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**2,3-Bis(methylene)bicyclo[2.1.1]hexane and
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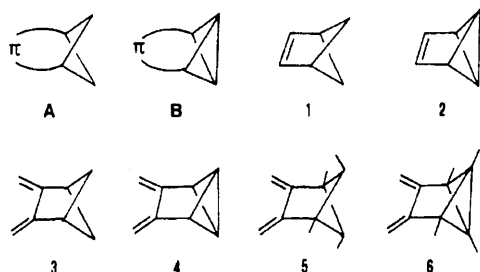
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The He (I) photoelectron spectra of 2-bicyclo[2.1.1]hexene (1), 2,3-bis(methylene)bicyclo[2.1.1]hexane (3), and 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (4) have been investigated. The assignment given is based on a ZDO model and semiempirical calculations. Together with the PE data of benzvalene (2), the reported data allow a comparison between 1-2 and 3-4. This yields a measure of the interactions between a cyclobutane or a bicyclobutane moiety and a double bond system within a ZDO model. The resonance integral found in the case of 1 and 3 amounts to -1.9 eV, that for 2 and 4, to -2.3 eV. The investigations furthermore reveal that the electronic factors which contribute to the higher reactivity of the bicyclobutane compounds amount to 5 kcal/mol.

Highly strained hydrocarbons have always attracted the interest of organic and physical organic chemists.¹ An interesting question in this area of chemistry is the differences between the influences of a cyclobutane and a bicyclobutane moiety on the properties of π -systems linked together as shown in A or B below. For geometric reasons



there are essentially three classes of compounds possible if we restrict ourselves to neutral closed shell cases; those where π stands for a two, a three, or a four carbon sp^2 bridge. The most simple case for a bridge with two sp^2 centers is 2-bicyclo[2.1.1]hexene (1) for model A and benzvalene (2) for model B. In the case of a butadiene bridge the ring system might be connected at the 1,4 positions or at the 2,3 positions of the butadiene fragment. The most simple examples for the latter case for A and B respectively are 2,3-bis(methylene)bicyclo[2.1.1]hexane (3) and 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (4).

A comparison between the reactivity toward tetracyanoethylene of the tetramethyl derivatives of 3 and 4, 5 and 6, revealed an acceleration of a factor of 3×10^7 for 6² with respect to 5. This large difference has been rationalized by the difference in the HOMO energy of 5 and 6. Since both compounds exhibit different steric requirements due to different geometries of the methyl groups at C(5,6) and C(1,6), respectively, part of the large difference in reactivity observed might be due to steric factors.³ This assumption is based on the observation that 3 reacts by a factor of 8.5×10^2 faster with TCNE than 5.³ The importance of electronic effects can be deduced from the fact that 4 reacts 3×10^2 faster than 3.⁴

To contribute to this discussion on the influence of a cyclobutane ring as compared with that of a bicyclobutane

Table I. Comparison between the First Measured Ionization Energies, $I_{v,j}$, with Calculated Orbital Energies of 1-4 (All Values in Electron Volts)

compd	band	$I_{v,j}$	assignment	$-\epsilon(\text{ZDO})$	$-\epsilon(\text{MIN-DO}/3^5)$
1	1	8.79	$4b_1(\pi)$	8.73	8.88
	2	10.84	$4b_2(\sigma)$	10.80	10.19
	3	11.6	$3b_1(\sigma)$	11.67	11.01
	4	12.0	$1a_2(\sigma)$	12.30	11.57
2 ^a	1	8.55	$4b_1(\pi)$	8.78	8.43
	2	9.75	$10a_1(\sigma)$	9.80	9.10
	3	10.83	$1a_2(\sigma)$	10.80	9.87
	4	12.18	$6b_2(\sigma)$	12.10	11.06
3	1	8.50	$2a_2(\pi)$	8.47	8.99
	2	10.0	$4b_1(\pi)$	9.80	9.94
	3	10.75	$6b_2(\sigma)$	10.80	10.11
	4	11.1	$3b_1(\sigma)$	12.10	11.48
4	1	8.27	$8a_2(\pi)$	8.30	8.50
	2	9.5	$9a_1(\sigma)$	9.80	8.88
	3	10.0	$3b_1(\pi)$	10.10	9.62
	4	11.2	$1a_2(\sigma)$	11.10	10.69
	5	11.75	$6b_2(\sigma)$	12.10	10.95

