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Nuclear Magnetic Resonance and Infrared Study of Hindered Rotation in Nitrosamines

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The proton magnetic resonance spectra of a series of nitrosamines are presented and interpreted in terms of hindered rotation about the N–N bond. It is concluded that the barrier to rotation in nitrosamines arises primarily as the result of partial double bond character of the N–N bond. Separate resonances are observed for the *cis* and *trans* isomers of benzylmethylnitrosamine, yielding a value for the 20° *cis/trans* isomer ratio of 1:3. ΔH for the *cis* $\rightarrow$ *trans* isomerization of benzylmethylnitrosamine is estimated to be less than 1 kcal. Temperature dependence studies of the magnetic resonance spectrum of N,N-dimethylnitrosamine yield values of 23 kcal. for the barrier to rotation about the N–N bond and 0.7×10^{13} sec.$^{-1}$ for the frequency factor for methyl reorientations, at 160°. On the basis of the n-m-r results, the infrared spectra of nitrosamines are reviewed and some new interpretations presented.

Introduction

The infrared spectra of nitrosamines have recently received considerable attention, especially by Haszeldine and co-workers.[2a,b] They conclude[2b] that "only in the vapor state is the nitroso group unaffected by strong interactions" and that both the ultraviolet and infrared spectra of the liquid and solutions are "best explained by assuming either intermolecular dipolar interaction or partial dimerization of the nitroso compounds to give $R_2N\cdot N(O^-)\cdot N^+(:O)\cdot NR_2$ analogous to C-nitroso dimers." They also conclude that rotational isomerism is possible in nitrosamines, but is less plausible than for nitrites and thus would play a minor role in producing the gross differences observed between the vapor and liquid (or solution) spectra.

In the present study, the proton magnetic resonance spectra of a series of nitrosamines are presented and interpreted in terms of hindered rotation about the N–N bonds. Absolute rotational configurations of unsymmetrically substituted nitrosamines are assigned on the basis of proton chemical shifts, and barriers to rotation about the N–N bonds are estimated from the temperature dependence of the magnetic resonance spectra. In view of the definite conclusions regarding the structure of this class of compounds as revealed by n-m-r, infrared studies were carried out concurrently and some new interpretations of these spectra are presented.

Experimental

The nitrosamines employed in this research were prepared by the classical method of nitrosation. A strong mineral acid solution of the secondary amine was treated with a solution of sodium or potassium nitrite. The reaction products were isolated and purified by standard techniques. A typical preparation is that of diethylnitrosamine.[3] Some of the physical properties of these nitrosamines are given in Table I.

N-m-r spectra were obtained by means of a Varian[4] high resolution nuclear magnetic resonance spectrometer and associated electromagnet. The spectrometer utilizes Bloch's[5] nuclear induction detection scheme. Proton magnetic resonance spectra were obtained at 30 and 40 Mc. and fields of approximately 7,050 and 9,400 gauss, respectively. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H_2O. Negative frequency displacements indicate resonances occurring at higher values of applied magnetic field (at constant frequency) than the proton resonance of H_2O. The cell used in the temperature studies is similar to that described by Bernstein, Schneider and Pople[6] in which heated or cooled nitrogen gas is circulated about a sample sealed in a 5 mm. o.d. Pyrex tube. The sample tube is surrounded by a small Dewar vessel which in turn fits into a receiver coil of 15 mm. diameter. The accuracy of the sample temperature determinations was about ±0.5°.

TABLE I

PHYSICAL CONSTANTS OF NITROSAMINES

Compound	n^tD	*t*, °C.	M.p., °C.	B.p., °C.	B.p., Mm.
Dimethylnitrosamine	1.4374	18	..	149–150	
Diethylnitrosamine	1.4386	20	..	177	
Diisopropylnitrosamine	....	..	46	194	
Di-*n*-butylnitrosamine	1.4447	24	..	133	30
N-Nitrosomorpholine	....	..	29	98	10
N-Nitroso-N-methylaniline	....	..	..	77	0.8
N-Nitroso-N-ethylaniline	....	..	..	108	3.7
N-Nitroso-N-methyl-*p*-toluidine	....	..	52.4	.....	..
Benzylmethylnitrosamine	1.5388	31.5	..	79	0.3

All infrared spectra were obtained on a model 21 Perkin–Elmer infrared spectrometer equipped with rock salt optics. With the exception of the experiments with D_2O in which CaF_2 windows were used, the windows of the gas and liquid cells were also rock salt.

Results and Discussion

Proton Magnetic Resonance Spectra of Nitrosamines. A. N,N-Dimethylnitrosamine and N,N-Diethylnitrosamine.—The room temperature 30 Mc. proton magnetic resonance spectrum of dimethylnitrosamine (Fig. 1) consists of two sharp resonances of equal intensity separated by a chemical shift of 19 c.p.s. Gutowsky and Holm[7] showed that if environmental exchange between two nuclei separated by a chemical shift $\delta\omega$ proceeds at an average rate of less than $1/\tau = \delta\omega/\sqrt{2}$, discrete resonances for the two non-equivalent nuclei are observed. However, if environmental exchange is proceeding at a rate greater than $\delta\omega/\sqrt{2}$, only a single resonance located between the resonance frequencies of the two non-equivalent nuclei in a "slowly" changing environment is observed. This analysis would imply then that if rotation about the N–N bond of dimethylnitrosamine proceeds at a rate of $2\pi(19)/\sqrt{2} = 84$ sec.$^{-1}$ or more, only a sin-

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(2) (a) R. N. Haszeldine and J. Jander, *J. Chem. Phys.*, **23**, 979 (1955); (b) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

(3) A. I. Vogel, *ibid.*, 1846 (1948).

