90. Electronic and Molecular Structure of Simple 3,3'-Bicyclopropenyls. Photoelectron Spectroscopy and Model Calculations

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Summary

The electronic and molecular structure of 3,3'-bicyclopropenyl (**1**) and its alkyl derivatives 3,3'-dimethyl-3,3'-bicyclopropenyl (**2**), dispiro[2.0.2.3]nona-1,5-diene (**3**), dispiro[2.0.2.4]deca-1,5-diene (**4**), dispiro[2.0.2.5]undeca-1,5-diene (**5**), and dispiro[2.0.2.6]dodeca-1,5-diene (**6**) are studied by means of photoelectron spectroscopy and model calculations. 'Through-bond' effects in model compound **1** are analyzed in detail, illustrating a general difficulty with NDO models. Low-energy photoelectron bands of **2–6** can be assigned to ejection of electrons from cyclopropenyl π- and *Walsh*-orbitals. Strong 'through-bond' coupling leads to splitting of the π-bands in the range 1.0–1.5 eV, while the strongly conformation-dependent splitting of the *Walsh*-bands allows conclusions concerning the preferred torsional angles. The preference of a *gauche*-conformation is predicted for **2** in the gas phase.

1. Introduction. – The four valence isomers of benzene, *i.e. Dewar* benzene, benzvalene, prismane and 3,3'-bicyclopropenyl, have attracted the interest of chemists for almost a century [1]. 3,3'-Bicyclopropenyl is probably the least stable of these four compounds [2–4] and has so far eluded synthesis, but several simple alkyl derivatives have been reported within the last decade (*e.g., cf.* [5]). In this paper

Scheme 1

1   2   3

4   5   6

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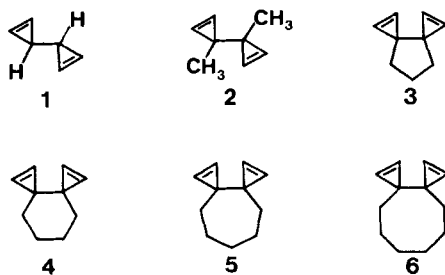
we report our investigations on the electronic and molecular structure of the 3,3′-bicyclopropenyls **1-6** *(Scheme 1)* by means of photoelectron (PE.) spectroscopy and/or empirical correlation procedures and model calculations.
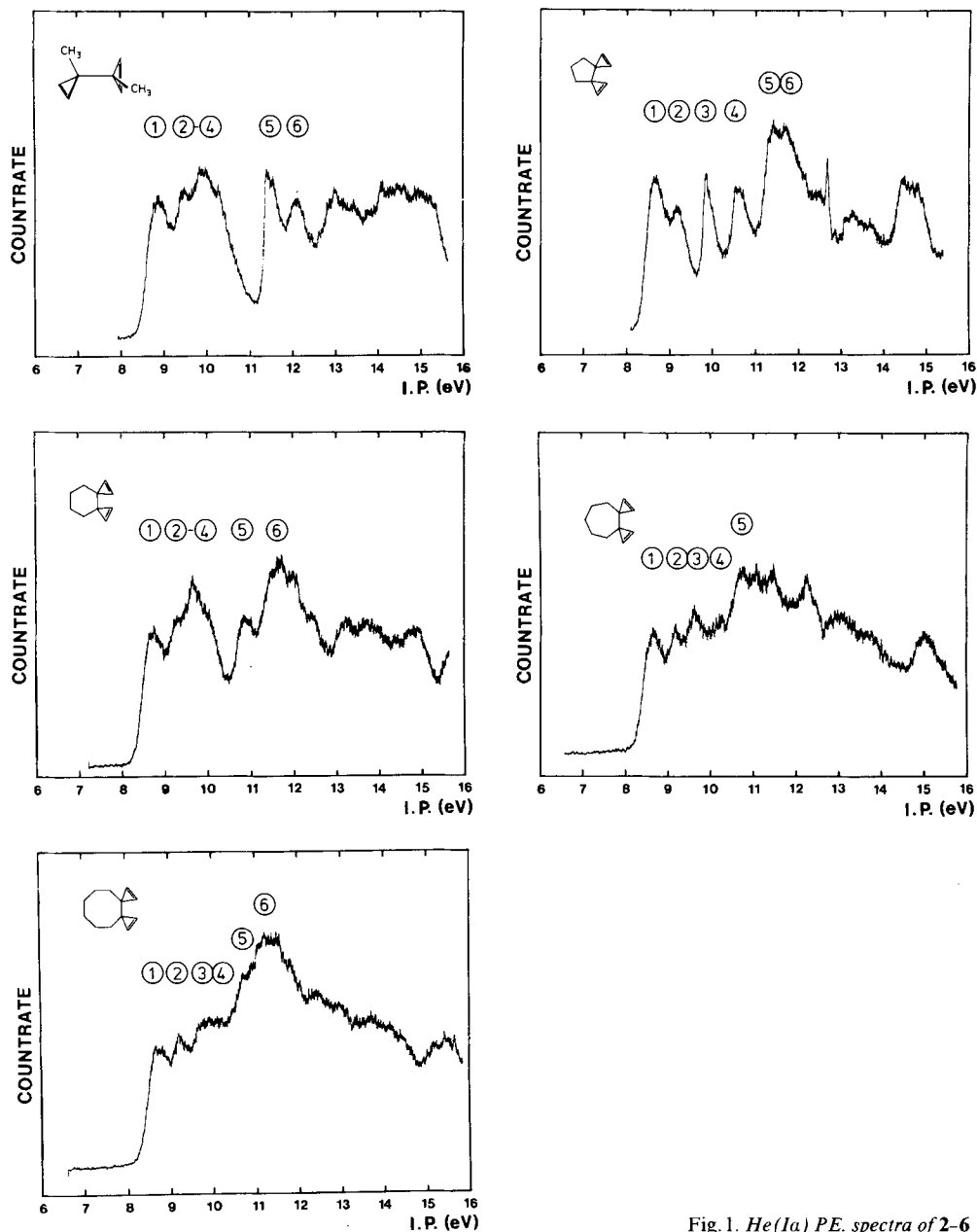

