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SINDO1 Investigations on the Low-lying States of some Three Membered Antiaromatic Systems

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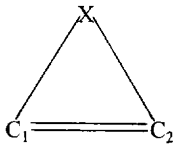
Abstract: The low-lying states of three membered ring systems are investigated by Configuration Interaction calculations using SINDO1 method. Though the ground state is moderately or highly antiaromatic in cyclopropenyl anion, azirene, oxirene and thiirene, the species exhibit moderate aromaticity in the excited states. The excited states of nonaromatic silirenyl anion and phosphirene are found to be antiaromatic.

INTRODUCTION

Cyclopropenyl anion **1** is the smallest antiaromatic carbocyclic system with 4π-electrons.[1] The parent ion and some of its derivatives are characterized as transient species by electrochemical techniques.[2,3] The formation and characterization of carbomethoxy derivative of **1** using gas phase methodology is reported for the first time in 1994 by Sachs and Kass.[4] The carbomethoxy cyclopropenyl anion is reported to be less stable than its acyclic analogue by approximately 14 kcal mol^{-1} which indicates that the former is significantly destabilized due to antiaromaticity. The isoelectronic heterocyclic systems such as 1*H*-azirene **2**, oxirene **3** and thiirene **6** are also elusive species and are detected only in rigid matrices as short lived intermediates.[5-9] The lack of stability in cyclopropenyl anion and the analogous heterocyclic species is attributed to antiaromaticity in these systems.[1] However in the phosphorus analog 1*H*-phosphirene **5**, a number of derivatives and complexes are synthesized as stable species.[10-13] Regitz has remarked on the basis of NMR evidences that there is no antiaromaticity in 1*H*-phosphirene.[13] The *ab initio* analysis of Bachrach[14] reveals that there is no structural, energetic or chemical evidence to suggest any antiaromatic character in 1*H*-phosphirene.



system	X
1	CH^-
2	NH
3	O
4	SiH^-
5	PH
6	S

Theoretical investigations[5,14-20] have been performed earlier on the ground states of the systems **1, 2, 3** and **5** but work on the excited states of these species is very limited. Davidson and Borden have examined the low-lying states of cyclopropenyl anion.[17b] Robb and coworkers studied the singlet and triplet states of oxirene in their investigation of Wolff Rearrangement of formyl methylene to oxirene.[16] In this work we present a comparative analysis of the degree of aromaticity in the low-lying excited states of the strained three membered ring systems **1** to **6**. Earlier theoretical studies on the excited states of some typical antiaromatic and nonaromatic molecules reveal that some of their low-lying excited states exhibit aromatic character.[21-23] In this work, we investigate the degree of aromaticity in the low-lying excited states of the species **1 - 6** which are expected to be versatile synthons through ring opening and ring expansion.[24]

COMPUTATIONAL PROCEDURE

The excited states of the species are studied using the CI version of the semiempirical SCF MO method SINDO1.[25-28] The suitability of the SINDO1 method in examining the behavior of the excited states is pointed out in the earlier works.[28] The special features of this method such as the inclusion of d-orbitals in the basis set of second row atoms and the use of charge dependent orbital exponents to account for the diffuse nature of electrons in molecular anions are described earlier.[26,28] The closed shell singlet states S_0 are optimized first at the SCF level using Newton-Raphson procedure. Vertical excitation calculations are then done including all singly

Table 1. SINDO1 Excitation energies (eV)

System	S_1		T_1	
	Type	Energy	Type	Energy
1	$\sigma (a_1) \rightarrow \pi^* (b_1)$	2.35	$\sigma (a_1) \rightarrow \pi^* (b_1)$	0.20
2	$\sigma (a_1) \rightarrow \pi^* (b_1)$	3.77	$\sigma (a_1) \rightarrow \pi^* (b_1)$	1.28
3	$\pi (a_2) \rightarrow \sigma^* (b_2)$	2.84	$\pi (a_2) \rightarrow \pi^* (b_1)$	1.08
4	$\sigma (a_1) \rightarrow \pi^* (a_2)$	4.06	$\sigma (a_1) \rightarrow \pi^* (a_2)$	2.51
5	$\sigma (b_2) \rightarrow \pi^* (a_2)$	3.00	$\sigma (b_2) \rightarrow \pi^* (a_2)$	2.33
6	$\pi (a_2) \rightarrow \sigma^* (b_2)$	1.79	$\sigma (b_2) \rightarrow \pi^* (a_2)$	0.57

excited configurations involving electronic excitation from three highest occupied orbitals to six lowest vacant MOs. The low-lying π-π*, π-σ* and σ-π* excited states are covered by this CI. The lowest excited triplet state T_1 and singlet state S_1 are studied by structural optimization. The degree of aromaticity in the excited states is determined by the bond-order definition of aromaticity.[29] According to this approach, the degree of aromaticity in a given electronic state is determined by the lowest ring bond order.[29,30] Recent critical analyses of different authors stress the role of σ-electrons in the aromaticity concept.[31-33] It is evident from these works that the π-electrons tend to have localized bonds while the σ-electrons tend to have delocalized bonds.[31-33] The computation of bond orders includes the contribution from the σ-as well as the π-electrons and thus the role of both σ- and π-electrons is taken into account while determining the degree of aromaticity.

