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THE PROTON MAGNETIC RESONANCE SPECTRA OF SOME AROMATIC NITROSO COMPOUNDS

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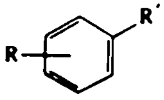
Abstract—Unusual chemical shifts are reported for *o*-alkylnitrosobenzenes. The origin of these shifts is considered. The PMR spectrum of *o*-nitrosotoluene is found to contain signals attributed to both monomeric and dimeric forms in carbon tetrachloride and *d*-chloroform solution.

o-NITROSOPROPYLBENZENE (**3a**) and *o*-butylnitrosobenzene (**4a**) were prepared in the course of a recent investigation of the reactivity of aromatic nitro and nitroso compounds towards triethyl phosphite.[1] Certain features of the PMR spectra of these compounds were unusual. A search of the literature gave no indication that the PMR spectra of nitrosobenzene or its simply alkyl derivatives have ever been discussed in any detail. A brief investigation of the PMR spectra of certain aromatic nitroso compounds was undertaken and the results are reported here. Shortly after completion of this work a paper reporting the PMR spectrum of nitrosobenzene and certain *para*-substituted derivatives appeared.[2]



R	$R^1 = NO$	$R^1 = NO_2$
H	**1a**	**1b**
o-Me	**2a**	**2b**
o-n-Pr	**3a**	**3b**
o-n-Bu	**4a**	**4b**
p-Me	**5a**	**5b**

RESULTS

The PMR spectra of the nitroso compounds can be conveniently discussed with reference to the corresponding nitro compounds. The data are given in Table 1.

The salient common feature of the spectra of **2a**, **3a** and **4a** is the appearance of single proton doublets (J = 8 c/s, additional small couplings are not resolved) near 6·2–6·3 ppm. These signals are assigned to the protons *ortho* to the nitroso function. The multiplicity of these signals indicates that they must be adjacent to either the nitroso or alkyl substituent. Alkyl substituents do not cause major changes in the shielding of adjacent ring protons.[5] The position of the high-field doublet in **2a** corresponds to an upfield shift of 0·9 ppm relative to the ring protons in toluene. The shift cannot be attributed to electron release by the nitroso substituent. The maximum upfield shift of *ortho* protons listed in major compilations[6] is the shift of

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[1] R. J. Sundberg, *J. Am. Chem. Soc.* **88**, 3781 (1966).

[2] I. R. King and G. W. Kirby, *J. Chem. Soc.* 1334 (1966).

TABLE 1. PMR SPECTRA OF SOME AROMATIC NITRO AND NITROSO COMPOUNDS IN PPM (FROM TMS)[a]

Compound	*o*-protons(s)	Benzyl protons	*m*, *p* protons
1a	(7·95)^{b,c}	—	7·5–8·1
1b	8·25^{c,d}	—	7·3–7·9
2a	6·25^{e}	3·29	7·0–7·7
2b	7·98^{f}	2·58^{g}	7·2–7·7
3a	6·17^{e}	3·83^{h}	7·0–7·7
3b	7·88^{f}	2·87^{h}	7·1–7·7
4a	6·17^{e}	3·85^{h}	6·9–7·7
4b	7·87^{f}	2·88^{h}	7·0–7·7
5a	7·81^{e,i}	2·40	7·35^{d}
5b	8·11^{e}	2·44^{j}	7·32^{d}

[a] The effect of concentration and solvents on peak position was examined in the case of **2a**. Except for the dimer Me peak small downfield shifts (2–3 c/s) of all peaks accompanied dilution of the solution in *d*-chloroform through the concentration range shown in Table 2. The largest shift in peak position observed in changing to CCl_4 as solvent was that of the high-field aromatic doublet which occurred at 5 c/s higher field (6·17 ppm) in CCl_4.

[b] *o*-Protons are not entirely resolved from aromatic multiplet; Lit.[5] 7·93. [c] Doublet, $J = 8$ c/s plus additional fine splitting. [d] Lit.[5] 8·25 ppm (in cyclohexane). [e] Doublet, $J = 8$ c/s. [f] Multiplet. [g] Lit.[4] 2·58 ppm. [h] Triplet, $J = 7·5–8$ c/s. [i] Lit.[5] 7·84 ppm. [j] Lit.[4] 2·48 ppm.

