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Pi-sigma interactions: Experimental evidence and its consequences for the chemical reactivity of organic compounds

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Abstract: The magnitude of π/σ interactions in nonplanar π systems and its dependence on the planarity, length and energy of the sigma frame is demonstrated by means of photoelectron spectroscopy. Its consequences for the reactivity of nonplanar π systems is discussed in the case of fragmentation reactions, light-induced [2+2]cycloaddition reactions, addition reactions of sesquinorbornene, 1,6-methano[10]annulene, 1,6-8,13-bismethano[14]annulene and Diels Alder reactions with isodicyclopentadiene.

INTRODUCTION

Usually organic chemists consider only the π electrons in planar π-systems like ethylene or benzene because these electrons mostly determine the reactivity of these systems and because it is easier to deal with just the π electrons*. This simple view received support in the early days of theoretical organic chemistry from the Hückel theory (ref.1) in which the role of σ electrons was at most considered as a perturbation. When a methyl group is attached to the π-system, e.g. in propylene or toluene, the concept of hyperconjugation has to be introduced to take care of the π/σ interaction as a perturbation. In those compounds, however, where the σ-frame of the π-system is bent, as in the bent double bond of bicyclo[1.1.0]butene$\Delta^{1,3}$ (1), syn-sesquinorbornene (2) or in a strained p-cyclophane like 3 the π/σ mixing is already very important and can not be neglected or treated as a perturbation as suggested by model calculations (ref.2-4).

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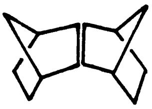

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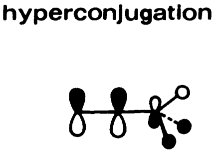
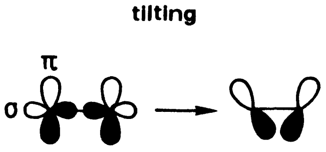
* Throughout this paper we shall use a one-electron picture where electrons are described by atomic and molecular orbitals of σ and π symmetry.

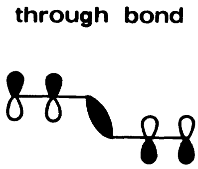
In the first part of this article we will present recent spectroscopic evidence that π/σ interactions can be large. In the second part we will discuss its implication for the chemical reactivity of several systems (ref.5).

In our discussions we will use arguments derived from molecular orbital theory to describe the electronic structure of molecules. To demonstrate the magnitude of π/σ interactions we will rely on the results of He(I) photoelectron (PE) spectroscopy. This method allows us via Koopmans' theorem (ref.6) to correlate directly the measured vertical ionization energies $I_{v,j}$ with the calculated orbital energies (ε_j): $I_{v,j} = -\varepsilon_j$. The demonstration is usually done by comparing the energy-split or the sequence of the valence MO's of a molecule where no π/σ interaction occurs with another one in which π/σ interaction occurs.

To make things clear we subdivide the π/σ interactions into what is called usually hyperconjugation, π/σ interaction due to bending (tilting) and through-bond interaction as shown below.







EXPERIMENTAL EVIDENCE

Hyperconjugation

There is much experimental evidence from electron absorption spectroscopy and PE spectroscopy on π systems that alkyl groups exhibit a strong electron donating effect. This effect has been dealt with theoretical (ref.7) and is commonly used in textbooks of organic chemistry; therefore we will leave this paragraph by comparing the first two ionization energies in benzene with that of toluene as shown in Figure 1. For reasons of symmetry the methyl group interacts only with a' and not with a", and thus the former is destabilized by 0.24 eV.

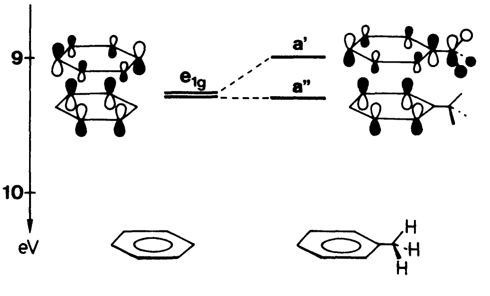
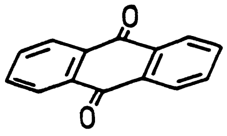


Fig.1 Comparison between the first PE bands of benzene and toluene. A schematic drawing of the highest occupied MO's is added at left and right.

Effect of bending

We will demonstrate that the effect of π/σ mixing is due to bending by comparing the first ionic states of anthraquinone(4) (ref.8) with the corresponding states of syn-bishomoanthraquinone (5)(ref.9) as shown in Figure 2.