^a Data from ref 5.

ring, we have investigated the He (I) photoelectron (PE) spectra of 1, 3, and 4 and carried out molecular orbital (MO) calculations of different degrees of sophistication. A comparison of the data between 1 and 2⁵ as well as 3 and 4 should allow us via the application of Koopmans' assumption⁶ to assess the orbital sequence of the highest occupied MO's as well as the interaction parameter between the π -system and strained ring moiety. This in turn allows us to test the results of MO calculations as well as conclusions drawn in earlier studies on these and related systems.⁷

PE Spectra of 1-4. In Figure 1 we show the PE spectra of 1, 3, and 4. The PE spectrum of 2 has been reported

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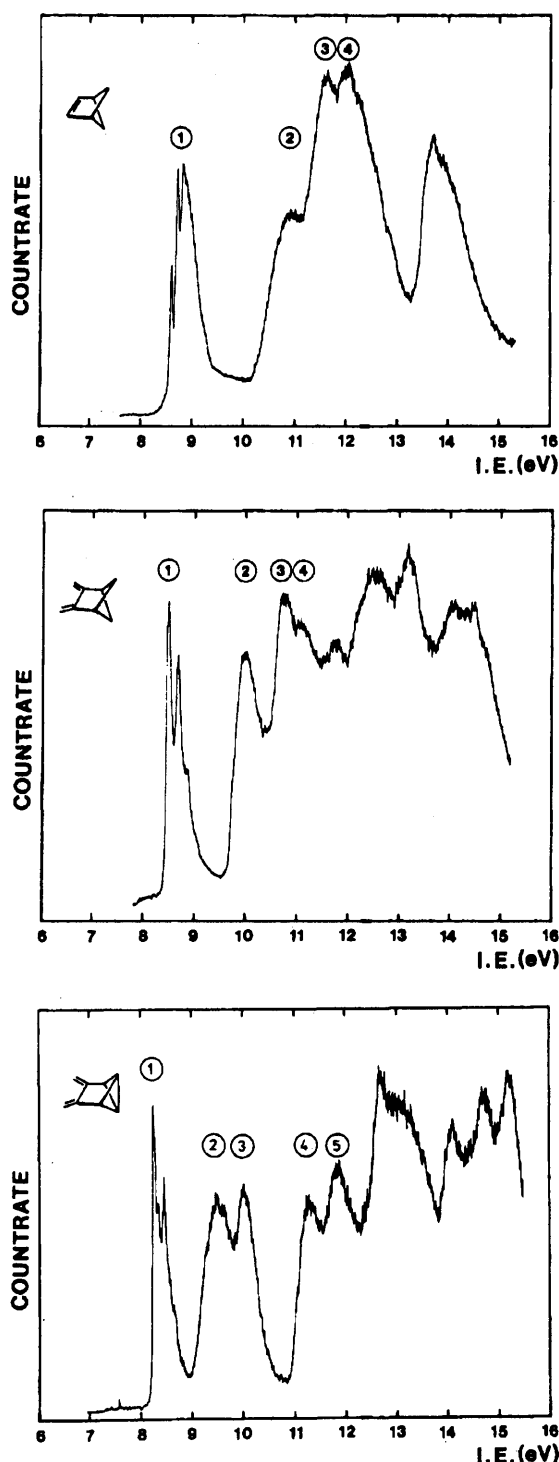


Figure 1. PE spectra of 1 (top), 3 (center), and 4 (bottom).

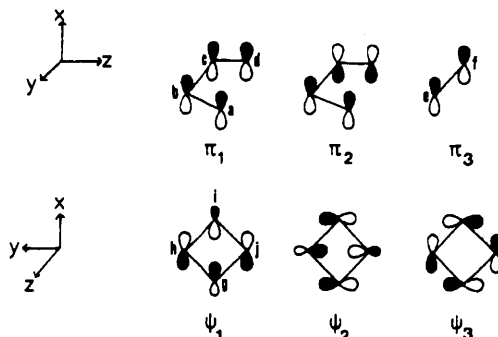
previously.⁵ Common to all three spectra is a band between 8 and 9 eV showing vibrational fine structure. The measured vertical ionization energies, I_{vj} , are collected in Table I for the first few bands.

