On the Stability of the Tetramers of Carbon Monoxide, Hydrogen Isocyanide, and Vinylidene. A Molecular Orbital Theoretical Rationalization

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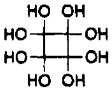
Semiempirical extended-Hückel and *ab initio* molecular orbital calculations at the correlated second-order Møller-Plesset (MP2) level of theory predict that the ground state electronic configuration of tetraoxocyclobutane (**3**) is different from those of its congeners [4]radialene (**5**) and tetraiminocyclobutane (**4**). In the singlet ground state of **3**, only three out of the four σ MOs describing the C−C σ bonds of the cyclobutane ring are occupied, while in the case of **4** and **5**, all four C−C σ MOs are occupied. By going from **5** to **3**, an electron density shift from the cyclobutane carbon atoms to the terminal C, N, and O atoms is observed. The calculated total natural orbital population for the cyclobutane carbon atoms diminishes from 4.01 (**5**) to 3.78 (**4**) and 3.64 (**3**). The MP2/6-31G*+ZPVE//MP2/6-31G* (ZPVE: zero-point vibrational energy) *ab initio* calculations predict that four CO molecules are more stable than the tetramer **3** by 32.8 kcal/mol. For **4** and **5**, however, the tetramers are more stable than four $^1\Sigma_g^+$ CNH or four $^1A_1$ CCH_2 by 61.6 and 322.3 kcal/mol, respectively. Furthermore, on the C_8H_8 energy surface, the $^1A_{1g}$ ground state of **5** lies 122.4 kcal/mol below four $^1\Sigma_g^+$ C_2H_2 molecules.

Introduction

Tetraoxocyclobutane (**3**) is unknown, and attempts to prepare this species have led at most to the isolation of its tetrahydrate **1** or to the squaric acid **2** and the squarate ion $\mathbf{3}^{2-}$.[1,2] However, its imino derivatives **4** and [4]radialene (**5**) are stable molecules.[3−5]



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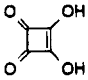

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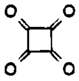

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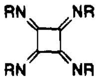

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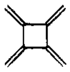

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In this paper, we provide a simple rationale for these differences based on the electronic structure of these species and compare its stability on the basis of detailed *ab initio* calculations. In the case of **4**, the calculations were carried out for the tetramer of hydrogen isocyanide.

Qualitative Considerations

To discuss the electronic structure of **3** and **4**, we start with that of [4]radialene (**5**). The frontier orbitals of **5** can be described as four C−X (X = CH_2) σ bonds, four C−C σ MOs localized along the ring, the familiar Walsh orbitals of cyclobutane,[6] four π MOs, and four π^* MOs. For clarity, only three of them, the LUMO, the HOMO, and one of the Walsh type orbitals, are shown in Figure 1.

Substitution of all four CH_2 groups by oxygen atoms produces two effects: (a) the π and the π^* MOs are stabilized and (b) the C−C σ MOs are destabilized considerably. According to the basic principles of the first-order perturbation MO theory,[7] the first effect is mainly due to the higher electronegativity (3.5) of oxygen as compared to carbon (2.5).[8] It affects all π MOs and also to a small extent the C−O σ MOs (see Table 1). The large destabilization of C−C σ MOs is due to a stronger antibonding interaction of the 2p lone pair type orbitals at the oxygen atoms with the C−C σ skeleton as compared to the C−C and C−H interactions in **5**. As a net effect, it results in a crossing between the a_{2u} ($1\pi^*$) and the b_{2g} (4σ) level. As a result, only three out of the four σ MOs describing the C−C σ bonds in the four-

