1,8-Diaza-bicyclo[5.4.0]undec-7-en (DBU) in 15 ml Diäthyläther versetzt. Nach 1stdg. Rühren bei RT. wird DBU-Hydrobromid abfiltriert, mehrmals mit wenig Äther gut ausgewaschen und das Filtrat anschliessend bei einer Badtemp. von max. 75° i.V. (zur Abtrennung letzter Reste DBU · HBr) in eine gekühlte (–78°) Vorlage übergetrieben. Die anschliessende Destillation über eine *Vigreux*-Kolonne (10 cm) liefert 3,1 g (46,9%) reine Substanz vom Sdp. 46–47°/30 Torr.

$C_7H_{12}Si$ (124,3) Ber. C 67,66 H 9,73% Gef. C 67,61 H 9,78%

1.4. *1,1-Dimethyl-1-silacyclohexa-2,4-dien-tricarbonyleisen* (**1**). 1 g (8 mmol) 1,1-Dimethyl-1-silacyclohexa-2,4-dien und *ca.* 4 g $Fe(CO)_5$ werden in 2 ml Benzol in einem evakuierten Bombenrohr während 13 Std. auf 150–160° erhitzt. Nach Öffnen des Rohres und Abpipettieren der gelben Lösung von wenig Ungelöstem destilliert man Benzol bei *ca.* 30°/100 Torr ab und fraktioniert den Rückstand über eine *Vigreux*-Kolonne (5 cm); Sdp. 59°/0,55 Torr, Ausbeute 1,5 g (69%).

$C_{10}H_{12}FeO_3Si$ (264,1) Ber. C 45,47 H 4,58 Fe 21,14% Gef. C 45,48 H 4,59 Fe 20,91%

2. 1,1-Dimethyl-1-silacyclohexadienyl-tricarbonyleisen-hexafluorophosphat(2). – Bei 0–10° wird eine Lösung von 1 g (3,8 mmol) **1** in 3 ml Methylenchlorid mit der Lösung von 1,6 g (4 mmol) Triphenylmethyl-hexafluorophosphat in 6 ml Methylenchlorid versetzt, kurz kräftig durchgerührt und die dunkelrote Lösung bei 0–10° *ca.* 3 Std. belassen. Das abgeschiedene, kristalline **2** filtriert man ab, wäscht es mit kleinen Portionen Methylenchlorid bis zum Farbloswerden des Filtrates und trocknet i.V. bei RT. Man erhält 1,2 g (80%) **2** vom Smp. 175–177° (Zers.), das eventuell zur weiteren Reinigung bei 30–40° in möglichst wenig Aceton gelöst und (nach Abtrennen von eventuell Ungelöstem) bei 0° kristallisiert werden kann. – NMR. (Aceton-d_6; 60 MHz, internes TMS): δ (ppm) 0,075 (*s*, 3 H, *exo*-CH_3); 0,96 (*s*, 3 H, *endo*-CH_3); 3,89 (*m*, 2 H an C(2) + C(6)); 7,01 (*m*, 3 H an C(3) + C(4) + C(5)).

$C_{10}H_{11}F_6FeO_3PSi$	Ber. C 29,43	H 2,72	F 27,93	Fe 13,68	P 7,59%
(408,1)	Gef. ,, 29,29	,, 2,80	,, 27,70	,, 13,84	,, 7,44%

LITERATURVERZEICHNIS

[1] *W. Fink*, Helv. *58*, 1205 (1975).
[2] *W. Fink*, Helv. *57*, 167 (1974).
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[5] *R. Benkeser & R. F. Cunico*, J. organometal. Chemistry *4*, 284 (1965).

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33. Electronic Structure, Molecular Conformation and Reactivity of Benzonorbornadiene Systems[1]

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(7. III. 75)

Summary. From the photoelectron spectra of benzonorbornadiene (**1**) and its 9-isopropylidene derivative (**2**) the energy and an approximate wave function for the highest occupied orbitals is obtained. With these results the differential reactivity of the systems in *Diels-Alder* additions with 'inverse electron demand' is discussed on the basis of frontier orbitals. For the ground state of **2** similar non-bonded interactions between the isopropylidene unit and the double bond or the benzene ring are indicated. Conformational equilibria in 9-aza derivatives of **1** are discussed in view of these findings.

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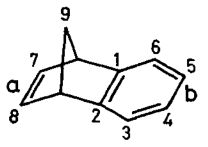
[1] Part I of: 'Weak molecular complexes with hydrocarbon donors'.

Introduction. – Recently, *Diels-Alder* additions to the double bond a of **1** and **2** (symmetry C_s) were reported using different cycloaddends [1].