To interpret the spectra we make use of the assumption that the measured ionization energies, I_{vj} , can be directly correlated to the calculated orbital energies ($-\epsilon_j = I_{vj}$) (Koopmans' theorem)⁶ derived for the ground state.

To estimate the orbital energies we apply a simple zero differential overlap model (ZDO model) which has been

used for other cyclobutane derivatives and benzvalene.^{5a} In this model, the relevant interaction scheme is worked out in the usual Hückel type treatment.

ZDO Model for 1 and 3. The wave functions for the fragments of 1 and 3 are the well-known HMO's⁹ of ethylene and butadiene as well as the Walsh-type MO's of cyclobutane.¹⁰ These MO's are schematically represented below. The corresponding wave functions together



with their irreducible representatives in the point group C_{2v} are given in eq 1-6. In these equations the $p_{\mu i}$'s are

$$\pi_1(b_1) = 0.372(p_{xa} + p_{xd}) + 0.602(p_{xb} + p_{xc}) \quad (1)$$

$$\pi_2(a_2) = 0.602(p_{xa} - p_{xd}) + 0.372(p_{xb} - p_{xc}) \quad (2)$$

$$\pi_3(b_1) = 0.707(p_{xe} + p_{xf}) \quad (3)$$

$$\psi_1(b_1) = 0.5(\phi_{xe} - p_{xe} + \phi_{xi} - p_{xi}) \quad (4)$$

$$\psi_2(b_2) = 0.5(p_{ye} - \phi_{ye} + p_{yi} - \phi_{yi}) \quad (5)$$

$$\psi_3(a_2) = 0.5(p_{ye} - p_{xe} - p_{yi} + p_{xi}) \quad (6)$$

pure p_{μ} atomic orbitals, while the $\phi_{\mu i}$'s are sp^n hybrid atomic orbitals parallel to the μ axis. In the case of cyclobutane the lowest occupied Walsh orbital (a_{1g} in D_{2h})¹⁰ is omitted since for reasons of symmetry it has no interaction partner on the side of the π -systems.

To construct the wave functions of 1 and 3 the atomic orbitals at the centers e and f of the ethylene fragment and b and c at the butadiene fragment have to be combined with those at centers h and j of the cyclobutane ring. The choice of a unique wave function for ψ_1 and ψ_2 is difficult, semiempirical calculations suggest, however, that the orbital density at all four centers is about equal.¹¹

For the basis orbital energies we use for ethylene

$$\epsilon(\pi) = -9.6 \text{ eV} \quad (7)$$

a value which has been used in previous studies.¹² This value incorporates the inductive effect of the four membered ring attached to it in 1 and 3.

To assess the basis orbital energy of the cyclobutane fragment we assume an inductive effect of the olefinic moiety in 1 and 3 to be 0.2 eV which yields

