of aliquots of methanol in THF until 1 equiv had been added revealed that only the anion IIIa had been protonated. Finally, reaction of 10 equiv of IIId with I equiv of the anion of 1,1,3-triphenylpropene revealed a complete absence of the anion IIIa.[12] Since a minimum of 10% anion formation would be detectable and a 10-fold excess was used, we conclude that the pK_a of IIId is at least 2 pK_a units greater than that of 1,3,3-triphenylpropene (26.6).[13]

Electrochemical Measurements. Electrochemical measurements were performed in DME/0.5 M $[(n\text{-}C_4H_9)_4N]ClO_4$ vs. a Ag/AgI reference electrode. A three-electrode IR-compensated system with a platinum auxiliary electrode was used throughout. Details of the construction of the reference electrode are given in ref 14 and 15. Cyclic voltammetry was performed at a platinum wire electrode on a PAR Model 170 electroanalytical system at 21 °C.

The cyclic voltammograms confirmed the reversibility of the first oxidation step ($R^- \rightarrow R\cdot + 1e$, at approximately −1.00 to −1.20 V in all cases.)[16] Potential sweep rates from 5 to 500 mV s^{-1} were used. The minimum value allowed by convection and diffusion was 5 mV s^{-1}. The ratios between the anodic and cathodic peak currents, $i_p(a)/i_p(c)$, were unity and independent of sweep rate. The potential separation between peaks was constant at ~72 mV. The reversible one-electron reduction of anthracene observed at −1.87 V in this system exhibited a peak separation of 66 mV under similar conditions.

The second oxidative process, occurring at approximately +0.4 to +0.6 V for the various compounds, is completely irreversible, probably due to rapid capture of the cation by another molecule of anion. This was independent of sweep rate, up to the maximum sweep rate available, 1000 mV s^{-1}. For this irreversible process use of E_p values as a measure of cation stability depends upon the condition that the rate of the chemical step following electron transfer be independent of substitution. This will be obeyed for the cation–anion recombination.[17]

Acknowledgment. We acknowledge with gratitude assistance in the preparation of compounds by Mr. R. Bruen and Mr. C. Migdal.

Registry No. Ia, 76429-99-7; Ib, 76430-00-7; Ic, 76430-01-8; Id, 68494-28-0; IIa, 76430-02-9; IIb, 76430-03-0; IIc, 76430-04-1; IId, 69340-84-7; IIIa, 76430-05-2; IIIb, 76430-06-3; IIIc, 76430-07-4; IIId, 76430-08-5; IVa, 40006-86-8; IVb, 2216-49-1; IVc, 13948-08-8; 4-(trimethylsily)bromobenzene, 6999-03-7; *p*-dibromobenzene, 106-37-6; trimethylsilyl chloride, 75-77-4; benzophenone, 119-61-9; [4-(trimethylsilyl)phenyl]diphenylcarbinol, 50653-05-9; [4-(trimethylsilyl)phenyl]diphenylchloromethane, 76446-92-9; bis[4-(trimethylsilyl)phenyl]phenylmethyl chloride, 76446-93-0; ethyl benzoate, 93-89-0; bis[4-(trimethylsilyl)phenyl]phenylcarbinol, 50653-06-0; ethyl *p*-(trimethylsilyl)benzoate, 18028-09-6; diethyl carbonate, 105-58-8; tris[4-(trimethylsilyl)phenyl]carbinol, 76430-09-6; tris[4-(trimethylsilyl)phenyl]methyl chloride, 76430-10-9.

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Evidence for a Strong Through-Bond Interaction in *anti*-Tricyclo[6.4.0.0^{2,7}]dodecatetraene

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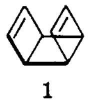
The He(I) photoelectron spectra of *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraene (6) and bicyclo[4.2.0]octa-2,4-diene (7) have been recorded. The first bands in the PE spectrum of 6 and 7 could be assigned based on a ZDO model and semiempirical calculations. The ZDO model reveals a resonance integral between the butadiene moiety and four-membered-ring fragment of $\beta = -1.5$ eV. In the case of 6 the first two bands are split by 0.6 eV which is due to through-bond interaction between the π system and the four-membered ring. A comparison with other systems showing two π systems in an anti arrangement to a σ system reveals a large through-bond effect.

