Conformations of Pyrrolidinium Ion Studied by Molecular Orbital Calculations

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Ab initio HF/6-31G(d, p) and density functional theory B3LYP/6-31G(d, p) calculations were carried out to investigate the conformations of pyrrolidinium ion. Two conformations, corresponding to twisted (C2) and envelope (Cs) forms were optimized. Vibrational analysis showed that the twisted form is at a local minimum point and the envelope form at a saddle point. The energy difference between the conformations is ca. 2 kJ mol^{-1}.

Key words: Pyrrolidinium Ion; Conformation; HF; DFT.

It is well known that cyclopentane is puckered and performs pseudorotation taking twisted (C2) and envelope (Cs) conformations with a quite low barrier for interconvertions [1, 2]. Recent ab initio calculations at the HF-SCF level with the 6-31G(d, p) basis set showed that the C2 form is more stable by 1.1 cal mol^{-1} [3]. Pyrrolidinium ion, $C_4H_8NH_2^+$, isoelectronic with cyclopentane, is expected to perform a similar motion, but the puckered geometries and the energy difference between the conformations may be different from those of cyclopentane owing to the heterocyclicity [4].

Recently, we studied $(C_4H_8NH_2)_2MCl_6$ (M = Sn, Te, and Pt) by single crystal X-ray diffraction and ^{35}Cl NQR and showed the cations take a conformation close to the C2 form in the crystals [5]. Since the pyrrolidinium ions are loosely packed in these crystals owing to the bulky complex anions, the stable conformation of the isolated cation is thought to have the C2 form. Our preliminary calculation of semi-empirical MO using the PM3 method also showed that the C2 conformation is more stable than the Cs one [5]. In the present note we have used the ab initio Hartree-Fock (HF) method and the density functional theory (DFT) to calculate the expected conformations and the energies.

All calculations were performed with the Gaussian 98 [6] package. The HF and Becke's three parameter hybrid DFT-HF method [7] with Lee-Yang-Parr correlation functional [8] (B3LYP) with the 6-31G(d, p) basis

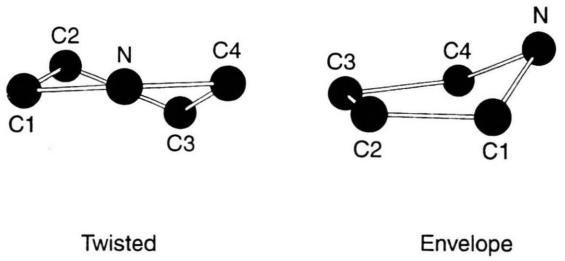

Fig. 1. The two conformations of $C_4H_8NH_2^+$.

Table 1. Bond lengths (Å), bond angles (°), and torsion angles (°) at twisted and envelope conformations of $C_4H_8NH_2^+$ ion calculated by PM3, HF/6-31G(d, p) and B3LYP/6-31G(d, p).

	Twisted			Envelope		
	PM3	HF	B3LYP	PM3	HF	B3LYP
N–C1	1.525	1.525	1.543	1.521	1.506	1.523
C1–C2	1.526	1.525	1.529	1.527	1.531	1.535
C2–C3	1.525	1.530	1.537	1.529	1.551	1.560
C3–C4	1.526	1.525	1.529	1.527	1.533	1.537
C4–N	1.525	1.525	1.543	1.521	1.507	1.523
N–C1–C2	106.60	103.99	104.00	106.31	103.33	103.41
C1–C2–C3	106.26	103.42	103.63	107.39	105.91	106.12
C2–C3–C4	106.26	103.42	103.63	107.45	106.02	106.23
C3–C4–N	106.60	103.99	104.00	106.40	103.60	103.66
C4–N–C1	107.99	108.39	107.87	106.85	105.21	104.97
N–Cl–C2–C3	20.81	33.22.	33.30	15.04	24.74	24.50
C1–C2–C3–C4	–25.81	–41.68	–41.95	–1.00	–1.77	–1.68
C2–C3–C4–N	20.79	33.20	33.27	–13.44	–21.88	–21.81
C3–C4–N–C1	–7.93	–12.72	–12.73	22.89	38.23	37.81
C4–N–C1–C2	–7.96	–12.76	–12.77	–23.50	–39.35	–38.86

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set were used for the geometry optimization and vibrational frequency calculations. The full optimizations without symmetry restrictions were carried out starting from the C2 and Cs conformations of the $C_4H_8NH_2^+$ ion obtained by the PM3 method [9]. Two stationary points were found corresponding to the C2 and Cs conformations (Figure 1). The optimized data are shown in Table 1 together with the initial geometries calculated by PM3. The bond lengths except C–N bonds, the bond angles and the torsion angles of both conformations produced by the HF and B3LYP calculations result to be very similar. For the C–N bonds, the B3LYP method gives longer bonds than the HF method. The PM3 calculations show flatter conformations, as pointed out by Dobado et al. [4].

The vibrational analysis shows that the C2 conformation corresponds to a potential energy minimum. On the other hand, the Cs conformation is found to be a saddle point of first order from the presence of an imaginary frequency. This result is somewhat surprising because the Cs conformations of other saturated five-membered ring compounds, such as cyclopentane, tetrahydrofuran, and tetrahydrothiophene, are reported to be stable [4]. The difference in the electronic energy between the C2 and Cs conformations calculated by HF/6-31G(d, p) is 2.0 kJ mol^{-1}, while that evaluated by B3LYP/6-31G(d, p) is 2.4 kJ mol^{-1}. Although these values are much larger than the energy difference obtained for cyclopentane [2, 4], they are still small compared to the energies of intermolecular interactions in solids. This is the reason why the pyrrolidinium ion can take various conformations in the crystals [10].

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