$$\epsilon(\psi_1) = \epsilon(\psi_2) = -10.8 \text{ eV} \quad (8)$$

$$\epsilon(\psi_3) = -12.3 \text{ eV} \quad (9)$$

as the corresponding orbital energies. These values are

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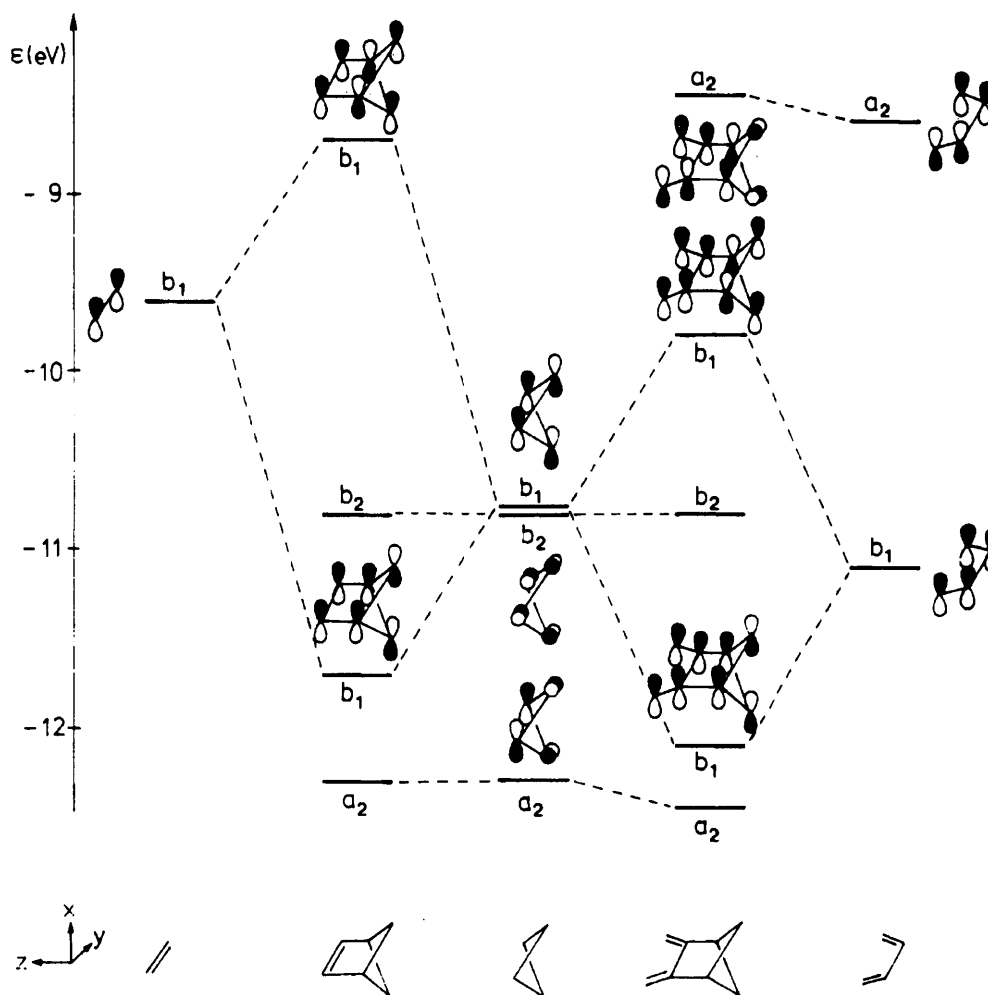


Figure 2. Interaction diagram between the basis orbital energies of a cyclobutane fragment (center) and an ethylene (left) or butadiene unit (right) to yield the valence orbitals of 1 and 3.

based on the PE data of cyclobutane¹³ and have been discussed in detail previously.^{11,12,14}

For the basis orbital energies for the *cis*-butadiene unit connected to the ring system at positions 2 and 3 we use

$$\epsilon(\pi_2) = -8.6 \text{ eV} \quad (10)$$

and

$$\epsilon(\pi_1) = -11.1 \text{ eV} \quad (11)$$

These values are lowered by 0.2 eV if the butadiene bridge is connected at the terminal centers 1 and 4.¹⁴

For the resonance integral β which describes the interaction between a p_μ atomic orbital on the π -system and a p_γ atomic orbital on the cyclobutane ring separated by one carbon-carbon single bond we adopt

$$\beta = \langle p_\mu | \mathcal{H} | p_\gamma \rangle = -1.9 \text{ eV}$$

This value has been tested in several systems.^{11,12,14,15}

Using the above wave functions, basis orbital energies and the resonance integral just discussed we are able to set up the secular equations for 1 and 3. Solving the

corresponding equations leads to the eigenvalues listed in Table I. As can be seen from Table I the values obtained by the ZDO approach compare well with the experimentally determined band positions.