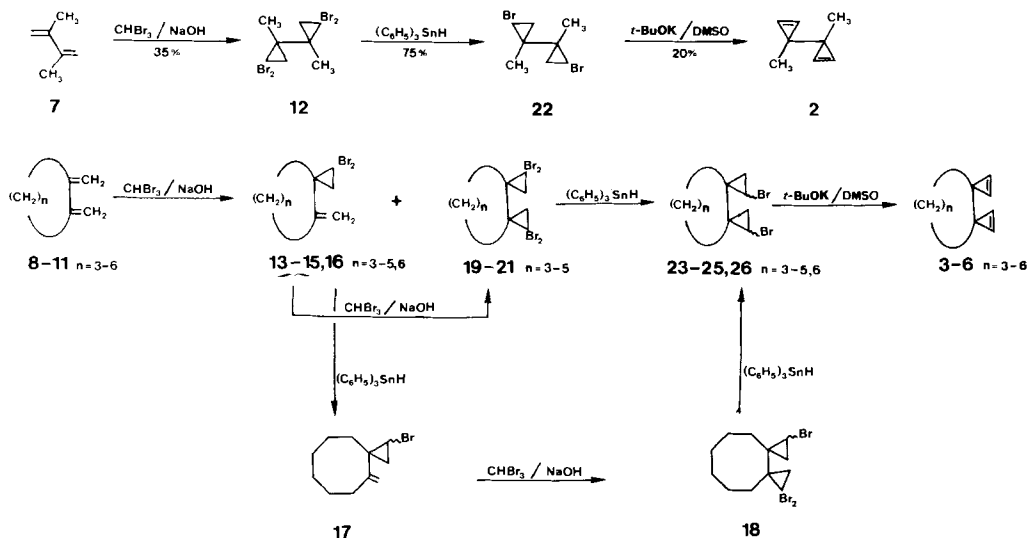Fig. 1. *He(Ia) PE. spectra of* **2–6**

Apart from the historical interest, the electronic structure of 3, 3′-bicyclopropenyl derivatives is interesting for a number of reasons. They offer ideal possibilities for the study of 'through-bond' interactions [6] [7] between formally separated double bonds. We shall consider 1 as a model system and discuss the applicability of NDO-type theories. Secondly, we are interested in the conformation-dependent interaction between cyclopropene *Walsh*-type orbitals in 1-6, in relation to the corresponding interactions in bicyclopropyl and its homologues which we have previously studied in detail [8–12]. In this connection we wish to explore the possibility for estimation of structural parameters, in particular the torsional angle of 2, on the basis of the PE. data.

The He(Iα) gas-phase PE. spectra of 2-6 are shown in *Figure 1* and measured ionization energies I_v are listed in *Table 1*. The compounds were synthesized following the general procedures (*cf.* [5] [13]). As indicated in *Scheme 2*, the starting materials were 2,3-dimethylbutadiene (7) and the 1,2-dimethylidenecycloalkanes 8-11 for 2 and 3-6, respectively. The cyclic dienes were prepared from the pertinent

Table 1. *Measured vertical ionization energies* $I_{V,J}$ *and calculated orbital energies* ε_J(eV)

Compound	J	$I_{V,J}$	Orbital assignment	$-\varepsilon_J$(MINDO/3)	$-\varepsilon_J$(SPINDO)	
2	①	8.8$_4$	11a(π^+)	8.60	9.88	[$\theta = 75°$]
	②	9.5	10a(w_A^-)	8.94	10.23	
	③	~ 10.0 ⎱	10b(w_A^+)	9.25	10.45	
	④	~ 10.3 ⎰	9b(π^-)	9.83	10.54	
	⑤	11.5	9a(w_S^+)	10.68	12.03	
	⑥	12.2	8b(w_S^-)	11.48	12.66	
3	①	8.6$_3$	12a(π^+)	8.39	9.63	[$\theta = 30°$]
	②	9.1$_3$	11a(w_A^-)	8.58	9.97	
	③	9.7$_8$	11b(π^-)	9.64	10.50	
	④	10.5$_1$	10b(w_A^+)	9.99	10.78	
	⑤	11.4 ⎱	10a(w_S^+)	10.49	12.13	
	⑥	11.7 ⎰	9b(w_S^-)	10.92	12.02	
			8b(σ)	11.18	12.40	
4	①	8.7$_3$	14a(π^+)	8.53	9.82	[$\theta = 60°$]
	②	9.2	13a(w_A^-)	8.75	10.07	
	③	~ 9.7 ⎱	12b(w_A^+)	9.11	10.57	
	④	~ 10.0 ⎰	11b(π^-)	9.85	10.36	
	⑤	10.9$_2$	12a($w_S^+ - \sigma$)	10.37	11.63	
	⑥	11.6	11a($\sigma + w_S^+$)	11.16	12.66	
			10b(w_S^-)	11.28	12.07	
			10a(σ)	11.31	12.15	
5	①	8.6$_6$	π^+			
	②	9.2$_0$	w_A^-			
	③	9.6$_4$	π^-			
	④	~ 10.2	w_A^+			
	⑤	10.7				
6	①	8.6$_6$	π^+			
	②	9.1$_4$	w_A^-			
	③	~ 9.6 ⎱	w_A^+			
	④	~ 10.8 ⎰	π^-			
	⑤	11.2				

Scheme 2

cycloalkanones *via* a *Mannich* reaction followed by a *Wittig* reaction and *Cope* elimination of the aminoxide. The dienes reacted with an excess of bromoform and sodium hydroxide under phase-transfer conditions, yielding the tetrabromobicyclo-propane derivatives **12** and **19–21**. Reduction to **22** and **23–25**, respectively, with triphenyltinhydride and elimination of HBr with potassium *t*-butoxide finally yielded the bicyclopropenyls **2–5**. In the case of diene **11**, the corresponding tetra-bromobicyclopropyl was not obtained and a slightly modified procedure was applied in order to obtain the bicyclopropenyl **6**, as indicated in the *Scheme*.

