Protonation Effect on C-N Bond Length of Alkylamines Studied by Molecular Orbital Calculations

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Z. Naturforsch. **55 a,** 769–771 (2000); received August 8, 2000

Molecular orbital calculations were performed for the six saturated alkylamines (CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, $(CH_3)_2CHNH_2$, $(CH_3)_3CNH_2$), their protonated cations ($CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$, $(CH_3)_2CHNH_3^+$, $(CH_3)_3CNH_3^+$), and $(CH_3)_4N^+$ using the Hartree-Fock, second-order Møller-Plesset, and density functional theory methods with the 6-311+G(d,p) basis set. Protonation lengthens the C-N bonds of the amines by 0.05 - 0.08 Å and shortens the C-C bonds of $CH_3CH_2NH_2$, $(CH_3)_2CHNH_2$, and $(CH_3)_3CNH_2$ by ca. 0.01 Å.

Key words: Protonation; Amine; HF; DFT.

Protonation of the nitrogen atom of the primary amines XNH_2 ($X = CH_3$, OH, F, CN, CHO, and NO_2) was investigated by Hopkinson and Csizmadia using ab initio molecular orbital calculations [1]. They found that the protonation results in an increase in the N-X bond length with changes of 0.132, 0.193, and 0.212 Å occurring for X = CN, HCO, and NO_2, respectively. For methylamine the increase was 0.079 Å. It would be erroneous to deduce the properties of the cation from the C-N bond length of the amine, as pointed out in case of the tert-butylammonium ion [2]. Recently, Zeroka et al. performed detailed calculations using MP2/6-311G(d,p) for methylamine, ethylamine and their cations [3, 4] to examine the infrared spectra of these molecules. They noticed that the C-N bond increased, while the C-C bond decreased on protonation of ethylamine. In the present note we have used the ab initio Hartree-Fock (HF), second-order Møller-Plesset (MP2), and density functional theory (DFT) methods with a large basis set of 6-311+G(d,p) to investigate the protonation effect on the C-N and C-C bond lengths for the six saturated alkylamines, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, $(CH_3)_2CHNH_2$, and $(CH_3)_3CNH_2$, and to obtain reliable data for the bond lengths of alkylammonium cations in gas phase.

The geometry of isolated amines in gas phase is obtainable by diffraction and spectroscopic methods, such as electron diffraction and microwave spectroscopy. But that of the corresponding cations is difficult to determine experimentally, and thus its structure is usually deduced from data obtained in the liquid and solid phase where inter molecular interactions are believed to affect the geometry considerably. Thus, the molecule orbital calculation is a suitable method to estimate the geometry of isolated ions.

All calculations were performed with the Gaussian 98 [5] package. The HF, MP2 and Becke's three parameter hybrid DFT-HF methods [6] with Lee-Yang-Parr correlation functional (B3LYP) [7] and Perdew/Wang 91 (B3PW91) [8] with the 6-311+G(d, p) basis set were used for geometry optimization and vibrational frequency calculations. The full optimizations without symmetry restrictions were carried out starting from the all staggered conformations of the amines and the cations. The stable conformations were confirmed by the vibrational analysis which shows only real frequencies for the optimized conformers.

The C-N bond lengths calculated for the methyl-substituted amines and ammonium ions are listed in Table 1 together with the values determined by microwave and electron diffraction measurements. All methods except for HF reproduce the C-N bonds of the amines. By the protonation, the C-N bond lengths of these amines increase by ca. 0.05 Å and the lengths of dimethylammonium and trimethylammonium ions

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Table 1. C-N bond lengths (Å) of methyl-substituted amines and ammonium ions, and the C-N bond difference ΔC-N (Å) between the amine and the ammonium.

	HF	MP2	B3LYP	B3PW91	Expt.
CH_3NH_2	1.454	1.464	1.465	1.459	1.471 - 1.474 [9 - 13]
$CH_3NH_3^+$	1.505	1.507	1.515	1.504	
ΔC-N	0.051	0.043	0.050	0.045	
$(CH_3)_2NH$	1.447	1.458	1.457	1.451	1.455 - 1.462 [14, 15]
$(CH_3)_2NH_2^+$	1.496	1.501	1.508	1.499	
ΔC-N	0.049	0.043	0.051	0.048	
$(CH_3)_3N$	1.446	1.455	1.456	1.449	1.451 - 1.454 [14, 16]
$(CH_3)_3NH^+$	1.493	1.498	1.506	1.497	
ΔC-N	0.047	0.043	0.050	0.048	
$(CH_3)_4N^+$	1.494	1.498	1.507	1.499	

become almost equal to that of tetramethylammonium ion.

