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The Calculation of Monocyclic Molecular Structures Using MINDO/3

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A comparison is made of the experimentally determined structures for some 4, 5, and 6 membered monocyclic rings and the MINDO/3 calculated structures. Among several systematic deficiencies the calculated ring structures are found to be too flat. This is attributed to the fact that MINDO/3 underestimates 1,4-eclipsing interactions.

Key words: Ring conformation – Monocyclic molecular structures.

1. Introduction

The semi-empirical SCF-MO method, MINDO/3, developed by M. J. S. Dewar [1] and his group at the University of Texas at Austin, has been used to calculate molecular structures and energies for a variety of compounds [2–5]. Despite its extensive application by Dewar et al., there has been little work done relating to the determination of molecular structures of puckered monocyclic compounds. MINDO/3's predictive ability with regard to these systems would be useful to know for chemists who wish to apply the method to the calculation of reaction path properties in reactions involving cyclic reactants, transition states, and products. Indeed, since MINDO/3 has in the past demonstrated systematic deficiencies for several classes of compounds [2–5], a study involving monocyclic compounds is a necessity if reaction path calculations of the above type are to have any significance. With this in mind, we present below the results of calculations by MINDO/3 on ten monocyclic compounds. These results are compared with experiment.

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2. Molecules Studied and Computational Details

There was some difficulty in finding experimental structures, due to the difficulty of treating these particular types of compounds with common structural determination techniques, such as microwave spectroscopy and X-ray crystallography. The prevalence of oxygen containing molecules included in the study is related to this, in that such experimental methods are more easily applied to these substances than, for example, aliphatic compounds.

The compounds that were studied, with the reference to their experimental structures, are: equatorial-propylene ozonide [6], ethylene carbonate [7], diglycollic anhydride [8], trioxane [9], 1,3-dioxolane [10], trans-1,2-cyclobutanedicarboxylic acid [11], β-propiolactone [12, 13], trimethylene oxide [14], 3-methylene-cyanocyclobutane [15], and chlorocyclobutane [16].

With some exceptions, the calculations were carried out with no symmetry assumed and all degrees of freedom optimized. Those molecules for which symmetry was assumed are starred in Table 1.

3. Results

The results of the calculations are presented in Table 1.

4. Discussion and Conclusions

We found four systematic deficiencies in MINDO/3 from our calculations. First MINDO/3 tends to underestimate C–O single bond distances. Second, internal ring angles are somewhat overestimated. Third, as found by Bingham, Dewar, and Lo for cyclohexane and cyclohexene [2], the method predicts geometries which are considerably closer to planarity than are actually observed. Finally, MINDO/3 does not seem to be able to reliably predict lowest energy cyclic conformers. These four deficiencies are not necessarily independent but likely are interrelated as we will show below.

That MINDO/3 should underestimate C–O single bond distances in rings is not surprising since the same deficiency has been noted in acyclic systems [3]. Table 1 shows this effect to be quite pervasive; it is present in all the oxygen-containing compounds we studied. The magnitude of the error appears to be the same in cyclic as in acyclic molecules, i.e. from a few hundredths of an Ångstrom up to almost a tenth of an Ångstrom. Note that the same systematic effect is not observed for C–C single bonds in our calculations nor in those reported by Bingham et al.

The very high percentage of ring bond angles which we find to be over-estimated in these heterocyclic systems is more surprising since there does not appear to be an analogous deficiency with acyclic molecules [2, 3]. Bingham and Dewar also report that internal ring angles for hydrocarbons are quite accurately predicted by MINDO/3.

