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Local Orbital Study of Bonding in Small Rings: Cyclopropane, Thiirane, Oxirane, and Aziridine

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The nature of the bonding in the three-membered ring molecules cyclopropane, thiirane, oxirane, and aziridine has been investigated through *ab initio* FSGO calculations. The direct correspondence between floating spherical Gaussian orbitals and specific chemical bonds has been used to study the degree of "bond bending". In accord with chemical intuition, it is demonstrated that the C–C ring bond becomes progressively more bent as the bond length is reduced. C–C bonds are found to be more flexible than C–N (O, S) bonds. The sizes and locations of carbon-heteroatom bond orbitals and C–H bond orbitals are also discussed.

Key words: Cyclopropane – Thiirane – Oxirane – Aziridine

The chemical nature of the "bent bonds" in molecules with small rings has been the subject of many investigations during the last decade. In some cases – such as the studies by Clark [1] and by Bonaccorsi *et al.* [2] – comparative calculations exploring how the bonding varies from system to system have also been conducted. As far as we are aware, all of these computations employed atom-centered basis sets and followed the molecular orbital approach. Since the classical concept of a bent bond is associated with a localized bond or bond orbital, as opposed to a molecular orbital, Bonaccorsi *et al.* used by the Foster-Boys localization procedure to indirectly generate localized orbitals in their calculations. These localized orbitals were then analyzed in terms of bond-bending and related concepts. There is, however, an *ab-initio* method which directly yields bond orbitals, without reference to atom-centered basis functions – the floating spherical Gaussian orbital (FSGO) method proposed by Frost [3]. Earlier FSGO calculations on cyclopropane [4] and cyclopropene [5] have demonstrated that small ring systems can be successfully treated. Accordingly, we have conducted a comparative FSGO study of bonding in cyclopropane, thiirane, oxirane, and aziridine. Our aim has

Table 1. Energies and dipole moments[a]

Molecule	E (FSGO)	E (SCF)[b]	E (SCF)[c]	μ (FSGO)	μ(SCF)[b]	μ (SCF)[c]	μ (Expt)[d]
C_3H_6	−98.890	−115.998	−116.752	0	0	0	0
C_2H_5N	−112.446	−131.805	−132.658	1.72	2.10	1.77	1.90
C_2H_4O	−129.138	−151.395	−152.369	2.91	2.35	1.19	1.89
C_2H_4S	−408.767	−456.002	−474.516	4.63	5.17	0.84[e]	1.85

[a] Energies in hartrees, dipole moments in debyes.

[b] See Ref. [1].

[c] See Ref. [2].

[d] Taken from Nelson, R. D., Jr., Lide, D. R., Jr., and Maryott, A. A. (eds.), National Standard Reference Data Series – NBS10 (National Bureau of Standards, Washington, D.C., 1967).

[e] If sulfur *d* orbitals were not included in the basis, a value of 1.56 D was obtained.

not been to rival the numerical accuracy of large atom-centered basis set calculations, but rather to determine and analyze wavefunctions which are both 1) obtained via non-empirical quantum mechanics and 2) readily translatable into the terms and ideas of classical chemistry.

Table 1 lists the total energies and dipole moments computed for the four molecules, and includes similar results determined by Clark [1] (using a small atom-centered Gaussian basis set) and by Bonaccorsi, Scrocco, and Tomasi [2] (using a minimal basis set of STO's). Calculations were done at experimental geometries. Although the FSGO results are poorer energetically, a surprising degree of consistency is observed; for cyclopropane, aziridine, and oxirane the FSGO energies are, respectively, 85.25, 85.31, and 85.30 percent of Clark's values and 84.70, 84.76, and 84.75 percent of Bonaccorsi's energies. This indicates that the level of the FSGO description of all these first-row molecules is uniform. The FSGO wavefunction for thiirane is relatively more accurate, in that E_{FSGO} is 89.64 and 86.14 percent of the two respective SCF energies. Although all three heterocyclic molecules have similar experimental dipole moments, none of the three sets of theoretical calculations reflects this similarity. The results for C_2H_4S are particularly poor, and it is apparent that in strained rings large basis sets are needed to accurately calculate dipole moments.