In Figure 2 we show on the left the interaction diagram for the π -MO of an ethylene fragment with the HOMO's of a cyclobutane moiety giving rise to the valence levels of 1. On the right of the same figure, the corresponding interaction scheme for 3 is displayed, involving the cyclobutane Walsh MO's and the π -MO's of a butadiene fragment. The two interaction diagrams represent the results of the ZDO model. As can be seen from the left diagram on Figure 2 there is a considerable shift of $b_1(\pi)$ of the ethylene unit when the two fragments are joined. This interaction is mainly based on the small energy difference (1.2 eV) of the basis orbital energies of $b_1(\pi)$ of the ethylene bridge and $b_1(\psi_2)$ of the cyclobutane unit. For 3 (right side of Figure 2) the HOMO of the butadiene fragment ($a_2(\pi)$) is hardly shifted by interaction although the interaction parameter between the two fragments is the same in 1 and 3. This is due to the larger difference in the corresponding basis orbital energies (3.9 eV). As anticipated from the reasons just discussed the energy split between $b_1(\pi)$ of the butadiene unit and $b_1(\psi_2)$ of the cyclobutane moiety is relatively large (Figure 2).

ZDO Model for 2 and 4. To treat 2 and 4 similarly to 1 and 3 we have to define the proper wave functions and

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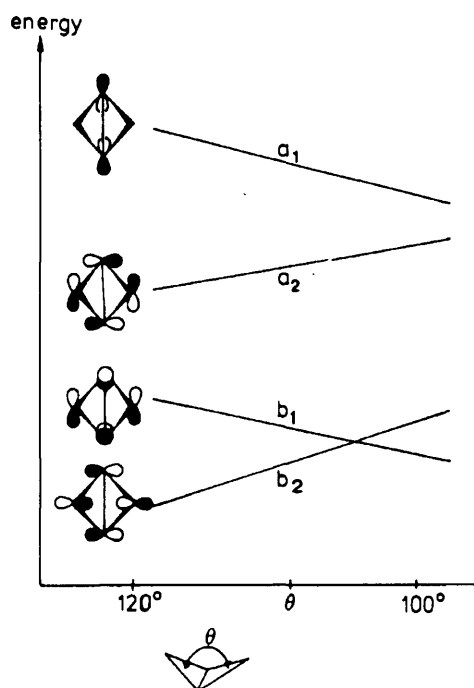
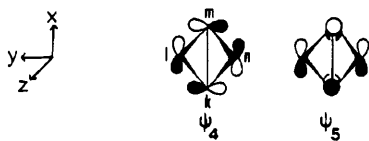


Figure 3. Schematic representation of the valence MO's of bicyclobutane as a function of θ .

the basis orbital energies of the bicyclobutane moiety. A value for the resonance integral can be obtained by fitting the calculated values to the observed band positions of the PE spectra. MO calculations¹⁶ as well as PE investigations^{17,18} on bicyclobutane revealed four high lying valence orbitals, $7a_1$, $1a_2$, $4b_2$ and $3b_1$ (see Figure 3). For our discussion we rely on a recent investigation¹⁹ comparing the different bonding models proposed for bicyclobutane in the literature.^{16,17,20,21} For reasons of symmetry only two MO's ($1a_2$ and $3b_1$) or only one ($3b_1$) possess the correct symmetry to interact with the butadiene or ethylene fragment, respectively. Recent investigations show that both the valence MO's ($1a_2$ and $3b_1$) can be approximated by the following equations assuming that the coefficients at all four positions are about equal in magnitude. This assumption is in line with the results of semiempirical and ab initio calculations.



$$\psi_4(a_2) = 0.5(p_{y_k} - p_{x_l} - p_{y_m} + p_{x_n}) \quad (12)$$

$$\psi_5(b_1) = 0.5(\phi_{z_k} - p_{x_l} - \phi_{z_m} - p_{x_n}) \quad (13)$$

As in (4)–(6) the p_{μ} 's are pure p_n atomic orbitals, while the ϕ_{μ} 's are sp^n hybrid atomic orbitals roughly parallel to the μ axis.

To assess the basis orbital energies of the four highest occupied MO's of the bicyclobutane fragment we should keep in mind that they depend very strongly on the dihedral angle, θ , as indicated in Figure 3. This is well documented by MO calculations.^{5a}

