Theoret. Chim. Acta (Berl.) 50, 145–158 (1978)

THEORETICA CHIMICA ACTA

Orbital Interactions in *anti*- and *syn*- Tricyclooctadienes and Their Homoderivatives

Photoelectron Spectra and Molecular Orbital Calculations

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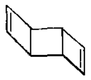
Photoelectron spectroscopy and molecular orbital calculations of the Extended Hückel, MINDO/3 and STO-3G Hartree–Fock type have been applied to *anti*- and *syn*-tricyclo[4.2.0.0^{2,5}]octadiene (**1** and **2**) and their homo and bishomo derivatives. The resulting ordering of the one-electron levels for **1** and **2** are $7a_g(\pi_+)$, $[6b_u(\sigma), 5b_u(\pi_-)]$, $4a_u(\sigma)$, $3a_u(\sigma)$ and $7a_1(\pi_+)$, $5b_2(\sigma)$, $6b_2(\pi_-)$, $3a_2(\sigma)$, $4b_1(\sigma)$, respectively. The present results differ substantially from those previously published.

Key words: Tricyclooctadienes, PE spectra and MO calculations of ~

1. Introduction

The ordering of the highest occupied molecular orbitals (MOs) of *anti*- and *syn*-tricyclo[4.2.0.0^{2,5}]octadiene, **1** and **2**, has been a matter of controversy for some time. Different MO calculations give widely divergent results; in fact, different orderings of the "plus" and "minus" π type combinations (see below) for **2** have been realized [1–4]. As discussed in detail by Heilbronner and Schmelzer [5], this discrepancy is due to extreme sensitivity of the competition between "through-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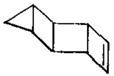
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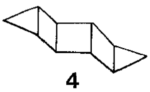
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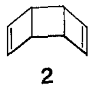
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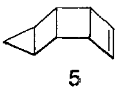
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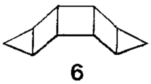
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space" and "through-bond" interactions with respect to small changes in MO approximation and molecular geometry. Analysis of the photoelectron (PE) spectra of **1** and **2** within Koopmans' approximation [6] has not clarified the orbital energy picture for these isomers. Two essentially different assignments of the first four bands in the spectra to specific MOs have been suggested. The first assignment [1] was based on empirical estimates of the "through-space" and "through-bond" effects, while the second [3] relied entirely on the results of semi-empirical calculations of the MINDO/2 type.

In an attempt to resolve this discrepancy we have recorded the PE spectra of the homo-derivatives **3** to **6**. Correlation with PE bands in this series should provide additional evidence for the ordering of the levels in **1** and **2**. Furthermore, these compounds offer interesting opportunities for a study of the interaction of high-lying valence orbitals of cyclobutane with ethylenic π-orbitals and cyclopropane Walsh-orbitals. This was of particular interest in connection with a recent study of the thermal rearrangement of these molecules [7] and PE spectroscopic investigations of other and related small ring compounds [8]. The interpretation is based on qualitative considerations and on the results of several types of MO calculations, including non-empirical calculations of the STO-3G type [9].

2. Experimental

The PE spectra of **1** and **2** are available from earlier studies [1, 3]. The syntheses of the compounds **3** to **6** were carried out according to the directions published previously [7], and the PE spectra were recorded at room temperature on a PS 18 instrument (Perkin Elmer Ltd., Beaconsfield, England) with a He(I) light source. The spectra were calibrated with argon; a resolution of about 20 meV on the argon line was obtained. The PE spectra of **3** to **6** are shown in Fig. 1.

3. Calculations

Calculations on the species **1** to **6** were carried out by approximate semi-empirical valence electron methods of the extended Hückel (EH) [10], SPINDO/1 [11], and MINDO/3 [12] type, and by a non-empirical Hartree–Fock method with a minimal STO-3G basis [9]. The simple EH calculations were based on a crude estimate of the molecular geometries. All C–C bond lengths were taken as 1.5 Å, the C=C distances as 1.35 Å and the C–H distances as 1.1 Å; dihedral angles of fused rings were taken as 120°. The remaining calculations were based on structures calculated by the MINDO/3 method. Optimization of all structural parameters with no symmetry restrictions led to a geometry of C_{2h} symmetry in the case of **1** and C_{2v} symmetry in the case of **2**. C_s symmetry was assumed for the compounds **3** and **5**, C_{2h} was assumed for **4** and C_{2v} for **6**. The calculated structures are given in Table 1. The results of the SPINDO/1 method were essentially identical for *anti*- and *syn*-isomers and thus failed to reproduce the trends of the PE spectra. Hence, no further use has been made of SPINDO/1 results in the ensuing study. To illustrate the geometry dependence of the calculated MO energies, MINDO/3

