

6 π Aromaticity in Four-Membered Rings

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Abstract: 6 π aromaticity has been investigated for a number of four-membered rings by ab initio MO methods. The rings were fully optimized within the symmetry constraints. The order of the stationary points was established by calculating the harmonic frequencies of the normal modes. It is shown that carbocycles show no 6 π aromaticity, in contrast with the nitrocycles. The stability of the planar D_{nh} rings is determined by two factors: the bond strength in the ring and the stability of the planar orientation of the ring substituent. The latter is strongly influenced by 1,3 π repulsions, which result from the fact that in 6 π four-membered rings the two highest occupied π molecular orbitals are 1,2-nonbonding and 1,3-antibonding. The role of the hydrogen substituents is investigated by the inclusion of polarization functions on the ring atoms. It is found that the p_z - d hybridization reduces the electron repulsion by "bending" the π frame outward, thereby increasing the electron density above the hydrogen bond. This stimulates the out-of-plane vibrations of the hydrogen atoms as shown by smaller force constants.

Aromaticity in conjugated hydrocarbon rings has been studied extensively for more than a century.¹ In principle, aromaticity is not restricted to hydrocarbons and may well include both homo- and heterocyclic rings. Concepts of aromaticity have been successfully applied in theories of chemical structure and reactivity. Our understanding of aromatic molecules rests primarily on the $4n + 2$ π -electron criterion, known as Hückel's rule, describing the delocalization of π electrons. Recently, however, there has been some debate in literature concerning the origin of aromaticity.²⁻¹¹ Following Berry's suggestion,¹² Shaik et al.,² applying a valence-bond correlation diagram model, proposed that the π components of benzene are unstable toward localizing distortions and that the D_{6h} symmetry is imposed by the σ frame, which opposes the π propensities. In addition to ab initio quantum chemical calculations^{2,3} supporting their conclusions, the instability of hexazine (hexaazabenzene),¹³ the all-nitrogen analogue of benzene, gives a clear example of the fact that aromaticity is not simply the result of topological properties of electron count and mode of delocalization. Although the provocative model of Shaik and Hiberty has been criticized by various authors,⁶⁻⁸ similar conclusions have been reached by Stanger and Vollhardt,³ Epiotis,⁴ and Voter and Goddard.⁵ Yet another challenge to the view that π -electron delocalization is the basis of aromaticity is provided by spin-coupled valence-bond calculations by Cooper et al.¹⁴ It is argued that the aromatic characteristics of benzene arise from the symmetric coupling of electron spins around the ring and that

the π electrons are essentially localized in deformed atomic orbitals.

Related to its origin is the definition of aromaticity.¹ Besides chemical and thermal stability, several criteria have been envisaged to distinguish between aromatic and nonaromatic compounds, e.g., ring currents, diatropicity in the ¹H NMR spectrum or bond distance equalization.¹⁵ Many of the experimental comparisons that are used for elucidating or describing aromaticity are, however, not conclusive since they critically depend on the choice of an appropriate reference structure or are very often not applicable to heterocyclic or inorganic molecules. Likewise, a variety of theoretical approaches has been advanced.¹⁶⁻²⁰ Most of them concentrate on the calculation of resonance energies, based on the additivity of bond energies in acyclic polyenes^{16,17} or graph theoretical considerations.¹⁸⁻²⁰ Very recently, Zhou and Parr introduced the absolute and relative hardness, related to the HOMO-LUMO gap as a criterion for aromaticity.²¹ It is clear that aromaticity is a complex phenomenon that cannot be explained by a single indicator. However, inherent in many definitions of aromaticity is the geometry criterion,²² i.e., the planarity of the system and the lack of bond length alternation. Realizing that it is not a strictly necessary nor sufficient criterion, we will attribute aromatic character for the purpose of this paper to those stable planar four-membered rings that exhibit the highest possible rotational symmetry and resist all distortions from this conformation.

The fact that several classes of compounds exist whose properties are not correctly predicted by the $4n + 2$ π -electron criterion necessitates a wider search for aromatic character among homo- and heteronuclear rings. A special class of potential aromatic ring systems, whose properties have not been investigated into detail, is formed by the electron-rich rings. By electron richness it is indicated that a compound possesses more π electrons than necessary to develop a simple Lewis-type model. As an example, consider a ring consisting of alternating CH and O fragments. Each carbon atom in the ring adds one electron to the π frame,

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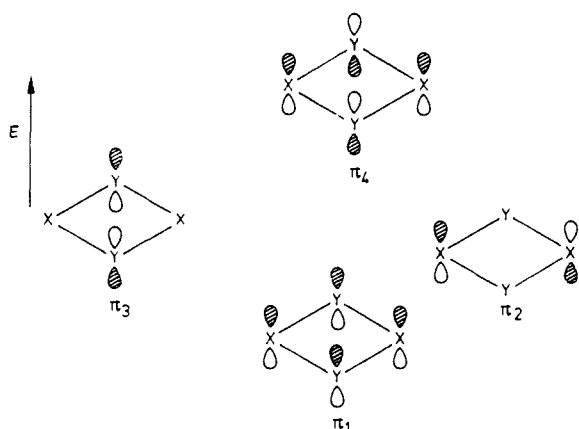


Figure 1. Schematic representation of the 4π orbitals of $(XY)_2$ rings.

whereas oxygen adds two electrons.

We investigated four-membered rings containing six π electrons since they are the smallest electron-rich rings that can be aromatic according to Hückel's rule. Despite their expected aromaticity, only a few stable 6π four-membered rings with a planar, delocalized conformation are known. This instability has been ascribed to the fact that the excess electrons fill nonbonding or even antibonding orbitals. Figure 1 shows the π MO scheme for homocyclic and heterocyclic four-membered rings. The filled π_2 and π_3 are 1,2-nonbonding and 1,3-antibonding, which results in a repulsive contribution to the π frame.

In the present paper we report quantum chemical calculations at 3-21G and 6-31G* levels of several electron-rich four-membered rings. We have investigated the stability and distortive properties of several homo- and heteronuclear rings within the following constraints: (i) six π electrons, (ii) four bonds of the same type for optimal delocalization in the ring, (iii) only neutral or doubly charged species, and (iv) hydrogen as substituent.

Considering the first-row elements, the cyclobutadiene dianion ($C_4H_4^{2-}$),²³ 1,3-diazetene ($C_2H_2N_2H_2$),²⁴ and 1,3-dioxetene ($C_2H_2O_2$),²⁴ which fulfil these criteria, have already been studied theoretically at ab initio level. Neither of these structures was reported to possess a stable planar conformation. The lack of aromaticity has been attributed to several factors, viz. (i) strong repulsive 1,3-interactions, (ii) electrostatic repulsions in charged systems, and (iii) electronegativity differences in heterocyclic rings that favor electron localization. The role of the hydrogen atoms, substituted on the ring atoms, in deformation from planarity, however, has not been envisaged.

For rings incorporating second-row or heavier atoms, several stable species have been isolated and identified (e.g., N_2S_2 ,²⁵ S_4^{2+} ,²⁶ Se_4^{2+} ,²⁷ and Te_4^{2+}).²⁸ In these compounds stabilization has been attributed to d-orbital participation, reducing the antibonding nature of π_2 and π_3 orbitals.²⁹⁻³¹

The calculations for a number of first-row and second-row cyclic systems reveal that 6π aromaticity can be expected for several homo- and 1,3-heteronuclear rings of varying overall charge (e.g., N_4^{2-} , $N_4H_4^{2+}$, and N_2S_2). For species that favor (partial) electron localization and whose planar geometries do not correspond to a true energy minimum of the potential hypersurface (e.g., $C_4H_4^{2-}$ and $C_2H_2O_2$), a detailed analysis of the preferred distortions and stable geometries is presented.

It will be shown that 6π aromaticity in four-membered rings first of all depends on the nature of the constituting ring fragments, giving the requested balance between bonding and distortive properties. This gives support to Shaik's conclusions regarding the importance of the σ frame in the discrimination between aromaticity and antiaromaticity. The calculations reveal a substantial difference between the 3-21G and 6-31G* basis sets. The basis set dependence can be attributed to the polarization functions on the ring atoms. These functions strengthen the ring by increasing the bond strength and reducing the 1,3-repulsion, but at the same time they destabilize the planar orientation of ring substituents. The latter effect is a result of the contribution of the polarization functions to the π frame. The repulsion is reduced but electron density above the planar-oriented hydrogen bond increases, thereby favoring out-of-plane relaxation.

