refluxed for 20 h. The workup was the same as for **45**. **48**: yield, 0.55 g (33%); mp 105 °C dec; ^{1}H NMR δ 4.56 (s, 5 H, Cp-*H*), 2.94 (d, 2 H, *J* = 19.4 Hz) and 2.53 (d, 2 H, *J* = 20.5 Hz) (Me$_2$C=CC*H*$_2$), 2.24–2.34 (m, 2 H) and 1.88–1.97 (m, 2 H) (C*H*$_2$CH$_2$CH$_2$C*H*$_2$), 1.66 (s, 6 H, C*H*$_3$), 1.72–1.84 (m, 2 H) and 1.41–1.53 (CH$_2$C*H*$_2$C*H*$_2$CH$_2$); ^{13}C NMR δ 137.7 and 123.9 (*C*=*C*), 81.2 and 71.8 (cyclobutadiene), 80.5 (Cp-*C*), 31.6, 24.4, and 23.4 (*C*H$_2$), 21.4 (*C*H$_3$); IR 1672, 1103, 997, 800 cm^{-1}, MS (EI) *m/z* 310 (64), 124 (55), 59 (100). Anal. Calcd for C$_{19}$H$_{23}$Co: C, 73.54; H, 7.47. Found: C, 73.36; H, 7.46.

4,9,14,19-Tetraisopropylideneheptacyclo[10.8.0.0^{2,6}.0^{2,11}.0^{7,11}.0^{6,17}.0^{7,16}]eicosa-1^{12},16-diene (49). **47** (100 mg, 0.15 mmol) was dissolved in a mixture of 50 mL of cyclohexane and 20 mL of acetonitrile. Ce(N-H$_4$)$_2$(NO$_3$)$_6$ (500 mg, 0.91 mmol) was then added, and the mixture was stirred for 18 h at room temperature. Water (50 mL) was added, and the layers were separated. The aqueous layer was extracted several times with cyclohexane. The combined organic layers were then dried over MgSO$_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel/petroleum ether (bp 40–65 °C): yield, 56 mg (88%); colorless crystals, mp >250 °C; ^{1}H NMR (CD$_2$Cl$_2$) δ 3.09 (d, 4 H, *J* = 13.8 Hz) and 2.78 (d, 4 H, *J* = 14.1 Hz) (Me$_2$C=

CC*H*$_2$C=), 2.21 (d, 4 H, *J* = 16.4 Hz) and 2.12 (d, 4 H, *J* = 17.6 Hz) (Me$_2$C=CC*H*$_2$CR$_3$), 1.70 (s br, 12 H) and 1.57 (s br, 12 H) (C*H*$_3$); ^{13}C NMR δ 141.8 (endocyclic *C*=*C*), 135.9, 126.8, 126.6, and 121.7 (Me$_2$C=*C*), 59.9 (cyclobutane), 30.6 and 28.5 (*C*H$_2$), 21.2 and 20.9 (*C*H$_3$); IR 2904, 2856 cm^{-1}; UV (cyclohexane) λ_{max} 240 nm (sh). Anal. Calcd for C$_{32}$H$_{40}$: C, 90.51; H, 9.49. Found: C, 90.32; H, 9.40.

Skipped Cyclic Ene- and Dienediynes. 2. Models for the Homoconjugation between Double and Triple Bonds[†]

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Abstract: The molecular structures of the skipped dienediynes 4,9-dimethylene-1,6-cyclodecadiyne (**1**) and (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**2**) have been determined by X-ray analysis. These studies reveal a chair conformation for both compounds. The intramolecular distances between the triple bonds are 3.003 (9) Å for **1** and 3.363 (10) Å for **2**. The distances between the termini of the double and triple bonds amount to 2.490 (12) Å for **1** and 2.469 (8) Å for **2**. The PE spectra of **1** and **2** together with 12 congeners have been recorded. The assignment of the first 5–6 PE bands is based on the comparison of the PE spectra of related species as well as on MO calculations. These investigations provide clear-cut evidence for homoconjugation between double and triple bonds.

Introduction

Since the original proposal of Winstein,[1] homoconjugation between double bonds has been investigated frequently by means of different methods.[2] Systematic investigations dealing with the concept of homoconjugation between triple bonds[3] or even between double and triple bonds are rare or nonexistent, mainly because sufficiently simple yet conformationally rigid model systems have not been available. From the results of work on the electronic properties of cyclic dialkynes (type I),[4,5] it became obvious that we would obtain ideal model compounds for the study of homoconjugation between other π-systems and triple bonds if we were able to replace the central carbon atom of one or two (CH$_2$)$_3$ bridges in a cyclic dialkyne with such a π-system, thus generating cyclic diynes of types II and III.
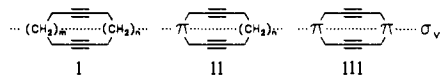
By interaction of the triple bonds in cyclic dialkynes (type I) four π-MOs are formed, the energetical sequence of which depends both on the transannular distance between the alkyne units as well as on the symmetry of the highest σ-orbital of the (CH$_2$)$_n$ bridges.[4,5] Two of these π-orbitals are symmetrical, and the other two are antisymmetrical with respect to the vertical plane of symmetry (σ_v) between the alkyne units (see below). If the additional π-systems in the bridges of type II and type III mol-

ecules are symmetrical with respect to σ_v, as is the case for both endo- and exocyclic C=C double bonds, homoconjugative orbital interaction is only possible with the symmetrical and not with the antisymmetrical set of triple bond orbital combinations. Thus, the energy differences between correlated MOs in cyclic dialkynes (type I) and in "skipped" enediynes (type II) or dienediynes (type III) (in which double and triple bonds are always separated from each other by one saturated carbon atom[6]) should yield information on homoconjugative interactions between double bonds and triple bonds. Also, this comparison should provide experimental evidence for the proposed electronic structure of cyclic dialkynes, which hitherto has mainly been based on the assignment of ionization energies according to MO calculations.