Table 1. Geometries

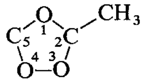
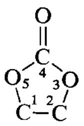
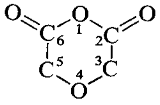
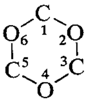
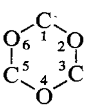
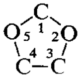
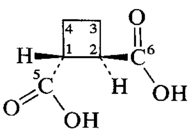
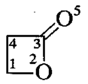
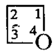
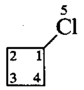
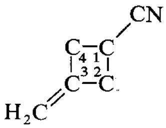
Compound	Calculated (observed) geometries bondlengths in Ångstroms, angles in degrees
 e-propylene ozonide	O^1C^2: 1.389(1.423); C^2O^3: 1.398(1.399); O^3O^4: 1.404 (1.471); O^4C^5: 1.379 (1.411); C^5O^1: 1.375 (1.423); $O^1C^2O^3$: 109.8 (105.6); $C^2O^3O^4$: 107.0 (99.7); $O^3O^4C^5$: 106.1 (99.2); $O^1C^2O^3O^4$: −0.4 (+41.0); $C^2O^3O^4C^5$: +3.5 (−49.2)
 ethylene carbonate	C^1C^2: 1.518 (1.52); C^2O^3: 1.378 (1.40) O^3C^4: 1.374 (1.33); $C^1C^2O^3$: 105.7 (102); $C^2O^3C^4$: 109.4 (109); $O^3C^4O^5$: 109.4 (111); C^1–C^2 axis makes an angle of 2.3° with the O^3–C^4–O^5 plane (exptl. = 20°)
 diglycollic anhydride*	O^1C^2: 1.347 (1.38); C^2C^3: 1.521 (1.49); C^3O^4: 1.366 (1.41); O^4C^5: 1.366 (1.41); C^5C^6: 1.521 (1.49); O^1C^6: 1.347 (1.38); $O^1C^2C^3$: 111.7 (116.9); $C^2C^3O^4$: 116.0 (111.9); $C^3O^4C^5$: 122.4 (110.7); $C^2O^1C^6$: 133.4 (121.2) $O^1C^2C^3O^4$: −15.2(−21.4); $C^2C^3O^4C^5$: +34.0 (+58.3); $C^3C^2O^1O^6$: −3.5 (−15.7)
 trioxane (chair)	C^1O^2: 1.369 (1.42); O^2C^3: 1.370 (1.42); C^3O^4: 1.371 (1.42); O^4C^5: 1.370 (1.42); C^5O^6: 1.369 (1.42); O^6C^1: 1.367 (1.42); $C^1O^2C^3$: 118.8 (110.4); $O^2C^3O^4$: 118.9 (109.6); $C^3O^4C^5$: 118.1 (110.4); $O^4C^5O^6$: 119.3 (109.6); C_3 axis: the oxygen plane is 0.075 Å above the carbon plane (0.462)
 trioxane (boat)	C^1O^2: 1.369; O^2C^3: 1.372; C^3O^4: 1.368; O^4C^5: 1.367; C^5O^6: 1.367; O^6C^1: 1.366; $C^1O^2C^3$: 118.4; $O^2C^3O^4$: 119.7; $C^3O^4C^5$: 119.5; $O^4C^5O^6$: 119.8; $C^1O^2C^3O^4$: −16.7; $O^2C^3O^4C^5$: +2.2; $C^3O^4C^5O^6$: +11.5
 1,3-dioxolane	C^1O^2: 1.383 (1.42); O^2C^3: 1.378 (1.42); C^3C^4: 1.513 (1.54); C^4O^5: 1.379 (1.42); O^5C^1: 1.379 (1.42); $C^1O^2C^3$: 106.8 (108); $O^2C^3C^4$: 106.7 (108); $C^3C^4O^5$: 106.0 (108); $C^1O^2C^3C^4$: +7.0 (+30.3); $O^2C^3C^4O^5$: −7.6 (−20.7)

Table 1. (cont.)

Compound	Calculated (observed) geometries bondlengths in Ångstroms, angles in degrees
 trans-1,2-cyclobutenedi-carboxylic acid*	C^1C^2: 1.578 (1.517); C^2C^3: 1.545 (1.553); C^3C^4: 1.516 (1.553); C^1C^5: 1.523 (1.493); $C^2C^3C^4$: 88.3 (87.5); $C^1C^2C^3$: 88.5 (88.8); $C^4C^1C^2C^3$: −8.3 (−20.1); angle between planes $C^2C^1C^4$-$C^2C^3C^4$: 168.0 (149)
 β-propiolactone	C^1O^2: 1.389 (1.45); O^2C^3: 1.373 (1.45); C^3C^4: 1.521 (1.53); $C^1O^2C^3$: 94.4 (89); $C^1C^2C^3$: 83.9 (83); $O^2C^3C^4$: 90.9 (94); $C^1O^2C^3C^4$: 0.6 (0)
 trimethylene oxide	C^1C^2: 1.513 (1.549); C^2C^3: 1.511 (1.549); C^3O^4: 1.389 (1.449); $C^1C^2C^3$: 83.4 (84.5); $C^1O^4C^3$: 92.6 (92.0); $C^2C^1O^4$: 92.0 (91.7); $C^1C^2C^3O^4$: −0.03 (0)
 chlorocyclobutane	C^1C^2: 1.521 (1.525); C^2C^3: 1.527 (1.550); C^1Cl^5: 1.786 (1.775); $C^2C^1C^4$: 90.8 (90.5); Angle between $C^2C^1C^4$-$C^2C^3C^4$ planes: 175.3 (160)
 3-methylene cyanocyclobutane[a]	C^1C^2: 1.544 (1.54); C^2C^3: 1.519 (1.496); $C^1C^2C^3$: 91.5°; $C^2C^3C^4$: 89.4°; $C^4C^1C^2$: 87.5 (90.8); The angle between the 4–1–2 and 4–3–2 planes: 176° (162.8°)

[a] The given experimental structure is consistent with but not completely determined by the observed microwave spectrum.

The tendency for MINDO/3 to overestimate the planarity of cyclic molecules has been noted by Bingham et al. [2] for cyclohexane and cyclohexene. We have noted a similar effect in all our systems and conclude that this behavior appears to be quite general. The magnitude of the discrepancy between observation and calculation is quite large, involving in some cases differences in dihedral angles of 20°–40°. Bingham and Dewar [2] have suggested that the ring flattening is due to an overestimation of non-bonded H · · · H repulsions. We question such an explanation on several grounds. First the flattening of cyclic compounds simultaneously increases 1,3-hydrogen distances and decreases the energetically more important 1,2 hydrogen distances. It would be expected that overestimation of

H···H non-bonded repulsions would favor the puckered rather than the planar conformations.

