

(Z,Z)-4,9-Dimethylene-1,6-cyclodecadiene: Crystal Structure and Photoelectron Spectrum

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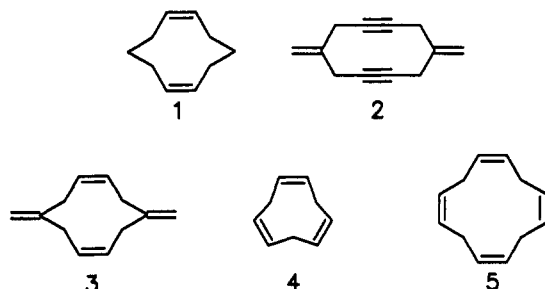
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(Z,Z)-4,9-Dimethylene-1,6-cyclodecadiene (**3**) has been prepared via cis-hydrogenation of 4,9-dimethylene-1,6-cyclodecadiyne (**2**). An X-ray investigation of single crystals shows that **3** adopts an armchair conformation in the solid state. The photoelectron spectrum of **3** shows four different ionization energies in the region between 8.9 and 9.6 eV, which have been assigned to four combinations of double-bond π -orbitals by comparison with the results of MO calculations. Thus, it is shown that in the gas phase the armchair conformation is also predominant. No through-space but considerable through-bond interactions between the double bonds of **3** are revealed by the photoelectron spectrum and the MO calculations.

Introduction

In 1963, Dale predicted that cyclic dienes can exist in unstrained conformations provided that both double bonds have the same geometry and are linked together by two polymethylene chains of the same odd number of CH₂ units.¹ One of the best-known examples of this type of cyclic compounds is (Z,Z)-1,6-cyclodecadiene (**1**), and a



considerable number of congeners of **1** such as 4,9-disubstituted, 4,4,9,9-tetrasubstituted,² and 4,9-bis(hetero)³ derivatives of **1** have been investigated with respect to their molecular conformations.^{4,5} It is generally agreed that there are two main conformations known as the "armchair" and "hammock" form (see Figure 1); however, different mechanisms have been proposed for the ring inversion of the armchair conformation.^{3,4} Quite surprisingly, there is no complete crystal structure analysis of **1** or one of its above-mentioned carbocyclic derivatives, whereas the structure of a 4,9-disila derivative of **1** has been established.⁶ An electron diffraction investigation of **1** indicated that the armchair conformation should be preferred in the gas phase.⁵ In the course of our work concerning the reactions of cyclic dialkynes with various electrophiles we came across the 4,9-dimethylene derivative of **1** which we prepared by hydrogenation of 4,9-

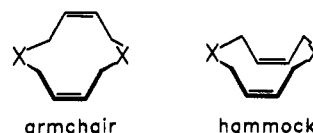


Figure 1. Main conformations of (Z,Z)-1,6-cyclodecadiene derivatives.

dimethylene-1,6-cyclodecadiyne (**2**) under the influence of the Lindlar catalyst.⁷ In this paper we report on the structure of (Z,Z)-4,9-dimethylene-1,6-cyclodecadiene (**3**) in the solid state as well as on the electronic properties of **3** which are revealed by its photoelectron spectrum.

X-ray Structure Determination of 3. An X-ray structure determination has been carried out on single crystals of **3**, which were obtained from petroleum ether (bp 30–40 °C) at –20 °C. Atomic coordinates of **3** are listed in Table I; bond lengths and angles are given in Figure 2. In the crystal, **3** adopts an armchair conformation (Figure 2). It is remarkable that the molecular symmetry (C_{2h}) of this conformation is completely maintained in the crystal, as the molecules of **3** have the site symmetry $2/m$ (space group $Cmca$, $Z = 4$). The distance between the C3 carbon atoms of the exocyclic double bonds and the closest carbon atom (C1) of the endocyclic double bonds amounts to 2.508 (1) Å. This value is similar to the corresponding distance between sp² carbon atoms of related skipped cyclic polyenes such as (Z,Z,Z)-1,4,7-cyclononatriene ("trishomobenzene", **4**) (2.46 Å)⁸ and (Z,Z,Z,Z)-1,4,7,10-cyclododecatetraene ("tetrahomocyclooctatetraene", **5**) (2.48 Å)⁹, which is isomeric to **3**.