The properties of individual bonding orbitals and relevant geometric factors are presented in Table 2. α denotes an orbital exponent, δ measures the perpendicular displacement of the orbital center from the bond axis, and the multiplier m_{AB} is defined as the bond axis projection of the distance from atom A to the bond orbital center divided by the A–B bond length.

Since the exponent of an orbital is a measure of its size, one notes from Table 2 that there is a rather significant variation in size of C–C orbitals among the four compounds. Part of this variation can be attributed to differences in the C–C bond length; however, studies on unstrained C–C single bonds [6] suggest that the $\alpha(R)$ dependence accounts for less than half of the observed variation. Furthermore, the ring C–C orbitals, with an average exponent of 0.345, are significantly more diffuse than the typical acyclic C–C orbital for a bond of similar length ($\alpha \simeq 0.370$)

Table 2. Properties of bonding orbitals[a, b]

Bond	Property	C_3H_6	C_2H_4S	C_2H_5N	C_2H_4O
C–C	α	0.3249	0.3598	0.3390	0.3553
	δ	0.0687	0.1236	0.1955	0.3429
	R	2.8535	2.8195	2.7987	2.7817
X–C	m	0.5000	0.3551	0.3176	0.1802
	α	0.3249	0.2629	0.3783	0.5116
	δ	0.0687	0.0755	0.0515[c]	0.0132
	R	2.8535	3.4374	2.7873	2.7136
	∠CXC	60.00°	48.42°	60.27°	61.67°
C–H	m	0.6103	0.6062	0.6242[d]	0.6330
	α	0.3624	0.3855	0.3760[d]	0.3902
	R	2.0580	2.0371	2.0475	2.0447
	∠HCH	115.10°	115.74°	115.72°	116.54°
N–H	m			0.4843	
	α			0.4278	
	R			1.9200	

[a] Bond lengths in bohr; bond angles in degrees.
[b] δ = perpendicular distance from bond axis to orbital center.
[c] The distance from the bond axis in the CNC plane is 0.0191.
[d] These are average values; the two different kinds of C–H orbitals had slightly different (~0.002) exponents and multipliers.

[6]. Presumably this extra diffusiveness is due to the interaction between neighboring ring bond orbitals. Indeed, in the two molecules with the most compact C–C bonds, thiirane and oxirane, the center of the C–O(S) orbital is relatively far from the C–C orbital (due to the length of the C–S bond and the high electronegativity of oxygen), while in cyclopropane and aziridine the neighboring ring orbitals are substantially "closer". All the C–C bonds are bent, in that the orbital centers lie off the C–C axis, outside of the ring. There is, however, a dramatic difference in the degree of bending associated with the different compounds. Cyclopropane is only slightly bent, while the C–C bond orbital in oxirane is centered more than one-third of a bohr off the bond axis![1] Fig. 1 shows that $\delta(R_{CC})$ is a smooth curve, which suggests that the key factor in determining δ is the internuclear distance. As R_{C-C} decreases, the bond "bows out" – in striking accord with the model of a chemical bond as a piece of plastic which bends as the ends are brought closer together. In fact, if one defines the bond length not as the internuclear distance but instead as the length of an arc connecting the nuclei and passing through the bond orbital center, this new C–C bond length is nearly constant through this series of molecules. We anticipate that Fig. 1 could be used to estimate the degree of C–C bending in other three-membered rings, and further predict that, given the rate of increase of $\delta(R)$ as R decreases, it is unlikely that

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[1] The localized orbitals in Ref. [2] display this same trend, but not to the same extent.

