Tetrahedron Letters,Vol.28,No.49,pp 6151-6154,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

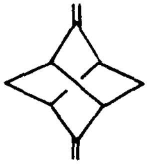
2,4-DIMETHYLENETRICYCLO[3.3.0.0^{3,7}]OCTANE AND 2,9-DIMETHYLENETRICYCLO[4.3.0.0^{3,8}]NONANE. SYNTHESIS AND THROUGH-SPACE INTERACTIONS.

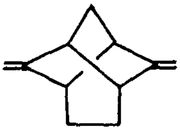
Rolf Gleiter* and Bernd Kissler

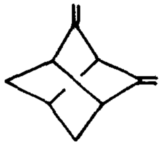
Institut für Organische Chemie der Universität Heidelberg,
Im Neuenheimer Feld 270, D-6900 Heidelberg

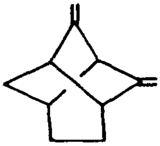
A four step synthesis of the title compounds 3 and 4 is reported. The HeI$_\alpha$-PE-spectra of both compounds reveal a considerable through-space interaction of the π-systems.

In connection with our studies on electronic interactions of π-systems across twisted six- or seven-membered rings as in 1 or 2[1], our attention was also focused on the isomers 2,4-dimethylenetricyclo[3.3.0.0^{3,7}]octane (3) and 2,9-dimethylenetricyclo[4.3.0.0^{3,8}]nonane (4).


1


2

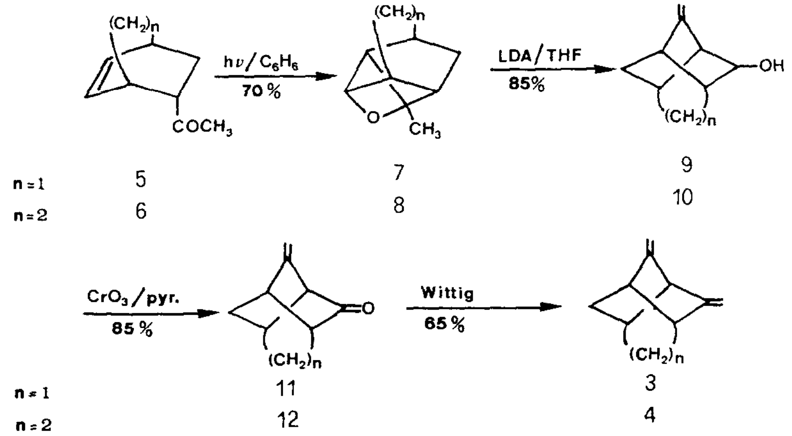

3


4

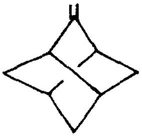
The dienes 3 and 4 were prepared from the known[2] ketones 11 and 12 by the Wittig reaction with methyltriphenylphosphonium bromide/sodium amide (see **Scheme 1**). The synthesis of ketones 11 and 12 was carried out as described[2], except that we were able to optimize the cleavage of the oxetanes 7 and 8[3] by treatment with LDA/THF at room temperature[4]. The ketones 11 and 12 could also be converted to the monoenes 13 and 14 by the Wolff-Kishner reaction[5].

To probe the interactions between the double bonds of 3 and 4, we used HeI$_\alpha$-photoelectron (PE) spectroscopy. The first ionization energies of 3, 4, 13

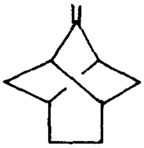
Scheme 1



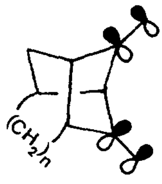
and 14 are collected in **Table 1**. We note that the π bands of 13 and 14 are placed at the center of gravity of the first two bands of 3 and 4.



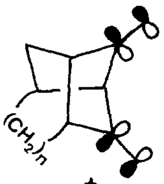
13



14



π^-



π^+

To interpret the PE-data, we compared the calculated orbital energies (ε_j) with the recorded vertical ionization energies ($I_{v,j}$) assuming the validity of Koopmans' theorem[6]. Both methods of calculation (MINDO/3[7] and HAM/3[8]) predict considerable splitting between π^- (HOMO) and π^+ and a significant admixture of σ-orbitals. A detailed analysis of the canonical wave functions revealed that the initial through space interactions of the π-systems are superimposed on π-σ-interactions, resulting in an overall decrease of the "pure" π-π-splitting by about 50%. In both compounds 3 and 4 we encounter a stronger destabilization of π^+ compared to π^-. The σ-admixture to the π-wave functions amounts to 21%(π^+)and 14%(π^-) for 3 and 28%(π^+)and 10%(π^-) for 4, respectively.

The strong π-π-interactions could be demonstrated by the spontaneous reaction of dienes 3 and 4 with N-phenyltriazolinedione (PTAD), which gave the crystalline homo Diels-Alder adducts 15 and 16.