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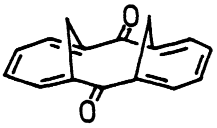

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The six ionic states of the first band in the PE spectrum of 4 overlap very strongly and are due to ionizations from two σ orbitals (n_+,n_-) and four π orbitals as shown in Figure 2. Reduction of symmetry from D_{2h}(4) to C_{2v}(5) allows a mixing between $a_2(n_-)$ and $a_2(\pi)$ as well as $b_2(n_+)$ and $b_2(\pi)$. Since both MO's have similar energies the interaction is quite large as can be seen from Fig.2. As a result of the strong π/σ interaction the $2p_\pi$-orbitals are tilted considerably.

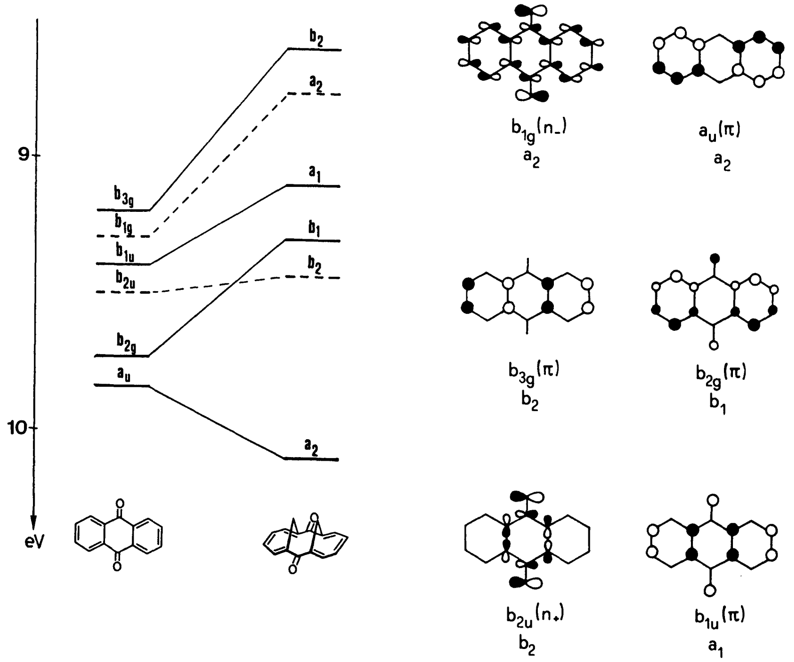


Fig.2 Comparison between the first bands of 4 and 5(left) and schematic drawing of the highest occupied MO's of 4(right). The irreducible representation in the point group D_{2h} and C_{2v} is given below each wave function.

Through-bond interaction

As shown by model calculations (ref.10) the interaction of π systems via σ bonds (through-bond interactions (ref.11)) depends strongly on the chain length and on the energy difference between π and σ orbitals. We will demonstrate the importance of the first factor by comparing the first bands

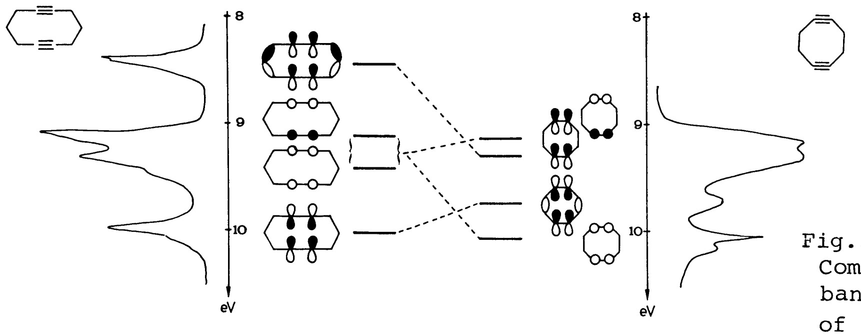
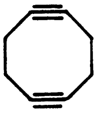


Fig.3
Comparison of the first bands of the PE spectra of 6 and 7.

