibilities of eight N-arylsydnones were measured by the Gouy method. Assuming that the influence of the conjugation between aryl and sydnonyl groups on diamagnetism is practically negligible, the molar susceptibility of unsubstituted sydnone was estimated as 38.7. Its isotropic part 24.57 was evaluated from the values for five of the contributing ionic forms calculated by the Gray-Cruickshank's method. From the magnitude of the exaltation of molar susceptibility which is equal to one third of an anisotropic part, the author suggested that the aromatic character of a sydnone ring is in the same order with those of furan and pyrrole rings. Four derivatives of N-phenylsydnone which have a substituent in meso-ionic ring were also measured, and the agreements between the observed and the calculated molar susceptibilities were found to be good within the limit of the latter's estimation.

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[23] G. Hazato et al, *Sci. Repts. Research Insts. Tohoku Univ., Ser.* A, **5**, 278 (1953); **6**, 193 (1954).