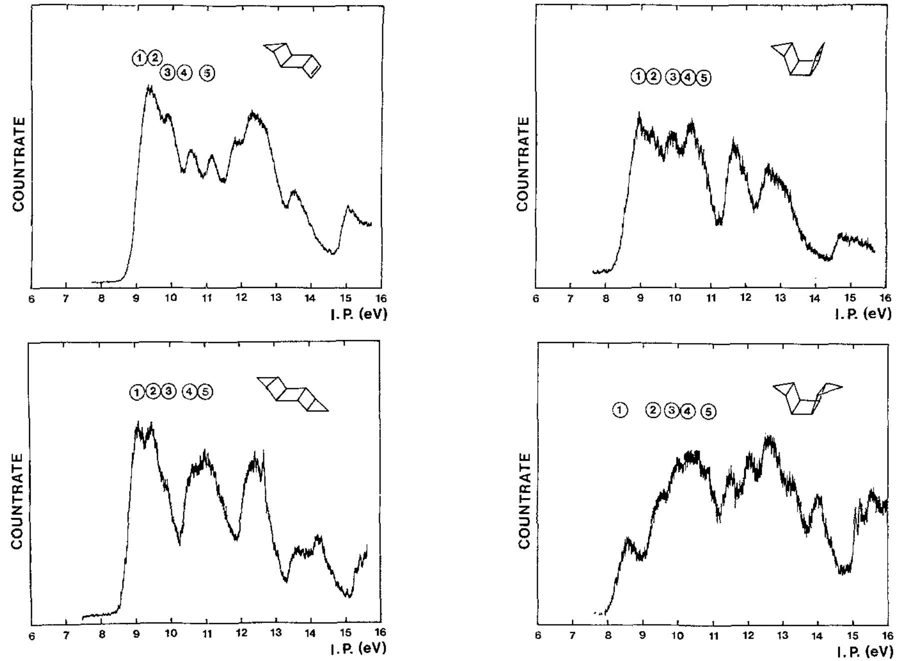
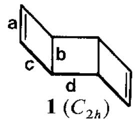
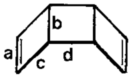
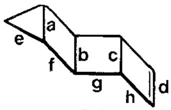
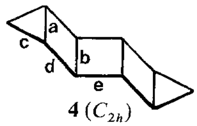
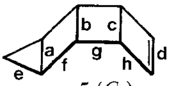
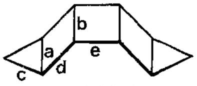


Fig. 1. Pe spectra of **3** to **6**

Table 1. Geometries of the carbon skeletons of **1** to **6** calculated by MINDO/3. Distances are in Å ($1Å = 10^{-10}$m)

 **1** (C_{2h})	a = 1.350, b = 1.589, c = 1.519, d = 1.548, cd = 121.49°
 **2** (C_{2v})	a = 1.350, b = 1.585, c = 1.520, d = 1.553, cd = 125.72°
 **3** (C_s)	a = 1.556, b = 1.589, c = 1.587, d = 1.350, e = 1.503, f = 1.532, g = 1.546, h = 1.518, ef = 116.51°, fg = 121.00°, gh = 121.48°
 **4** (C_{2h})	a = 1.556, b = 1.588, c = 1.503, d = 1.522, e = 1.544, cd = 116.45°, de = 120.90
 **5** (C_s)	a = 1.557, b = 1.584, c = 1.584, d = 1.351, e = 1.502, f = 1.533, g = 1.551, h = 1.519, ef = 116.35°, fg = 125.27°, gh = 126.20°
 **6** (C_{2v})	a = 1.557, b = 1.583, c = 1.503, d = 1.534, e = 1.549, cd = 116.18°, de = 125.67°

results are presented for the regular geometries mentioned above, as well as for the optimized geometries.

The calculations were performed at the Hochschul-Rechenzentrum der TH Darmstadt and the Rechenzentrum der Universität Erlangen-Nürnberg.

4. "Through-Space" and "Through-Bond" Interactions in 1 and 2

Before turning to the results for **3** to **6**, it is first instructive and useful to consider in simple terms the interactions affecting the π-type orbitals in **1** and **2**:

