Ring Puckering and Methylene Rocking in Cyclobutane

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Summary Calculations of the ring puckering potential in cyclobutane show no double minimum potential unless methylene rocking is introduced.

A CONSIDERABLE number of recent papers have been concerned with the puckering of four-membered rings.[1–5] Ueda and Shimanouchi[6] have analysed the i.r. spectrum of cyclobutane and shown the puckered (D_{2d}) geometry to be more stable than the planar (D_{4h}) geometry by 1·28 kcal./mole at a puckering angle of 34°. The adoption of a non-planar structure is usually attributed to a balance between (1) ethane-like torsional effects, which tend to cause puckering by reducing the eclipsing of non-bonded hydrogens, and (2) the decrease in $\angle$CCC on puckering, which increases ring strain and thereby tends to preserve planarity.[3] By using empirical torsional, bond stretching, and angle bending functions, Gwinn and co-workers[2,3] have successfully matched the microwave data and reproduced the double minimum potential in O^--, S^--, and Se^--substituted four-membered rings. They assumed that the nuclear displacements are curvilinear, *i.e.*. CC and CH bond lengths and HCH angles are preserved during the puckering. Also included is the restriction *that the methylene groups remain bisected by their local* CCC *angle* (we call this the puckering motion "proper").

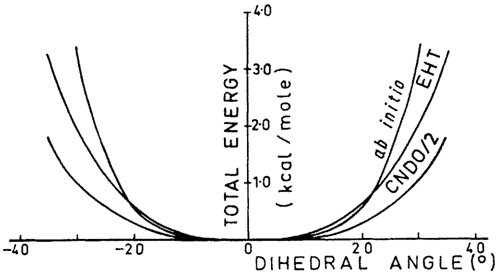

FIGURE 1. *Potential curves for the puckering motion by three different methods. Experimental bond distances and* HCH *angles are used.*

Using these assumptions and the experimental bond distances and angles (r_{C-C} = 1·556, r_{C-H} = 1·095 Å, $\angle$HCH = 116°)[7] we have calculated the potential barrier for this puckering motion in three different quantum-mechanical levels of approximation: 1) the Extended Hückel theory (E.H.T.),[8] 2) the CNDO/2 method,[9] and 3) a full *ab initio* calculation using a minimum Slater basis set. The result is shown in Figure 1, where total energy (in kcal./mole) is plotted against the dihedral angle (defined as 180° − β, Figure 2). The calculations all fail to yield a double minimum potential: the planar form of cyclobutane is more stable, and the energy increases continuously on puckering.

This surprising result suggests that there may be additional distortions on puckering. A complete CNDO/2 geometry optimization was carried out in the four variables: dihedral angle, C–C bond distance, C–H bond distance, and $\angle$HCH. The assumption of curvilinear displacements was verified, *i.e.* no change in bond lengths or $\angle$HCH occurs during puckering proper. (Optimized results give r_{C-C} = 1·49, r_{C-H} = 1·12 Å, $\angle$HCH = 106° at all dihedral angles up to 40°). However, the total energy again increases continuously with dihedral angle, contrary to experiment.

We then considered the possibility that other distortions occur which accompany the change in dihedral angle so as to stabilize the puckered geometry. In particular, *rocking* of the CH_2 groups relative to the CCC plane can increase the staggering of adjacent hydrogens. Thus, the methylene rocking angle was added as a fifth variable in the CNDO/2 calculation. Figure 2 shows this rocking motion in the puckered geometry. The potential curves at the optimized geometry, both with and without CH_2 rocking, are shown in Figure 3.

A double minimum potential is now observed when rocking is introduced, with a potential minimum at a dihedral angle of 20° and a methylene rocking angle of 3°. (The amount of rocking necessary to give the minimum energy increases from 0° in the planar configuration to 4° at a dihedral angle of 40°, always so as to increase the staggering of adjacent hydrogens.) However, the barrier height of 0·31 kcal./mole is still significantly smaller than the experimental value of 1·28 kcal./mole. A novel feature of this calculation is that puckering proper brings no stabilization and that stability in the nonplanar configuration requires an additional rocking of the methylene groups.

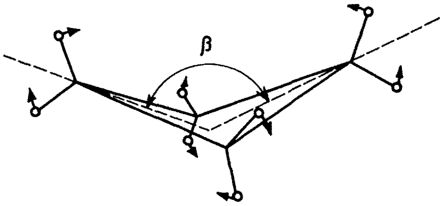

FIGURE 2. *Rocking motion in the puckered geometry, with dihedral angle* = 180° − β. (*The direction of rocking shown will increase the staggering of adjacent hydrogens*).

Note added in proof. In a recent study of the silacyclobutane molecule[10] Laane and Lord have mentioned the possibility of a strong mixing between puckering and rocking modes to such an extent that the ring-puckering motion is not a normal mode of vibration.

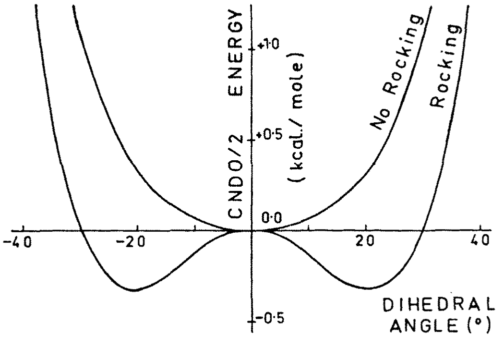

FIGURE 3. *Optimized* CNDO/2 *potential curves for the puckering motion, with and without rocking of methylene groups.*

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[1] G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1953, **75**, 5634.
[2] S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, *J. Chem. Phys.*, 1960, **33**, 1643; S. I. Chan, J. Zinn, and W. D. Gwinn, *ibid.*, 1961, **34**, 1319; S. I. Chan, T. R. Borgers, J. W. Russell, H. L. Strauss, and W. D. Gwinn, *ibid.*, 1966, **44**, 1103.
[3] D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, 1966, **44**, 3467.
[4] A. B. Harvey, J. R. Durig, and A. C. Morrissey, *J. Chem. Phys.*, 1969, **50**, 4949.
[5] A. C. Luntz, *J. Chem. Phys.*, 1969, **50**, 1109.
[6] T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, 1968, **49**, 470.
[7] R. C. Lord and B. P. Stoicheff, *Canad. J. Phys.*, 1962, **40**, 725.
[8] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.
[9] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289. The program used was a modified version of QCPE 91.
[10] J. Laane and R. C. Lord, *J. Chem. Phys.*, 1968, **48**, 1508.