Interactions in 2,8,9-Trifunctional [3.3.3]Propellanes

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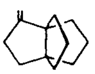
The He(I_α) photoelectron (PE) spectra and electronic spectra of the 2,8,9-trifunctional [3.3.3]propellanes 3, 6, 8, and 9 together with the corresponding 2-mono- and 2,8-difunctional species have been recorded. The PE investigations reveal a small split between the π bands in the PE spectra of 2 and 3 and the n-lone pair bands in those of 7 and 9. This is rationalized by assuming a small through-space interaction among the functional groups. A considerable π-n splitting is found in the case of 5, 6, and 8. This splitting is due to a fairly strong interaction of n and π orbitals with the σ frame of the corresponding propellane. The first band of the electronic spectra of 6, 8, and 9 is assigned to π* ← n transitions on the basis of CNDO/s-CI calculations. These investigations suggest a small split among the lowest unoccupied π* orbitals.

Wechselwirkungen bei [3.3.3]Propellanen mit funktionellen Gruppen in 2-,8- und 9-Stellung

Die He(I_α)-Photoelektronen (PE)-Spektren und die Elektronen-Spektren der in 2-,8- und 9-Stellung funktionalisierten [3.3.3]Propellane 3, 6, 8 und 9 wurden zusammen mit den in 2-Stellung bzw. den in 2,8-Stellung funktionalisierten Derivaten aufgenommen. Die PE-Untersuchungen zeigen eine kleine Aufspaltung zwischen den π-Banden in den PE-Spektren von 2 und 3 und den n-Banden von Verbindungen 7 und 9. Dies wird auf eine kleine räumliche Wechselwirkung der funktionellen Gruppen zurückgeführt. Bei 5, 6 und 8 findet man eine beträchtliche π-n-Aufspaltung. Diese Aufspaltung ist durch eine starke Wechselwirkung zwischen n- und π-Orbitalen mit dem σ-Gerüst des entsprechenden Propellans bedingt. Die ersten Banden der Elektronenspektren von 6, 8 und 9 wurden aufgrund von CNDO/s-CI Rechnungen π*←n-Übergängen zugeordnet. Diese Untersuchungen sprechen für eine kleine Aufspaltung der tiefsten unbesetzten Orbitale.

Propellanes are interesting model compounds for studying structure-reactivity relationships[1]. Of special interest with respect to investigations of the interaction of proximate π and/or n-orbitals are 2,8,9-trifunctional [3.3.3]propellanes like **3**, **6**, **8**, and **9**, which provide a sterically fixed framework for three proximate C=C or C=O double bonds. To study the interaction among the valence orbitals of these compounds we used He(I_α) photoelectron (PE) and UV/VIS spectroscopy. Together with **3**, **6**, **8**, and **9**, whose syntheses have been reported[2], we also studied the 2-mono- and 2,8-difunctional propellanes **1**, **2**, **4**, **5**, and **7**, which have been prepared in recent years[3,4].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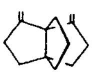
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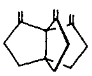
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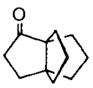
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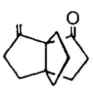
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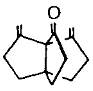
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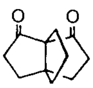
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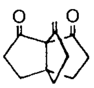
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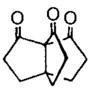
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PE Spectra

The PE spectra of the 2,8,9-trifunctional [3.3.3]propellanes **3**, **6**, **8**, and **9** are shown in Figure 1. While the spectrum of **3** shows only one broad feature in the low energy region, two peaks are found for **9** at 9.3 and 9.8 eV. The ratio of the areas below the envelopes amounts to 2:1. In the PE spectra of the less symmetrical species **6** and **8** (C_{2v}) three peaks at low energy can be distinguished. The recorded vertical ionization energies, $I_{v,j}$, of **1**–**9** are collected in Table 1.

To interpret these data we proceed empirically by comparing the spectra of the trifunctional species with the mono- and difunctional compounds. This has been carried out in Figure 2.

