Inorganic Analogues of Cyclic Organic Molecules

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Ab initio SCFMO calculations are given for inorganic systems related to the hydrocarbon rings $C_3H_3^+$, C_3H_6, C_4H_4, C_4H_8, and C_6H_6. The molecules studied belong to the same symmetry group and/or are isoelectric with the hydrocarbon rings, and include H_3^+, H_4, H_6, N_3^+, N_4, N_6, O_3, O_4, and several others. Preferred geometries and energies are reported for single-ζ and double-ζ basis sets. The relationship between the hydrocarbon rings and their inorganic analogues is shown. Although lone-pair repulsions destabilize the inorganic rings, their possible existence as molecules, intermediates, and transition states is discussed.

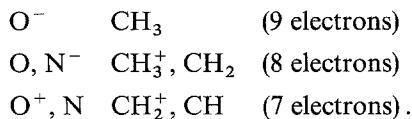*Key word:* Inorganic ring systems with equal atoms

1. Introduction

The predictive power of Walsh's rules [1, 2] for determining molecular geometry is well-established for triatomic systems of the form AH_2, AB_2, and HAB. It has been shown by Buenker and Peyerimhoff [3] that it is possible to extend Walsh's rules to more general systems of substituted triatomics, such as H_nAB_2, in order to make geometry predictions for more complex molecules. This is true because hydrogen substitution can alter the position of valence orbital energies without altering their angular dependence, and the preferred bond angle is determined by following the variation of sums of orbital energies. Thus, for example, it was shown that the energy variation on angle bending in ozone is quite similar to that in the isoelectronic molecule C_3H_6, with minima occuring in both cases near 60° (ring) and 120° (bent) geometries [4–7].

In this paper we consider the possible inorganic analogues of the hydrocarbon rings $C_3H_3^+$ (cyclopropenyl cation), C_3H_6 (cyclopropane), C_4H_4 (cyclobutadiene), C_4H_8 (cyclobutane), and C_6H_6 (benzene). These molecules have received considerable attention because, for example, $C_3H_3^+$ and C_6H_6 form prototype aromatic molecules while C_4H_4 is antiaromatic [8]; C_3H_6 and C_4H_8 are also important systems in organic chemistry and have been thoroughly studied by molecular orbital techniques [9–11]. We shall make use of the well known properties of such molecules in the present study.

We can classify organic and inorganic systems as analogues provided that
1) They are isoelectronic. The following replacements can be considered:

$$O^- \qquad CH_3 \qquad \text{(9 electrons)}$$
$$O, N^- \qquad CH_3^+, CH_2 \qquad \text{(8 electrons)}$$
$$O^+, N \qquad CH_2^+, CH \qquad \text{(7 electrons)}.$$

2) They belong to the same symmetry group (isosymmetric).

When these two conditions are fulfilled, it is highly likely that the organic and inorganic molecules will have the same electronic configuration, and hence a similar geometry (some exceptions will be discussed). Under certain circumstances, which have been discussed in the recent review by Buenker and Peyerimhoff [45], the isosymmetric requirement is unnecessary. This allows extension of results obtained for ABA systems, for example, to include ABC systems.

To illustrate the use of the two criteria of equivalence given above, consider a possible inorganic analogue of cyclopropane (D_3h symmetry, 24 electrons) which is cyclic ozone (D_3h, 24 electrons). Figure 1 shows a system of localized orbitals where the equivalence between CH bonds and oxygen lone pairs is revealed; the high symmetry ensures a comparable orbital energy diagram for both molecules.
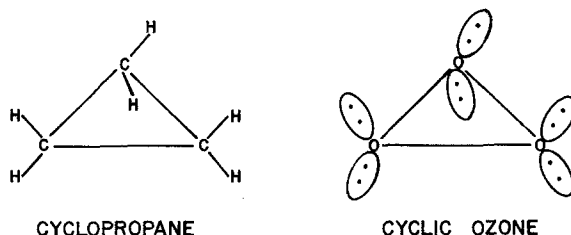