Recent photoelectron (PE) spectroscopic investigations[1] and model calculations[2] indicate that a four-membered ring interacts strongly with a double-bond system connected in 1,2 and 1,3 positions. Relevant examples are the PE spectra of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octadienes[3,4] 1 and 2 as well as tricyclo[3.3.0.0^{2,6}]octene (3)[5] and bicyclo[4.1.1]octa-2,4-diene (4).[6] Missing links in this series are the *syn*- and *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraenes 5 and 6 as well as bicyclo[4.2.0]octa-2,4-diene (7). In this paper we report our PE spectroscopic investigations of 6 and 7.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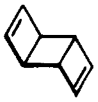
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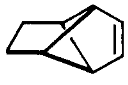
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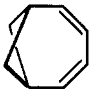
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Photoelectron Spectra. The He(I) PE spectra of 6 and 7 are shown in Figure 1. The recorded first vertical ion-

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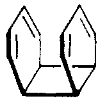
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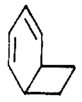

7

ization potentials ($I_{V,J}$) are collected in Table I. The PE spectrum of **6** shows two bands (1 and 2) clearly separated from strongly overlapping bands starting at 10 eV. Band 1 shows a typical Gaussian shape while band 2 exhibits a steep onset and vibrational fine structure. The energy difference between band 1 and 2 is found to be 0.60 eV. The PE spectrum of **7** shows, like all butadiene derivatives, one band around 8 eV separated by a 2-eV gap from a region of strongly overlapping bands.

To interpret both PE spectra we make use of Koopmans' theorem.[7] In this approximation the measured vertical ionization potential, $I_{V,J}$, is set equal to the negative value of the orbital energy ϵ_J ($-\epsilon_J = I_{V,J}$). This allows the correlation of orbital energies with the energies of PE bands. The orbital energies were calculated by a ZDO model using parameters obtained from previous investigations of vinylcyclobutane derivatives[5,6] and by semiempirical calculations using the MINDO/3[8] and extended Hückel (EH)[10] methods.

ZDO Model. To estimate the orbital energies of the first bands we first consider the LCAO wave functions of the interacting fragments and the corresponding basis orbital energies.

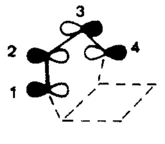
(a) Wave Functions. For the highest occupied molecular orbital (HOMO) of the butadiene unit in **7** the Hückel wave function is given by eq 1. In the case of **6**

$$\psi_1 = 0.372(\pi_2 - \pi_3) + 0.602(\pi_1 - \pi_4) \qquad (1)$$

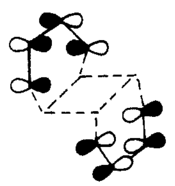
there are two linear combinations (eq 2). All three (ψ_1,

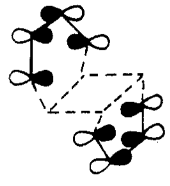
$$\psi_{2,3} = (1/2^{1/2})(\psi_1 \pm \psi_1) \qquad (2)$$

ψ_2, ψ_3) are shown below.



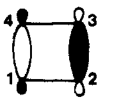
Ψ_1,a''

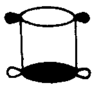

Ψ_2,a$_u$

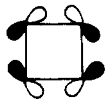

Ψ_3,b$_g$

The irreducible representations according to which these wave functions transform in the point group C_s (for **7**) and C_{2h} (for **6**) are listed below the drawings.