(4) Varian Associates, Palo Alto, Calif.

(5) F. Bloch, W. W. Hansen and M. E. Packard, *Phys. Rev.*, **70**, 474 (1946).

(6) H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc. (London)*, **A236**, 515 (1956).

(7) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

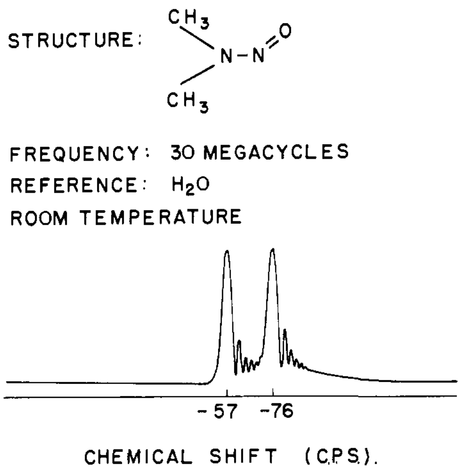


Fig. 1.—Proton magnetic resonance spectrum of N,N-dimethylnitrosamine.

gle, structureless proton resonance absorption located at −66.5 c.p.s. would be expected. The appearance of two separate resonances in the room temperature proton magnetic resonance spectrum of dimethylnitrosamine indicates then that a barrier to rotation about the N–N bond exists that is of sufficient magnitude to reduce the rate of methyl reorientations to less than 84 sec.$^{-1}$ at room temperature.

The primary contributors to the electronic structure of dimethylnitrosamine are the two resonance forms of Fig. 2. The observation of two separate methyl resonances shows clearly that the configuration of dimethylnitrosamine must be planar, or at least nearly planar, inasmuch as a configuration in which the plane containing the N–N–O group is perpendicular to the plane containing the C–N–C group would be incapable of giving rise to the observed non-equivalence of the methyl groups. The barrier to rotation about the N–N bond of nitrosamines probably stems largely from the partial double bond character of the N–N bond produced as the result of overlap between the p-orbitals of the two nitrogen atoms. While the n-m-r results alone do not establish an absolutely planar configuration for nitrosamines, consideration of the origin of the barrier as stemming from the contribution of resonance form II to the electronic structure of these molecules would seem to require a planar configuration.

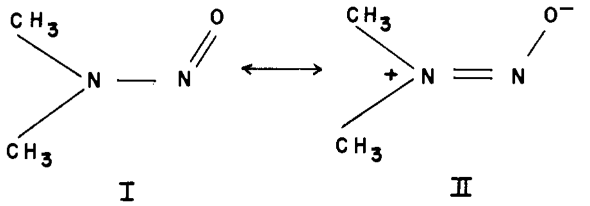


Fig. 2.—Resonance structures of N,N-dimethylnitrosamine.

The assignment of the two proton resonances of dimethylnitrosamine to the methyl groups respectively *cis* and *trans* to the oxygen atom cannot be made on the basis of existing concepts of the origin of chemical shifts in molecules. The non-equivalence of the two methyl groups of dimethylnitrosamine could be ascribed to non-equal inductive effects transmitted through the σ-bond skeleton to the protons of the methyl groups. An alternative or perhaps complementary mechanism would be to ascribe the chemical shift between the two methyl groups to field effects between the oxygen atom and the two methyl groups situated at different distances from the oxygen atom. Such a field effect, as well as the more conventional inductive effect, may be operating to produce the observed paramagnetic shift of CH_2 proton resonances relative to CH_3 proton resonances in, say, diethyl ether. If such be the case, the −57 c.p.s. resonance of dimethylnitrosamine may be assigned to the methyl groups *cis* to the oxygen atom (the *cis* group being the closer to the oxygen atom and presumably the more strongly affected by field effect interactions with the oxygen atom), and the −76 c.p.s. resonance, to the methyl group *trans* to the oxygen atom.

The proton magnetic resonance spectrum of diethylnitrosamine is shown in Fig. 3 and consists of two superimposed quadruplets in the >CH_2 region and two superimposed triplets in the $-CH_3$ region. The appearance of two ethyl resonances in diethylnitrosamine again indicates that hindered rotation about the N–N bond occurs in this compound. At 30 Mc., the chemical shift between the >CH_2 proton resonances in the two isomeric forms is 24 c.p.s., and between the two $-CH_3$ resonances, 8 c.p.s. An observable shift of 8 c.p.s. between the methyl proton resonances indicates that the room temperature average rate of reorientation about the N–N bond of diethylnitrosamine must be less than about $2\pi(8)/\sqrt{2} = 36$ sec.$^{-1}$.

