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EXCITED STATES OF ANTIAROMATIC SYSTEMS [1]

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Abstract - SINDO1 studies were performed to optimize the geometry of excited states of some antiaromatic molecules. It is discussed how such states can exhibit aromatic character upon suitable electronic excitation. The nodal pattern of the molecular orbitals involved in the electronic excitation are used to invoke bond equilization in excited states. We have investigated singlet and triplet excited states of five-membered rings C_4H_5B, $C_5H_5^+$ and C_5H_4O containing four π electrons and bicyclic systems bicyclo-(1,1,0)-butadiene, bicyclo-(2,2,0)-hexatriene and benzocyclobutadiene. It is seen that in bicyclo-(2,2,0)-hexatriene, both the bicyclic structure and the 1,4-diradical structure determine the equilibrium geometry.

1. Introduction

In a previous paper [2] we have shown how the nodal properties of the occupied π molecular orbitals (MOs) play a decisive role in the characterization of aromaticity in cyclic electron systems. In particular, the change in the degree of aromatic character accompanying electronic excitation can easily be interpreted by the nodal behavior of the "essential orbitals", i.e., the molecular orbitals that are involved in the electronic excitation.

It is a common experience that the lowest unoccupied molecular orbital (LUMO) contains one more nodal plane than the highest occupied molecular orbital (HOMO). This leads to the conclusion that the process of exciting an electron from a bonding MO to a vacant MO, results in weakening of the bonds. This may be seen from the decrease of the sum of the bond order values. This behavior is also observed in aromatic systems, the excited states of which are shown to have weakened ring bonds as reflected by ring bond length expansion [3-5]. In consequence the aromatic character is reduced in the excited states. In fact our recent studies show that the aromatic character is decreased significantly or lost in the excited states of 6 π electron ring systems [6,7].

The highest occupied and lowest unoccupied molecular orbitals in cyclobutadiene (CBD) and cyclooctatetraene (COT) illustrate that in these cases there are equal numbers of nodal planes in the HOMO and LUMO. Further, in these cases it is seen that the nodal patterns in the HOMO and LUMO complement each other, i.e., when the HOMO contributes local bonding between two neighboring atoms p and q, the LUMO provides antibonding of equal magnitude and vice versa. Thus, an electronic excitation from the HOMO to the LUMO will cancel the bond alternating effect of the HOMO [2]. Structural optimization of these excited states of CBD and COT has revealed that they are moderately aromatic [2], though their ground states are antiaromatic and nonaromatic, respectively [8]. The analysis of nodal properties gives a clue that the excited states of nonaromatic and antiaromatic molecules can attain aromatic character when the essential orbitals have the required nodal properties.

In this paper, we examine the excited of some small antiaromatic molecules at the SINDO1 level [9]. The main goal of this work is to establish that the excited states of antiaromatic molecules can exhibit aromatic character. Our study is motivated by the fact that the synthesis and characterization of the small antiaromatic systems pose great difficulty due to the instability inherent in these systems [10]. We have seen that aromaticity is connected with kinetic stability [2,11,12]. Identification of kinetically stable aromatic excited states in the antiaromatic molecules by theoretical studies may provide the experimentalists with an easy access to these unstable systems, by way of deexcitation. These aromatic excited states may eventually open up new pathways for reactions involving the antiaromatic species.