2. 'Through-bond' coupling in *1*. – The parent compound **1** provides a particu-larly simple example for 'through-bond' interaction between two formally separated double bonds. Discounting the σ-bonds of the 3-membered rings, the interaction takes place *via* a single ethanediylidene unit, comprising the central $C(3), C(3')$-bond and the two adjoining C, H-bonds. In this section we discuss the mechanism of the interaction using simple models and semiempirical computational procedures, thereby obtaining a basis to estimate the corresponding effects in **2–6**.

The three occupied semi-localized orbitals of the ethanediylidene unit can be represented in terms of the simple *Hückel*-type '*Linear Combination of Bond Orbitals*' (LCBO) model proposed recently [14]. This model uses localized bond orbitals σ_{CC} and σ_{CH} and considers only geminal interactions. With the basis ener-gies $A_{CC} = A_{CH} = -17.0$ eV and $B_{gem} = -2.0$ eV the eigenvalues $\varepsilon_1 = -19.8$, $\varepsilon_2 = -17.0$, and $\varepsilon_3 = -14.2$ eV are calculated (*cf. Fig. 2*).

Introduction of the cyclopropene π-orbital into the LCBO formalism is straight-forward. The effective basis energy A_π for cyclopropene is expected to be somewhat lower than the corresponding value for more typical ethylenic double bonds, because of the shorter bond length [15] and the 'reversed polarity' (a result of inter-action between π- and σ^*-orbitals) [16] in the case of cyclopropene. We shall assume
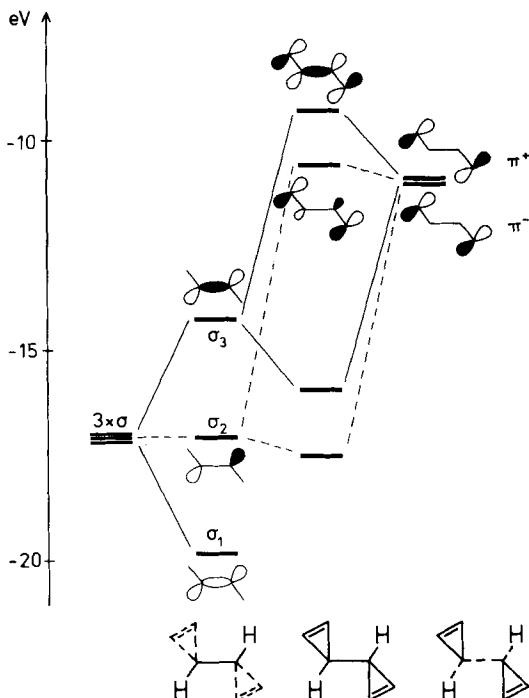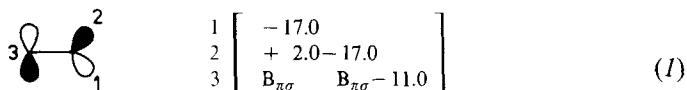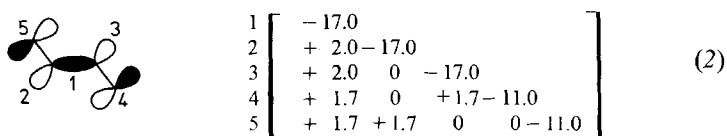
Fig. 2. *Empirical correlation diagram illustrating the simple derivation of 'through bond' effects in* **1** ('Through space' interaction between the π-orbitals is assumed to be negligible, as in the case of the *anti*-conformation indicated, *cf. (2)*)

$$\begin{array}{c} 1 \\ 2 \\ 3 \end{array} \begin{bmatrix} -17.0 & & \\ +2.0 & -17.0 & \\ B_{\pi\sigma} & B_{\pi\sigma} & -11.0 \end{bmatrix} \qquad (1)$$

that A_π for cyclopropene is intermediate between the values for ethylene (-10.5 eV) and acetylene (-11.4 eV) and adopt the value $A_\pi = -11$ eV. Regarding the resonance integrals involving the π-orbitals we shall consider only nearest-neighbour terms and assign a common value $B_{\pi\sigma}$ irrespective of the type of σ-bond involved. We estimate this value from a consideration of the LCBO problem for cyclopropene with inclusion of the two methylene σ_{CH^-} and the π-orbital (*1*). Reproduction of the first ionization energy of cyclopropene, 9.9 eV [17–19], requires a $B_{\pi\sigma}$-value of 1.7 eV (positive because of the choice of phases in (*1*)).

The LCBO secular problem for **1** including the three ethanediylidene σ-orbitals and the two π-orbitals is indicated in (*2*). 'Through-space' interaction between the

$$\begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array} \begin{bmatrix} -17.0 & & & & \\ +2.0 & -17.0 & & & \\ +2.0 & 0 & -17.0 & & \\ +1.7 & 0 & +1.7 & -11.0 & \\ +1.7 & +1.7 & 0 & 0 & -11.0 \end{bmatrix} \qquad (2)$$

π-orbitals is assumed to be negligible, as in the case of the *anti*-conformation indicated (torsional angle $\theta = 180°$). Diagonalization of the matrix yields for the two highest eigenvalues (3).

$$\varepsilon\,(\pi^+) = -\ 9.3\ \text{eV}$$
$$\varepsilon\,(\pi^-) = -\ 10.6\ \text{eV} \tag{3}$$

Here π^+ and π^- indicate wave functions with dominant contributions from the π-orbitals, as indicated in *Figure 2* (74% and 92% π-character, respectively).

