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Structure and Photoelectron Spectrum of 3,3′-Bicyclopropenyl[†]

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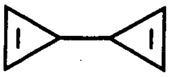
Abstract: The X-ray crystal structure of thermally sensitive 3,3′-bicyclopropenyl (mp 198 K) has been determined at 103 K using a miniature-zone melting procedure with focused infrared light. The structural parameters calculated for the anti conformer using the Hartree–Fock self-consistent field procedure with a 3-21 G basis set compare well with the experimental data. The photoelectron spectrum of **1**, which exhibits three peaks of different heights well separated from a smaller fourth one, can be interpreted in terms of about a 2:1 mixture of anti and gauche conformers, respectively, in the gas phase.

Introduction

The valence isomers of benzene have attracted the attention of chemists for well over a century.[1] Although Dewar benzene, benzvalene, and prismane have been known for some time, the fourth member of this family, 3,3′-bicyclopropenyl (**1**), has only recently been prepared.[2] Apart from the historical interest, the bicyclopropenyls have been the object of considerable interest with regard to interactions between the isolated double bonds.[3] These interactions of nonconjugated π-systems fall into a number of categories including overlap through space (homoconjugation,[4] spiroconjugation[5]) or, as recognized more recently, through the σ-framework of the molecule. The latter effect is often referred to as a "through-bond" interaction.[6] 3,3′-Bicyclopropenyl is of interest in this regard, as several theoretical calculations predict that this system will experience conjugation through the σ-framework.[7,8] In this paper we report the structure and photoelectron spectrum of **1** as well as model calculations which support the experimental work.



Results and Discussion

A. Molecular Structure. The X-ray crystal structure of **1** (mp 198 K) has been determined at 103 K using a miniature-zone melting procedure with focused infrared light (see Experimental Section). As predicted by semiempirical calculations,[4] the conformation of **1** in the solid state was found to be anti with C_i symmetry (Figure 1). With intermolecular H···H separations of 2.86 Å, the crystal packing of **1** is assumed not to cause significant distortions. The unit cell is presented in Figure 2. The interatomic distances in **1** (Table I) reveal several interesting features. The most salient is the central bond, which is extremely short (1.503 (1) Å) for a formal C(sp^3)–C(sp^3) bond, indicating significant rehybridization of the bridging atoms. This is also apparent from the C3′–C3–H3 angle of 113.7 (6)°, and the C3–C3′–(center C1,C2) of 124.7°.

The double bond is comparable to the double bond in cyclopropene, which was determined by microwave spectroscopy[9] to be 1.2939 (4) Å; however, the cyclic single bonds with C(sp^2)–C(sp^3) atoms are slightly longer (1.512 (1) Å) than those in cyclopropene (1.509 (1) Å). This may be attributed to the fact that, in general, bond distances in the gas phase are found to be longer than those in the solid state.

Table I. Interatomic Distances and Angles for 1

	Bond Lengths (Å)		
C3–C1	1.510 (1)	C3–C2	1.513 (1)
C3–H3	0.999 (12)	C3–C3′	1.503 (1)
C1–C2	1.290 (1)	C1–H1	0.951 (12)
C2–H2	0.914 (14)		
	Bond Angles (deg)		
C1–C3–C2	50.5 (1)	C1–C3–H3	118.9 (7)
C2–C3–H3	117.7 (6)	C1–C3–C3′	120.9 (1)
C2–C3–C3′	121.1 (1)	H3–C3–C3′	113.7 (6)
C3–C1–C2	64.8 (1)	C3–C1–H1	146.0 (8)
C2–C1–H1	149.1 (8)	C3–C2–C1	64.7 (1)
C3–C2–H2	146.7 (7)	C1–C2–H2	148.6 (7)

Table II. Calculated Relative Energies ΔE (kcal/mol) for the Anti (θ = 180°) and Gauche Conformations of 3,3′-Bicyclopropenyl[a]

method	θ (deg)	ΔE
3-21G	180	0.48
	47.6	
STO-3G	180	0.56
	45	
4-31G[b]	180	0.10
	45	

[a] The energy for the anti conformer was set to 0. [b] Based on structural parameters derived with the STO-3G basis set.