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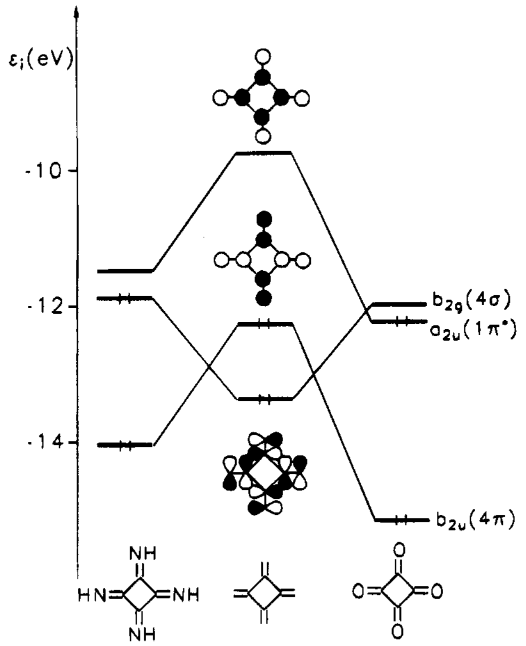

Figure 1. Correlation between the frontier orbital energies of **3**–**5**. The values are derived from an extended-Hückel calculation.

Table 1. Sum of the One-Electron Energies (eV) for the C–C and C–X^a σ MOs and for the C–X^a π MOs of 3 and 4 Relative to Those of 5 (Extended-Hückel Results)

compd	$\sum_{i=1}^{4} \epsilon_i\sigma(C-C)$	$\sum_{i=1}^{4} \epsilon_i\sigma(C-X^a)$	$\sum_{i=1}^{4} \epsilon_i\pi(C-X^a)$
3	+28.6	−0.2	−8.8
4	+3.5	−4.2	−5.0
5	0.0	0.0	0.0

[a] X = O (**3**), NH (**4**), CH_2 (**5**).

membered ring are occupied. The result is a weakening of the C–C bonds in **3** and, furthermore, a small HOMO–LUMO gap (Figure 1). The replacement of all four CH_2 groups of **5** by four NH moieties has much smaller effects on the π stabilization and σ (C–C) destabilization (see Table 1 and Figure 1). Again this is due to a smaller value for the electronegativity of nitrogen (3.0)[8] and to smaller repulsive interactions between the lone pairs on nitrogens and the σ Walsh type orbitals. These smaller effects reduce only the HOMO–LUMO gap in **4** but maintain the same MO configuration as in **5** (see Figure 1, left side). Thus, for **4** and **5**, one can expect a singlet ground state with a configuration of $(4\pi)^2(4\sigma)^2(1\pi^*)^0$ (denoted later as *S*1) and for **3** a singlet $(4\pi)^2(1\pi^*)^2(4\sigma)^0$ (denoted later as *S*2) or a triplet $(4\pi)^2(4\sigma^1)(1\pi^*)^1$. If for the bonds localized along the cyclobutane ring one assumes that a σ bond contributes more to the stabilization than a π bond, then both possible ground state configurations of **3** should be energetically less favorable than those of **4** and **5**. In the next section, we discuss the stability of **3**–**5** on the basis of *ab initio* calculations.

Ab Initio Calculations on 3, 3^{2-}, 4, and 5

Computational Details. All calculations were carried out with a 6-31G* basis using the Gaussian 92 system of programs.[9] The geometries of the lowest singlet and triplet states of **3**–**5** were gradient-optimized at the Hartree–Fock (HF) and at the correlated second-order Møller–Plesset (MP2) levels of theory. We note that, during geometry optimizations, the singlet $^1A_{1g}$ (S2) of **5** converges to $^1A_{1g}$ (S1) and the lowest triplet state is $^3B_{1g}$ $((4\sigma)^2(4\pi)^1(1\pi^*)^1)$. For $\mathbf{3}^{2-}$, we have only optimized the geometry of its ground state $^1A_{1g}$ $((4\pi)^2(4\sigma)^2(1\pi^*)^2)$. The geometry optimizations were performed under D_{4h} (**3**, $\mathbf{3}^{2-}$, and **5**) and C_{4h} (**4**) symmetry constraint. In order to check the stationarity of the structures and to obtain vibrational frequencies together with zero-point vibrational energy (ZPVE), the HF/6-31G*//HF/6-31G* and MP2/6-31G*//MP2/6-31G* equilibrium geometries of the lowest states were used for analytical calculations of the Hessian matrices. For estimation of the stability of the tetramers **3**–**5** with respect to the four monomers, reference data for the CO $(^1\Sigma_g^+)$, CNH $(^1\Sigma_g^+)$, and CCH_2 $(^1A_1)$ molecules were calculated. In addition, we have calculated the reference data for hydrogen cyanide and acetylene, the more stable isomers of hydrogen isocyanide and vinylidene, respectively. The HF and MP2 total and relative energies are collected in Table 2. Optimized geometrical parameters are presented in Table 3. ZPVE, stabilization energies, and harmonic frequencies are given in Tables 4 and 5. Table 6 summarizes the results of natural population analysis (NPA).[10]

