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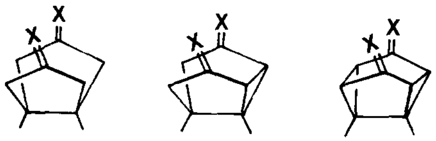
THROUGH BOND AND THROUGH SPACE INTERACTION IN 1,5-DIMETHYL-3,7-DIMETHYLENE-TETRACYCLO[3.3.0.0^{2,8}.0^{4,6}]OCTANE

Rolf Gleiter and Gerhard Jähne

Institut für Organische Chemie der Universität Heidelberg
Im Neuenheimer Feld 270, D-6900 Heidelberg (W-Germany)

Summary: The synthesis of the hydrocarbons 4-6 has been achieved via Wittig reaction from the diketones 1-3. By means of He(I)photoelectron spectroscopy it is shown that the interaction between the π-fragments in 4-6 increases strongly.

Recently we demonstrated by means of He(I)photoelectron (PE) spectroscopy that the interaction between the 2p-lone-pairs on the oxygen atoms increases considerably in the series 1, 2, and 3 mediated by the σ-skeleton[1].



X=O 1 2 3

X=CH_2 4 5 6

To explore the prevailing interaction between the π-moieties, we have prepared 4-6 by applying the Wittig reaction to 1-3 as indicated in (1). Under the reaction conditions indicated we obtained 4-6 in yields between 20 % and 50 %[3].

$$1 - 3 \xrightarrow[\substack{(C_6H_5)_3P\text{-}CH_3{}^+Br^- \\ 80^\circ\ C/2d}]{\text{DMSO, NaH}} 4 - 6 \qquad (1)$$

In Tab. 1 the measured ionization energies (I.E.) are compared with the orbital energies (ε_j) obtained by model calculations[4] using the HAM/3[6] procedure.

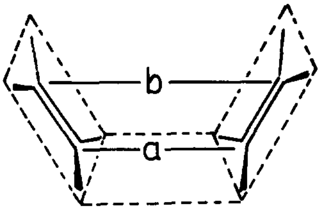
Table 1: Comparison between the measured vertical ionization energies (I.E.) of 4-6 and the calculated orbital energies (ε_j) according to HAM/3. (w = Walsh-typ orbital, ΔI and $\Delta\varepsilon$ indicate the difference between π_+ and π_-). All values in eV.

compound	band	I.E.	assignment	$\lvert\Delta I\rvert$	$-\varepsilon_j$	$\lvert\Delta\varepsilon\rvert$
	1	8.9	b_1 (π_-)	0.2	8.53	0.2
4	2	9.1	a_1 (π_+)		8.74	
(C_{2v})	3	10.3	σ		10.85	
	1	8.36	a' (π_+)	0.4	8.43	0.37
5	2	8.77	a'' (π_-)		8.80	
(C_s)	3	9.60	a'' (w)		9.74	
	1	7.89	a_1 (π_+)		8.19	
6	2	8.93	a_2 (w)	1.26	8.94	1.07
(C_{2v})	3	9.15	b_1 (π_-)		9.26	
	4	9.93	b_2 (w)		10.06	

As seen from Tab. 1 we observe a strong increase in the splitting between the energies of the orbitals $\pi_+ = 1/\sqrt{2}(\pi_1 + \pi_2)$ and $\pi_- = 1/\sqrt{2}(\pi_1 - \pi_2)$ where π_1 and π_2 denote the localized π-orbitals in 4-6.

To interprete the data we divide the interaction prevailing in the systems 4-6 into a spatial part (through space) and an interaction which is mediated via the σ-skeleton (through bond)[7].

To estimate the spatial interaction we have carried out model calculations on two ethylene molecules in the spatial arrangement identical to that one of 4, 5 and 6 using the HAM/3 procedure which has proved to be a valuable guide (see Tab. 1). The following distances (a, b) between the carbons have



been assumed[4].

4: a = 4.04 Å, b = 6.29 Å;
5: a = 3.11 Å, b = 4.74 Å;
6: a = 2.87 Å, b = 4.84 Å.

The calculated split between π_- and π_+ is found to be:
0.04 eV (4),
0.12 eV (5), and
0.17 eV (6).

