Magnetochemical Study of Nitroso Compounds

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Introduction

Since the early investigation of Pascal[1], little attention has been paid to the magnitude of diamagnetic susceptibility of nitroso compounds. Pascal treated the nitroso group as equivalent to the carbonyl group, and assigned +3.46[2] for the constant of the oxygen atom in the former group. But his value was supported by measurements on three compounds only, namely nitrosobenzene, N-nitrosopiperidine, and N-nitrosodiethylamine. Since nitroso compounds show deep color and a tendency to form dimer, some authors[3] proposed a triplet structure to the nitroso group. Although Wilson[4] found nitrosobenzene and *p*-nitrosodimethylaniline to be diamagnetic and did not accept the above-mentioned suggestion, he did not give any value of susceptibility of these two compounds. Farquharson[5] examined the susceptibility of nitrosobenzene, as a solid, as a melt and as a solute in benzene and acetic acid. His results showed that this compound is less diamagnetic in a molten or dissolved state than in a solid state.

It seems of interest to measure the susceptibility of some nitroso compounds, both in solid and dissolved states, in order to test the validity of Pascal's constant for the oxygen atom in the nitroso group, and to throw further light on the extraordinary change of diamagnetism found by Farquharson.

Experimental

Materials.—Nitrosobenzene[6], recrystallized from ethanol, m. p. 66–67°C. *p*-Nitrosotoluene[7], from ethanol, m. p. 48.5–49.5°C. *p*-Nitrosodimethylaniline[8], from petroleum ether, m. p. 87.5–88°C. *p*-Nitrosodimethylaniline hydrochloride[8], prepared from purified free base and hydrochloric acid, m. p. 177°C (decomp.). *p*-Nitrosodiethylaniline[9], from petroleum ether, m. p. 87.5°C. *p*-Nitrosonitrobenzene[10] from ethanol, 119–120°C. *m*-Nitrosonitrobenzene[10], from ethanol, m. p. 89–90°C. 2-Methyl-2-nitrosopropane, provided by Dr. F. Iimura, used without further purification. N-Nitrosodiethylamine[11], b. p. 170–170.5°C/756 mmHg. $n_D=1.4412$ at 13.0°C. N-Nitrosodiphenylamine[12], from ligroin, m. p. 68.5–69.5°C. *p*-Benzoquinone[13], sublimed in vacuum, m. p. 114°C. *p*-Nitrosophenol[14], from toluene, m. p. 124°C (decomp.). α-Naphthoquinone[15], sublimed in vacuum, m. p. 124°C. α-Nitro-α-naphthol[16], from ethanol, m. p. 190°C (decomp.). β-Naphthoquinone, commercial product, used without further purification, m. p. 125–130°C (decomp.). β-Nitroso-α-naphthol[16], from ethanol, m. p. 146–148°C (decomp.). α-Nitroso-β-naphthol[17], from ligroin, m. p. 109°C.

Magnetic Measurement.—The measurements were carried out by the Gouy method as previously described[18], using two specimen tubes, a small one (ca. 0.32 cc.) for solid specimens and a large one (ca. 1.20 cc.) for liquids. For some compounds, the susceptibility was also determined by measuring the susceptibility of the solution, and assuming that the additivity law holds for the constituents of the solution. The following solvents were used for this purpose, acetic acid ($\chi=-0.534$), dioxan (-0.570), toluene (-0.716), and concentrated hydrochloric acid (-0.675).

Results and Discussion

In Table I are presented molecular weight, and specific and molar susceptibilities for the specimens of C- and N-nitroso compounds measured, together with the values calculated by Pascal's constants for the molar susceptibility. In the cases of C-nitroso compound, the observed values of molar susceptibility are in serious disagreement with the calculated ones. For the estimation of constant of the oxygen atom in nitroso group, Pascal used nitrosobenzene alone as an example of this series of compounds, and his value is appreciably less diamagnetic than those presented by Farquharson and by us, therefore the calculated values for C-nitroso compounds have no meaning except for the convenience of the following discussion.

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[1] P. Pascal, *Bull. soc. chim. France*, **9**, 336 (1911).

[2] Susceptibility values have been multiplied by 10^6 throughout this paper.

[3] L. Pauling, *J. Am. Chem. Soc.*, **53**, 3225 (1931) and references cited there.

[4] E. B. Wilson Jr., ibid., **56**, 747 (1934).