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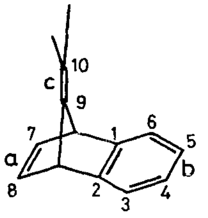

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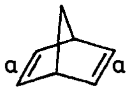

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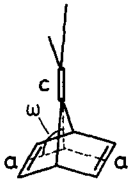

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A remarkable feature was that the reaction rates for **1** and **2** were roughly similar for 'normal' additions, while **2** showed a significant rate increase as compared with **1** for additions 'with inverse electron demand'. These results were explained on the basis of the shape and the energy of the frontier orbitals (HOMO and LUMO) of the

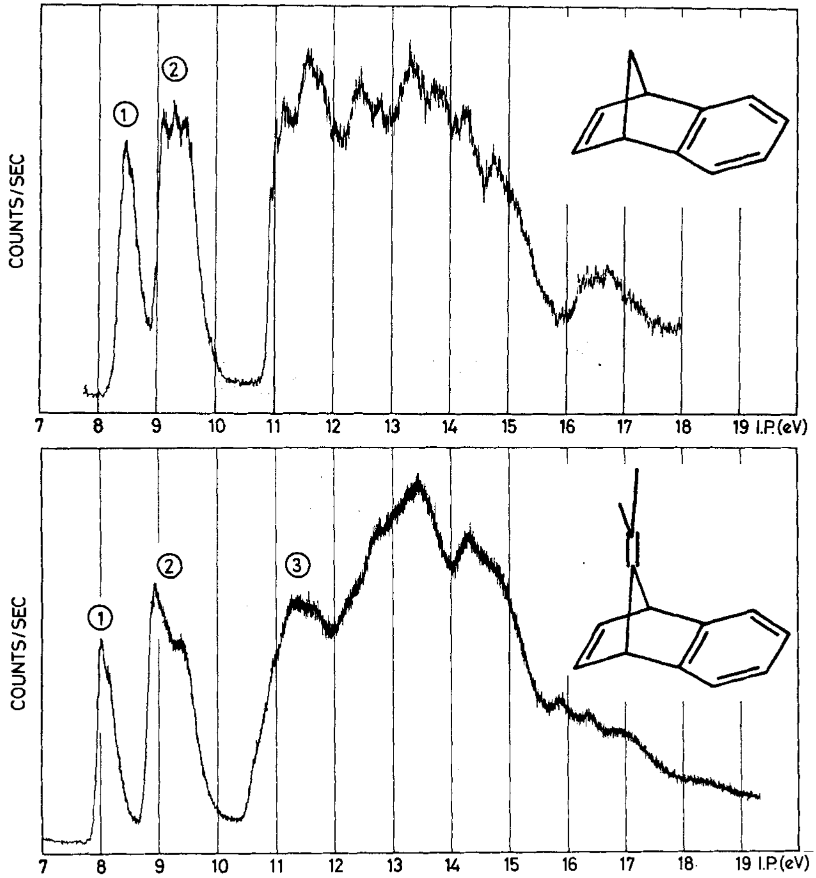


Fig. 1. a) *Photoelectron spectrum of* **1**, b) *Photoelectron spectrum of* **2**

model systems **3** and **4**, deduced from photoelectron (PE.)-studies [2]. Furthermore, it was concluded that there is no necessity to invoke 'secondary orbital overlap' between the cycloaddends and the exocyclic double bond c in **2**, in the case of the 'normal' additions.

In this paper the electronic structure of **1** and **2**, derived from their PE.-spectra (see Fig. 1), is described and the results are shown to support the above cited qualitative conclusions. In view of this, some structural features of **2** are discussed and a more quantitative correlation between electronic structure and reactivity of various bicyclic systems is put forward using frontier-orbital perturbation theory. In a following paper the charge-transfer (CT.)-spectra of **1** and **2** will be discussed and the ground state structure of the complexes elucidated.

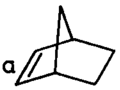
PE.-Results. – Fig. 1a shows the PE.-spectrum of **1**. Experience, as well as the ratio of areas of the band systems ② / ① = 2.1, suggests that the latter are due to electron removal from three MO's; they involve predominantly the three π-basis functions π_a, π_b^S [2]) and π_b^A the two latter being the highest lying-occupied π-MO's of benzene.

In the PE.-spectrum of **2** (Fig. 1b), the corresponding ratio is ② / ① = 2.7, indicating that the additional π-MO, resulting from the introduction of the exocyclic double bond c, is covered by ②. Unfortunately, here only two vertical ionization potentials (IP_V) are resolved.

For **1** and **2** the third nodeless π-MO of benzene is hidden by the complex high energy band system starting at ③ and due to σ-ionizations. This will not be further discussed.