0·8 ppm found in aniline and N-methylaniline.[6] The nitroso group is considered to be weakly electron-withdrawing, σ *para* = +0·123.[7]

The fact that high-field doublets appear in the spectra of the *o*-alkylnitrosobenzenes **2a**, **3a** and **4a**, while **1a** and **5a** show no comparable signals, demonstrates that the presence of an *ortho* substituent is required for the unusual shift to be observed. The signals due to the benzyl protons in **2a**, **3a** and **4a** are found at abnormally *low* field. Thus, the position of the Me singlet in *o*-nitrosotoluene (**2a**) is downfield by 0·89 ppm relative to the Me signal in the *para* isomer **5a**. Similarly, the benzyl methylene signals in *o*-nitrosopropylbenzene (**3a**) and *o*-butylnitrosobenzene (**4a**) are shifted 0·96 and 0·97 ppm downfield from the methylene signals in the corresponding nitro compounds **3b** and **4b**.

The PMR spectra of 4·2 and 12·8% by wt solutions of *o*-nitrosotoluene are shown in Fig. 1. In addition to the Me singlet at 3·3 ppm a singlet is also found near 2·5 ppm. The relative intensity of the high-field singlet drops as the solution is diluted. The high-field signal is therefore attributed to the Me groups of nitrosotoluene dimer present in equilibrium in solution. This observation confirms an earlier conclusion of Hammick[8] based on apparent mol wt in benzene, that *o*-nitrosotoluene is partially dimerized in solution. The apparent ratio of protons of the various types as determined by integration of the spectra are recorded in Table 2.

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[4] P. R. Wells and P. G. E. Alcorn, *Austr. J. Chem.* **16**, 1108 (1963).

[5] I. Yamaguchi, *Mol. Phys.* **6**, 105 (1963).

[6] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance* pp. 258–259. McGraw-Hill, New York (1959).

[6] P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.* **78**, 3043 (1956).

[7] H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).

[8] D. L. Hammick, *J. Chem. Soc.* 3105 (1931).