We have chosen representative examples of monocyclic and bicyclic antiaromatic molecules for our study. It may be pointed out that in a bicyclic molecule on can characterize aromaticity/antiaromaticity in two different ways. The most common way is to take into consideration only the perimeter of the molecule, neglecting the intraannular bond. The second approach is based on the local criteria for aromaticity of the individual rings [13,14]. In our work, we consider the molecular perimeter to characterize aromaticity in the bicyclic systems in line with the ring current concept [8]. From the different kinds of aromaticity indices [15-22], those based on the resonance energy concept [15-19] have been widely used. A disadvantage of the resonance energy approach is that one has to choose a reference system and for studying the excited states, the choice of a reference system is ambiguous. The molecules we have studied and the numbering systems used are shown in Fig. 1. The five-membered cyclic systems containing four π electrons, 1, 2 and 3 are classified as antiaromatic [23,24]. Borol 1 is unknown experimentally. Cyclopentadienone 3 is reported to dimerize by a Diels Alder reaction . Cyclopentadienyl cation 2 is predicted to have a triplet ground state [25] which is confirmed by EPR spectroscopic studies [26]. At D_{5h} symmetry, the triplet is shown to be 17 kcal/mole more stable than the lowest singlet [25]. Structural optimization of the closed shell singlet at the SINDO1 level leads to C_{2v} symmetry for the lowest singlet. This closed shell singlet is found to be antiaromatic according to the bond order criterion [8]. The bicyclic system, bicyclobutadiene 4 has antiaromatic character. 1,4-didehydrobenzene 5 is moderately aromatic according to the ring current criterion [8], but the resonance energy methods [18,19] classify it as highly antiaromatic. The seeming contradiction is resolved if one considers that the molecule is destabilized across the diagonal bond, but bond equalization along the perimeter allows a ring current. Benzocyclobutadiene is moderately antiaromatic in character. We have studied the low-lying triplet and singlet states. Usually these excited states arise from π - π^*, π - σ^* and σ - π^* excitations. The main effect of the excitation associated with the change in the nodal pattern of the essential orbitals is reflected by the changes in the bond orders, and the change in aromatic character can easily be determined using the bond order criterion.

2. Computational procedure

We start from the ground state structures of the molecules optimized at the SINDO1 level [9]. We then perform a calculation for the vertical excitation involving 17 configurations which includes the ground state and all singly excited configurations arising from the two highest occupied orbitals to four lowest vacant orbitals. We look at the nodal patterns of the essential orbitals of the low-lying vertical states T_1, T_2, S_1 and S_2. If the nodal patterns are such that the electronic excitation favors strengthening of the ring bonds as compared to that in the ground state, then it will be reflected by the changes in the bond order values. In particular, there will be an increase in the lowest ring bond order. An examination of the lowest ring bond order provides an important guideline in investigating aromaticity in the excited states of the nonaromatic and antiaromatic systems. If this preliminary examination of bond orders obtained in a vertical excitation indicates the possibility of the aromaticity in the lowest singlet and triplet excited states, then we have optimized the structures of these states by the Newton-Raphson procedure

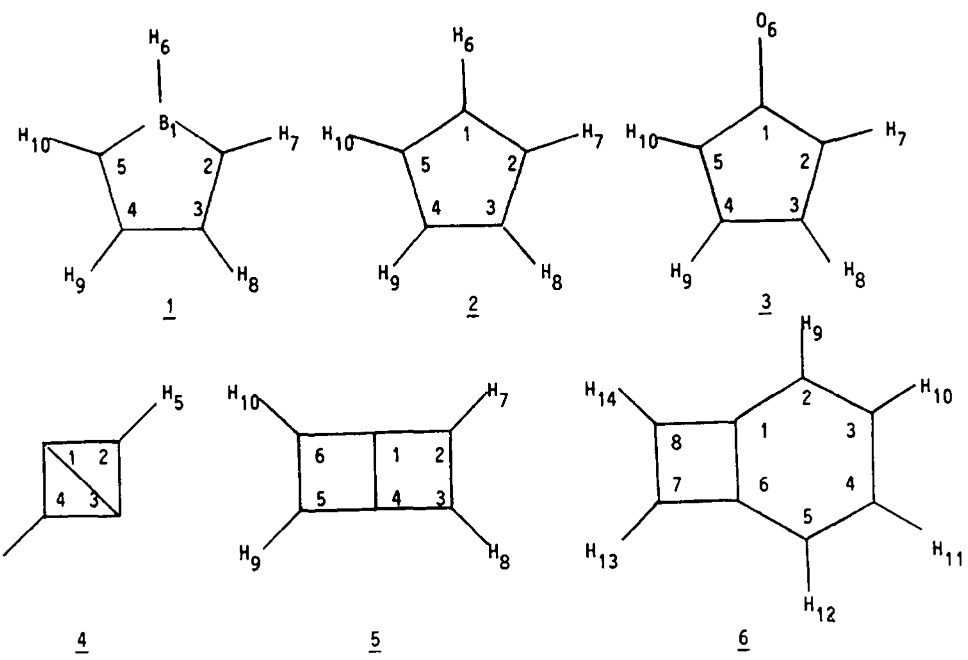

Fig. 1: Labeling and numbering of molecules

using the energy difference method for the first and second derivatives.