CYCLOPROPANE   CYCLIC OZONE

Fig. 1. Localized orbitals (sp^3 hybridization assumed) for cyclopropane and cyclic ozone

The point which emerges from the analogy is that ozone should exist as a *stable ring*. In fact, the ground state geometry of ozone is bent at 116° [12], but there is a deep secondary minimum for cyclic ozone at 60° [4–7]. Inspection of resonance structures for bent ozone (below),
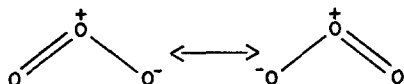
and simple replacement by isoelectronic groups (O, CH_2), (O^+, CH), (O^-, CH_3) leads to a prediction in the reverse direction — there should be a stable hydrocarbon of form
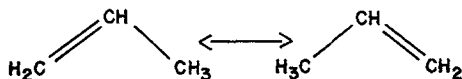
which, of course, is propylene, a structural isomer of cyclopropane[1]. Note that in this case we have dropped requirement [2] of symmetry equivalence and still retained some predictive power. In other cases we can drop the requirement that the systems be isoelectronic; as will be shown for the hydrogen rings the requirement of symmetry equivalence (belonging to the same point group) can lead to interesting analogies with the hydrocarbon rings. We now begin a systematic investigation of the inorganic analogues.

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[1] There are some traps to be avoided in this process. Ozone has equal bond lengths, propylene does not. Propylene cannot be represented by resonance structures since the presence of hydrogens makes the positions non-equivalent. Another error can occur where there are partially occupied degenerate orbitals; compare O_2 and ethylene.

2. Method of Calculation

Calculations reported in this paper use either a minimum basis (single-ζ, hereafter called SZ) or double-ζ (DZ) basis of Slatertype exponential orbitals in an *ab initio* SCFMO calculation. The molecular orbital program used was obtained from Stevens and has been discussed in recent publications [13, 14] (the integral package is obtainable from the Quantum Chemistry Program Exchange as QCPE 161).

Table 1. Computed total energies for the cyclic molecules and ions

Molecule	r (bohr)	Basis set	Energy (hartree)	Comment	Ref.
H$_2$	1.40	SZ	$-$ 1.1281	$\zeta = 1.20$	a
	1.40	DZ	$-$ 1.1283	$\zeta = 0.90, 1.20$	a
	1.40	1s, 1s', 2p	$-$ 1.1669	full CI	[25]
	1.40		$-$ 1.1745	exact	[20]
H$_3^+$	1.66	SZ[e]	$-$ 1.2699	$\zeta = 1.40$	a
	1.66	large	$-$ 1.3397	full CI	[19]
	1.66	large	$-$ 1.342	est. (± 0.001)	[19]
H$_4$	2.30	SZ[e]	$-$ 1.9834	$^3A_{2g}$, $\zeta = 1.029$	a
	2.30	DZ	$-$ 2.0079	$^3A_{2g}$, 0.90, 1.20	a
	2.40	1s, 1s', 2p	$-$ 2.0909	$^3A_{2g}$, full CI	[25]
H$_6$	2.06	SZ[e]	$-$ 3.2081	$\zeta = 1.10$	a
	1.86[e]	DZ	$-$ 3.2408	$\zeta = 0.90, 1.20$	[26]
N$_2$	2.178[e]	SZ	$-$ 108.5694	Clementi ex.	[27]
	2.075[e]	DZ	$-$ 108.8644	Huzinaga ex.	[27]
	2.0675	large	$-$ 108.9928	near H-F	b
N$_3^+$	2.580[e]	SZ	$-$ 162.389	ion-optimized	[27]
	2.655[e]	DZ	$-$ 162.597	Huzinaga ex.	[27]
N$_4$	2.714[e]	SZ	$-$ 216.925	$^3A_{2g}$, Clem. ex.	[27]
	2.700	DZ	$-$ 217.240	$^3A_{2g}$, Huzin. ex.	[27]
N$_6$	2.606[e]	SZ	$-$ 325.468	Clementi ex.	[27]
O$_2$	2.280	SZ	$-$ 149.0906	$^3\Sigma_g^-$, Clem. Ex.	a
	2.280	SZ	$-$ 149.0825	$^3\Sigma_g^-$, 7.66, 2.28	a
	2.280	DZ	$-$ 149.5623	$^3\Sigma_g^-$, Clementi ex.	a
	2.280	large	$-$ 149.6639		c
O$_3$	2.670[e]	SZ	$-$ 223.5568		[5]
	2.730	DZ	$-$ 224.1793		[7]
	2.730	DZ$^+$	$-$ 224.2794		[7]
O$_4$	2.67[e]	SZ	$-$ 298.1081	$\zeta = 7.66, 2.28$	a
	2.84[e]	DZ	$-$ 298.9546	Clementi ex.	a
C$_3$H$_6$	2.76	GTO	$-$ 116.8974		d
C$_4$H$_4$	2.691	GTO	$-$ 153.42	$^3A_{2g}$	[41]
C$_4$H$_8$	2.929	SZ	$-$ 155.8370		[11]

