Further Theoretical Studies of the Structure and Electronic Spectrum of Cyclobutadiene *

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The possible geometries for cyclobutadiene and the electronic spectra corresponding to those geometries were calculated by a modified Pariser-Parr method with inclusion of doubly-excited as well as singly-excited configurations in calculating the π-energy. The bond lengths of the most stable forms agreed well with previous calculations where the empirical parameters used in the π-energy calculation were different from those used here, and where only singly-excited configurations were included. With these additional refinements, the rectangular singlet is calculated to be more stable than the square triplet. It is noted that the geometry predicted to have the lowest energy is a function of the approximations employed.

Mögliche Geometrien und die zugehörigen Spektren von Cyclobutadien wurden nach Pariser-Parr unter Einschluß der einfach und zweifach angeregten Konfigurationen berechnet. Die Bindungslängen der stabilsten Form stimmen gut mit früheren Rechnungen mit anderen gewählten Parametern überein, bei denen nur die einfach angeregten Konfigurationen berücksichtigt worden waren. Und zwar ergibt sich, daß eine rechteckige Form (Singulett) stabiler als die quadratische (Triplett) ist. Allerdings hängt diese Geometrie von den gewählten Parametern ab.

Les géométries possibles du butadiène et les spectres électroniques correspondants ont été calculés par une méthode de Pariser-Parr motifiée avec interaction de configurations avec les états mono et diexcités des électrons π. Les longueurs de liaison des formes les plus stables sont en accord avec celles obtenues précédemment avec des paramètres empiriques différents dans un calcul ne tenant compte que des configurations monoexcitées. Dans notre calcul amélioré le singulet rectangulaire est plus stable que le triplet carré. La géométrie la plus stable dépend de l'approximation utilisée.

Introduction

In an earlier paper, the energies of cyclobutadiene with different possible geometries were calculated using the modified Pariser-Parr method for calculating the π-energy and the Westheimer Method for the σ-energy [1]. With all singly-excited states included in the CI Matrix, it was found that the triplet π electronic configuration of the square form was more stable than the singlets of either the square form or the most stable rectangular form. However, in a quite different approach, Dewar [2] found the reverse to be true, although the geometries obtained for both the square and rectangular forms were similar by either method of calculation. Since the method of calculating the total energy [3] used in the earlier paper [1] was different from and inferior to the method we later developed [6] to fit the spectra of a wider selection of compounds, we thought it would be instructive to redo the calculations on cyclobutadiene by employing the latter method, which also includes doubly-excited configurations in the CI treatment.

The equation for the compression energy for the σ system was redetermined. By a slightly different approach (see Appendix) from that given by the previous papers [1, 3] the equation found and used in the present work is

$$E = 29.5\,(r - 1.574)^2$$

where r is the bond length expressed in Å, and E is in eV. The constants in the above equation were chosen to yield an equilibrium bond length of 1.334 Å for ethylene and 1.510 Å for zero-bond-order ethylene. Use of this equation also yields bond lengths for benzene and butadiene which are in satisfactory agreement with experiment. See Table 1 for details.

Table 1. *Calculated and experimental bond lengths (Å) and energies (eV) for butadiene and benzene*

	Bond Length calc.	Energy calc. (from calc. bond lengths)			Bond Length Experimental	Energy calc. (from exp. bond lengths)		
		E_π	E_σ	E_T		E_π	E_σ	E_T
Benzene	1.399	−89.106	5.392	−83.714	1.397	−89.229	5.516	−83.713
Butadiene	1.344, 1.456	−55.979	3.516	−52.462	1.344, 1.468	−55.906	3.446	−52.461

Results and Discussion

The bond lengths leading to a minimum of total energy for cyclobutadiene were sought for the square singlet, square triplet, and rectangular singlet. The results are presented in Table 2. The energies calculated with inclusion of singly-excited configurations only, and with inclusion of both singly and doubly-excited configurations are also presented in Table 2.

Table 2. *The calculated geometries and energies for different possible electronic structures of cyclobutadiene*

Structure[c]	R_{12}	R_{23}	E_σ	E_π[a]	E_T[a]	E_π[b]	E_T[b]
S-triplet	1.422	1.422	2.710	−56.009	−53.299	−56.009	−53.299
S-singlet	1.427	1.427	2.534	−55.133	−52.599	−56.287	−53.754
R-singlet	1.331	1.498	3.807	−57.186	−53.379	−57.768	−53.961

   [a] Configuration interaction up to and including all singly-excited configurations.
   [b] Configuration interaction up to and including all doubly-excited configurations.
   [c] S = square; R = rectangular.

The results indicate that the singlet of the rectangular form is the most stable among the three possible forms. This is contrary to the previous calculation using a similar method. The difference between the two methods which caused the contrary results seemed to lie in the way the resonance integrals (β) and the Coulomb integrals (γ) were obtained. In the previous method, the β and γ vs. distance curves were determined in a highly empirical manner specifically to fit the electronic spectrum of benzene. In the present method, they were related to their theoretical counterparts and were found to yield good electronic spectra

of a variety of compounds. We therefore feel that the present calculation is more reliable. Another quite unexpected finding in the present calculation was that with the inclusion of doubly-excited configurations, the singlet of the square form becomes more stable than the triplet. The cause for this difference is that the singlet ground configuration interacts strongly with its doubly-excited configurations, while the triplet does not interact with any of the doubly-excited configurations.