The shape and energy of the MO's associated with the ionizations in ① and ②, and originating from a mixing of the π-basis functions cited above, are deduced as follows:

Choice of basis orbital energies. – 1) The basis orbital energy $A(\pi_a, \mathbf{6})$ is expected to be similar to $\varepsilon(\pi_a, \mathbf{5}) = -8.97$ eV [2] due to the remoteness of the additional



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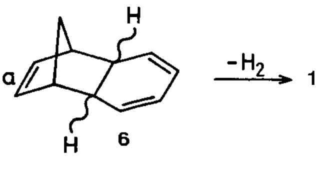

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butadiene unit[3]). Dehydrogenation of **6** leads to **1**, the π_a-orbital thus having experienced the same inductive perturbation as the π-basis orbitals of **3** when formed from **5**, ($\delta A(\pi_a) = -0.15$ eV [2]); accordingly:

$$A(\pi_a, \mathbf{1}) = A(\pi_a, \mathbf{3}) = -9.12 \text{ eV}. \tag{1}$$

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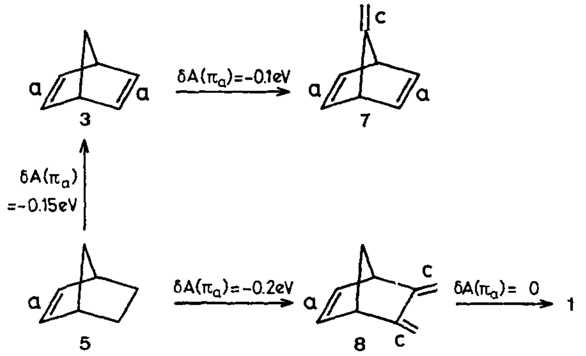
[2]) The indices S, A indicate the symmetry behaviour of these basis functions with respect to the mirror plane in **1** and **2**.

[3]) This proposal is supported by the fact that the energy of the π-MO in 3-hexene (–9.02 eV [3]) and the π-basis energy found for 1,5-cyclooctadiene (–9.05 eV [4]) are virtually identical.

Another approach is provided as follows:



(2)

(3)

On introduction of c into **3** leading to **7**, $\delta A(\pi_a)$ was found to be -0.1 eV [5] (2). Conversion of **5** to **8** involves addition of two exocyclic double bonds of type c; hence

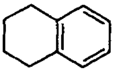
$$\delta A(\pi_a) = -0.2 \text{ eV}. \tag{4}$$

Since further substitution with a remote double bond (**8** → **1**) leads to no change in $A(\pi_a)$, we obtain

$$A(\pi_a, \mathbf{1}) = A(\pi_a, \mathbf{5}) - 0.2 \text{ eV} = -9.17 \text{ eV}. \tag{5}$$

Subsequently the mean between the results of (1) and (5), $A(\pi_a, \mathbf{1}) = -9.15$ eV, is used.

2) The two benzene basis orbital energies of **1**, $A(\pi_b^S)$ and $A(\pi_b^A)$ are derived as follows: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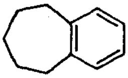
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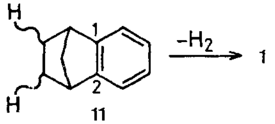

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For **9** and **10**, $\varepsilon(\pi_b^S) = -8.44$ eV and $\varepsilon(\pi_b^A) = -8.96$ eV [6], which are expected to be also valid for **11**. As cited above for **5** → **3**, $\delta A(\pi_a) = -0.15$ eV which is also applicable to **11** → **1**.

However, the orbital densities at C(1) and C(2) in **11** differ from those of π_a in **5** by a factor of 1/2 for π_b^S and 1/6 for π_b^A. This leads to

$$\begin{aligned} A\left(\pi_b^S, \mathbf{1}\right) &= -8.44 \text{ eV} - \frac{1}{2} \cdot 0.15 \text{ eV} = -8.52 \text{ eV}, \\ A\left(\pi_b^A, \mathbf{1}\right) &= -8.96 \text{ eV} - \frac{1}{6} \cdot 0.15 \text{ eV} = -8.99 \text{ eV}. \end{aligned} \tag{6}$$

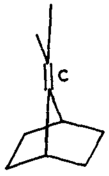
3) For **2**, the basis orbital energies derived for **1** are corrected for the inductive effect of the additional exocyclic double bond c. For **3** → **4**, $\delta A(\pi_a) = +0.1$ eV was found [2]. Thus

$$A(\pi_a, \mathbf{2}) = A(\pi_a, \mathbf{1}) + \delta A(\pi_a) = -9.05 \text{ eV}. \tag{7}$$

4) By analogy with (7), the inductive effect of double bond c on π_b^S and π_b^A in th benzene moiety of **2** results in:

$$\begin{aligned} A\left(\pi_b^S, \mathbf{2}\right) &= A\left(\pi_b^S, \mathbf{1}\right) + \frac{1}{2} \cdot 0.1 \text{ eV} = -8.47 \text{ eV} , \\ A\left(\pi_b^A, \mathbf{2}\right) &= A\left(\pi_b^A, \mathbf{1}\right) + \frac{1}{6} \cdot 0.1 \text{ eV} = -8.97 \text{ eV} . \end{aligned} \quad (8$$

5) The basis orbital energy of π_c in **2** is derived as follows:



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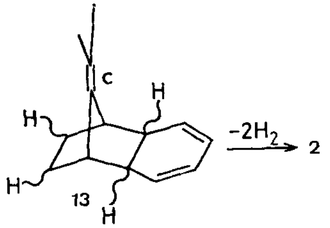