In cases where the nodal properties indicate that S_1 and T_1 cannot attain aromatic character, we have looked for the possibility of aromaticity in the higher states T_2 or T_3 and S_2 or S_3. We have optimized those states which are likely to be aromatic.

Unrestricted Hartree-Fock (UHF) calculations at the SINDO1 level for the triplet of cyclopentadienyl cation 3 show that the triplet is lower in energy than the closed shell singlet state. We have also studied excited singlet S_1 and the triplet by closed shell calculations involving configuration interaction (CI).

3. Results and discussion

3.1. Structures and aromaticity

3.1.1. Monocyclic systems

The occupied π molecular orbitals (MOs) of the ground state of molecules 1, 2 and 3 are classified in the C_{2v} group. The nodal patterns of $\pi_1(b_1)$ and $\pi_2(a_2)$ in borol 1 and cyclopentadienyl cation 2 are analogous to the π MOs b_{3u} and b_{2g} of cyclobutadiene. In cyclopentadienone 3 the corresponding orbitals are π_1 and π_3, respectively. The $\pi(a_2)$ orbital has a nodal plane passing through the bond C_3C_4 and the opposite vertex. The presence of two electrons in the a_2 orbital causes bond alternation in the ring. In molecules 1 and 2 the C_3C_4 bond is found to be the weakest ring bond with bond orders 1.14 and 1.04, respectively. The local bonding contribution of the $\pi_1(b_1)$ orbital to the bond C_3C_4 outweighs the antibonding contribution arising from $\pi_2(a_2)$. It is thus clear that the lowering of this bond order well below that of the normal single bond order 1.25, as obtained in all-valence electron calculations, is caused by the strain in the σ frame. In 3, the appearence of the additional MO π_2 is responsible for the weakening of the ring bonds adjacent to the carbonyl group. This bond order is 1.17. In this case also, it is clear that the antiaromaticity arises from the σ frame.

The optimized structures and bond orders of ground and low-lying excited states of 1, 2 and 3 are presented in Table 1. The T_1 and S_1 states of 1 and 2 and T_1 and S_2 of 3 originate from the $\pi - \pi^*$ excitation $a_2 - b_1$. The nodal planes of these essential orbitals are such that the regions

Table 1: Bond lengths (Å), bond angles (degrees) and bond orders of equilibria of electronic states of monocyclic rings 1, 2 and 3

Internal coordinate[a]	S_0			$T_1(\pi-\pi^*)$			$S_1(\pi-\pi^*)$			$S_2(\pi-\pi^*)$
	1	2	3	1	2	3	1	2	3[c]	3
X_1C_2	1.602	1.485	1.572	1.560	1.450	1.527	1.558	1.450	1.530	1.563
C_2C_3	1.348	1.362	1.353	1.440	1.450	1.475	1.423	1.450	1.418	1.377
C_3C_4	1.569	1.586	1.532	1.426	1.450	1.388	1.439	1.450	1.436	1.478
X_1Y_6	1.167	1.097	1.218	1.159	1.090	1.215	1.159	1.090	1.224	1.206
C_2H_7	1.072	1.085	1.078	1.070	1.090	1.071	1.071	1.090	1.077	1.075
C_3H_8	1.081	1.090	1.076	1.075	1.090	1.072	1.075	1.090	1.072	1.071
$C_5X_1C_2$	106.9	112.0	102.8	102.8	108.0	100.8	102.6	108.0	97.9	96.6
$X_1C_2C_3$	104.6	105.1	108.6	108.6	108.0	110.5	108.3	108.0	113.1	113.1
$C_2C_3C_4$	111.9	108.9	110.0	110.3	108.0	109.1	110.4	108.0	107.9	108.1
$Y_6X_1C_2$	126.6	124.0	128.6	127.9	126.0	129.6	128.0	126.0	131.0	131.7
$H_7C_2C_3$	125.2	129.9	127.1	121.9	126.0	124.1	121.4	126.0	122.7	132.1
$C_4C_3H_8$	120.9	123.0	123.0	123.6	123.6	126.0	125.6	123.3	126.0	125.7
bond orders										
X_1C_2	1.28	1.44	1.17[b]	1.48[b]	1.60[b]	1.35[b]	1.48[b]	1.60[b]	1.21[b]	1.30[b]
C_2C_3	2.05	2.01	2.09	1.57	1.60[b]	1.56	1.65	1.60	1.87	1.65
C_3C_4	1.14[b]	1.04[b]	1.25	1.67	1.60[b]	1.77	1.60	1.60	1.48	1.66