Second, we have performed additional calculations on cyclohexane and trioxane the results of which also argue against the Bingham–Dewar hypothesis. In these calculations, the ring atoms of both molecules were locked into the experimental geometry and the positions of the hydrogens attached to the ring optimized. The sum of all the two-centre H···H energies was calculated and compared with the same quantity for the completely optimized cyclohexane and trioxane. Obviously, the total energies of the fully optimized structures were found to be lower than the partially optimized structures. If the H···H repulsions are the predominant factor in driving each molecule from the more puckered experimental geometry to the flattened MINDO/3 fully optimized structure, then the difference in two-center H···H repulsions should constitute a large part of the total energy difference between partially and fully optimized geometries. As Table 2 shows, we do not observe this.

In fact, with cyclohexane the H···H energy actually increases in going from the experimental to the MINDO/3 optimized structure.

Third, Bingham *et al.* report that MINDO/3 underestimates the barrier to rotation in ethane. If non-bonded H···H repulsions were overestimated, one would expect an overestimation of the barrier to rotation.

The underestimation of the rotational barrier in ethane suggests a more likely cause for ring flattening. If 1,4 C···C or C···O non-bonded repulsions involving the ring atoms are similarly underestimated, then one might indeed expect an increased tendency towards planarity. We decided to test this hypothesis by comparing the MINDO/3 calculated energies for various conformations of a model system, *n*-butane, since in the planar rings the 1,4 C···C interactions are all analogous to the methyl-methyl eclipsed conformation of this molecule. The results are summarized in Table 3 together with the available experimental and *ab initio* SCF-MO conformational energies.

These results clearly indicate that the rotational barrier in *n*-butane is indeed underestimated by MINDO/3, as anticipated. We therefore conclude that the

Table 2. H–H two-center energies

	Partial optim. (eV)	Full optim. (eV)	Change (eV)
Trioxane:			
two-center H–H energies	1.629	1.564	−0.065
Total Energy	−1402.556	−1403.387	−0.831
Cyclohexane:			
two-center H–H energies	4.446	4.798	0.352
Total energy	−939.643	−940.022	−0.379

Table 3. Barriers to internal rotation in n-butane

Conformational change	MINDO/3 Calc. Barrier (kcal/mol)	Exptl. (kcal/mol)[a]	*ab initio* (kcal/mol)[b]
gauche → anti	0.4	2.9–3.4	2.5–2.8
gauche → gauche	2.0	5.3–5.9	6.0–6.8

[a] Ito, K.: J. Am. Chem. Soc. **75**, 2430 (1953); Piercy, J. Rao, M.: J. Chem. Phys., **46**, 3951 (1967)
[b] Hoyland, J.: J. Chem. Phys. **49**, 2563 (1968); Radom, L. Lathan, W. Hehre, W. Pople, J.: J. Am. Chem. Soc. **95**, 693 (1973)

ring flattening may well be due to an underestimation of 1,4 eclipsing interactions by MINDO/3.

It should be mentioned that the tendency towards planarity in MINDO/3 calculated ring structures may be responsible for the observed opening of internal ring angles. Strictly from the geometry of cyclic compounds, flattening the ring necessitates increasing the internal angles. Note, however, that the shortened C–O bonds should have the opposite effect on ring planarity. The systematic shortening of these bonds is expected to make the rings more puckered because of the increased repulsion between eclipsed, or nearly eclipsed ring atoms. That MINDO/3 errors on the side of too much planarity is probably attributable, once again, to the underestimation of 1,4 non-bonded repulsions.

Since MINDO/3 predicts ring geometries which are too flat and since the distinction between different ring conformations (such as boat and chair forms of six-membered cyclic molecules) becomes less pronounced as the rings become flatter, one might then anticipate that the magnitude of calculated energy differences between different conformations would also decrease. For example, diglycollic anhydride can exhibit both boat and chair conformations with the boat form being the experimentally observed structure. In agreement with this, MINDO/3 suggests that both conformations correspond to minima on the conformational potential energy surface. However, because of the flatness of the ring, the structures of the two conformations are not markedly different and their computed energies differ by only 0.07 kcal/mol, a chemically insignificant amount. A similar situation is encountered with trioxane where the boat and chair forms have a calculated energy difference of only 0.23 kcal/mol. Once again, the energy difference is almost insignificant. It is noteworthy, and not surprising considering the small energy differences between different conformations, that MINDO/3 incorrectly predicts the preferred conformation of trioxane. The molecule has been found to prefer the chair conformation [9, 17] while MINDO/3 suggests the boat form is more stable. Based on these results, one must conclude that MINDO/3 is an inadequate tool for the determination of the conformations of cyclic molecules. Not only does it fail to correctly predict the structures of the allowed conformational isomers of a molecule, but it also fails to reliably predict the relative energies of these structures.

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