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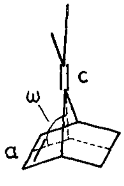

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$A(\pi_c, \mathbf{13})$ is expected to be similar to $\varepsilon(\pi_c, \mathbf{12}) = -8.49$ eV [2] due to the remoteness of the additional perturbing butadiene unit in **13**. The inductive effect on π_c upon **13** → **2** will be equal to $\delta A(\pi_c) = -0.3$ eV, already known for **12** → **4** [2]. Hence

$$A(\pi_c, \mathbf{2}) = -8.49 \text{ eV} - 0.3 \text{ eV} = -8.79 \text{ eV}. \quad (9)$$

Interaction of basis orbitals in **1**. – As a preliminary approach the interaction of the basis orbitals was derived using off-diagonal elements (B) previously deduced for **3** [2]. These of course had to be modified in view of the different coefficients for the π_b-orbitals at C(1) and C(2) in **1**. We obtained

$$\begin{aligned} B\left(\pi_a \pi_b^S, \mathbf{1}\right) &= B\left(\pi_a \pi_a, \mathbf{3}\right) \cdot \frac{1}{\sqrt{2}} = -0.30 \text{ eV} , \\ B\left(\pi_a \pi_b^A, \mathbf{1}\right) &= 0 \quad \text{by symmetry.} \end{aligned} \quad (10)$$

In Fig. 2 the resulting orbital pattern (i) is compared with the experimental orbital energies, indicating a need for an increase in $\pi_a \ldots \pi_b^S$ interaction; indeed perfect agreement with experiment is obtained for $B(\pi_a \pi_b, \mathbf{1}) = -0.40$ eV (ii). The eigenfunctions ψ_1, ψ_2, ψ_3 associated with the calculated orbital energies ε_1, ε_2, ε_3 are also given. It can be seen, that about 80% of the π-charge is concentrated for ψ_1 on π_b^S and for ψ_3 on π_a, as $\psi_2 = \pi_b^A$ (ε_2 (**1**) $= A(\pi_b^A, \mathbf{1})$) for reasons of symmetry.

Interaction of basis orbitals in **2**. – Based on the results in Fig. 2 (ii) discussed for **1** above we chose

$$B(\pi_a \pi_b^S, \mathbf{2}) = B(\pi_a \pi_b^S, \mathbf{1}) = -0.40 \text{ eV}. \quad (11)$$

The interaction of π_c with π_a was taken as equal to that found for **4** [2]

$$B(\pi_c \pi_a, \mathbf{2}) = B(\pi_c \pi_a, \mathbf{4}) = -0.45 \text{ eV}. \quad (12)$$

Assuming the same atomic coupling parameter β to be valid for the $\pi_c \ldots \pi_b^S$ interaction (*i.e.* $\beta_{7,9} = \beta_{1,9}$) yields the off-diagonal element

$$B\left(\pi_c \pi_b^S, \mathbf{2}\right) = B\left(\pi_c \pi_a, \mathbf{4}\right) \cdot \frac{1}{\sqrt{2}} = +0.318 \text{ eV.}^{4)} \qquad (13)$$

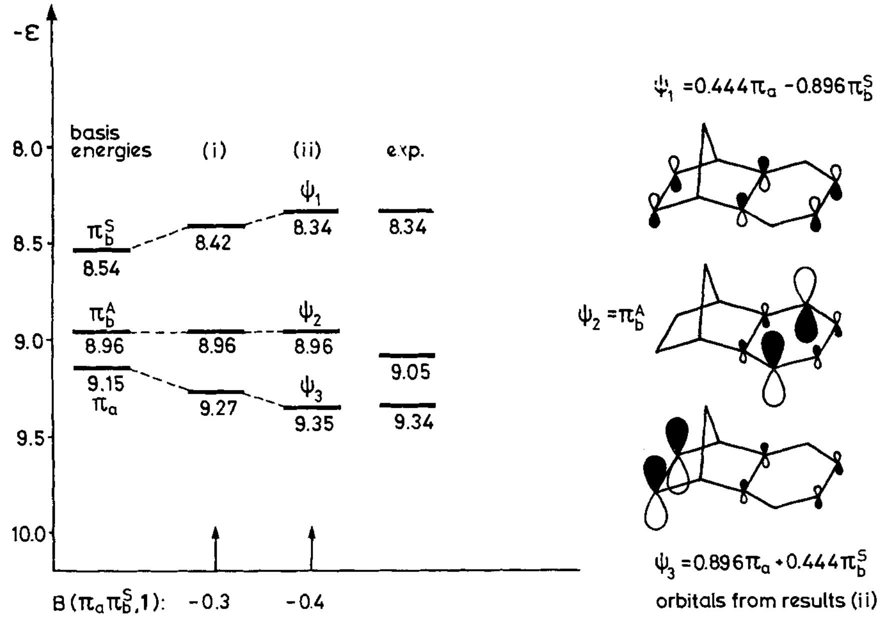


Fig. 2. *Comparison between theoretical and experimental orbital energies for* **1**. *Wave functions for the three highest occupied orbitals of* **1**

