Short Communication

An *Ab Initio* Molecular Orbital Calculation of the Molecular Structure and Conformational Preferences of Imidazolidine and 1,3-Dioxolane

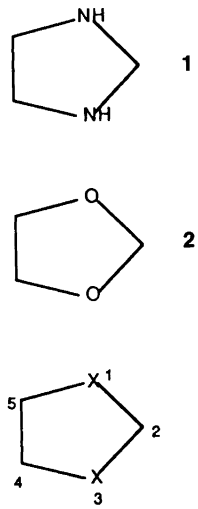
Anne Skancke[a] and Lev Vilkov[b]

[a]Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, N-9001 Tromsø, Norway and [b]Department of Chemistry, Moscow State University, 119899, GSP, Moscow, V-234, USSR

Skancke, A. and Vilkov, L., 1988. An *Ab Initio* Molecular Orbital Calculation of the Molecular Structure and Conformational Preferences of Imidazolidine and 1,3-Dioxolane. – Acta Chem. Scand., Ser. A 42: 717–720.

The conformations of saturated five-membered rings containing IV, V and VI main group elements have been studied by a number of methods. [1,2] It has been confirmed that such rings are non-planar, and may pseudorotate with a barrier depending on the endo- and exocyclic substituents. The main factor leading to deviation from planarity of the ring with eclipsed bond orientation is the torsional moment around the single bond. This torsional moment may be compensated for by a decrease in the bond angles leading to a non-planar form. Such conformations may be described by a number of different parameters, but for stereochemical studies dihedral angles are the preferred ones. A large dihedral angle in a five-membered ring corresponds to a large torsional moment around this bond, the latter being also correlated with the inherent barrier of internal rotation.

By successively replacing one CH_2 group of cyclopentane by NH and O, respectively, one should expect a gradual change in the pseudorotation barriers, parallelling the situation for non-cyclic systems provided the torsional moment is the decisive factor. However, the most recent *ab initio* molecular orbital calculations for cyclopentane,[3] pyrrolidine[4] and oxolane (tetrahydrofuran)[3] showed that there is no regular change in the pseudorotation barriers for these molecules (the numerical values are 0, 1.66 and 0.74 kcal mol^{-1}, respectively). It should be pointed out, however, that the higher value for pyrrolidine may in part be attributed to the fact that the calculations for this compound were carried out with a 4-21G basis set augmented with polarization functions on the nitrogen only. Furthermore, pyrrolidine is found to have an energy minimum for a C_s ("envelope") conformation with an axial N–H bond,[4] whereas for the case of oxolane a C_2 conformation ("twist") is preferred.



Scheme 1.

Table 1. Energies (in a.u.) for imidazolidine and 1,3-dioxolane. Numbers in parentheses are energy differences (in kcal mol^{-1}).

	Imidazolidine		1,3-dioxolane	
	C_s	C_2	C_s	C_2
3-21G//3-21G	−225.8630	−225.8632	−265.3103	−265.3113
n.of imag-freq.	0	0	1	0
6-31G*//3-21G	−227.1249	−227.1246	−266.7863	−266.7870
MP2(6-31G*)/HF/3-21G	−227.8375(0)	−227.8365(0.6)	−267.5227(0)	−267.5238(−0.7)
3-31G*//6-31G*	−227.1280	−227.1276	−266.7923	−266.7926
MP2(6-31G*)/HF/6-31G*	−227.8398(0)	−227.8388(0.6)	−267.5237(0)	−267.5240(−0.2)

We report here the results of *ab initio* calculations for a related pair of molecules, viz. imidazolidine (**1**) and 1,3-dioxolane (**2**) (Scheme 1). These molecules contain two heteroatoms (N−H or O in 1,3 positions) and consequently only one C−C bond. Since a C−C bond in acyclic molecules has a larger barrier to internal rotation than a C−N or C−O bond,[5] our choice of molecules should provide a simple model system for testing the importance of this rotation.