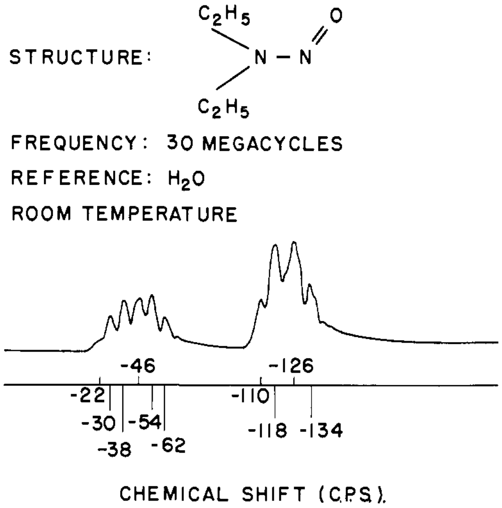


Fig. 3.—Proton magnetic resonance spectrum of N,N-diethylnitrosamine.

B. Rotational Barrier of N,N-Dimethylnitrosamine.—The temperature dependence of the 40 Mc. proton magnetic resonance spectrum of N,N-dimethylnitrosamine is shown in Fig. 4. The chemical shift between the two methyl resonances has begun to decrease at a temperature of 150°, and is reduced to zero at temperatures in excess of 180°. At 180°, therefore, rotation about the N–N bond of

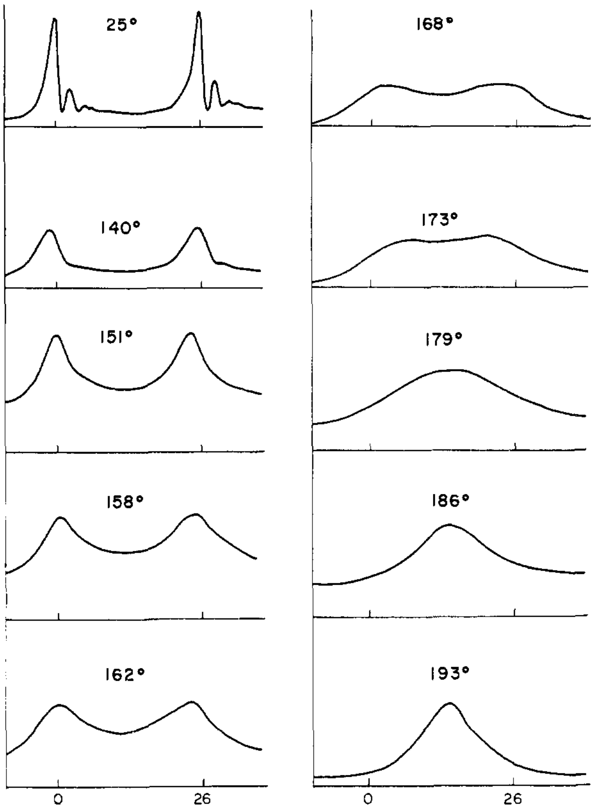


Fig. 4.—Temperature dependence of the 40 Mc. proton magnetic resonance absorption of N,N-dimethylnitrosamine.

dimethylnitrosamine proceeds at a rate of about 110 sec.$^{-1}$. If the absolute rate equation is assumed to apply, a free energy of activation of about 23 kcal. is obtained for reorientations about the N–N bond of nitrosamines.

Gutowsky and Holm[7] have developed expressions describing the behavior in nuclear magnetic resonance of a system containing two non-equivalent nuclear environments between which exchange of resonating nuclei is possible. They have shown that for the special case in which the numbers of exchanging nuclei in the two environments are equal and the resonance line widths are small compared to the chemical shift between nuclei in the two environments, the observed chemical shift, $\delta\omega_e$, is given by the expression

$$\delta\omega_e = \left(1 - \frac{2}{\tau^2\,\delta\omega^2}\right)^{1/2} \delta\omega \qquad (1)$$

where τ is the average time an exchanging nucleus spends in a given environment and $\delta\omega$ is the chemical shift between nuclei in the two environments at temperatures at which the rate of the exchange process can be characterized as "slow," *i.e.*, $\tau\delta\omega >> 1$. Equation 1 is applicable to N,N-dimethylnitrosamine in that the numbers of methyl protons in the two environments are equal, and the ratio of $\delta\omega$ to the methyl proton line widths is in excess of 10.

Gutowsky and Holm assumed that the reorientation process behaved as a typical rate process and that the rate equation was of the form

$$k = \nu_0 \exp(-E_a/RT) \qquad (2)$$

where k is the rate constant, ν_0 is the frequency factor, and E_a is the barrier to rotation. Since in their formulation $k = 1/2\tau$, equation 2 was rewritten as

$$\log_{10}(1/\tau\delta\omega) = \log_{10}(2\nu_0/\delta\omega) - E_a/2.3RT \qquad (3)$$

A plot of $\log_{10}(1/\tau\delta\omega)$ *vs.* $1/T$ for N,N-dimethylnitrosamine is given in Fig. 5. The slope yields a value of 23 kcal. for E_a and the intercept, a value of 0.7×10^{13} sec.$^{-1}$ for ν_0.