of the PE spectrum of cycloocta-1,5-diyne (6)(ref.12) with that of cyclodeca-1,6-diyne (7)(ref.13). In 6 both π fragments are connected by a C_2H_4 chain, whereas in 7 a C_3H_6 unit connects the acetylenic parts. Both spectra (Fig.3) differ in so far as the first four ionic states are clearly separated in the spectrum of 7 while in 6 they overlap strongly. This remarkable difference can be rationalized by assuming a larger interaction of the "out-of-plane" π MO's (b_{2g}, b_{3u}) in 6 due to the smaller separation between the two acetylenic moieties in this compound (2.8 Å) as compared to 7 (3.0 Å), and to a strong π/σ interaction of a_g(π) in the case of 6 and of b_{1u}(π) in the case of 7 (see above). This strong π/σ interaction leads to different HOMO's for both compounds.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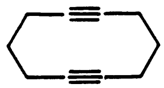
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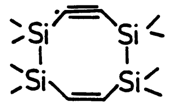
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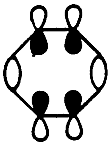
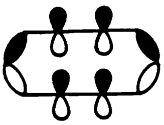
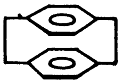

a_g


b_{1u}

The basis orbital energy of the interacting σ bonds can also be varied either by replacing the C-C bonds by Si-Si bonds (e.g.8)(ref.14), by imposing additional strain, or by replacing the hydrogens by fluorine. These effects will be illustrated by comparing the first bands of the PE spectra of [2.2]paracyclophane (9)(ref.15) with those of [1:2,9:10]bismethano[2.2]paracyclophane (10)(ref.16), the octafluoro[2.2]paracyclophane(11) (ref.15) and the octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane (12)(ref.17) as shown in Fig.4. It is seen that the energy of the b_{3u} orbital varies by more than 3 eV. Again the HOMO of 9 and 11 is different from that of 10 and 12 due to π/σ interaction.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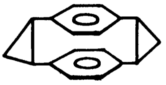
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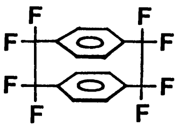
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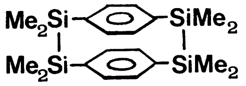
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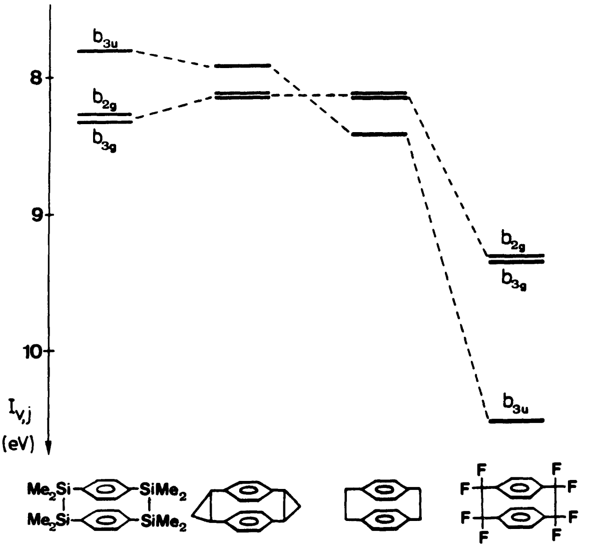


Fig. 4 Comparison of the first PE bands of 9-12.

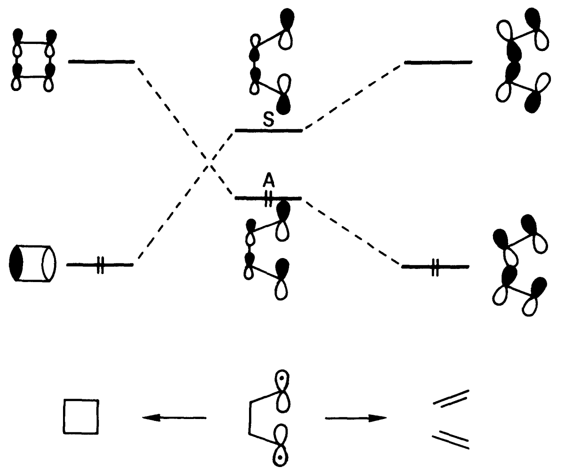


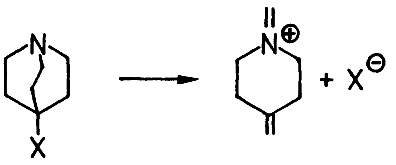
Fig.5 Correlation of the frontier orbitals of tetramethylene with those of cyclobutane (left) and two ethylenes (right).