[a] X = C,B Y = H,O [b] aromaticity index [c] $\sigma-\pi^*$

which are antibonding or nonbonding in the a_2 orbital are bonding in the $b_1(\pi^*)$ orbital and vice versa. Thus it is evident that the $\pi - \pi^*$ excitation $a_2 - b_1$ will reduce the bond alternation caused by the a_2 orbital in the ground state. It may easily be verified that the $a_2 - b_1$ excitation in 1, 2 and 3 is analogous to the $\pi_2(b_{2g}) - \pi_3^*(b_{1g})$ excitation in cyclobutadiene [2]. In the latter case, the excitation brings about bond equalization and makes the S_1 and T_1 states moderately aromatic [2]. The bond orders of the optimized structures reveal that the triplet of 1, 2 and 3 are indeed moderately aromatic. The π-π* singlets of 1 and 2 also possess moderately aromatic character. However, in 3, the π-π* singlet state S_2 is found to be nonaromatic due to significant contribution from σ-σ* excitation which weakens the ring bonds adjacent to the carbonyl group. But the π electrons are delocalized in the rest of the ring as shown by the bond order values of 1.65, 1.66 and 1.65. The σ - π* singlet state S_1 of 3 is found to be nonaromatic.

It is seen from Table 1 that the structures of the π - π* singlet and triplet of cyclopentadienyl cation studied by RHF-CI calculations are identical to the open shell calculations of the triplet. In this system the excited states have D_{5h} geometry. However, in the excited states of 1 and 3 it is not possible to achieve perfect bond equalization because of the polarization of electrons by the heteroatoms present.

3.1.2. Bicyclic systems

Bicyclo-(1,1,0)-butadiene

The ground state of this molecule was recently studied by Schleyer [27]. Only MP2/6-31G* calculations resulted in a comparable stability of bicyclobutadiene and the rearranged carbene. MNDO and 4-31G calculations put the carbene relatively much too low with a negligible barrier of 1 kcal/mol from 4. With SINDO1 we get results closer to MP2/6-31G*, but we find 5 more stable than the carbene by 5 kcal/mol, compared to -5.7 kcal/mol in the latter. The system of bicyclo-(1,1,0)-butadiene can be viewed as a perturbed CBD in which an intraannular bond is formed between atoms 1 and 3 which are diagonally across the ring. The occupied π MO's in the ground state show that the antibonding contributions of HOMO π_2 between bonded atoms 1,4 and 2,3 is

Table 2: Bond lengths (Å), bond angles, dihedral angles (degrees) and bond orders of equilibria and transition state (TS) of low-lying singlet and triplet states of bicyclo-(1,1,0)-butadiene 4

Internal coordinate	S_0	T_1', T_1''	T_1(TS)	S_1'	S_1''
C_1C_3	1.678	1.763	1.855	1.770	1.854
C_1C_2	1.298	1.390	1.353	1.379	1.362
C_4C_3	1.298	1.390	1.353	1.379	1.362
C_2C_3	1.614	1.441	1.479	1.390	1.473
C_4C_1	1.614	1.441	1.479	1.390	1.473
C_2H_5	1.064	1.069	1.066	1.070	1.066
$C_1C_2C_3$	69.4	77.0	81.7	79.5	81.6
$C_1C_4C_3$	69.4	77.0	81.7	79.5	81.6
$C_1C_3C_4$	64.2	52.8	52.1	50.5	51.8
$C_3C_1C_2$	64.2	52.8	52.1	50.5	51.8
$C_1C_3C_2$	46.4	50.2	46.2	50.0	46.6
$C_3C_1C_4$	46.4	50.2	46.2	50.0	46.6
$C_3C_2H_5$	132.1	136.7	137.6	137.0	137.6
$C_2C_3C_1C_4$	180.0	150.5, 209.5	180.0	145.0	179.5
$C_1C_3C_2H_5$	180.0	153.4, 206.6	179.5	157.0	178.7
		bond orders			
C_1C_3	1.01	0.96	0.82	1.04	0.83
C_1C_2	2.18	1.60	1.76	1.58	1.74
C_2C_3	0.93[a]	1.50[a]	1.20[a]	1.52[a]	1.22[a]