Results and Discussion

Relative Energies. The HF/6-31G*//HF/6-31G* results predict the singlet S1 as a ground state of **3**, **4**, and **5** (Table 2). The frequency calculations confirm the stationarity (no imaginary frequencies were detected) of the singlets S1 on the SCF potential energy surface (Table 4).

The lowest excited state is a triplet with an energy of 9.7 (**3**), 69.2 (**4**), and 33.9 (**5**) kcal/mol above the ground states. At the HF/6-31G*+ZPVE//HF/6-31G* level, the tetramers **4** and **5** are more stable than four monomer molecules by 24.4 (**4**) and 321.0 (**5**) kcal/mol. In the case of **3**, however, four CO molecules are more stable by 98.5 kcal/mol. This large difference makes an experimental detection of the C_4O_4 tetramer very unlikely. Some years ago, Reine *et al.* discussed the stability of the dimer structures C_2O_2 and C_2S_2.[11] For both molecules, the $^3\Sigma_g^-$ electronic state was detected as a minimum on the respective potential energy hypersurface, with an energy that lies below the lowest spin-allowed dissociation limit, $^1\Sigma_g^+ + {}^3\Pi$. We note that a $^3\Pi$ CO lies 139 kcal/mol above the $^1\Sigma_g^+$ ground state.[12] Taking into account that for **3** the HF/6-31G*//HF/6-31G* singlet–triplet energy difference is only 9.7 kcal/mol, a correct description of the ground state electronic structure (*i.e.* singlet *vs* triplet) is necessary for the discussion of the possible spin-allowed dissociation path. It is well-known that the post-SCF methods where correlation effects are included into the calculation procedures are better suited to predict the relative energies of the particular electronic states. Accordingly, we have repeated the geometry optimizations for the lowest states of **3**–**5** and $\mathbf{3}^{2-}$ at the MP2

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Table 2. Total and Relative Energies of the Lowest Singlet and Triplet States of the Tetramers 3–5 and of Their Monomers CO, CNH, and CCH_2 as Well as of the Isomers HCN and C_2H_2[a]

		HF/6-31G*//HF/6-31G*			MP2/6-31G*//MP2/6-31G*		
compd	state	E_T	E_{rel}	Δ^b	E_T	E_{rel}	Δ^b
3	$^1A_{1g}$ (S1)	−450.811 247	0.0	+88.0	−452.006 219	+25.7	
	$^3B_{1u}$	−450.795 813	+9.7		−452.002 010	+28.4	
	$^1A_{1g}$ (S2)	−450.708 345	+64.6		−452.047 212	0.0	+23.6
CO	$^1\Sigma_g^+$	−112.737 877			−113.021 215		
4	^1A_g (S1)	−371.489 892	0.0	−43.0	−372.621 815	0.0	−75.1
	^3B_u	−371.379 610	+69.2		−372.531 424	+56.7	
	^1A_g (S2)	−371.211 180	+174.9		−372.513 785	+67.8	
CNH	$^1\Sigma_g^+$	−92.855 328			−93.125 542		
5	$^1A_{1g}$ (S1)	−307.487 649	0.0	−272.4	−308.488 283	0.0	−342.6
	$^3B_{1g}$	−307.433 564	+33.9		−308.387 230	+63.4	
	$^3B_{1u}$	−307.244 084	+152.8		−308.250 638	+149.1	
CCH_2	$^1A_1$	−76.763 395			−76.985 574		
HCN	$^1\Sigma_g^+$	−92.875 197			−93.158 944		
C_2H_2	$^1\Sigma_g^+$	−76.817 826			−77.066 794		

[a] Total and relative energies are in hartrees and kilocalories per mole, respectively. [b] $\Delta = E_T(C_4X_4) - 4E_T(CX)$: X = O (**3**), NH (**4**), and CH_2 (**5**).

