

AB INITIO STUDY OF CYCLOBUTADIENE IN EXCITED STATES: OPTIMIZED GEOMETRIES, ELECTRONIC TRANSITIONS AND AROMATICITIES

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Abstract—An *ab initio* SCF-CI study of planar cyclobutadiene (CB) in ground and excited states has been carried out. The equilibrium geometries of some valence and Rydberg states have been calculated, as well as the energies of the vertical (absorption and emission) and non-vertical transitions. Using the optimized geometries, it is discussed how the aromaticity changes upon excitation of CB to the lowest-lying singlet and triplet states. The following conclusion is made: upon excitation to the fluorescent (S_1) or phosphorescent (T_1) states, the aromaticity of the anti-Hückel system cyclobutadiene increases significantly, whereas that of the Hückel system benzene decreases.

Cyclobutadiene (CB) has been the subject of numerous theoretical and experimental studies, and the interest in its structure and properties has been constantly increasing in recent years.¹ The interest in CB is due not only to its unusual chemical and physical properties, but also to the fact that it is the first representative of the $4n$ π -electron "anti-aromatic" systems.

While the ground state of CB is already comparatively well studied, information as to its excited states is rather scarce; mostly, vertical transition energies have been calculated (see Refs. [4, 7, 9, 99, 102, 104, 105] in Ref. [1]). The purpose of the present communication is to determine the equilibrium molecular geometries of the low-lying singlet and triplet states, their energies and character, as well as to calculate the vertical (absorption and emission) and non-vertical (adiabatic) electronic transitions of CB. Such information is always of special importance for molecular photophysics and photochemistry of organic compounds.^{2,3} In addition, knowledge of the geometry of the excited states could be used for a qualitative estimation of the change in aromaticity upon the excitation of the molecule to a given electronically excited state. This would allow to extend the concepts "aromaticity" and "antiaromaticity" to photoexcited states.

Method of calculation

The *ab initio* SCF calculations employed a basis of Gaussian lobe functions with the exponents of the 3-21G basis set 4 augmented by a diffuse (s, p) basis set at the carbon atoms. The corresponding exponent was chosen to be 0.05 so that Rydberg states could be taken into account. For the ground state as well as for the lowest electronically excited singlet and triplet states of the C_4H_4 molecule the equilibrium geometries were estimated. Geometry parameters involved are the two CC distances of the rectangular skeleton of the carbon atoms. The cyclobutadiene molecule was assumed to be planar with $CH = 1.08$ Å and $CCH = 135^\circ$ in ground and excited states.

In order to obtain excited states a limited CI treatment was carried out in which the notion of the molecular orbital is still retained. Only those singly excited configurations were used which have a common occupied MO as origin from which the excitations are performed. This concept can be realized most conveniently within the formalism of improved virtual orbitals.^{5,6}

This method has been successfully applied for singly excited states.⁷ In the case of degenerate or nearly degenerate doubly excited electronic configurations as they occur with C_4H_4 additional work has to be done as follows. As is well known in this case the Hartree-Fock state does not represent a state with a symmetry appropriate to D_{4h} . The HF state, however, can be used to yield the states ${}^3A_{2g}$ and ${}^1B_{2g}$ with the corresponding wave functions $1/\sqrt{2}(e_g^x \bar{e}_g^y \pm \bar{e}_g^x e_g^y)$ which obviously are energetically separated by twice the exchange integral between e_g^x and e_g^y . The separation can then be used to locate the states ${}^1B_{1g}$ and ${}^1A_{1g}$, for which the HF state lies exactly between them, with the wave functions $1/\sqrt{2}(e_g^x \bar{e}_g^x \mp e_g^y \bar{e}_g^y)$. This somewhat qualitative concept was also used for reduced symmetry $D_{4h} \rightarrow D_{2h}(e_g \rightarrow b_{2g} + b_{3g})$, in which the HF state splits to $(b_{2g})^2$ and $(b_{3g})^2$, and therefore a 2×2 secular equation must be solved. This is possible because the exchange integral between e_g^x and e_g^y (b_{2g} and b_{3g}) changes only slightly upon distortion from the square geometry.

RESULTS AND DISCUSSION

Description of electronic states

In the past many quantum chemical investigations have been performed on the CB molecule in order to find out the nature of the ground state and its geometry. All these results are summarized in the review¹ and therefore we can restrict ourselves to an overall comparison of our data, listed in Table 1, with those in the literature. All recent computational attempts unequivocally predict a rectangular singlet ground state due to Jahn-Teller distortion, and a slightly higher located triplet state with square configuration. The most reliable geometry

Table 1. Optimized geometries and energies of non-vertical (adiabatic) transitions