The calculations were performed using the Gaussian 86 computer programme.[6] The geometries were optimized using the gradient method with a 6-31G* basis set. In the end points of geometry optimizations, single-point calculations have been carried through at the MP2(6-31G*) level. The energies are reported in Table 1, which also gives the corresponding energies at the 3-21G level. As is seen from the table, the C_s and C_2 forms are quite close in energy for both molecules, with a slight preference for C_s for imidazolidine and for C_2 for 1,3-dioxolane.

Table 2 gives the calculated geometries for the two symmetries for both molecules, and illustrations are given in Fig. 1. For imidazolidine, only the axial forms at the nitrogen atoms were obtained as stationary points. It should be noted that the pseudorotational potential surface also contains several other forms (e.g. "half-twist"); these have been omitted in the present work which has focused on the highest symmetry forms. For 1,3-dioxolane, comparison is made

Table 2. Geometry parameters (in Å and degrees) as calculated at the 6–31G* level. The numbering of atoms is given in accordance with Scheme 1.

Parameter	Imidazolidine		1,3-Dioxolane			
	C_2	C_s	C_2	C_s	C_2[a](exp)	C_2[b](exp)
X1-C2	1.465	1.454	1.395	1.387	$1.423(1)_{av}$	1.430(2)
X1-C5	1.460	1.463	1.404	1.404		1.415(2)
C4-C5	1.530	1.559	1.519	1.543	1.542(6)	1.530(4)
$(C-H)_{av}$	1.084	1.083	1.083	1.083	1.106	1.095(4)
X-H	0.995	1.001				
∠X1C2X3	108.1	107.7	107.8	106.5	108.7(24)	107.6(5)
∠C2X1C5	106.5	104.2	108.3	107.0	105.8(24)	106.7(4)
∠CC X1	103.7	105.7	102.3	104.0	101.0(4)	102.1(23)
τX3C4C5X1	37.6	0	21.3	0	41.8(31)	38.4(6)
∠XCX-XCCX		35.11		33.7		

[a]From Ref. 7. [b]From Ref. 8.

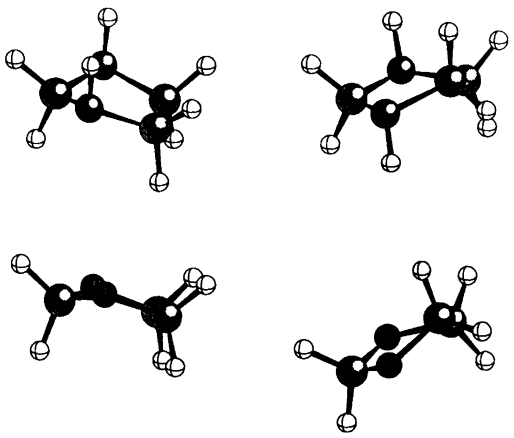


Fig. 1. Plots of molecular structures of C_s and C_2 forms of imidazolidine and 1,3-dioxolane.

with recent electron diffraction results by Hilderbrandt and coworkers[7] and unpublished data of Hedberg.[8] The overall comparison is reasonably good, although our computed data give C–O distances somewhat shorter than the experimental ones. These distances are critically dependent on the basis set, and calculations with the smaller 3-21G basis set give C–O bond distances 0.04 Å longer. There is an interesting discrepancy in the C–C distances, since our computed C–C distance for the C_2 form is shorter than the experimental value for the C_2 form; this latter value is, however, in good agreement with our C–C distance for the C_s form (as expected, these nonpolar bonds are less basis set dependent, the 3-21G set giving values about 0.015 Å longer). No experimental structural information is available for imidazolidine.