As for **1**

$$B(\pi_c \pi_b^A, \mathbf{2}) = B(\pi_a \pi_b^A, \mathbf{2}) = 0. \qquad (14)$$

The resulting eigenvalues of **2** are shown in Fig. 3 (i). Comparison with the experimental spectrum shows almost perfect agreement, suggesting furthermore that the peak at 8.9 eV involves ionization from the accidentally degenerate orbital pair ψ_2 and ψ_3. The corresponding eigenfunctions ψ_1 to ψ_4, to be discussed later, are shown in Fig. 4.

Orbitals of **2** *from interaction of those of* **1** *with* π_c. – An alternative approach consists of constructing the MO's ψ_1 to ψ_4 of **2** using as a basis the MO's obtained for **1** (Fig. 2 (ii)), for which the respective energies are corrected by inclusion of the inductive effect of π_c. Since ψ_1 and ψ_3 of **1** are strongly dominated by π_b^S and π_a, resp., and $\psi_2 = \pi_b^A$ we have according to (7):

$$A(\psi_3, \mathbf{2}) = \varepsilon_3(\mathbf{1}) + 0.1 \text{ eV} = -9.24 \text{ eV} \qquad (15)$$

---

4) The positive sign in (13) follows from the negative signs chosen in (11) and (12); it is important to note the *Moebius*-topology of the three interacting π-systems a, b and c.

and according to (8):

$$\begin{aligned} A(\psi_1, \mathbf{2}) &= \varepsilon_1(\mathbf{1}) + 0.1 \cdot \frac{1}{2}\,\mathrm{eV} = -8.29\,\mathrm{eV}, \\ A(\psi_2, \mathbf{2}) &= \varepsilon_2(\mathbf{1}) + 0.1 \cdot \frac{1}{6}\,\mathrm{eV} = -9.03\,\mathrm{eV}, \end{aligned} \tag{16}$$

taking now for the ε-values those experimentally observed (Fig. 2). The basis energy $A(\pi_c, \mathbf{2})$ of the exocyclic double bond c is given by (9).

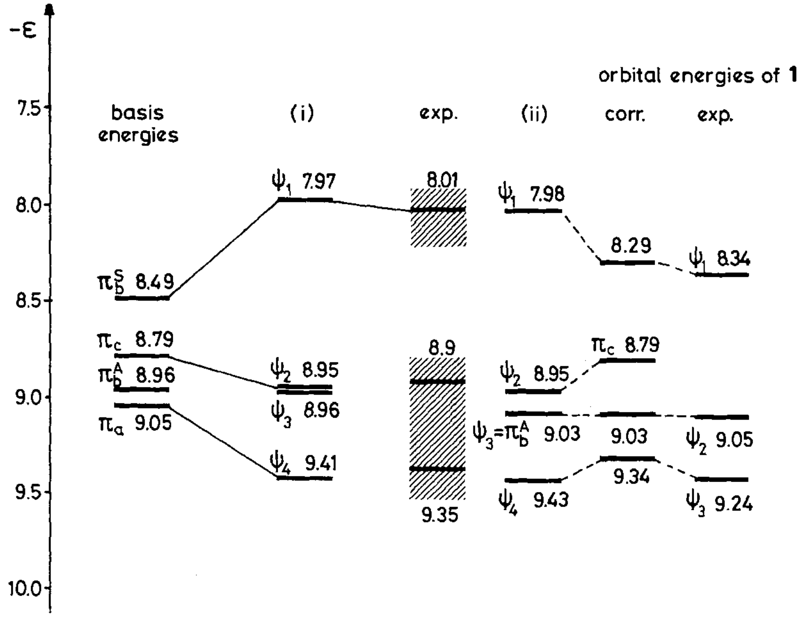
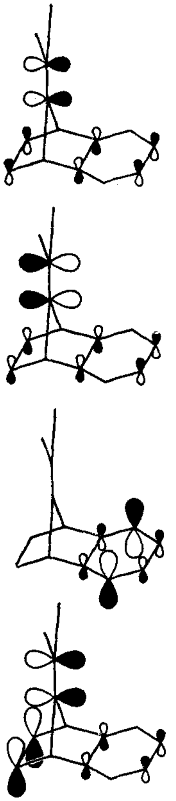


Fig. 3. *Comparison between theoretical and experimental orbital energies for* **2**

Using the optimal atomic interaction parameters obtained for **2** (*cf.* (11), (12) and (13)) and the appropriate coefficients in π_c and in the MO's of **1**, the off-diagonal elements are found to be:

$$\begin{aligned} B(\psi_1 \pi_c, \mathbf{2}) &= +0.484\,\mathrm{eV}, \\ B(\psi_2 \pi_c, \mathbf{2}) &= 0, \\ B(\psi_3 \pi_c, \mathbf{2}) &= -0.260\,\mathrm{eV}. \end{aligned} \tag{17}$$