[a] This work.
[b] Cade, P. E., Sales, K. D., Wahl, A. C.: J. Chem. Phys. **44**, 1973 (1966).
[c] Schaefer, H. F.: J. Chem. Phys. **54**, 2207 (1971).
[d] Siu, A. K. Q., St. John 3rd, W. M., Hayes, E. F.: J. Am. Chem. Soc. **92**, 7249 (1970).
[e] Optimized.

For neutral molecules we use Clementi's [15] best-atom exponents for SZ basis sets and Huzinaga [16] best-atom exponents for DZ basis sets, unless otherwise noted. Some optimization was done to find the best exponents for ions. Where open-shell situations are encountered, two techniques are used: Nesbet's method of symmetry and equivalence restrictions [17] in an open shell calculation, or a limited configuration interaction. All of the computed energies, together with the results of other workers, have been collected in Table 1.

3. Hydrogen Rings

Consider the symmetric rings of hydrogen atoms having molecular formulas H_3^+, H_4, and H_6. Respective symmetries for the rings are D_{3h}, D_{4h}, and D_{6h} so by criterion [2] we look for analogies with the isosymmetric hydrocarbon rings $C_3H_3^+$, C_4H_4, and C_6H_6. In Fig. 2 the orbital energy patterns (based on SZ results), which are completely symmetry determined, are shown. These orbital energies were obtained for the geometries and exponents listed in Table 1, which are nearly optimum. Inspection of the orbital energies with reference to the energy of a hydrogen $1s$ orbital (-0.5 hartree) shows that, from orbital energy considerations alone, H_2, H_3^+, and H_6 should be stable while H_4 is unstable. Exactly the same energy level diagram forms the basis for the Hückel $4n + 2$ rule for the stability of pi-systems, from which follows the stability of $C_3H_3^+$ and C_6H_6 (aromatic), and instability of C_4H_4 (antiaromatic). We now ask: Is there evidence, experimental or theoretical, concerning the stability of hydrogen rings?

