at room temperature. The complex was the decomposed with glacial acetic acid, and the solvent was removed under reduced pressure. Water (20 mL) was added, and the mixture was extracted with $CHCl_3$ (3 × 25 mL). To the combined extracts was added 15% hydrochloric acid (25 mL), and the mixture was refluxed for 4 h and then cooled, and the organic layer was separated. The aqueous layer was extracted once with $CHCl_3$, and the combined extracts were washed with saturated brine, dried (Na_2SO_4), and concentrated. Chromatography on silica gel (10:1 petroleum ether–EtOAc) gave 3.22 g (78%) of pure **8**: IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (CDC13) δ 1.19 (t, 3 H), 2.1–3.1 (m, 10 H), 4.0 (q, 2 H), 5.8 (m, 3 H).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.78; H, 8.78.

Azulene-5-carboxylic Acid (9). A mixture of diene **8** (2.06 g, 0.01 mol) and DDQ (100 mg) in benzene (75 mL) was refluxed for 14 h. The solution was cooled, filtered, diluted with ether, and washed with aqueous $NaHCO_3$ solution. A 20% NaOH solution (25 mL) was added to the organic phase, and the solution was stirred at 25 °C for 4 h. The organic layer was separated, and the aqueous phase was extracted once with benzene. The combined extracts were washed successively with water, dilute hydrochloric acid, and water, then dried (Na_2SO_4), and concentrated. The residue was crystallized (EtOAc–petroleum ether) to give violet crystals of **9** (1.2 g, 65%): mp 202–203 °C (lit.[9] mp 206–207 °C).

Acknowledgment. Financial support was provided by the Department of Science and Technology, and the Government of India is gratefully acknowledged. We also thank Dr. R. Balasubramanian for his help.

Registry No. **2**, 867-13-0; **3**, 99377-24-9; **4**, 99377-25-0; **5**, 7148-07-4; **6**, 99377-26-1; **7**, 99377-27-2; **8**, 99377-28-3; **9**, 1202-03-5; bromoacetone ethylene ketal, 33278-96-5.

An ab Initio Study of the Cyclobutadiene Dianion and Dication

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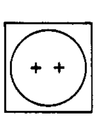
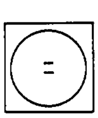
Received August 27, 1985

Hückel's rule predicts that both the dication (**1**) and dianion (**2**) of cyclobutadiene should be aromatic. Ion **1** contains two π electrons ($4n + 2$, $n = 0$) and ion **2** six π electrons ($4n + 2$, $n = 1$). However, more recent Hückel calculations with a Mulliken–Parr type of reference structure predict both to be nonaromatic (REPA = -0.001β).[1]

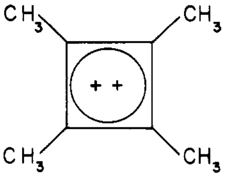


1



2

The little experimental evidence available seems to suggest that neither ion is particularly stable. While the parent dication **1** is unknown, Olah, Bollinger, White, and Mateescu have reported the synthesis of the tetramethyl and tetraphenyl derivatives (**3** and **4**).[2,3] However, their syntheses of **3** and **4** were later questioned by van der Hout-Lodder, de Haan, van de Ven and Buck because of the temperature dependence of the ^{13}C NMR spectrum of **4**.[4,5] They suggested that what Olah and co-workers had observed were the dications in equilibrium with their monocations. Olah and Staral subsequently published more details of the syntheses of **3** and **4** and reported the formation of first the monocations and subsequently the dications.[6] They concluded that if the equilibrium is present, the dication must be by far the dominant species. Perhaps the best evidence for the lack of strong π stabilization in **1** is an ab initio calculation reported in 1978.[7] It was found that the dication **1** is not planar but rather a puckered square (D_{2d}) with a dihedral angle of 144.2°.



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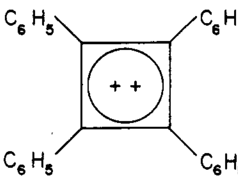
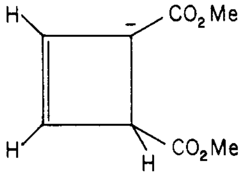


4

McKennis, Brener, Schweiger, and Pettit[8] obtained evidence for the formation of dianion **2**; but they characterized it as being highly reactive since it apparently abstracted protons from THF. More recently Garratt and Zahler[9] measured the pK_a of **5** and concluded that the dianion formed from **5** has no special stabilization. They suggested that even the parent dianion **2** will be nonaromatic.