Solution of the secular problem yields the eigenvalues indicated in Fig. 3 (ii), which are in good agreement with those obtained by approach (i) as well as with experiment. This is further supported by the shape of the associated eigenfunctions which are found to be identical with those from (i), depicted in Fig. 4.



$$\psi_1 = .696\pi_b^S + .534\pi_c - .480\pi_a$$

$$\psi_2 = .693\pi_b^S - .674\pi_c + .255\pi_a$$

$$\psi_3 = \pi_b^A$$

$$\psi_4 = .188\pi_b^S + .510\pi_c + .839\pi_a$$

Fig. 4. *Eigenfunctions for the four highest occupied orbitals of* **2**, *obtained by approach* (*ii*) (*see text*)

Discussion. – *Interpretation of the rates of cycloaddition to* **1** *and* **2**. As briefly summarized in the introduction, the rate enhancement of *Diels-Alder* additions with 'inverse electron demand' resulting from the introduction of a 9-isopropylidene group into **1** was discussed in [1] on the basis of the known changes in electronic structure of the model system **4** as compared with **3**. It included a consideration of the various contributions to the (proposed) rate determining depression ($\delta\varepsilon$) of the highest occupied MO (HOMO) of the donor-hydrocarbon X:

$$\delta\varepsilon(X) = -\frac{H^2(X,Y)}{\varepsilon(Y) - \varepsilon(X)} \qquad (18)$$

where $\varepsilon(X)$ = HOMO-energy of different donor-monoenes X

$\varepsilon(Y)$ = LUMO-energy of acceptor addend Y

$H^2(X,Y)$ = HOMO-LUMO interaction term.

The logarithm of the rate constant ($\log k(X)$) was taken to be a monotonic function of $\delta\varepsilon(X)$.

For small variations in the rate constant one might assume proportionality between $\log k(X)$ and $\delta\varepsilon(X)$. Hence

$$\log k(X) = -C_1 \frac{H^2(X,Y)}{\varepsilon(Y) - \varepsilon(X)} \; ; \quad C_1 > 0 \; . \tag{19}$$

The present PE.-analysis for **1** and **2**, together with the results where Y was tropone fixes the values for $\log k(X)$[5] and $\varepsilon(X)$ for X = **1**, **2**, **3** and **5**. Since each of these substrates possesses a plane of symmetry passing through the double bond to be attacked by Y, the two HOMO-coefficients of this double bond are equal in magnitude. Denoting the square of this coefficient by $c^2(X)$ we obtain: $c^2(\mathbf{5}) = 0.5$ and $c^2(\mathbf{3}) = 0.25$ by symmetry, $c^2(\mathbf{1}) = 0.099$ and $c^2(\mathbf{2}) = 0.115$ from Fig. 2 and Fig. 4, respectively. Expansion of the numerator of (19) shows: $H^2(X,Y) = C_2 \cdot c^2(X)$ (C_2 is a constant). Inserting this into (19), with subsequent slight manipulation, yields

$$\frac{c^2(X)}{\log k(X)} = C_3 \cdot \varepsilon(X) + C_4 \text{ (where X is } \mathbf{1, 2, 3, 5}) \; , \tag{20}$$

where $C_3 = (C_1 \cdot C_2)^{-1}$, $C_4 = -C_3 \cdot \varepsilon(Y)$. In Fig. 5 this relationship is shown graphically for the four substrates.

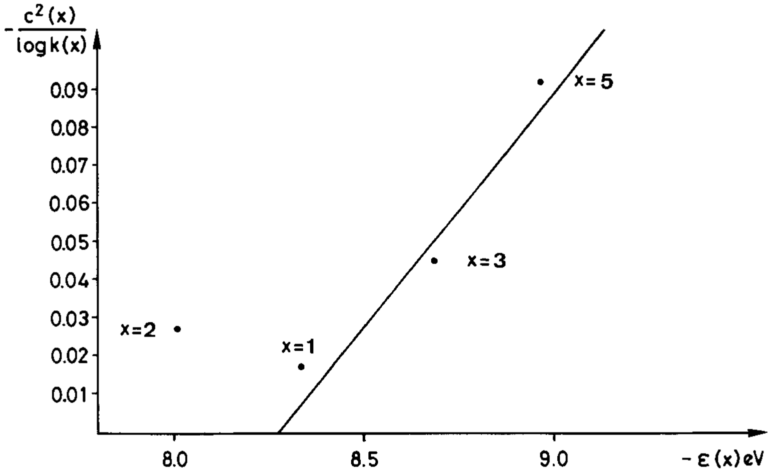


Fig. 5. *Graphical expression of equation (20)*

It can be seen that for **1**, **3** and **5** a linear relationship is roughly fulfilled, thus supporting the view expressed in [1] that the differential reactivity of the unsaturated norbornane systems discussed there in *Diels-Alder* additions with 'inverse electron demand' can only be rationalized if both the energy and the shape of the donor-HOMO's at the site of attack are taken into account. The point for X = **2** however deviates markedly from the correlation and from monotonic functionality. Apparently the rate of cycloaddition here is too low for a HOMO-LUMO interaction of the type encountered in **1**, **3** or **5** and better agreement could be obtained by de-

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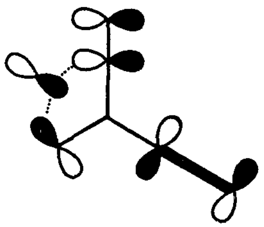
[5] Since **3** contains two equivalent double bonds, the measured rate of addition was corrected by a statistical factor of 2.