These results clearly show that the through space interaction in 4-6 is small and that the increase of splitting encountered in the series 4-6 is due to an increase in the π/σ interaction.

Analyzing the MO's of 4-6 shows a strong increase in the π/σ mixing for π_+ whereas the interaction between π- and the σ frame remains essentially constant (see Fig. 1).

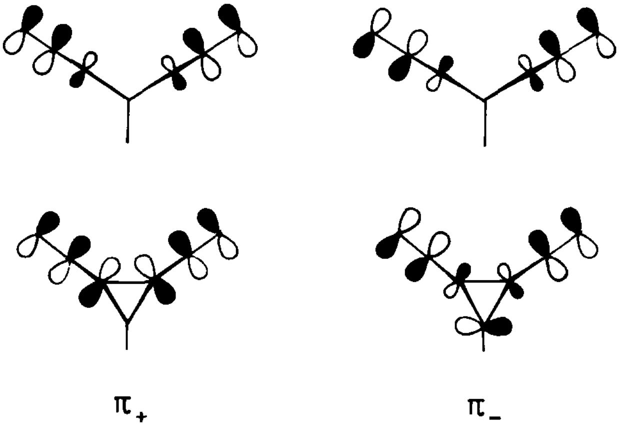


Fig. 1: Schematic drawing of a_1 (π_+) and b_1 (π_-) of 4 (top) and 6 (bottom) according to a MINDO/3 calculation.

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References and Notes:

1) G. Jähne, R. Gleiter, Angew.Chem. 95, 500 (1983), Angew. Chem., Int. Ed. Engl. 22, 488 (1983); Angew. Chem. Suppl. 1983, 661^{2}.

2) Related systems to **1**-**3** have been reported by:
K. Kratzat, F.W. Nader, T. Schwarz, Angew. Chem. 93, 611 (1981), Angew. Chem., Int. Ed. Engl. 20, 589 (1981); L.S. Miller, K. Grohmann, J.J. Dannenberg, L. Todaro, J. Am. Chem. Soc. 103, 6249 (1981); R. Gompper, M.-L. Schwarzensteiner, Angew. Chem. 94, 447 (1982), Angew. Chem., Int. Ed. Engl. 21, 438 (1982); H.-D. Martin, C. Heller, J. Werp, Chem. Ber. 107, 1393 (1974).

3) Compounds **4**-**6** have been characterized by elemental analysis as well as by their ^{1}H-, ^{13}C-NMR, IR, UV and Mass spectra. Selected data are:
4:b.p. 70-75°C (36 Torr, kugelrohr); IR (film) 1650 cm^{-1}; ^{1}H-NMR (60 MHz, CDCl$_3$) δ: 4.9-4.77 (4H, m), 2.33-2.20 (8H, m); ^{13}C-NMR (75.46 MHz, CDCl$_3$) δ: 150.69 (s), 106.54 (t), 50.52 (s), 45.76 (t), 61.64 (q).
5: b.p. 72-75°C (40 Torr, kugelrohr); IR (film) 1650 cm^{-1}; ^{1}H-NMR (90 MHz, CDCl$_3$) δ: 4.86 (4H, m), 2.53 (2H, d (≈15 Hz), m), 2.03 (2H, d (≈15 Hz), m), 1.98 (2H, s), 1.30 (3H, s), 1.20 (3H, s); ^{13}C-NMR (75.46 MHz, CDCl$_3$) δ: 150.90 (s), 104.92 (t), 48.87 (s), 44.29 (s), 43.24 (d), 22.84 (q), 15.20 (q).
6: b.p. 65-70°C (30 Torr, kugelrohr); IR (film) 1655 cm^{-1}; ^{1}H-NMR (90 MHz, CDCl$_3$) δ: 4.83 (4H, s), 1.83 (4H, s), 1.33 (6H, s); ^{13}C-NMR (75.46 MHz, CDCl$_3$) δ: 148.27 (s), 102.34 (t), 39.94 (d), 38.98 (s), 14.21 (q); UV (cyclohexane) λ_{max}: 228 nm ($\log \varepsilon = 4.246$).

4) Since the geometry of **4**-**6** is not known we have minimized their heat of formation by varying all geometrical parameters assuming C_{2v} (**4**, **6**) and C_s (**5**) symmetry using the MINDO/3 method[5].

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