Since a similar bond length (anti conformer[10] X-ray structure 1.4924 (4) Å, gas electron diffraction[11] 1.508 Å) between the two rings of bicyclopropyl has been encountered and was also found to be shorter than the cyclic C(sp^3)–C(sp^3) distances[10] (1.5052 (3) vicinal, 1.5046 (4) distal) for this system, we ascribe this effect to the higher s character of this bond as compared to a normal C–C bond.[12] In vinylcyclopropene,[13] the double bond is even

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[†] Dedicated to Professor William von Eggers Doering on the occasion of his 75th birthday.

[‡] Universität-GH Essen.

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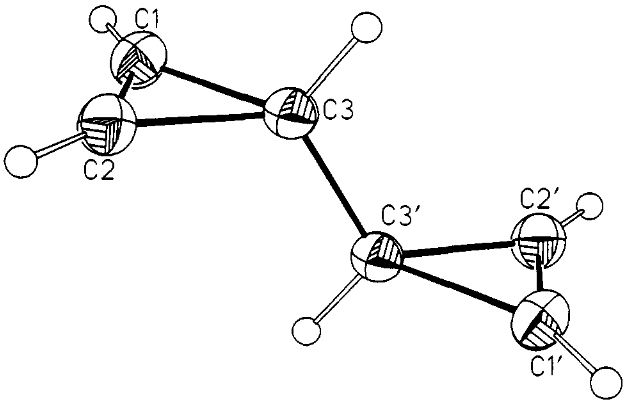


Figure 1. Molecular structure of 1. The ellipsoids are drawn at the 50% level.

Table III. Structural Parameters for 1 As Calculated with the 3-21G Basis for the Anti and Gauche Conformers

	Bond Lengths (Å)			
	C1–C2	C2–C3	C1–C3	C3–C3′
anti	1.285	1.520	1.520	1.497
gauche	1.284	1.516	1.520	1.503

Bond Angles (deg)

	C1–C3–C2	C2–C3–C3′	C2–C3–C3′–C2′	C1–C3–C3′–C1′	H3–C3–H3′–C3′
anti	50.0	120.3	121.4	121.4	180.0
gauche	50.05	120.39	10.98	106.10	–47.57

shorter (1.279 (1) Å) than in **1**, and the conjugation in the exocyclic C–C bond shortens the distance to 1.476 (1) Å, as observed for **1**.

In contrast to **1**, the hexa-*tert*-butyl derivative[14] was found to exist exclusively in the gauche conformation as a result of the severe steric interactions between the *tert*-butyl groups. This results in a lengthening of the central C–C bond to 1.570 (3) Å. The cyclic C–C bonds (1.550 (2), 1.536 (2) Å) are also longer, but the double bond (1.294 (2) Å) agrees well with **1**.

B. Calculations. (i) Structural Parameters. The total energy of **1** as a function of the torsional angle θ has been plotted in Figure 3, where θ is defined as the angle H3–C3–C3′–H3′. To calculate the geometrical parameters of **1** and its potential energy as a function of θ, we have applied the Hartree–Fock self-consistent field (HF-SCF) procedure using the software Gaussian 86[15] with a 3-21G[16] basis set. Each point of the potential curve shown in Figure 3 has been optimized with a 3-21G basis set. Two minima were found in the gas phase, with an energy difference of 0.48 kcal/mol in favor of the anti conformer. The prediction of a local minimum at θ = 45–50° is consistent with earlier calculations using a partially optimized geometry with a STO-3G basis set.[8] The predicted dihedral angles θ for the local minima as well as the energy difference between the gauche and anti conformers are presented in Table II.

The calculated energy difference of 0.5 kcal/mol (3-21G) leads to a statistically corrected ratio of the anti to the two gauche conformers of approximately 1.24:1. The structural parameters derived using the 3-21G basis set are shown in Table III.