5

We have carried out an initial search of the potential surface of **2** with the 3-21G basis set.[10,11] Several geometries were examined: trapezoid (C_{2v}), rectangle (D_{2h}), puckered square (D_{2d}), rhombus (D_{2h}), square (D_{4h}). However, all led to a square geometry, which was the highest symmetry considered. The optimized square had a C–C bond distance of 1.470 Å and a C–H bond distance of 1.088 Å and an energy of −152.37661 au. Reoptimization of the square with the 6-31G* basis[10] gave values of 1.455 and 1.077 Å and an energy of −153.24573 au.

To be certain that the square structure was a minimum on the potential surface, a vibrational analysis was undertaken with the 6-31G* basis. It was found that for the E_g distortion (**6**) the energy decreased relative to the square structure and, thus, that indeed the square is not a minimum on the potential surface of the cyclobutadiene dianion. Structure **6** has lower symmetry (C_s) than any previously examined. Further optimization was then carried out with a C_s symmetry constraint. This was done with both the 3-21G and 6-31G* basis sets, and the results

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(1) Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471.

(2) Olah, G. A.; Bollinger, J. M.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3667.

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(5) van der Hout-Lodder, A. E.; de Haan, J. W.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 156.

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(11) Although the 3-21G basis set was developed for neutral molecules, L. Radom (*Aust. J. Chem.* **1976**, *29*, 1635) has shown that with the similar 4-31G basis excellent agreement between calculated and experimental geometries was obtained for a number of mono- and dianions.

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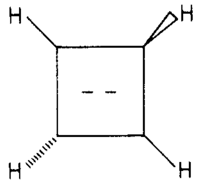
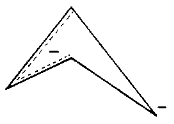


6

are given in Figure 1 along with those for cyclobutadiene[12] and its dication.[7] Examination of the geometry (Figure 2) found for the dianion indicates not only that the degree of puckering is much less than that found for the dication but that its overall structure is quite different. The two long and two short C–C bonds along with the position of hydrogen attached to C-4 suggest that the dianion consists of a localized negative charge at C-4 and an allylic anion (C_1–C_2–C_3) as in 7.



7

It appears therefore that there is little driving force toward conjugation of six π electrons in the dianion.

Comparison of the 6-31G* and 3-21G results (see Figure 1) indicates that the larger basis set brings about no significant changes in the geometries of cyclobutadiene or its dication and dianion. Some minor trends are apparent. The 6-31G* carbon–carbon bonds are somewhat shorter and carbon–hydrogen bonds are slightly longer than those computed with the 3-21G basis set. Also very small changes occur with the various angles. Hence, it appears that the smaller 3-21G basis set is quite sufficient for determining the geometries of these species.

In light of the results for the dianion, a possible C_s structure was also examined for the dication since this was not one of the structures previously considered.[7] The starting geometry used in the search (STO-3G) was strongly distorted (long and short C–C bonds); however, after a rather lengthy search the structure converged to that found earlier (D_{2d}) by Krogh-Jespersen, Schleyer, Pople, and Cremer.[7]

An allylic species such as 7 might be expected to exhibit as appreciable effect of electron correlation on its structure. Therefore, we carried out an additional set of calculations at the MP2 level to determine qualitatively whether the same structure results. The MP2 optimization was also found to give a bent structure with C_s symmetry as 7. The primary change was that the long and short carbon–carbon bonds differed by only 0.05 Å, as compared to a difference of 0.14 Å in the SCF optimization.

One question that remains is whether the highest energy electrons are bound in the dianion. Table I shows that with the 6-31G* basis the energies of the four highest occupied orbitals are positive. A single-point calculation at the 6-31G* geometry was done with an added diffuse p-function on each carbon (6-31G* + diffuse p).[13] Even with this basis set the two highest occupied orbitals are positive in energy. A similar situation was found for the square (D_{4h}) dianion mentioned above. To evaluate the influence of a counterion, $Li^+C_4H_4^{2-}$ was examined with the 3-21G basis. Its geometry was optimized with the C_{4v} symmetry constraint and is given in Figure 3. It is seen that the major effect of the lithium on the structure is the distortion of the hydrogens out of the plane of the carbons and away from the lithium, but the C–C bond distances and skeletal angles are very similar to those found for the square dianion in the absence of the lithium (1.470 Å). The highest occupied molecular orbital (HOMO) is now bound (energy = −0.0084 au), and the total energy is −160.160 31