Method

All the geometries were optimized completely^{32,33} at closed-shell restricted Hartree-Fock (RHF) level with two split-valence basis sets. We used the 3-21G basis set³⁴ to find stationary points on the potential surface. To improve the quality of the basis set, the extended 6-31G* set,³⁵ with polarization functions on ring atoms, was used. The orbital exponents of the polarization function were $\alpha = 0.2$ for Li; $\alpha = 0.8$ for C, N, and O; and $\alpha = 0.65$ for S. The 6-31G** basis set was used to establish the role of the hydrogen bond. The orbital exponent used for the polarization functions on the hydrogen atoms was $\alpha = 1.1$. For some bare rings (N_4^{2-} and O_4^{2+}), a TZVP basis set³⁶ was used to probe the quality of the 6-31G* basis set in describing the geometry and frequencies at HF level. The orbital exponents of the polarization functions were $\alpha = 0.98$ for N and 1.28 for O. To improve the results of the 6-31G* calculations, the dianions were also investigated with diffuse functions in the basis set. The exponents used in the 6-31+G* and 6-31++G** basis sets were $\alpha = 0.0360$ for H, 0.0438 for C, and 0.0639 for N.³⁷

The optimized geometries are subject only to overall molecular symmetry constraints. To obtain the symmetry of the minimum, the following strategy can be developed: First, optimize the molecule in its highest symmetry and calculate the harmonic frequencies. Second, make a picture of the normal modes associated with the imaginary frequencies. For degenerate vibration modes allowance must be made for both distortions. Last, make a superposition of these modes. The result will most likely be the symmetry of the lowest local minimum. Exceptions will occur when new imaginary-frequency modes arise during the geometry optimization. The new modes, which preserve their imaginary frequencies, will lower the symmetry of the minimum. Other minima will arise when these new modes stabilize an original energy-lowering mode. Hence, to find all the local minima on the potential surface, all the stationary points have to be calculated. This is done by the following procedure: For every molecule the conformation with the highest symmetry (D_{4h} or D_{2h}) was used as a starting point. For the optimized geometry a vibrational analysis was undertaken^{33,38} to find the order of the stationary point. In case a particular conformation possesses no imaginary frequencies no further attempts were made to find conformations of lower symmetry. For stationary points with one or more

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Table I. Total Energies (au) of the Conformations for Four-Membered (XY)₂ Rings (Number of Imaginary Frequencies in Parentheses)

X	Y	charge	compd	sym	3-21G	6-31G*	other		
CH	CH	-2	1	<i>D</i> _{4h}	-152.376 61 (3)	-153.245 72 (3)	-153.255 69 (3) ^a		
							-153.381 28 (3) ^b		
					2	<i>D</i> _{2d}	-152.379 36 (2)	-153.254 21 (2)	
					3	<i>C</i> _{2h} (1)	-152.389 26 (2)	-153.264 07 (2)	
					4	<i>C</i> _s (1)	-152.394 00 (1)	-153.269 25 (1)	
					5	<i>C</i> _{2h} (2)	-152.401 10 (2)	-153.280 54 (1)	
					6	<i>C</i> _s (2)	-152.401 52 (0)		
					7	<i>C</i> ₂	-152.405 29 (0)	-153.282 18 (0)	
CH	N	-2	8	<i>D</i> _{2h}	-184.228 86 (2)	-185.320 48 (2)	-185.325 51 (2) ^a		
							-185.429 29 () ^{b,c}		
							-185.448 21 (2) ^{b,d}		
CH	NH	0	9	<i>C</i> _{2h}	-184.245 81 (1)				
					10	<i>C</i> _s	-184.260 85 (0)	-185.352 80 (0)	
					11	<i>D</i> _{2h}	-185.752 04 (1)	-186.791 34 (3)	-186.805 10 (3) ^a
CH	O	0	12	<i>C</i> _{2h}	-185.756 06 (1)				
					13	<i>C</i> _s	-185.762 20 (0)	-186.806 78 (1)	
					14	<i>D</i> _{2h}	-225.142 29 (1)	-226.425 82 (2)	-226.431 26 (2) ^a
					15	<i>C</i> _{2h}	-225.153 92 (1)		
N	N	-2	16	<i>C</i> _s	-225.192 68 (1)	-226.470 12 (0)	-217.423 25 (0) ^e		
					17	<i>D</i> _{4h}	-216.047 75 (0)	-217.348 95 (0)	-217.454 51 (0) ^f
								-218.764 86 (1) ^a	
NH	N	0	18	<i>D</i> _{2h}	-217.484 25 (0)	-218.755 59 (1)			
					19	<i>C</i> _{2h}		-218.757 12 (0)	
NH	NH	2	20	<i>D</i> _{4h}	-217.890 00 (0)	-219.152 72 (0)	-219.172 30 (0) ^a		
					21	<i>D</i> _{2h}	-256.829 53 (1)	-258.321 89 (0)	
N	O	0	22	<i>C</i> _{2v}	-256.836 92 (0)				
					23	<i>D</i> _{2h}	-257.019 98 (0)	-258.541 18 (1)	-258.552 16 (1) ^a
					24	<i>C</i> _{2h}		-258.542 15 (1)	
NH	O	2	25	<i>C</i> _s		-258.542 70 (0)			
					26	<i>D</i> _{2h}	-899.170 91 (0)	-903.770 99 (0)	
					27	<i>D</i> _{4h}	-296.033 49 (2)	-297.782 87 (0)	-297.903 26 (0) ^f
S	O	2	28	<i>D</i> _{2h}	-938.885 26 (0)	-943.678 85 (0)			
S	S	2	29	<i>D</i> _{4h}	-1581.230 35 (0)	-1589.159 88 (0)			

^a6-31G**. ^b6-31++G**. ^cSinglet containing 6π electrons. ^dLowest singlet (4π electrons). ^e6-31+G*. ^fTZVP.

imaginary frequencies we used the corresponding vibration modes to find out how the symmetry breaks when the molecule distorts to conformations of lower energy.

Results

The total energies and the order of the stationary points are given in Table I. The geometries with *D*_{2h} or *D*_{4h} symmetry are summarized in Table II and their most important frequencies in Table III. Table IV comprises the geometry data and imaginary harmonic frequencies of the stationary points on the cyclobutadiene dianion potential energy surface. The geometries and frequency data of conformations with *C*_{2h} and *C*_s or *C*_{2v} symmetry are listed in Tables V and VI, respectively. Finally, in Table VII the results of the calculations of dianions with counterions are collected.

1. Rings Containing Carbon (1–16). Four-membered rings containing six π electrons exhibit π repulsion between opposite atoms. By opposite atoms we indicate those ring atoms that exchange positions when rotated about a 2-fold axis perpendicular to the ring. The negative overlap, which correlates with the repulsion, between opposite atoms is large for carbon compared to nitrogen or oxygen. This is evident since a larger nuclear charge of the ring atoms leads to less diffuse orbitals resulting in a decrease of the 1,3 negative overlap. The stability of a particular conformation depends on 1,2-bonding and 1,3-repulsion, as well as on the flexibility of the ring. In this section we examine the stability of carbocycles containing first-row elements only.

Considering our restrictions on the rings to study, four carbon-containing cycles remain: the cyclobutadiene dianion (C₄H₄²⁻), the 1,3-diazetene dianion (C₂H₂N₂²⁻), 1,3-diazetine (C₂H₂N₂H₂), and 1,3-dioxetene (C₂H₂O₂). In a planar ring system (*D*_{4h} or *D*_{2h}) the repulsion can be reduced by out-of-plane vibrations of the ring substituents. Two opposite substituents can vibrate in or out of phase (ungerade or gerade). The filled π₂ and π₃ are 1,3-antibonding (Figure 1) and favor gerade vibrations. To minimize negative overlap, the normal modes with the lowest frequencies vibrate out of phase, i.e., degenerate E_g vibrations in *D*_{4h} and B_{2g} or B_{3g} vibrations in *D*_{2h} symmetry (Figure 2). This, however, does not imply a direct correlation between 1,3-repulsion

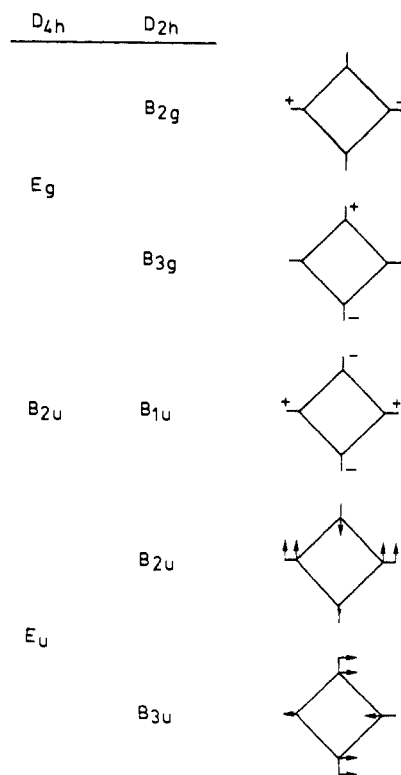


Figure 2. Important normal vibrational modes in relaxation of four-membered rings.

and the frequencies of these modes. The inclusion of polarization functions on the ring atoms reduces the repulsion but simultaneously lowers the frequencies of the out-of-plane vibration modes. Other important normal modes are B_{2u}/B_{1u} vibrations in *D*_{4h}/*D*_{2h} symmetry.