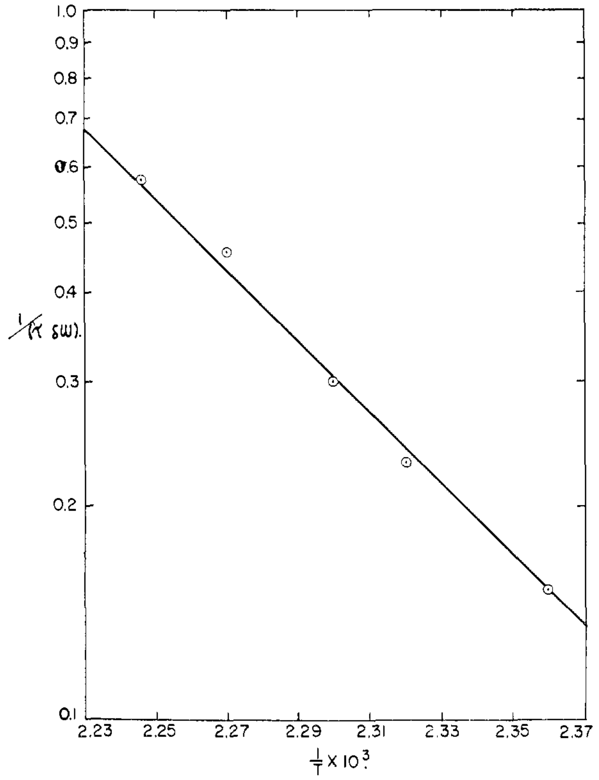


Fig. 5.—$1/\tau\delta\omega$ *vs.* $1/T$ for N,N-dimethylnitrosamine.

Hydrogen bonding of the form postulated by Haszeldine[2b] between the protons of the alkyl groups and the oxygen atom of nitrosamines probably could not contribute more than 3–5 kcal. to the barrier to rotation about the N–N bond. The 23 kcal. barrier found for dimethylnitrosamine suggests then that the barrier to rotation arises largely from partial double bond character of the N–N bond. The barrier to rotation about the N–N bond in dimethylnitrosamine is considerably higher than the barriers to rotation about the C–N bond of 7 and 12 kcal. found,[7] respectively, for dimethylformamide and dimethylacetamide. This suggests that resonance structures of the form of II of Fig. 2 are more important for nitrosamines than for amides.

C. Benzylmethylnitrosamine.—The proton magnetic resonance spectrum of benzylmethylnitrosamine (Fig. 6) is too complex to arise from a single isomeric species. The resonance at 42 c.p.s. is that of the phenyl protons, the two at −16 and −29 c.p.s. are those of the $>CH_2$ group, and the two at −63 and −84 c.p.s. are those of the $-CH_3$ group. The doublings of the $>CH_2$ and $-CH_3$ resonances are ascribed to the coexistence of the two

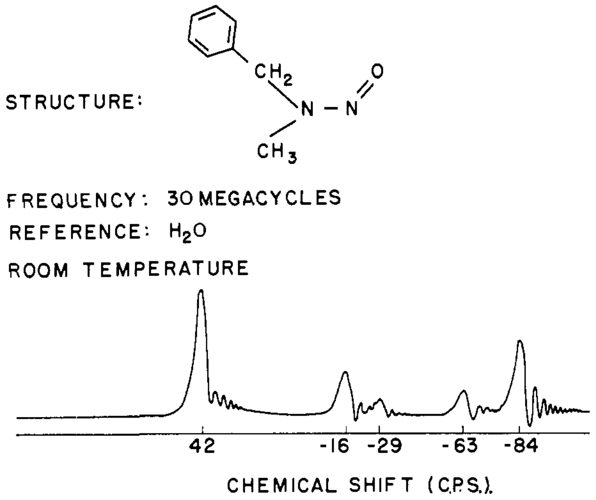


Fig. 6.—Proton magnetic resonance spectrum of benzylmethylnitrosamine.

isomeric forms of benzylmethylnitrosamine (Fig. 7). If it is assumed that proximity of the terminal oxygen atom of the nitroso group induces a shift in the $>CH_2$ and $-CH_3$ proton resonances in the direction of lower resonance fields (at constant frequency), the −16 and −84 c.p.s. resonances can be assigned to the $>CH_2$ and $-CH_3$ groups, respectively, of the isomer in which the $-CH_3$ group is *trans* to the oxygen atom. Similarly, the −29 and −63 c.p.s. resonances can be assigned to the $>CH_2$ and $-CH_3$ groups, respectively, for the isomer in which the $-CH_3$ group is *cis* to the oxygen atom. This analysis is borne out by the coalescence of the two peaks assigned to the $>CH_2$ group and the two peaks assigned to the CH_3 group at temperatures above 200° where the reorientation process is too rapid for the observation of separate resonances assignable to the *cis* and *trans* forms.

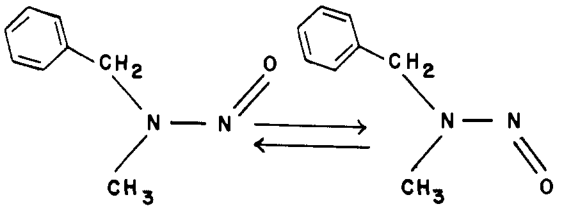


Fig. 7.—*cis-trans* isomers of benzylmethylnitrosamine.