The H_3^+ ion has been observed in the mass spectrometer [18]. From data on appearance potentials, the estimated enthalpy change for $H_2 + H^+ \rightarrow H_3^+$ is -115 kcal/mole. In an extensive quantum mechanical calculation of the
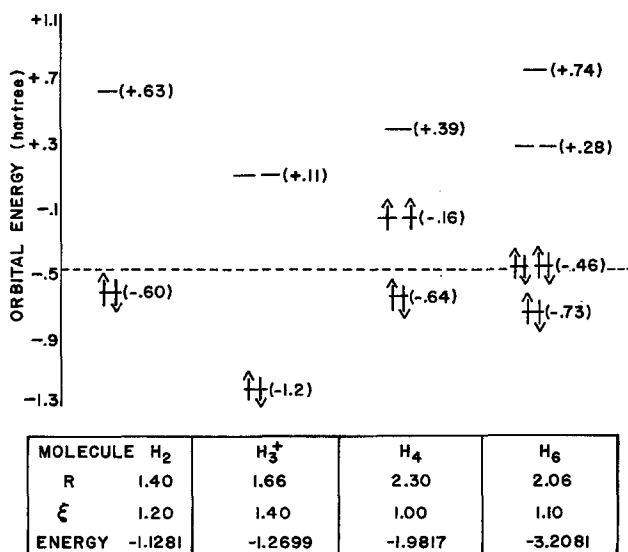

MOLECULE	H_2	H_3^+	H_4	H_6
R	1.40	1.66	2.30	2.06
ξ	1.20	1.40	1.00	1.10
ENERGY	-1.1281	-1.2699	-1.9817	-3.2081

Fig. 2. SZ orbital energies for hydrogen rings. Dashed line = energy of a hydrogen $1s$ orbital (-0.5 hartree)

preferred geometry of H_3^+ by Csizmadia et al. [19], by extrapolation of their CI result they obtained

$$\text{Energy of } H_3^+ \text{ (exact)} = -1.342 \pm 0.001 \text{ hartree}.$$

The preferred geometry was cyclic with $r = 1.66$ bohr. Since the exact energy of H_2 [20] is -1.1745 hartree (at the potential minimum), the computed energy difference from $H_2 + H^+$ is 105 kcal/mole, in reasonable agreement with the experimental value of 115. Thus, the H_3^+ ion forms a stable ring.

The search for a low energy H_4 molecule has provided a challenge to theoreticians, following the shock tube study by Bauer and coworkers [21] of the $H_2 + D_2 \rightarrow 2HD$ isotopic exchange reaction. They observed the low activation energy of 42 kcal/mole [21, 22] and proposed a *molecular* exchange mechanism, involving a vibrationally excited $H_2(D_2)$ in a four-center transition state. The atomic exchange mechanism,

$$H_2 \rightarrow 2H, \quad H + D_2 \rightarrow HD + D$$
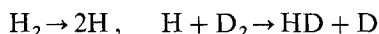
was considered to be ruled out on kinetic grounds. An exhaustive search by *ab initio* techniques [23–25] for any four-center transition state which lies below the energy required for the atomic exchange mechanism has never revealed such a transition state. It now appears unlikely that such a transition state will be found.

The reason for the instability of square planar H_4 is evident from inspection of Fig. 2, where the "antiaromatic" nature of the occupied H_4 orbitals is shown. By contrast, H_6 appears stable and this led the author to propose the possibility that the exchange reaction proceeds through a *six-center* transition state [26]. DZ calculations on the energy of H_2, H_4, and H_6 showed $E(H_4) - 2E(H_2) = 156$ kcal/mole, i.e. H_4 is a high energy form, but $E(H_6) - 3E(H_2) = 90$ kcal/mole, which is below the dissociation energy of H_2. The reaction was studied along both concerted termolecular and two-step bimolecular paths. In each case the relatively low energy of H_6 was the essential part of the mechanism. Thus, the hydrogen rings show useful analogies to the hydrocarbon rings, a fact which follows from their symmetry-determined orbital energy patterns. Although the true mechanism of this reaction must still be considered to be in doubt, some recent molecular beam results [49] on reactions of this type lend support to the idea of a 6-center transition state.

