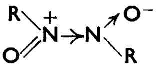
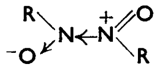
222. *The Structures and Stabilities of the Dimeric Forms of Nitroso-compounds.*

By J. W. SMITH.

The molecular polarisation and molecular refraction of the more stable form of dimeric nitrosomethane, as determined from measurements on dilute solutions in benzene, differ only by 7·5 c.c. This difference is much smaller than would be expected for a structure which permits rotation about a N–N bond. If, however, the N–N linkage is assumed to have essentially a double-bond character, and the dimer studied is the *trans*-form, the result can be interpreted in terms of a fairly high atom polarisation, the major contribution to which arises from the bending of the polar N–O bonds. A reason for the different stabilities of the dimeric forms of various nitroso-compounds is suggested.

THE structures of the dimeric forms of organic nitroso-compounds have been a subject of speculation. From the chemical properties, and particularly the *ortho-para*-directing character of the group in the dimeric forms of aromatic nitroso-compounds, Hammick, New, and Sutton [1, 2] inferred in 1932 that they were best represented by a form of resonance state frequently suggested at that time and involving, in this case, high-frequency alternation between structures (I) and (II). Of the other possibilities, structure (III) was rejected as being inadmissible on chemical evidence, and structures (IV) and (V) were rejected as suggesting too stable a molecule.


(I)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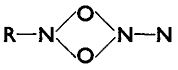
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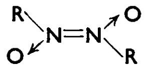
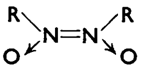

(IV)


(V)

In carbon tetrachloride solution at 0° the dissociation of the dimeric form of 2 : 5-dimethyl-2-nitrosohexane is slow. Hence Hammick, New, and Williams [2] were able to study the change of the dielectric constants of these solutions with time, and thence to derive the values at zero time. From the results so obtained they inferred that the dipole moment of the dimeric form was about 1 D. Similarly, from measurements on benzene solutions containing the known equilibrium proportions of monomer and dimer, they obtained a value of about 1·5 D for the moment of the dimeric form of nitrosomesitylene. They interpreted these results as supporting the structure they proposed, since the molecule would be expected to have a small moment due to rotation about the central N–N bond out of the *trans*-configuration which the molecule would tend to assume owing to the repulsion of similar dipoles.

In interpreting the results of their measurements on nitrosomesitylene solutions, however, Hammick, New, and Williams assumed that the difference between the molecular polarisations of nitrosobenzene and the monomeric form of nitrosomesitylene is equal to the difference between the values for nitrobenzene and nitromesitylene. They therefore made the tacit assumption that the difference between the dipole moments of nitrosobenzene and the monomeric form of nitrosomesitylene is much greater than the difference between the moments of nitrobenzene and nitromesitylene. This is not justified, and it is noticeable that their values for the molecular polarisation of the dimeric form of nitrosomesitylene are least for the solutions in which the ratio of dimer to monomer is greatest, so the true moment of the dimeric form is probably much smaller than the value they derived.

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[1] Hammick, *J.*, 1931, 3105; Hammick, New, and Sutton, *J.*, 1932, 742.

[2] Hammick, New, and Williams, *J.*, 1934, 29.

The determination of the dipole moment of a compound from measurements on solutions containing other polar molecules is always rather uncertain, especially when the concentration of other polar molecules changes with the concentration of the species under consideration. Until recently, however, no stable dimeric nitroso-compound was available for study, but it has now been shown by Gowenlock and Trotman [3] that dimeric nitrosomethane exists in two fairly stable forms. By analogy with the azo- and azoxy-compounds they suggest that these are the geometrical isomers (IV) and (V), the more stable dimer *A* being the *trans*-form. This view is supported by both chemical and spectroscopic evidence.

It appears to be impossible to measure the dipole moments of both forms by the dilute solution method, as the less stable dimer *B* passes rapidly into dimer *A* in the non-polar solvents which are suitable for these measurements. However a small sample of dimer *A* was kindly placed at the author's disposal by Dr. B. G. Gowenlock, and the results of measurements on its solutions in benzene are shown in the table, where α, β, and γ are the mean values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, and the remaining symbols have their usual significance.

Polarisation data for the dimer A *of nitrosomethane in benzene solution at 25°.*

$100w$	0·0000	0·4791	0·8237	1·1690
ε	2·2741	2·2759	2·2774	2·2790
v	1·14460	1·14296	1·14180	1·14063
n_D	1·4980	1·4980	1·4980	1·4980

$\alpha = 0{\cdot}40_4$, $\beta = 0{\cdot}340$, $\gamma = 0{\cdot}00$; whence $P_{2\infty} = 28{\cdot}7$ c.c., $[R_D]_2 = 21{\cdot}2$ c.c.

If the difference between $P_{2\infty}$ and $[R_\infty]_2$ were to be interpreted as arising from a permanent dipole moment, the value of the latter would be 0·61 D. A *trans*-form of the dimer, as in (IV), should have zero moment, whilst the *cis*-form, as in (V), would be expected to have a moment at least as great as that of *cis*-azoxybenzene [4] (4·68 D). Any structure which permits even a restricted rotation about the N–N bond should lead to a moment much in excess of 0·6 D. The evidence suggests, therefore, that the molecule is essentially rigid and symmetrical, with the oxygen, nitrogen, and carbon atoms all in one plane.