The structural parameters calculated for the anti conformer compare well with the experimental data presented in Table I. We notice that the bond length between C3 and C3′ is found and

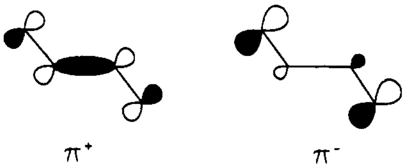
Table IV. Comparison between the Recorded Vertical Ionization Energies $I_{v,j}$ and the Calculated Orbital Energies[a] ϵ_j for **1** in Anti and Gauche Conformations[b]

band	$I_{v,j}$	$-\epsilon_j$ (anti)	$-\epsilon$ (gauche)
1	9.05	9.29 ($8a_g$, π^+)	9.34 (11a, π^+)
2	9.70	9.79 ($3b_g$, W_{A^+})	
3	10.22	10.33 ($7b_u$, π^-)	10.12 (10a, W_{A^-}) 10.21 (10b, π^-)
4	11.46		11.86 (9b, W_{A^+})
5	12.22	12.71 ($7a_g$, W_{S^+}) 12.89 ($3a_u$, W_{A^-})	
6	12.8		13.51 (9a, W_{S^+})
7	13.0		13.79 (8b, W_{S^-})

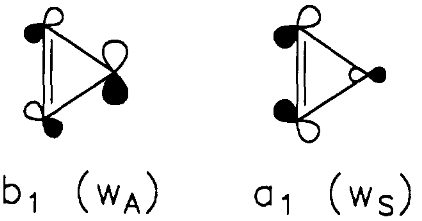
[a] The orbital energies were calculated with a 3-21G basis set. [b] All values in eV.

calculated to be shorter for the anti (1.497 Å) than for the gauche (1.503 Å) conformer. This is consistent with the bond lengthening observed for the gauche conformation of the *tert*-butyl derivative described above.

(ii) Orbital Sequence. The highest occupied MOs of **1** have been discussed extensively in an earlier study.[7] Therefore, we will present only the most salient results here. Model calculations reveal two π-MOs which are separated considerably in energy due to different through-bond coupling. As indicated below for the anti conformer, the π^+ linear combination interacts strongly with the central H–C–C–H unit, while the interaction between π^- and the σ-frame is small. Model calculations using a 3-21G basis set predict eigenvalues of $\epsilon(\pi^+) = -9.29$ eV and $\epsilon(\pi^-) = -10.33$ eV for the anti conformation of **1**. The π-character of the corresponding wave functions amounts to 67% for π^+ and 77% for π^-.



In addition to the π-MOs, it is also necessary to consider the Walsh-type MOs of **1**. For the derivation of these, we utilize the fact that each cyclopropene unit contributes on symmetric (W_S) and one antisymmetric (W_A) Walsh-type orbital (see below).



Photoelectron (PE) investigations on cyclopropene suggest that there is a large separation between the energies of both basis orbitals (PE bands for W_A = 10.9 eV, W_S = 12.7 eV).[17] This difference justifies the treatment of both sets separately as a first approximation. This yields the symmetric and antisymmetric linear combination of the W_A set (W_{A^+}, W_{A^-}) and the W_S set (W_{S^-}, W_{S^+}), as shown in Chart I.

Next to each schematic drawing of the wave function, we list the irreducible representation in the point groups C_{2v} (syn), C_2 (gauche), and C_{2h} (anti).[18] A change from C_{2v} or C_{2h} symmetry

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(18) Note that the signs of W_{a^-}, W_{S^+}, W_{s^-}, and W_{A^+} are defined for the syn conformation. On going from the syn (C_{2v}) to the anti (C_{2h}) conformation (rotation around the C3–C3′ bond), the two 2p orbitals at the 3 and 3′ position of W_{a^-} adopt the same sign while those of the W_{S^+} linear combination adopt the opposite sign. The same rotation is used in earlier papers on bicyclopropenyl[7] and bicyclopropyl.[19]