$$\pi_+ = (\pi_a + \pi_b)/\sqrt{2}$$

$$\pi_- = (\pi_a - \pi_b)/\sqrt{2}$$

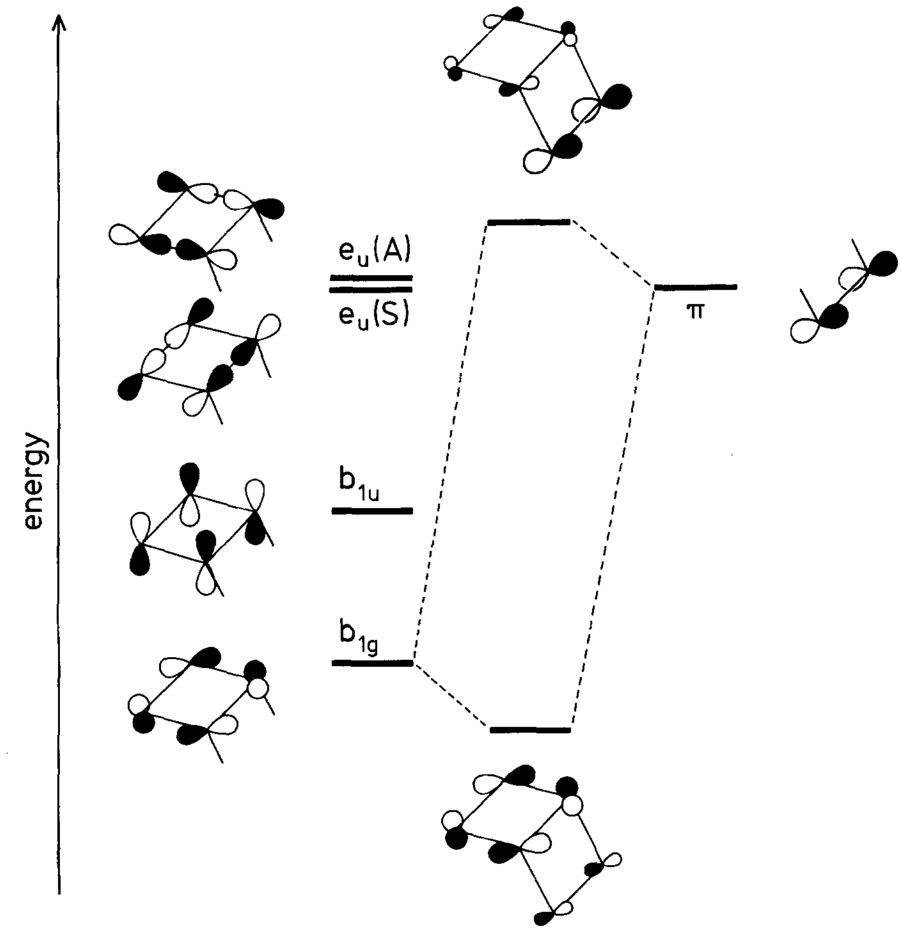
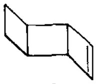


Fig. 2. Conjugative interaction between an ethylenic π-orbital and the b_{1g} Walsh-type orbital of cyclobutane (D_{4h})

π_+ and π_- are the symmetry adapted linear combinations of the ethylenic π-orbitals π_a and π_b. As discussed in detail previously [1], the "through-space" effect is negligible in the case of **1**, while in the case of **2** this effect can be expected to stabilize π_+ and destabilize π_- by about 0.2 eV, yielding a total split of ~0.4 eV. In order to estimate the "through-bond" effect, the valence MO's of the central cyclobutane ring require inspection. The approximate shape of the four highest occupied MOs of cyclobutane [13] and the π orbital of ethylene, arranged according to a bicyclo[2.2.0.]hexene geometry, are illustrated in Fig. 2. In contrast to the case where the π system is bridging the 1,3 positions of the four-membered ring [8b, 13b, 14], there is no significant interaction between the π orbital and the highest occupied cyclobutane orbitals, e_u, in the present 1,2-disubstituted case. Interaction with the $e_u(A)$ component is forbidden by symmetry, and interaction with the $e_u(S)$ component vanishes due to poor overlap. Significant interaction is possible with the lower lying b_{1g} orbital (Fig. 2). In **1** and **2** "through-bond" interaction via this orbital does not affect the π_- combination, but destabilizes the totally symmetric π_+ combination by an amount which should be of similar magnitude in the *anti-* and *syn*-isomer [1]. Provided the effective energy of the basis orbitals π_a and π_b can be derived, this magnitude can be estimated from the PE spectrum of **1** (where the "through-space" contribution is negligible). In the previous investigation [1] the basis orbital energy was estimated from the first ionization energy $I_{V,1}$ of the monoene **7** as 9.2_5 eV. Introduction of a second double bond in **7** to yield **1** was considered to lower the π basis orbital energy by 0.3_5 eV,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leading to $-9.2_5-0.3_5=-9.6$ eV for the energy of the basis orbitals π_a and π_b in **1** and **2**. However, it was not taken into consideration that conjugative interaction of the kind outlined in Fig. 2 is operative in monoene **7** as well as in dienes **1** and **2**. The observed energy of the π level of **7** must be corrected for this destabilizing effect in order to obtain the proper basis orbital energy. This means that the energies of the basis orbitals of **1** and **2** are lower than the -9.6 eV assumed in [1]. We contend that a much improved agreement with the PE data can be obtained if the basis orbital energies are taken as ~ -10.0 eV. This is evident from the correlation diagram in Fig. 3 which illustrates the derivation of the energies of the π_+ and π_- orbitals. An important change relative to [1] is the fact that the π_+ and π_- energies obtained for **2** clearly correspond to the first and the third PE band, respectively, leaving the second band to ionization of a σ level. The ordering in **1** is probably also π_+, σ, π_- which leads to a higher degree of consistency than π_+, π_-, σ. However, considering the near-degeneracy of the second and third ionization energies of **1**, this result is less certain than the ordering obtained for **2**.