For reasons obvious from the pertinent interaction diagram in *Figure 2*, 'through-bond' coupling destabilizes the totally symmetric π^+-combination much more effectively than the π^--combination, leading to the appreciable split of 1.3 eV. The LCBO prediction is consistent with the results of non-empirical STO-3 G and 4-31 G calculations (1.40 and 1.14 eV) [4], indicating that the simple picture is essentially correct.

However, the π-level splittings predicted by a number of semiempirical procedures are widely scattered, as shown in *Table 2*. Most NDO-type methods predict

Table 2. *Splitting of the π-levels* $a_g(\pi^+)$ *and* $b_u(\pi^-)$ *for* anti-*bicyclopropenyl* (1) *calculated by various computational methods* (for calculational details, see *Sect. 7*)

Method	$\varepsilon\,(\pi^+) - \varepsilon\,(\pi^-)$ [eV]	Method	$\varepsilon\,(\pi^+) - \varepsilon\,(\pi^-)$ [eV]
CNDO/2	2.77	CNDO/S	0.77
STO-3G [4]	1.40	EHT	0.75
EWMO	1.29	MNDO	0.65
4-31G [4]	1.14	SPINDO	0.63
MINDO/3	1.02	INDO	0.48

splittings which are considerably smaller than those obtained by the more exact methods. To study the origin of this discrepancy it is instructive to reformulate the results of the semiempirical procedure in terms of the LCBO formalism. In (4) and (5) we give the *Fock* matrix for 1 in a truncated basis of localized bond orbitals corresponding to the diagram in (2), using MINDO/3 [20] and a recently developed INDO procedure [21], respectively. Diagonalization of these matrices yields $\varepsilon\,(\pi^+)$- and $\varepsilon\,(\pi^-)$-values which are within $\sim 1\%$ of the energies obtained by the full calculations, indicating that all essential interactions are considered in (4) and (5).

$$
\text{MINDO/3} \quad
\begin{matrix}
1 \\ 2 \\ 3 \\ 4 \\ 5
\end{matrix}
\begin{bmatrix}
-19.06 & & & & \\
+4.05 & -16.28 & & & \\
+4.05 & +0.48 & -16.28 & & \\
+1.51 & -0.57 & +1.79 & -10.71 & \\
+1.51 & +1.79 & -0.57 & 0.00 & -10.71
\end{bmatrix}
\tag{4}
$$

$$
\text{INDO} \quad
\begin{matrix}
1 \\ 2 \\ 3 \\ 4 \\ 5
\end{matrix}
\begin{bmatrix}
-21.49 & & & & \\
+4.70 & -19.44 & & & \\
+4.70 & +0.94 & -19.44 & & \\
+1.50 & -1.12 & +2.07 & -12.00 & \\
+1.50 & +2.07 & -1.12 & 0.00 & -12.00
\end{bmatrix}
\tag{5}
$$

An important difference between the two matrices concerns the magnitude of the elements corresponding to next-neighbour interactions. In particular, the elements F_{42} and F_{53} corresponding to 'through-space' interaction between next-neighbour π- and σ_{CH}-orbitals are predicted by the INDO version to be twice as large (-1.12 eV) as predicted by MINDO/3 (-0.57 eV). Setting the F_{42}- and F_{53}-elements equal to zero in (4) and (5) leads to the prediction of practically identical π-splittings in both cases, $\Delta\pi = 1.9$ eV. However, with inclusion of these elements π^+ is stabilized and π^- is destabilized, leading to predicted splittings 0.5 and 1.1 eV, respectively. In other words, the predicted 'through-bond' effect is extremely sensitive to the magnitude of next-neighbour interactions (which are neglected in the *Hückel*-type LCBO model (2)). However, it is important to realize that next-neighbour terms in NDO theories are essentially spurious, because of an inadequate treatment of overlap effects [22–24]. As an artifact, NDO theories predict too negative next-neighbour $F_{\pi\sigma}$-elements (π and σ in-phase). These next-neighbour interactions tend to oppose the dominant 'through-bond' mechanism, a result of the alternating phases of the important σ relay-orbitals. This leads to the prediction of unrealistically small splittings of the π-levels as compared with the results of more rigorous methods[2]. In the case of MINDO/3, this artifact seems to be largely compensated by the tendency of this method to place σ-levels at comparatively low binding-energies, thereby reinforcing the 'through-bond' interaction; in the case of CNDO/2 [30], however, the artifact is strongly overcompensated. Among the NDO methods considered in *Table 2*, MINDO/3 comes closest to the *ab initio* predictions, due to a fortunate cancelation of errors[3]. In the following we consider primarily results obtained with this method.

For simplicity we have so far considered only the *anti*-conformation of **1**. Other interactions than those represented in *(2)*, *(4)* and *(5)* may become important for conformations with torsional angle θ lower than 180°. 'Through-space' interaction between the π-orbitals is maximal for θ-values close to zero, but *ab initio* [4] as well as MINDO/3 calculations indicate that this effect is much less significant than the 'through-bond' effect, amounting to a few tenths of an eV. For dihedral angles close to 90°, considerable interaction between a π-orbital on one ring and a w_A' *Walsh* orbital *(8)* on the other is predicted by MINDO/3, leading to strongly avoided crossing of the $b(\pi^-)$- and $b(w_A^+)$-levels as shown in *Figure 3*. The interaction is mainly of 'through-bond' character, involving the $C(3)$, H- and $C(3')$, H-bond orbitals. Unfortunately, *Greenberg & Liebman* [4] who performed *ab initio* calculations on **1** did not consider this effect; in fact, they let the $b(\pi^-)$- and $b(w_A^+)$-levels become degenerate in their STO-3 G correlation diagram for a θ-value between 90° and 120°. Probably the avoidance of the crossing escaped their attention.