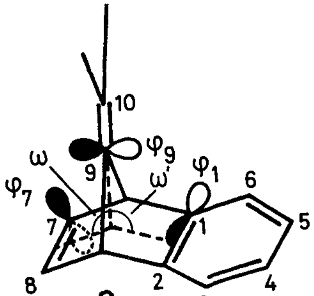
crease of such interaction. Taking our value for $\varepsilon(\mathbf{2})$ as valid this suggests a smaller value for C_2, which could result if the incoming addend exerts additional, but destabilizing interaction with parts of the HOMO centered at non-reacting moieties of **2**. Inspection of this orbital (Fig. 4) indicates that the space above the reacting double bond contains a significant fraction from the HOMO centered at the exocyclic isopropylidene unit. Since the two HOMO-fractions have an out-of-phase relationship, overlap of the incoming LUMO with both of them, as indicated below, may well lead to a smaller interaction term for **2**.



In [1] it was pointed out that the observed rate increase for **2** does not necessitate the idea of (stabilizing) secondary interaction between the addend and the exocyclic isopropylidene double bond. The present analysis suggests in addition that this interaction in fact takes place on a HOMO-LUMO basis in a destabilizing manner, leading to decreased reactivity of **2**, relatively speaking.

Earlier theoretical treatments of cycloaddition reactions have in most cases correlated differential reactivity only with changes in orbital energies, thus assuming the numerator in (18) to be constant for the whole series [7]. Recently however it has been recognized that the shape of the frontier orbitals, *e.g.* calculated using the CNDO/2-method, also contributes valuable information [8]. In the present paper the numerator in (18) is discussed using PE.-spectroscopic (= 'experimental') results as a basis.

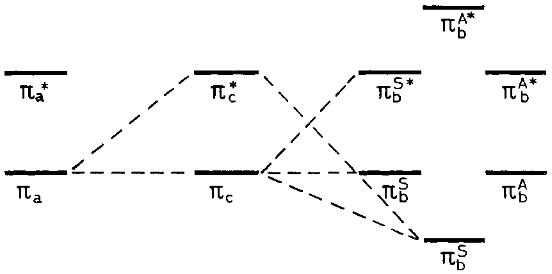
The conformation of **2**. In [2] it was pointed out that the interaction between a and c in **4** was significantly larger than that in **14**. On this basis it was suggested that $\omega(\mathbf{14}) > \omega(\mathbf{4})$. Clearly this prediction is reasonable since ground-state conjugative destabilization [9] between the bonding a- and c-levels ('closed-shell repulsion') may be reduced in **14** by an increase in the angle ω as compared with that required by the molecular symmetry of **4**.



2

In this respect **2** presents an interesting structure for exploring the relative importance of such destabilizing interactions between two double bonds (c and a) in relation to a third double bond and a benzene ring (c and b). The PE.-results for **2** discussed above were compatible with equal atomic coupling parameters for the two interacting pairs. Hence in **2** $\omega \approx \omega'$ or, for the respective closed-shell repulsions, E(a ... c) $\approx$ E(b ... c) is suggested. We advance some further arguments, both theoretical and experimental, which support this hypothesis:

The diagram below shows the HMO-levels of the π-systems embodied in **2**. The correlation lines indicate those energetically relevant pair interactions which, on the basis of symmetry arguments, occur between the π_c-orbitals and the π_a- or the π_b-orbitals:



As expected both over-all interactions turn out to be repulsive since both involve conjugative destabilization between bonding levels which outweigh stabilizations due to depression of filled levels by empty levels. However it is not immediately evident that for the resulting destabilizing interaction energies E(a ... c) > E(b ... c); although for the degenerate orbital interactions $\pi_a \ldots \pi_c > \pi_c^S \ldots \pi_c$ (assuming $\omega = \omega'$) due to larger coefficients of the a-system, there is an additional $\pi_b^S \ldots \pi_c$ interaction. We therefore resorted to the perturbation treatment outlined by *Salem* [10]. Using his terminology the total interaction energies turned out to be

$$E(a \ldots c) = -\beta S^2 (k^2 - 6k + 1),$$

$$E(b \ldots c) = -\beta S^2 \left(\frac{11}{9} k^2 - 6k + 1.5\right) \qquad (21)$$