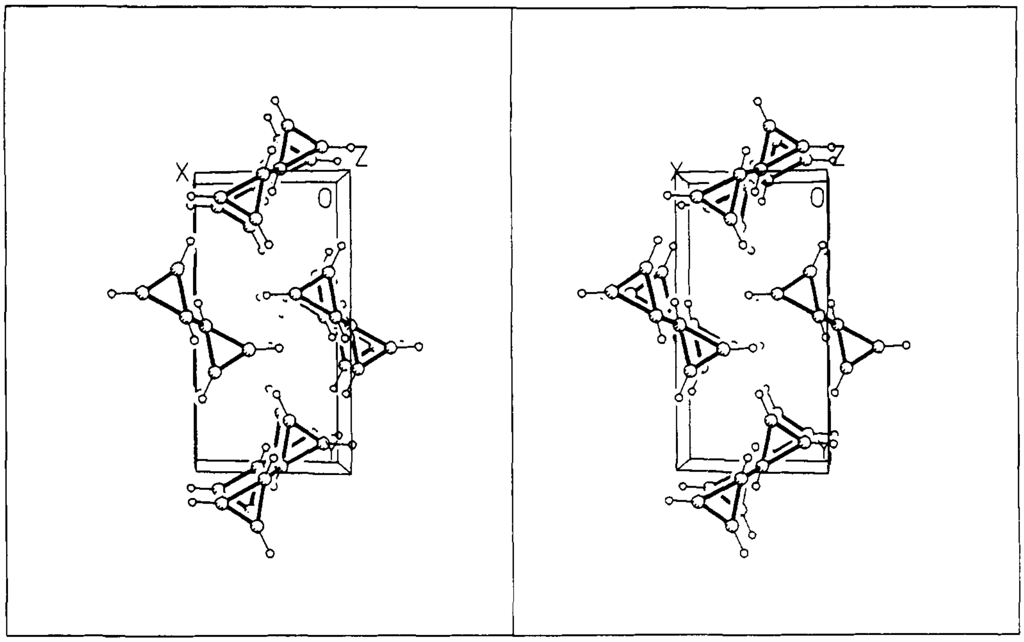
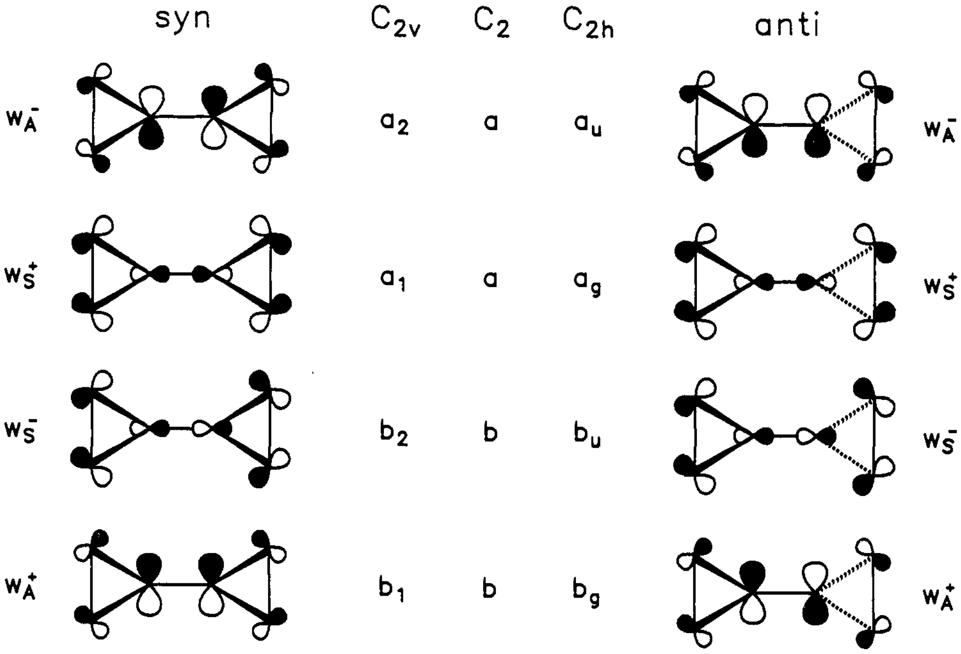


Figure 2. Stereoview of the molecular packing of **1**.