[a] aromaticity index

compensated by the bonding contributions arising from π_1. Hence from π MO consideration alone, the molecule should be classified as nonaromatic. But the highly strained σ frame causes antiaromaticity. This is reflected by the usually large single bond length of 1.614 Å for the bonds C_1C_4 and C_2C_3. The double bonds C_1C_2 and C_3C_4 are 1.298 Å each which is much shorter than the normal double bond distance. At the first sight, an attempt to bring about bond equalization in such a perimeter seems doubtful. In Table 2 we present geometry and bond order of some low-lying excited states. Both S_1 and T_1 originate from HOMO - LUMO (π - π^*) excitation. Two consequences of this excitation are as follows: First, the removal of an electron from the π_2-orbital can reduce by 50% the bond alternation caused by the presence of two electrons in π_2. The second aspect is that the σ^* orbital is antibonding along the cross bond C_1C_3. Though the magnitude of antibonding is comparable to that in the π MO, it can be effective in elongating the intraannular bond C_1C_3 since in the σ^* the antibonding is directed along this bond.

The extension of the 1,3 bond may help in relieving the σ strain in the system. The resultant effect would be manifested by the structure and aromatic character of the adiabatic excited states which we discuss in the following paragraph. The vertical states T_2 and S_3 arise from π - π^* excitation. The nodal plane and the MO coefficients are such that in the bicyclobutadiene perimeter, the region where the HOMO (π_2) contributes to bonding, π^* contributes to antibonding of equal magnitude and vice versa. In other words, it implies that the π - π^* electronic excitation mentioned above will cancel the bond alternation arising from π_2 orbital. Also it can be seen that the intraannular bond C_1C_3 will be weakened considerably since there is a dominant antibonding contribution from the π^* orbital. The aromaticity index of 1.34 obtained by the vertical calculation for the T_2 and S_3 states points out that these states have borderline nonaromatic-moderately aromatic behavior. This shows that the net delocalization around the ring due to the π electrons in π_1 MO is largely cancelled by the σ strain. Structural optimization leads to enhanced aromaticity in these states T_2 and S_3. The vertical states T_3 and S_2 arise from π - σ^* excitation where the σ^* is antibonding with respect to carbon hydrogen bonds. There is a bonding contributions from σ^* along the cross bond. This has a tendency to bring the carbon atoms 1 and 3 closer together which is reflected by strengthening of this bond with a bond order of 1.22. We have not pursued calculations of these states further, since it is expected that the σ strain would increase by the shortening of the 1,3 bond which will eventually destabilize these states. Search for energy minima on the potential hypersurfaces for the T_1 and S_1 states of bicyclobutadiene furnishes interesting results. For the triplet state we have come across a planar nonaromatic transition state and two distinct nonplanar minima. We denote these triplet minima as T_1' and T_1''. It is seen that the minima of T_1' and T_1'' correspond to two isomers which are obtained by "folding in" and "folding out" of the two cyclopropene fragments with respect to the intraannular bond C_1C_3. The folding angle of the perimeter amounts to 29.5°. Our calculations demonstrate that the interconversion of the two forms T_1' and T_1'' takes place via the planar transition state TS of T_1. Such a situation was predicted by Toyota and Nakajima [28] with dihedral angles at about 30°. The optimized geometries and bond orders of these states are listed in Table 2. T_1' and T_1'' are moderately aromatic having the aromaticity indices 1.50. It is found that the ring bond lengths along the perimeter of the triplet minima are in the range 1.39 to 1.44 Å. It may be surprising to note that this range of ring bond lengths is achieved from the ground state values of 1.298 and 1.614 Å. So an understanding of structures and properties of such excited states cannot be brought about by vertical calculation alone. The present study clearly points out the necessity of structural optimization.

The singlet state S_1 is found to have two minima, denoted as S_1' and S_1''. S_1' is nonplanar by 35° and is found to be moderately aromatic. The structure of S_1' is very similar to T_1' (Table 2). S_1'' is nonaromatic, but planar. Incidentally, the structures of TS of T_1 and S_1'' are almost identical. As expected, the intraannular bond C_1C_3 is lengthened considerably in the triplets T_1' and T_1'' and the singlet S_1' and S_1''. The nonplanarity in the states T_1', T_1'' and S_1' causes significant mixing of the essential orbitals.