A comparison of **1**–**3** shows that the interaction among the π bonds is minute. A somewhat larger split ($\beta \approx 0.15-0.2$ eV) is found by comparing the mono-, bis-, and tris-carbonyl compounds **4**, **7**, and **9**. The small split in both cases is rather unexpected in view of the apparent favourable arrangement of the double bonds in **2** and **3** for homoconjugation or for lone-pair interaction in **7** and **9**.

As in **3** a similar small interaction has been observed in the related trivinylmethane[5]. The small interaction encountered in **2**, **3**, **7**, and **9** can best be rationalized by considering the distances between the double bonds. Unlike barrelene, where all three double bonds are arranged parallel to each other, the double bonds in **2**, **3**, **7**, and **9** diverge. The distances between the inner atoms (positions 2, 8, and 9) amount to 2.6 Å, while the outer centers are about 3.3 Å apart. This divergence mitigates the spatial interactions in all the samples with two and three substituents considerably. For **6** and **8** the split encountered (see Figure 2) is relatively large. In view of the above discussion this outcome cannot

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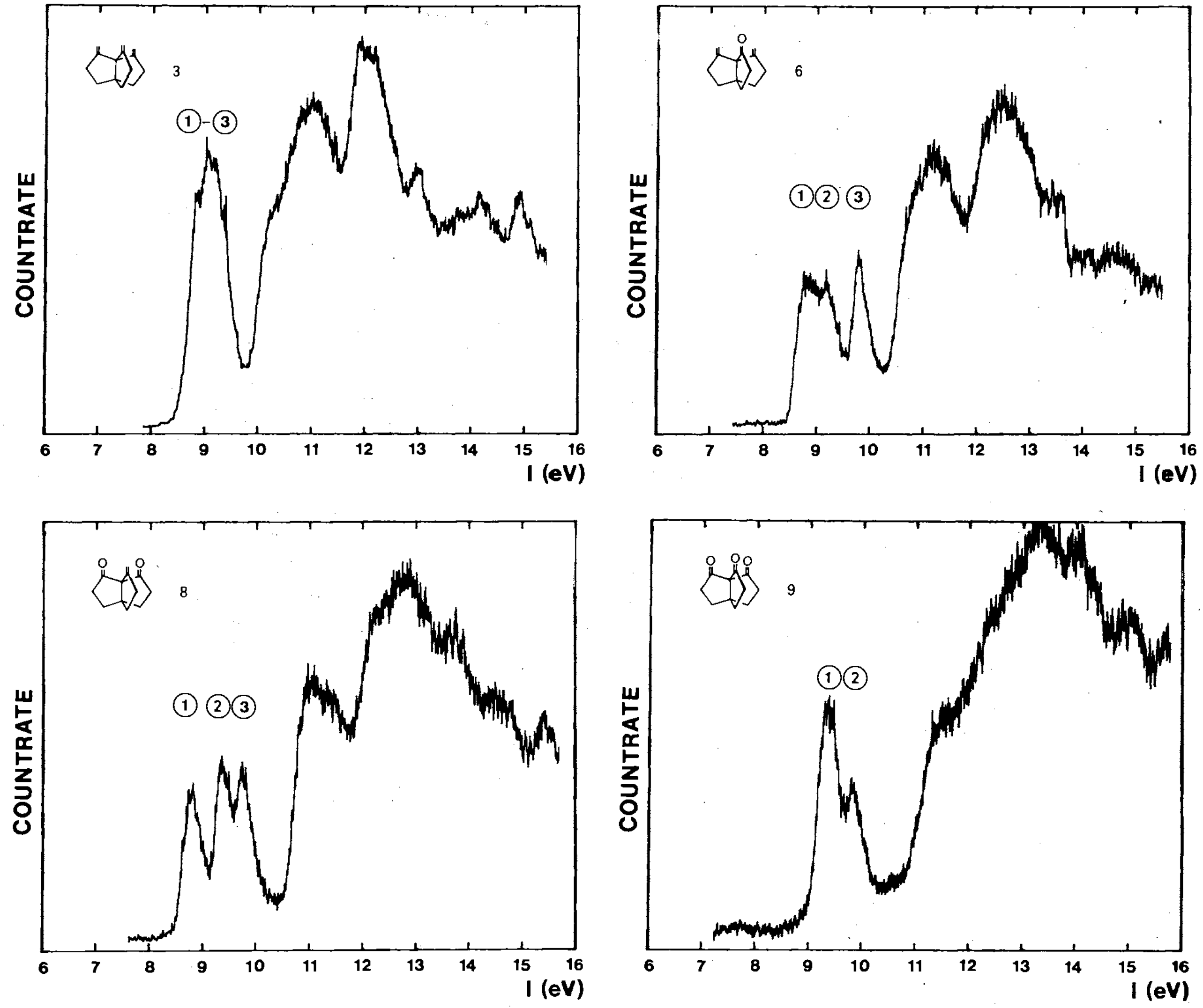