RESULTS AND DISCUSSION

Excitation Energies

Table 1 presents the adiabatic excitation energies of the lowest singlet and triplet excited states of **1** - **6**. Although experimental values of the transition energies are not available for comparison, earlier works[21-23,27,34-36] show that the SINDO1 triplet energies agree closely with experimental values while singlet energies are higher by about 1 eV.

In its most symmetrical geometry cyclopropenyl anion **1** belongs to D_{3h} symmetry and according to π-electron treatment, the triplet diradical should be the ground state due to the presence of two electrons in a pair of degenerate π-MOs.[17] However, there is non-D_{3h} distribution of π electron density in the closed shell singlet state that causes the σ-MOs of **1** to deviate from D_{3h} symmetry in S_0.[17] Borden has pointed out that a proper description of wavefunction of S_0 of **1** should include CI in the σ and π spaces. Further in **1** large second order Jahn-Teller effect operates on the lowest singlet state, distorting its geometry considerably.[17] This distortion can bring the singlet state S_0 below the triplet state T_1. The present structural optimization study with SCF calculations on S_0 and CI calculations on S_1 and T_1 reveals that in **1**, the triplet is the lowest state and the closed shell singlet lies 0.39 eV higher in energy. However when CI calculations are performed on S_0 of **1** using singly and doubly excited configurations originating from three highest occupied MOs to six lowest unoccupied MOs, S_0 is found to be the ground state lying 0.20 eV lower than the triplet state. *Ab initio* study shows that the closed shell singlet is the ground state of 1.[17] In the species **2** - **6**, the perturbation caused by the heteroatom, lifts the degeneracy of the highest occupied π-MOs and thus the closed shell singlet states are the ground states.

The structural optimization study reveals that the triplet state of oxirene is ππ* in origin as found by *ab initio* study.[16] However, the SINDO1 excitation energy of oxirene triplet is about 1 eV lower than the *ab initio* value of 2.24 eV obtained by 6-31G* calculations.[16] The remaining singlet and triplet states investigated are of the type σπ* or πσ*. In cases where there is significant deviation from planarity, it is found that the σ and π orbitals mix considerably. For convenience, the orbital representations belonging to C_{2v} symmetry are retained in Table 1.

Molecular geometries and degree of Aromaticity

Ground States. Table 2 presents the SINDO1 optimized geometries of the ground states of the species studied. The results show that oxirene and thiirene are planar and retain C_{2v} symmetry in the ground state. The remaining species are significantly nonplanar about the atom X as revealed by the dihedral angles HCCX and CCXH. The SINDO1 geometries of the ground states show good agreement with the ab initio geometries except in the CC and CX bond lengths. The SINDO1 CC bond lengths in the singlet S_0 are in the range 1.297 Å - 1.320 Å and are very close to standard CC double bond length while the adjacent ring bonds CX are found to be shorter than the respective CX single bonds. The *ab initio* CC bonds are considerably shorter while the CX bonds

Table 2. Molecular geometries^{a} in the closed-shell state S_0

	1	2	3	4	5	6
CC	1.313	1.302 $(1.256)^{b}$	1.297 $(1.268)^{c}$	1.325	1.309 $(1.283)^{d}$	1.295
CX	1.505	1.441 $(1.490)^{b}$	1.444 $(1.486)^{c}$	1.867	1.790 $(1.821)^{d}$	1.814
CH	1.062	1.060 $(1.065)^{b}$	1.058 $(1.062)^{c}$	1.058	1.063 $(1.070)^{d}$	1.065
XH	1.138	1.024 $(1.008)^{b}$	--	1.474	1.436 $(1.418)^{d}$	--
CCX	64.1	63.1 $(65.1)^{b}$	63.3 $(64.7)^{c}$	69.2	68.6 $(69.4)^{d}$	69.0
CCH	140.5	153.0 $(156.8)^{b}$	160.0 $(161.6)^{c}$	134.0	143.3 $(144.8)^{d}$	152.9
CXH	115.0	113.0 $(108.7)^{b}$	--	103.8	102.0	--
HCCX	193.0	193.8	180.0	175.0	176.5	180.0
CCXH	103.1	102.4	--	96.0	95.2 $(77.6)^{d}$	--

a values inside parentheses correspond to ab initio results.