Table 3. Optimized Structural Parameters of the Tetramers 3–5 and of the Monomer Molecules[a]

		HF/6-31G*//HF/6-31G*					MP2/6-31G*//MP2/6-31G*				
compd	state	C–C	C–X[b]	X–H[b]	HXC[b]	XCC[b]	C–C	C–X[b]	X–H[b]	HXC[b]	XCC[b]
3	$^1A_{1g}$ (S1)	1.551	1.173			135.0	1.560	1.215			135.0
	$^3B_{1u}$	1.550	1.168			135.0	1.561	1.192			135.0
	$^1A_{1g}$ (S2)	1.571	1.151			135.0	1.521	1.216			135.0
3^{2-}	$^1A_{1g}$	1.467	1.241			135.0	1.493	1.268			135.0
4	^1A_g (S1)	1.513	1.244	1.008	111.3	138.0	1.512	1.278	1.031	109.2	138.9
	^3B_u	1.517	1.241	1.002	118.7	138.5	1.510	1.253	1.021	118.1	131.1
	^1A_g (S2)	1.542	1.213	0.991	135.7	138.9	1.489	1.276	1.013	128.1	138.5
5	^1A_g (S1)	1.497	1.319	1.075	121.5	135.0	1.493	1.341	1.086	121.4	135.0
	$^3B_{1g}$	1.435	1.393	1.074	121.1	135.0	1.456	1.371	1.084	121.3	135.0
	$^3B_{1u}$	1.528	1.330	1.076	121.2	135.0	1.510	1.322	1.090	122.0	135.0
CO	$^1\Sigma_g^+$		1.114					1.151			
CNH	$^1\Sigma_g^+$		1.154	0.985	180.0			1.187	1.003	180.0	
CCH_2	$^1A_1$		1.294	1.077	120.2			1.309	1.088	120.4	
HCN	$^1\Sigma_g^+$		1.133	1.059	180.0			1.177	1.069	180.0	
C_2H_2	$^1\Sigma_g^+$	1.185		1.057			1.217		1.066		

[a] Distances are given in angstroms and bond angles in degrees. [b] X = O (**3** and **3^{2-}**), N (**4**), and C (**5**).

Table 4. Calculated Zero-Point Vibrational Energy (ZPVE) and Stabilization Energy (Δ) of the Ground State Tetramers C_4X_4 with Respect to Four Ground State Monomers CX[a]

		HF/6-31G*//HF/6-31G*			MP2/6-31G*//MP2/6-31G*		
compd	state	*i*	ZPVE	Δ^b	*i*	ZPVE	Δ^b
CO	$^1\Sigma_g^+$	0	3.49		0	3.03	
3	$^1A_{1g}$ (S1; D_{4h})	0	24.45	+98.5	0	21.26	+58.5
3	$^1A_{1g}$ (S2; D_{2d})	3[c]			0	21.28	+32.8
CNH	$^1\Sigma_g^+$	0	9.93		0	9.87	
4	^1A_g (S1)	0	58.39	−24.4	0	53.0	−61.6
CCH_2	$^1A_1$	0	16.39		0	15.16	
5	$^1A_{1g}$ (S1)	0	87.15	−321.01	0	80.9	−322.3
HCN	$^1\Sigma_g^+$	0	11.29		0	9.99	
C_2H_2	$^1\Sigma_g^+$	0	18.48		0	16.15	