Table II. Geometry Data for D_{2h}/D_{4h} Conformations^a

X	Y	compd	basis set	XY	$\angle YXY$	XH	YH
CH	CH	1	3-21G	1.470	99.0	1.088	1.088
			6-31G*	1.454	90.0	1.094	1.094
			6-31G**	1.454	90.0	1.093	1.093
CH	N	8	6-31++G**	1.452	90.0	1.079	1.079
			3-21G	1.427	97.0	1.089	
			6-31G*	1.389	98.2	1.095	
CH	NH	11	6-31G**	1.389	98.2	1.094	
			6-31++G*** ^b	1.383	97.7	1.081	
			6-31++G*** ^c	1.359	101.2	1.078	
CH	O	14	3-21G	1.384	88.6	1.056	0.991
			6-31G*	1.364	88.9	1.061	0.990
			6-31G**	1.364	89.0	1.061	0.989
CH	O	14	3-21G	1.370	90.9	1.053	
			6-31G*	1.325	92.8	1.059	
			6-31G**	1.325	92.8	1.058	
N	N	17	3-21G	1.427	90.0		
			6-31G*	1.353	90.0		
			6-31+G*	1.349	90.0		
NH	N	18	TZVP	1.348	90.0		
			3-21G	1.382	96.3	0.993	
			6-31G*	1.319	96.4	0.993	
NH	NH	20	6-31G**	1.319	96.4	0.991	
			3-21G	1.345	90.0	1.027	1.027
			6-31G*	1.299	90.0	1.022	1.022
N	O	21	6-31G**	1.300	90.0	1.021	1.021
			3-21G	1.399	86.7		
			6-31G*	1.302	87.8		
NH	O	23	3-21G	1.364	91.3	1.066	
			6-31G*	1.276	92.2	1.047	
			6-31G**	1.276	92.1	1.045	
N	S	26	3-21G	1.732	93.7		
			6-31G*	1.614	90.7		
			exp.	1.654	90.4		
O	O	27	3-21G	1.428	90.0		
			6-31G*	1.278	90.0		
			TZVP	1.271	90.0		
S	O	28	3-21G	1.681	77.7		
			6-31G*	1.588	81.6		
S	S	29	3-21G	2.240	90.0		
			6-31G*	1.990	90.0		
			exp. ^d	2.0	90.0		

^a Distances in angstroms, angles in degrees. ^b Singlet containing 6π electrons. ^c Lowest singlet (4π electrons). ^d Depends on the counterion.

Vibrational analysis for the four-membered carbocycles in D_{4h}/D_{2h} symmetry shows that these systems are unstable toward distortion. The largest imaginary harmonic frequency corresponds with a gerade vibration (Table III). This means that these systems lower their energy by an out-of-plane relaxation of the two opposite hydrogen atoms to give a C_{2h} conformation. For some of the carbocycles a second imaginary frequency is obtained corresponding with an ungerade vibration. Both vibrations involve the hydrogens attached to carbon. The instability of the planar conformations suggests that the distortive propensity of the π system is strong enough to overcome the σ -imposed symmetrical geometry. In the following sections we will describe the characteristics of 6π four-membered homo- and heterocarbocycles. The parent cyclobutadiene dianion will be elaborated in some detail because it possesses many of the characteristic properties and deformation modes encountered in these systems.

1.1. The Cyclobutadiene Dianion ($C_4H_4^{2-}$, 1-7). Ab initio calculations on the dianion of cyclobutadiene have already been reported by Hess et al.²³ However, no full vibrational analysis of the stationary points on the potential hypersurface was presented. In the search for stable molecular geometries we started by calculating the harmonic frequencies of the optimized planar (D_{4h}) conformation 1 of the cyclobutadiene dianion (Figure 3). The D_{4h} geometry optimization was performed within four different basis sets (Table II). The 6-31G** basis set was included to establish the importance of polarization functions on hydrogen in the calculation of the harmonic frequencies of the out-of-plane vibrations, whereas the 6-31++G** basis set was employed to test the effect of diffuse functions in the description of this di-

Table III. Harmonic Frequencies (cm^{-1}) of D_{4h} and D_{2h} Conformations

X	Y	compd	basis set	E_g		B_{2u}		E_u	
				B_{2g}	B_{3g}	B_{1u}	B_{2u}	B_{3u}	
CH	CH	1	3-21G	847i	847i	437i	826	826	
			6-31G*	1059i	1059i	741i	874	874	
			6-31G**	1025i	1025i	697i	874	874	
CH	N	8	6-31++G**	279i	279i	417i	926	926	
			3-21G	867i		326i	807	681	
			6-31G*	1023i		503i	978	838	
CH	NH	11	6-31G**	999i		472i	981	849	
			6-31++G**	1269		256i	1112	1244	
			3-21G	499i	471	460	988	924	
CH	NH	11	6-31G*	758i	389i	283i	1031	975	
			6-31G**	734i	343i	215i	1033	974	
			3-21G	690i		135	941	727	
CH	O	14	6-31G*	863i		420i	1057	866	
			6-31G**	843i		384i	1060	870	
			3-21G			746	677	677	
N	N	17	6-31G*			894	972	972	
			6-31+G*			857	981	981	
			TZVP			880	954	954	
NH	N	18	3-21G	321		635	593	895	
			6-31G*	456i		495	987	1111	
			6-31G**	401i		523	978	1117	
NH	NH	20	3-21G	564	564	662	957	957	
			6-31G*	101	101	481	1117	1117	
			6-31G**	178	178	487	1115	1115	
N	O	21	3-21G			635	847	626i	
			6-31G*			865	1136	729	
			6-31G**			522	695	755	
NH	O	23	3-21G	252		481	1055	1110	
			6-31G*	370i		503	1060	1117	
			6-31G**	330i		336	650	548	
N	S	26	3-21G			535	679	945	
			6-31G*			744	928	928	
			6-31G**			734	938	938	
O	O	27	3-21G			249	1076i	1076i	
			6-31G*			415	717	389	
			TZVP			517	903	301	
S	O	28	3-21G			83	201	201	
			6-31G*			247	571	571	
			6-31G**						

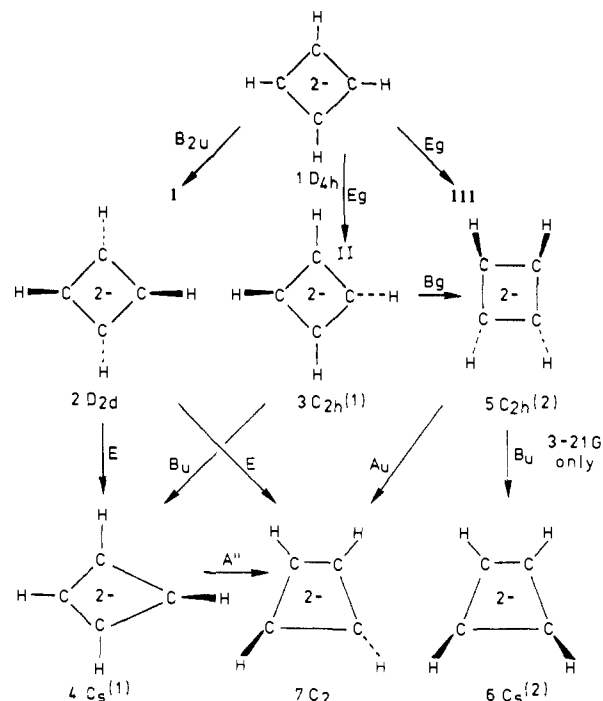


Figure 3. Stationary points of the cyclobutadiene dianion, their symmetry, and their energy-lowering vibrations.

anionic species. At all computational levels the D_{4h} conformation is unstable, and a total of three imaginary frequencies was es-