4. Nitrogen Rings

Using a system of hybrid orbitals common to both nitrogen and carbon, the nitrogen rings and their organic analogues are shown in Fig. 3. Because the two systems are isoelectronic and isosymmetric, their MO energy level diagrams will be quite similar. Where the form of the MO's is completely symmetry determined, as is the case for the *pi*-MO's, the pattern must be identical. By analogy, then, N_3^+ and N_6 should form stable aromatic systems whereas N_4, like C_4H_4, should be antiaromatic and unstable. However, N_2 is the stable form of nitrogen and obviously a closer examination is in order.
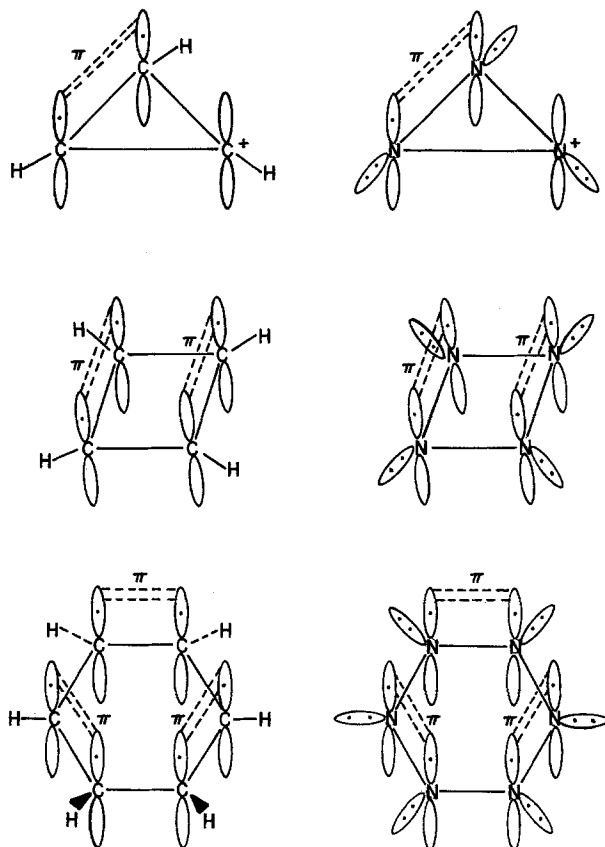
Fig. 3. N_3^+, N_4, and N_6 and their organic analogues cyclopropenyl$^+$, cyclobutadiene, and benzene

An extensive study of these rings [27] led to the following conclusions (energies and optimized distances appear in Table 1):

1) Although the most stable form of N_3^+ is linear and asymmetric [28], there is a secondary minimum for cyclic N_3^+.

2) N_4 is highly destabilized relative to two molecules of N_2. In a DZ basis, the observed order of stability is

$$2N_2 > N_2 + 2N > \text{tetrahedral } N_4 > \text{square } N_4.$$
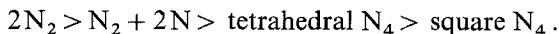
Relative energies in hartree are $2N_2$ (0.0); tetrahedral (0.436), square planar triplet (0.488). The N_4 species lie above the dissociation energy of N_2 (0.360 hartree).

3) N_6 lies 0.240 hartree above $3N_2$ in a SZ basis and shows some stabilization relative to N_4 in the same basis.

4) SZ basis sets appear to seriously overestimate the stability of the small rings, when compared to DZ calculations. For example, for N_4 in an SZ basis relative energies are $2N_2$ (0.0), rectangular singlet (0.204), square planar triplet (0.214), tetrahedral (0.218).

These results can be understood by considering the nature of the bonds $N \equiv N$, $N = N$, and N–N. The extremely stable triple bond, and rather unstable double and single bonds have been explained [29, 30] on the basis of lone pair repulsions, e.g. as in diimide (I) and hydrazine (II).

In fact the ground state geometry of I is trans [46] and of II is skewed [47]; for these geometries the lone pair repulsions are clearly lessened but apparently still quite destabilizing (thus leading to weakened double and single bonds). In this regard, it is striking that protonation of N_2H_4 to produce $N_2H_5^+$, followed by another protonation to give the $N_2H_6^{++}$ ion leads to a series of bond distances which are 1.47, 1.45, and 1.42 Å respectively [43], apparently due to the lessening of lone-pair repulsive effects on protonation. This effect of the sigma-system apparently swamps the more modest energy effect coming from the stability, or lack of it, in the *pi*-system. Nevertheless, the secondary minimum for cyclic N_3^+ and the relative stability of N_6 compared to N_4 can be understood by reference to the hydrocarbon analogues.