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(2) Reviews: (a) Winstein, S. *Spec. Publ.-Chem. Soc.* **1967**, *21*, 5. (b) Warner, P. M. In *Topics in Nonbenzenoid Aromatic Chemistry*; Hirokawa Publishing Co.: Tokyo, 1977; Vol. 2, p 183. (c) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. (d) Heilbronner, E. In *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*, The Jerusalem Symposia on Quantum Chemistry and Aromaticity, III, The Israel Academy of Science and Humanities, Jerusalem, Israel, 1971, p 58. (e) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369 and references therein.

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(5) Gleiter, R.; Kratz, D.; Schäfer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258.

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We have recently synthesized[7] a series of 10 skipped cyclic enediynes and dienediynes. The dienediynes are the following: 4,9-dimethylene-1,6-cyclodecadiyne (**1**), (Z,Z)-4,10-cyclo-dodecadiene-1,7-diyne (**2**), 10-methylene-(Z)-4-cycloundecene-1,7-diyne (**3**), and 4,9-diisopropylidene-1,6-cyclodecadiyne (**4**).
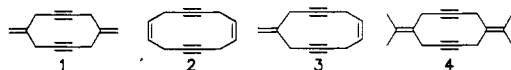
The cyclic enediynes are 4-methylene-1,6-cyclodecadiyne (**5**), 4-methylene-1,6-cycloundecadiyne (**6**), (Z)-4-cycloundecene-1,7-diyne (**7**), (Z)-4-cyclododecene-1,7-diyne (**8**), 4-iso-propylidene-1,6-cyclodecadiyne (**9**), and 4-isopropylidene-1,6-cycloundecadiyne (**10**). According to perturbation theory,[8] the
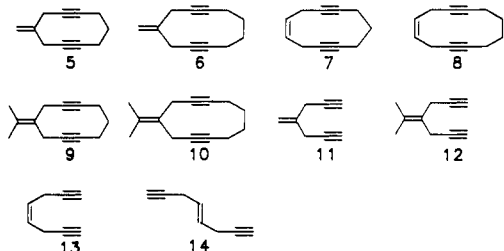
energy shift which is due to homoconjugative interactions strongly depends on the basis orbital energies of the interacting systems. In order to estimate these energies and for comparison, we also needed the acyclic skipped enediynes 4-methylene- and 4-iso-propylidene-1,6-heptadiyne (**11**[9] and **12**[7]) as well as (E)- and (Z)-4-octene-1,7-diyne (**13** and **14**)[10–12] and the cyclic diynes 1,6-cyclodecadiyne (**15**), 1,6-cycloundecadiyne (**16**), and 1,7-cyclododecadiyne (**17**).[4,5]
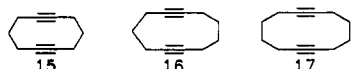
The isopropylidene-substituted diynes **4**, **9**, and **10** are serving as counterproofs for the expected homoconjugation effects in the other cyclic systems, since the orbital energy of the double bonds in these systems should be too high for a sizeable homoconjugative interaction with the symmetrical triple bond orbital combinations mentioned above. We therefore expected the ionization energies of the symmetrical triple bond orbital combinations of **4**, **9**, and **10** to have nearly the same values as in the parent systems **15** and **16**. The method of choice to investigate the interactions prevailing in **1–10** is He(I) photoelectron (PE) spectroscopy. The structural parameters of the enynes are important for the discussion of their electronic properties; therefore, we have investigated the structure of the key compounds **1** and **2** by the X-ray technique. In the following sections we will report on these investigations.

Structures

(a) Structures of 1 and 2. To compare the structural parameters of **1** and **2** with their congeners **15**[4] and **17**,[4] we carried out X-ray investigations on single crystals of **1** and **2**. Both molecules crystallize in a chair conformation as presented in Figure 1. In this figure we have listed the most relevant distances and angles of both molecules.[13] At the endocyclic sp² centers of **1** we note

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(10) Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron Lett.* **1963**, *5*, 313.

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(13) For both **1** and **2**, there are two independent molecules situated on two different crystallographic centers of symmetry in the unit cell. The numbers given in Figure 1 and in the discussion are averaged values of chemically equivalent distances and angles. The scatter is given in brackets. The standard deviations of the individual values, which can be found in the supplementary material, are 0.001–0.002 Å and 0.1–0.2°.
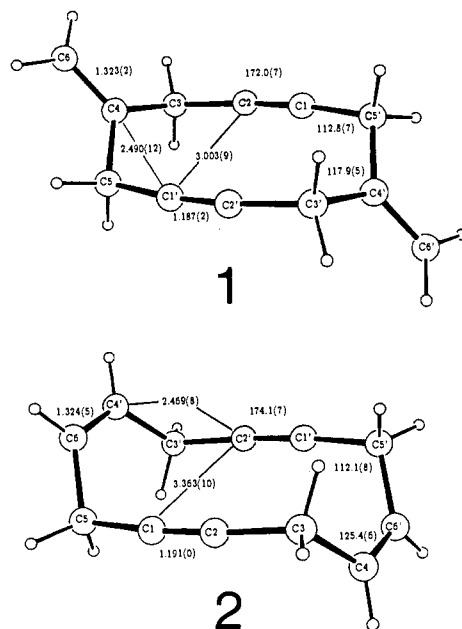
Figure 1. Geometry of **1** and **2** as determined by an X-ray investigation. The most relevant bond lengths (Å) and bond angles (deg), averaged for chemically equivalent values for both independent molecules, are given. The scatter is put in parentheses. The standard deviations are 0.001–0.002 Å and 0.1–0.2°, respectively.[13]