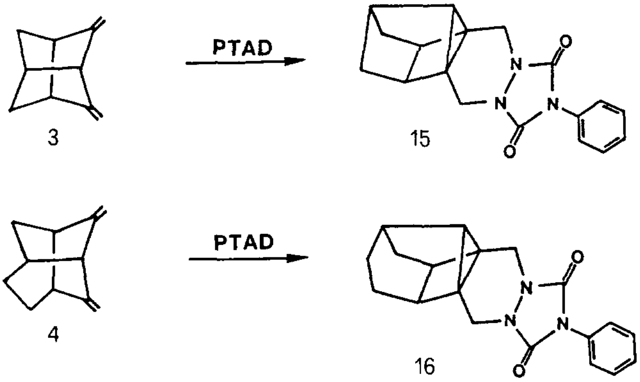


Table 1 Comparison between the first ionization energies, $I_{v,j}$, of 3, 4, 13 and 14 with calculated orbital energies. Values in eV.

compound	$I_{v,j}$	assignment	$-\varepsilon_j$(MINDO/3)	$-\varepsilon_j$(HAM/3)
3	8.60	a"(π^-)	9.03	8.96
	9.40	a'(π^+)	9.56	9.35
	10.5	σ	10.28	10.46
4	8.70	a"(π^-)	9.07	8.96
	9.26	a'(π^+)	9.47	9.23
	10.1	σ	10.00	10.17
13	8.96	b(π)	9.34	9.12
	10.2	b(σ)	9.92	10.26
14	9.00	b(π)	9.40	9.01
	9.75	b(σ)	9.73	9.95

We are grateful to the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft for financial support. B.K. thanks the state Baden-Württemberg for a scholarship during his dissertation.

References and Notes:

Dedicated to Professor Emanuel Vogel on the occasion of his 60th birthday

1) B. Kissler, R. Gleiter, **Tetrahedron Letters,** 26, 185 (1985); R. Gleiter, B. Kissler, C. Ganter, Angew.Chem.in press.

2) M. Nakazaki, K. Naemura, Y. Kondo, **J.Org.Chem.** 41, 1229 (1976). The authors cleaved the oxetanes 7 and 8 by action of either LiNEt$_2$ in benzene (27% yield) or perchloric acid in methanol (28% yield), the latter reagent causes the production of a side-product.

3) R.R. Sauers, J.A. Whittle, **J.Org.Chem.** 34, 3579 (1969); R.R. Sauers, K.W. Kelly, **J.Org.Chem.** 35, 498 (1970); R.R. Sauers, W. Schinski, **Tetrahedron Letters,** 79 (1969).

4) Most relevant spectroscopic data of 3, 4, 14; 15 and 16:

3: ^{1}**H-NMR** (300 MHz, CDCl$_3$) δ: 4.30 (4H,s), 2.77 (1H,m), 2.65 (2H,m), 2.48 (1H,m), 1.53(4H,s). ^{13}**C-NMR** (75 MHz, CDCl$_3$) δ: 160.6, 92.4, 48.7, 43.5, 43.4, 37.1.
4: ^{1}**H-NMR** (300 MHz, CDCl$_3$) δ: 4.64 (1H,s), 4.48 (1H,s), 4.46 (1H,s), 4.40 (1H,s), 2.90 (1H,d, J=5.7 Hz), 2.62 (1H,m), 2.17 (1H,m), 1.87-1.36 (6H,m). ^{13}**C-NMR** (75 MHz, CDCl$_3$) δ: 159.8, 156.4, 98.3, 94.8, 53.3, 43.5, 39.8, 34.4, 32.0, 26.8, 25.8.
14: ^{1}**H-NMR** (200 MHz, CDCl$_3$) δ: 4.51 (1H,s), 4.31 (1H,s), 2.69-2.59 (1H,d,br, J=5.0 Hz), 2.44-2.35 (1H,m), 2.32-2.23 (1H,m), 2.12-2.00 (1H,m),1.82-1.62 (1H,m), 1.60-1.23 (7H,m). ^{13}**C-NMR** (75 MHz, CDCl$_3$) δ: 161.7, 96.2, 47.6, 42.9, 38.5, 37.4, 33.9, 33.5, 27.7, 26.7.
15: **mp** 204-205°C; ^{1}**H-NMR** (200 MHz, CDCl$_3$) δ: 7.63 (1H,m), 7.45-7.42 (2H,m), 7.40-7.35 (2H,m), 4.05 (2H,d, J=12.0 Hz), 3.86 (2H,d, J=12.0 Hz), 2.77 (1H,s,br), 2.60 (2H,s,br), 1.93 (1H,d, J=3.3 Hz), 1.50 (2H,dd, J_1=10 Hz, J_2=3.3 Hz), 1.00 (2H,d, J=10 Hz).
16: **mp** 203-204°C; ^{1}**H-NMR** (300 MHz, CDCl$_3$) δ: 7.55-7.35 (5H,m), 4.11 (1H,d, J=12.0 Hz), 4.05 (1H,d, J=12.0 Hz), 3.94 (1H,d, J=12.0 Hz), 3.84 (1H,d, J=12.0 Hz), 2.59 (1H,d, J=8.4 Hz), 2.48-2.41 (2H,m), 1.85 (1H,d, J=5.3 Hz), 1.71-1.16 (6H,m).

5) Monoene 13 proved to be identical with a sample obtained by degradation of D_{2d}-dinoradamantane-2-carboxylic acid. See: M. Nakazaki, K. Naemura, N. Arashiba, **J.Org.Chem.** 43, 888 (1978).

6) T. Koopmans, **Physica,** 1, 104 (1934).

7) R.C. Bingham, M.J.S. Dewar, D.H. Lo, **J.Am.Chem.Soc.** 97, 1285 (1975).

8) L. Asbrink, C. Fridh, E. Lindholm, **Chem.Phys.Letters,** 52, 63; 69(1977).

(Received in Germany 7 September 1987)