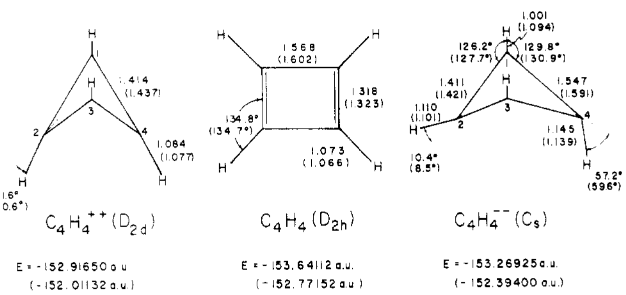


Figure 1. Optimal geometries of cyclobutadiene,[12] its dication,[7] and dianion computed with 6-31G* basis and 3-21G (in parentheses). For the dication and dianion, the dihedral angles made by $C_1C_2C_3$ and $C_3C_4C_1$ planes are 137.4° (140.4°) and 163.1° (164.4°), respectively. In the dianion the dihedral angle made by $C_2C_1C_4$ and $C_2C_3C_4$ planes is 167.62° (168.39°). The dashed lines bisect the $C_1C_2C_3$ and $C_1C_4C_2$ angles. Bond distances are in Angstroms and angles in degrees; energies are in atomic units. The conversions of 1 au of length = 0.529 177 06 Å and 1 au of energy = 627.5092 kcal/mol were used throughout.[14]

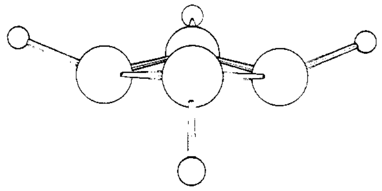


Figure 2. ORTEP[15] drawing of the dianion of cyclobutadiene.

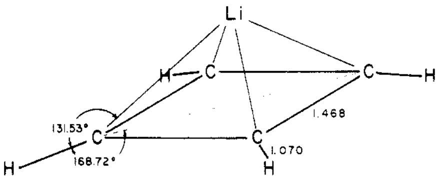


Figure 3. Optimized geometry (3-21G) of $Li^+C_4H_4^{2-}$ with a C_{4v} symmetry constraint. The lithium lies 1.078 Å above the plane of the carbons. Bond distances are given in Angstroms and angles in degrees.

Table I. Orbital Energies (au) of the Filled Orbitals of the Cyclobutadiene Dianion

symmetry	6-31G*/6-31G*	6-31G* + diffuse p/6-31G*
A′	−10.7633	−10.8658
A″	−10.7185	−10.8519
A′	−10.7185	−10.8519
A′	−10.7090	−10.8394
A′	−0.6324	−0.7503
A″	−0.3690	−0.4754
A′	−0.3593	−0.4619
A′	−0.2046	−0.3027
A′	−0.1780	−0.2771
A″	−0.0331	−0.1415
A′	−0.0267	−0.1227
A″	0.0303	−0.0834
A′	0.0716	−0.0277
A′	0.2197	0.1316
A″	0.2439	0.1637

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[12] Hess, B. A., Jr.; Čársky, P.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 695.

[13] The diffuse p had an exponent of 0.034 as recommended by: Dunning, T. H., Jr.; Hay, P. J. In "Modern Theoretical Chemistry"; Schaefer, H. F.; III, Ed.; Plenum Press: New York, 1977; Vol. 3, p 1.

[14] Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1973**, *2*, 663.

[15] Johnson, C. K. "ORTEP II, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

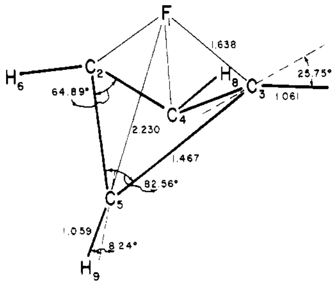

Figure 4. Optimized geometry (3-21G) of $F^-C_4H_4^{2+}$ with a C_{2v} symmetry constraint. The C_2–H_6 and C_3–H_7 bonds form an angle of 25.75° with the bisectors of $\angle C_4C_3C_5$ and $\angle C_4C_2C_5$ and are on the opposite side of the planes formed by these angles from the fluorine. The C_4–H_8 and C_5–H_9 bonds form an angle of 8.24° with the bisectors of $\angle C_2C_4C_3$ and $\angle C_2C_5C_3$ and are on the same side of the planes formed by these angles as the fluorine.

au. This suggests that the highest filled orbital of the C_s structure for the dianion is also likely to be bound when a cation is introduced.