[a] X = O (**3**), NH (**4**), and CH2 (**5**). All values are given in kilocalories per mole. [b] $\Delta = E_T(C_4X_4) - 4E_T(CX)$ corrected for ZPVE. [c] $^1A_{1g}$ (S2; D_{4h}) value.

level of theory. In the case of **4** and **5**, the MP2/6-31G*+ZPVE//MP2/6-31G* results confirm the singlets S1 as local minima on the MP2 energy surface lying 61.6 (**4**) and 322.3 kcal/mol (**5**) below the dissociation limits 1 and 2, respectively.

$$^1A_g\ (\mathrm{S1}):\ (\mathrm{CNH})_4 \rightarrow 4\,^1\Sigma_g^+\ \mathrm{CNH} \qquad (1)$$

$$^1A_{1g}\ (\mathrm{S1}):\ (\mathrm{CCH_2})_4 \rightarrow 4\,^1A_1\ \mathrm{CCH_2} \qquad (2)$$

The dissociation products from eqs 1 and 2, the hydrogen isocyanide and vinylidene, have been studied extensively, both, experimentally[13,14] and theoretically.[15,16] The MP2/6-31G*+ZPVE//MP2/6-31G* calculations predict that hydrogen cyanide, HCN, lies 20.8 kcal/mol below the local minimum of the CNH molecule. This value can be compared to the experimental data obtained by Ellison and co-workers.[13d] These authors suggest that CNH lies somewhere between 17.2 and 26.5 kcal/mol above HCN enthalpy. We note that values between 10 and 15 kcal/

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Table 5. Comparison of Harmonic Vibrational Frequencies (cm^{-1}) Calculated at the MP2/6-31G*//MP2/6-31G* Level with Available Experimental Data[a]

		3^{2-}			5		
symmetry	selection rule	normal vibration	calcd	ref 20	normal vibration	calcd[b]	ref 21
		ν_1	1817	1794	ν_1	3013	2988
A_{1g}	R(p)	ν_2	693	723	ν_2	1684	1681
					ν_3	1410	1434
					ν_4	670	683
A_{1u}	inactive				ν_5	678(0)	
A_{2g}	inactive	ν_3	835(0)		ν_6	3097(0)	
A_{2g}	inactive				ν_7	1063(0)	
					ν_8	503(0)	
A_{2u}	IR	ν_4	255(27)	259	ν_9	821(176)	894
					ν_{10}	189(6)	210
		ν_5	1666	1594	ν_{11}	3011	3020
B_{1g}	R(dp)	ν_6	620	647	ν_{12}	1621	1662
					ν_{13}	1363	1390
					ν_{14}	565	600
B_{1u}	inactive				ν_{15}	595(0)	
		ν_7	1048	1123	ν_{16}	3099	3084
B_{2g}	R(dp)	ν_8	251	294	ν_{17}	1186	1195
					ν_{18}	846	857
					ν_{19}	216	237
		ν_9	508(0)		ν_{20}	803(0)	
B_{2u}	inactive	ν_{10}	73(0)		ν_{21}	499(0)	
					ν_{22}	50(0)	
		ν_{11}	637	662	ν_{23}	808	891
E_g	R(dp)				ν_{24}	730	751
					ν_{25}	304	357
		ν_{12}	1647(1123)	1530	ν_{26}	3098(9)	3082
		ν_{13}	1088(31)	1090	ν_{27}	3012(5)	3031
		ν_{14}	308(3)	350	ν_{28}	1607(0)	
E_u	IR				ν_{29}	1387(16)	1409
					ν_{30}	1127(6)	1160
					ν_{31}	786(1)	805
					ν_{32}	242(1)	265

[a] IR intensities (km/mol) are given in parentheses. [b] Scaled by a factor of 0.94.