In this section, the primitive derivation of the π orbital energies for **1** and **2** has been discussed in some detail. We find that adjustment of the basis orbital energy leads to a consistent assignment of bands in the PE spectra to π_+ and π_- levels

(Fig. 3). This assignment is essentially similar to the one suggested by Bodor, Chen and Worley [3] as far as the π levels are concerned. It will be shown in the following that this result is supported by correlation with the results for **3** to **6**.

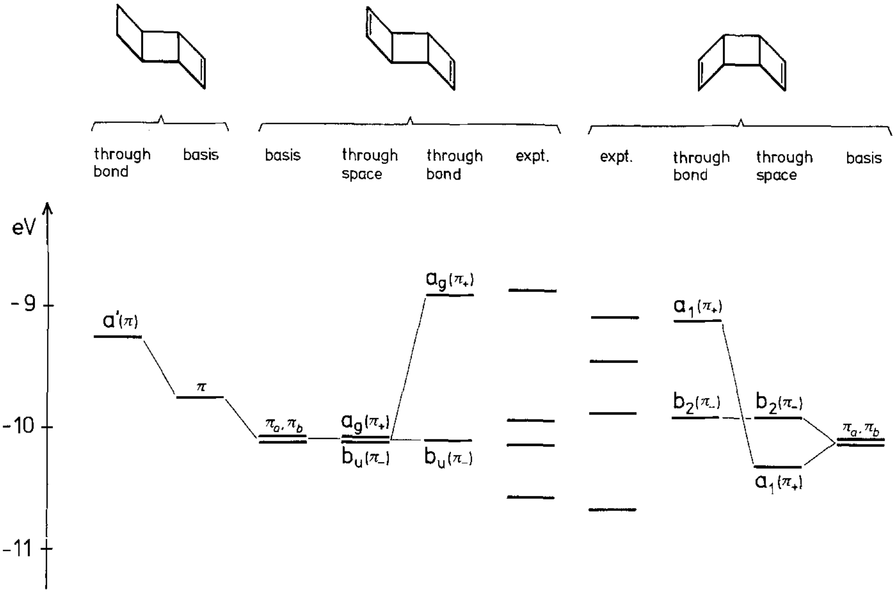


Fig. 3. Correlation of π levels in **7**, **1** and **2** illustrating the simple derivation of "through-space" and "through-bond" contributions

5. Correlation of Orbitals in the Series 1 to 6

Consider first the interaction between the highest occupied orbitals of cyclobutane and cyclopropane linked in 1,2 fashion. Strong interaction is expected between the highest occupied e_u orbitals of the cyclobutane ring and the e'-type Walsh orbitals of cyclopropane [15, 13b, 13d], as outlined in Fig. 4. Inductive effects have been assumed to destabilize the $e'(S)$ orbital of the disubstituted cyclopropane more than the $e'(A)$ orbital due to the larger amplitude of the former on the substituted centers. As regards the e_u orbitals of a 1,2 disubstituted cyclobutane, inductive effects can be expected to affect the $e_u(S)$ and $e_u(A)$ components to about the same degree. However, interaction with bonding and anti-bonding cyclopropane orbitals not shown in the diagram will tend to destabilize the $e_u(S)$ orbitals relative to the $e_u(A)$ orbital, and this may affect the relative ordering of the two intermediate resulting levels indicated in Fig. 4. The diagram is easily extended to the case of two cyclopropane groups attached symmetrically to a cyclobutane group as in **4** and **6**. The orbital interactions are worked out in Fig. 5.

Inspection of the relative orientation of p orbitals on joined centers indicates that the overlap between the cyclopropane Walsh orbitals (e.g. $e'(S)$) and the cyclobutane b_{1g} orbital is negligible (cf. Figs. 2 and 4). This implies that the conjugative