Since there was some evidence which suggested that cyclobutadiene has a singlet ground state, and tetramethylcyclobutadiene appears likely to have a triplet ground state [5], calculations were also made to compare the energies of the methyl-substituted cyclobutadienes in their various geometric forms. The results show that as the number of methyl groups increases, the energy difference between the singlet of the rectangular form and the triplet or singlet of the square form decreases. However, the change in the difference in energy is only a few hundreds of an eV. The spectra of each of the three possible forms were calculated and are presented in Table 3.

Calculations including triply-excited configurations were also carried out, as these do make some difference in some cases [6]. It was found that the ground state energies remained practically unchanged as expected, and the calculated spectra differed from those given in Table 3 only for transition energies which exceeded 9 eV.

Table 3. *The calculated spectra of the most stable forms of cyclobutadiene*

Molecule	Transition energy		f
	eV	mμ	
S cyclobutadiene (singlet)	1.14	1084.5	0
	1.72	722.8	0
	5.88	210.8	0.09
	6.08	204.1	0
	8.22	150.9	0
	9.26	134.0	0.39
S cyclobutadiene (triplet)	3.05	406.8	.01
	3.27	379.4	.2
	7.04	176.2	—
	7.16	175.7	—
R cyclobutadiene (singlet)	2.45	506.5	0
	2.63	471.3	0
	6.27	197.7	0.21
	7.22	171.8	0.01
	9.08	136.6	0
	9.90	125.2	0.88

While we do not feel completely confident of the prediction that the rectangular singlet will be found to be the stable form of cyclobutadiene (because the calculated energy difference is small), we do feel confident that the electronic spectrum can be used to establish which form is under examination in an experimental study.

The singlet is predicted to show only forbidden or faintly allowed bands above 210 mμ in the ultraviolet, while the triplet will show strong absorption at about 380 mμ, which will almost certainly lead to the compound being strongly colored.

Appendix

The total energy E_T can be expressed as $E_T = E_\pi + E_\sigma$ where E_π is the energy due to the π system, and E_σ the energy due to the σ system. The π energy is obtained with the VESCF-CI method with inclusion of penetration effects and all singly and doubly excited states. The σ energy is assumed to obey the relation $E_\sigma = \dfrac{k}{2} (r - r_0)^2$ where the constants k and r_0 are to be determined.

Since at the equilibrium bond length r_e, the total energy is a minimum $(dE_T/dr)_{r=r_e} = 0$, or $(dE_\pi/dr)_{r=r_e} = -(dE_\sigma/dr)_{r=r_e}$ and $(dE_\sigma/dr)_{r=r_e} = k(r_e - r_0)$. Therefore, if we have information on $(dE_\pi/dr)_{r=r_e}$ for two molecules the values of k and r_0 can be found. The desired information can be obtained by using ethylene and zero-π-bond-order ethylene as references. The bond length of ethylene is taken to be 1.334 Å, and of zero-π-bond-order ethylene, to be 1.510 Å.

The principle of the method used to determine $(dE_\pi/dr)_{r=r_e}$ is as follows: On a plot of E_π vs. r; if we take the point at $r = r_x$ and connect it to the point at $r = r_e$, the slope changes with the position of r_x. As r_x approaches r_e, or Δr approaches zero, the slope approaches (dE_π/dr) at $r = r_e$. Therefore by calculating $\Delta E_\pi/\Delta r$ at different values of Δr, the value of (dE_π/dr) at $r = r_e$ can be obtained by interpolation.

The calculations on ethylene are shown in Table 4, and $(dE_\pi/dr)_{r=1.344\text{Å}}$ is found to be 14.132 eV/Å.

Table 4

r_x (Å)	E_π (eV)	Δr (Å)	$\Delta E/|\Delta r|$
1.315	−26.87967	0.019	14.398
1.320	−26.80668	0.014	14.326
1.325	−26.73442	0.009	14.257
1.330	−26.66286	0.004	14.188
1.334	−26.60611	0	(14.132) by interpolation
1.340	−26.52182	−0.006	14.048
1.345	−26.45233	−0.011	13.980
1.350	−26.38354	−0.016	13.911
1.355	−26.31540	−0.021	13.843

(Note: the plot of $\Delta E/|\Delta r|$ vs. Δr in this range is a straight line.) Similarly, from calculations on zero bond order ethylene, (dE_π/dr) at $r = 1.510$ Å is found to be 3.749 eV/Å. Hence we have

$$k(1.334 - r_0) = -14.132$$
$$k(1.510 - r) = 3.749 .$$

Solving the above two simultaneous equations, we find, $r_0 = 1.574$ Å and $k = 58.99395$ eV/Å thus $E_\sigma = 29.50(r - 1.574)^2$ eV.

References

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