Interaction of Walsh Orbitals in Rotanes. Photoelectron Spectroscopic Investigation

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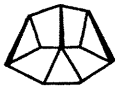
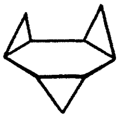
Summary He I photoelectron spectroscopic investigations of bicyclopropylidene (**4**), [3]rotane (**5**), and [4]rotane (**6**) reveal considerably larger resonance integrals for (**4**) and (**5**) compared with values reported for bicyclopropyl and tricyclopropyl derivatives.

THE electronic interaction between cyclopropane rings has so far been studied only with model compounds like (**1**) and (**2**), in which the cyclopropane rings are connected with each other *via* two centres.[1] We are currently studying the polycyclopropylidenes ([*n*]rotanes†) (**3**) ($n = 1$—6),[2] in which two or more cyclopropane rings are linked *via* one centre only, and related molecules by photoelectron (P.E.) spectroscopy. We report here results for bicyclopropylidene (**4**),[3a] [3]rotane (**5**),[3b] and [4]rotane (**6**).[3c]


(**1**)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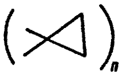
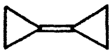


(**3**)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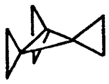
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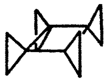
(**6**)

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† [3]Rotane is trispiro[2.0.2.0.2.0]nonane and [4]rotane is tetraspiro[2.0.2.0.2.0.2.0.]dodecane.

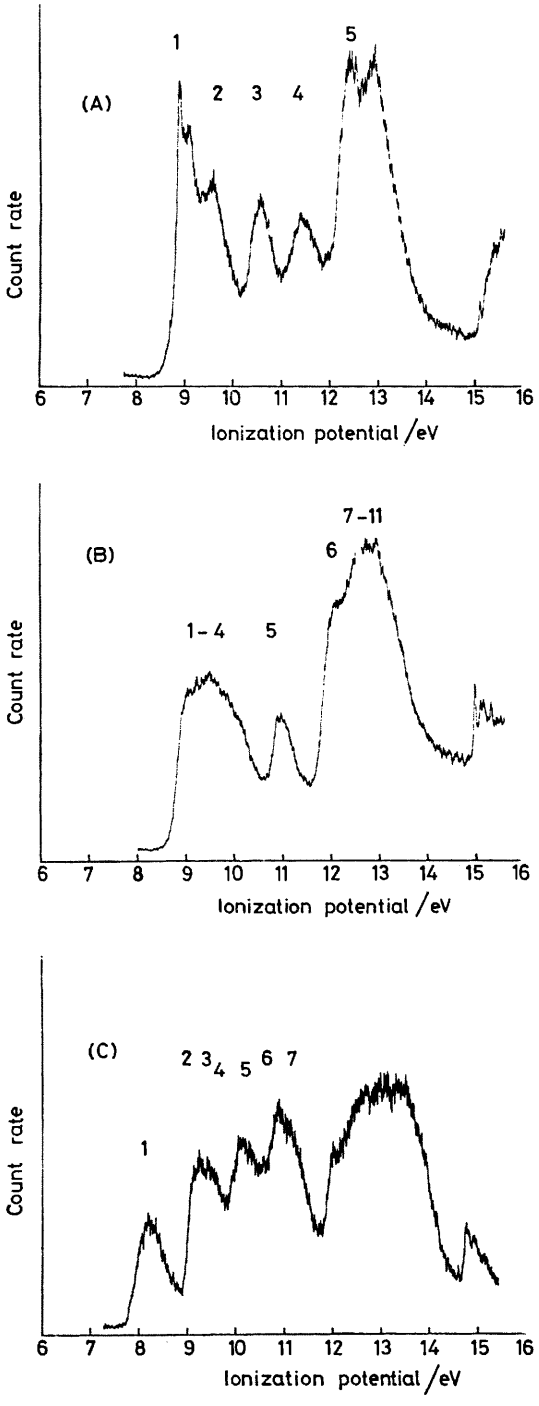

FIGURE 1. Photoelectron spectra of (4), (A); (5), (B); and (6), (C).

The P.E. spectra‡ of (4)—(6) are shown in Figure 1. The measured vertical ionization potentials are compared with molecular orbital energies, ϵ_J, obtained from MINDO/3[4] and STO 3G[5] calculations (Table) making use of Koopmans' theorem,[6] ($-\epsilon_J = I_{V,J}$), in the assignment of the P.E. bands.

TABLE. Observed vertical ionization potentials, $I_{V,J}$, and calculated orbital energies for (4), (5), and (6). All values in eV (1 eV = 96.49 kJ/mol).

Band	$I_{V,J}$	Assignment[a]	MINDO/3	STO 3G
Compound (4) (D_{2h})				
1	8·93	$2b_{1u}(\pi)$	−9·29	−7·95
2	9·63	$2b_{1g}$(W)	−8·80	−8·84
3	10·58	$4a_g$(W)	−9·93	−10·64
4	11·48	$3b_{2u}$(W)	−11·23	−11·94
5	12·48	$2b_{3u}$(W)	−12·02	−12·44
Compound (5) (D_{3h})				
1	9·12	$3e''$	−9·21	−9·15
2	9·32			
3	9·52	$5e'$	−9·22	−9·15
4	10·02			
5	11·02	$4a_1'$	−10·38	−11·04
6	12·22	$3a_1'$	−11·84	−12·39
7	12·68	$2e''$	−11·93	−12·53
8				
9	13·03	$4e'$	−11·83	−12·84
10				
11	13·32	$1a_2''$	−12·79	−13·19
Compound (6) (D_{4h})				
1	8·22	$2b_{2u}$	−8·30	−7·71
2	9·21	$5e_u$	−9·18	−9·42
3	9·42			
4	10·12	$3e_g$	−10·09	−10·18
5	10·32			
6	10·91	$2b_{1g}$	−10·74	−11·28
7	11·21	$4a_{1g}$	−10·75	−11·30

[a] The numbering of the orbitals refers to the valence orbitals only.

Adopting the assignment in the Table the split between the bonding linear combination of the Walsh e_A orbitals (Figure 2) amounts to 2·84 eV ($2b_{1g} - 2b_{3u}$) for (4), 4·10 eV ($3e'' - 1a_2''$) for (5), and 2·00 eV ($2b_{2u} - 3e_g$) for (6). These measured energy differences correspond to values for the resonance integral between linked $2p$ atomic orbitals of the adjacent cyclopropane rings of −2·14, −2·05, and −1·50 eV for (4), (5), and (6), respectively. The variation of the resonance integral is consistent with the expected change of hybridization of the joined centres, being close to sp in (4) and (5) and close to sp^2 in (6). It is of particular interest

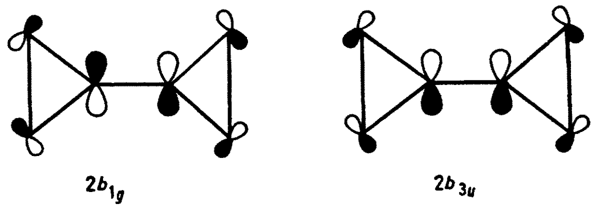

FIGURE 2. Bonding linear combination of the Walsh e_A orbitals for (4).

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‡ The He I P.E. spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer and calibrated with Ar.

that the interaction parameter found for (**4**) and (**5**) is considerably larger than that ($\beta = -1{\cdot}73$ eV) reported for (**1**), (**2**), and bicyclopropyl.[7]

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