Since the cyclobutadiene molecule is expected to be more stable in its rectangular singlet rather than square triplet form, we might look for a similar stabilization in rectangular N_4. However, the SZ calculations show a stabilization of only 0.01 hartree relative to the square triplet. Thus a DZ calculation on rectangular N_4 would be expected to give an energy ca. 0.48 hartree above $N_2 + N_2$. The lack of CH bonding, or, alternatively, the presence of interacting lone pairs in the sigma-system, leads to a significant destabilization in cyclic N_4 relative to cyclobutadiene [27, 41].

It was predicted by Longuet-Higgins and Orgel [31] that cyclobutadiene would be stabilized by interaction with a transition metal, primarily through a stabilizing interaction with the degenerate *pi* non-bonding orbital on C_4H_4 and the metal *d*-orbitals. The subsequent synthesis of cyclobutadieneiron tricarbonyl by Pettit and coworkers [32] verified this hypothesis. It has been proposed by Shusturovich *et al.* [33, 34] that a complex of the form


may have exceptional stability, and could be involved in the fixation of molecular nitrogen. Since the *pi*-orbitals are essentially identical with those in cyclobutadiene (although slightly lower in energy), the argument is well-founded. However, the results given in this paper on N_4 render it unlikely that such a complex could achieve sufficient stability through this interaction to overcome the inherent instability of the N_4 ring.

5. Oxygen Rings

The relationship between ozone and cyclopropane was discussed by Buenker and Peyerimhoff [3]. The existence of a double minimum in the bending potential for ozone has been shown by several authors [4–7], where one form corresponds to the cyclic (60°) molecule and a second form to the bent ($\sim 116°$) geometry. Again, the SZ calculations drastically overemphasize the ring stability [5] but the DZ calculations predict an energy almost competitive with that of bent ozone [4, 6, 7]. The chemistry of ozone has been discussed on this basis [5, 6].

The cyclization of ozone involves an orbital crossing from an occupied *pi* non-bonding orbital to an occupied sigma bonding orbital. This can be seen, in reverse direction, to be analogous to the ring opening of cyclopropane to produce a trimethylene diradical (below):
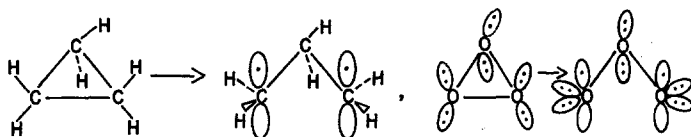
Although bent ozone is stable and trimethylene is not, there should be an activation energy for each process. SZ calculations by Salem and coworkers [9, 10] on cyclopropane for the process indicated give a barrier height of 0.083 hartree, while for cyclic → bent ozone the barrier height is 0.134 hartree in a SZ calculation [5], 0.050 hartree in a DZ calculation [4]. The analogy is useful for understanding the electronic changes in the reaction, as shown in more detail by Buenker and Peyerimhoff [3, 48].

It may be noted here that optimized SZ calculations [5] predict cyclic ozone to be 48 kcal/mole *more* stable than bent ozone, while in a CNDO/2 calculation [7] cyclic ozone is preferred by 300 kcal/mole! A GVB calculation [6] favors the bent species by approximately 35 kcal/mole, whereas a DZ calculation favors bent ozone by ca. 10 kcal/mole [4, 7]. It is probable that calculations beyond the Hartree-Fock limit would further favor the bent form, since in that geometry CI will be more important due to the presence of low lying vacant orbitals [5, 44].