3. 'Through-bond' coupling in 2–6. – The essential features of the interaction diagram for **1** in *Figure 2* also apply to the alkyl derivatives **2–6**, and similar splittings of the π-levels are expected for these compounds. This expectation is con-

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[2] The results of this analysis are applicable also to the related systems with 'through bond' interactions *via* three bonds (see, *e.g.* [25–29]).

[3] Similar cancelation of errors is demonstrated by comparison of MINDO/3 and STO-3 G results for tricyclo[4.2.0.0^{2,5}]octadienes [26].
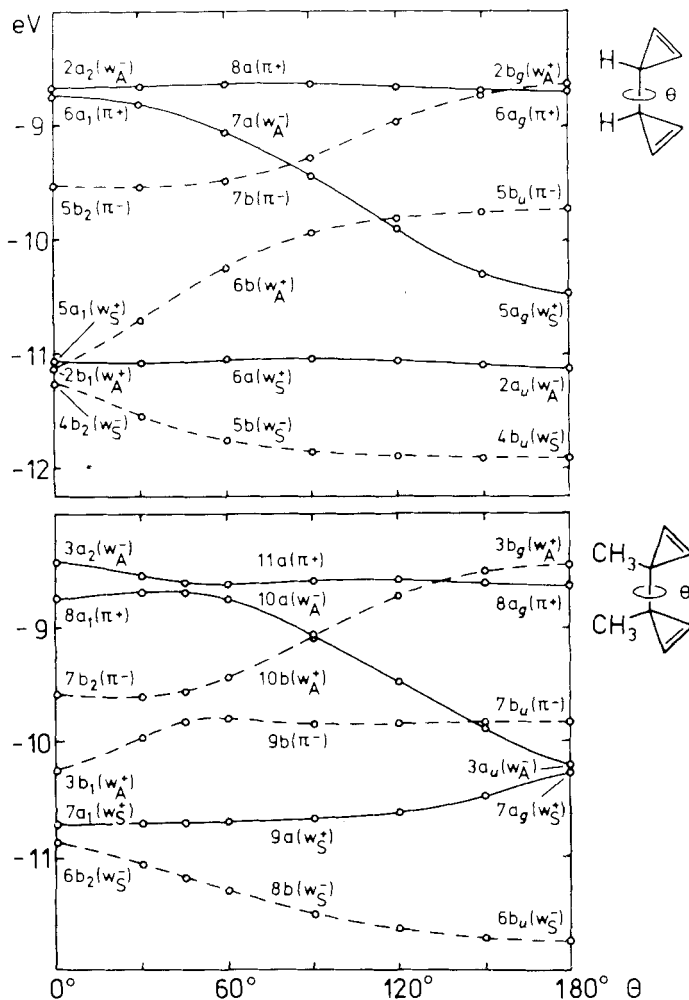
Fig. 3. *MINDO/3 orbital energies for* **1** *and* **2** *as a function of torsional angle* θ *($\theta = 0°$ relates to the C_{2v} syn-, $\theta = 180°$ to the C_{2h} anti-conformation)*

firmed by comparison of the MINDO/3 results for **1** and **2** in *Figure 3*. However, the inductive and hyperconjugative effects of the alkyl groups tend to destabilize the *Walsh* orbitals more strongly than the π-orbitals; this leads to corresponding shifts of the 'avoided crossings', which according to MINDO/3 calculations occur for a θ-value close to 45° in the case of **2**. As a result, the interaction between the $b(\pi^-)$- and $b(w_A^+)$-levels is much less drastic in this case since the levels tend to cross in a conformational region where the $\pi - w_A'$ 'through-bond' interaction is insignificant. The interaction is further reduced by delocalization of the orbitals into the alkyl groups.

In the case of **3** and **4** the σ-systems involved in the $\pi - \pi'$ 'through-bond' coupling are related to those of cyclopentane and cyclohexane, respectively. Inspection of the highest occupied totally symmetric orbitals of these cycloalkanes indicates that in the case of **3**, high-lying ideally shaped orbitals (*e. g.*, the cyclopentane 12a (σ_{CC})-orbital [31]) are available for strong interaction with the π^+-combination, but not in the case of **4**. The corresponding cyclohexane orbitals are delocalized over the whole ring, a consequence of the high symmetry of the preferred chair conformation, and tend to be significantly C,H-bonding [31]. As a consequence, we observe a marked difference in the shape of the π^+-type orbitals of **3** and **4** as indicated schematically (6) and (7). It is apparent that the 'through-bond' destabilization is relatively inefficient in the case of **4**; moreover, the π-lobes are rotated in such a way that 'through-space' stabilization is increased. The balance of contributions is such that a slightly lower binding energy is calculated (and observed) for **3** than for **4** *(Table 1)*. This trend is the opposite of what one might have expected on consideration of a larger destabilizing inductive effect in the case of **4** and a smaller torsional angle in the case of **3**, favouring 'through-space' stabilization.


(6)
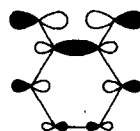
(7)

4. Walsh orbitals in 2–6.

4. *Walsh* orbitals in 2–6. – In the preceding sections, *Walsh* orbitals were mentioned briefly in connection with their interaction with π-type orbitals in **1** and **2**. Here the *Walsh* orbital system of bicyclopropenyl compounds is considered in slightly more detail.