b HF/6-31G** - ref.18; c HF/6-31G* - ref.16; d HF/6-31G* - ref.14

are longer than the SINDO1 lengths. It may be noted that the SINDO1 CC and CP bond lengths of 1.309 and 1.790 Å respectively in phosphirene agree well with the corresponding experimental values of 1.303 and 1.784 Å observed in 1-chloro-2-phenyl-3-*tert*-butylphosphirene.[10] The XH bond is distorted significantly from the CCX ring plane in the species **1, 2, 4** and **5**. The dihedral angles CCXH in these systems are 103.1, 102.4, 96.0 and 95.2° respectively which reflect pronounced pyramidalization around atom X. The dihedral angle CCPH of 95.2° in phosphirene is in reasonable agreement with the STO-3G[19] and 6-31G*[14] values of 94.2 and 77.6° respectively.

Table 5 shows that the CX bond order values are in the range 0.99 - 1.17Å for the species **1, 2, 3,** and **6**. These values reflect that in the ground state the CX bonds are weaker than the standard CX single bonds having bond order of about 1.25. Thus in the closed shell singlet species the CX bonds are the weakest ring bonds and determine the degree of aromaticity. The weakening of the CX bonds originates from the highest occupied π-MO which is antibonding along CX. The aromaticity indices are 1.03 and 0.99 respectively in the planar oxirene and thiirene and are classified as highly antiaromatic according to the bond order definition. Antiaromaticity in the closed shell singlet states of **1** and **2** is less pronounced due to significant pyramidalization around X which relieves the ring strain. It may be noted that in the ground states of **4** and **5**, the SiC and PC bond orders are 1.21 and 1.24 respectively which show that they are as strong as the respective single bonds. The bond order definition of aromaticity classifies silirenyl anion and phosphirene to be nonaromatic in their ground states. Our observation regarding the nonaromatic nature of phosphirene ground state is in agreement with the conclusion of Regitz who attributed the stability of 1*H*-phosphirene over 2*H*-phosphirene by assuming that the former has "no antiaromatic character".[13] Further, the present result is in complete accordance with the conclusion of Bachrach, based on rigorous ab initio computations[14], that there is no destabilization arising from antiaromaticity in **5**. This agreement between our finding and the experimental as well as *ab initio* results regarding the nonaromatic nature of phosphirene indicates that the comparative analysis of the three membered ring species reported in this work are reliable. Though there is no report sofar on silirenyl anion, the present analysis predicts it to be nonaromatic in nature.

Excited States. The geometries in the lowest excited singlet S_1 and the triplet T_1 are presented in Tables 3 and 4. In the S_1 of **1**, **2** and **3** the CC ring bond is lengthened by about 0.08 - 0.10 Å and the CX bonds are shortened roughly by the same extent. In the singlet excited states of **4** and **5**, the bond lengths do not differ much from those in the ground states. The changes in the bond lengths in the excited states can easily be explained from the nodal patterns of the molecular orbitals that participate in the excitation. It is seen that in the optimized geometries of S_1, the highest occupied MOs $\sigma(a_1)$ in **1** and **2** and $\pi(a_2)$ in **3** have the same nodal property, i.e., bonding along CC and antibonding along CX. Further, the $\pi*(b_1)$ and the $\sigma*(b_2)$ are antibonding along CC and nonbonding along CX. Thus the electronic excitation in S_1 of **1, 2** and **3** results in more delocalization of

Table 3. Molecular geometries in the excited singlet state S_1

	1	**2**	**3**	**4**	**5**	**6**
C C	1.393	1.408	1.379	1.336	1.305	1.329
C X	1.415	1.362	1.360	1.875	1.802	1.745
C H	1.089	1.089	1.097	1.060	1.070	1.084
X H	1.096	1.024	--	1.484	1.457	--
C C X	60.5	58.9	59.5	69.1	68.8	67.6
C C H	152.4	154.0	178.0	131.0	141.6	140.5
C X H	129.0	124.5	--	155.4	82.5 124.9	--
H C C X	235.5	250.5	180.0	178.3	178.2	180.0
C C X H	118.2	114.5	--	146.3	179.5	--

Table 4. Molecular geometries in the triplet state T_1[a]