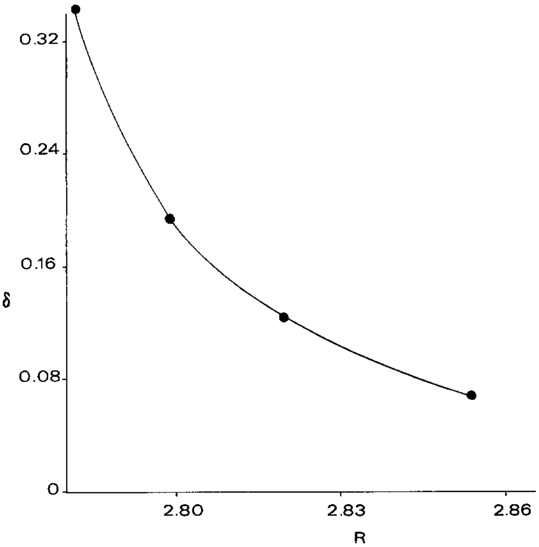

Fig. 1. Dependence of the perpendicular displacement of the C–C bond orbital from the C–C bond axis on C–C bond length

C–C bonds significantly shorter than that in oxirane will be found in three-membered rings.

As we have shown elsewhere [7], FSGO multipliers reflect electronegativity differences and can even be used to define an electronegativity scale. In these ring systems the C–S, C–N, and C–O bond multipliers follow the chemically anticipated trend, $m_{OC} < m_{NC} < m_{SC}$. The actual numerical values are 0.18, 0.32, and 0.35, whereas from our previous work [7], on unstrained molecules we would have anticipated the respective values 0.24, 0.32, and 0.46. The agreement for the C–O and C–N bonds is satisfactory, but the C–S multiplier of 0.35 seems too small, and suggests an overly electronegative sulfur; 0.46 would be more reasonable. This might be the result of a deficiency in the FSGO model, although the very small C–S–C bond angle[2] (48.4°) might enhance the effective electronegativity of sulfur through *d*-orbital participation or interaction between the two C–S bonds in thiirane.

The C–S, C–N, and C–O bond orbital exponents, as expected, increase as the bond length decreases. The δ values for these bonds are, however, somewhat surprising in that the degree of bond bending is relatively small. The in-plane bending of the carbon-heteroatom bond in aziridine and oxirane is less than 10% of the carbon–carbon bending. This trend of greater flexibility for C–C bonds is

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[2] The original reference to the experimental structure of thiirane, Ref. [8], cites a C–S–C angle of 65° 48′, which is entirely inconsistent with their other bond angles and bond lengths, and must be a misprint. From the other geometric data provided in this reference, we find the C–S–C angle to be 48.4°. Note that this misprint has been propagated in the chemical literature (Rohmer, M. M., Roos, B.: J. Am. Chem. Soc. **97**, 2025 (1975)).

also supported (with different magnitudes) by the "perpendicular localized orbital dipole moments" calculated by Bonaccorsi, Scrocco, and Tomasi [2].

Studies on unstrained hydrocarbons have shown that both α_{CH} and m_{CH} depend on the local chemical environment [6]. On that basis, we anticipated that the C–H orbitals of ring molecules would be intermediate in character between the methylene C–H orbitals of propane and the $=CH_2$ orbitals of ethylene. This is, in fact, the case for cyclopropane and thiirane. Oxirane, and to a lesser extent aziridine, behave differently. In these last two molecules, the C–H bond orbitals have moved significantly toward the terminal H atoms; this electron flow is contrary to what might have been expected from electronegativity considerations. The observed C–H multipliers do correlate with the C–C–X bond angle, but this does not provide a rationale for the electron flow. It is possible that interactions with lone pair electrons on the heteroatom or with the highly bent C–C bond electrons are the root cause of this phenomenon, or that it is just an artifact of the FSGO method.

In conclusion, the FSGO model wavefunctions of these four three-membered ring molecules provide, at an energetically consistent level of accuracy, a simple description of how the bond orbitals behave. One observes that 1) C–C bond orbitals are more diffuse than in similar unstrained bonds, 2) the bending in a C–C bond has a simple dependence on the C–C bond length, 3) heteronuclear ring bonds are less flexible than C–C bonds, 4) the location of the orbital center of the C–X bonding orbital is monitored by electronegativity differences, and 5) the factors influencing ring-adjacent C–H orbitals are not yet clear.

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