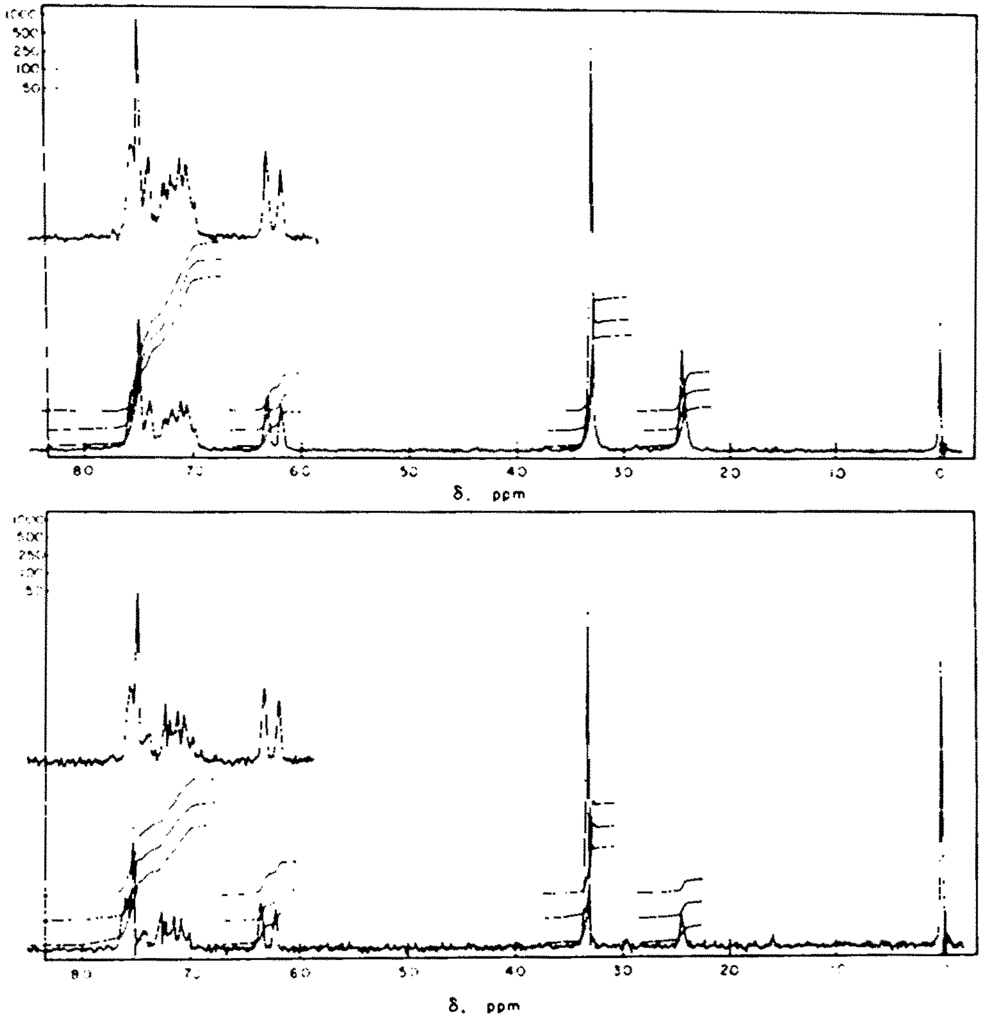

FIG. 1. NMR Spectra of *o*-Nitrosotoluene in *d*-Chloroform. Top: 12·8% by wt; Bottom: 4·2% by wt.

TABLE 2. INTEGRATION RATIO[a] FOR *o*-NITROSOTOLUENE

Conc[b]	Aromatic Multiplet	Doublet	Low-Field Singlet	High-Field Singlet	% Dimerization
12·8	3·3	0·70	2·2	0·78	26
7·8	3·4	0·83	2·4	0·58	19
4·2	3·3	0·89	2·65	0·34	11

[a] Expressed as number of protons taking the combined integrals of the two high-field singlets as equal to 3 protons.

[b] Wt. % in *d*-chloroform containing approximately 1% TMS.

Two conclusions can be drawn from the integration data. The per cent dimerization has been calculated on the basis of the relative ratio of the two Me singlets. The calculated values are shown in column 6 of Table 2. The second important conclusion which can be reached is that the high-field doublet in the aromatic region is due to the *ortho* protons in the monomer only.

The *ortho* protons of the dimer fall in the aromatic multiplet, i.e., the dimer exhibits no unusual chemical shifts. This conclusion is drawn from the ratio of the integral of the *ortho* hydrogen doublet to the low-field methyl singlet which is nearly 1:3 in each of the solutions studied. In contrast the ratio of the integral of the doublet to the sum of the integral of the two methyl signals drops from 1:4·3 to 1:3·4 as the solution is diluted from 12·8 to 4·2% by wt.

Similar evidence for the existence of an equilibrium dimer concentration is found in CCl_4 solution but the extent of dimerization is markedly reduced. In a 1·67 molar solution (~13% by wt) in CCl_4 the extent of dimerization is about 9·7% whereas in 1·05 molar solution it is 5·9%. There is no evidence that either *o*-nitrosopropylbenzene or *o*-nitrosobutylbenzene are appreciably dimerized in solution. A single triplet attributable to the benzyl methylene group is observed in each case.

DISCUSSION

The most striking features of the chemical shift data presented in Table 1 are the magnitude of the shifts involved and the dependence of the unusual shifts on the presence of an *ortho*-substituent. The shifts observed for the *ortho* protons and the benzyl hydrogens are both larger than those previously observed for most other functional groups. For example, the chemical shifts of neighboring Me groups due to the anisotropy of the nitro group have previously been examined.[4] The shifts due to nitro groups appear to be much smaller than those observed in the nitroso derivatives examined here. The *o*-Me signal in the spectrum of *o*-nitrotoluene is shifted downfield only 0·22 ppm relative to toluene.[4] In hindered polymethylnitrobenzenes small upfield shifts are observed.[4]

In the absence of steric interactions with adjacent groups the effect of a nitroso group on *o*-protons must be a downfield shift of about 0·6 ppm. This value is obtained by comparison of the value 7·95 ppm for the *ortho* protons in **1a** vs. 7·37 for benzene and of the *ortho* protons in **5a** (7·81 ppm) relative to toluene (7·17 ppm). The total upfield shift of the proton adjacent to the nitroso group which results when a Me group is placed adjacent to the nitroso function is 1·56 ppm (**2a** vs. **5a**). In contrast, the difference in the position of the *ortho* proton resonances of the corresponding nitro compounds in **2b** and **5b** is only 0·13 ppm. A relative large shift has, however, been observed in 1-nitro-2-methylnaphthalene. The 8-proton in this compound appears 0·64 ppm higher than the corresponding proton in 1-nitronaphthalene.[3]