The highest occupied Walsh orbitals of the cyclobutane[11] fragment are indicated below together with their irreducible representations in C_{2h} and C_s. In all three wave functions indicated, the coefficients of the basis atomic orbitals φ have the same magnitude ($0.50\varphi_n$) at each center n. For reasons of symmetry only the wave functions belonging to the irreducible representation A_u (A''), i.e., ψ_2 (ψ_1) and ϕ_2, will interact with each other.







	Φ_1	Φ_2	Φ_3
C_{2h}	b$_u$	a$_u$	a$_g$
C_s	a'	a"	a'

(b) Basis Orbital Energies and Interaction Parameters. To estimate the basis orbital energy of the cyclobutane ring we assume as previously[5,6] that the inductive shift of one butadiene unit amounts to 0.2 eV. From this and the PE data of cyclobutane[12] we obtain eq 3 and 4.

$$\epsilon(\phi_2) = -10.6 \text{ eV for } \mathbf{6} \qquad (3)$$

$$\epsilon(\phi_2) = -10.8 \text{ eV for } \mathbf{7} \qquad (4)$$

For the basis orbital energy of a butadiene unit attached to a cyclobutane ring we assume eq 5. This value we take

$$\epsilon(\psi_1) = \epsilon(\psi_3) = -8.5 \text{ eV} \qquad (5)$$

from the PE spectrum of **6** (band 2). It is very close to the basis orbital energy assumed in previous studies (−8.4 eV).[5,6]

In order to set up the interaction matrices for **6** and **7**, the off-diagonal elements have to be calculated. For **6** we obtain eq 6 and for **7** we obtain eq 7. Considering β values

$$H_{\psi_1,\phi_2} = 4 \times 0.425(0.5)\langle \pi_1|\mathbf{H}|\varphi_1\rangle = 0.850\beta \qquad (6)$$

$$H_{\psi_2,\phi_2} = 2 \times 0.602(0.5)\langle \pi_1|H|\varphi_1\rangle = 0.602\beta \qquad (7)$$

in the range −1.9 to −1.4 eV, the best fit between experiment and calculation is obtained for $\beta = -1.5$ eV. (By using slightly different basis orbital energies on vinylcyclobutane derivatives a β value of −1.25 eV has been advocated in the literature.[13]) Our result for β is considerably smaller than the value obtained for **3** and **4** (−1.9 eV) by using the same basis orbital energies. We ascribe this discrepancy to the smaller overlap in the case of **6** and **7** where p AO's on linked centers are not parallel as in **3** or **4** but are tilted by about 30° (see later). The comparison given in Table I shows an excellent agreement between the ZDO model and experiment. The estimated chosen basis orbital energy for the highest occupied Walsh orbital of the cyclobutane ring in **7** corresponds very well to the value measured for band 3. Also the missing vibrational fine structure of band 1 is noteworthy in comparison with the first band of the PE spectrum of **4**;[6] it is indicative of a σ/π interaction for the HOMO of **7**.

A beautiful confirmation of the assignment suggested for **6** is obtained by consideration of the shape of the PE bands. The Gaussian shape of band 1 indicates ionization from an orbital with significant σ-bonding character, while band 2 appears as a typical π band similar to the characteristic first PE band of compounds containing a *cis*-butadiene[5,14] unit. This is consistent with the assignment of band 1 to the $7a_u(\pi_+)$ MO, which according to the ZDO treatment incorporates 31% Walsh orbital character. In