Figure 1. PE spectra of **3**, **6**, **8**, and **9**

be rationalized by invoking a spatial interaction among n and π orbitals. Probably, a small through-space interaction is overruled by a large through-bond effect.

To check our qualitative argumentation we have carried out semiempirical calculations using the MINDO/3 method[6]. We chose this method because it proved to be quite reliable with respect to the calculated orbital energies in the case of other carbonyl compounds in which CO groups and/or C = C double bonds are held together in close proximity[7]. The results of the MINDO/3 calculations are collected in Table 1. A comparison between the ionization energies and the negative values of the calculated orbital energies shows a close agreement. This indicates that Koopmans' approximation[8] is valid, at least for the outer valence region of **1**–**9**. The predicted splitting pattern by the MINDO/3 method very closely resembles that shown in Figure 2.

The MO calculations also support our presumption of an interaction between the π and n orbitals with the σ frame in **5**, **6**, and **8**. To exemplify this we show in Figure 3 an interaction scheme which leads to the MO sequence predicted for **5**. The n orbital at the oxygen atom of the CO group and the π orbital of the olefinic double bond interact weakly with each other through space which leads to a small splitting of the n + π linear combination below the n − π combination. Due to the strong interaction of the n + π linear combination with the σ frame a reversal of the sequence results. A similar pattern is observed for **6** and **8**, i.e. the bonding linear combination is predicted to be higher in energy than the antibonding one (see Table 1).

Electronic Spectra of 6, 8, and 9

The UV/VIS spectra of **6**, **8**, and **9** show one broad band around 300 nm with low intensity and considerable fine structure ($\Delta\tilde{\nu} \approx 1100\ \mathrm{cm}^{-1}$) (see Table 2). This first band is followed by bands with higher energy. In the case of **6** we recorded one further band at 205 nm, for the two other samples two further bands were found. While the energy of the first band remains essentially constant for all three compounds, the energy of the other bands varies strongly with the number of CO groups (see Table 2). The relatively small

Table 1. Comparison between the first vertical ionization energies, $I_{v,j}$, with the calculated (MINDO/3) orbital energies (ε_j) of **1**–**9**. All values in eV

compound	band	$I_{v,j}$	assignment	$-\varepsilon_j$ (MINDO/3)
1	1	9.0	13a″(π)	9.37
2	1	8.9	20a′(π)	9.39
	2	9.1	15a″(π)	9.39
3	1	8.9	12e(π)	9.30
	2	9.0		
	3	9.2	$3a_2$(π)	9.48
4	1	8.9	20a′(n)	9.33
5	1	8.9	n + π	9.09
	2	9.5	π − n	9.89
6	1	8.9	22a′($n+\pi_1+\pi_2$)	8.96
	2	9.20	15a″($\pi_1-\pi_2$)	9.50
	3	9.80	21a′($n-\pi_1-\pi_2$)	10.12
7	1	9.1	15a′(n)	9.34
	2	9.4	20a″(n)	9.83
8	1	8.77	15a″($n_1+n_2+\pi$)	9.04
	2	9.35	22a′(n_1-n_2)	9.76
	3	9.75	14a″($\pi-n_1-n_2$)	10.30
9	1	9.3	12e(n)	9.61
	2			
	3	9.8	$10a_1$(n)	10.26