Table IV. Geometry Data and Imaginary Harmonic Frequencies of Stationary Points on the C₄H₄²⁻ Potential Energy Surface

compd	sym	basis set	geometry data ^a	imag freq ^b
2	D _{2d}	3-21G	CC = 1.481, CH = 1.095, ∠HC, CCC = 15.2	788 (E)
		6-31G*	CC = 1.468, CH = 1.103, ∠HC, CCC = 18.1	814 (E)
3	C _{2h} (1)	3-21G	CC = 1.478, C ₁ H ₁ = 1.112, C ₂ H ₂ = 1.086	774 (B _g)
		6-31G*	∠C ₁ C ₃ C ₂ = 44.8, ∠H ₁ C ₁ , C ₁ C ₂ C ₄ = 35.0 CC = 1.460, C ₁ H ₁ = 1.121, C ₂ H ₂ = 1.092	442 (B _u) 921 (B _g)
4	C _s (1)	3-21G	∠C ₁ C ₃ C ₂ = 44.7, ∠H ₁ C ₁ , C ₁ C ₂ C ₄ = 36.1 C ₁ C ₂ = 1.421, C ₃ C ₄ = 1.592	461 (B _u) 717 (A'')
		6-31G*	C ₁ H ₁ = 1.101, C ₂ H ₂ = 1.095, C ₄ H ₄ = 1.139 ∠H ₂ C ₂ C ₁ = 127.7, ∠H ₁ C ₁ , C ₁ C ₂ C ₃ = 8.5 ∠H ₄ C ₄ , C ₄ C ₃ C ₂ = 59.6, ∠H ₂ C ₂ , C ₂ C ₁ C ₄ = 27.1 ∠C ₁ C ₂ C ₃ C ₄ = 164.6	745 (A'')
5	C _{2h} (2)	3-21G	C ₁ C ₂ = 1.475, C ₁ C ₃ = 1.509, CH = 1.109	398 (A _u)
		6-31G*	∠HC ₁ C ₂ = 124.4, ∠HC, CCC = 36.1 C ₁ C ₂ = 1.455, C ₁ C ₃ = 1.485, CH = 1.118	147 (B _u) 309 (A _u)
7	C ₂	3-21G	∠HC ₁ C ₂ = 124.0, ∠HC, CCC = 37.0 C ₁ C ₂ = 1.514, C ₂ C ₃ = 1.379, C ₁ C ₄ = 1.666	
		6-31G*	C ₁ H ₁ = 1.132, C ₂ H ₂ = 1.099, ∠C ₁ C ₂ C ₃ = 95.1 ∠H ₁ C ₁ C ₄ = 113.7, ∠H ₂ C ₂ C ₃ = 131.0 ∠H ₁ C ₁ , C ₁ C ₄ C ₂ = 58.1, ∠H ₂ C ₂ , C ₂ C ₃ C ₁ = 8.3 ∠C ₁ C ₂ C ₃ C ₄ = 8.9	
6	C _s (2)	3-21G	C ₁ C ₂ = 1.476, C ₂ C ₃ = 1.385, C ₁ C ₄ = 1.590	
		6-31G*	C ₁ H ₁ = 1.133, C ₂ H ₂ = 1.109, ∠C ₁ C ₂ C ₃ = 93.8 ∠H ₁ C ₁ C ₄ = 116.2, ∠H ₂ C ₂ C ₃ = 130.7 ∠H ₁ C ₁ , C ₁ C ₄ C ₂ = 54.4, ∠H ₂ C ₂ , C ₂ C ₃ C ₁ = 14.3 ∠C ₁ C ₂ C ₃ C ₄ = 6.7	
			C ₁ C ₂ = 1.526, C ₂ C ₃ = 1.391, C ₁ C ₄ = 1.597	
			C ₁ H ₁ = 1.122, C ₂ H ₂ = 1.105, ∠C ₁ C ₂ C ₃ = 93.9	
			∠H ₁ C ₁ C ₄ = 116.1, ∠H ₂ C ₂ C ₃ = 128.7	
			∠H ₁ C ₁ , C ₁ C ₄ C ₂ = 53.5, ∠H ₂ C ₂ , C ₂ C ₃ C ₁ = 21.0	

^a Distances in angstroms, angles in degrees. ^b Frequencies in reciprocal centimeters.

Table V. Geometry Data for C_{2h} Conformations^a

X	Y	compd	basis set	XY	XH	YH	∠X ₁ X ₂ Y	∠H ₁ X ₁ X ₁ YY
CH	CH	3	3-21G	1.478	1.112	1.086	44.8	35.0
			6-31G*	1.460	1.121	1.092	44.7	36.1
CH	N	9	3-21G	1.442	1.122		48.4	38.3
			3-21G	1.393	1.067	0.991	44.2	30.7
CH	NH	12	3-21G	1.386	1.067		45.3	38.5
NH	N	19	6-31G*	1.322	0.997		48.1	22.3
NH	O	24	6-31G*	1.280	1.048		46.0	20.4

^a Distances in angstroms, angles in degrees.

Table VI. Geometry Data for C_s and C_{2v} Conformations^a

X	Y	compd	basis set	X ₁ Y	X ₂ Y	∠YX ₁ Y	∠X ₁ YYX ₂	θ ₁ ^b	θ ₂ ^b	θ ₃ ^b
CH	CH	4	3-21G	1.421	1.592	96.2	164.6	8.5	59.6	27.1
			6-31G*	1.412	1.547	95.1	162.9	10.2	57.4	30.7
CH	N	10	3-21G	1.335	1.637	110.7	173.9	3.7	71.1	
			6-31G*	1.314	1.538	109.1	173.7	6.1	66.9	
CH	NH	13	3-21G	1.323	1.542	96.6	171.4	5.5	65.7	10.0
			6-31G*	1.314	1.479	95.3	168.6	7.7	61.8	17.5
CH	O	16	3-21G	1.272	1.703	108.7	172.4	1.0	80.0	
			6-31G*	1.244	1.583	108.2	172.6	1.8	76.2	
N	O	22	3-21G	1.298	1.597	99.2	180.0			
NH	O	25	6-31G*	1.240	1.354	97.0	172.9	7.3	48.1	

^a Distances in angstroms, angles in degrees. ^b θ₁ = ∠HX₁, X₁YY, θ₂ = ∠HX₂, X₂YY, and θ₃ = ∠HY, YXX.

Table VII. Total Energies (au) and Geometry Data^a for D_{4h} Cyclobutadiene and Cyclotetrazene Dianion Lithium Complexes (Li₂X₄)

X	compd	basis set	XX	XH	Li-center	E
CH	30	3-21G	1.481	1.068	1.794	-167.662 27
		6-31G**	1.461	1.073	1.770	-168.613 83
N	31	3-21G	1.438		1.750	-231.274 10
		6-31G*	1.355		1.765	-232.612 71

^a Distances in angstroms.

published, a 2-fold degenerate E_g and one B_{2u} vibration (Table III). The latter one was not reported by Hess et al. It appears

that the geometry (Table II) does not change dramatically upon addition of polarization or diffuse functions but that a significant change in harmonic frequencies is obtained when the basis set is augmented with a single set of diffuse exponents. All energy-lowering vibrations of the D_{4h} conformation are out-of-plane distortions. Geometry optimization along the B_{2u} mode, which has the smallest imaginary frequency, results in a puckered square 2 with D_{2d} symmetry (path I). The E_g modes lead to the two different structures 3 and 5 of C_{2h} symmetry (paths II and III). In path II we restricted the out-of-plane distortion to two protons. Structures 3 and 5 were optimized at both 3-21G and 6-31G* levels. Ordering these points with respect to their energies gives

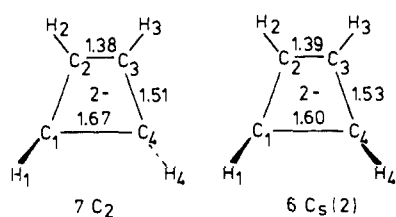


Figure 4. Optimal geometries of the cyclobutadiene dianion at the 3-21G level.

a decrease from D_{2d} via $C_{2h}(1)$ to $C_{2h}(2)$ (Figure 3). The order of these conformations correlates with the imaginary frequencies and the employed distortion restrictions in case of a degenerate vibration. A subsequent vibrational analysis on the three structures 2, 3, and 5 reveals that neither of them corresponds to a local minimum. In fact, this can be expected because we, somewhat arbitrarily, divided the overall relaxation into three independent routes. It was found that conformations 2, 3, and 5 possess two imaginary frequencies at the 3-21G level. At the 6-31G* level this number is reduced to a single one for the $C_{2h}(2)$ conformation (5). It is noteworthy that, in contrast to the D_{2d} and $C_{2h}(1)$ geometries, the $C_{2h}(2)$ structure possesses bond alternation in the ring.