[5] J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

[6] "Organic Syntheses", (1945), **25**, 80.

[7] E. Bamberger and A. Rising, *Ann.*, **316**, 257 (1901).

[8] A. Baeyer and H. Caro. *Ber.*, **7**, 963 (1874).

[9] "Organic Syntheses", Coll. Vol., (1943) **2**, 223.

[10] E. Bamberger and R. Hübner, *Ber.*, **36**, 3803 (1903).

[11] A. Geuther, *Ann.*, **128**, 151 (1863).

[12] E. Fischer' ibid., **190**, 67 (1878).

[13] "Organic Syntheses", Coll. Vol., (1948) **1**, 482.

[14] J. L. Bridge, *Ann.*, **277**, 79 (1893).

[15] C. E. Groves, *J. Chem. Soc.*, **26**, 209 (1873).

[16] R. Henriques and M. Ilinski, *Ber.*, **18**, 704 (1885).

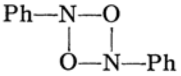
[17] "Organic Syntheses", Coll. Vol. (1948) **1**, 411.

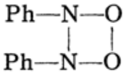
[18] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

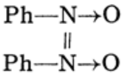
TABLE I
DIAMAGNETIC SUSCEPTIBILITIES OF NITROSO COMPOUNDS

Substance	M. w.	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$		
			Obs.	Calcd.	Lit
Nitrosobenzene	107	0.552	59.1	54.2	55.0[1] 60.2[5]
p-Nitrosotoluene	121	0.582	70.4	66.1	—
p-Nitrosodimethylaniline	150	0.489	73.3	86.4	—
p-Nitrosodiethylaniline	178	0.520	92.6	110.1	—
p-Nitrosonitrobenzene	152	0.433	65.8	60.5	—
m-Nitrosonitrobenzene	152	0.434	66.0	60.5	—
N-Nitrosodiethylamine	102	0.581	59.3	61.0	60.6[1]
N-Nitrosodiphenylamine	198	0.559	110.7	111.9	—

As it is well known that nitrosobenzene exists as dimeric form in the solid state, the calculated molar susceptibility must be computed for this structure. But the structure of dimeric nitrosobenzene has not been determined yet. Ingold and Piggott[19] and Pauling[3] suggested the structure (I) containing the nitrogen-oxygen ring which is analogous to that of dimeric nitric oxide[20]. On the other hand, the chemical evidence favors the structure in which nitrogen atoms are bound together, and Stewart[21] and Hammick[22] proposed the structures (II) and (III) respectively.


(I)


(II)


(III)

The same apparent molar susceptibility is computed by Pascal's law to be −58.2 or −60.2 for the structures (I) and (II), using the constitutional correction constant for four-membered carbon ring +3.05[23] or +1.1[24] instead of the unknown one for nitrogen-oxygen ring. For the structure (III), −59.2 is estimated from the observed value for azobenzene −105.3[25] with the aid of the system of Gray and Cruickshank[26]. All of these calculated molar susceptibilities are in good agreement with the observed one, and we cannot decide the most probable one among these three structures. The differences between the observed and calculated molar susceptibilities of *p*-nitrosotoluene, and *m*- and *p*-nitrosonitrobenzenes can be interpreted similarly, but those of *p*-nitrosodialkylanilines, which are less diamagnetic than the calculated values in contrast with the above-mentioned cases, must be considered further.

In the dissolved state, nitrosobenzene and its derivatives are blue or green, and cryoscopic data[22] show that they exist mainly as monomeric form. As *p*-nitrosodialkylanilines are green even in the solid state, they have certainly the nitroso group which is chromophoric, and the depression of diamagetism may be attributed to this distinctive character. With the purpose of confirming this view we examined the susceptibility of the solution, and the values of these compounds were calculated by the direct application of Wiedemann's additivity law. The results are in Table II, with the calculated molar susceptibilities given by Pascal's constant for nitroso group.

It should be noted that the observed molar susceptibilities are from 10 to 18 units less diamagnetic than the calculated values in all of the C-nitroso compound. The depression is also found in nitrosobutane, and we thus conclude that this depression is attributed to the presence of nitroso group attached to a carbon atom, and its magnitude is affected by the conjugation with aromatic nucleus and the other substituents. Consequently, the magnetic contribution of the nitroso group as a whole in these compounds is paramagnetic of the order of 10 units. In the cases of the N-nitroso compound, the molar susceptibility does not depend on the states, i. e. solid, liquid and dissolved, and they agree with the calculated values within the accuracy of measurements and estimations. From the magnetic standpoint, it is apparent that the nitroso group attached to a nitrogen atom is unlike that attached to a carbon atom.