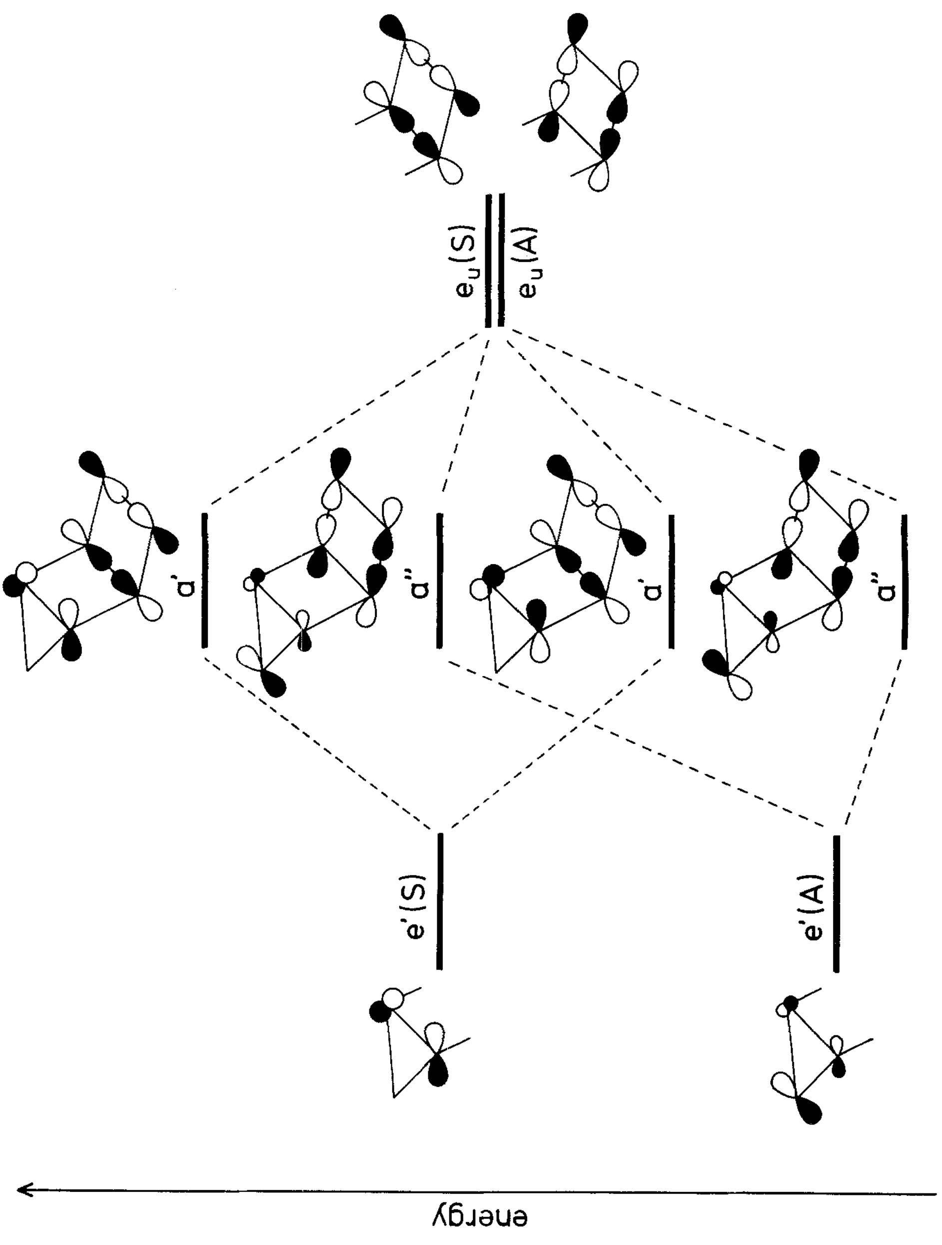


Fig. 4. Interaction of the highest occupied e_u orbitals of cyclobutane and the highest occupied e' orbitals of cyclopropane in relation to **3** and **5**