A *cis/trans* isomer ratio of 24:76 is obtained by comparing the integrated intensities of the −16 and −29 c.p.s. CH_2 resonances or the −63 and −84 c.p.s. CH_3 resonances. Within the accuracy of the intensity measurements (about ±10%), the 24:76 *cis/trans* isomer ratio of benzylmethylnitrosamine is unchanged over the temperature range of 20 to 150°. The energies of the two forms of benzylmethylnitrosamine must therefore be similar, with ΔH for the *cis* → *trans* conversion being less than about 1 kcal. The similarity of energies of the *cis* and *trans* isomers of benzylmethylnitrosamine is perhaps not surprising since the sizes and electrical properties of the CH_3 group and the $>CH_2$ group of the benzyl substituent are similar.

D. N-Nitroso-N-methylaniline and N-Nitroso-N-ethylaniline.—The proton magnetic resonance spectrum of N-nitroso-N-methylaniline is given in Fig. 8. The peak at 44 c.p.s. is assigned to the phenyl protons and the one at −70 c.p.s., to the methyl protons. Since only a single methyl proton resonance is observed, either only one of two rotational isomers possible to N-nitroso-N-methylaniline is present in concentrations detectable by n-m-r, or rotation about the N–N bond is proceeding so rapidly that only an "averaged" methyl resonance is observed. Similar results are obtained for N-nitroso-N-ethylaniline in that only single phenyl and ethyl proton resonances are observed.

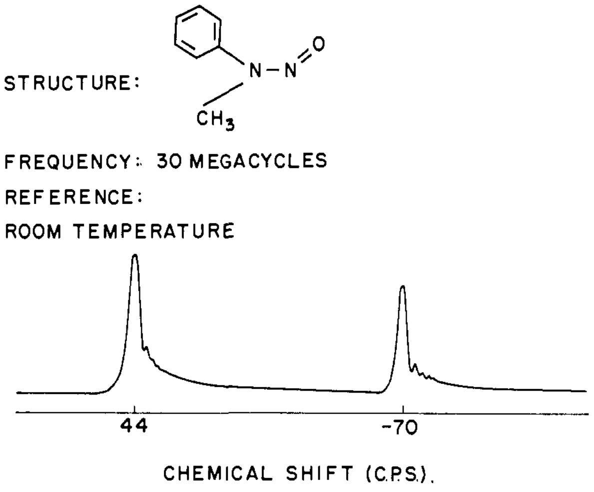


Fig. 8.—Proton magnetic resonance spectrum of N-nitroso-N-methylaniline.

In view of the large *cis/trans* chemical shifts encountered in the nitrosamine systems, it is estimated that as little as 5% of one isomer could be detected. Thus if rotation about the N–N bonds of N-nitroso-N-methylaniline and N-nitroso-N-ethylaniline is highly hindered in the sense that separate resonances for the *cis* and *trans* forms should be observable, the isomer ratio must exceed about 20:1. A high isomer ratio is not unreasonable for the phenylalkylnitrosamines in view of the dissimilarity of the N-substituents for each of these compounds.

An alternative explanation for the appearance of single methyl and ethyl proton resonances for these compounds is similar to that proposed by Gutowsky and Holm[7] as a possible reason for the observation of only single N-methyl proton resonances for N-methylformanilide and N-methylacetanilide. Contributions of resonance structures such as II of Fig. 9 might be expected to reduce substantially the barrier to rotation about the N–N bond from values obtained in compounds for which these structures are not possible. The spectrum of N-nitroso-N-methylaniline was observed at −50° in an attempt to "freeze-in" two isomers in the event of "fast" rotation at room temperature, but without success. Using the frequency factor obtained for dimethylnitrosamine, the computed value of E_a for the phenylalkylnitrosamines required, in the n-m-r sense, for "fast" rotation about the N–N

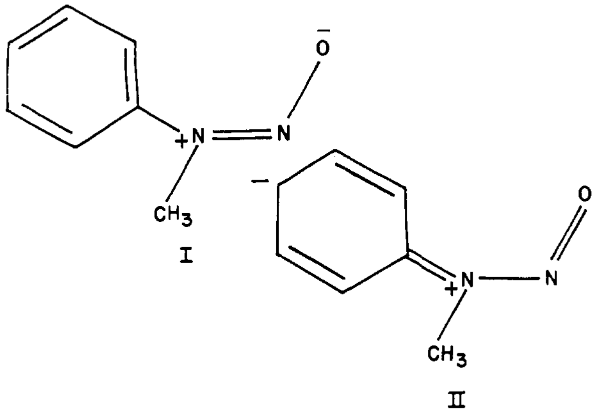


Fig. 9.—Some resonance structures of N-nitroso-N-methylaniline.

bond at −50° is less than 6 kcal. In view of the barrier of 23 kcal. found for dimethylnitrosamine, an upper limit of 6 kcal. for E_a for the phenylalkylnitrosamines in the event of "fast" rotation implies a very considerable contribution of II of Fig. 9 to the electronic structure of phenylalkylnitrosamines.

