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STRUCTURE AND PUCKERING POTENTIAL OF AZETIDINE,  $(\text{CH}_2)_3\text{NH}$   
STUDIED BY ELECTRON DIFFRACTION  
AND AB INITIO CALCULATIONS

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Azetidine has been investigated by the restricted Hartree-Fock (RHF) method and Rayleigh-Schrödinger-Møller-Plesset (RSMP) perturbation theory in order to gain additional information from a previous electron diffraction study.<sup>1</sup>

A simultaneous optimization of all structural parameters showed that the degree of ring puckering,  $q$ , depends on the size of the basis set in a way similar to that observed for cyclobutane;<sup>2</sup> that is, with small basis sets  $q$  is severely underestimated.<sup>3</sup> Only with polarization functions in the basis can a reliable  $r_e$  structure be obtained. Our best RHF structure is as follows:  $q = 0.23 \text{ \AA}$ ; C-N  $1.467 \text{ \AA}$ ; C-C  $1.541 \text{ \AA}$ ; N-H  $1.001 \text{ \AA}$ ;  $\text{C}_2\text{H}_{\text{ax}}$   $1.089 \text{ \AA}$ ;  $\text{C}_2\text{H}_{\text{eq}}$   $1.084 \text{ \AA}$ ;  $\text{C}_3\text{H}_{\text{ax}}$   $1.083 \text{ \AA}$ ;  $\text{C}_3\text{H}_{\text{eq}}$   $1.082 \text{ \AA}$ ;  $\phi$  (ring dihedral angle)  $24.9^\circ$ ;  $\angle\text{HC}_2\text{H}$   $108.7^\circ$ ;  $\angle\text{HC}_3\text{H}$   $109.3^\circ$ ;  $\angle\text{C}_{2,4}\text{NH}$   $50.7^\circ$ ;  $\tau_1$  ( $\text{HC}_2\text{H}$  rock)  $2.4^\circ$ ;  $\tau_2$  ( $\text{HC}_3\text{H}$ )  $3.6^\circ$ ;  $\omega$  ( $\text{HC}_2\text{H}$  torsion)  $2.0^\circ$ ;  $\beta$  ( $\text{HC}_2\text{H}$  bending)  $0.7^\circ$ .

Inclusion of electron correlation at the RSMP level increases  $q$  and the HCH rocking angles ( $q = 0.27 \text{ \AA}$ ;  $\phi = 28.0^\circ$ ;  $\tau_1 = 2.5^\circ$ ;  $\tau_2 = 4.1^\circ$ ), while  $\text{C}_{2,4}\text{NH}$  is decreased to  $47.5^\circ$ .

Obviously, azetidine is slightly more puckered than cyclobutane. The re-interpretation of the electron diffraction data<sup>1</sup> without shrinkage corrections and using the assumption  $\tau_1 = \tau_2$  leads to  $\tau_{\text{av}} = 2.0(3.0)^\circ$  and  $\phi = 31.5(2.5)^\circ$ ; the latter result is not virtually different from that reported earlier ( $33.1(2.4)^\circ$ ).<sup>1</sup> Thus, the coupling between  $\tau$  and  $\phi$  is less strong than claimed by Catalán et al.<sup>5</sup> On the other hand, recent experimental results obtained for cyclobutane<sup>6</sup> are in qualitative accord with our findings.