Table I. Crystallographic Data of **1** and **2**

compound	1	2
crystal system	triclinic	triclinic
space group	P1̄	P1̄
Z	2	2
a (Å)	7.626 (1)	7.422 (1)
b (Å)	7.879 (1)	7.714 (2)
c (Å)	9.844 (2)	9.424 (2)
α (deg)	65.59 (1)	112.50 (1)
β (deg)	73.32 (2)	90.68 (2)
γ (deg)	59.70 (1)	110.67 (1)
crystal size (mm)	0.5 × 0.5 × 0.3	0.5 × 0.5 × 0.35
unique reflections	2208	2217
observed reflections ($I \geq 2.5\sigma(I)$)	1518	1662
R factor	0.044	0.041
diffractometer	Enraf-Nonius CAD4	
scan	ω–2θ	
radiation	Mo Kα	
structure solving	MULTAN[21]	

a reduction of the bond angle within the ring (117.9 (5)°) from the usual values. The triple bonds are bent (172.0 (7)°). Both triple bonds are arranged parallel to each other, with a transannular distance of 3.003 (9) Å. At the sp² centers of **2** we note an enlargement of the bond angle within the ring (125.4 (6)°). The triple bonds are slightly less bent (174.1 (7)°) than in **1**, and the transannular distance between the parallel triple bonds is 3.363 (10) Å. The reduction of the angle at the sp² center in **1** we ascribe to the repulsion between the exomethylene groups and the ring atoms. The enlargement of the sp² angles in **2** reduces the transannular repulsion between the triple bonds.

A comparison of the molecular parameters of **1** and **15**[4] shows great similarity, which can be traced back to the mentioned reduction in the angle at the ring sp² center in **1** to 117.9° and an enlargement of the angle at centers 4 and 9 in **15** (115.9°). The comparison of the molecular parameters of **2** and **17** shows considerable differences in the crystal. For **2** we have found a chair conformation with parallel triple bonds. In the case of **17** a twisted chair–chair conformation was found in which the triple bonds were inclined by 24°, and the distance between them was found to be 4.06 Å, considerably longer than in **2**.

The distance between the endocyclic sp² center and the adjacent sp center in **1** amounts to 2.490 (12) Å. In the case of **2** the distance between the termini of the double bond and the adjacent

Skipped Cyclic Ene- and Dienediynes. 2

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Table II. Atomic Coordinates and Equivalent Displacement Parameters (U_{eq}) of 1 and 2[a]

Compound 1

atom	x	y	z	$U_{eq} \times 10^3$ (Å²)
C1A	−0.0482 (2)	0.5723 (2)	0.6413 (1)	44 (1)
C2A	0.1193 (2)	0.4349 (2)	0.6397 (1)	45 (1)
C3A	0.3206 (2)	0.2672 (2)	0.6157 (1)	53 (1)
C4A	0.3840 (2)	0.2875 (2)	0.4515 (1)	45 (1)
C5A	−0.2595 (2)	0.7379 (2)	0.6277 (1)	53 (1)
C6A	0.5465 (2)	0.3190 (2)	0.3809 (2)	67 (2)
C1B	0.3299 (2)	0.2299 (2)	0.0041 (1)	47 (1)
C2B	0.4969 (2)	0.2181 (2)	−0.0275 (1)	47 (1)
C3B	0.7146 (2)	0.1732 (2)	−0.0666 (2)	54 (1)
C4B	0.8344 (1)	0.0077 (2)	−0.1418 (1)	44 (1)
C5B	0.1361 (2)	0.2126 (2)	0.0500 (2)	53 (1)
C6B	0.9154 (2)	0.0517 (2)	−0.2823 (2)	60 (1)

Compound 2

| atom	x	y	z	$U_{eq} \times 10^4$ (Å²)
C1A	−0.2164 (2)	−0.0886 (2)	−0.1418 (1)	500 (4)
C2A	−0.1784 (2)	−0.2238 (2)	−0.1364 (1)	482 (4)
C3A	−0.1177 (2)	−0.3755 (2)	−0.1160 (1)	544 (4)
C4A	0.0887 (2)	−0.3473 (1)	−0.1419 (1)	554 (4)
C5A	−0.2460 (2)	0.0943 (2)	−0.1315 (2)	598 (4)
C6A	−0.2464 (2)	0.2271 (2)	0.0346 (2)	583 (4)
C1B	0.4405 (2)	−0.2594 (1)	0.4766 (1)	474 (4)
C2B	0.3120 (2)	−0.2035 (2)	0.5181 (1)	460 (4)
C3B	0.1642 (2)	−0.1174 (2)	0.5677 (1)	546 (4)
C4B	0.2423 (2)	0.0773 (2)	0.7127 (1)	519 (4)
C5B	0.6059 (2)	−0.3118 (2)	0.4187 (2)	625 (4)
C6B	0.6599 (2)	−0.2615 (2)	0.2813 (1)	556 (4)

[a] U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Structural Parameters of 1–10 as Derived from MMX Calculations

diyne	α^a (deg)	θ^b (deg)	d (Å)^c
1	172	0	3.0
2	171	1	3.5
3	170, 174^d	2	3.1, 3.3^d
4	170	1	3.0
5	172, 172^d	0	3.0, 3.0^d
6	174, 177^d	12	3.5, 3.2^d
7	176, 172^d	1	3.1, 3.3^d
8	170, 172^d	15	4.1, 3.8^d
9	170, 170^d	4	3.0, 3.0^d
10	174, 175^d	3	3.5, 3.1^d

[a] Bond angle at the triple bonds. [b] Inclination angle between opposite triple bonds. [c] Transannular distance between the acetylenic carbon atoms. [d] First value: C1; second value: C2.

triple bond is found to be 2.469 (8) Å. These values are similar to the distances between the termini of the double bonds found in 1,4,7-cyclononatriene (2.46 Å),[14] a homoconjugated olefin. The crystallographic data of 1 and 2 and the atomic coordinates are listed in Tables I and II.