A similar θ value as in 4 is expected in tricyclo-[3.1.0.0^{2,6}]hexane (7). To estimate the basis orbital energies for the bicyclobutane⁵ unit we use for $\epsilon(a_2)$ the value obtained from the PE spectrum of 2:

$$\epsilon(a_2) = -10.8 \text{ eV} \quad (14)$$

To estimate the values for $\epsilon(a_1)$, $\epsilon(b_1)$, and $\epsilon(b_2)$ we start from the first ionization energies of 7.^{5,22} To correct the energies for the inductive effect of the C_2H_4 bridge we compared them with those MO's of 2 which are not affected by conjugation, i.e., $10a_1$, $1a_2$, and $6b_1$. A comparison yields an average difference of 0.6 eV. If we assume that this factor corrects for the C_2H_4 bridge we end up with the following basis orbital energies for the bicyclobutane fragment:

$$\epsilon(a_1), -9.8 \text{ eV}; \epsilon(b_1), -12.0 \text{ eV}; \epsilon(b_2), -12.1 \text{ eV} \quad (15)$$

These values are very close to those derived earlier for bicyclobutane using different arguments.⁵ Since b_1 depends very strongly on θ (see Figure 3) the value estimated above is probably too low.

Varying the resonance integral β between -1.8 to -2.4 eV yields the best agreement between calculation and experiment by using a value of -2.3 eV. This value must be considered as a upper bound for β due to the uncertainties in determining the basis orbital energies for the bicyclobutane fragment. Nevertheless a value smaller than -2 eV seems unrealistic. The interaction diagram shown in Figure 4 is based on the basis orbital energies and the β value just discussed. The calculated ZDO values are also listed in Table I. The comparison between calculated and experimental values for 2 and 4 (see Table I) shows a good agreement for the first bands.

Our assignment of the first PE bands is based on these calculations. It is further supported by considering the shape of the bands. The first band in the PE spectrum of 4 shows vibrational fine structure with a steep onset, typical for weakly bonding MO's. In line with this band-shape consideration are the results of our ZDO model which show that the wave function of a_2 of 4 is strongly localized at the π fragment. All the other four MO's show more or less strong σ participation. This results in the observed Gaussian shape of bands two-five of 4. A further confirmation of our assignment just discussed is found by comparing the first bands of the PE spectrum of 4 with those of 6.¹⁸ We encounter (Figure 5) a shift toward lower ionization energies due to the methyl groups. The shift found for the first band (0.4 eV) and third band (0.7 eV) is smaller than for band two (0.9 eV) and band four (1.4 eV). These observations are in line with the assumption that bands one and three are due to ionizations from π orbitals while the wave functions of the second and fourth orbital are strongly localized in the bicyclobutane part.

Semiempirical Calculations. To compare the ZDO results with those of all valence electron calculations we have carried out MINDO/3 calculations⁸ on 1 to 4. Since the geometrical parameters of 3 and 4 are not known we have optimized the heat of formation (ΔH_f°) of 1–4 with respect to their geometrical parameters assuming C_{2v} symmetry. The most relevant parameters are shown in

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(22) A reinvestigation of the PE spectrum of 7 revealed for the first two bands the values 9.2 eV and 10.0 eV.¹⁸