Starting from the three points found, we continued the geometry optimization using 3-21G and 6-31G* throughout. Since we optimized the planar ring along the B_{2u} mode and left the E_g unaltered, at least one degenerate imaginary frequency is expected. Indeed, the D_{2d} conformation exhibits a 2-fold degenerate E mode with an imaginary frequency, identical with the E_g mode of the planar molecule. Hence, the energy of the D_{2d} structure can be lowered via similar relaxation modes used for the planar ring. Superposition of paths I and II results in the $C_s(1)$ structure 4 depicted in Figure 3. As discussed above, path II is a restricted relaxation and must result in a conformation with at least one imaginary frequency. Optimization within this symmetry constraint leads to a conformation in which three carbons constitute an allylic fragment with a three-center four-electron system. The remaining C-H fragment lies strongly out of plane to minimize 1,3-repulsion. The energy of $C_s(1)$ lies between that of the $C_{2h}(1)$ and $C_{2h}(2)$ structures. The $C_s(1)$ structure is identical with the one reported by Hess et al. but does not correspond to a stable molecular arrangement. In fact, vibrational analysis at both 3-21G and 6-31G* shows that this conformation possesses a single large imaginary frequency, belonging to an A'' mode. An imaginary frequency for a C_s geometry suggests that the true minimum possesses no symmetry at all. However, removal of the C_s constraint by a small deformation and further optimization results in conformation 7 with a 2-fold axis (C_2). Vibrational analysis points out that this structure corresponds to a local minimum. Starting from D_{2d} , we reach the same stable C_2 geometry directly if we use the mode corresponding to a combination of paths I and III.

Having established one minimum, we now must attend to the imaginary frequencies of the $C_{2h}(1)$ and $C_{2h}(2)$ arrangements. As mentioned above, the $C_{2h}(1)$ geometry possesses two imaginary frequencies. The mode corresponding to the smallest imaginary frequency can be regarded as the difference of paths II and III (Figure 4). This B_g mode leads to the $C_{2h}(2)$ conformation. The largest imaginary frequency corresponds to a B_u mode similar to path I and results in the $C_s(1)$ structure, from which the stable C_2 geometry can be reached. These calculations suggest that the order at which the different paths are followed is not important. For the $C_{2h}(2)$ conformation we expect one imaginary frequency belonging to an A_u mode similar to the B_{2u} mode of the planar ring. However, the two imaginary frequencies found at 3-21G level for the $C_{2h}(2)$ structure indicate that not all stationary points have been established yet.

At 3-21G level the $C_{2h}(2)$ geometry can break down to either C_s or C_2 symmetry. The largest imaginary frequency leads to the familiar C_2 geometry, resulting from the combination of paths I and III. This result reveals that the B_u mode stabilizes along the relaxation! The $C_s(2)$ structure 6, which appears to be a local

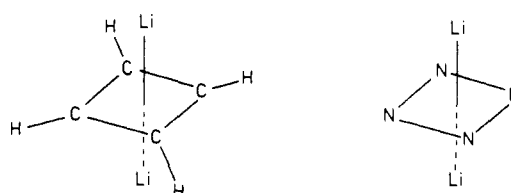


Figure 5. D_{4h} geometries of $Li_2C_4H_4$ and Li_2N_4 .

minimum, is a result of a mode whose frequency became imaginary during the optimization down from D_{4h} . The fact that this conformation is a local minimum indicates that now the A_u mode is stabilized. A second minimum is not obtained at 6-31G* level.

Summarizing the results, it is evident that despite six π electrons the cyclobutadiene dianion is not aromatic but favors distortion toward a ring structure containing three different C-C bonds of C_s (6) or C_2 (7) symmetry. These two structures are very much alike but differ by the orientation of the hydrogen atoms attached to the longest C-C bond (Figure 4). The C_s conformation 6 has a cis orientation, whereas the energetically favored C_2 structure 7 possesses a trans orientation. In both conformations the shortest C-C linkage can almost be regarded as a double bond. The negative charge is primarily confined to the two adjacent tetrahedral carbon atoms separated by the longest C-C bond. If the cyclobutadiene dianion exists as an intermediate, these results predict an electrophilic addition to take place at the neighboring positions with the largest negative charge to give 1,2-substituted 3-cyclobutene. This is in agreement with the formation of the dianion claimed by McKennis et al.³⁹

Hess et al.²³ have addressed the question whether the highest energy electrons are bound in the dianion since the orbital energies of the highest occupied orbitals are positive. We evaluated several aspects of this problem. Augmenting the basis sets with diffuse functions on carbon and hydrogen (6-31++G**) lowers the HOMO energies for the D_{4h} conformation only partially, from 0.28 to 0.19 au. A 6-31++G** RHF SCF calculation of the cyclobutadiene dianion with a C_2 molecular geometry identical with 6 leads to an alternative singlet state of lower energy due to a change in the symmetry of the occupied MO's. On attempted geometry optimization, starting from 6, a D_{2h} structure similar to the neutral cyclobutadiene molecule is obtained with four π electrons and two extra σ electrons.⁴⁰ Apparently, the electrons use the additional freedom provided by the diffuse functions to leave the dianion, rather than giving an improved description of the bonding.

Another possibility to overcome the problems associated with the calculation of negative ions is the introduction of counterions. To evaluate their effect, $Li_2C_4H_4$ was examined within the 3-21G and 6-31G** basis sets. The results of these calculations, in Table VII, reveal that $Li_2C_4H_4$ possesses a stable D_{4h} conformation with an Li^+ nucleus on either side of the ring (Figure 5). Similar structured capped annulene rings have led to the introduction of a $4n + 2$ interstitial electron rule describing aromaticity in three dimensions.⁴¹ A Mulliken population analysis shows that the effective charge on each Li nucleus amounts to approximately +0.25 au (6-31G**). The orbital energies indicate that all electrons are now bound ($E(\text{HOMO}) = -0.23$ au).

1.2. The 1,3-Diazetene Dianion ($C_2H_2N_2^{2-}$, 8-10). The planar (D_{2h}) conformation 8 of the 1,3-diazetene dianion possesses imaginary frequencies for the B_{2g} and B_{1u} modes at both 3-21G and 6-31G* levels. Each of the individual modes leads to a stationary point with a lower energy. The B_{2g} mode gives a C_{2h} (9) and the B_{1u} mode a C_{2v} conformation. A combination of these modes results in C_s structure 10 (Figure 6). In the C_s geometry three ring atoms combine to form a carbon-centered allylic fragment with two short C-N bonds ($\text{HCN}_2^{\cdots}\text{CH}^-$). The other carbon is

(39) McKennis, J. S.; Brener, L.; Schweiger, J. R.; Pettit, R. *J. Chem. Soc., Chem. Commun.* 1971, 365.

(40) Geometry data for the D_{4h} singlet 4π cyclobutadiene dianion in the 6-31++G** basis set: CC = 1.569 Å, CC = 1.324 Å, CH = 1.074 Å, $\angle\text{HCC} = 135.4$, $E = -153.4392$ au.

(41) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1982, 104, 4782.

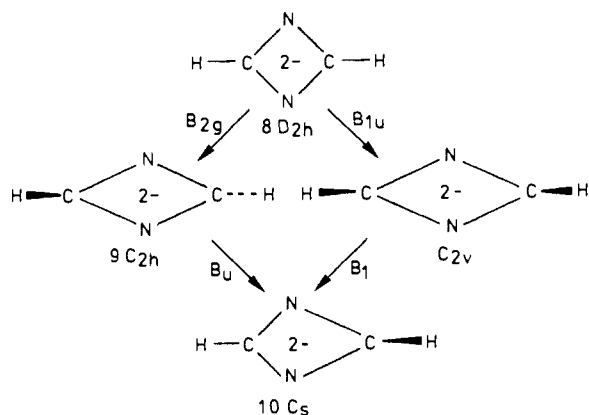


Figure 6. Stationary points of the 1,3-diazetene dianion, their symmetry, and their energy-lowering vibrations.

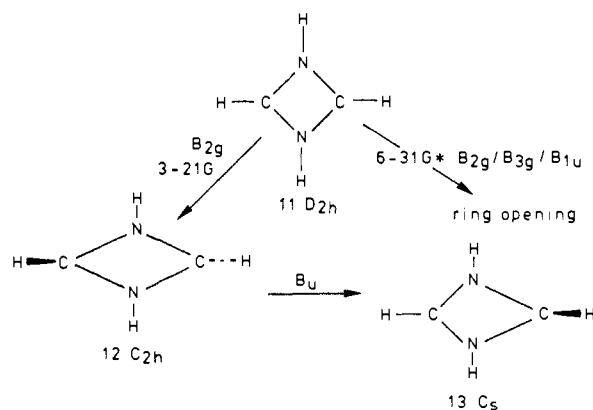


Figure 7. Stationary points of 1,3-diazetine, their symmetry, and their energy-lowering vibrations.

connected via long C–N bonds with the hydrogen atom strongly out of plane. The vibrational analysis at 3-21G level points out that the C_s conformation is a local minimum. In a 6-31G* basis set the C_s geometry remains stable. The difference between the short and long C–N bonds, however, is reduced.