	1	**2**	**3**	**4**	**5**	**6**
C C	1.482	1.440	1.420 (1.440)	1.333	1.295	1.382
C X	1.427	1.381	1.357 (1.367)	1.856	1.855	1.745
C H	1.079	1.070	1.056 (1.059)	1.067	1.078	1.080
X H	1.088	1.015	--	1.477	1.447	--
C C X	58.7	58.6	58.5 (58.2)	68.9	69.5	66.7
C C H	132.0	139.2	163.0 (168.3)	132.5	142.3	135.3
C X H	126.0	114.7	--	158.5	76.2 117.0	--
H C C X	232.0	238.8	180.0 (180.0)	182.5	184.5	235.0
C C X H	116.2	106.3	--	167.6	179.5	--

[a] values inside parentheses correspond to 6-31G* values - ref.16

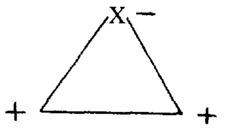
electrons. The calculated aromaticity indices of 1.39, 1.46 and 1.48 respectively show that these species are moderately aromatic. The singlet excited state of silirenyl anion involves the transition $\sigma(a_1) \rightarrow \pi^*(a_2)$. Both the σ and π^* orbitals are bonding along CC but antibonding along CX. As the antibonding along CX is more pronounced in π^*, the excitation weakens the CX bond further and S_1 of **4** becomes highly antiaromatic. In the phosphirene singlet, both the σ and π^* orbitals mix with each other and attain common nodal behavior. The CX bonds are weakened slightly compared to the ground state. Our calculations lead to the observation that the PH bond in phosphirene is tilted significantly from the C_2 axis of the CCP ring. The π and σ^* orbitals that are involved in generating the S_1 state of thiirene have complementary nodal characters. This results in the elongation of CC bond by 0.034 Å and shortening of the CS bonds by 0.069 Å and the excited state becomes nonaromatic as compared to the highly antiaromatic ground state. Other major changes observed in the singlet excited states pertain to the nonplanarity around the atom X. Nonplanarity is more pronounced around the unique carbon in **1** and nitrogen in **2** as compared with their ground states. Phosphirene becomes nearly planar in the excited state.

Table 5. Bond orders (Aromaticity indices) in the low-lying states

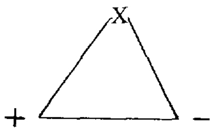
		1	**2**	**3**	**4**	**5**	**6**
State	bond			bond orders			
S_0	CC	2.10	2.20	2.27	2.05	2.19	2.33
	CX	(1.14)[a]	(1.17)[a]	(1.03)[b]	(1.21)[c]	(1.24)[c]	(0.99)[b]
S_1	CC	(1.39)[d]	(1.46)[d]	1.56	1.96	1.92	1.82
	CX	1.42	1.53	(1.48)[d]	(0.99)[b]	(1.17)[a]	(1.21)[c]
T_1	CC	(1.43)[d]	(1.38)[d]	(1.35)[d]	1.95	2.04	1.66
	CX	1.46	1.49	1.43	(1.03)[b]	1.13 (1.08)[a]	(1.31)[d]

a - moderately antiaromatic b - highly antiaromatic c - nonaromatic d - moderately aromatic.

The geometries of the triplet states T_1 are found to be similar to the corresponding singlet excited states when the excitations involved are of the same origin. The excitation is different in oxirene triplet and also in thiirene triplet. The CC bonds are longer in the triplet states of **1**, **2**, **3** and **6** as compared to those in the singlet excited states. In phosphirene triplet, the CP bonds are elongated to 1.855 Å. Thiirene triplet becomes nonplanar as seen from the dihedral angle HCCS which is 235°. It exhibits moderate aromatic character. Lowest triplets of silirenyl anion and phosphirene are highly antiaromatic with aromaticity indices 1.03 and 1.06 respectively. It may be noted that the SINDO1 geometry of oxirene triplet shows close agreement with the *ab initio* result at 6-31G* level.



$\pi(a_2)$



$\pi(b_1)$

CONCLUSION

Among the three membered 4π electron systems studied in this work, phosphirene is found to be nonaromatic in its ground state, in agreement with experimental and *ab initio* findings. The present study predicts that the ground state singlet of silirenyl anion is also nonaromatic. Oxirene and thiirene are highly antiaromatic in the ground state. The SINDO1 molecular geometry of phosphirene agree very closely with the experimental value in substituted phosphirene. Significant structural changes are noticed in the excited states of cyclopropenyl anion, azirene, oxirene and thiirene. Excited states of phosphirene and silirenyl anion are found to be moderately or highly antiaromatic while the remaining species studied are moderately aromatic in the excited states.

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