The most logical interpretation of the critical part the *ortho*-alkyl substituent plays in determining the nature of the shift of the *ortho* proton is that a steric interaction between the alkyl group and the nitroso group forces the nitroso substituent into a conformation different from that in the unsubstituted derivatives. Supporting this view is the fact that the presence of an *ortho*-substituent is known to increase the tendency towards dimerization of aromatic nitroso compounds. This "ortho-effect" is clearly operating in the case of *o*-nitrosotoluene since the NMR spectrum gives evidence of the presence of dimer in solution. However, it is a matter of controversy as to whether the effect of an *ortho*-substituent on the extent of dimerization is primarily an effect on the dimer or the monomer.[9] We have examined the ultraviolet spectrum of *o*-nitrosotoluene in order to assess the possibility that the nitroso group has been forced out of planarity in *o*-nitrosotoluene. Pertinent spectral data for nitrosobenzene, *o*-nitrosotoluene and nitrosomesitylene are recorded in Table 3.

TABLE 3. UV ABSORPTION DATA

Nitrosobenzene[a]	281 (3·96)	304 (3·84)	750 (1·62)
o-Nitrosotoluene	288 (3·96)	310 (3·85)	750 (1·50)
Nitrosomesitylene[b]	295 (4·02)	321 (4·04)	790 (1·53)

[a] A. Schors, A. Kraaijeveld and E. Havinga, *Rec. Trav. Chim.* **74**, 1243 (1955).

[b] K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.* **78**, 1113 (1956).

The shifts of the band positions roughly parallel those observed for the corresponding aromatic aldehydes[10] but no intensity drop with *ortho* substitution is noted. Forbes and Mueller[11] have concluded that in 2-methylbenzaldehyde the CO group is displaced from the plane of the aromatic ring by 31° on the basis of changes in intensity of absorption but Bloor and Burawoy[12] have presented evidence which suggests that such calculations give values for the interplanar angle which are too large. Recent estimates[13] of interplanar angles in acetophenones on the basis of ^{13}C magnetic resonance spectra have generally been lower than estimates derived from UV spectral data. It therefore seems reasonable to adopt a value of about 20° as the maximum distortion from planarity in *o*-nitrosotoluene since it seems unlikely that the lone electron pair on nitrogen would cause more steric interference with the adjacent Me substituent than does the formyl proton in *o*-methylbenzaldehyde. The deviation from planarity may well be zero if the tendency towards dimerization is the result of steric effects in the dimer.

The C—N—O bond angle in *o*-nitrosotoluene is presumably roughly 120°. The nitrogen atom is considered to be trigonally hybridized with a lone pair in an sp^2 orbital.[14] The angle has apparently not been measured experimentally, but for H—N═O, which Linnett and Rosenberg[15] consider to be structurally analogous to nitrosobenzene, the H—N—O angle has been found to be 108·5°.[16] Furthermore, C—N—O bond angles of 120° have been assumed in theoretical calculations of electronic transition energies of nitrosobenzene and nitrosomethane.[17] Figure 2 depicts the most favorable conformation for *o*-nitrosotoluene.

When it is assumed that a large portion of the *o*-nitrosotoluene molecules adopt this conformation a qualitative explanation of the fact that the *o*-Me group and the *o*-hydrogen experience markedly different shielding by the nitroso function is possible. In *o*-nitrosotoluene the oxygen atom is constrained to the area of the *o*-hydrogen

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[9] R. R. Holmes, *J. Org. Chem.* **29**, 3076 (1964).

[10] E. A. Braude and F. Sondheimer, *J. Chem. Soc.* 3754 (1955).

[11] W. F. Forbes and W. A. Mueller, *Canad. J. Chem.* **34**, 1347 (1956).

[12] J. E. Bloor and A. Burawoy, *Tetrahedron* **20**, 861 (1964).

[13] K. S. Dhami and J. B. Stothers, *Tetrahedron Letters* 631 (1964).

[14] B. Gowenlock and W. Lüttke, *Quart. Rev.* **12**, 321 (1958); W. Lüttke, *Angew. Chem.* **69**, 99 (1957).

[15] J. W. Linnett and R. M. Rosenberg, *Tetrahedron* **20**, 54 (1964).

[16] F. W. DALBY, *Canad. J. Phys.* **36**, 1336 (1958).