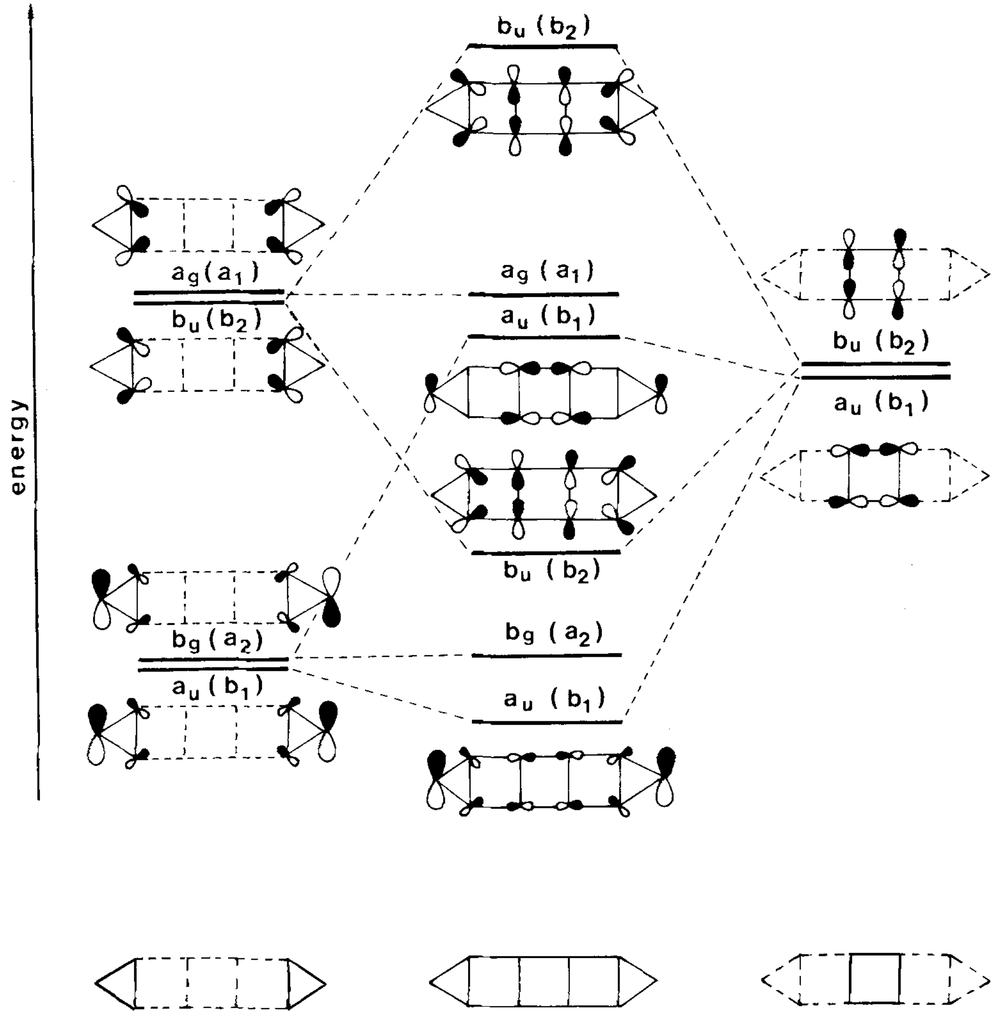


Fig. 5. Interaction of the highest occupied e_u orbitals of cyclobutane and symmetry adapted combinations of the highest occupied e' orbitals of two cyclopropane units in relation to **4** and **6**

interactions in the "mixed" compounds **3** and **5** are noncompetitive; the cyclopropane Walsh orbitals and the ethylenic π orbital tend to interact with different orbitals of the cyclobutane ring. "Through-bond" coupling via the central ring should thus be minimal, and a simple superposition of the diagrams in Fig. 2 and Fig. 4 should be a satisfactory representation.

Guided by the interaction diagrams in Figs. 2, 4 and 5, it is possible to correlate one-electron energy levels for **1** to **6**. Observed and calculated energies are collected in Table 2 and Table 3, and diagrammed in Fig. 6 and Fig. 7. Unfortunately, inspection of the calculated results makes it clear that the predicted ordering of the levels depends critically on the choice of method and input geometry (cf. introduction). How, then, can a consistent assignment of PE bands to specific MOs be arrived at?

Table 2. Observed ionization energies $I_{V,J}$ and calculated MO energies ε_J for the *anti* species **1**, **3** and **4** (energies in eV; 1 eV ≈ 96.487 kJ/mole)

				$-\varepsilon_J$			
Cpd.	Band	$I_{V,J}$	MO[a]	EH	MINDO/3		STO-3G
1[d] (C_{2h})	1	8.96	$7a_g(\pi_+)$	12.09[b]	8.79[b]	8.79[c]	7.24[c]
	2	9.93	$6b_u$	11.93	9.24	9.13	9.11
	3	10.13	$5b_u(\pi_-)$	12.94	9.93	9.99	8.68
	4	10.57	$4a_u$	12.78	9.71	9.52	10.11
	5	11.6	$3a_u$	13.48	10.80	10.84	11.24
3 (C_s)	1	9.3	$15a'$	11.59	8.61	8.75	8.31
	2	9.3	$14a'(\pi)$	12.42	9.18	9.27	7.88
	3	9.86	$8a''$	12.46	9.34	9.44	9.88
	4	10.46	$13a'$	12.73	9.80	9.73	9.68
	5	11.06	$7a''$	13.12	10.22	10.21	10.41
4 (C_{2h})	1	9.1	$8b_u$	11.49	8.36	8.67	8.10
	2	9.5	$9a_g$	12.17	9.03	9.21	8.75
	3	9.8	$5a_u$	12.22	8.98	9.30	9.59
	4	10.6	$7b_u$	13.12	10.31	10.06	10.04
	5	10.9	$4a_u$	12.96	9.98	10.19	10.47

[a] Assignment from present work. Numbering refers to valence orbitals only.
[b] Estimated regular geometry, see text.
[c] Geometry optimized by MINDO/3 (Table 1).
[d] Ionization energies from Refs. [1, 3].

The most rigorous of the applied methods, the non-empirical STO-3G Hartree–Fock method, predicts both π levels to lie above the σ levels in **1** and **2**. This seems to support the assignment suggested in [1]. However, comparison with the results for the homo derivatives **3**–**6** indicates that the STO-3G result is not reliable. Consider, for instance, the variation of the first ionization energy in the series **2**, **5** and **6**; the observed binding energy is constantly decreasing while the STO-3G results show the opposite trend (Fig. 7). The observation that the first ionization energy of **2** is higher than that of **5** proves beyond reasonable doubt that if the first level in **2** is a π level, then the first level in **5** is a σ level. This follows from the fact that all calculations predict a stabilization of the highest occupied π level when going from **2** to **5** (it is furthermore consistent with the observed relatively low binding energy of the first level of **6**, which is necessarily of σ type). The STO-3G results are undoubtedly in error by predicting the π levels at too low binding energy relative to the σ levels, leading to a reversal of the two highest occupied levels in the case of **5**. The same conclusion is arrived at by a consideration of trends in the series **1**, **3** and **4** (Fig. 6). A shift of STO-3G π energies for **1**, **2**, **3** and **5** towards higher binding energies in order to obtain consistency with the PE data for **3**