As is evident from the rather large C—C=C bond angle at the endocyclic double bonds (C1—C1'—C2'': 127.9 (1)°), there is some ring strain present in **3**, which can be traced back to C...C and H...H interactions parallel to the double bonds (C2...C2'' = 3.167 (2) Å; H1...H1' = 2.14 (2) Å). This effect has been predicted by Almenningen et al.⁵ for the parent hydrocarbon **1**, and it somewhat contradicts the original claim of **1** to be a completely unstrained molecule.^{1b,c}

Electronic Properties of 3. In the photoelectron spectrum of **3** (Figure 3), four different ionization energies arising from π -type MOs can be detected in the region

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Table I. Atom Coordinates and Equivalent Thermal Parameters of the Carbon Atoms of 3

atom	x	y	z	$U_{eq}^a \times 10^4 (\text{\AA}^2)$
C1	0.4582 (1)	0.0539 (1)	0.2689 (1)	493 (5)
C2	0.3996 (1)	0.1267 (1)	0.4028 (1)	512 (5)
C3	0.3489 (1)	0.0000	0.5000	492 (7)
C4	0.2647 (1)	0.0000	0.5000	707 (11)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

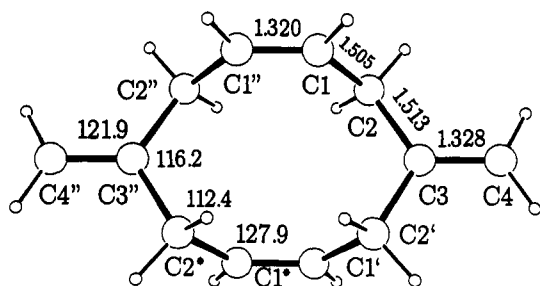


Figure 2. Molecular structure of 3 with bond lengths (Å) and angles (deg). The standard deviations are 0.001–0.002 Å and 0.1°.

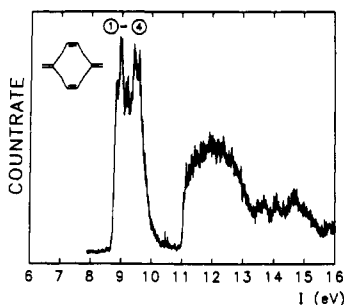


Figure 3. PE-spectrum of 3.

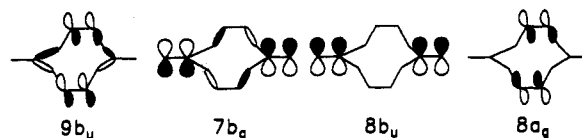
Table II. Comparison between the Recorded Vertical Ionization Energies, $I_{v,j}$, of 3 and the Calculated Orbital Energies, ϵ_j , for the Armchair (C_{2h}) and the Hammock (C_{2v}) Conformation of 3 (All Values in eV)

band	$I_{v,j}$	assnt	$-\epsilon_j (C_{2h})$		$-\epsilon_j (C_{2v})$	
			MINDO/3	3-21G	MINDO/3	3-21G
1	8.97	9b _u	9.04 (9b _u)	9.17	8.84 (8b ₁)	8.50
2	9.17	7b _g	9.33 (7b _g)	9.32	9.28 (8b ₂)	9.34
3	9.43	8b _u	9.56 (8b _u)	9.65	9.61 (10a ₁)	9.61
4	9.55	8a _g	9.60 (8a _g)	9.70	9.81 (9a ₁)	10.19

between 8.9 and 9.6 eV (see Table II). This contrasts with the behavior of 5⁹ (a 12-membered ring isomer of 3), the photoelectron spectrum of which shows only one broad band in the same region. Clearly, this indicates the predominance of one rather rigid conformation in the gaseous sample of 3, whereas in the case of 5 the individual π -ionizations remain unresolved as a result of overlapping bands of various conformations. (The contrast between the conformational rigidity of 3 and the high flexibility of 5 is also evident from ¹H NMR investigations in solution^{2,4a,9}). In Table II, the experimental ionization energies of 3 are compared for the results of MO calculations (MINDO/3¹⁰ and 3-21G¹¹) which have been carried out for both the armchair (C_{2h}) and the hammock (C_{2v}) conformations (for both calculations, the same geometry

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Figure 4. Schematic drawing of the four π -MO's of 3.