CONSEQUENCES FOR REACTIVITY

In the preceding sections we have seen that π/σ interaction may change the symmetry of the HOMO in a series of compounds. This change should have strong implications on the reactivity of the molecules if its reactivity is frontier-orbital controlled (ref.18). Cases for which such a symmetry change will be discussed are fragmentation reactions and light-induced [2+2]cycloadditions. Further consequences of the reactivity are caused by changing the shape of the wave functions by polarization or by π/σ mixing (tilting) as shown above.

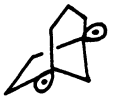
Symmetry change

Heterolytic fragmentations(e.g. 13 → 14) are widely spread reactions in organic chemistry (ref.19). It has been shown (ref.20) that the electronic requirements for an allowed fragmentation in a system like 13 or its



13 **14**

corresponding cation is the level ordering of the frontier orbitals. If the antisymmetric (A) MO is below the symmetric one (S), fragmentation is an allowed reaction. In Figure 5 this situation is shown at the right. This condition is met by maximal through-bond coupling of the empty cation orbital and the nitrogen lone pair. In those cases where the sequence S below A is found, ring closure is allowed and fragmentation is forbidden (Fig.5 left) even though the conformational requirements (ref.20) for the fragmentation are met. As examples for this latter case we can put forward the biradicals 15, 16 and 17 which can be postulated in the reaction of the corresponding dihalides with alkali metals (ref.21). Another example is the photofragmentation of exo-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (18) to its endo isomer (19) and tricyclo[4.3.0.0^{2,5}]nona-3,8-diene (20). This fragmentation has been rationalized by involving through-bond interaction (ref.22).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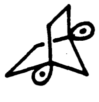
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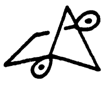
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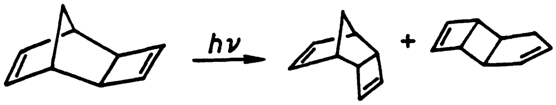

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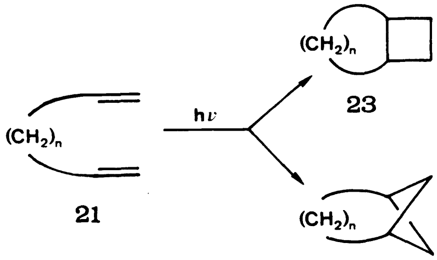
The light-induced [2+2]cycloaddition of α,ω-dienes (21) depends on the number of methylene groups (ref.23). For n = 2 one observes mainly 1,3-bridged cyclobutanes (22); for n = 1 and 3 the 1,2-bridged products (23) dominate.



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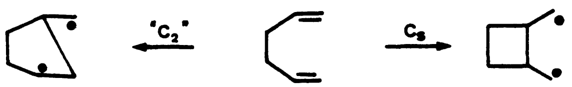
Besides steric factors, electronic factors involving π/σ interactions have also been proposed (ref.24). A correlation of the first excited state of 21* (n=2) with a low excited state of the two possible biradical intermediates 24 and 25 leads to the conclusion that for both reaction paths the electronic contribution to the activation energy is about the same. For 25, however, the steric hindrance in the transition state (27) is less than for 24 where an eclipsed conformation in the transition state (26) seems likely. For 21 (n=3) a similar correlation (ref.24) yields a considerable electronic contribution to the activation energy only for a head-to-tail mode of ring closure.



25 21(n=2) 24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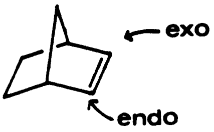
Polarization and tilting

Second-order orbital interactions (ref.25) are important for understanding regio-and stereo-selectivity in substitution and cycloaddition reactions. The effect of hyperconjugation by polarization of the frontier orbitals on the regioselectivity of aromatic substitution or on cycloaddition reactions has been reviewed extensively (ref.18). Here we only mention that hyperconjugation contributes to the selectivity of norbornene (28) towards exo-addition (ref.26,27) and the structure and reactivity of sesquinorbornene (2) in its ground and excited state (ref.27,28).