As for the cyclobutadiene dianion, the calculations of the 1,3-diazetene dianion were repeated with a 6-31++G** basis set. On attempted reoptimization of the original D_{2h} geometry, two different singlet states were obtained (Tables I and II). The lowest energy form does not correspond to a 6 π -electron configuration, but contains only 4 π electrons. Again this result is similar to the case of the cyclobutadiene dianion (vide supra).

1.3. 1,3-Diazetine ($C_2H_2N_2H_2$, 11–13) and 1,3-Dioxetene ($C_2H_2O_2$, 14–16). The neutral molecules 1,3-diazetine and 1,3-dioxetene have already been studied at ab initio level by Budzelaar.²⁴ Their planar geometries (11 and 14) possess a single imaginary frequency at the 3-21G level, corresponding to a B_{2g} mode (Figures 7 and 8). Taking only this mode into account, one would expect a stable C_{2h} conformation for these molecules (12 and 15). The resulting rings possess a mirror plane through the opposite CH bonds. To verify whether these conformations are energy minima, we optimized both molecules within this symmetry constraint. Vibrational analysis in 3-21G reveals that these structures are transition states between two C_s conformations (13 and 16). Apparently, the B_{1u} and the B_{2g} modes are coupled for these rings.

For 1,3-diazetine it was found that the optimized C_s ring corresponds to a local minimum with a small barrier for ring opening.⁴² At the 6-31G* level, however, the D_{2h} conformation has three imaginary frequencies. A barrierless ring opening takes

(42) A C_s structure of a 6 π -electron four-membered ring similar to 13 has recently been described by Sanchez et al. for a 1,3-diaza-2-phosphete monoanion. This structure contains a 4 π -allylic NCN⁺ fragment and a 2 π sp³-hybridized phosphorus moiety. Roques, C.; Kim, T.; Mazières, M. R.; Majoral, J. P.; Wolf, R.; Sanchez, M. Lecture at the XI. International Conference on Phosphorus Chemistry, Tallinn, USSR, 1989.

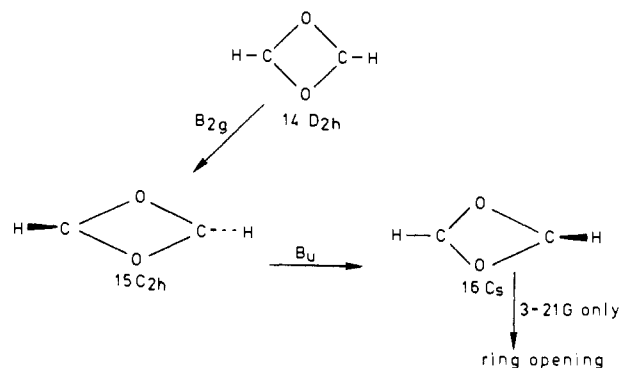


Figure 8. Stationary points of 1,3-dioxetene, their symmetry, and their energy-lowering vibrations.

place by a linear combination of the B_{2g} and B_{3g} modes corresponding to the imaginary frequencies. The C_s conformation has become a transition state of a 1,3 C shift. For 1,3-dioxetene the opposite situation is found. In 3-21G the C_s conformation is a transition state whereas in 6-31G* it appears to be a local minimum on the potential surface.

The reason for their different behavior is caused by the protons attached to the nitrogen atoms. The role of the protons can be explained when we order the normal modes by increasing force constants as shown in Figure 2 and Table III. For both molecules and at both levels we find the B_{2g} – B_{3g} – B_{1u} – B_{3u} – B_{2u} sequence. The first three modes are a result of out-of-plane vibrations of protons. The presence of a proton on both nitrogen atoms is necessary to have a B_{3g} mode. The vibration of this mode disrupts an allylic fragment formed in a C_s conformation. When both B_{2g} and B_{3g} modes possess imaginary frequencies, which is more likely for the 6-31G* basis set, energy lowering will take place by ring opening. In the absence of the B_{3g} mode, ring opening proceeds via a planar deformation that involves the B_{3u} mode. In contrast with the B_{3g} mode, the force constant of the B_{3u} mode increases on going from the 3-21G to the 6-31G* level. Apparently, large basis sets make the σ frame of the ring more rigid, which is indicated by the smaller bond lengths. On the other hand the protons move out of plane easier due to the presence of polarization functions on the ring atoms.

2. All Nitrogen Rings (17–20). The chemistry of experimentally known nitrogen homocycles is limited to two classes of compounds until now.⁴³ The first class is formed by the saturated three-membered rings (triaziridines) and the second consists of pentazoles (N_5H). The intriguing question whether the all-nitrogen analogue of benzene (hexazine) is stable enough to be detected attracted the interest of several groups since the report of its formation.^{44–47} High-level ab initio calculations suggest that the D_{6h} conformation might be a local minimum on the potential surface.¹³ The nitrogen analogue of the cyclopentadienyl anion has been studied at the ab initio level as a potential ligand and was found to be more stable than hexazine.⁴⁸ However, no experimental evidence for its existence has been found. Considering the large difference in stability between benzene and hexazine, it is of interest to study the stability of the all-nitrogen analogues of the cyclobutadiene dianion. Three nitrocycles having four nitrogens fulfil our specifications, i.e., four equal bonds and 6 π electrons. Ordered by the number of hydrogens attached these are the cyclotetrazeno dianion (N_4^{2-}), the neutral 1,3-dihydro-cyclotetrazeno ($N_2H_2N_2$), and the cyclotetrazeno dication ($N_4H_4^{2+}$). These species are isoelectronic and contain 30 electrons like the cyclobutadiene dianion. Since nitrogen has a larger

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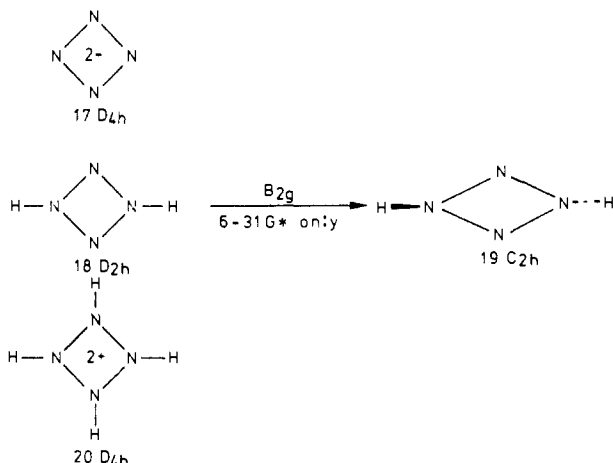


Figure 9. Stationary points of the all-nitrogen rings, their symmetry, and their energy-lowering vibrations.

nuclear charge, its atomic orbitals are less diffuse, which leads to a reduction of the repulsion in the π frame. Our ab initio calculations show that all three ring systems are stable in their planar (D_{2h} or D_{4h}) conformation at the 3-21G level (Figure 9).

2.1. The Cyclotetrazene Dianion (N_4^{2-} , 17). The optimized D_{4h} conformation of the cyclotetrazene dianion (17) possesses no imaginary harmonic frequencies and is therefore stable toward geometry distortions. Nevertheless, the positive eigenvalues of the degenerate highest occupied molecular orbitals indicate that the dianion possesses unbound electrons. Despite the negative charge and the unbound electrons, the cyclotetrazene dianion appears to possess the most stable planar conformation of the studied 6π four-membered rings. Optimization at 6-31G* level leads to smaller N–N bonds and higher frequencies for all six modes. The highest energy electrons, however, remain unbound. Even after inclusion of a diffuse set of functions to the basis set (6-31+G*), this result remains unaltered. At the 6-31G* level the B_{2u} vibration (ring puckering) is the lowest frequency mode. The overall high frequencies suggest that the D_{4h} cyclotetrazene dianion is indeed an example of 6π aromaticity in four-membered rings. The lack of substituents on the ring rules out the possibility of out-of-plane relaxation by fragments attached to the ring. Ring puckering is unfavorable since puckering decreases the bond angles, which in turn increases the ring strain. Apparently, the N–N bond strength is large enough to overcome the strain. The role of the substituents can be examined by adding two or four hydrogen atoms to the bare nitrogen ring (vide infra).

As for the cyclobutadiene dianion, we investigated the cyclotetrazene dianion also with two Li^+ counterions. The optimized geometry data of Li_2N_4 (Figure 5) are given in Table VII and are very similar to those of $Li_2C_4H_4$. A vibrational analysis shows that Li_2N_4 is a stable molecular conformation.