Chart I. Definition of W_{A^-}, W_{S^+}, W_{S^-}, and W_{A^+} for the Syn (left) and Anti (right) Conformation of **1**[15]



to the lower C_2 symmetry allows the W_A and W_S orbitals to mix (see Chart I). This is seen in Figure 4, where the orbital energies of the highest occupied MOs of **1** are shown as a function of the torsional angle θ. Reducing the symmetry, the W_{A^+} and W_{S^-} set at 0° and the W_{S^+} and W_{A^-} set at 180° repel each other strongly. For dihedral angles close to 90°, a considerable interaction between $b(\pi^-)$ and $b(W_{A^+})$ is encountered (avoided crossing). The curves shown in Figure 4 were obtained with a HF-SCF calculation using a 3-21G basis set. They closely resemble those obtained by the MINDO/3 method.[7]

C. PE Spectrum. The PE spectrum of **1** (Figure 5) exhibits three peaks of different heights which are well separated from a smaller fourth one. The recorded vertical ionization energies are listed in Table IV. For the interpretation of the spectrum, we assume the validity of Koopman's theorem,[20] i.e., the recorded vertical ionization $I_{v,j}$ is set equal to the negative value of the calculated orbital energy ϵ_j;$I_{v,j} = -\epsilon_j$. The close similarity between the orbital pattern derived for various alkylated bicyclopropenes and the experimental results justifies this assumption.[7] According to the MO calculations discussed in the previous section, we must assume that a mixture of the anti and gauche conformers populate the gas phase. In this regard, comparison of the orbital sequence calculated for $\theta = 50°$ with that for $\theta = 180°$ leads to two noticeable differences. At 180° we expect three nearly equally spaced bands [$8a_g(\pi^+)$, $3b_g(W_{A^+})$, and $7b_u(\pi^-)$] well-separated (2 eV) from two close bands [$7a_g(W_{S^+})$ and $3a_u(W_{A^-})$] (see also Table IV), while W_{S^-} is predicted at much higher energy. For the gauche conformer we expect the bands originating from $10a(W_{A^-})$ and $10b(\pi^-)$ to be very close together. The band from $9b(W_{A^+})$ is anticipated to be well separated (1.6 eV) from those bands arising from 10a and 10b and $9a(W_{S^+})$ and $8b(W_{S^-})$. In Figure 6 we have compared the PE spectrum with calculated ionization energies (3-21 G level) of a 2:1 anti:gauche mixture. A reasonable agreement between calculation and experiment could be found

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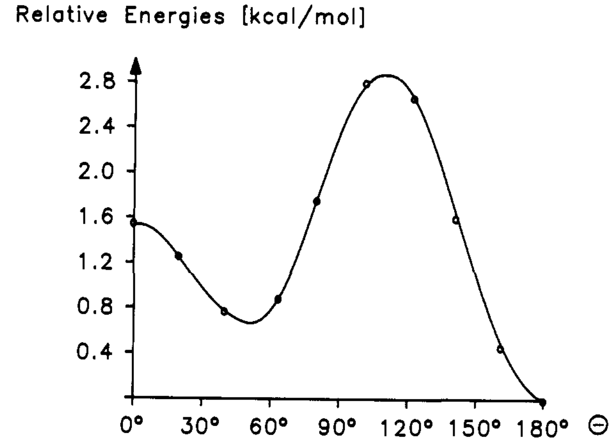

Figure 3. Relative energies (3-21G) for **1** as a function of the torsional angle θ.

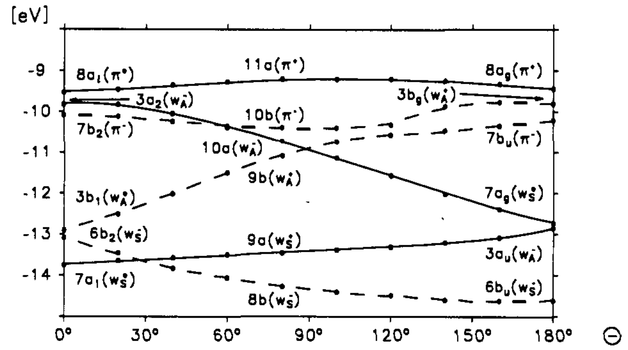

Figure 4. Orbital energies (3-21G) for **1** as a function of the torsional angle θ.