(as derived from a MINDO/3 calculation) has been used). The experimental split of the π -MOs of 3 amounts to 0.58 eV. Both calculation methods predict a similar value (MINDO/3: 0.56 eV; 3-21G: 0.53 eV) only for the armchair conformation, whereas in the case of the hammock form the calculated values are much larger (MINDO/3: 0.97 eV; 3-21G: 1.69 eV). Thus, it is safe to assume that the armchair conformation is largely preferred in the gas phase. The four lowest ionization energies of 3 are therefore assigned to the π -MOs of 3 on the basis of the MO calculations (and using Koopmans' theorem¹²) for the armchair conformation as shown in Table II. In Figure 4, the π -MOs of 3 are drawn schematically. According to this assignment, the energy split between the two combinations of the endocyclic double bonds (9b_u and 8a_g) amounts to 0.58 eV, which is quite similar to the corresponding value of the parent compound 1, for which a value of 0.5 eV has been reported.¹⁴ Obviously, there is no significant through-space interaction between the endo- and the exocyclic double bonds of 3. According to the MO calculations, the appearance of four different π -ionization energies in the photoelectron spectrum of 3 is a consequence of π/σ -interactions. The endo- and the exocyclic double bonds can be considered as two independent sets of π -systems with the orbital energy split within each set arising exclusively from through-bond interactions¹⁴ via the σ -skeleton of the 10-membered ring.

Conclusions

We have shown that (Z,Z)-4,9-dimethylene-1,6-cyclodecadiene (3) adopts an armchair conformation in the solid state as well as in the gas phase. The symmetry of this conformation (C_{2h}) is completely maintained in the crystal. The armchair is not entirely unstrained as indicated by rather large bond angles at the endocyclic double bonds. Unlike the skipped cyclic diene-diyne,⁶ the skipped cyclic tetraene 3 shows no effects of cyclic homoconjugation. However, the π -orbitals of the double bonds of 3 are split into four energetically different levels by through-bond interactions via the σ -skeleton of the 10-membered ring.

Experimental Section

Compound 3 was synthesized as reported previously.⁸ Colorless prisms crystallized from petroleum ether (bp 30–40 °C) at –20 °C. Sum formula C₁₂H₁₆; $M_r = 160.3$ g/mol; orthorhombic; $Cmca$; $Z = 4$; $a = 15.777$ (2) Å, $b = 8.271$ (1) Å, $c = 7.647$ (1) Å; $V = 997.9$ (4) Å³; $D_x = 1.067$ g/cm³; Mo K α , $\lambda = 0.71073$ Å, $\mu = 0.553$ cm⁻¹; $F(000) = 352$; crystal size 0.5 × 0.5 × 0.3 mm; Enraf-Nonius CAD-4 diffractometer; $\omega - 2\theta$ scan method; 665 data up to $\sin \theta/\lambda = 0.66$ Å⁻¹; 662 unique reflections: 442 intensities with $I \geq 2.5\sigma(I)$; three standard reflections: 333, 242, 621. Absorption ignored.

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The structure was solved using Sir88.¹⁶ The structure was refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for C and isotropic thermal parameters for H. 45 parameters, $R = 0.037$, $R_w = 0.045$ ($w = 4F^2/\sigma^2F^2 + (0.03F^2)^2$); $S = 2.02$; (Δ/σ_{\max}) < 0.01; largest peak 0.106 e/Å³. Atom coordinates and thermal parameters of **3** are listed in Table I.

The photoelectron spectrum of **3** was recorded on a Perkin-Elmer PS 18 instrument at ambient temperature and calibrated with Ar.

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