State	Symmetry	CC ₁	CC ₂ [Å]	E [eV]	Character of state
S ₀	¹ A _g	1.526	1.316	0.00 *	ground state
	¹ B _{1g}	1.439	1.439	0.38	
S ₁	¹ B _{2g}	1.436	1.436	2.56	valence
S ₂	¹ A _{1g}	1.436	1.436	2.69	valence
S ₃	¹ B _{3g}	1.49	1.39	6.04	Rydberg (π+σ*)
		1.43	1.43	6.45	
T ₁ (T ₀)	³ A _{2g}	1.440	1.440	0.19	valence
T ₂	³ B _{3u}	1.51	1.41	5.71	Rydberg (π+π*)
T ₃	³ B _{2u}	1.49	1.39	5.90	Rydberg (π+π*)

*Total energy: -152.792 a.u. All Rydberg state geometries are given with an accuracy of two digits after the decimal point due to the flatness of the energy surface. The Herzberg convention for the assignment of states has been used throughout this paper.²⁹

parameters for the singlet state (C—C=1.57 and C=C=1.34 Å) and for the triplet state (C—C=1.45 Å)⁸ are well reproduced by the results presented here in Table 1. A further important geometry parameter of the singlet ground state is seen to be the height of the energy barrier which occurs at the square configuration. The height of this barrier decides the static or dynamic nature of the calculated rectangular equilibrium geometry. Our value of 9 kcal/mole is in accord with the range of 12–13 kcal/mole given in recent studies.^{8,9} The singlet-triplet energy separation, however, shows a shrinkage which is typical for our simple method, but the correct ordering is still retained.

With the exception of the ground and lowest triplet state, the properties of excited states have been reviewed up to now mainly by means of vertical transitions.¹ Geometry optimizations of excited states have not yet been performed systematically. For example, the early study of Buenker and Peyerimhoff yielded a non-square "equilibrium geometry" for the triplet state of CB in contrast to all later findings. This is probably due to the fact that geometries were not optimized sufficiently within their calculation scheme.^{1,10} As can be seen from Table 1, except for the singlet ground state all the excited valence states show a square configuration with almost the same CC distance of about 1.44 Å. The lowest singlet and triplet states of Rydberg type, however, show rectangular equilibrium geometries which are not so

pronounced as that for the ground state. The perimeter is increased for Rydberg states with respect to valence states.

In Table 2 our vertical absorption transitions are juxtaposed to some of the latest results found in the literature. There is no full agreement with respect to the ordering of the two lowest excited valence singlet states. Especially for the states ¹B_{1g}(¹B_{2g}) and ¹A_g(¹A_{1g}) a reversed ordering is obtained by *ab initio* SCF-CI calculations.^{9,10} In contrast, the results obtained by EOM and PPP-CI are in good agreement with our results.^{11,12}

In addition to vertical excitations, which can be compared with experimental absorption transitions, the equilibria of excited states allow the discussion of vertical emission transitions which for CB are quite different from absorption transitions as can be seen from Table 3. In our calculation the states ¹B_{2g} and ¹A_{1g} are almost equal in energy, while Jafri and Newton have found the ¹A_{1g} state somewhat lower in energy.⁹

Absorption and emission vertical transitions

The calculated absorption and emission transitions to the first three singlet and first three triplet states are shown in Tables 2 and 3, respectively, and the O—O electronic transitions are given in Table 1. The longest wavelength absorption transitions ¹B_{1g}←¹A_g and ³B_{1g}←¹A_g are in good agreement with some theoretical calculations (and with experimental data for the singlet

Table 2. Absorption transitions (Franck-Condon) [eV] (a) Our results, (b) EOM[12], (c) PPP-CI[11] Experiment 3.54–4.13 eV[1]

	¹ A _g → ³ B _{1g}	¹ A _g → ¹ B _{1g}	¹ A _g → ¹ A _g *	¹ A _g → ³ B _{3u}	¹ A _g → ³ B _{2u}	¹ A _g → ¹ B _{3g}
a)	1.12	3.46	4.90	5.96	6.00	6.10
b)	1.12	3.67	5.36	6.11	6.27	-
c)	-	3.52	4.35	-	-	-

Table 3. Emission transitions (Franck-Condon)[eV] using equilibrium geometries given in Table 1.

${}^3A_{2g} \rightarrow {}^1B_{1g}$	${}^1B_{2g} \rightarrow {}^1B_{1g}$	${}^1A_{1g}^* \rightarrow {}^1B_{1g}$	${}^3B_{3u} \rightarrow {}^1A_g$	${}^3B_{2u} \rightarrow {}^1A_g$	${}^1B_{3g} \rightarrow {}^1A_g$
~ 0	2.18	2.31	5.25	5.74	5.88

absorption $S_1 \leftarrow S_0$). It can be seen from Table 2 that the Stokes shift $\Delta E_{St} = \Delta E_{abs} - \Delta E_{em}$ is anomalous ($> 5000 \text{ cm}^{-1}$)¹³ for all transitions between the ground and valence excited states. These results seem reasonable, since in the Stokes shift is reflected the change in geometry upon excitation of the molecule.^{2,14} This change is rather large for the valence excited states and smaller for the Rydberg states (in Table 1).

The T_1 (${}^3A_{2g}$) phosphorescence state of CB lies very close to the ground state (0.19 eV) and the transition energy $T_1 \rightarrow S_0$ is ~0. This is conducive to intensive radiationless deactivation of the T_1 state, i.e. experimental observation of phosphorescence of CB cannot be expected.

