Structure and Conformation of Methylated Hydroxylamines

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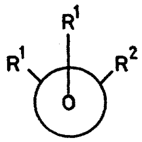
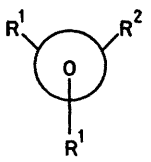
Summary Electron diffraction studies show that methylated derivatives of hydroxylamine exist in two conformations differing by a 180° rotation about the N–O bond, as predicted by M.O. calculations, but with a much smaller free energy difference than the calculations would suggest.

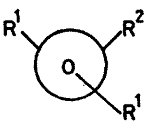
MOLECULAR ORBITAL calculations on hydroxylamine suggest that the molecule has 2 minima (**1a**) and (**1b**) on the potential function to rotation about the N–O bond, that the preferred conformation has the non-bonded electron densities *trans* (**1b**), and that there is an appreciable (*ca.* 12 kcal mol^{-1}) barrier to internal rotation.[1–3] Of these predictions only the second has until now been verified experimentally,[4] although many authors have implicitly accepted the first of these conclusions and used it in their arguments.[5] In this communication we present the first experimental evidence in support of the first of these conclusions from an electron diffraction study of four methylated derivatives of hydroxylamine.



(a)

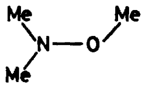


(b)

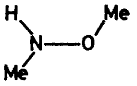


(c)

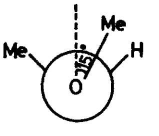
(1); $R^1 = R^2 = H$
(2); $R^1 = R^2 = Me$
(3); $R^1 = Me, R^2 = H$



(2)



(3)



(3a)

The radial distribution curve of the trimethyl derivative (**2**) (Figure) shows two 'long' C · · · C distances at *ca.* 270 and 310 pm arising from the *cis* (**2a**) and *trans* (**2b**) conformations. The *trans* conformation is the major contributor (*ca.* 75%). Similar proportions are observed for the *NO*-dimethyl derivative (**3**), but here the *cis* conformation (**3a**) appears to have the CNOC dihedral angle increased by *ca.* 15° presumably due to methyl repulsions. For the *O*- and *N*-monomethyl derivatives we observe only one (*trans*) conformation, but note that there are no 'long' C · · · C distances in these compounds to facilitate detection of the minor conformers. The minor conformers, if they exist, must be close to the *cis* forms. For compounds (**2**) and (**3**) if the *cis* conformers are replaced by the *gauche* conformers (**2c** and **3c**), appreciably poorer fits to the experimental data result. We have not, however, ruled out the possibility of small amounts of other conformers being present.

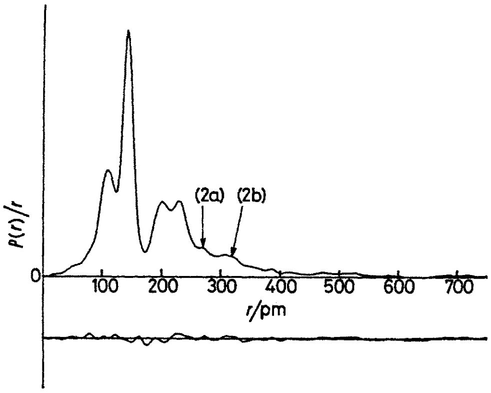


FIGURE. Radical distribution curve for trimethylhydroxylamine (**2**).

We note that the M.O. calculations of Pederson and Morukama,[1] and Fink, Pan, and Allen[2] predict that the energy of the *cis* conformer of hydroxylamine should be 7—11 kcal mol^{-1} above that of the *trans* conformer. The calculations of Radom, Hehre, and Pople[3] on hydroxylamine and its *O*- and *N*-methyl derivatives give similar values although the methyl substituents appear to lower the energy difference slightly. In contrast, our observations on

TABLE. Structural parameters on compounds studied averaged over all conformations

	H_2NOH[a]	MeNHOH	H_2NOMe	MeNHOMe	Me_2NOMe
r(C–N)/pm	—	143·8(17)	—	143·7(12)	144·7(4)
r(C–O)/pm	—	—	138·9(2)	138·1(7)	137·2(6)
r(N–O)/pm	145·3(2)	146·4(12)	146·2(2)	148·8(7)	149·6(7)
∠CNO/°	—	107·1(3)	—	103(2)	105·5(7)
∠NOC/°	—	—	108·0(2)	109(2)	109·1(9)

[a] Ref. 3.

the trimethyl and *NO*-dimethyl derivatives show free energy differences of only *ca.* 0·6 kcal mol^{-1}.

Structural data averaged over all conformers of the compounds studied are reported in the Table. Detailed discussion of the results will follow in the full papers.[6]

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[1] L. Pedersen and K. Morukama, *J. Chem. Phys.*, 1967, **46**, 3941.

[2] W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, 1967, **47**, 895.

[3] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 2371.

[4] S. Tsunekawa, *J. Phys. Soc. Japan*, 1972, **33**, 167; R. A. Y. Jones, A. R. Katritzky, S. Saba, and A. J. Sparrow, *J.C.S. Perkin II*, 1974, 1554; P. A. Giguere and I. D. Liu, *Canad. J. Chem.*, 1952, **30**, 948; R. E. Nightingale and E. L. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 4092.

[5] See for example: M. Raban and G. W. J. Kenney, *Tetrahedron Letters*, 1969, **17**, 1295; W. Walter and E. Schaumann, *Annalen*, 1971, **747**, 191; F. G. Riddell, P. Murray-Rust, and J. Murray-Rust, *Tetrahedron*, 1974, **30**, 1087.

[6] F. G. Riddell, E. S. Turner, D. W. H. Rankin, and M. R. Todd, unpublished results.