(b) Structures of 3–10. Since no single crystals of 3–10 were available, we carried out force field calculations (MMX) on these molecules to derive the molecular parameters. We chose this method because the calculated parameters for 1 and 2 compare quite well with the X-ray data. It should be mentioned that the MINDO/3 method also gave very satisfactory results. In Table III we have collected the most relevant data for 3–10. In Figure 2 the conformations of 1–10 are shown. As anticipated, in the 10-membered rings smaller distances (3.0 Å) between the triple bonds are found than in the larger rings (3.1–4.1 Å). With the exception of 6 and 8, the triple bonds are predicted to be oriented almost parallel to each other. In the case of 6 the angle of inclination is predicted to be 12° and in 8 to be 15°. The distance between the nearest termini of the endo double bond and the triple
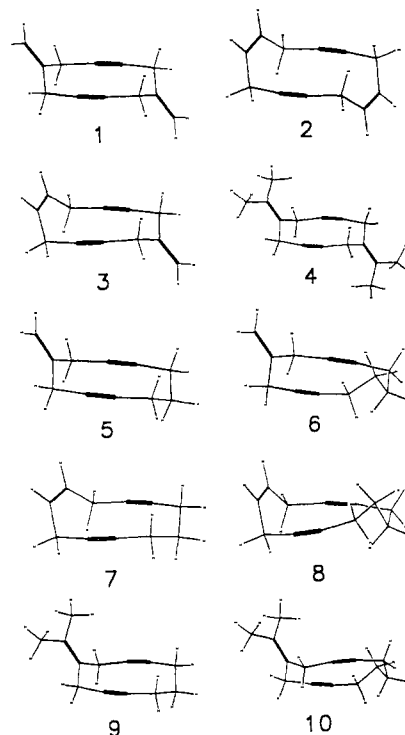
**Figure 2.** Conformations of 1–10 as derived from MMX calculations.

bond is found to be 2.4 Å in all cases; for the exo double bond this value is calculated to be 2.5 Å. The angles at the triple bonds vary between 170° and 176° (see Table III). The endocyclic bond angles at the sp² atoms were found to be 120° for the methylene groups, 116° for the isopropylidene groups, and 125° for the endocyclic double bonds, except in 7 where this angle was calculated to be 124°.

Photoelectron Spectra

In interpreting the He(I) photoelectron (PE) spectra in the low-energy region, we assume that the recorded vertical ionization energies, $I_{v,j}$, can be directly correlated with the calculated negative values of the molecular orbital energies, ϵ_j (Koopmans' theorem[15]). Before presenting the PE spectroscopic results on 1–14, we will briefly discuss the results of the investigations on 15–17.[4,5] The π-MOs in these species can be differentiated into a set of two π_i-orbitals which lie "in the molecular plane" that is defined by the two parallel triple bonds, π^1 and π^2, and a set of two π_o-orbitals which are perpendicular to this plane. Within both sets two linear combinations can be formed, one of which is bonding, π^+, and one of which is antibonding, π^-, with respect to the vertical plane of symmetry between the triple bonds (σ_v, see the Introduction).

$$\pi_i^\pm = 1/\sqrt{2}(\pi_i^1 \pm \pi_i^2) \text{ and } \pi_o^\pm = 1/\sqrt{2}(\pi_o^1 \pm \pi_o^2)$$

The PE spectroscopic investigations on 15 reveal a strong interaction between π_i^- and the σ-frame of the propano groups. Thus the band which is assigned to the ionization from π_i^- ($I_{v,1} = 8.47$ eV) is considerably separated (by 1.5 eV) from the π_i^+-band (10.02 eV). The sequence of the π_o-bands is less clear-cut, because semiempirical and ab initio (3-21G basis) calculations suggest[4] the assignment of the second band in the PE spectrum of 15 (9.12 eV) to be π_o^+ and the third one (9.42 eV) to be π_o^-. These results
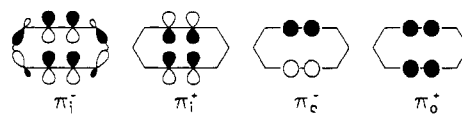
are due to a stronger hyperconjugative interaction of π_o^+ with the adjacent CH₂ groups as compared to π_o^- (predicted by the calculations). An empirical assignment[5] places π_o^- at lower ionization

(14) Roth, W. R.; Bang, W. P.; Göbel, B.; Sass, R. L.; Turner, R. B.; Yü, A. P. *J. Am. Chem. Soc.* **1964**, *86*, 3178.

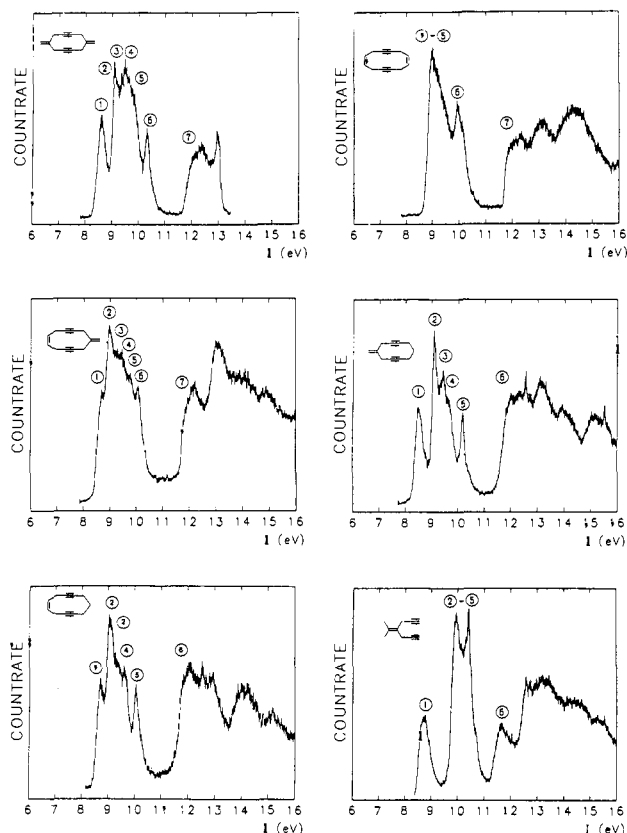(15) Koopmans, T. *Physica* **1934**, *1*, 104.