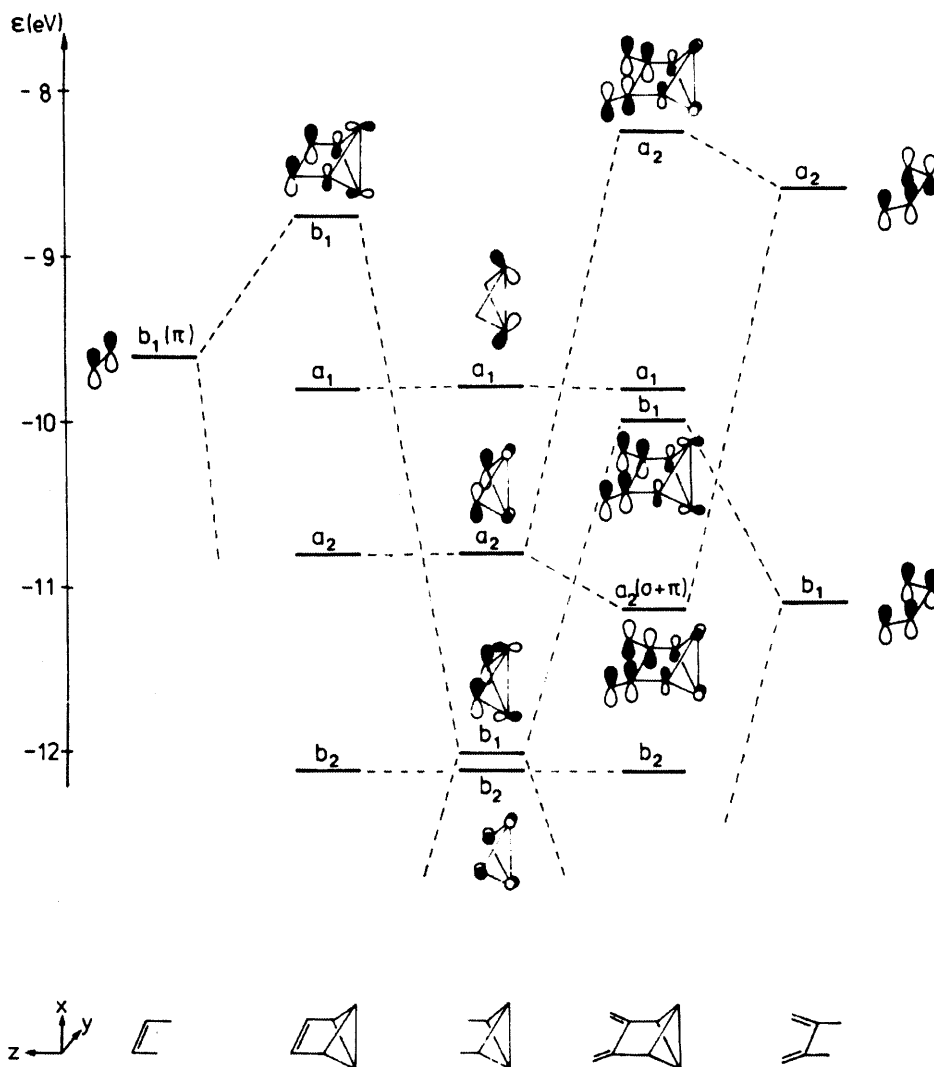


Figure 4. Interaction diagram between the basis orbital energies of a bicyclobutane fragment (center) and an ethylene (left) or butadiene fragment (right) to yield the valence MO's of 2 and 4, respectively.

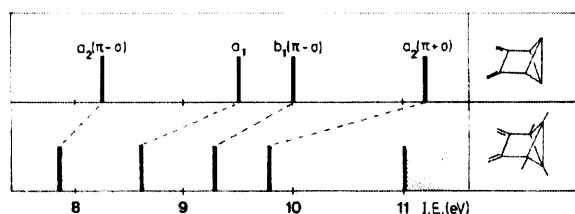


Figure 5. Comparison between the first bands of the PE spectra of 4 and 6.

Figure 6 together with the calculated values for the heat of formation.²³ For 1 and 2 the comparison with the experimental determined structural parameters²⁴ is made. The agreement between experiment and calculation is remarkably good. The heat of formation reported for 2 (87 kcal/mol)²⁵ is in good agreement with the predicted

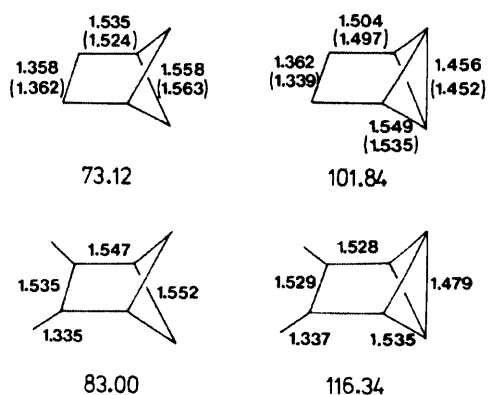


Figure 6. Calculated (MINDO/3) bond length for 1-4 together with heats of formation in kcal/mol. For 1 and 2 the experimental bond lengths are given in brackets.

value (Figure 6). It is interesting to note that the bonds connecting the ring system with the olefinic part are

(23) To define the dihedral angles in the four-membered ring of 1 and 3 the following distances are given: 1, 1-4 = 2.10 Å, 5-6 = 2.82 Å; 3: 1-4 = 2.11 Å; 5-6 = 3.30 Å. To define the flap angle in 2 and 4, the following distances are given: 2, 1-4 = 2.17 Å; 4, 1-4 = 2.17 Å.