The paramagnetic contribution of the nitroso group found here is very weak, if we compare it with that found in the substance with a permanent magnetic moment.

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19) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 168 (1924).

20) W. J. Dulmage, E. A. Meyers and W. N. Lipscomb, *J. Chem. Phys.*, **19**, 1432 (1951).

21) Cited in reference 3.

22) D. Ll. Hammick, *J. Chem. Soc.*, **1931**, 3105.

23) J. Farquharson and M. V. C. Sastri, *Trans. Faraday Soc*,, **33**, 1474 (1937).

24) P. Pascal, *Compt. rend.*, **181**, 656 (1925).

25) Y. Matsunaga, This Bulletin, **29**, 308 (1956).

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

TABLE II

DIAMAGNETIC SUSCEPTIBILITIES OF NITROSO COMPOUNDS IN THE DISSOLVED STATE

Solute	Solvents*	No. of Detn.	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Molar Suscept. $(-\chi_M)$ Calcd.
Nitrosobenzene	A	3	0.372		
	T	2	0.393	41.0	54.2
p-Nitrosotoluene	D	1	0.440		
	T	1	0.435	53.0	66.1
p-Nitrosodimethylaniline	T	2	0.490	73.5	86.4
p-Nitrosodiethylaniline	T	2	0.691	92.4	110.1
2-Methyl-2-nitrosopropane (Nitrosobutane)	D	1	0.489	42.5	52.5
N-Nitrosodiethylamine	D	1	0.569		
	T	1	0.587	59.0	61.0
N-Nitrosodiphenylamine	D	1	0.545		
	T	1	0.566	110	111.9

* A: acetic acid. D: dioxan. T: toluene.

Therefore, if we assume that the apparent difference is due to the partial compensation of diamagnetism by the paramagnetic contribution of triplet state, the molecule may be excited at the rate of the order of one thousandth. This assumption seems to be improbable for the following two reasons. In the first place, the excitation energy expected from the magnetic data is about 7 kcal. mol.$^{-1}$, and this is only one fifth of that suggested from the spectroscopic data27). In the second, the state of the substance may somewhat affect the magnitude of the excitation energy, and also the apparent paramagnetic contribution of the nitroso group. But *p*-nitrosodialkylanilines do not show such a tendency28). In another explanation of the contribution of the nitroso group, we must consult Van Vleck's equation29) for the molar susceptibility of a polyatomic molecule with no resultant electron spin moment, namely,

$$\chi_M = -\frac{Ne^2}{6mc^2}\sum r^2 + \frac{2}{3}N\sum_{n'\neq n}\frac{|m^0(n';n)|^2}{h\nu(n';n)}$$

where $m^0(n';n)$ is a non-diagonal element of the matrix for the angular momentum of the system, $\nu(n';n)$ is the frequency corresponding to $n';n$ transition, and the other terms have their usual physical significance. If the second term is dominant in the nitroso group, the magnetic contribution of this group as a whole may be feebly paramagnetic and independent of temperature. Such examples are not rare in inorganic compounds, but in organic compounds, the second term is usually smaller than the first one, and the case found here is very striking. However, we wish to emphasize that there is no essential difference between diamagnetism and temperature-independent paramagnetism, and the sign of the susceptibility depends only on the magnitude of these two terms.

TABLE III

DIAMAGNETIC SUSCEPTIBILITIES OF QUINONES AND THEIR MONOXIMES

Substance*	M. w.	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Molar Suscept. $(-\chi_M)$ Diff**	Molar Suscept. $(-\chi_M)$ Lit.
p-Benzoquinone	108	0.355	38.4	—	41.3 30), 40.0 31), 38.2 32), 34.4 33)
p-Nitrosophenol	123	0.412	50.7	12.3	50.3 1)
α-Naphthoquinone	158	0.465	73.5	—	73.8 21), 73.0 33),
α-Nitroso-α-naphthol	173	0.530	91.8	18.3	—
β-Naphthoquinone	158	0.430	67.9	—	—
β-Nitroso-α-naphthol	173	0.478	82·7	14.8	—
α-Nitroso-β-naphthol	173	0.485	83.9	16.0	—

* Monoximes are indicated by the name of isomeric nitrosophenol.