[17] R. Basu, *Theoretic Chimica Acta* **2**, 7 (1964); R. L. McEwen, *J. Chem. Phys.* **34**, 547 (1961).

whereas the *o*-Me group is near the lone pair on the nitrogen of the nitroso group. Steric interference with the Me group prevents adoption of the conformation in which the nitroso function has rotated 180°. In nitrosobenzene and other nitrosobenzenes lacking *ortho*-substituents the nitroso group is free to rotate. The two *ortho* hydrogens experience averaged shielding from both conformations of the nitroso group and large shifts due to the anisotropy of the functional group are not observed.

The nitro group would not be expected to show the same sensitivity to *ortho*-substitution. The nitro group is symmetric towards rotation about the C—N bond by 180° so that even if non-planar conformations are adopted the substituents on both sides of the ring will experience roughly equivalent shielding effects.

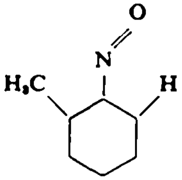

FIG. 2. Preferred Conformation of *o*-Nitrosotoluene.

Nevertheless, the electronic structure of the nitroso group must be such that the shielding of neighboring nuclei are very sensitive to their position relative to the nitroso group. Dahlquist and Forsen[19] have been able to measure the PMR spectra of two rotational isomers of furan-2-aldehyde. The difference in chemical shift observed for the 3-proton in the two rotamers is only 0·15 ppm. Thus, a proton adjacent to an aldehyde group seems to be much less sensitive to the orientation of an aldehyde group than does a proton adjacent to a nitroso group. This data and the fact that neither the nitro nor dimerized nitroso function show the large effects observed in the nitroso monomers suggest that the presence of an unshared electron pair on the nitrogen atom in the monomer may be a principal source of the unusual shielding effects. Saito and Nukada[20] have attributed the paramagnetic anisotropy of the hydroxyimino group to the presence of a lone pair on the nitrogen atom.

It is interesting that rather large shifts of the *o*-methyl signals in *o*-toluic acid and methyl *o*-toluate have been reported. Thus, the *o*-methyl signal of methyl *o*-toluate is found at 2·85 and whereas in the *p*-methyl toluate the corresponding signal appears at 2·52.[18] Similarly the Me signal in *o*-toluic acid is found 0·61 ppm downfield from the corresponding signal in *p*-toluic acid.[21] A combination of steric and magnetic anisotropic effects similar to those proposed for *o*-nitrosotoluene must also be in operation in this case.

If the origin of the unusual shielding of the *o*-proton in *o*-nitrosotoluene involves steric constraint of the nitroso function one might expect the spectrum to be temperature dependent. The spectrum was therefore recorded at 28°, 55°, 70° and 80°. The position of the doublet of the *ortho* hydrogen shifted downfield by 5 c/s as the temperature increased over this range. The signal of the Me group apparently shifted upfield by 2 c/s as the temperature was raised from 28° to 80°. Other peaks shifted 1 c/s or

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[18] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 58. Pergamon Press, New York (1959).

[19] K.-I. Dahlquist and S. Forsen, *J. Phys. Chem.* **69**, 4062 (1965).

[20] H. Saito and K. Nukada, *J. Mol. Spectr.* **18**, 1 (1965).

[21] W. J. LeNoble, J. LuValle and A. Leifer, *J. Phys. Chem.* **66**, 1188 (1962).

less. While these small shifts are in the direction expected, the fact that the shielding of both the *o*-proton and the Me group are still distinctly abnormal must mean that there is still a strong preference for a single conformation of the nitroso group at 80°.

The appearance of signals attributable to both the dimeric and monomeric forms demonstrates that the frequency of the exchange of individual Me groups between the two possible environments (dimer *vs* monomer) cannot be large relative to the frequency shift between the two signals. The detailed studies necessary to extract quantitative information about the rate of the exchange from the spectral data have not been undertaken.

EXPERIMENTAL

The synthesis of most of the compounds examined is described elsewhere.[1] Commercial samples of nitrobenzene and the nitrotoluenes were used. The spectra were recorded using a Varian A-60 instrument. Unless otherwise noted the solvent was *d*-chloroform and soln concentration was 0·15 g per ml solvent. TMS was used as an internal standard. The calibration of instrument was checked periodically with a Chf standard. The shifts recorded in Table 1 are the apparent centers of the multiplets in the case of triplets and doublets.

The variable temp measurements were made using a Varian Associates V-6040 Variable Temp Controller. The temps were estimated to ±3° from the shift in the ethylene glycol spectrum. The soln was an 0·925 molar (7·3% by wt) soln of *o*-nitrosotoluene in CCl_4 containing 2% t-butyl alcohol.

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