1,4-Didehydrobenzene

The closed shell ground state of this molecule <u>5</u> is classified as moderately aromatic by the ring current criterion while the resonance energy methods [18,19] declare it as antiaromatic due to the weak intraannular bond. Investigation of the occupied π MOs reveals that the π orbitals of 5 are similar to those in benzene and behave as a perturbed benzene system. In 5, the molecule has only C_s group symmetry. This is reflected by the unequal MO expansion coefficients and the removal of degeneracy in the MOs. However, the nodal planes are essentially unaltered as compared to the case in benzene. The reduced molecular symmetry in 5 brings about partial localization of the π electrons along the perimeter and the system has a moderately aromatic character. It may be pointed out that the π system provides a net antibonding contribution towards the intraannular bond C_1C_4. The low bond order of 0.74 for this bond reflect that there is only σ bonding between the 1 and 4 positions. The bonding in the ground state was already discussed [29,30]. According to the vertical excitation calculation, T_1 arises from a π - π^* excitation. The π^* orbital is bonding between the carbons 1 and 4 while the π MO is antibonding between these atoms. As far as the molecular perimeter is concerned, the regions which are bonding in π are antibonding in π^* and vice versa. This will reduce the π delocalization as compared to that in the closed shell system. Both the vertical and optimized calculations of the T_1 state show that it is nonaromatic in character, having the aromaticity index 1.24. The optimized structures of 5 are presented in Table 3.

It is found that the structural optimization leads to the elongation of the four bonds adjacent to the intraannular bond in such a way that they are equal and approach single bond value. The remaining two bonds are shortened, both to 1.348 Å. The 1,4 bond is elongated to 1.627 Å, though there is bonding contribution to this bond from the π^* MO, probably to relieve the strain in the four-membered rings. The two rings are folded with respect to the intraannular bond C_1C_4.

Table 3: Bond lengths (Å), bond angles, dihedral angles (degrees) and bond orders of ground and excited states of bicyclo-(2,2,0)-hexatriene 5

Internal coordinate	S_0 C_{2v}	$T_1(\pi\text{-}\pi^*)$ C_s	$T_2(\sigma\text{-}\pi^*)$ C_s	$S_1(\sigma\text{-}\pi^*)$ C_s
C_1C_2	1.379	1.509	1.428	1.428
C_2C_3	1.507	1.348	1.392	1.392
C_1C_4	1.589	1.627	2.035	2.035
C_1C_6	1.447	1.509	1.428	1.428
C_5C_6	1.412	1.348	1.392	1.392
C_2C_7	1.076	1.071	1.072	1.072
C_6H_{10}	1.077	1.071	1.072	1.072
$C_1C_2C_3$	91.7	95.3	103.0	103.0
$C_2C_1C_4$	88.3	84.7	77.0	77.0
$C_6C_1C_4$	86.5	84.7	77.0	77.0
$C_1C_6C_5$	93.5	95.3	103.0	103.0
$C_1C_2H_7$	134.8	131.4	127.0	127.0
$C_1C_6H_{10}$	132.7	131.4	127.0	127.0
$C_2C_1C_4C_5$	180.0	132.0	216.9	216.9
$C_1C_4C_3H_8$	180.0	173.0	172.5	172.5
		bond orders		
C_1C_2	1.75	1.24[a]	1.52[a]	1.52[a]
C_2C_3	1.49	2.01	1.87	1.87
C_1C_6	1.47[a]	1.24[a]	1.52[a]	1.52[a]
C_5C_6	1.83	2.01	1.87	1.87
C_1C_4	0.73	1.02	0.29	0.29

[a] aromaticity index

The dihedral angle $C_2C_1C_4C_5$ shows that the two rings are folded by 48°. Consequently the carbon atoms 2, 3, 5 and 6 are shifted below the transannular bond by 0.56 Å. The nonplanarity of the system involves considerable σ - π mixing. The LUMO π^* orbital of the ground state has dominant σ character in T_1 at the 1,4 positions directed along the intraannular bond. The valence of carbon is 2.85 for the positions 1 and 4 and it reflects that the π - π^* triplet T_1 is a 1,4 diradical. It may be pointed out that this π - π^* triplet state is analogous to the ${}^3B_{1g}$ state of benzene. Although both are 1,4 diradicals with quinoidal structure, in benzene the triplet is planar and weakly aromatic [7] while in 1,4-didehydrobenzene it is nonplanar and nonaromatic. Another important difference between the two is that the former is a π diradical while the latter is a σ diradical. The distortions in the internal ring bond angles in the triplet of 5 are about 5° from that of a rectangle.