The O_4 molecule is isoelectronic with cyclobutane and may therefore possess an energy minimum in the square planar form. All experimental measurements on O_4 [35–37] suggest that it is a loosely bound dimer of O_2, consisting of two slightly perturbed O_2 molecules of ill-defined geometry. More to the present interest is the observation of the isotopic exchange reaction $^{16}O_2 + ^{18}O_2 \rightarrow 2\,^{16}O-^{18}O$ in shock tube studies [38, 39], the mechanism of which may be either atomic, via dissociation of O_2 and then $^{16}O + ^{18}O_2 \rightarrow ^{16}O-^{18}O + ^{18}O$, or molecular, via a four center transition state. The experimental data show that a molecular mechanism is preferred [38]. We report here calculations on the stability of the four membered ring O_4, to test the feasibility of the exchange pathway through this structure.

Results for a square planar ring are given in Table 1. Once again the SZ calculations favor the ring relative to the DZ calculations, and by a substantial

Table 2. Molecular orbitals of cyclobutane and O_4 (D_{4h} symmetry)

Orbital symmetry	Orbital type	C_4H_8 orbital energy (eV)[a]	O_4 orbital energy (eV)[b]
$1a_{1g}$	$1s$	-304.850	-562.068
$1e_u$	$1s$	-304.849	-562.076
$1b_{2g}$	$1s$	-304.847	-562.079
$2a_{1g}$	σ	-29.539	-44.387
$2e_u$	σ	-23.678	-35.305
$2b_{2g}$	σ	-19.504	-25.835
$1a_{2u}$	π_b	-17.287	-18.688
$3a_{1g}$	σ	-16.712	-17.202
$1e_g$	π_{nb}	-14.133	-13.507
$1b_{1g}$	σ	-12.715	-17.893
$1b_{1u}$	π_{ab}	-11.624	-8.941
$3e_u$	σ	-11.050	-12.677
$2a_{2u}$	π^*	$+13.972$	none
$4e_u$	σ^*	$+15.194$	$+9.390$
$4a_{1g}$	σ^*	$+16.699$	none
$1a_{2g}$	σ^*	$+17.036$	$+13.175$
$2e_g$	π^*	$+18.895$	none
$5e_u$	σ^*	$+19.289$	none
$3b_{2g}$	σ^*	$+19.926$	$+13.469$
$2b_{1u}$	π^*	$+23.567$	none
$4b_{2g}$	σ^*	$+24.005$	none

[a] Reference [11].
[b] $1s = 7.66$, $2s = 2p = 2.28$, $r = 2.67$ bohr.

amount. Ignoring the question of correlation energy problems due to the open shell in O_2, simple subtraction in the same basis set gives; for $2O_2 \rightarrow O_4$,

$$\Delta E(SZ) = -298.1081 - 2(-149.0825) = 0.0567 \text{ hartree} = 36 \text{ kcal/mole},$$

$$\Delta E(DZ) = -298.9546 - 2(-149.5623) = 0.170 \text{ hartree} = 107 \text{ kcal/mole}.$$

Both calculations show an O_4 energy below that of the experimental O_2 dissociation energy, 118 kcal/mole [40]. It was found that distortion of the O_4 molecule along the normal modes of the square [11] leads to an increase in the total energy along each mode, so the square form represents a potential minimum, not a transition state (SZ basis). The magnitude of the barrier to be overcome during the decomposition of cyclic O_4, and hence its computed stability, will be the subject of a future publication (which will include a search for the lowest energy exchange pathway).