ε values for all bands suggest assigning all the transitions between 200 and 350 nm to π* ← n transitions. This assignment is confirmed by a CNDO/s-CI[9] calculation taking into account singly excited configurations only. The results (Table 2) of these calculations indicate that all the observed UV bands in **6**, **8**, and **9** are due to transitions from the three highest occupied MO's (see Table 1) to the three lowest unoccupied MO's. The latter are π* in character. The energy separation between the three lowest unoccupied π* MO's of **3**, **6**, **8**, and **9** is predicted to be at most 0.8 eV, i.e. the interaction among the unoccupied MO's is predicted to be as small as that between the occupied ones. In the case of **6** and **8** the LUMO's with π* character are: 16a″, 17a″, and 23a′. For **9** the CNDO/s calculation predicts 13e and $4a_2$. As shown in Table 2 several configurations usually contribute to one transition. The agreement between calculation and experiment is satisfactory.

Concluding Remarks

Our investigations of the 2,8,9-trifunctional [3.3.3]propellanes **3**, **6**, **8**, and **9** reveal only a minor through-space interaction. It is so small that in the case of **5**–**8** the sequence of the highest occupied MO's is dominated by an interaction between the σ frame and the n orbitals. The

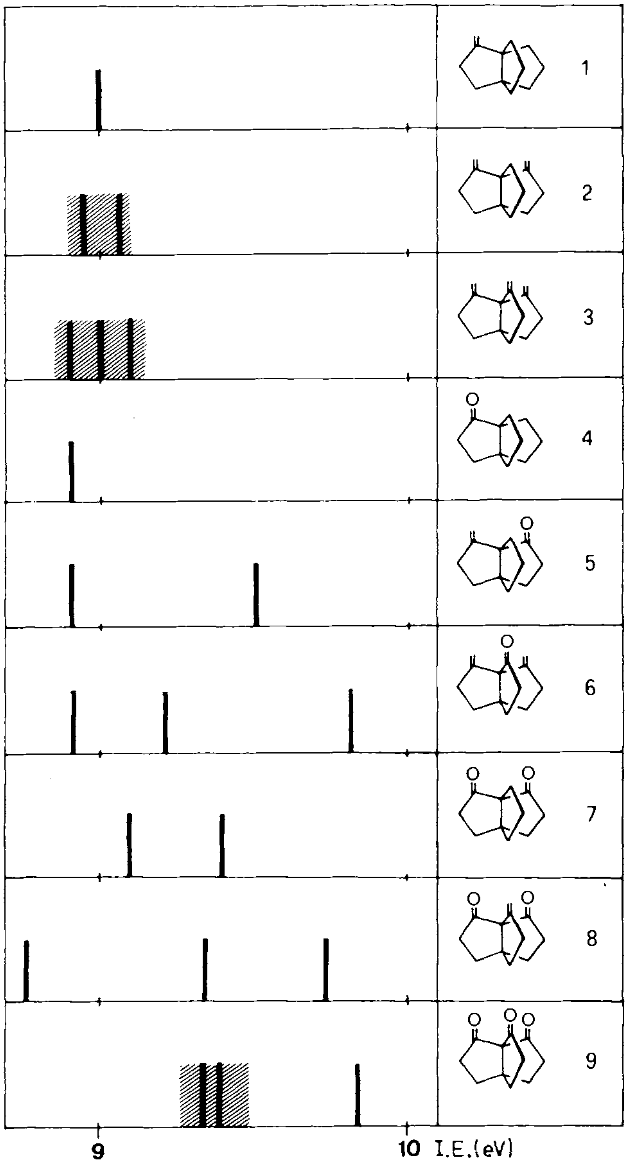

Figure 2. First ionization energies of **1**–**9**

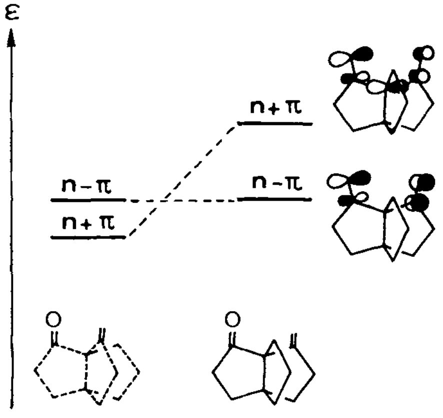

Figure 3. Qualitative diagram showing the interaction between the n orbital of the CO group, the π MO of the ethylene part, and the σ frame in **5**