Infrared Spectra.—The conclusion reached by Haszeldine[2b] that the spectral changes between the gas and condensed phases of nitrosamines are primarily caused by dimerization is supported by this investigation. However, dimerization of the type $R_2N{\cdot}N(O^-){\cdot}N^+(:O)NR_2$ appears unlikely because of the positive nature of the amine (not the nitroso) nitrogen atom (see Fig. 2). The alternative dimer structure of Fig. 10 would seem to be more consistent with the observed high barrier to rotation about the N–N bond of nitrosamines, resulting presumably from an important contribution of resonance form II of Fig. 2 to the electronic structure of nitrosamines.

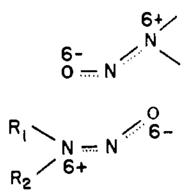
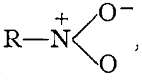


Fig. 10.—Possible structure of dimeric nitrosamines.

A. Dimethylnitrosamine.—Since dimethylnitrosamine is the simplest of this series of compounds, it was studied in greater detail than the others, and conclusions derived are extended to the more complicated structures.

Of the 27 vibrational modes of dimethylnitrosamine, there are 10 stretching and 17 deformation vibrations. Of the 10 stretching frequencies, 4 are concerned primarily with the C_2—N—N=O skeleton, 6 (with some degeneracy) with the CH stretching. The four stretching frequencies of the skeleton are of main concern to us, although, as will be seen, some of these lie in the same regions as the methyl deformations. Without deuterated compounds, therefore, assignments of the stretching modes are subject to considerable uncertainty, especially for the more complicated members of the series. If it is assumed that the four stretching vibrations of interest can be regarded as group frequencies, they can be assigned to N=O, N—N, and C—N (symmetrical) and C—N (asymmetrical). The spectrum of dimethylnitrosamine vapor at 100° shows only three, rather than four strong peaks in the 1000–1600 cm.$^{-1}$ region. The highest frequency (1493 cm.$^{-1}$) can be assigned to the N=O vibration, and the 1017 cm.$^{-1}$ band to the N—N vibration. The peak at 1294 cm.$^{-1}$ may be assigned to one of the C–N vibrations because of the similarity in position to the C–N vibrations in amines.[8] The other C–N vibration, although allowed, must be of very low intensity, or the two C–N vibrations are coincident and not resolved. Haszeldine and Jander[2a] noted a shoulder on the high frequency side of the 1294 cm.$^{-}$ band (at 1310–1330 cm.$^{-1}$) which became a strong band in solution and in the liquid. It seems unlikely this band in the liquid is due to a large increase in intensity of the C–N vibration in solution but is more readily attributed to one of the C–N vibrations of the dimer. The very weak bands of the vapor at 1410 and 1450 cm.$^{-1}$ are reasonably assigned to the symmetrical and asymmetrical methyl deformations, respectively. Two weak bands at longer wave lengths (848 and 795 cm.$^{-1}$) have not been assigned. The former appears to be a perpendicular vibration and might be the N-NO out-of-plane deformation.

If it is assumed that the vapor is monomeric, the N=O absorption lies at a lower frequency than would be expected for true double bond absorption. The N=O frequencies in alkyl nitrites, for example, lie between 1620 and 1685 cm.$^{-1}$.[9] Even alkyl nitro compounds where the double bond character of the N=O bonds is reduced by resonance with charged forms such as  $R-\overset{+}{N}\begin{smallmatrix}\nearrow O^-\\ \searrow O\end{smallmatrix}$, etc., absorb near 1560–1500 cm.$^{-1}$ (asymmetric mode). The shift to still longer wave lengths in nitrosamines supports the appreciable contribution of resonance form II of Fig. 2.

The spectrum of liquid dimethylnitrosamine differs considerably from that of the gas. A weak shoulder at ~1475 cm.$^{-1}$ can be associated with the N=O vibration of a small amount of the monomeric form. The strong 1440 and 1406 cm.$^{-1}$ absorptions are believed to arise from the dimer. Although these frequencies lie in the same region as the $-CH_3$ deformations, the latter vibrations would not be expected to give rise to the strongest bands in the spectrum. The shifts to lower frequencies and the appearance of more than one N=O band for the dimer would be expected for the postulated structure. Two strong bands also are evident in the CN stretching region at 1316 and ~1285 cm.$^{-1}$, and are attributable to the dimer since the monomer concentration (as judged from the low monomer N=O intensity) must be very small. Stabilization of the charge-separated resonance form by dimerization would be expected to give rise to an increase in the N–N frequency. The expected shift is

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(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(9) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

TABLE II

INFRARED FREQUENCIES OF DIMETHYLNITROSAMINE (CM.$^{-1}$)

	N-O stretching frequency[b]		CN stretching frequencies		N-N stretching frequencies	
	Monomer	Dimer	Monomer	Dimer	Monomer	Dimer
Gas at 100°	1493(s)	....	1294(s) 1310–1330(m)	.....	1017(s)	....
50% soln. in D_2O	1490(s)	1442(s) 1408(s)		1288(s)[a] 1340(s)	....	....
10% soln. in CCl_4	1470(s, sh)	1445(s) 1405(s)		1293(s)[a] 1315(s)	....	1042(s)
10% soln. in $CHCl_3$	1480(m, sh)	1450(s)		1290(s)[a] 1322(s)	....	1045(s)
Pure liquid	1475(w, sh)	1440(s) 1406(s)		1285(s)[a] 1316(s)	....	1049(s)