** Monoxime (obs.) − Quinone (obs.).

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27) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **67**, 994 (1945).

28) The validity of this assumption was completely denied. According to Dr. I. Miyashita, Hokkaido University, *p*-nitrosodialkylanilines do not show paramagnetic absorption (private communication).

29) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Oxford University Press, Oxford (1932), p. 275.

30) P. Pascal, *Bull. soc. chim. France*, **9**, 177 (1911).

31) K. S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc.*, **A234**, 265 (1935).

32) H. Mikhail and F. G. Baddar, *J. Chem. Soc.*, **1944**, 590.

33) E. D. Bergmann et al., *J. chim. phys.*, **49**, 474 (1952).

Pascal concluded that nitrosophenol exists as quinone monoxime in the crystal, comparing its molar susceptibility to the calculated value using his own constants. However, as already shown, owing to the paramagnetic contribution of nitroso group it seems to be difficult to decide whether the magnitude of molar susceptibility favors the quinone monoxime form. We measured also some of quinone monoxime, and the values are compared with those of the parent quinones. The results are presented in Table III. The values of the molar susceptibility increment associated with the transition $>C=O \rightarrow >C=N-OH$ markedly depend on the nature of the rest of the molecule, and they are more diamagnetic than those found in the aliphatic series which were reported as from 7.4 to 11.7 units[34]. Hence it appears that the oxime group cannot localize π-electrons in the aromatic nucleus so strongly as carbonyl group, and the evaluation of the molar susceptibility of quinone monoxime by a set of constants is difficult.

TABLE IV

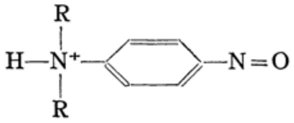
DIAMAGNETIC SUSCEPTIBILITIES OF *p*-NITROSODIALKYLANILINE HYDROCHLORIDES

Ion	Molar Suscept. ($-\chi_M$)				
	Obs.	Calcd.			
		A_1	A_2	B_1	B_2
p-Nitrosodimethylaniline$+H^+$	79.9*	73.9	93.0	77.0	82.7
p-Nitrosodiethylaniline$+H^+$	101**	93.2	116.7	100.7	106.4

* Hydrochloride (103.3) $-$Chloride ion (23.4)[35].

** Apparent susceptibility of free base in hydrochloric acid solution.

Nitrosodialkylanilines form the salts with inorganic acids, and the color change from green to yellow suggests the disappearence of the distinctive nature of the nitroso group. In order to elucidate the structure of the cation, we examined their susceptibilities measuring the susceptibility of the crystalline salt or the hydrochloric acid solution. The observed values shown in Table IV will be compared with the calculated values of some of the models of the cation. The value A_1 is for the monomeric anilinium ion (IV), and the value A_2 for the dimer. However, the former computed on the basis of the observed susceptibility for the free base is too small and the latter given by Pascal's law is too large.


(IV)


(V)

The possible other structure is (V), in which the hydrogen ion is attached to the oxygen atom in the nitroso group. The expected values for this stucture are somewhat obscure, because the most similar compound the susceptibility of which is known is quinone monoxime, and the substitution of carbonyl group by $>C=NR_2$ may affect the degree of localization of aromatic electrons. If the transition $>C=O \rightarrow >C=NR_2$ does not affect the magnetic contribution of aromatic electrons, the value B_1 may be expected, and if the delocalization occurs in this transition again to a similar extent to that found in the transition from quinone to its monoxime, the value B_2 may be expected. The observed values are in the expected ranges, and seem to be consistent with the structure (V).

Summary

The magnetic susceptibility of nine nitroso-compounds, as solids and as solutes, were measured by the Gouy method. The constant for the nitroso group attached to a carbon atom was found to be paramagnetic of the order of 10 units. The author suggested that the second term in Van Vleck's equation for the diamagnetism of a molecule is dominant in this case. Some quinones and their monoximes were also measured, and it appeared that the ability of the oxime group to localize aromatic electrons is less than that of the carbonyl group. In addition, the structure of nitrosodialkylaniline hydrochloride was discussed from the magnetic standpoint.

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[34] C. M. French and D. Harrison, *J. Chem. Soc.*, 1955, 3513.

[35] V. C. G. Trew, *Trans. Faraday Soc.*, 37 476 (1941).