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Table I. Comparison between Vertical Ionization Potentials, $I_{V,J}$, and Calculated Orbital Energies, ϵ_J, of 6 and 7[a]

band	$I_{V,J}$	assignment	ZDO	MINDO/3	EH
			7 (C_s)		
1	8.25	9a″ (π)	−8.21	−8.48 (9a″)	−11.85 (9a″)
2	10.35	8a″ (σ)		−9.64 (12a′)	−11.69 (12a′)
3	10.8	12a′ (W)	−10.8	−10.14 (8a″)	−13.02 (8a″)
4	11.2	7a″ (π)	−11.1	−11.00 (7a′)	−13.58 (7a′)
			6 (C_{2h})		
1	7.85	$7a_u(\pi_+ - W)$	−7.91 ($7a_u$)	−8.19 ($7a_u$)	−11.62 ($7a_u$)
2	8.52				
	8.71	$6b_g(\pi_-)$	−8.52 ($6b_g$)	−8.82 ($6b_g$)	−12.22 ($6b_g$)
	8.90				
3	10.15	$8b_u$ (W)		−9.34 ($8b_u$)	−12.41 ($8b_u$)
4	10.4	$6a_u(\sigma)$	−10.6	−9.87 ($6a_u$)	−12.87 ($6a_u$)
				−10.22 ($9a_g$)	−13.22 ($9a_g$)
				−11.00 ($8a_g$)	−13.71 ($8a_g$)
				−11.32 ($5b_g$)	−13.84 ($5b_g$)
5	11.0	$5a_u(\pi_+ + W)$	−11.21 ($5a_u$)	−11.39 ($5a_u$)	−13.85 ($5a_u$)
6	11.2				

[a] All values in eV.

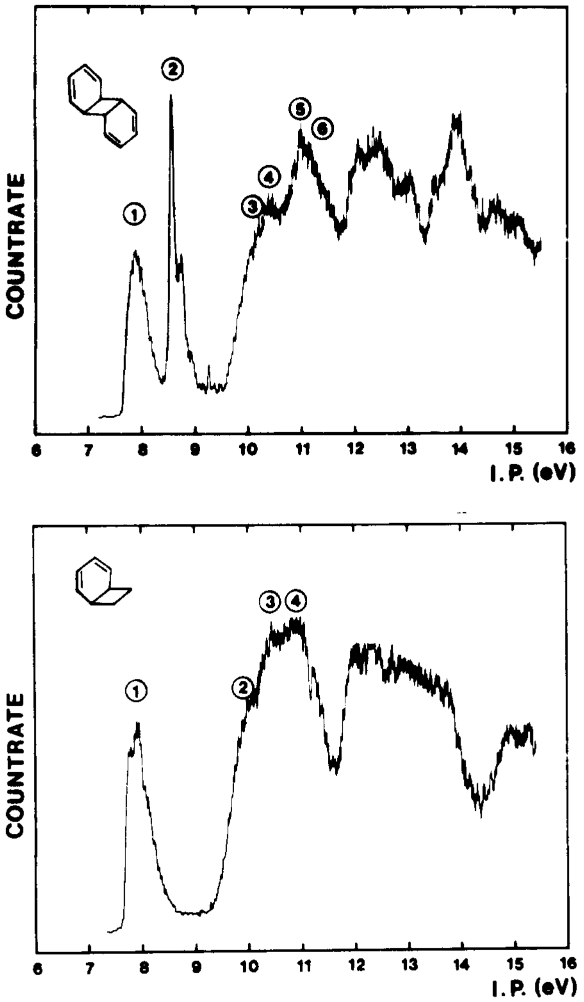
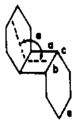


Figure 1. PE spectra of 6 and 7.

Table II. Geometries of the Carbon Skeletons of 6 and 7 Calculated by MINDO/3[a]

7 (C_s), H_f = 37.53 kcal/mol

$a = 1.541$, $b = 1.581$; $c = 1.507$, $d = 1.351$, $e = 1.471$, $f = 1.521$, $\alpha = 123.4°$, $ab = 88.9°$, $af = 91.1°$, $cd = 122.9°$, $de = 121.5°$



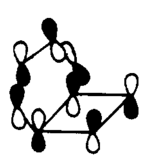
6 (C_{2h}), H_f = 82.75 kcal/mol

$a = 1.558$, $b = 1.575$, $c = 1.506$, $d = 1.351$, $e = 1.471$, $\alpha = 127.0°$, $cd = 122.8°$, $de = 121.5°$

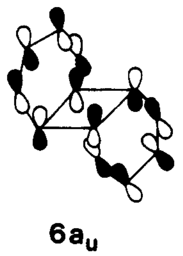
[a] Distances are in Å (1 Å = 10^{-10} m).

contrast, the $6b_g(\pi_-)$ orbital is of purely butadiene π character, consistent with the assignment of band 2 to this MO.