The presence of a drastic change in the lengths of the C-C bonds upon excitation from ${}^1A_g(S_0)$ to ${}^1B_{2g}(S_1)$, accompanied with a change in symmetry $D_{2h} \rightarrow D_{4h}$ (Table 1) should according to general photophysical principles^{15,16} lead to a crossing of the potential hypersurfaces of the S_1 and S_0 states in the neighbourhood of the equilibrium point of the S_1 state, i.e. to radiationless deactivation; in addition, the emission transition ${}^1B_{2g} \rightarrow {}^1B_{1g}$ is forbidden. In contrast to the general case, however, the potential hypersurface of CB in ground state has two minima and the energy gap between the S_0 and S_1 hypersurfaces in the equilibrium point of the S_1 state is rather large, 2.18 eV. This leads to the conclusion that CB could exhibit a weak fluorescence in the region of 550–600 nm.

Finally we shall consider the energy difference between the vertical absorption and the non-vertical transition, which can be used as a rough estimate for the steepness of the potential hypersurface of a given excited state. It can be seen from Tables 1 and 2 that the S_1 and S_2 states of CB (which are of identical geometry) differ strongly, for the hypersurface of the S_2 state should be more steep than that of S_1 ; the S_1 and T_1 states have comparable, with respect to steepness, hypersurfaces.

Aromaticity in ground and excited states

From the many different theoretical and experimental means of estimating aromaticity (for a recent overview see ref. 17), we choose to use here the degree of alternation in the bond lengths^{18–21} in different equilibrium geometries of CB. Thus strong alternations in the bond lengths is interpreted as antiaromaticity (weak electron delocalisation), weak or no alternation as aromaticity (strong electron delocalisation), and intermediate alternation as non-aromaticity (intermediate electron delocalisation). To distinguish between different cases of no alternation (square geometry), a "longer" bond length is interpreted (cf Dewar²²) as decreased "effective π -bond energy", and thus decreased aromaticity.

In the present paper we shall try to give a qualitative

answer as to how the aromaticity of CB changes upon excitation, more specifically upon excitation to the lowest-lying fluorescent (S_1) and phosphorescent (T_1) states. It can be seen from Table 1 that the rectangular ground state of CB exhibits a very strong alternation of bond lengths, stronger even than characteristic of the typical non-aromatic compounds (linear trans-polyenes) 1.36–1.46 Å.²³ This is in full agreement with all other studies¹ which place CB together with the antiaromatic systems. Upon excitation of CB from the ground S_0 (1A_g) state to the excited S_1 (${}^1B_{2g}$), S_2 (${}^1A_{1g}$), and T_1 (${}^3A_{2g}$), the geometry of the molecule changes strongly and the bond length alternation disappears (Table 1). Similar results were obtained by us for the S_1 state in a PPP calculation (including full π -space CI) of CB using S_0 geometry taken from Table 1. Using Coulson-Golebiewski's relation,²⁴ we have obtained a square geometry $CC = 1.428 \text{ \AA}$ for the S_1 state. These states are square in their equilibria and the π -electrons are evenly delocalized along the 4-membered ring. The calculated bond lengths lie in the range of aromatic C-C bond lengths (~1.38–1.44 Å, see for instance²³ and cf. 1.421 Å for graphite²³). All this indicates that the antiaromaticity of CB strongly decreases in S_1 , S_2 , and T_1 states, and that probably these states should have to a certain degree an aromatic character. For the T_1 state these results are in qualitative agreement with the conclusions of Baird.²⁵ Because of the greater C-C bond lengths in the square equilibrium excited states, it is also to be expected that the aromaticity of these states is lower than that of benzene, the tropylium cation and the pentadienyl anion in ground state- $CC \sim 1.4 \text{ \AA}$.²³

In the framework of the present approach, the experimental values for the bond lengths in excited S_1 (${}^1B_{2u}$) and T_1 (${}^3B_{1u}$) benzene (1.434 Å and 1.433 Å, respectively^{26–28}) should also indicate a similar decrease in aromaticity upon excitation.

Thus we come to the following conclusion: upon excitation to the fluorescent S_1 , phosphorescent T_1 states the aromaticity of the Hückel system benzene decreases, whereas that of the anti-Hückel system cyclobutadiene increases significantly.

An experimental indication supporting the above conclusion with respect to CB would be its relative photochemical stability upon irradiation in its first absorption band. Indeed, CB is obtained mainly photochemically and decomposes relatively slowly and upon lengthy irradiation (to acetylene).¹ Conversely, CB in ground state decomposes and/or dimerizes rapidly (upon heating).¹

As seen from Table 1, the Rydberg excited states of CB are characterized by strong bond length alternation, although not so strong as in the ground state. As these states are rather highlying, it is hardly meaningful to estimate their aromatic character.

A more detailed study of aromaticity of some Hückel and anti-Hückel systems in excited states is in progress.

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