with

$$\beta = \langle \varphi_1 | H | \varphi_9 \rangle = \langle \varphi_7 | H | \varphi_9 \rangle < 0,$$

$$S = \langle \varphi_1 | \varphi_9 \rangle = \langle \varphi_7 | \varphi_9 \rangle > 0,$$

where k is a proportionality factor. Using the values k = 2.85 and $\beta = -3$ eV (22) as recommended by *Salem* [10] and the overlap integral S = 0.064, calculated on the basis of the observed geometry for the norbornadiene **3** ($\omega = \omega' = 124.5°$ [11]) yields

$$E(a \ldots c) - E(b \ldots c) = +0.7 \text{ kcal/mol.} \qquad (23)$$

Taking 0.5 kcal/mol for the angle-deformation energy[6]) at each of the bridgehead carbons in **2**, (23) leads to

$$124.5° < \omega < 124.5° + 0.1 \text{ rad.} \qquad (24)$$

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[6]) Defined for an angle deformation of 0.1 rad.

Such a small deformation may well not lead to a perceptible difference between the two coupling parameters mentioned above.

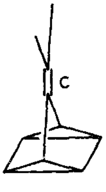
This result is further supported by MINDO/2-calculations [12] of the molecular energy of **2** as a function of ω, ω'. (To keep the costs of computation within tolerable limits, $\omega + \omega' = 249°$ was assumed on the basis of the structural analysis for **3** [11]). The minimum energy conformation of **2** is found for

$$\omega = 124.5° + 3°. \tag{25}$$

In a recent discussion of the electronic structure of **15** and **16** [13] it was concluded that the interactions between the quadricyclane moiety and c in **15** or the heteroatom lone pair n in **16** exhibit closely resembling features.

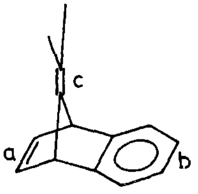
Applied to the present case, the closed-shell repulsion $E(a \ldots c) \approx E(b \ldots c)$ found above in **2** predicts $E(a \ldots n)$ in **17** to be about equal to $E(b \ldots n)$ in **17a**; *e.g.* the two invertomers **17** and **17a** having roughly the same energy. Actually the equilibrium constant K for **17**/**17a** is 1.5 for R = Cl, X = H [14]; 0.33 for R = CH_3, X = Cl and 0.18 for R = CH_3, X = F [15], which suggests that for R = H, X = H the equilibrium may not be displaced by much toward one invertomer, although in [16] only one species could be observed under NMR.-conditions. Note, however, that in accord with (23), (24) the invertomer **17a** is favoured.

For **18** (R = H), where the destabilizing interaction $\pi_a \ldots \pi_c$ is lacking, $\omega < \omega'$ should hold by analogy with **14**.



15

16



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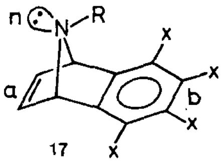
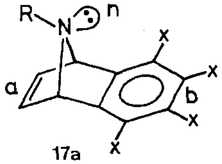
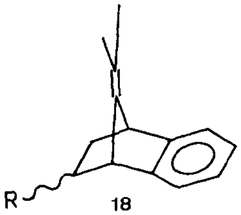


17



17a



18

Actually, the solvolysis rates of the epimeric pair of tosylates **18** (R = OTs) are roughly equal [17], indicating a similar degree of anchimeric assistance by the benzene ring in the case of the *exo*-, or by the isopropylidene group in the case of the *endo*-tosylate. This, however, does not exclude the possibility that the same observations were made with $\omega > \omega'$ in **18**, as the interaction between the backlobe of the developing positivized hybrid orbital with either of the unsaturated groups presumably involves little or no vertical stabilization [18]. (See [19] for a striking example of th kind).

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34. Syntheses of (2*R*,4′*R*,8′*R*)-α-Tocopherol and (2*R*,3′*E*,7′*E*)-α-Tocotrienol

by **John W. Scott, Fred T. Bizzarro, David R. Parrish** and **Gabriel Saucy**

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(24. X. 75)

Summary. Reaction of trimethyl-hydroquinone with methyl vinyl ketone in acidic methanol gave *rac.*-2-methoxy-2,5,7,8-tetramethyl-chroman-6-ol (**8**). This acetal was converted in four steps to *rac.*-(6-hydroxy-2,5,7,8-tetramethyl-chroman-2-yl)acetic acid (**13**). Acid **13** was readily resolved with α-methyl-benzylamine to give the (*S*)-enantiomer **14**. Treatment of the unwanted (2*R*)-isomer with acid regenerated **13**, thus leading to an efficient use of this compound. Employing a side chain derived from phytol, **14** was converted to (2*R*, 4′*R*, 8′*R*)-α-tocopherol (**1d**, 'natural' vitamin E). A reaction sequence from **14** involving two highly stereoselective *Claisen* rearrangements has provided the first total synthesis of (2*R*,′*E*, 7′*E*)-α-tocotrienol (**2d**).