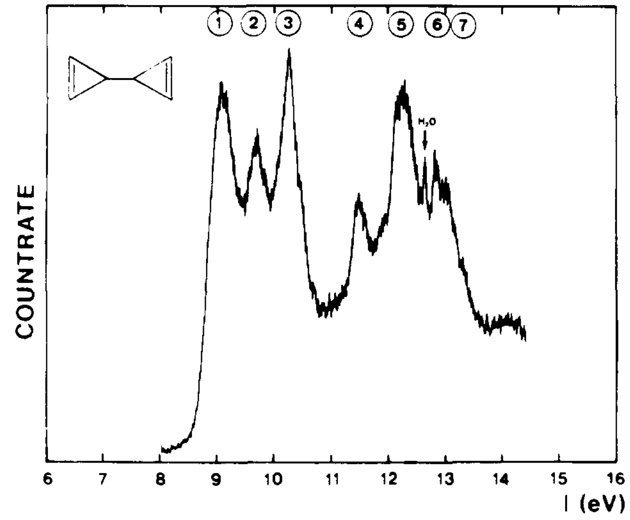

Figure 5. He(I) PE spectrum of **1**.

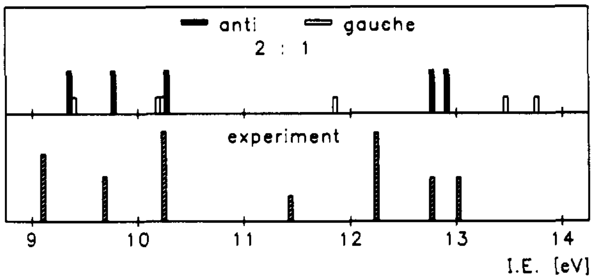

Figure 6. Comparison between the calculated (3-21G) ionization energies for a 2:1 mixture of anti:gauche **1** with the experiment. The different intensities are indicated by the height of the bars.

only if we assumed that both conformers are present in the gas phase. The assumed ratio of about 2:1 for the anti:gauche mixture in the gas phase would result in an energy difference of 0.8 kcal/mol between the two conformers.

Experimental Section

A. X-ray Structure Determination. **1** was prepared as described previously[2] and condensed from the cooling trap of a vacuum line directly into a capillary at 100 K. After the capillary had been sealed, a specially constructed device[21] allowed the capillary to be transferred directly to the diffractometer at 100 K. There the sample was warmed to 194 K, which is slightly below its melting point. By the focusing of the infrared portion of a halogen lamp onto the capillary with a parabolic mirror,[22] a molten zone was produced within the capillary. The mirror was moved by computer-assisted control to produce a cyclindric single crystal that was cooled to 103 K. The cell dimensions, calculated from 25 centered reflections, are as follow: a = 4.8901 (9), b = 9.4400 (18), and c = 5.1604 (10) Å, β = 102.261 (14)°, V = 232.78 (7) Å^3, Z = 2, monoclinic, space group $P2_1/n$, ρ = 1.114 g cm^{-3}, μ = 0.06 mm^{-1}, data collection of 5294 intensities ($2\theta_{\max}$ = 90°, Mo Kα radiation) merged to 1927 intensities (R_{merg} = 0.0242) of which 1442 were treated as observed ($F_o \geq 4\sigma(F)$). Structure solution by direct methods and refinement of carbon atoms anisotropically and hydrogen atoms isotropically without any constraints gave R = 0.044, R_w = 0.050, 41 parameters, maximum residual electron density 0.45 eÅ^{-3}.

B. PE Spectra. The He(I$_\alpha$) gas-phase PE spectrum of **1** was recorded at room temperature on a PS 18 instrument (Perkin-Elmer Ltd., England) and calibrated with reference to Ar lines (15.76 and 15.94 eV) and Xe lines (12.13 and 13.44 eV). A resolution of about 20 meV on the Ar line was obtained.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (5 pages); tables of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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