The excited states T_2 and S_1 of 5 originate from the HOMO-LUMO excitation σ - π^*. There is one to one correspondence in the bonding and antibonding relation between the σ and the π^* MO's. Thus the vertical excitation calculations shows that there is no significant change in the bond orders upon excitation and the states T_2 and S_1 retain the moderately aromatic character. The σ orbital has a bonding contribution along the intraannular bond C_1C_4. Excitation of one electron from the σ orbital may help in relieving the σ strain in the system by way of elongating the C_1C_4 bond. Indeed, structural optimization results in considerable elongation of this bond with a distance of separation of 2.035 Å. Both T_2 and S_1 are found to have the same structure. The bond order of C_1C_4 is reduced to 0.30 which shows that there is essentially no transannular bond. It is also noticed that the four bonds adjacent to the 1,4 positions become equal with bond lengths 1.428 Å. Each of the remaining two bonds have bond lengths of 1.387 Å. Thus it is clear that the perimeters of T_2 and S_1 of 5 have bond lengths which are in the acceptable range

Table 4: Bond lengths (Å), bond angles (degrees) and bond orders of equilibria of singlet and triplet states of benzocyclobutadiene 6

Internal coordinate	S_0	T_1	S_1
C_1C_2	1.395	1.460	1.440
C_2C_3	1.462	1.381	1.400
C_3C_4	1.392	1.466	1.430
C_1C_6	1.494	1.564	1.614
C_1C_8	1.553	1.442	1.424
C_7C_8	1.359	1.438	1.435
C_2H_9	1.080	1.076	1.076
C_3H_{10}	1.080	1.076	1.076
C_8H_{14}	1.075	1.069	1.070
$C_6C_1C_2$	119.4	118.8	118.4
$C_1C_2C_3$	119.4	118.2	117.9
$C_2C_3C_4$	120.7	123.0	123.7
$C_6C_1C_8$	87.5	87.5	86.4
$C_1C_8C_7$	92.5	92.5	93.6
$C_1C_2C_9$	120.6	119.4	120.0
$C_2C_3H_{10}$	118.7	119.0	118.2
$C_1C_8H_{14}$	132.4	134.5	134.0
		bond orders	
C_1C_2	1.90	1.65	1.70
C_2C_3	1.55	1.81	1.74
C_3C_4	1.91	1.56	1.64
C_1C_6	1.40	1.17	1.07
C_1C_8	1.11[a]	1.50[a]	1.52[a]
C_7C_8	2.05	1.61	1.62

[a] aromaticity index

for an aromatic ring. The bond angles are distorted considerably in the T_2 and S_1 states as compared with the ground state. The individual four membered rings are folded by 36.9° relative to the C_1C_4 bond. At the optimized structures of T_2 and S_1, the π^* orbital is dominated by σ contributions at C_1C_4 positions, similar to the situation in the π - π^* triplet. The valence of carbon is 2.74 for C_1 and C_4. Thus we see that the σ - π^* states T_2 and S_1 of 5 are σ 1,4 diradicals with nonplanar quinoidal structures. Both these states are found to be moderately aromatic. The aromaticity index is 1.52.

The excitation energies presented in Table 5 show that the σ - π^* triplet T_2 is lowered significantly by structural optimization. The energy difference between the closed shell singlet S_0 and the σ - π^* triplet is 1.8 kcal/mol. Such a low energy difference between the closed shell singlet and the triplet indicates that the system 5 may be regarded as a closed shell singlet with some diradical character. The singlet state is predicted to be the ground state of 5 by ab initio [29], MINDO/3 and MNDO [37] calculations. Bergman and coworkers [32] have presented evidence that the closed shell singlet is the reactive state in 5. It is also found to be a stable intermediate [33]. The energy barrier between the closed shell and diradical forms is predicted to be 3.0 and 4.6 kcal/mol respectively by MNDO and MINDO/3 [27]. The energy difference of 1.8 kcal/mol obtained by the SINDO1 calculations are near to the MNDO value [27]. However, the structures predicted for the triplet by MNDO CI show a difference of about 0.05 Å, for the bond lengths as compared with our values.