Table 2. Observed and calculated (CNDO/s-CI) transitions for **6**, **8**, and **9**. All spectra were recorded in *n*-hexane

Com-pound	Band	← Experiment		→	← Calculation	→
		λ [nm]	$\tilde{\nu}$ [cm^{-1}]	ε	$\tilde{\nu}$ [cm^{-1}]	Leading Configuration (%)
6	A	324	30900	50	30700	$16a''(\pi^*) \leftarrow 22a'(n,\pi)(25)$;
		312	32100	100		$16a''(\pi^*) \leftarrow 21a'(n,\pi)(24)$;
		301	33300	120		$17a''(\pi^*) \leftarrow 22a'(n,\pi)(24)$
		291	34400	110		$17a''(\pi^*) \leftarrow 21a'(n,\pi)(24)$
		286	35000	90		
	B	205	48800	9600	49100	$23a'(\pi^*) \leftarrow 22a'(n,\pi)(49)$;
					49300	$16a''(\pi^*) \leftarrow 15a'(\pi)(45)$;
						$23a'(\pi^*) \leftarrow 15a''(\pi)(74)$
8	A	330	30300	140	32220	$23a'(\pi^*) \leftarrow 15a''(n,\pi)(28)$;
		315	31750	110		$23a'(\pi^*) \leftarrow 14a''(n,\pi)(37)$;
						$17a''(\pi^*) \leftarrow 22a'(n)(25)$
		303	33000	130	33020	$23a'(\pi^*) \leftarrow 22a''(n)(45)$;
		292	34250	125		$17a''(\pi^*) \leftarrow 14a''(n,\pi)(25)$;
						$17a''(\pi^*) \leftarrow 15a''(\pi,n)(15)$
		285	35100	110		
	B	229	43700	2190	53040	$23a'(\pi^*) \leftarrow 15a''(n,\pi)(66)$;
					54380	$23a'(\pi^*) \leftarrow 14a''(n,\pi)(14)$
						$16a''(\pi^*) \leftarrow 15a''(n,\pi)(86)$
9	A	324	30900	140	30390	$13e(\pi^*) \leftarrow 12e(n)(80)$
		310	32300	250		
		298	33600	390		
		288	34700	390		
		280	35700	360		
		272	36800	270		
	B	251	39800	790	31130	$13e(\pi^*) \leftarrow 12e(n)(40)$;
		242	41300	1010		$13e(\pi^*) \leftarrow 10a_1(n)(23)$;
						$4a_2(\pi^*) \leftarrow 12e(n)(25)$
	C	221 (sh)	45250	6920	50190	$13e(\pi^*) \leftarrow 12e(n)(98)$
		216	46300	6080		

relatively high energy of the first absorption band in the electronic spectra ($\tilde{\nu} \approx 30000$ cm^{-1}) indicates that the interaction between the π* MO's is also very moderate. In line with this supposition is our observation that none of the 2,8,9-trifunctional [3.3.3]propellanes can be reduced electrochemically.

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Experimental

The syntheses of **1**–**9** have been reported[2–4]. – The He(I) photoelectron spectra of the analytically pure compounds were recorded on a Perkin Elmer PS 18 instrument. The recording temperatures were: **1**–**5** room temperature, **6**: 50°C, **7**: 80°C, **8**: 90°C, and **9**: 150°C. The electronic spectra were recorded in *n*-hexane with a Cary 17D.

Because the geometry of only one compound (**9**) is known from X-ray investigations[10], we have optimized the heat of formation of **1**–**9** with respect to their geometrical parameters using the MINDO/3 procedure. A comparison between the calculated and experimental values for the bond lengths of **9** agrees within ±0.02 Å for all bonds except the central one. For the latter MINDO/3 predicts 1.61 Å while the X-ray investigation reveals 1.523 Å.

CAS Registry Numbers

1: 111917-14-7 / **2**: 112112-57-9 / **3**: 58461-87-3 / **4**: 88288-20-4 / **5**: 112138-33-7 / **6**: 58435-05-5 / **7**: 112138-34-8 / **8**: 112112-58-0 / **9**: 64940-50-7

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