Communications to the Editor

Nonplanar Structures of Cyclobutadiene Dications

Sir:

Olah and coworkers have prepared a number of methyl, phenyl, and fluorine substituted cyclobutadiene dications in superacid media, but little detailed structural information is available. The parent dication is not yet known in solution although C4H42+ species of undetermined structure may have been encountered in the gas phase. Huckel molecular orbital theory predicts the aromatically stabilized 2s-electron ground-state geometry (I). The resulting conclusions have never been subjected to critical examination. We present here the results of ab initio molecular orbital calculations which suggest that the parent cyclobutadiene dication, as well as the tetramethyl derivative, is not planar, but prefers rather strongly puckered geometries (II and IV) instead.

The cyclobutadiene dication geometry was optimized within two overall molecular symmetry contraints, D4h (I) and D2d (II), using the Gaussian 70 series of programs and three basis sets, minimal STO-3G, split valence 4-31G, and a basis set containing a split valence as well as polarization functions on carbon, 6-31G*. The CI-C, and C-H bond lengths of I were optimized simultaneously with a procedure based on the conjugate gradient scheme of Davidon, Fletcher, and Powell.

At all calculational levels, II was the lowest energy structure for the cyclobutadiene dication. The calculated barrier to inversion through the D4h form (I) increases in the restricted Hartree-Fock (RHF) approximation with improvement in the geometry of the valence molecular orbitals (Table I). The decrease in symmetry from D4h to D2d allows greater mixing among the orbitals; in particular, the 3e, orbital which is the 1,2-bonding, 1,3-antibonding Walsh-type ring orbital of p, and py character (Figure 1). The energetic advantages arising from puckering are clearly reflected in the energies of the valence molecular orbitals (Table I). The decrease in symmetry from D4h to D2d allows greater mixing among the orbitals; in particular, the 3e, orbital which is the 1,2-bonding, 1,3-antibonding Walsh-type ring orbital of p, and py character (Figure 1). The energetic advantages arising from puckering are clearly reflected in the energies of the valence molecular orbitals (Table I).

Table I. Orbital Energies \( \epsilon (\text{au}) \) of Planar (I) and Puckered (II) Cyclobutadiene Dications (RHF/STO-3G).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>( \text{I, } D_{4h} )</th>
<th>( \text{II, } D_{2d} )</th>
<th>Difference, ( \epsilon (\text{I} - \text{II}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1g (LUMO)</td>
<td>-1.4041</td>
<td>-1.4141</td>
<td>+0.0261</td>
</tr>
<tr>
<td>1a2 (( \sigma ))</td>
<td>-0.9679</td>
<td>-0.9691</td>
<td>+0.0012</td>
</tr>
<tr>
<td>3e,</td>
<td>-1.0496</td>
<td>-1.0670</td>
<td>+0.0174</td>
</tr>
<tr>
<td>1b1g</td>
<td>-1.1020</td>
<td>-1.0962</td>
<td>-0.0058</td>
</tr>
<tr>
<td>2b2g</td>
<td>-1.1990</td>
<td>-1.2153</td>
<td>+0.0163</td>
</tr>
<tr>
<td>3a1g</td>
<td>-1.2155</td>
<td>-1.2155</td>
<td>0.0000</td>
</tr>
<tr>
<td>3e,</td>
<td>-1.4041</td>
<td>-1.4051</td>
<td>+0.0010</td>
</tr>
<tr>
<td>2a1g</td>
<td>-1.7488</td>
<td>-1.7747</td>
<td>+0.0259</td>
</tr>
</tbody>
</table>

* At RHF/6-31G*, the 2b2 orbital is lower in energy than the 3e,.

At RHF/6-31G*, the 2b2 orbital is lower in energy than the 3e,.

Figure 1. Schematic representation of the 1b1g, the 2b2g, and one of the 3e, molecular orbitals.

puckering of the cyclobutadiene dication as well, although the concomitant changes in molecular geometry and symmetry also are important. The energetic advantages arising from puckering are clearly reflected in the energies of the valence molecular orbitals (Table I). The decrease in symmetry from D4h to D2d allows greater mixing among the orbitals; in particular, the 3e, orbital which is the 1,2-bonding, 1,3-antibonding Walsh-type ring orbital of \( p_2 \) and \( p_3 \) character (Figure 1). The major stabilization on going from D4h to D2d occurs in the 3e, orbitals and is lowered primarily through enhanced overlap in the D2d geometry (II), in which the C1-C2 and C3-C4 distances are shortened by 0.02 and 0.09 A, respectively, relative to those in I (RHF/6-31G*). In both the 2b2g and 3e, orbitals, the C-H bond back lobes point toward each other inside the ring (Figure 1). In the 2b2g orbital two nodal planes bisect the C-C bonds, resulting in an absence of electron density in the center of the ring. Puckering forces the orbitals out of plane, and 1,3 bonding develops pairwise between the back lobes. The stabilization is so large that the 2b2 orbital energy drops below...
the 3a1 (RHF/6-31G*). The degenerate 3e, orbitals (Figure 1) are strongly 1,3 antibonding. Puckering decreases this 1,3 antibonding by tilting the hybrid orbitals and reducing their overlap. This effect also results from strong mixing with the LUMO εg (Dαg) set of p2 orbitals upon distortion and is enhanced by the slight bending of the hydrogens.