Benzocyclobutadiene

The fusion of a CBD ring with a benzene ring results in a transfer of π electron density from the CBD unit to the benzene unit, partially localizing the π electrons in the latter. Consequently in the CBD fragment there is only one double bond. The bond common to the two rings C_1C_6 has character in between a single bond and a delocalized ring bond. In Table 4 we present geometry and bond orders of 6.

It is clear that in the ground state, the four membered ring has the weakest ring bonds due to the strain factor which overrides the limited π delocalization in the four membered ring. The low-lying triplet and singlet states T_1 and S_1 arise from HOMO-LUMO π - π* excitation. In both the HOMO and the LUMO, the nodal patterns complement each other. Thus the bond alternation which occurs in the perimeter of 6 in the ground state will be reduced in the excited states T_1 and S_1. It is particularly interesting to note that in 6 the HOMO and LUMO. Thus the HOMO-LUMO excitation in 6 is expected to equalize efficiently the perimeter from the CBD unit. The common bond C_1C_6 will be weakened by the excitation since the HOMO is bonding between the atoms 1 and 6 while the LUMO is antibonding for this atomic pair. These qualitative deductions are confirmed by the structural optimization study. In T_1 and S_1, it is seen that the bond lengths of the perimeter range between 1.466 to 1.381 Å and 1.400 to 1.435 Å respectively (Table 4). Planarity is retained in the excited states. The weakest ring bonds have bond orders of 1.50 and 1.52 respectively for T_1 and S_1 which reflect that both these states possess moderately aromatic character.

3.2. Excitation energies

In Table 5 we have collected the SINDO1 vertical and adiabatic excitation energies for the low-lying states of molecules 1 to 6.

Table 5: Adiabatic and vertical (in parentheses) excitation energies (eV) of ring 1 - 6

System	T_1	S_1	T_2	S_2
1	1.60 (2.65)	3.07 (3.82)		
2	0.26^c(1.12)	1.20 (2.04)		
3	2.26 (3.52)	3.94 (4.23)		4.58 (5.15)
4	0.97 (2.54)	1.77^a(2.94) 2.09^b		
5	0.43 (2.41)	0.65 (2.78)	0.08 (2.51)	
6	1.74 (2.90)	3.13 (4.26)		

a S_1' b S_1'' c RHF; -0.15 eV UHF

The values presented for the cyclopentadienyl cation are based on RHF-CI calculations. According to these calculations the triplet of 2 lies above the closed shell ground state by 0.26 eV. But the unrestricted HF calculations at the SINDO1 level show that the triplet lies 0.15 eV below the closed shell ground state. At the D_{5h} geometry of the triplet the closed shell singlet is 0.64 eV higher than the triplet state obtained by the CI study. The low excitation energies for the excited states of 1,4 didehydrobenzene reveals the contribution of the diradical structures to the equilibrium geometry.

A PPP calculation for the vertical excitation energy of benzocyclobutadiene 6 has been reported by Vogler and Ege [34]. They obtain 2.93 eV for the $^1B_2$ state. Our ionization potential of 7.75 eV for the ground state compares favorably with the experimental PE value of 7.87 eV [35] and the MNDO PERTCI value of 7.55 eV [36].

4. Conclusions

The present study illustrates that antiaromatic systems can exhibit aromatic character upon suitable electronic excitation. The nodal pattern of the essential orbitals which are involved in the electronic excitation play a major role in characterizing aromaticity in the excited states. It is found that even σ - π* or π - σ* excitation can induce aromaticity in the excited states of antiaromatic molecules by way of relieving the σ strain. We have identified aromaticity in the excited states of five-membered rings containing four π electrons, borol 1, cyclopentadienyl cation 2 and cyclopentadienone 3 and the bicyclic systems bicyclo-(1,1,0)-butadiene, bicyclo-(2,2,0)-hexatriene and benzocyclobutadiene. The calculated adiabatic excitation energies reveal that in bicyclo-(2,2,0)-hexatriene there may exist an equilibrium between the aromatic bicyclo structure and the aromatic 1,4 diradical structure. The diradical is predicted to be nonplanar by 37°. Finally it is confirmed that antiaromatic systems have low-lying excited states compared to aromatic systems.

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