	Unassigned long wave length dimer band
Gas at 100°	..
50% soln. in D_2O	..
10% soln. in CCl_4	684(s)
10% soln. in $CHCl_3$	685(s)
Pure liquid	683(s)

[a] Either monomer or dimer or both. [b] s = strong; m = medium; w = weak; sh = shoulder.

observed, the 1017 cm.$^{-1}$ peak in the gas is found at 1049 cm.$^{-1}$ in the liquid. An additional band, not present in the gas phase, appears at 683 cm.$^{-1}$ in the liquid.

The spectrum of dimethylnitrosamine liquid was obtained at 130° (just below the boiling point) and little difference from the room temperature spectrum was observed. Thus, the difference in gas and liquid phase spectra does not appear to be a temperature effect but is a reflection of the change of state.

The spectra of solutions of dimethylnitrosamine were more like those of the liquid phase spectra than that of the gas. In a 10% solution in CCl_4 the two strong dimer bands were evident at 1455 and 1405 cm.$^{-1}$, and the monomer shoulder ($\sim$1470 cm.$^{-1}$) was stronger than in the liquid. Two strong bands were evident again in the C–N stretching region (at 1315 and 1293 cm.$^{-1}$). The N–N frequency lay at 1042 cm.$^{-1}$. A chloroform solution has weak bands in the same region as the N=O vibration that interfere somewhat with position assignments, but Haszeldine and Jander's published spectrum[2b] indicates that the monomer shoulder (>1460 cm.$^{-1}$) is somewhat lower (relative to the dimer bands at $\sim$1445 and 1408 cm.$^{-1}$) in $CHCl_3$ than in CCl_4. The C–N doublet is again observed as strong bands at 1322 and 1290 cm.$^{-1}$. The N–N frequency is again near 1040 cm.$^{-1}$. Both of these solutions show the strong band, attributable to dimer, at 683 cm.$^{-1}$. Finally, the spectrum of a 50% solution of dimethylnitrosamine in D_2O was obtained. A strong band at 1490 cm.$^{-1}$ which readily can be attributed to the monomer is of comparable intensity to the dimer N=O bands at 1446, 1409 and 1390 cm.$^{-1}$. The appearance of three bands in the N=O region of the dimer may be explained by a $-CH_3$ deformation vibration becoming evident because of the decreased intensity of dimer bands due to partial dissociation in this solvent. The 1390 cm.$^{-1}$ band is tentatively assigned to the symmetrical methyl deformation. Further evidence for partial dissociation of the dimer in D_2O is that the relative intensities of the bands change on dilution to a 25% solution, the 1490 cm.$^{-1}$ monomer band increasing relative to the dimer bands. Two CN vibrations are again evident at 1340 and 1288 cm.$^{-1}$. The infrared frequency assignments of dimethylnitrosamine in these solvents are shown in Table II.

Liquid dimethylnitrosamine appears from the foregoing analysis to be largely dimeric, but at concentrations of $\sim$10% in $CHCl_3$ or CCl_4 there is a small amount of dissociation to the monomer. At concentrations as high as 50% in D_2O there is an appreciable amount of each form. Cryoscopic and ultraviolet measurements are usually made at such low concentrations that the monomeric form would predominate. In fact, it was found that Beer's law was obeyed for both H_2O and $CHCl_3$ solutions of dimethylnitrosamine at all concentrations low enough for the ultraviolet measurements (*i.e.*, less than about 1% by volume). Thus ultraviolet shifts of about 30 mμ from CCl_4 to H_2O solutions are associated with changes in dielectric constant or hydrogen bonding and not with dimer formation.

B. Other Alkyl Nitrosamines.—The infrared spectra of several other nitrosamines have been examined and regularities in their spectra observed. Interpretation, of course, becomes difficult because of increased molecular complexity and, in particular, because of the increased absorption of the $>CH_2$ deformation frequency in the region of the N=O vibrations. For this reason, assignment of even the N=O monomer frequencies is open to doubt, and the multiplicity of bands in the dimer N=O (1460–1430 cm.$^{-1}$) region makes assignment of these virtually impossible. Table III lists the tentative assignment of the monomer N=O vibrations in the liquid, in CCl_4 solution, and in the vapor phase for those compounds that have been studied.

In the straight chain aliphatic nitrosamines, dimethyl, diethyl and dibutyl, there is essentially one strong peak in the 1050 cm.$^{-1}$ or N–N stretching region. However, in diisopropylnitrosamine and in N-nitrosomorpholine there are several bands in this region, and assignment becomes uncertain. These two compounds show other characteristics which do not fall in line with the other compounds as seen in Table III.

