The Structure and Conformation of Hydroxylamine and its Methylated Derivatives

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MO calculations show that hydroxylamine and methylated hydroxylamines exist in two conformations 2.8–6.3 kcal mol^{-1} apart in energy, and that the length of the N–O bond does not change upon methylation.

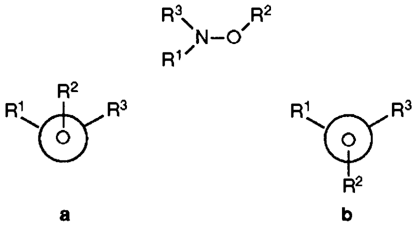
As part of a study to develop molecular mechanics parameters for the N–O bond we recently examined the literature for information concerning the structure of hydroxylamine and its methylated derivatives. Infrared,[1] microwave,[2] and X-ray[3] evidence indicated an N–O bond length of approximately 1.46 Å and the *trans* conformation (**1b–6b**, Fig. 1) as the exclusive conformation. MO calculations[4] suggested that the hydroxylamines existed in the *trans* conformation with a substantial energy difference (7–11 kcal mol^{-1}) (1 cal = 4.184 J) between the *trans* conformers and the *cis* conformers (**1a–6a**, Fig. 1). In contrast to these results, electron diffraction studies by Riddell and coworkers[5] suggest that the energy difference

Table 1 Structural parameters from electron diffraction[5b]

	H_2NOH	H_2NOMe	MeHNOH	Me_2NOH	MeHNOMe	Me_2NOMe
r(C–N)/Å	—	—	1.420(4)	—	1.439(1)	1.442(5)
r(C–Q)/Å	—	1.388(4)	—	—	1.374(8)	1.350(6)
r(N–O)/Å	1.453(2)	1.463(3)	1.477(2)	—	1.496(9)	1.513(9)
∠(CNO)/°	—	—	107.7(2)	—	104.5(2)	102.6(7)
∠(NOC)/°	—	108.7(3)	—	—	[109]	109.3(1)
Δ*G*(*c*-*t*)/kcal mol^{-1}	>4.0	>4.0	?	—	0.6	0.6

Table 2 Structural parameters from *ab initio* calculations

	H_2NOH	H_2NOMe	MeHNOH	Me_2NOH	MeHNOMe	Me_2NOMe
r(C–N)/Å	—	—	1.4594	1.4574	1.4601	1.4574
r(C–O)/Å	—	1.4212	—	—	1.4221	1.4222
r(N–O)/Å	1.4515	1.4479	1.4522	1.4559	1.4487	1.4526
∠(CNO)/°	—	—	105.99	104.82	105.77	104.69
∠(NOC)/°	—	107.02	—	—	107.21	107.19
Δ*G*(*c*-*t*)/kcal mol^{-1}	5.95	3.40	4.50	2.81	4.60	6.31



1; $R^1 = R^2 = R^3 = H$
2; $R^1 = Me, R^2 = R^3 = H$
3; $R^1 = R^3 = H, R^2 = Me$
4; $R^1 = R^3 = Me, R^2 = H$
5; $R^1 = R^2 = Me, R^3 = H$
6; $R^1 = R^2 = R^3 = Me$

Fig. 1

between conformers is only 0.6 kcal mol^{-1} in compounds **5** and **6**, and that the *cis* conformers are present at room temperature. In addition they found significant changes in the N–O and C–O bond lengths upon methylation (Table 1). In the trimethyl derivative **6** the C–O bond seemed unusally short (1.351 *vs.* 1.428 Å in MeOMe[6]), and the N–O bond seemed unusually long (1.514 Å).

We performed an *ab initio* study of hydroxylamine and its methylated derivatives in order to resolve questions about the bond lengths and the energy differences between conformers. All computations were performed with the GAUSSIAN 90[7] suite of programs. Hartree–Fock energies and optimized structures were determined with the 6-31G*[8] basis set. Second-order Møller–Plesset[9] (MP2) perturbation theory was used to correct the structures and energies for the effect of electron correlation. Compounds **1, 3, 4** and **6** have a plane of symmetry defined by the N–O–R^2 atoms which bisects the R^1–N–R^3 angle. To simplify the calculations on these molecules they were constrained to maintain C_s symmetry. Stationary points were confirmed to be minima by numeric harmonic vibrational frequency analysis. Computed enthalpies were corrected for zero-point vibrational energy. The results of our calculations on the *trans* conformers are shown in Table 2.

We find an average N–O bond length of 1.4515 Å, in good agreement with the IR, microwave, and X-ray data. The average C–O bond length of 1.4218 Å is in good agreement with the experimental value found in dimethyl ether. Unlike Riddell and coworkers we find no discernable trends in either the N–O, or the C–O bond lengths. In addition, we find energy differences between the *cis* and *trans* conformers of compounds **5** and **6** which are substantially higher than those observed in the electron diffraction work.

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