The second and the third PE. band of cyclopropene at 10.9 and 12.7 eV correspond to ejection of electrons from w_A and w_S *Walsh*-type orbitals (8) [17–19]. The shape of these orbitals is similar to that of the *Walsh* orbitals of cyclopropane [31–33], but in the case cyclopropene the w_S-orbital is stabilized by almost 2 eV relative to the w_A-orbital. To construct a model for the *Walsh* orbitals of 3,3'-bicyclopropenyls, one might as a first approximation assume that orbitals derived from cyclopropene w_A and w_S can be considered independently, *i. e.* that interaction between a (w_A^-)- and a (w_S^+)- and between b (w_A^+)- and b (w_S^-)-type orbitals (9) is negligible. This is a poor approximation in the corresponding case of bicyclopropyls where the interaction is essential for torsional angles close to 90° [8] [9] [12], but it might be acceptable for bicyclopropenyl derivatives because of the large separation

(8)

$b_1(w_A)$ $a_1(w_S)$

$$a(w_A^-) \qquad\qquad b(w_A^+)$$

$$a(w_S^+) \qquad\qquad b(w_S^-)$$

(9)
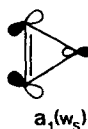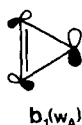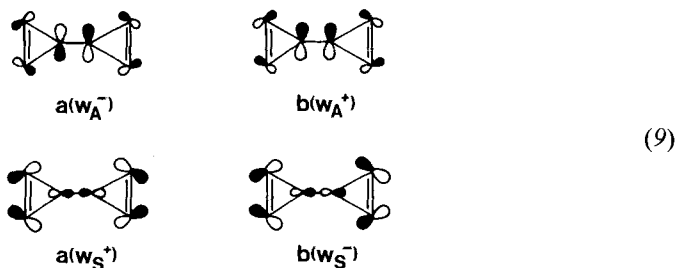
in energy between w_A and w_S basis orbitals. Within this very simple model we predict for the splitting in energy of the w_A^-- and w_A^+-combinations:

$$
\begin{aligned}
E_a(w_A^-) - E_b(w_A^+) &= 2\langle w_A | H | w_A' \rangle \\
&= 2\left(\frac{2}{\sqrt{6}}\right)^2 \langle t_3 | H | t_3' \rangle \\
&= \frac{4}{3}\beta_{ww'} \cos\theta
\end{aligned}
$$

(10)

Here we have assumed that the shape of the cyclopropene w_A-orbital is similar to that of the corresponding orbital of cyclopropane, which implies that the coefficient of the 'tangential' p-atomic orbital at the 3-position (t_3) is close to $2/\sqrt{6}$ [8] [34]. $\beta_{ww'}$ in (10) indicates the resonance integral involving 'tangential' p-atomic orbitals in the 3,3'-positions for torsional angle $\theta = 0°$. The effective $\beta_{ww'}$-value for bicyclo-propyl has been estimated to be *ca.* 1.7 eV [34], and we thus obtain for 1:

$$E_a(w_A^-) - E_b(w_A^+) \approx 2.3 \cos\theta$$

(11)

This empirical prediction is in accordance with the MINDO/3 results for θ-values close to 0° and 180° ($\Delta w_A = 2.4$ eV), but is of limited interest in the intermediate region because of extensive orbital mixing, particularly with $b(\pi^-)$ and $a(w_S^+)$ (*cf. Fig. 3*). However, introduction of alkyl groups in the 3,3'-positions serves to reduce this orbital mixing markedly, thereby improving the usefulness of the cosine relation for predictive purposes. The alkyl substitution diminishes the w_A-amplitude at the 3,3'-positions, causing a reduction in the numerical constant in (11). According to MINDO/3, the splitting in the case of 2 is

$$E_a(w_A^-) - E_b(w_A^+) \approx 1.8 \cos\theta$$

(12)

and in the case of 3 and 4

$$E_a(w_A^-) - E_b(w_A^+) \approx 1.6 \cos\theta$$

(13)

5. Assignment of the PE. bands. – On the basis of the results in the preceding sections we discuss the assignment of the lowest few PE. bands of 2-6 within *Koopmans'* approximation ($\varepsilon_{MO} = -I_v$) [35]. We shall assume that bands in the low
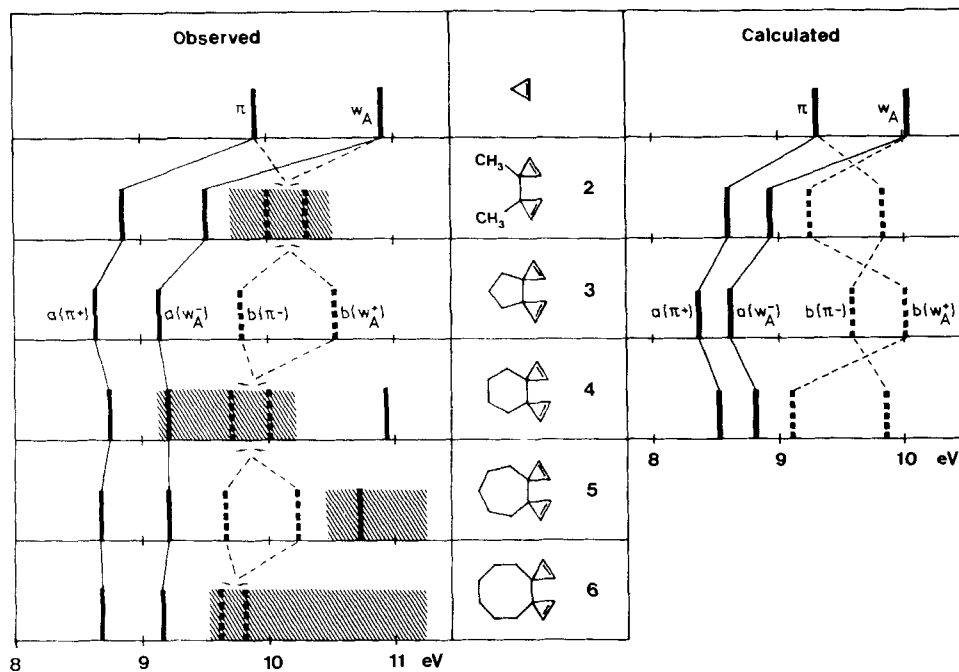
Fig. 4. *Correlation of observed ionization energies for* 2-6 (left) *and of orbital energies calculated by MINDO/3 for* 2-4 (right)

energy region 8.5–10.5 eV are due to ejection of electrons from orbitals of predominantly π- and w_A-character and that the first PE. band in all cases corresponds to the $a(\pi^+)$-level. The resulting assignment is indicated in *Table 1* and in the correlation diagram in *Figure 4* which also displays for comparison the results of some MINDO/3 calculations.