If each nitrogen atom is linked to the other, and to one of the oxygen atoms, by σ-bonds, there remain six electrons (one from each oxygen atom and two from each nitrogen atom) for π-bond formation. Ignoring the hyperconjugative effect of the methyl groups, and assuming the O–N and N–N resonance integrals to be each equal to β, L.C.A.O. treatment indicates that if the coulombic integrals of the nitrogen and oxygen atoms are taken as equal ($\alpha_O = \alpha_N$) the mobile bond orders of the N–O and N–N bonds are 0·448 and 0·725, respectively. Alternatively, if α_O is taken as $\alpha_N + \beta$, the mobile bond orders are 0·354 and 0·927, respectively. It also indicates that the formal charges on the oxygen and nitrogen atom are $-0{\cdot}725$ and $+0{\cdot}725$, respectively, when $\alpha_O = \alpha_N$, and $-0{\cdot}853$ and $+0{\cdot}853$, respectively, when $\alpha_O = \alpha_N + \beta$.

These calculations indicate that the mobile bond order of the N–N bond is the greater the smaller is the electronegativity of the nitrogen atoms. In the dimeric forms of nitrosomethane the hyperconjugative effect of the methyl groups will tend to increase the π-electron density in the O–N–N–O system and effectively to decrease the electronegativity of the nitrogen atoms, thus increasing the double-bond character of the N–N linkage and increasing its stability. In the dimeric forms of nitrosobenzene, on the other hand, conjugation with the phenyl groups will have exactly the reverse effects and so weaken the N–N bond. This may account for the facts that the dimeric form of nitrosobenzene is very unstable, and that the greatest stability of the dimeric form is encountered when the

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[3] Gowenlock and Trotman, *J.*, 1955, 4190.

[4] Gehrckens and Müller, *Annalen*, 1933, **500**, 296.

nitroso-group is linked to a primary carbon atom, where hyperconjugative effects are greatest.[5] It is also pertinent that the most stable dimer of an aromatic nitroso-compound appears to be that of nitrosomesitylene, where steric effects restrict its conjugation with the O–N–N–O system.

If, therefore, the stable dimer *A* of nitrosomethane has essentially the structure (IV), the molecule contains two fairly large opposed dipoles, so a rather large atom polarisation is to be expected. Hence it seems most probable that the $P_{2\infty} - [R_D]_2$ difference of 7·5 c.c. should be attributed to this cause. Since the N–O bonds have some double-bond character, the main contribution to the atom polarisation will probably arise from bending vibrations of these bonds in the C–N=N–C plane. Bond stretching and probably also the out-of-plane bending will be associated with much higher force constants, and hence their contributions will be only small. Hence, as a first approximation, the whole of the atom polarisation can be attributed to in-plane bending, and the system regarded as two one-dimensional oscillators. The expression for the atom polarisation then becomes ${}_AP = 8\pi N^2\mu^2{}_1/9k_b$, where μ_1 is the effective moment of the N–O bond, and k_b is the in-plane bending force constant in erg/radian^2. As in all similar instances it is difficult to estimate the effective value of μ_1. It is unsafe to use the result of the molecular-orbital calculation quoted above, since this method tends to exaggerate the charge distribution. The value is likely to be larger than the moment of *trans*-azoxybenzene[4] (1·705 D), since in the latter compound the true N–O bond moment is partly compensated by the lone-pair moment at the second nitrogen atom. When it is assumed that the $P_{2\infty} - [R_D]_2$ difference represents the whole of the atom polarisation, and a value of $\mu_1 = 1{\cdot}7$ D is used, it follows that $k_b = 6{\cdot}4 \times 10^{-13}$ erg/radian^2, whilst the more probable value of $\mu_1 = 2{\cdot}2$ D leads to $k_b = 10{\cdot}7 \times 10^{-13}$ erg/radian^2. The latter value compares closely with the figure of 12×10^{-13} erg/radian^2 for the bending of the two C=O bonds in the plane of the ring in benzoquinone, a figure based on an ${}_AP$ value[6] of 8·8 c.c. and an effective bond moment of 2·5 D. This value of the force constant for benzoquinone predicts an absorption band at 113 cm.$^{-1}$, very close to the value of 120 cm.$^{-1}$ observed by Cartwright and Errera,[7] thus indicating that the treatment of each C=O bond as a one-dimensional oscillator is reasonable. The double-bond character of the N–O bonds is probably less than that of the C-O bonds, but nevertheless the behaviours are likely to be closely parallel. In the present instance the frequency predicted by a force constant of $10{\cdot}7 \times 10^{-13}$ erg/radian^2 corresponds with an absorption band at about 100 cm.$^{-1}$, but no measurements extending so far into the infra-red region have been recorded.

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[5] Gowenlock and Trotman, *J.*, 1956, 1670.

[6] Hammick, Hampson, and Jenkins, *J.*, 1938, 1263; Boud and Smith, *J.*, 1956, 4507.

[7] Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138.