We have also studied the influence of a counterion on the structure of the dication of cyclobutadiene by optimizing the structure of $F^-C_4H_4^{2+}$ (Figure 4) with the C_{2v} symmetry constraint (3-21G basis). Although the basic puckered character of the ring remains, the two dihedral angles of the ring (102.9, 91.1°) are considerably smaller than those found in the dication in the absence of the fluoride ion (164.4°).

The structure of $C_4H_4^{2+}$ in the presence of two fluoride ions has been studied by Kos and Schleyer.[16] However, they imposed a planar C_{4v} structure on the $C_4H_4^{2+}$ group. As can be seen from the above results, this is a fairly poor approximation to the structure of this species, either with or without counterions.

In summary, it has been found that the addition of or removal of two electrons from cyclobutadiene leads to two very different structures both of which minimize overlap of their potential π systems, in agreement with our earlier prediction[1] of nonaromatic character for these two diions.

Acknowledgment. C.S.E. thanks the Air Force Office of Scientific Research for partial support of this work under Grants AFOSR-82-0100 and AFOSR-85-0072 DEF.

Registry No. 2, 36685-24-2.

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Methyl Group Functionalization in 6-Methylazulene

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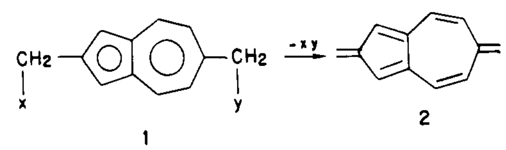
Received April 16, 1985

Our interest in the features of the electronic structures of unstable polyenes[1] that are revealed by photoelectron spectra led us to consider the azulylene family of which **2** is the 2,6-isomer. Gram quantitites of an appropriate precursor (**1**) are required to provide such spectra, and methods of functionalizing methyl groups on azulenes are not altogether trivial.[2] We therefore have developed a useful method that accomplishes this purpose for 6-methylazulene (Scheme I).[3]



The key metalation reaction was suggested by the previous results of Hafner.[4] Treatment of 6-methylazulene with sodium*N*-methylanilide in tetrahydrofuran generated sodium 6-methyleneazulenate. The solution of this sodium salt may then be converted to either the chloride (**3**) using trifluoromethanesulfonyl chloride[5] or alternatively the oxime (**4**) by treating the sodium salt with isoamyl nitrite. The chloride (**3**), as expected, is an excellent substrate for nucleophilic substitution.

Table I shows the results for a number of new compounds that are easily obtained by the reaction of 6-(chloromethyl)azulene with several nucleophiles. Competitive initial rate experiments for the reaction of **3**, compared with 1-(chloromethyl)naphthalene, were also investigated with the nucleophiles shown in Table I. The tabulated results indicate that 6-(chloromethyl)azulene reacts slightly faster than 1-(chloromethyl)naphthalene with anionic nucleophiles but at approximately the same rate with the uncharged nucleophile diethylamine. This could be rationalized by the polarity of the charge distribution of the nonalternant azulene system.[6]

The rates of solvolysis of certain arylmethyl chlorides have been measured and interpreted in terms of a molecular orbital treatment.[7] This model predicts a linear correlation between the logarithm of the solvolysis rate and the coefficient of the nonbonding molecular orbital at the methylene carbon atom of the corresponding carbocation. The respective HMO coefficients for the 1-methylnaphthalene and the 6-methylazulene systems are both 0.67. The equivalence of these coefficients suggests identical rates of solvolysis and S_N2 displacement[7] for the respective chlorides in satisfactory agreements with the experimental results. This model, using the HMO coefficients for the nonalternant azulene system, does not account for the high reactivity of 1-methylazulene derivatives[8] or the relatively low reactivity of 4-methylazulene derivatives,[4b] and the agreement between the model and experiments in the present case might be fortuitous.

The main point of the present work is that 6-(chloromethyl)azulene is now readily available via chlorination of 6-methylazulene and has been shown to be a reactive substrate in displacement reactions. Derivatives of this

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(2) Azulenes react rapidly with *N*-bromosuccinimide to give 1-bromo-substituted azulenes; see: Hafner, K.; Patzelt, H.; Kaiser, H. *Justus Liebigs Ann. Chem.* **1962**, *656*, 24.

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