2.2. 1,3-Dihydrocyclobutadiene ($N_2H_2N_2$, 18 and 19). Attaching two protons to the ring at opposite nitrogen atoms give the neutral molecule $N_2H_2N_2$. The presence of two protons on the ring reduces the symmetry and thereby the aromaticity of the species. Although the planar conformation 18 is stable at the 3-21G level, the gerade, out-of-plane vibration (B_{2g} mode) is weak. At the 6-31G* level the planar ring possesses one imaginary frequency. Hence, the addition of two protons leads to nonaromaticity. The imaginary frequency of the B_{2g} mode demonstrates that a C_{2h} restraint leads to a lower stationary point. Indeed, vibrational analysis of the optimized C_{2h} geometry at the 6-31G* level shows that this conformation (19) is a local minimum, which lies only 1 kcal/mol below the D_{2h} structure. A conformation containing an allylic arrangement like the one found for the 1,3-diazetene dianion is not formed. The relative stability of the nitrogen analogue can be attributed to the reduced 1,3-repulsion for nitrocycles. It can be concluded that both the 3-21G and 6-31G* calculations predict that the 1,3-dihydrocyclobutadiene ring is stable but is easily distorted from D_{2h} symmetry and therefore essentially nonaromatic.

2.3. The Cyclotetrazene Dication ($N_4H_4^{2+}$, 20). Adding another two protons to the bare nitrogens results in the formation of the dication of cyclotetrazene. The D_{4h} conformation 20 appears to be remarkably stable at 3-21G level. The stability of the cyclotetrazene dication compared to the isoelectronic cyclobutadiene dianion can be attributed to two factors, i.e., the reduction of the repulsive 1,3-interaction and the delocalization of positive charge over the hydrogens outside the ring. When we compare the dication with the neutral nitrocycle, it is evident that the stability of the dication is a result of its increased aromatic character. At the 6-31G* level the planar ring remains stable. However, the degenerate E_g modes (hydrogens out of plane) have a rather low frequency (101 cm^{-1}). Addition of polarization functions to the hydrogen basis set stabilizes the planar orientation of the hydrogen bond, which results in a slight increase of the frequency of the E_g mode only, which again illustrates the role of the substituents. The other modes remain unchanged.

3. Heterocyclic Nitrogen Rings (21–26). The chemistry of nitrogen–oxygen compounds⁴⁹ is very different from nitrogen–sulfur chemistry.⁵⁰ Rings containing only N–O bonds are unknown, whereas rings with 4, 6, 8 or 10 N–S bonds have been prepared and characterized over the last decades.⁵¹ On the other hand, a large number of acyclic N_xO_y compounds are known in contrast with their sulfur analogues. The unusual properties of the inorganic $(NS)_x$ polymer, such as its superconductive behavior, have led to a great number of investigations.²⁹ The monomer of this inorganic polymer is cyclodithiazene. This species is unique as far as it is the only experimentally known neutral molecule satisfying our criteria.^{52–55} Several experimental data are known. The calculated harmonic frequencies, for example, can be compared with the Raman spectra of N_2S_2 . However, the experimental assignment is controversial in the literature.^{54,55} While the oxygen analogue (N_2O_2) is unknown, the cis conformation of the asymmetric nitric oxide dimer has been synthesized at low temperatures.⁵⁶ The oxygen analogue of N_2S_2 , cyclodiazoxene (N_2O_2), has not yet been studied theoretically.

3.1. Cyclodiazoxene (N_2O_2 , 21 and 22). At the 3-21G level N_2O_2 appears to be unstable in the planar D_{2h} conformation 21. Examination of the B_{3u} mode belonging to the imaginary frequency reveals that the C_{2v} ring 22, with a C_2 axis through the nitrogen atoms, possesses a lower energy. Optimization of the C_{2v} geometry results in a conformation with a nitrogen-centered allylic fragment ($NO_2^+ \cdots N^-$) as depicted in Figure 10. This structure is similar to the carbon-centered conformation found for 1,3-dioxetene. However, there is no assist of substituents, which is indicative of a rather weak N–O bond. The formation of a nitrogen-centered allylic fragment instead of an oxygen-centered fragment can be attributed to the larger NN 1,3-repulsion. Vibrational analysis at this level shows that the distorted ring is stable. Reoptimization of the D_{2h} conformation with a larger basis set with polarization functions on the ring atoms (6-31G*) results in a ring with remarkable stability and aromatic character. The frequency of the B_{3u} mode changed from $626i$ to 729 cm^{-1} . A similar trend was found for the bare cyclotetrazene dianion (N_4^{2-}) but less pronounced. Overlap population analysis at both levels indicates that this trend is caused by the increased 1,2-overlap, whereas the 1,3-repulsion remains at the same level. The question whether N_2O_2 is experimentally accessible cannot be answered on the basis of these calculations only.

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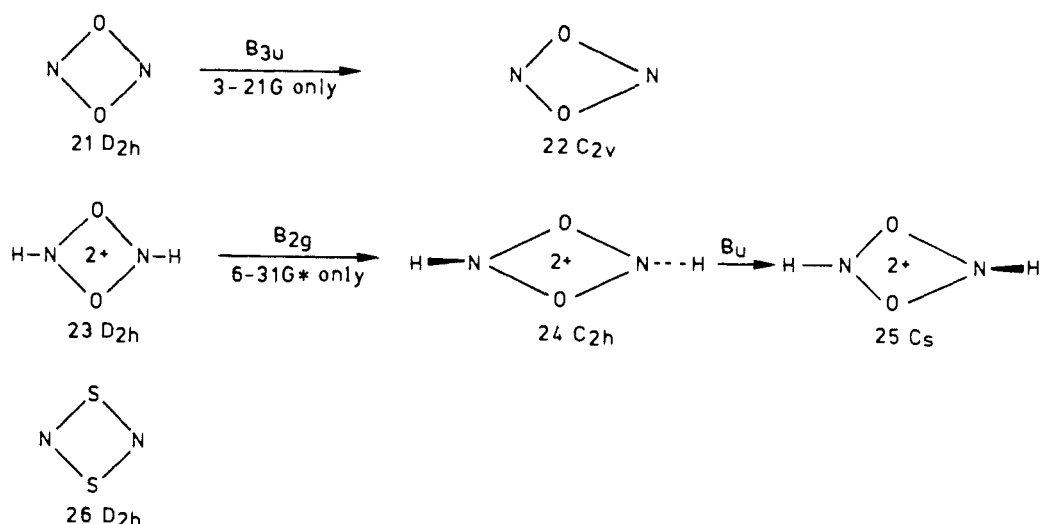


Figure 10. Stationary points of the heterocyclic nitrogen rings, their symmetry, and their energy-lowering vibrations.

3.2. The Cyclodiazoxane Dication ($N_2H_2O_2^{2+}$, 23–25). Adding hydrogen atoms to the nitrogen nuclei stabilizes the D_{2h} conformation **23** at the 3-21G level. Apparently, the reason for its stability is the increase of electron delocalization. This is reflected by the energy difference between the two highest occupied π orbitals, which decreases when we add hydrogen atoms to the bare ring. The D_{2h} conformation appears to be a transition state at 6-31G* level with one imaginary frequency belonging to a B_{2g} mode (Figure 10). Again, the analogy with the corresponding all-nitrogen ring ($N_2H_2N_2$) is remarkable. The resemblance between these compounds indicates that the electronegativity of NH lies about halfway between the values for N and O. Relaxation along the B_{2g} mode leads to a C_{2h} ring **24** similar to the one found for 1,3-dihydrocyclohexene ($N_2H_2N_2$). Force calculation on this geometry shows, however, that we have found another transition state. Further relaxation leads to a similar C_s conformation **25** as was found for 1,3-dioxetene. The small energy difference between these structures shows that the protons are nearly free in their out-of-plane vibrations.

3.3. Cyclodithiazene (N_2S_2 , 26). The substitution of oxygen by sulfur leads to longer bond lengths. The 1,3-repulsion, however, remains about the same. The most important difference with its oxygen analogue lies with the fact that the two highest π orbitals are nearly degenerate. Experimentally, a N–S distance of 1.654 Å and a S–N–S angle of 90.4° were found⁵³ (Figure 10). Extensive calculations at ab initio level have been performed by Karpfen et al.²⁵ They calculated the normal frequencies at SCF (4-21G*) and CEPA-PNO levels. The molecule is found to be stable at all levels, which suggests that N_2S_2 is an aromatic heterocyclic ring. This is supported by vibrational analysis of the D_{2h} conformation **26** at both 3-21G and 6-31G* levels. The harmonic frequencies at the 6-31G* level appear to be identical with those found at 4-21G* level by Karpfen et al. Apparently, an improvement of the s and p set has a minor effect on the force constants. However, in the same paper it is shown that inclusion of the correlation energy (CEPA-PNO) has a considerable effect on the frequencies. Comparing the calculated vibrations of N_2S_2 with N_2O_2 , it appears that the oxygen analogue is more stable at the 6-31G* level. A closer look at the modes shows a large difference in the frequency order of the modes. The lowest frequency mode for N_2O_2 is a B_{3u} distortion, which leads to a C_{2v} conformation with a nitrogen-centered allylic fragment. For N_2S_2 the ring-puckering mode (B_{1u}) is the lowest one, probably due to the reduced ring strain. The relatively low A_g breathing frequencies suggest a flexible ring too. The flexibility of the ring might be the most important reason why only cyclodithiazene could be synthesized.