Semiempirical Calculations. To test and to complete the assignment arising from the ZDO calculations we have calculated the molecular orbital energies by using the MINDO/3[8] and the EH[10] methods. Since the detailed structures of 6 and 7 are not known we have optimized their geometries within the MINDO/3 scheme[8] using a modified Fletcher–Powell search procedure.[9,15] The heats of formation as well as the geometrical parameters derived for the carbon skeletons are given in Table II. No symmetry constraints were adopted for any of the compounds. The structural parameters realized for the cyclobutane segments in 6 and 7 closely parallel those derived from electron-diffraction experiments on bicyclo[2.2.1]hex-2-ene[16] and tricyclo[3.3.0.0^{2,6}]oct-3-ene.[17] The semiempirical calculations confirm our assignment based on our ZDO model of the first, third, and fourth band of 7. For the assignment of band 2, appearing as a shoulder in the PE spectrum of 7, the assignment 8a″ is suggested. The 8a″ orbital (schematically shown below) can be looked at as a linear combination of the $1b_{1u}$ orbital[1] of the cyclobutane moiety with a σ orbital of the butadiene rest.



8a″



$6a_u$

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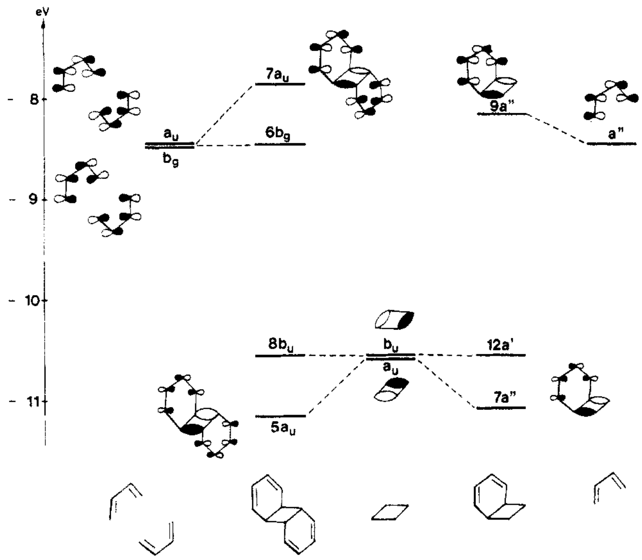


Figure 2. Orbital interaction diagram for **6** (left) and **7** (right) based upon perturbation theory.

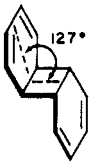
In the case of the PE spectrum of **6** the assignment based on our ZDO model of the first two bands is confirmed. The Walsh-type $8b_u$ orbital is predicted to be on top of $6a_u$. The latter orbital is closely related to that of $8a''$ and is indicated schematically. For $5a_u$ a value (−11.39 eV) close to that found with the ZDO model (−11.21 eV) is predicted. Between $6a_u$ and $5a_u$ both semiempirical methods predict three orbitals of σ type. Due to the broad overlapping bands in the PE spectrum in the region of 11 eV it is hard to judge if the suggested assignment is reasonable.