Figure 3. PE spectra of 1-3, 5, 7, and 12.

energy than π_o^+. For **16** the sequence of the bands parallels that of **15**; hence, the splitting of the bands is smaller, although $\Delta I(\pi_i)$ = 0.92 eV and $\Delta I(\pi_o)$ = 0.27 eV. In **17** we observed only two close-lying peaks at 9.13 and 9.38 eV, which indicates a very small interaction between the triple bonds. To elucidate the interactions in **1–4** and their congeners **5–14**, we recorded their photoelectron (PE) spectra. As examples we show the PE spectra of **1–3** together with those of **5, 7,** and **12** (Figure 3). We note strongly overlapping bands for the dienediynes **2** and **3**, but more easily recognizable bands for **1** and the enediynes, especially those with a 10- or 11-membered-ring skeleton. To correlate the different peaks with the MOs, we compared the spectra with those which can be easily assigned empirically (**11–14**) or with **15–17**, whose spectra have been interpreted recently.[4,5] The ionization energies of **1–14** are collected in Table IV.

In addition to the empirical correlation we also rely on MO calculations. Procedurally we use ab initio calculations with a 3-21G basis set[16] based on geometrical parameters derived from a MINDO/3[17] calculation (we used the MINDO/3 method because it has performed reasonably well for cyclic diacetylenes of medium ring size[5]); for **1** and **2** the experimental geometry has been used in addition to the above basis set. As there are hardly any differences in the ring geometry of the 10-membered rings **1, 4, 5, 9,** and **15,** their ionization energies can be correlated directly, without having to consider changes in the intramolecular distances between the interacting π-systems. We therefore start our discussion of the PE spectra with these systems.

PE Spectra of the 10-Membered Rings 1, 4, 5, and 9

(a) Ionization Energies of the Double Bonds and the Out-of-Plane Orbitals. To understand the PE spectra of **1** and **4**, we start by discussing the PE spectra of simpler models such as those of **5, 9, 11,** and **12.** In order to estimate the ionization energy of

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(17) (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975,** *97,* 1285. (b) Bischof, P. *J. Am. Chem. Soc.* **1976,** *98,* 6844.

Table IV. Measured Vertical Ionization Energies, $I_{v,j}$, and Calculated Orbital Energies of 1-14