TABLE III

INFRARED SPECTRA OF ALKYL NITROSAMINES

Nitrosamine	N=O frequencies of monomer peak			N-N frequency		
	Gas	Liquid	CCl_4	Gas	Liquid	CCl_4
Dimethyl	1493(s)	1475(w, sh)	1470(s, sh)	1017	1049	1042
Diethyl	1485(s)[a]	1470(m, sh)	1470(s)	..	1065	1063
Dipropyl	1487(s)[a]	1456(s)[a]	1460([a])	..	..	..
Diisopropyl	.....	1468(s)	1473(s)	..	..	..
Dibutyl	.....	1460(s, sh)	1465(s)	..	1077	1075
N-Nitroso-morpholine	.....	1450(w, sh)	1465(s)	..	..	..

[a] Taken from Haszeldine's data.[2a]

As the chain length increases, there is a progressive increase in intensity of the N=O band of the liquid relative to the others in the spectrum. This is interpreted as a reduced tendency toward dimerization which is particularly evident for the diisopropyl compound where the bulky nature of the isopropyl group may cause some steric hindrance in the dimer form. The multiplicity of bands in the 1000–1100 cm.$^{-1}$ region of this compound probably arises from both dimer and monomer contributions. A progressive small shift of the N=O frequency in the liquid to longer wave lengths also occurs as the chain length increases.

C. Unsymmetrically Substituted Nitrosamines.—This work has included a brief study of N-nitroso-N-methylaniline, N-nitroso-N-ethylaniline, N-nitroso-N-methyl-*p*-toluidine and benzylmethylnitrosamine. Table IV lists the N=O monomer frequencies, the phenyl frequencies in the 1500–1600 cm.$^{-1}$ region, and the N–N frequencies. In addition, a sharp phenyl band appears in the N–N region which shifts considerably in the benzyl compound. Once again these compounds show a multiplicity of peaks in the 1450–1380 cm.$^{-1}$ region which are believed to arise from the dimer form as well as from CH deformations.

TABLE IV

INFRARED FREQUENCIES OF UNSYMMETRICAL NITROSAMINES

Nitrosamine	Phenyl vibrations	1500 cm.$^{-1}$ region N=O stretching freq. of monomer	N–N stretching frequency	1050 cm.$^{-1}$ region vibrations
N-Nitroso-N-methylaniline (liq.)	1605(m) 1500(s)	1470(s)	1092(s)	1030(m)
N-Nitroso-N-ethylaniline (liq.)	1604(w) 1500(s)	1480(s)	1099(s) 1081(m, sh)	1033(m)
N-Nitroso-N-methyl-*p*-toluidine (60° melt)	1588(vw) 1515(s)	1460(s)	1090(s)	1018(m)
Benzylmethylnitrosamine (liq.)	1610, 1588(vw) 1500(m)	1450(s)	1042(s) 1027(s)	1077(m)
(CCl_4 soln.)	1610, 1588(vw) 1500(w)	1455(s)	1035(m, sh) 1027(s)	1080(m)

The N=O stretching frequency of the monomer is somewhat more intense in phenyl substituted nitrosamines than in the alkyl compounds, suggesting that the tendency toward dimerization is reduced by steric hindrance.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XX. Dielectric Relaxation Times and Molecular Shapes of Some Substituted Benzenes and Pyridines[1-3]

BY ANTHONY J. PETRO[4] AND CHARLES P. SMYTH

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Measurements of dielectric constant and loss at wave lengths of 1.25, 3.22 and 10.0 cm. and 300 m. have been carried out at 20, 40 and 60° on toluene, styrene, ethylbenzene, isopropylbenzene, *o*-xylene, *m*-xylene, *p*-chlorotoluene, α-picoline, 2- and 4-vinylpyridine, and 2- and 4-ethylpyridine in the pure liquid state and on solutions of *p*-chlorotoluene in benzene, *p*-xylene and *p*-dichlorobenzene. The relaxation times and viscosities are examined in relation to molecular size and shape. A regular increase in relaxation time with increasing size of the substituted group is observed for the benzene derivatives with the exception of styrene. The anomalous values for the latter are attributed to planarity of the molecule. The slightly polar hydrocarbons are compared with the polar pyridines after suitable internal field and viscosity corrections have been applied to the latter. The ratios of the molecular relaxation times and viscosities at constant temperature, or equivalently, the molecular relaxation times at constant viscosity, are found to be adequate in most cases for correlation of compounds of different polarity but similar size and shape. A similar correlation is made for *p*-chlorotoluene between the pure liquid and its solutions in non-polar solvents whose molecular sizes and shapes are similar to the solute. Activation energies for viscous flow and dielectric relaxation are compared on the basis of molecular size and shape and the mechanism of each process. The difference between the two quantities is found to be a maximum for the nearly planar molecules and to decrease with increasing bulk and irregularity of the substituted group.

The investigation into the relations between molecular size and shape and dielectric relaxation in liquids has been extended to a group of benzene and pyridine derivatives. Whereas the benzene and pyridine rings are rigid, symmetric and planar structures, substitution of one or more groups into the ring will alter the size and shape of the molecule as well as the planarity and possibly the rigidity. Furthermore, benzene and pyridine are only very slightly different in size and shape but differ markedly in polarity. Consequently, the effects of po-

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(2) This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Portions of this paper were read before the American Chemical Society, Physical and Inorganic Division, Atlantic City, N. J., Sept. 18, 1956.

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