LETTER

The Structures and Lower Electronic States of Cyclobutadiene

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Since the earliest times of the development of quantum chemistry, cyclobutadiene has been frequently studied from the theoretical standpoint together with benzene. The molecule is of special interest because of its peculiarities in many respects when compared with benzene. On its molecular structure Coulson1) and Craig2,3)* have supposed that the molecule, if it exists, should not be square as usually assumed but may be rectangular in form. Until now no quantitative work has been done about this problem or as to how the lower electronic states, especially the ground state, change their location in the energy level schema on varying the structure.

The present author has calculated the energy levels of all configurations arising from four π-molecular orbitals, assuming five different structures varying from the square (I) to the rectangle (V) having the normal single and double bond lengths. The standard ASMO method without configuration

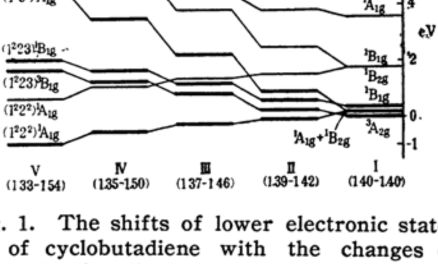

Fig. 1. The shifts of lower electronic states of cyclobutadiene with the changes of molecular dimensions.

Fine and thick stripes indicate the configuration energies computed by the ordinary ASMO method and by the method of atoms in molecules respectively. The ${}^3A_{2g}$ level in the square form (I) is taken as the reference state in both computations. (1.33–1.54), for instance, represents the short and long bond lengths in Å.

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1) C. A. Coulson, private communication to the present author; C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1947).

2) D. P. Craig, *Proc. Roy. Soc.*, **A 202**, 498 (1950).

3) D. P. Craig, *J. Chem. Soc.*, **1951**, 3175.

* And also the earlier work of J. E. Lennard-Jones and J. Turkevich, *Proc. Roy. Soc.*, **A 158**, 297 (1937).

interaction has been used at first. Next, to the results thus obtained has been added Moffitt's correction by the method of atoms in molecules.[4] Then the two sets of results have been compared. In the figure are shown the term values for only the lower energy states which are of primary importance for the present purpose. When comparing the ground state of (I) with that of (V) as obtained by the ASMO method, one might infer that the former would be more stable than the latter. On the other hand, according to the second treatment which seems to be more reliable, the lowest singlet level referred to the lowest triplet level is lowered throughout the five structures by 1.61 e. V. and the ground state of (V) is located about 0.9 e. V. below that of (I). The effect of configuration interaction has been known to be small, in general, in the method of atoms in molecules. To cite an example, in (I) the splitting (not shown in the figure) of degenerate $^1A_{1g}$ into $^1B_{1g}$ and $^1B_{2g}$ is only 0.3 e. V.[4,5] according to the method of atoms in molecules, whereas in the ordinary ASMO method it amounts to 3.5 e. V.[2] In the above, σ-bonds have been excluded from consideration; if these are taken into account the square form will still be unstable, because the energy gained in the modification process (V to I) of the σ-framework is relatively small (at most 3 kcal.). Now, it may safely be concluded that cyclobutadiene will not be stable in a square form and that, if it exists, it will take a rectangular form.

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