4. Oxygen and Sulfur Rings (27–29). For the group VI elements of the periodic table the corresponding X_4^{2+} rings possess 6π electrons. For X = S, Se, and Te the planar conformation is experimentally found to be stable.^{26–28} However, the oxygen

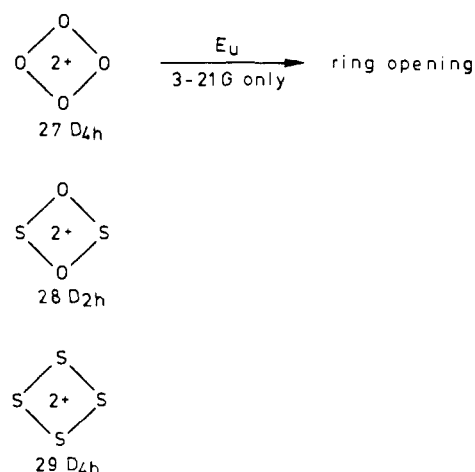


Figure 11. Stationary points of the rings containing group VI elements only, their symmetry, and their energy-lowering vibrations.

analogue is unknown. Neutral oxygen and sulfur rings have been studied theoretically.^{57–59} The puckered oxygen ring appears to be stable at high levels of theory.⁵⁷ According to this information there is no reason why the dication of this molecule should be unstable.

4.1. The Cyclotetraoxane Dication (O_4^{2+} , 27). Vibrational analysis of the planar conformation **27** in the 3-21G basis set results in one degenerate mode (E_u) with a large imaginary frequency ($1091i \text{ cm}^{-1}$). Examination of the distortion dictated by this mode suggests a ring opening to take place (Figure 11). Optimizing the open-chain isomer results in fragmentation. At the 3-21G level the dication apparently dissociates spontaneously into two dioxygen cations. At the 6-31G* level, however, the picture changes dramatically. The optimized D_{4h} geometry is stable, and the frequency of the E_u mode changes to 928 cm^{-1} . Comparing this result with the basis set dependence of N_4^{2+} and N_2O_2 , we see an increased effect on E_u vibrations for bare rings containing more electronegative atoms. The stabilization is a result of the extra polarization functions leading to stronger bonds. This illustrates the risks associated with conclusions based upon single-point calculations with geometries optimized at lower level.

4.2. The Cyclodithioxane Dication ($S_2O_2^{2+}$, 28). Since the behavior of the oxygen and sulfur rings is very different in the basis sets used, we studied the cyclodithioxane dication. Calculation of the harmonic frequencies points out that the optimized D_{2h} conformation **28** is stable at both levels (Figure 11). According

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to the frequencies, this species is more stable than the homocyclic sulfur ring. This makes the cyclothioxane dication an interesting target for synthesis, as well as further theoretical investigation.

4.3. The Cyclotetrathiane Dication (S_4^{2+} , 29). The D_{4h} conformation 29 of the homocyclic sulfur ring is stable at the 3-21G as well as at the 6-31G* level as might be expected since it is experimentally accessible²⁶ (Figure 11). The S-S bond length varies with the counterion used from 1.92 to 2.014 Å. A bond length of 1.99 Å found at 6-31G* level seems reasonable. A small basis set like 3-21G overestimates the bond length. The same trend was found for cyclodithiazene (N_2S_2). The large S-S bond length makes the ring flexible, which is illustrated by the low puckering frequency. The flexibility of the ring might be the main reason why the sulfur ring and its heavier analogues can be prepared more easily than the oxygen ring. The flexibility is an indication for a large quadratic region for this local minimum, e.g., the space in which all frequencies are real. Since ring strain increases the energy of the minimum most, a correlation between the size of this region and the ease of the synthesis might be expected.

Discussion

When we review the results, we see a remarkable difference between the four-membered carbocycles and nitrocycles. This dichotomy is similar to the different stability of benzene and hexazine¹³ (vide supra), but the order is reversed. For 6π -electron four-membered rings, the planar geometry of the carbocycles is unstable, whereas the planar nitrocycles are stable or form low-energy barriers between their minima. The calculations for the oxygen analogues display a strong basis set dependence. At the 6-31G* level, these rings are much more stable than their corresponding conformations at the 3-21G level. The most extreme example is the homocyclic oxygen ring O_4^{2+} , which fragmentizes at the 3-21G level but possesses a planar D_{4h} conformation at the 6-31G* level. The sulfur-containing rings (N_2S_2 , S_4^{2+}) are found to be stable at both levels of theory, in accordance with experimental results. Even the unknown $S_2O_2^{2+}$ ring is remarkably stable in both basis sets. The relative ease by which the π electrons can be accommodated by sulfur is expected to give an important contribution in stabilizing these rings.

The stability of the planar (D_{2h}/D_{4h}) conformation of 6π -electron four-membered rings primarily depends on the stability of the planar orientation of the ring substituents. For bare rings, the relaxation is limited to planar deformation and ring puckering. In general, the frequencies of these modes are rather high. The stability toward ring opening, following a deformation from planarity, is determined by the bond strength in the ring.

Concerning the stability of the planar orientation of the hydrogen bond, it appears that atoms possessing a more contracted π orbital stabilize the planar orientation due to the reduced mixing of the s orbital of hydrogen with the π frame by out-of-plane vibrations. The mixing is increased by an outward distortion of the p_z orbitals, stimulated by the π 1,3-repulsion. Concerning the

computational aspects, it is noteworthy that polarization functions on the ring atoms reduce the repulsion but simultaneously destabilize the planar hydrogen bond and that the inclusion of polarization functions on hydrogen does not result in a dramatic change of the geometry nor of the calculated harmonic frequencies that show a slight increase.

The bond strength in the ring is determined primarily by the combined effects of the nuclear charge and the σ molecular orbitals. Recent theoretical calculations suggest that the π -electron delocalization is not the most important driving force for aromaticity.² A possible stabilizing effect on the planar conformation by the π electrons is even reduced in the present four-membered rings as a consequence of the π 1,3-repulsion resulting from the filled antibonding molecular orbitals π_2 and π_3 (Figure 1). Due to a decrease of the size of the atomic π orbitals for electronegative elements, the π 1,3-repulsion is reduced and the planar conformation gains stability.

On basis of the aforementioned arguments the instability of the planar conformation of the cyclobutadiene dianion can be explained by the instability of the planar hydrogen bond as a result of the π 1,3-repulsion. Spontaneous ring opening is unlikely because the C-C σ bond is relatively strong. Due to the electronegativity difference of the ring atoms, which favors electron localization, it is not surprising that ring opening becomes more likely for the heterocarbocycles, since the bonds are weaker than the C-C bond. In conclusion, the substituted nitrocycles are more stable than their carbon analogues, due to a reduction of the repulsion and hence a more stable planar orientation of the hydrogen bonds.

The influence of the total charge of the molecule depends on its sign. The balance between nuclear repulsion and bond strength determines the stability of the positively charged molecules. This is best illustrated by the cyclotetraoxane dication at 3-21G and 6-31G* levels. The absence of polarization functions leads to relatively long and weak O-O bonds and fragmentation of the ring. At 6-31G*, however, the ring remains stable due to the strengthening of the O-O bonds. This demonstrates the importance of polarization functions in quantum chemical calculations on electronegative atoms. A negative charge increases the 1,3-repulsion, which results in an increase of the molecular orbital eigenvalues. For all dianions at all levels we found positive eigenvalues for the highest orbitals, which suggests that some electrons are unbound.

The present study shows that the occurrence of 6π aromaticity in four-membered rings is determined by the fine balance of stabilizing and distortive properties, which depends on the nature of the constituting ring atoms and the presence of ring substituents. It is clear that the planar stability of these molecules is not solely the result of the delocalization of the π electrons. Calculations at higher theoretical level are currently in progress to give conclusive answers on the aromatic character of 6π four-membered rings and to gain further insight in the origins of aromaticity.