Table 6. Total Occupancy of the Valence In-Plane (σ) and π Natural Orbitals of C and X in the MP2 Ground-States of 3–5

	3 (X = O)	**4** (X = N)	**5** (X = C)
C (cor)	1.999	1.999	1.999
σ: C (2s, $2p_x$, $2p_y$)	2.676	2.879	3.013
π: C ($2p_z$)	0.962	0.896	1.000
X (cor)	1.999	1.999	1.999
σ: X (2s, $2p_x$, $2p_y$)	4.719	4.396	3.362
π: X ($2p_z$)	1.503	1.088	0.982

mol were also suggested on the basis of either experiments[13a–c] or quantum chemical calculations.[15] In the case of **4**, our MP2/6-31G*+ZPVE//MP2/6-31G* calculations predict that four HCN molecules are more stable than the tetramer. Thus, **4** cannot be characterized to be the absolute minimum on the energy surface, lying 21.8 kcal/mol above the global minimum of four isolated $^1\Sigma_g^+$ HCN molecules. For vinylidene, the isomer of the well-known acetylene, quantum chemical calculations predict that both molecules are local minima on their potential energy surface.[16] Nevertheless, vinylidene should rather be considered as the effective transition structure for the experimentally known degenerate rearrangement in which the two hydrogen atoms of acetylene change places.[17] The experimental energy barrier for this rearrangement is not known; the theory predicts values between 0.9 and 8.1 kcal/mol depending on the calculation method.

The MP2/6-31G*+ZPVE//MP2/6-31G* results predict that acetylene is more stable by 50.0 kcal/mol. The negative ion photoelectron spectroscopic and gas phase proton transfer kinetic studies of Ervin *et al.*[14f] yielded for the acetylene–vinylidene isomerization energy a result of 47.4 ± 4 kcal/mol. For **5**, our MP2/6-31G*+ZPVE//MP2/ 6-31G* results predict that tetramethylenecyclobutane is also more stable than four acetylene molecules. Thus, on the C_8H_8 energy surface,

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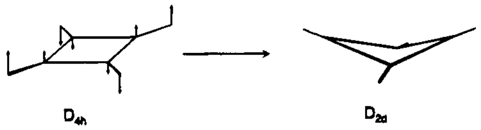
5 can be characterized as a deep local minimum lying 122.4 kcal/mol below the dissociation limit from eq 3.

$$^1A_{1g}(S1)\text{: } (CCH_2)_4 \rightarrow 4\,^1\Sigma_g^+\ C_2H_2 \qquad (3)$$

In the case of tetraoxocyclobutane (**3**), the MP2/6-31G*//MP2/6-31G* results predict the singlet $^1A_{1g}$ (S2) as the ground state of **3** whose energy is 28.4 kcal/mol lower than that of the $^1A_{1g}$ (S1) state (Table 2). Surprisingly, these results are very close to the qualitative description from the first section. However, the vibrational analysis shows one imaginary b_{2u} mode (21i cm^{-1}), suggesting that $^1A_{1g}$ (S2) of **3** is a transition state on the potential energy surface. An examination of the normal coordinates corresponding to this b_{2u} mode suggests a distortion from D_{4h} to D_{2d} symmetry (see below).



Consequently, we have reoptimized the singlet S2 of **3** in D_{2d} symmetry. The calculated energy lowering and the changes in the bond distances were minute, but the D_{2d} $^1A_1$ (S2) of **3** has all real frequencies and is a local minimum on the MP2 potential energy surface. Nevertheless, the MP2/6-31G*+ZPVE//MP2/6-31G* calculations predict that **3** lies 32.8 kcal/mol above the dissociation limit (eq 4).

$$D_{2d}\text{: } ^1A_1\ (S2)\ C_4O_4 \rightarrow 4\,^1\Sigma_g^+\ CO \qquad (4)$$

Furthermore, we have performed frequency calculations for the D_{4h} $^1A_{1g}$ (S1) state of **3**, and no imaginary frequencies were detected. Thus, the D_{4h} $^1A_{1g}$ (S1) state of **3** also represents a local minimum on the potential energy surface whose energy lies 58.5 kcal/mol above the dissociation limit (eq 5).

$$D_{4h}\text{: } ^1A_{1g}\ (S1)\ C_4O_4 \rightarrow 4\,^1\Sigma_g^+\ CO \qquad (5)$$