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predicted to be shorter for 2 and 4 compared with 1 and 3. This is in line with the larger resonance integral as discussed in the previous section.

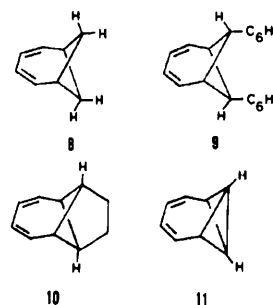
The agreement between calculated orbital energies (MINDO/3) and PE data is not satisfactory. Usually the high energy bands are predicted at too low energies, furthermore in case of 4 the MINDO/3 model predicts $9a_1$ at too low energies. It seems to be a general shortcoming of MINDO/3 to give too low binding energies for σ orbitals with a large p character (ribbon orbitals). However, the qualitative orderings are the same.

Discussion

Our PE spectroscopic investigations on 1-4 together with the ZDO treatment reveal a stronger interaction between the π -system and the bicyclobutane unit as compared to the cyclobutane fragment. The increase of interaction is exemplified in the different resonance integrals (2.3 eV vs. 1.9 eV) and it shows up in the lower ionization energy for 2 and 4 compared with 1 and 3.

In line with these findings is the marked difference in reactivity toward dienophiles encountered for 3 and 4⁴ as well as 5 and 6². The comparison of the PE results of 3 and 4 shows that the electronic contribution amounts to only 5 kcal/mol. The larger difference in reactivity in case of 5-6² we ascribe to steric effects as indicated in the introduction. Note, however, that in some cases²⁶ methyl groups show remarkable effects on ionization potentials. The syn hydrogen atoms at positions 5 and 6 of 3 are placed closer to the π -system than the corresponding hydrogens in 4. This shielding effect is expected to be seriously stronger for the methyl groups in 5 compared to 6. In line with these arguments is the observation that systems like 8^{14,27} or 9²⁸ do not

react or react slowly with *N*-phenyltriazolinedione, whereas 10²⁹ and octvalene (11)³⁰ react smoothly.



Experimental Section

The preparation of 1,³¹ 3,³ and 4⁴ has been described in the literature. For our PE spectroscopic investigations we used analytically pure material. The PE spectra have been recorded on a Perkin-Elmer PS 18 photoelectron spectrometer. The spectra were recorded at room temperature and were calibrated with argon and xenon. A resolution of 0.03 eV was achieved for the single bands and 0.1 eV for the shoulders.

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Registry No. 1, 822-41-3; 2, 659-85-8; 3, 50682-99-0; 4, 55678-69-8; 5, 55955-16-3; 6, 50590-86-8.

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Novel Photoinduced Functionalized C-Alkylations in Purine Systems¹

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The photoinduced reactions of metal enolates with 6-halopurine derivatives result in the formation, in high yields, of a variety of novel functionalized 6-alkylated purines that exist preferentially in the hydrogen-bonded enolic form in nonpolar solvents. High-field ¹H and ¹³C NMR data provide unambiguous support for the structures proposed. An $S_{RN}1$ mechanism is implicated in these photochemical transformations. The synthetic versatility of the photoproducts is illustrated by their conversion to other functionalized 6-substituted purines such as those bearing alkenyl, epoxy, and diol groups. Extension of the photochemical functionalized C-alkylation to purine nucleosides is described.

Carbon-carbon bond forming reactions are potentially very effective approaches to the synthesis of a wide variety of interesting functionalized nucleosides. However, this methodology has been of limited synthetic utility in the chemistry of purine nucleosides. For example, direct displacement of leaving groups such as methyl sulfone and halide by nucleophiles is limited to nucleophiles derived from carbons bearing one or two strong electron-withdrawing groups.² Purines can be converted to nucleophiles

by a metal-halogen exchange reaction, and the resulting intermediate may participate in alkylation reactions.³ However, these reactions must be conducted at very low temperatures (-130 °C) to avoid nucleophilic attack by the butyllithium in the first step and to minimize the relocation of the carbanion to the C-8 position in the lithiopurine intermediate. Although metal-catalyzed reactions have been used to synthesize C-6-alkylated purines, these re-

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