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PREPARATION AND SPECTROSCOPIC PROPERTIES OF CYCLODECA-1,6-DIYNE

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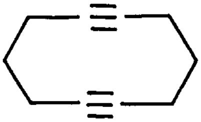
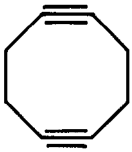
The preparation of cyclodeca-1,6-diyne(1) is reported. The PE results reveal a strong interaction between the in plane π molecular orbitals of 1.

Cyclodeca-1,6-diyne(1) has a pair of acetylenic residues separated by two trimethylene chains. The level of interaction between its triple bonds should differ from that in cycloocta-1,5-diyne (2)[1] where the linking is achieved by a pair of $(CH_2)_2$ units. In this communication, we describe the preparation of 1 and detail those spectroscopic features that are characteristic of the interaction prevailing in both 1 and 2. The use of 1 as a useful synthetic precursor will be detailed elsewhere.

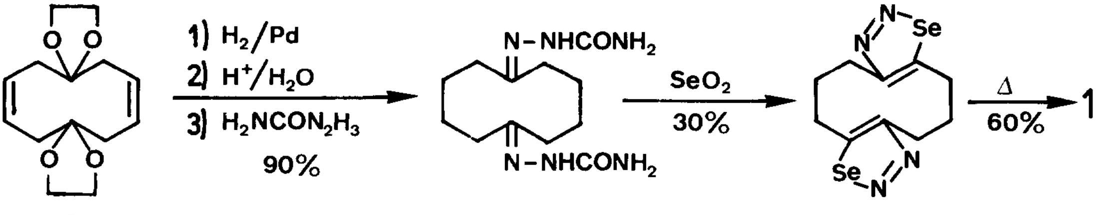


1



2

The starting point of our synthesis was the ketal 3[2]. Saturation of the peripheral double bonds, followed by deblocking with pyridinium tosylate and reaction with semicarbazide afforded the bissemicarbazone 4[3]. The subsequent transformation of 4 to the bisselenodiazole 5[3,4] set the stage for thermolytic conversion to 1[3].



3 4 5

The method of choice for probing the electronic interactions in compounds such as 1 is HE(I)photoelectron (PE) spectroscopy[5,6]. The PE spectrum of 1 which is illustrated in Figure 1 is characterized by four bands below 10.5 eV.

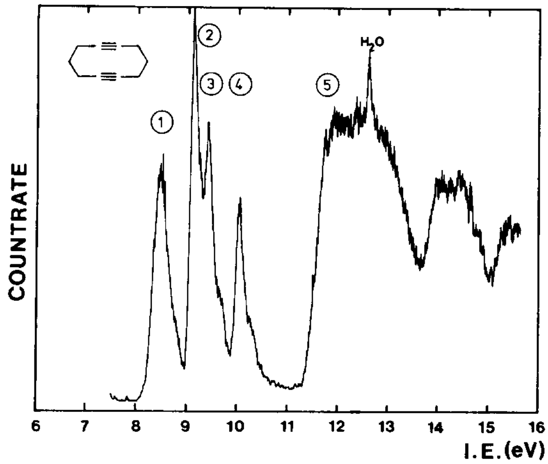


Figure 1 PE spectrum of 1

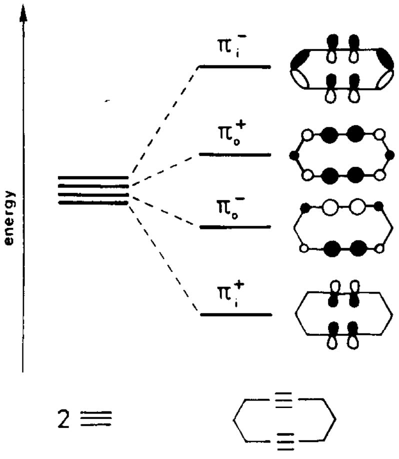


Figure 2 Qualitative drawing of the highest occupied MO's of 1

The PE bands of 2[5] and those of alkylacetylenes[7] suggest that the above bands (① - ④) be assigned to ionizations from the π-MO's of the acetylene fragments. Through application of MINDO/3[8] and Hartree-Fock-SCF calculations, with a minimal basis set (STO-3G)[9] as a guide this assignment was confirmed, provided that Koopmans' assumption[10] be adopted as valid. A comparison between the measured vertical ionization energies ($I_{v,j}$) and the calculated negative values of the orbital energies is given in the Table[11].

Table

Comparison Between the Vertical Ionization Energies ($I_{v,j}$) and Calculated Orbital Energies ($-\varepsilon_j$) of **1** (C_{2h}). Values in eV.

Band	$I_{v,j}$	assignment	$-\varepsilon_j$(MINDO/3)	$-\varepsilon_j$(STO-3G)
①	8.47	$6a_u(\pi_i^-)$	9.13	7.26
②	9.12	$7b_u(\pi_o^-)$	9.61	7.79
③	9.42	$5b_g(\pi_o^+)$	9.70	7.81
④	10.02	$8a_g(\pi_i^+)$	10.20	8.59
⑤	11.8	$7a_g(\sigma)$	10.81	11.62

Accordingly we assign the first four bands to ionizations from two linear combinations from the in plane ($\pi_i^\pm$) and two linear combinations from the out of plane ($\pi_o^\pm$) π - MO's.

In the latter case the interactions seem to be dominated by hyperconjugation (see Figure 2). For the in plane π-MO's through space and through bond interactions operate in the same direction thus giving rise to a large energy difference between $6a_u(\pi_i^-)$ and $8a_g(\pi_i^+)$ (see Figure 2 and Table).

The comparison between the PE results of **1** and **2**[5] demonstrates that the interactions between the in plane π-MO's depend on the chain length between the π units.

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References and Notes

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3 All compounds have been characterized by elemental analysis as well as by their ^{1}H, ^{13}C NMR, IR and mass spectra. Selected data:

4: mp. 228°C

5: mp. 175°C (decomp). ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ (ppm): 3.20-3.27 (2H,m), 3.01-3.08 (2H,m), 2.64-2.77(2H,m) ^{13}C NMR (75 MHz, CDCl$_3$, TMS)δ (ppm): 160.67, 158.78, 32.66, 25.05, 24.04

1: mp. 81°C, ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ (ppm): 2.33-2.29 (8H,m), 1.74-1.60 (4H,m); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ (ppm): 82,99, 25.17, 19.60.

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11 Since the detailed structure of 1 is unknown we have minimized all geometrical parameters with respect to the heat of formation (ΔH_f^o) using the MINDO/3 method. Also the HF/STO-3G calculations are based on this geometry.

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