We notice that similar conclusions were found for the ground states of C_2O_2 and C_6O_6 molecules.[11,18] Both HF and MP2 calculations exclude the triplet as a ground state of **3**. The failure of tetraoxocyclobutane to display a ground state electronic structure more stable than four ground state carbon monoxide may be attributed to the extreme stability of the isolated CO molecules. The C≡O molecule with a dissociation energy of 256 kcal/mol incorporates the strongest known chemical bond.[12] Furthermore, if we take into account the standard value of the third bond in C≡O (77 kcal/mol),[19] which should be broken to form tetraoxocyclobutane, it seems to be impossible to detect the C_4O_4 tetramer in experiments starting with free CO molecules, and other strategies are necessary to possibly reach this goal.

Molecular Geometries and Vibrational Frequencies. The molecular structures of $\mathbf{3}^{2-}$, **4**, and **5** are known from experimental investigations.[1g,3e,4,5] Although the X-ray data of $C_4O_4K_2{\cdot}H_2O$[1g] predict two distinct bond lengths for the C−C and C−O bond distances, a D_{4h} structure was assumed for $\mathbf{3}^{2-}$ with mean C−C and C−O distances of 1.457 and 1.259 Å, respectively. An analysis of the vibrational spectrum confirmed the D_{4h} structure of $\mathbf{3}^{2-}$. The investigations by Ito and West[20] showed that only the D_{4h} model gives a reasonable fit with the experimental data. The force constants calculated by Ito and West suggest longer bond distances than the X-ray mean values. We notice that the MP2/6-31G*//MP2/6-31G* C−C and C−O bond lengths are 1.493 and 1.268 Å, respectively. In Table 5, we compare the calculated MP2/6-31G*//MP2/6-31G* harmonic frequencies with the experimental values. To our knowledge, these are the first *ab initio* values for the vibrations in $\mathbf{3}^{2-}$. The agreement between theoretical and experimental data is good, giving additional support for the D_{4h} structure of $\mathbf{3}^{2-}$. In the case of **4**, the tetramer $(CNH)_4$ was not yet synthesized up to now. We compare its optimized structure with the experimental X-ray data obtained for the tetramer of phenylisocyanide.[3e] The difference between experimental and MP2/6-31G*//MP2/6-31G* C−C and C−N bond distances of **4** is only 0.006 and 0.001 Å, respectively. The calculated CCN bond angle of 138.9° reproduces the experimental value of 138.3°[3e] very well. It seems that the planar C_{4h} structure of $(CNH)_4$ is correctly predicted by the MP2 calculations.

The X-ray data for the most simple [4]radialene, the tetramethylenecyclobutane (**5**), are not known, and only [4]radialenes with large substituents were characterized by the X-ray experiments.[4] Due to steric repulsion, all these [4]radialenes adopt lower than D_{4h} symmetries with either planar or puckered cyclobutane rings. The experimental values for the C−C bonds of the cyclobutane ring varied from 1.466 to 1.508 Å and those for C=C bonds from 1.292 to 1.347 Å.[4,5] We notice that the respective MP2/6-31G*//MP2/6-31G* values calculated for **5** are 1.493 and 1.341 Å (Table 3). The vibrational analysis performed for **5** showed that tetramethylenecyclobutane adopts D_{4h} symmetry.[21]

In Table 5, we compare the calculated MP2/6-31G*//MP2/6-31G* harmonic frequencies of **5** with the experimental vibrations. The calculated frequencies are scaled by a factor 0.94. The scaling factor was chosen on the basis of the comparison between the calculated harmonic frequencies for $^1A_1$ vinylidene (1272, 1708, and 3207 cm^{-1}), with the experimental values of 1165 ± 10 cm^{-1} for the CH_2 scissors, 1635 ± 10 cm^{-1} for the CC stretch, and 3025 ± 30 cm^{-1} for the CH symmetric stretch reported by Burnett *et al.*[14d] The agreement between theory and experiment is very good. Thus, theory also unquestionably confirms the D_{4h} structure of **5**.