The PE. spectrum of **2** exhibits a group of four overlapping bands in the 8.5–10.5 eV region, followed by peaks at 11.5 and 12.5 eV. Under the assumption that the first band at 8.8 eV can be assigned to the $a(\pi^+)$-level, assignment of the second peak at 9.5 eV to a w_A-level is straightforward. The strongly overlapping bands close to 10.0 and 10.3 eV must be assigned to the second w_A-level and the $b(\pi^-)$-level; we leave open the ordering of these closely spaced, probably strongly 'mixed levels'. This assignment of the low-energy bands is consistent with the results of *Greenberg & Liebman* [4] and *Schweig et al.* [36] and is supported by correlation with data for cyclopropene **3** and **4** (cf. *Fig. 4*). Bands ⑤ and ⑥ can be assigned to a (w_s^+)- and b (w_s^-)-levels, respectively. Band ⑤ shows a remarkably steep onset and a partly resolved vibrational fine structure, similar to the w_S-band of cyclopropene [17] [18].

According to the *ab initio* study by *Greenberg & Liebman* [4] **1** has two low-energy structures, the *gauche-* ($\theta \approx 50°$) and *anti*-conformers, with very similar energies; at the 4–31 G level, the difference is of the order of 0.1 kcal/mol. The

authors assume that the *anti*-conformer is most stable, a tendency which they consider to be strengthened by the methyl substituents in the case of **2**. However, this assumption is not supported by the PE. data for **2**. According to the assignment discussed above, the absolute splitting of the w_A-bands of **2** falls in the range 0.5–0.8 eV. On the basis of (*12*), this splitting is consistent only with the assumption of a *gauche*-conformation. On the whole, consideration of observed and calculated data for the first six PE. bands indicates that contribution from the *anti*-conformer to the observed PE. spectrum is insignificant. (Similar conclusions were reached concerning simple bicyclopropyls [12]). MINDO/3 calculations yield a satisfactory correlation with the PE. data for **2**, **3** and **4** under the assumption of $\theta = 75°$ in the case of **2** (*cf. Fig. 4*).

The PE. spectrum of **3** exhibits four relatively well separated peaks in the low-energy region. Assignment of bands ① and ③ separated by 1.15 eV to the $a(\pi^+)$- and $b(\pi^-)$-levels, respectively, is straightforward. The steep onset and sharpness of band ③ is characteristic for bands corresponding to ejection of electrons from nearly localized π-type orbitals, *i.e.* the π^--orbital. The π-bands are more intense than bands ② and ④, which we assign to $a(w_A^-)$- and $b(w_A^+)$-levels, respectively; this observation is consistent with the fact that in case of cyclopropene, the π-band is much more intense than the w-bands [18] [19]. The energy splitting of the w_A-bands is equal to 1.4 eV, indicating according to (*13*) a dihedral angle θ close to 30°. This value is well within the conformational range confined by the torsional mobility of the 5-membered ring in **3** [37] [38]. The results of MINDO/3 and SPINDO [39] calculations on **3** for $\theta = 30°$ support the assignment indicated above and suggest assignment of the closely spaced bands ⑤ and ⑥ to two w_S-combinations, overlapping the onset of the compact σ-region.

In the case of **4** we again have strongly overlapping bands in the low-energy region, similar to the case of **2**. Indeed, the close similarity of the low-energy regions of the two spectra indicates similar torsional angles, thereby supporting our prediction concerning the preferred conformation of **2** (a similar correspondence is observed between the PE. spectra of the saturated analogues of **2** and **4** [12]). According to the tentative assignment indicated in *Table 1*, the splitting of the w_A-bands of **4** is similar to the corresponding value for **2**, 0.5–0.8 eV, indicating on the basis of (*13*) a torsional angle of approximately 60°. This value is consistent with the preference of a chair conformation of the cyclohexane ring in **4** [37]. According to MINDO/3 calculations, band ⑤ at 10.9 eV ist best assigned to the w_S^+-level, destabilized as a result of strong interaction with cyclohexane ribbon orbitals.

The PE. spectrum of **5** is similar to that of **3** in the sense that four maxima are discernible in the low-energy region. We tend to assign these bands as in the case of **3** (*Table 1*). In the PE. spectrum of **6** bands ③ and ④ apparently coalesce to one broad band with no well-defined maximum; in this respect, the spectrum is somewhat similar to the spectra of **2** and **4** and we suggest a similar assignment of the bands. Probably the effective bicyclopropenyl torsional angle is similar to that of **3** in the case of **5**, and similar to those of **2** and **4** in the case of **6**. In the latter case, the splitting of the w_A-levels is at least 0.5 eV which seems incompatible with a 'symmetrical crown' conformation of the 8-membered ring which would imply a θ-value very close to 90°; the PE. data are more consistent with the preference of

the energetically favoured 'extended crown' conformation [40] [41]. On the other hand, prediction of structural features for the mobile species **5** and **6** on the basis of the PE. spectra is probably overhazardous.