Table 3. Observed ionization energies $I_{V,J}$ and calculated MO energies ε_J for the *syn* species **2**, **5** and **6** (energies in eV; 1 eV≈96.487 kJ/mole)

				$-\varepsilon_J$			
				EH	MINDO/3		STO-3G
Cpd.	Band	$I_{V,J}$	MO[a]	[b]	[b]	[c]	[c]
2[d] (C_{2v})	1	9.08	$7a_1(\pi_+)$	12.20	8.90	8.83	7.29
	2	9.44	$5b_2$	11.83	9.16	8.90	8.81
	3	9.87	$6b_2(\pi_-)$	12.75	9.67	9.89	8.50
	4	10.67	$3a_2$	13.02	10.01	9.84	10.17
	5	10.9	$4b_1$	13.02	10.12	10.04	10.84
5 (C_s)	1	8.91	$15a'$	11.47	8.53	8.64	8.18
	2	9.3	$14a'(\pi)$	12.39	9.17	9.27	7.87
	3	9.9	$13a'$	12.77	9.83	9.56	9.34
	4	10.3	$8a''$	12.58	9.56	9.63	9.88
	5	10.6	$7a''$	12.86	9.83	9.98	10.29
6 (C_{2v})	1	8.5	$8b_2$	11.28	8.21	8.55	7.96
	2	9.4	$9a_1$	12.27	9.13	9.29	8.91
	3	~10.0	$(5b_1)$	12.39	9.20	9.41	9.57
	4	~10.3	$(7b_2)$	12.86	9.91	9.65	9.44
	5	~10.6	$(4a_2)$	12.58	9.58	10.04	10.31

[a] Assignment from present work. Numbering refers to valence orbitals only.
[b] Estimated regular geometry, see text.
[c] Geometry optimized by MINDO/3 (Table 1).
[d] Ionization energies from Refs. [1, 3].

and **5**, yields an ordering of σ and π levels in **1** and **2** which fully supports the results of the simple considerations in the previous section (Fig. 3). Similar results are obtained by the EH and MINDO/3 methods, provided that the need for separate correlation of π and σ levels is recognized. The resulting assignment is indicated in Tables 2 and 3 and Figs. 6 and 7.

These results are supported by a consideration of the trends related to the three highest occupied σ orbitals of **1** and **2**. All calculations without exception predict the ordering $6b_u$, $4a_u$, $3a_u$ in the case of **1** and $5b_2$, $3a_2$, $4b_1$ in the case of **2**. The $6b_u$ and $5b_2$ orbitals are related to the $e_u(S)$, the $4a_u$ and $3a_2$ orbitals to the b_{1u}, and $4b_1$ orbitals to the $e_u(A)$ orbital of the cyclobutane ring (Fig. 2). A considerably larger split is predicted for the $4a_u$ and $3a_u$ orbitals of **1** than for the related $3a_2$ and $4b_1$ orbitals of **2**. This can be explained by the fact that the interaction between these levels is forbidden by symmetry in the case of **2**. That the interaction is considerable in the case of **1** is indicated by the observation that the $3a_u$ orbital attains C–H bonding character at the bridgehead positions. The predicted intervals are in qualitative agreement with the large separation of the fourth and the fifth ionization energies of **1** (1.0 eV) and the small gap between the corresponding energies of **2** (0.3 eV).

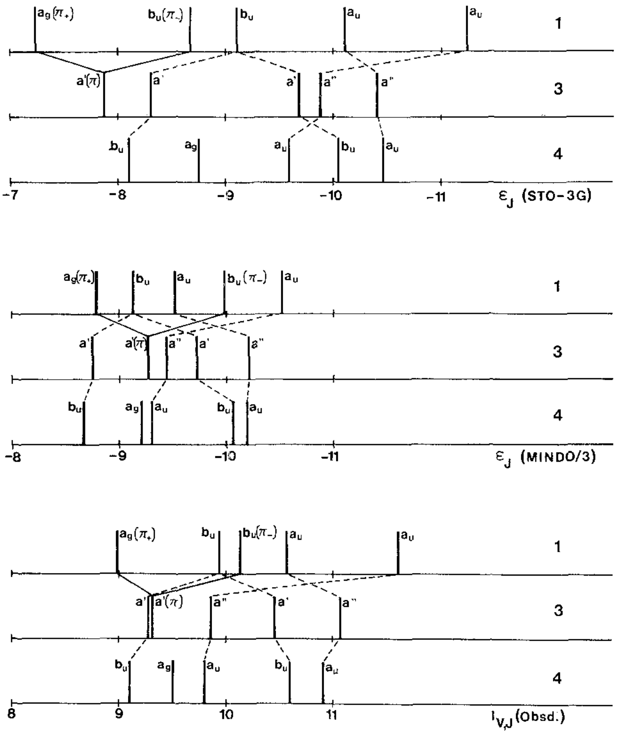
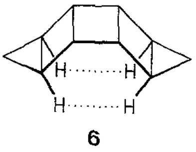


Fig. 6. Correlation of observed energies and energies obtained by MINDO/3 and STO-3G calculations for **1**, **3** and **4** (structures calculated by MINDO/3)