The change in 1,3 bonding also manifests itself in the Mulliken electronic population analysis. The total CI-C~ overlap populations in I are large and negative -0.359 (RHF/6-31G*), whereas in II the 1,3 interaction is indicated to be weakly bonding (C1-C3 overlap population = +0.076).

It is an oversimplification to attribute the puckering of the cyclobutadiene dications to any single effect. Nevertheless, part of the destabilizing 1,3 interactions in a four-membered ring may be relieved through puckering, and this geometrical alteration occurs despite the expected loss of resonance energy and the increase in angle strain. Orbital mixing and orbital reorientation, enhanced through pyramidalization, stabilize the puckered form. This interplay of effects seems to be fairly general and is to be found in isoelectronic four-membered ring systems containing boron as well.10 Substituents may change the preferred conformation; the strong donation of π electrons to the ring indicated by the NMR data suggests that planar substituted cyclobutadiene dications may also be found.

The tetrafluorocyclobutadiene dication is indicated (RHF/STO-3G) to be planar (V).11 However, the tetramethyl species, known experimentally, is calculated to be more stable puckered (IV)12 than planar (III).13 The RHF/STO-3G difference, 2.3 kcal/mol, is not much smaller than that for the unsubstituted species (I vs. II). Higher level calculations on III and IV, although not yet feasible, would probably also indicate a larger difference. This suggests the possibility of experimental verification of these predictions.13-14

Acknowledgments. This work was supported at Erlangen by the Fonds der Chemischen Industrie, at Carnegie-Mellon by NSF Grant CHE75-09808, and at Cologne by the Deutsche Forschungsgemeinschaft. We thank Professor George Olah and Professor R. G. Cooks for their interest. Computer programs written by Dr. Dieter Poppinger and by Dr. Hans-Ulrich Wagner and assistance provided by the Computer Centers at Cologne and at Erlangen facilitated this work.

References and Notes


(2) J. H. Beynon, A. Mathias, and A. E. Williams, Org. Mass. Spectrom., 5, 303 (1971); W. J. Hehre, private communication. The cyclobutadiene diation may not be the most stable isomer of C4H6. At the 4-31G optimized level, the pertubative method “C2H2CD2H2” (C2H2CD2H2) with R(C-C) = 1.339 Å. R(C-C) = 1.251 Å. R(C-H) = 1.087 Å. HCC = 120°, has an energy of -152.68998, and E(6-31G) = -152.01650.


(5) (a) Actually, Table 1 shows that the energy of the π orbital (1aπ) in I decreases slightly upon puckering.


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(10) (a) 3(CH)2(BH)2, K. Krogh-Jespersen, D. Cremer, J. D. Dill, P. v. R. Schleyer, and J. A. Popie, manuscript in preparation; (b) PM1, ref 3c.

(11) RHF/STO-3G structures and energies. (a) C4F42+, ref 3c; (b) C4H42-, ref 3c. (c) C4H42+, (III), C4 assumed carbon skeleton planar; R(C-C) = 1.467 Å (opt), R(OCC) = 1.507 Å (opt, (CH3 standard), E = -305.58622 au (compare with E = -303.68230 au given in ref 3b for the C4H42+ conformation). (d) C4(3H)1+ (IV), C4 assumed, obtained by allowing ill to puckering; R(OCC) = 1.459 Å, R(OCC) = 1.507 Å, θ1 = 126° (axial), θ2 = 0.230 Å (CH3 standard), dihedral angle between the C-C ring planes is 154.6°, E = -305.58622 au.

(12) The 1,2-dimethyl-3,4-dibenzylor 1,2-dimethyl-3,4-diisopropylcyclobutadiene dications might be suitable for this purpose by using NMR methods.

(13) We also considered the possibility that cyclobutadiene might have a non-planar carbon skeleton; however, such distortions produced no energy lowering in the triplet. The degenerate LUMO’s of I, which are strongly destabilized in the puckered conformation (II), are both singly occupied in triplet cyclobutadiene.

(14) The performance of the theory at levels used in this paper can be assessed by comparing the results on C4 hydrocarbons with experiment (W. J. Hehre and J. A. Pople, J. Am. Chem. Soc., 97, 6941 (1975)).

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Acarnidines, Novel Antiviral and Antimicrobial Compounds from the Sponge Acarlos erithacus (de Laubenfels)

Sir:

Extracts of the red-orange sponge Acarlos erithacus (de Laubenfels),1,2 from the Gulf of California have significant activity against Herpes simplex type 1,3 as well as against Bacillus subtilis,3,4 and Penicillium atrovenenum.3,5 We have followed these activities during fractionation and wish to report here the structures of a closely related group of compounds, the C120, C121, and C143 acarnidines (Ia-c), isolated from the extracts, which possess the biological activities noted above as well as activity against other microorganisms.3,5 The acarnidines have in common the unique substituted homopemidine skeleton shown (I) and differ in the fatty acid substituent R.

The acarnidines were isolated by extracting homogenized sponge with toluene–methanol (1:3) and partitioning with 1 N sodium nitrate solution. The antimicrobiol activity parameters, which were present in the aqueous phase, were extracted into chloroform and chromatographed on Sephadex LH-20 (methanol) and silica gel (CHC13–CH30H–concentrated NH3, 6:3:1) to give I in 0.2% yield, essentially free of impurities. Field desorption mass spectrometry (FDMS)6 of the oily mixture showed the most intense M + H ions at m/e 464 (1b), 466 (1a), and 488 (1c).