The extent of the analogy between O_4 and C_4H_8 can be seen by inspection of the orbital energies obtained in a SZ calculation for each. These orbitals and their symmetry designations in D_{4h} [11] are shown in Table 2. The oxygen orbitals are of course shifted to lower energy. The ordering is generally parallel, except that the π_{nb} (pi non-bonding, not shown) and π_{ab} (pi antibonding, below) orbitals in

O_4 are destabilized relative to the corresponding orbitals in C_4H_8 ($1e_g$ and $1b_{1u}$ orbitals, Table 2). This same effect

C$_4$H$_8$ ($1b_{1u}$)   O$_4$ ($1b_{1u}$)
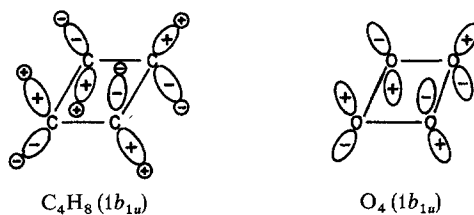
was observed in a study of C_4H_4 [41], where it was shown that the H-atoms play an important role in stabilizing the σ_{cc} antibonding molecular orbitals. No such possibility exists in O_4, and the $1b_{1u}$ MO, at -8.94 eV, lies well above the rest.

6. Other Rings

These arguments can be readily extended to mixed rings and larger systems. For example, the hypothetical molecules N_3H_3 and N_4H_4 are isoelectronic with C_3H_6 and C_4H_8 and may be expected to show minima for comparable geometries (below):

III   IV

V   VI
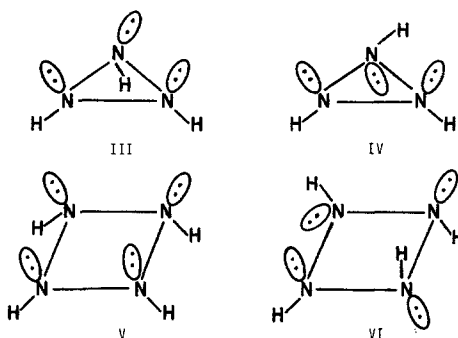
Structures III–V exhibit strong lone pair repulsions but VI should be relatively favored. However, the very weak single bond in hydrazine, which can also adopt a comparable geometry (below), renders all of these structures unstable. Why hydrazine,

bond energy = 38 kcal/mole,
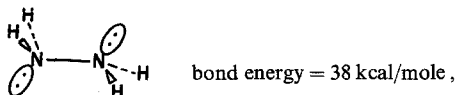
and also diimide, both of which can minimize lone pair repulsions by adoption of the trans structure, should be so unstable remains an interesting unsolved problem. The simple picture of lone pair-repulsions is insufficient, and one would like to know the extent of the lone pair-bond pair interaction.

A mixed 6-membered ring, trioxymethylene (VII, below) is isoelectronic with cyclohexane and probably exists in the chair conformation also. This ring forms in a low activation energy

$$VII \qquad VIII \qquad IX$$
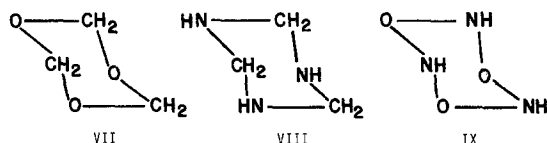
concerted polymerization involving three monomers of formaldehyde [42]. An analogous possibility for a nitrogen substituted system suggests itself (VIII) or even a mixed HNO system (IX), but in these cases the monomers $H_2C{=}NH$ and $HN{=}O$ are unstable and the reactions have not been observed.

7. Summary and Conclusions

By analogy with hydrocarbon rings through the establishment of a) isoelectronic, and b) isosymmetric criteria, one can discuss the stability of some hypothetical, but potentially observable molecules. Thus O_3 exists as a secondary minimum in cyclic form and O_4 could be involved in isotopic exchange; cyclic N_3^+ and N_6 show signs of stability whereas N_4 is very unstable; H_3^+ and H_6 are favored while H_4 is not, and extensions may be made to larger systems. The effect of lone pair repulsions reduces the stability of nitrogen and oxygen rings, which may nevertheless exist as minima or transition states in the reactions discussed. The presence of NH and OH bonds will serve to reduce these high energies by stabilizing the framework antibonding orbitals [41], and protonation of lone pairs can also add a stabilizing effect.

References

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