Natural Population Analysis. The MP2/6-31G*//MP2/6-31G* C−C bond lengths in the cyclobutane ring increase from 1.493 Å (**5**) to 1.512 Å (**4**) and 1.521 Å (**3**). It is interesting to note that the optimized C−C bond length in a perfectly stable $\mathbf{3}^{2-}$ is 1.493 Å. The calculated occupancy for the σ C−C natural bond orbital (NBO) decreases from 1.93 (**4** and **5**) to 1.82 (**3**). The occupancy of the C−X (X = C (**5**), N (**4**), and O(**3**)) σ NBOs remains unchanged, while those of the C−X π NBOs increase from 1.85 (**5**) to 1.87 (**4**) and 1.94 (**3**). By going from **5** to **3**, an increasing electron density shift is observed from the cyclobutane carbon atoms to the terminal C, N, and O atoms (Table 6). Both the in-plane (σ) and π natural atomic orbitals (NAOs) participate in the electron density

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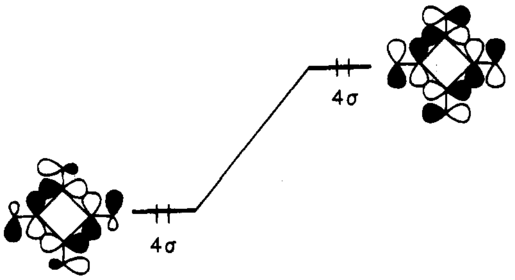
shift (Table 6). The integrated natural charge on the methylene group of **5** amounts to +0.06*e*, and those on NH and O of **4** and **3** amount to −0.16*e* and −0.29*e*, respectively. The total delocalization of electrons to the Rydberg NAOs amounts to 0.37*e* (**5**), 0.50*e* (**4**), and 0.56*e* (**3**). All the above features are in accord with the qualitative considerations from the first section. Furthermore, the lone pairs of oxygens which are able to interact with the Walsh type orbitals of the cyclobutane ring have pure p character, while those of nitrogen in **4** have 39% s and 61% p character. Consequently, the role of destabilization of the lone pairs in **3** is greater than that of those in **4** (see below).

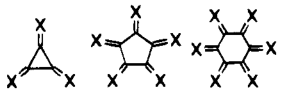


4 **3**

General Remarks

The optimized structures of **3** and 3^{2-} are close but not identical with those calculated by Radom and co-workers with STO-3G and 4−31G basis sets.[22]

In the case of **5**, HF and MP2 total energies corrected for ZPVE predict almost the same values for the stability of **5** with respect to four $^1A_1$ CCH_2 monomers (−321.0 (HF) vs −322.3 kcal/mol (MP2)) or four $^1\Sigma_g^+$ C_2H_2 molecules (−122.5 (HF) vs −122.4 kcal/mol (MP2)). For **4**, the MP2 results predict greater stability of the tetramer with respect to four $^1\Sigma_g^+$ CNH monomers than the HF results (−61.6 (MP2) vs −24.4 kcal/mol (HF)); however, the instability of **4** with respect to four $^1\Sigma_g^+$ HCN molecules is almost the same on both calculation levels (+20.1 (HF) vs +21.8 kcal/mol (MP2)). By going from HF/6-31G*+ZPVE//HF/6-31G* to MP2/6-31G*+ZPVE//MP2/6-31G* calculations, there is a relatively large decrease of the instability of the C_4O_4 tetramer with respect to four ground state monomer molecules (98.5 *vs* 32.8 kcal/mol). It is quite possible that further refinement of the theory would diminish this value. In the case of **3**, the large localization of the negative charge on oxygen atoms leads to greater electrostatic repulsion than in **4** and **5** and is responsible for the puckered ground state structure of **3**. The arguments put forward for **3** and **4** can be extended to the cyclic tri-, penta-, and hexaketones **6a**−**8a** and to their imino derivatives **6b**−**8b**. To our knowledge, the imines **6b**−**8b** are unknown.



X = O **6a** **7a** **8a**
X = NR **6b** **7b** **8b**

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