diyne	band	$I_{v,j}$	assignment	$-\epsilon_j$ (3-21G)	$-\epsilon_j$ (MINDO/3)
1 (C_{2h})	1	8.6	$5a_u(\pi_1^-)$	8.95 ($5a_u$)	9.02
	2	9.12	$4b_g(\pi_o^-)$	9.43 ($5b_u$)	9.46
	3	9.4	$5b_u(\pi_o^+)$	9.48 ($4b_g$)	9.59
	4	9.5	$5a_g(\pi_d^+)$	9.74 ($5a_g$)	9.58
	5	9.7	$4b_u(\pi_d^-)$	10.22 ($4b_u$)	10.17
	6	10.35	$4a_g(\pi_1^+)$	10.75 ($4a_g$)	10.22
2 (C_{2h})	1		$9a_g(\pi_d^+)$	9.35 ($9a_g$)	9.37
	2	9.0–	$8a_u(\pi_i^-)$	9.36 ($8a_u$)	9.53
	3		$6b_g(\pi_o^-)$	9.36 ($6b_g$)	9.48
	4	9.5	$8b_u(\pi_o^+,\pi_d^-)$	9.41 ($8b_u$)	9.50
	5		$7b_u(\pi_o^+,\pi_d^-)$	10.06 ($7b_u$)	10.12
	6	10.0	$8a_g(\pi_i^+,\pi_d^+)$	10.31 ($8a_g$)	9.71
3 (C_s)	1	8.7(sh)	$13a''(\pi_i^-)$	9.18 ($13a''$)	9.27
	2	9.08	$12a''(\pi_o^-)$	9.43 ($17a',\pi_{d(endo)}$)	9.41
	3	9.4	$17a'(\pi_o^+)$	9.46 ($12a''$)	9.53
	4	9.5	$16a'(\pi_d^+)$	9.92 ($16a',\pi_{d(exo)}$)	9.57
	5	9.75	$15a'(\pi_d^-)$	10.07 ($15a',\pi_o^+$)	10.10
	6	10.07	$14a'(\pi_i^+)$	10.54 ($14a'$)	9.92
4 (C_{2h})	1	8.4–	$10a_u(\pi_i^-)$	8.65 ($10a_u$)	8.94
	2		$12a_g(\pi_d^+)$	8.79 ($12a_g$)	8.99
	3	8.6	$11b_u(\pi_d^-)$	8.91 ($11b_u$)	9.21
	4	9.1	$9b_g(\pi_o^-)$	9.27 ($9b_g$)	9.52
	5	9.3	$10b_u(\pi_o^+)$	9.57 ($10b_u$)	9.68
	6	9.98	$11a_g(\pi_1^+)$	10.52 ($11a_g$)	10.14
5 (C_s)	1	8.53	$12a''(\pi_i^-)$	8.93 ($12a''$)	9.07
	2	9.13	$11a''(\pi_o^-)$	9.42 ($16a'$)	9.48
	3	9.48	$16a'(\pi_o^+)$	9.47 ($11a''$)	9.65
	4	9.65	$15a'(\pi_d)$	9.98 ($15a'$)	9.87
	5	10.23	$14a'(\pi_i^+)$	10.62 ($14a'$)	10.21
6 (C_s)	1	8.77	$14a''(\pi_i^-)$	9.37 ($14a''$)	9.35
	2	9.07	$13a''(\pi_o^-)$	9.52 ($13a''$)	9.57
	3	9.4	$17a'(\pi_o^+)$	9.62 ($17a'$)	9.59
	4	9.5	$16a'(\pi_d)$	9.86 ($16a'$)	9.77
	5	9.93	$15a'(\pi_i^+)$	10.14 ($15a'$)	9.72
7 (C_s)	1	8.70	$12a''(\pi_i^-)$	9.12 ($12a''$)	9.32
	2	9.09	$11a''(\pi_o^-)$	9.39 ($16a',\pi_d$)	9.45
	3	9.4	$16a'(\pi_o^+)$	9.44 ($11a''$)	9.58
	4	9.6	$15a'(\pi_d)$	9.72 ($15a',\pi_o^+$)	9.79
	5	10.06	$14a'(\pi_i^+)$	10.41 ($14a'$)	9.95
8 (C_s)	1	9.1	$14a''(\pi_o^-)$	9.22 ($14a''$)	9.41
	2		$13a''(\pi_i^-)$	9.28 ($13a''$)	9.60
	3	9.3	$17a'(\pi_d)$	9.36 ($17a'$)	9.48
	4		$16a'(\pi_o^+)$	9.61 ($16a'$)	9.80
	5	9.9	$15a'(\pi_i^+)$	10.08 ($15a'$)	9.65
9 (C_s)	1	8.4	$15a''(\pi_i^-)$	8.73 ($15a''$)	9.02
	2	8.6	$19a'(\pi_d)$	8.86 ($19a'$)	9.12
	3	9.1	$14a''(\pi_o^-)$	9.32 ($14a''$)	9.62
	4	9.3	$18a'(\pi_o^+)$	9.49 ($18a'$)	9.63
	5	10.0	$17a'(\pi_i^+)$	10.44 ($17a'$)	10.17
10 (C_s)	1	8.7	$17a''(\pi_i^-)$	8.69 ($17a''$)	9.11
	2		$20a'(\pi_d)$	8.76 ($20a'$)	9.13
	3	9.2	$16a''(\pi_o^-)$	9.05 ($16a''$)	9.51
	4		$19a'(\pi_o^+)$	9.39 ($19a'$)	9.61
	5	9.6	$18a'(\pi_i^+)$	10.23 ($18a'$)	9.93
11 (C_{2v})	1	9.63	$3b_1(\pi_d)$	9.52 ($3b_1$)	9.58
	2		$2a_2(\pi_o^-)$	10.41 ($2a_2$)	10.10
	3	10.5–	$7b_2(\pi_i^-)$	10.52 ($7b_2$)	9.91
	4	10.7	$8a_1(\pi_i^+)$	10.76 ($8a_1$)	10.11
	5		$2b_1(\pi_o^+)$	10.81 ($2b_1$)	10.53
12 (C_2)	1	8.75	$13b(\pi_d)$	8.88 ($13b$)	9.13
	2		$12b(\pi_i^-)$	10.01 ($12b$)	9.61
	3	9.95–	$12a(\pi_o^-)$	10.25 ($12a$)	10.00
	4	10.42	$13a(\pi_i^+)$	10.37 ($13a$)	9.82
	5		$11b(\pi_o^+)$	10.73 ($11b$)	10.40
13 (C_{2v})	1	9.6	$3b_1(\pi_d)$	9.43 ($3b_1$)	9.45
	2		$2a_2(\pi_o^-)$	10.53 ($2a_2$)	10.20
	3	10.3–	$7b_2(\pi_i^-)$	10.62 ($7b_2$)	9.99
	4	10.6	$8a_1(\pi_i^+)$	10.71 ($8a_1$)	10.14
	5		$2b_1(\pi_o^+)$	10.93 ($2b_1$)	10.56
14 (C_{2h})	1	9.60	$3a_u(\pi_d)$	9.35 ($3a_u$)	9.41
	2		$2b_g(\pi_o^-)$	10.54 ($2b_g$)	10.20
	3	10.35–	$8a_g(\pi_i^+)$	10.59 ($8a_g$)	9.90
	4	10.7	$7b_u(\pi_i^-)$	10.76 ($7b_u$)	10.34
	5		$2a_u(\pi_o^+)$	10.93 ($2a_u$)	10.56

a All values are in electronvolts.

Skipped Cyclic Ene- and Dienediynes. 2

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Figure 4. Comparison of the first PE bands of **5, 9, 11,** and **12.**
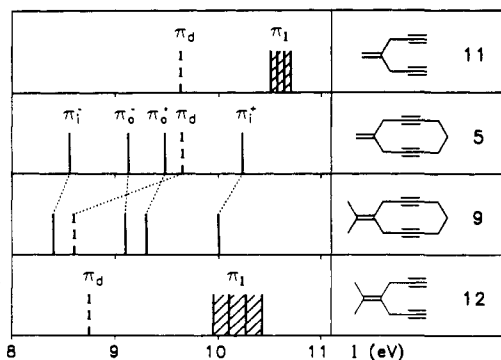

Figure 5. Comparison of the first PE bands of **1, 4, 5,** and **15.**

the π-MO localized at the exomethylene group, we compared the PE spectra of **11** and **12** with those of **5** and **9** (Figure 4). The PE spectrum of **11** shows one peak at 9.63 eV and four strongly overlapping bands centered around 10.6 eV. A comparison with the PE spectrum of 1,1-dimethylethene $(I_{v,1} = 9.44$ eV)[18] and the first bands of propyne $(I_{v,1} = 10.36$ eV)[19] suggested the assignment of the peak at 9.6 eV to the ionization from the double bond in **11** (π_d) and the bands at 10.6 eV to the triple bonds (π_t). The suggested assignment is corroborated by comparison of the PE bands of **11** with those of **12** (Figure 4, Table IV). This comparison leads to a shift toward lower energy for the first band by 0.88 eV and for the bands at higher energy by an average value of 0.4 eV, which is anticipated from first-order perturbation theory.[8]