Concluding Remarks. According to the analysis presented, the $7a_u(\pi_+)$ orbital is destabilized due to a through-bond interaction[18] with the corresponding Walsh orbital (a_u(W)) of the four-membered ring. This interaction is indicated in Figure 2. The energy difference between the unperturbed π niveau ($6b_g(\pi_-)$) and $7a_u(\pi_+)$ of **6** amounts to 0.60 eV. A comparison with the value found for **2** (0.97 eV)[3,4] and that for *anti*-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (**8**) (1.60 eV)[19] indicates a strongly varying energy difference between $a_u(\pi_+)$ and $b_g(\pi_-)$ in the systems **2**, **6**, and **8**. The observed energy shift can conveniently be analyzed by second-order perturbation theory.[20] According to this theory the energy shift, $\delta\epsilon$, of two interacting molecular orbitals, $\psi_a = \sum_i c_{ia}\varphi_{ia}$ with the orbital energy ϵ_a and $\psi_b = \sum_j c_{jb}\varphi_{jb}$ with the orbital energy ϵ_b, is given by eq 8. In this expression c_{ia} and c_{jb} are the coefficients of ψ_a and ψ_b at the sites where the interaction takes place and β_{ij} represents the matrix element of the perturbation operator. β_{ij} is approximately proportional to the overlap between the atomic orbitals φ_{ia} and φ_{jb}.

$$\delta\epsilon = \frac{\sum\limits_{ij}(c_{ia}c_{jb}\beta_{ij})^2}{|\epsilon_a - \epsilon_b|} \qquad (8)$$

To estimate the overlap of the π and σ systems in **2**, **6**, and **8** we can use the dihedral angle between the planes of the π system and the σ system. The values calculated (MINDO/3) are given below. It shows that β_{ij} should be a maximum for **8** and a minimum for **6**; the difference, however, should be moderate.

2



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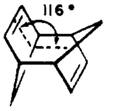

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Another difference between **2** and **8** on one side and **6** on the other is due to the coefficients in the numerator which are slightly smaller (0.425) for the butadiene system in **6** than for the ethylene bridge (0.500) in **2** and **8**.

The main factor, however, influencing the different π-level splittings in **2**, **8**, and **6** is due to the denominator. The basis orbital energies can be estimated as follows.

2: $\epsilon_\pi \approx -9.6$ eV $\epsilon_\sigma = -10.8$ eV $\epsilon_\pi - \epsilon_\sigma = 1.2$ eV
6: $\epsilon_\pi = -8.5$ eV $\epsilon_\sigma = -10.6$ eV $\epsilon_\pi - \epsilon_\sigma = 2.1$ eV
8: $\epsilon_\pi \approx -9.6$ eV $\epsilon_\sigma = -10$ to 10.5 eV $\epsilon_\pi - \epsilon_\sigma = 0.4$–0.9 eV

The energy difference ($\epsilon_\pi - \epsilon_\sigma$) obtained for **6** is considerably larger than the values found for **2** and **8**.

From this discussion we conclude that the smaller shift between $a_u(\pi_+)$ and $b_g(\pi_-)$ observed in the case of **6** compared to **2** and **8** is mainly due to the energy difference of the interacting fragment orbitals.

The shift toward lower binding energy of the HOMO of **6** due to the discussed through-bond interaction should manifest itself in the reactivity of **6**, e.g., toward dienophiles. Based on our investigations we predict a considerably higher reactivity of **6** with a dienophile, compared with **7**.

Experimental Section

The PE spectra have been measured with a PS18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England). Compound **7** was prepared via reduction of cyclooctatetraene with Zn.[21] The mixture of **7** and 1,3,5-cyclooctatriene (15% **7**) was separated by complexing cyclooctatriene with $AgNO_3$.[22] The residue was purified by distillation: $n^{20}{}_D$ 1.505; NMR ($CHCl_3$, Me_4Si) δ 2.3 (m, 4 H), 3.0 (m, 2 H), 5.5 (m, 4 H).

Compound **6**, previously prepared[23] on the basis of cyclooctatetraene, was obtained by a new synthesis[24] starting from norbornadiene.

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Registry No. 6, 21657-71-6; **7**, 3725-28-8; 1,3,5-cyclooctatriene, 1871-52-9.

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