The correlation of these σ levels with those in **3** to **6** is indicated in Figs. 6 and 7. The first and third σ orbitals of **1** and **2** are related to the e_u orbitals of cyclobutane and interact strongly with the Walsh orbitals of the cyclopropane rings as indicated in Figs. 4 and 5. The suggested correlation of the observed energies is that which is most consistent with the predicted trends. It is found to be in agreement with the assignment of π bands discussed above, although the reverse assignment of the first σ band and the second π band of **1** cannot be excluded due to the closeness of the peaks. Also, the assignment of the third to the fifth ionization energies of **5** and **6** is rather uncertain, partly due to the low resolution of this region in the PE spectrum of **6** and partly due to the strong sensitivity of the calculated results to variation of geometry. There are some indications that the geometry calculated for **6** is somewhat inadequate. Thus, the considerable destabilization of the $8b_2$ level of **6** relative to the first level of **5** is best reproduced by the calculations based



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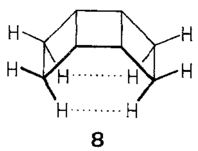

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on the estimated regular geometry. Apparently, the calculations based on the structure calculated by MINDO/3 tend to underestimate the "through-space" orbital interaction of the sterically interfering hydrogen atoms in **6**. The $8b_2$ and $4a_2$ orbitals have significant amplitudes on the interacting hydrogens and are particularly sensitive to variation of the H ... H distance. This distance is 2.0 Å for the estimated structure, but 3.0 Å for the geometry predicted by MINDO/3 (under the assumption of C_{2v} symmetry). The experimental structure of *syn*-tricyclo[4.2.0.0^{2,5}]octane (**8**) seems to indicate that the estimated structure is closer to reality as far as the H ... H distance is concerned. The corresponding distance in **8** is 2.13 Å [16].

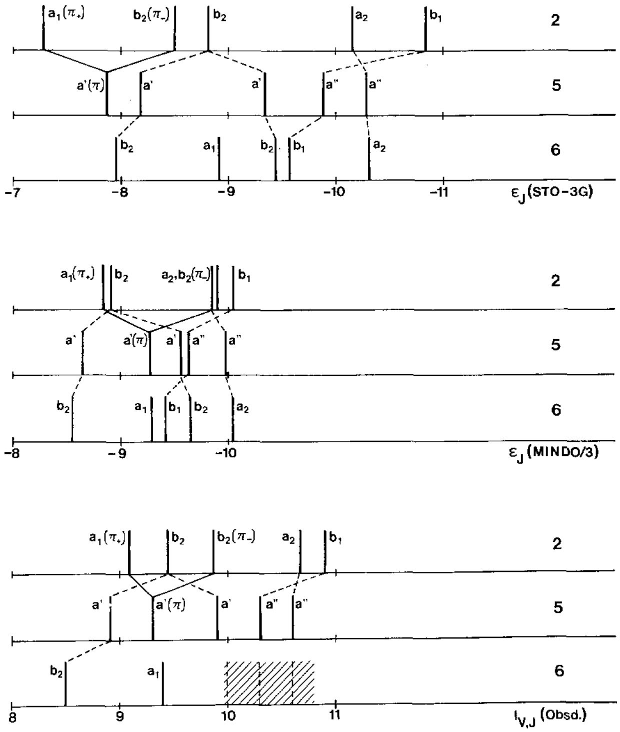

Fig. 7. Correlation of observed energies and energies obtained by MINDO/3 and STO-3G calculations for **2**, **5** and **6** (structures calculated by MINDO/3)

6. Concluding Remarks

Assignment of the ionization energies of **1** and **2** to individual molecular orbitals suggested in this paper is at variance with either of the two previously published. The suggested assignment of the π_+ and π_- levels is consistent with the results of Bodor, Chen and Worley [3]; however, we cannot agree with their assignment of five σ levels in case of **1** and four σ levels in case of **2** between 9 and

11 eV. The present results indicate that two and three σ levels, respectively, are present in this region.

None of the applied MO methods yields perfect agreement with the PE data for **1** to **6**. MINDO/3 and STO-3G results are about equally useful for correlation of the bands (perhaps with a slight preference for MINDO/3), provided σ and π levels are treated separately. It is not known whether the apparent failure of the STO-3G type calculations in predicting the correct ordering of π and σ levels is due to limitations inherent in the method (poor basis), inadequate input geometries, or a deviation from Koopmans' theorem. Furthermore, the compounds are probably particularly bad cases for the theoretical prediction of the PE spectra [5]; we feel that the assignment proposed in this paper, based on correlation of bands in a series of related compounds, is the best one can do at present, but accurate calculations [17] going beyond Koopmans' theorem and based on experimental geometries are called for.

Acknowledgement. The work in Darmstadt was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The work at the Ohio State University was financed by The National Science Foundation. We are grateful to Dr. P. Hofmann (Erlangen) for carrying out some *ab initio* calculations.

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Received April 17, 1978/July 4, 1978