The comparison of the PE spectra of **5** and **11** (Figure 4) suggests assigning band 3 or 4 of the PE spectrum of **5** to the ionization of the π-MO at the double bond (π_d). The other four peaks are assigned to the ionization of π-MOs at the triple bonds. The latter we classify as the "in-plane" linear combinations π_i^+ and π_i^- and the "out-of-plane" linear combinations π_o^+ and π_o^-, as discussed in the previous paragraph for **15–17.** We chose to assign the third band in the PE spectrum of **5** to the ionization from π_o^+ and the fourth band to π_d because both calculation methods predict this sequence. According to the 3-21G calculation, the energy of the π_o^+ orbital is only slightly affected by the introduction of the double bond(s) in **1** and **5**, since the through-space interactions of these orbitals are largely compensated by hyperconjugation effects with the allylic–propargylic C–H bonds. By following this choice the empirical band sequence for **1, 4, 5,** and **15** parallels the one derived from the 3-21G calculations (see below). The ionization from the exomethylene double bond(s) in **1** and **5** we ascribe to the band at 9.6–9.8 eV. The comparison between the bands of **5** and **9** (Figure 4) as well as between **1** and **4** shows the anticipated low-energy shift of the π_d-band(s) by 1.1 eV.
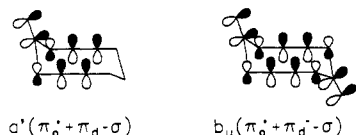

The observation that the second band in the series **1, 5,** and **15** remains at constant energy (see Figure 5) is best explained by assigning it to π_o^- since, due to its nodal properties,[8] this orbital should not be affected by the double bonds. This assignment is further supported by the fact that the energy of the π_o^- combination also remains unchanged in **4** and **9** as well as in the larger rings (see below).

(b) Ionization Energies of the In-Plane Orbitals. In Figure 5 we have correlated the first PE bands of **15** with those of **1, 4,** and **5.** The slight shift of the first band in **1** and **5** (π_i^-) toward higher energy is understandable if we recall that in **15** the strong

split between π_i^- and π_i^+ is due to an intense through-bond interaction of π_i^- with the highest σ-orbitals of the propano chains. Replacement of the sp³ center either at C(4) or at both C(4) and C(9) in **15** by an sp² center of the exomethylene group(s) will diminish the through-bond interaction somewhat by lowering the basis orbital energy for the corresponding σ-orbitals. In **4** and **9** this small effect is overcompensated by an increase of the energy of the propano chain orbitals caused by the methyl groups. Consequently, we find a slight shift of π_i^- toward lower ionization energy. Most interestingly, the comparison between **1** or **5** and **15** shows a significant shift of π_i^+ in **1** (+0.33 eV) and **5** (+0.21 eV) toward higher ionization energy (Figure 5). We consider this to be clear-cut evidence for a homoconjugative interaction between the double bond(s) and the triple bonds in **1** and **5**. The resulting linear combinations are shown schematically.
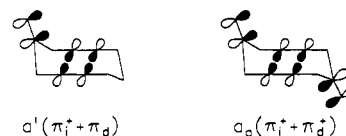
The change from **1** to **4** and from **5** to **9** resulted in the anticipated strong shift of π_d toward lower energy, which indicates a large energy difference between the basis orbital energies of the double and triple bond(s) in **4** and **9**. As a consequence, in **4** and **9** the homoconjugative effects between the double bond(s) and π_i^+ should be a lot weaker than in **1** and **5**. The PE spectra fully confirm this prediction, since the ionization energies assigned to the π_i^+ orbitals of **4** and **9** are almost identical with the corresponding value of **15** $(\pi_i^+(15), 10.02$ eV; $\pi_i^+(4), 9.98$ eV; $\pi_i^+(9), 10.0$ eV). This is a clear counterproof for the proposed homoconjugative interactions in **1** and **5**.

PE Spectra of the 11- and 12-Membered Rings 2, 3, 6–8, and 10

The assignment of the PE spectra of **2, 3,** and **8** is hampered by the fact that only the first and last band in the area between 8.8 and 10.2 eV can be recognized clearly. In the region in between, we find mainly strongly overlapping bands. Our assignment relies on the results of the MO calculations, qualitative considerations, and the comparison with **6, 7,** and the 10-membered rings.

To understand the electronic structure of the 11-membered rings qualitatively, we have compared the PE spectra of **3, 6, 7,** and **16** in Figure 6. The first band and the last band are assigned to π_i^- and π_i^+, respectively. This follows from the correlation with the first and last bands of **16** and is confirmed by the MO calculations. Again, in the case of **6,** we find a strong stabilization of π_i^+ by homoconjugation with the exomethylene group, which is completely analogous to the situation in **1** and **5.** The "counterproof" works equally well as for the 10-membered rings, as the ionization energies assigned to the π_i^+ combinations of **10** and **16** are almost identical $(\pi_i^+(10), 9.68$ eV; $\pi_i^+(16), 9.69$ eV).

In the case of **3** and **7,** there are considerable differences in the ring geometry as compared to **16.**[5] Whereas in **16** the triple bonds are calculated to be inclined by 10.2° (MMX), in **3** and **7** they

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(19) Carlier, P.; Dubois, J. E.; Masclet, P.; Mouvier, G. *J. Electron Spectrosc. Relat. Phenom.* **1975,** *7,* 55 and references therein.
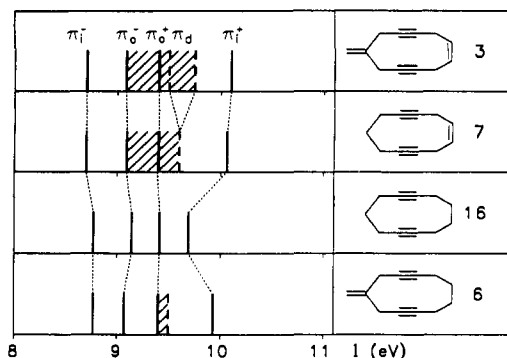
Figure 6. Comparison of the first PE bands of **3**, **6**, **7**, and **16**.