6. Concluding remarks. – The most significant results of this investigation can be summarized as follows: *a*) the π-type orbitals of 3, 3'-bicyclopropenyl derivatives interact strongly 'through-bond', leading to an energy splitting in the order of 1–1.5 eV; *b*) using 3,3'-bicyclopropenyl as a model system, fundamental difficulties with the NDO approximation are demonstrated. The very satisfactory performance of the MINDO/3 method is largely due to a fortunate cancelation of errors; *c*) the conformation-dependent splitting of the w_A-type levels allows conclusions concerning the preferred conformation in the gas phase. The preference of a *gauche*-conformation is predicted for **2**; the PE. data for **3** and **4** are consistent with structures inferred from molecular models.

7. Calculations. – Semiempirical CNDO/2 [31], CNDO/S [42], INDO [21], SPINDO [39], MINDO/3 [20], MNDO [43], EWMO [44] and EHT [45] calculations were carried out using computer programs available (with the exception of the recently developed INDO version [21]) through QCPE, Indiana University. The molecular geometries were taken as those predicted by MINDO/3 calculations under the assumption of C_2-symmetry, except for the torsional angle θ of the 3, 3'-bicyclopropenyl moiety which was treated as an input parameter (the MNDO result for **1** in *Table 2* refers to the MNDO structure). Localized bond orbitals according to the *Edmiston-Ruedenberg* procedure [46] were calculated using computer programs generously supplied by Dr. *P. Bischof* and Dr. *M. C. Böhm*. In the case of MINDO/3, localized π-orbitals were not obtained directly by the intrinsic localization procedure, but were constructed by suitable linear combination of near-degenerate C=C 'banana'-bond orbitals.

8. Experimental Part. – *General remarks.* The PE. spectra have been recorded with a *PS 18* spectrometer (*Perkin Elmer Ltd.,* Beaconsfield, England) at r. t. The spectra were calibrated with Ar; a resolution of about 20 meV on the Ar-line was obtained. The ^{1}H-NMR. spectra were determined with a *Varian EM 360* (60 MHz) and *Bruker WH 300* (300 MHz) spectrometer.

If not otherwise noted we followed the preparative procedures given by *Landeer* and *van Straten* [13].

Preparation of 1,1-dibromo-4-methylidenespiro[2. 7]decane (**16**). To a mixture of 17 g (0.125 mol) **11**, 253 g (1 mol) CHBr₃, 43 g (0.5 mol) CH₂Cl₂, 1 g hexadecyltrimethylammonium bromide (HTAB) (*ca.* 3 mmol) and 2 ml ethanol, 29 g of a 50% aq. solution of NaOH (1 mol) were added at 0°. The mixture was stirred vigorously 2 h at 0°, 45 h at 50° and then poured into 1 l sat. NaCl-solution. The organic phase was collected, washed with 2N HCl and sat. NaCl-solution. The organic extract was dried over Na₂SO₄ and the solvent removed. After distilling the excess CHBr₃ (32°/3 Torr) the residue was passed through alumina (20 g Al₂O₃/neutral) using cyclohexane as solvent. After evaporation of the solvent the residue was destilled; b.p. 110°/0.01 Torr. – ^{1}H-NMR. (60 MHz, CCl₄): 1.62 (*m*, 12 H); 2.25 (*m*, 2 H); 4.98 (*m*, 1 H); 5.18 (*m*, 1 H).

Preparation of 1-bromo-4-methylidenespiro[2.7]decane (**17**). Treating 14.5 g **16** (0.047 mol) in abs. ether with 16.5 g (0.047 mol) $(C_6H_5)_3SnH$ according to [13] 8.35 g (78%) **17** were obtained. The product was purified by distillation (63°/0.15 Torr) and identified by chemical analysis.

Preparation of 1,1,6-tribromodispiro[2.0.2.6]dodecane (**18**). To a mixture of 8.35 g **17** (0.036 mol), 185 g bromoform (0.73 mol), 0.35 g HTAB (*ca.* 1 mmol) and 2 ml ethanol, 29 g of a 50% aq. NaOH-solution (0.365 mol) were added at 0°. The whole reaction has been carried out under N_2-atmosphere. The mixture was stirred vigorously 2 h at 0° and then 65 h at 20° and then poured into 400 ml sat. NaCl-solution. The same workup procedure was applied as described for **16**. After evaporation of the solvent the non-reacted **17** was removed by distillation. The remaining oily residue was dissolved in *ca.* 20 ml pentane and cooled with dry ice, 3.2 g colorless crystals of **18** were obtained (22%). – IR. (Nujol): 1250*m*, 1235*s*, 1050*s*, 1032*s*, 693v.*s*. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 2.92 (*m*, 1 H); 2.51 (*m*, 1 H); 1.96 (*m*, 3 H); 1.77 (*m*, 4 H); 1.58 (*m*, 4 H); 1.16-1.44 (*m*, 3 H); 1.00 (*m*, 1 H).

Preparation of 1,5-dibromodispiro[2.0.2.6]dodecane (**26**). The preparation of **26** from **18** was achieved according to [13] in 56% yield.

Preparation of dispiro[2.0.2.6]dodeca-1,5-diene (**6**). Compound **26** (1.45 g, 4.5 mmol) was reacted with *t*-BuOK (1.5 g, 13.5 mmol) in DMSO according to [13]. The crude products were chromatographed twice on *Silicagel 60 (Merck)* using pentane as solvent. The first fraction contained the desired product. After evaporation most of the solvent (30 cm *Vigreux* column), the last residues of the solvent were removed at $-196°$ *i.v.* (10^{-6} Torr), obtaining 115 mg (0.72 mmol) **6**. Its purity was controlled by GC. – ^{1}H-NMR. (300 MHz, $CDCl_3$): 1.44 (*m*, 4 H); 1.55 (br. *s*, 4 H); 1.70 (*m*, 4 H); 7.10 (*s*, 4 H) [13].

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