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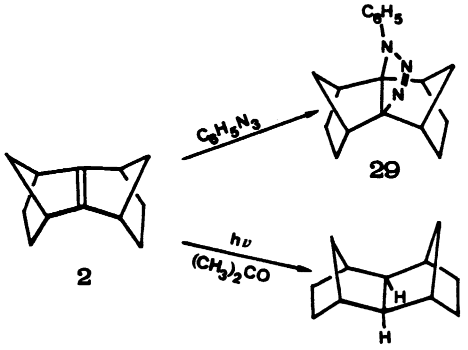
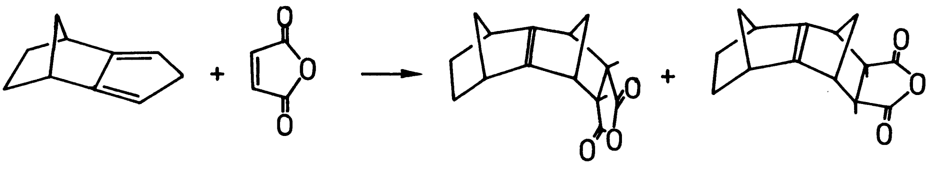


Recently a number of cases have been found where π/σ interactions influence the stereoselectivity of cycloadditions. The Diels-Alder reaction of isodicyclopentadiene (31) and related compounds (ref.29,30) yields mainly addition from the endo surface (syn to the C_2H_4 bridge) of the diene moiety (ref.29) as exemplified by the reaction of 31 with maleic anhydride (32). These reactions have been rationalized by invoking π/σ interactions (ref.25,29,30). In the case of 31 and related species MO calculations suggest a considerable mixing of the lowest occupied π MO (π_S) with high lying σ MO's with a strong p character. As a result of this interaction a tilting of this MO is predicted as shown below. It is seen that the rotation leads to a significant difference in the electron distribution of the syn and anti side. The consequences for this tilting on the reactivity is indicated in Figure 6.



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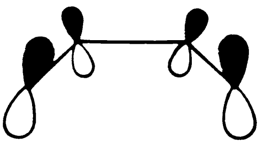


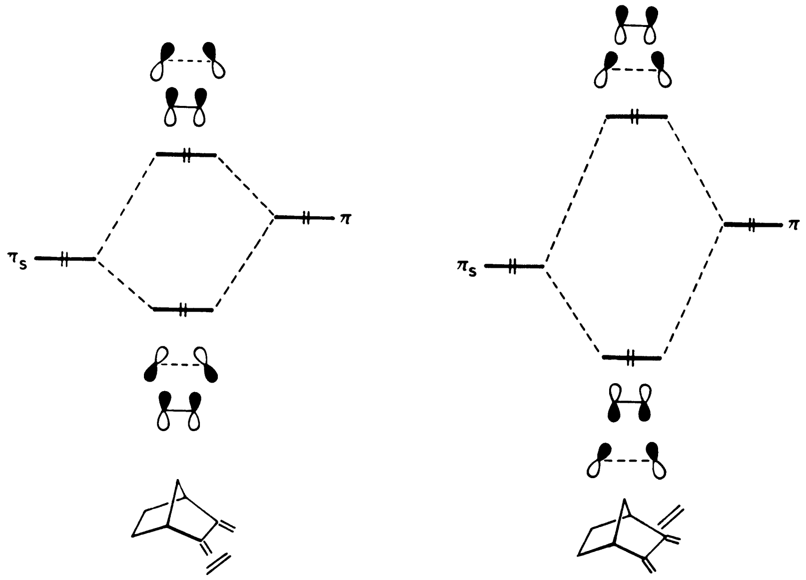
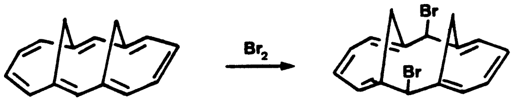


Fig.6 Qualitative diagram of the interaction between π_S of the butadiene unit in 31 with a π bond. On the left, below plane approach. On the right, above plane approach.

If the dienophile adds from below (Figure 6 left) the antibonding interaction between π_S of the butadiene moiety and the HOMO of the dienophile is smaller than in the case of syn attack (Figure 6 right). This is due to the different overlap between the rotated $2p_\pi$ orbitals at the terminal carbon atoms of the butadiene fragment and the dienophile. The consequences of the orbital tilting and steric counterarguments(ref.31) are currently being investigated by modifying the geometry of the dienophile and the diene.

Other reactions, in which stereoselectivity has been rationalized by π/σ interaction, are the reactions of Br_2 with 1,6-methano[10]annulene (35)(ref.32) and syn-1,6:8,13-bismethano[14]annulene (36)(ref.33). In both cases the addition of bromine occurs from the sterically more hindered side, syn to the methano bridge as shown for 36 below. For both cases MO calculations (ref.32,33) predict a tilting of the HOMO and/or the HOMO-1 away from the CH_2 group(s). Similar arguments as mentioned before can be used to understand the substitution from the sterically more hindered side.



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