For 1,3-dioxolane, one of the recent electron diffraction studies[7] has shown that there is a very low barrier (~0.3 kcal mol^{-1}) for pseudorotation, and the C_2 form of the molecule corresponds to an energy minimum. However, the electron-diffraction data were little sensitive to the different conformations, the value for pseudorotation was fixed and the two C–O bonds were assumed equal. There is an earlier *ab initio* calculation of oxolane,[3] but in the latter calculation certain geometry parameters were fixed and correlation energy was not included. Nevertheless, the results of this calculation are in good agreement with experiment, yielding a C_2 conformation and a pseudorotation barrier of 0.79 kcal mol^{-1}.

In an attempt to establish the nature of the stationary points, we have calculated analytical frequencies at the level HF(3-21G)/HF/3-21G (see Table 1). On the basis of these calculations, both the C_s and the C_2 forms are at energy minima for imidazolidine. At our highest calculational level, the former conformer is the more stable by 0.6 kcal mol^{-1}. However, the existence of one low frequency for each form indicates a very small barrier to internal rotation. For the C_s form, this is found to be 61 cm^{-1} (A'' symmetry) and for the C_2 form 44 cm^{-1} (B symmetry). For 1,3-dioxolane, one imaginary frequency of A'' symmetry (114.2i) is found for the C_s form, which is therefore found to be at an energy maximum. The C_s form of 1,3-dioxolane is more stable than the C_s form by 0.2 kcal mol^{-1}. The small barrier to pseudorotation may be responsible for the longer C–C bond encountered in the experimental work.

In conclusion, we have found a consistency in trends giving smaller barriers for the disubstituted systems imidazolidine and 1,3-dioxolane than has been found for pyrrolidine, oxolane and the parent cyclopentane. This is in accordance with what would be expected if the C–C torsion is the decisive factor in the magnitude of the barrier. Although our energy differences are small, they are supported by the frequency calculation. Table 1 also gives data for calculations at the MP2(6-31G*)/HF/3-21G, and it is seen that the same qualitative conclusion would be reached at this level.

The conformational preference of pyrrolidine and imidazolidine (the N-containing pair) is the envelope (C_s), while oxolane and 1,3-dioxolane (the O-containing pair) both prefer the twist (C_2) conformation.

A molecular mechanics calculation (MM2) by Nørskov-Lauritsen and Allinger[9] predicts the C_s form of 1,3-dioxolane to be the more stable, but this result hinges critically upon the data chosen for parameterization. In the case of a system having two functional groups which may interact, the parameterization scheme becomes particularly important, and unfortunately the experimental material available for such parameterization is scarce.

References

1. Cremer, D. and Pople, J. A. *J. Am. Chem. Soc. 97* (1975) 1358.
2. Vilkov, L. V., Mastryukov, V. S. and Sadova, N. I. *Determination of Geometrical Structure of Free Molecules,* Mir Publishing, Moscow 1983, Chap. XI.
3. Cremer, D. *Isr. J. Chem. 23* (1983) 72.
4. Pfafferott, G., Oberhammer, H., Boggs, J. E. and Caminati, W. *J. Am. Chem. Soc. 107* (1985) 2305.
5. Veillard, A. In: Orville-Thomas, W. J., Ed., *Internal Rotation in Molecules,* Wiley, New York 1974, p. 385.
6. Frisch, M. J., Binkley, J. S., Schlegel, H. B., Raghavachari, K., Melius, C. F., Martin, L., Stewart, J. J. P., Bobrowicz, F. W., Rohlfing, C. M., Kahn, L. R., DeFrees, D. J., Seeger, R. R., Whiteside, R. A., Fox, D. J., Fleuder, E. M. and Pople, J. A. *Gaussian 86,* Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1984.
7. Shen, Q., Mathers, T. L., Raeker, T. and Hilderbrandt, R. L. *J. Am. Chem. Soc. 108* (1986) 6888.
8. Hedberg, K. *Personal communication.*
9. Nørskov-Lauritsen, L. and Allinger, N. *J. Comput. Chem.* (1984) 326.

Received May 23, 1988.