The C-N and C-C bond lengths of $CH_3CH_2NH_2$, $(CH_3)_2CHNH_2$, $(CH_3)_3CNH_2$ and their cations are listed in Table 2 together with the experimental data. Ethylamine and isopropylamine have two staggered conformations, i. e., trans and gauche forms, the former being more stable than the latter [4, 16, 20, 21]. The differences in the electronic energy between the two forms of ethylamine obtained in the present calculations with HF/6-311+G(d,p), MP2/6-311+G(d,p), B3LYP/6-311+G(d,p), and B3PW91/6-311+G(d,p) are 0.79, 0.76, 0.017, and 0.17 kJ mol^{-1}, respectively, and those of isopropylamine are 1.8, 2.4, 1.5, and 1.2 kJ mol^{-1} in the same order. It is noticeable that the DFT methods gave a quite low energy difference between the two forms of ethylamine.

For the amines, the C-C bonds are longer than the C-N bonds. The protonation causes the C-N bonds to become longer and the C-C bonds shorter, resulting in the C-N bonds being longer than the C-C bonds in the cations. The difference of the C-N bond lengths between the amine and the corresponding cation increases in order of $CH_3CH_2NH_2$ < $(CH_3)_2CHNH_2$ < $(CH_3)_3CNH_2$, as if the CH_3 group pushed out the NH_3^+ group in the cations.

Table 2. C-N and C-C bond lengths (Å) of ethylamine, isopropylamine, tert-butylamine, and their protonated cations, and the C-N and C-C bond differences (Å) between the amine and the ammonium ion.

	HF	MP2	B3LYP	B3PW91	Expt.
$CH_3CH_2NH_2$ (trans)					
C-N	1.454	1.464	1.466	1.460	1.470(10) [17]
C-C	1.528	1.529	1.533	1.528	1.531(6)
$CH_3CH_2NH_2$ (gauche)					
C-N	1.456	1.467	1.469	1.462	1.475(10) [17]
C-C	1.522	1.523	1.526	1.521	1.524(6)
$CH_3CH_2NH_3^+$					
C-N	1.517	1.517	1.532	1.520	
C-C	1.517	1.517	1.517	1.512	
ΔC-N *	0.063	0.053	0.066	0.060	
ΔC-C *	–0.011	–0.012	–0.016	–0.016	
$(CH_3)_2CHNH_2$ (trans)					
C-N	1.460	1.469	1.473	1.466	1.469(13) [18]
C-C	1.525	1.524	1.529	1.524	1.529(5)
$(CH_3)_2CHNH_2$ (gauche)					
C-N	1.459	1.468	1.472	1.465	
C-C	1.526	1.525	1.530	1.525	
	1.532	1.532	1.537	1.532	
$(CH_3)_2CHNH_3^+$					
C-N	1.530	1.527	1.547	1.534	
C-C	1.520	1.520	1.522	1.517	
ΔC-N *	0.070	0.058	0.074	0.068	
ΔC-C *	–0.005	–0.004	–0.007	–0.007	
$(CH_3)_3CNH_2$					
C-N	1.465	1.472	1.478	1.471	1.493(6) [19]
C-C	1.531	1.528	1.536	1.530	1.529(4)
	1.537	1.536	1.544	1.538	1.536(4)
$(CH_3)_3CNH_3^+$					
C-N	1.542	1.535	1.562	1.547	
C-C	1.526	1.524	1.528	1.524	
ΔC-N	0.077	0.063	0.084	0.076	
ΔC-C	–0.005	–0.004	–0.008	–0.006	
	–0.011	–0.012	–0.016	–0.014	

* Difference between the trans form and the cation.

We are grateful to Prof. H. Tanaka, Okayama University, for his help in carrying out the MO calculations. This work was supported by Grant-in-Aid for Scientific Research (B) (No. 10440208) from the Ministry of Education, Science, Sports and Culture, Japan.

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