are oriented parallel and the distance between C1 and C7 is about 0.2 Å shorter than in **16**. Therefore, the through-space interaction and the resulting energy split between the two in-plane combinations must be somewhat larger than in **16**, a fact which can be clearly seen in a slight decrease of the ionization energy of the π_i^- combination in **3** and **7**. However, in **3** and **7** we also observe a much stronger shift of π_i^+ toward higher ionization energy, which provides clear evidence for the stabilization of π_i^+ by homoconjugation with the endocyclic double bond. Since the second band in **3**, **6**, **7**, and **16** remains rather constant (9.1 eV), we assign it to the ionization event from π_o^-. This assumption is based on the fact that π_o^- is not interacting with the double bonds for reasons of symmetry (as already discussed in connection with the PE spectrum of the 10-membered rings), and it is supported by the fact that the energy thus assigned to π_o^- is almost identical with the corresponding values of the 10-membered rings.

The PE spectra of **13** and **14** (Table IV) reveal that there is no significant difference in ionization energy between the endocyclic double bond in **3** and **7** and a methylene double bond as in **6**. Both spectra show one band at 9.6 eV, which is assigned to the ionization from the double bond and which is well separated from a broad peak of four triple bond ionizations around 10.5 eV (Table IV). Therefore, and in analogy to the 10-membered rings, we assign band 3 of the PE spectra of **3**, **6**, and **7** to the ionization from π_o^+. Band 4, and in the case of **3** also band 5, we assign to the ionization from the double bonds. In the case of **3** and **7**, this assignment differs from the results of the calculations (Table II). From a comparison of the experimental values with the results of the calculations for **11**, **13**, and **14**, we conclude that the calculations tend to underestimate the ionization energy of the internal double bonds; for this reason we support the empirical assignment.

As in the case of **3** and **7**, there are differences in the ring geometry between **2** and **8** and their parent system **17**.[4] The distances between the acetylenic carbon atoms in **8** (4.1 and 3.8 Å) are somewhat shorter than the distances in **17** (4.06 Å); however, they are still considerably longer than the van der Waals distance (3.4 Å)[20] and the triple bonds remain skewed. Thus we do not expect significant differences in the through-space interactions of the triple bonds between **8** and **17**. In changing from **17** to **8**, the energy of π_i^- should therefore remain constant, but in **8** π_i^+ should be considerably stabilized by homoconjugation with the endocyclic double bond. As in **2** the triple bonds are parallel and the distance between them (3.36 Å) is close to the van der Waals value; a slight shift of π_i^- toward lower ionization energy can be anticipated, but the stabilization of π_i^+ by homoconjugation should still be the dominating effect in causing a stronger split between the in-plane orbitals compared to **17**. In Figure 7 we have correlated the PE bands of **2**, **8**, and **17**. As
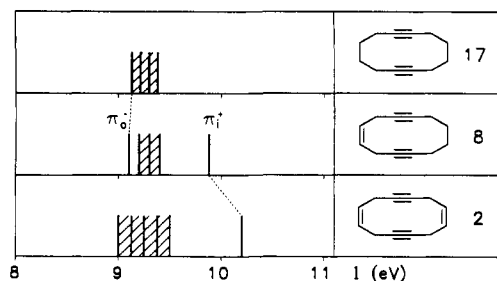
Figure 7. Comparison of the first PE bands of **2**, **8**, and **17**.

we find strongly overlapping bands in the PE spectra of **2** and **8**, it is impossible to assign individual ionization energies to all MOs. However, the predictions discussed above are fully confirmed. According to the 3-21G calculation, we assign the highest ionization energies of **8** (9.1 eV) and **17** (9.13 eV) to the π_o^- orbital. As expected, these values are almost identical with the corresponding energies of the 11- and 10-membered rings. According to the 3-21G calculations, the broad peak at 9.3 eV in the PE spectrum of **8** is assigned to the ionizations from π_o^-, π_o^+, and π_d, and the first ionization peak of **2** (9.0–9.5 eV) is assigned to the ionizations from π_i^-, π_o^-, π_o^+, and the two π_d combinations. The strong overlap of the first five ionizations in the PE spectrum of **2** is not surprising as the 3-21G method predicts the four highest MOs of **2** to have almost identical energy. From the first ionization bands of **2** and **8** we learn that in fact there is no considerable destabilization of π_i^- in these two molecules as compared to **17**. This confirms our prediction that the geometrical differences between **2**, **8**, and **17** do not cause a significant change in the through-space interactions of the triple bonds within this series. The peak at 9.88 eV in the PE spectrum of **8** and at 10.0 eV in that of **2** we assign to linear combinations which result from the interaction between π_i^+ and the double bond(s). As the geometrical differences are not important, the strong shift of the ionization assigned to π_i^+ in **8** and **2** (Figure 7) can be attributed to homoconjugation between the double and the triple bonds. The resulting linear combinations are shown schematically.

$a'(\pi_i^+ + \pi_d)$ $a_g(\pi_i^+ + \pi_d^*)$

Conclusions

The X-ray investigations on **1** and **2** show that the structural requirements for homoconjugative interactions between the double bonds and triple bonds are met. The distances between the termini of the double and triple bonds are as close as in the corresponding olefinic models. The PE spectroscopic investigations on **1–10** reveal a sizeable homoconjugation between the double and triple bonds. It is evidenced by a high-energy shift of bands by about 0.2 eV per double bond. To our knowledge this is the first time that such an interaction has been shown. The PE investigations furthermore reveal a confirmation of the assignment of the second band in the PE spectra of **15** and **16** to π_o^-. This assignment is in contrast to the prediction of calculations.

Supplementary Material Available: Tables of atomic coordinates of the hydrogen atoms, anisotropic displacement factors of the carbon atoms, bond lengths, bond angles, and selected interatomic distances of **1** and **2** (3 pages). Ordering information is given on any current masthead page.

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