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CONSEQUENCES OF σ-π-INTERACTION IN [2.2]-PARACYCLOPHANE

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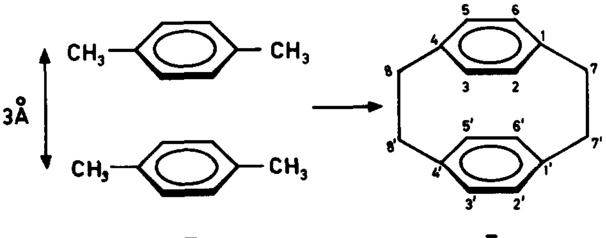
The particular conditions prevailing in the electronic structure of [2.2]-paracyclophane (I) manifest themselves, among other things, in the electronic spectrum of this molecule as compared to that of dibenzyl (1). For the interpretation of the electronic spectrum two model-approximations have been used: One follows the LCAO-CI procedure developped by Pariser, Parr and Pople (2). The other is the use of an exciton mechanism including charge transfer states (3). Both methods are based on the π-approximation and neglect the σ-core.

For I this assumption of σ-π-separability is not valid. In this molecule two bonds (7-7' , 8-8' ; see below) are parallel to the π-orbitals of the benzene rings and therefore available for σ-π-interaction.



II I

The correlation diagram (see fig. 1) which corresponds to the hypothetical dehydrogenation of II to I yields an indication of the size of this interaction.

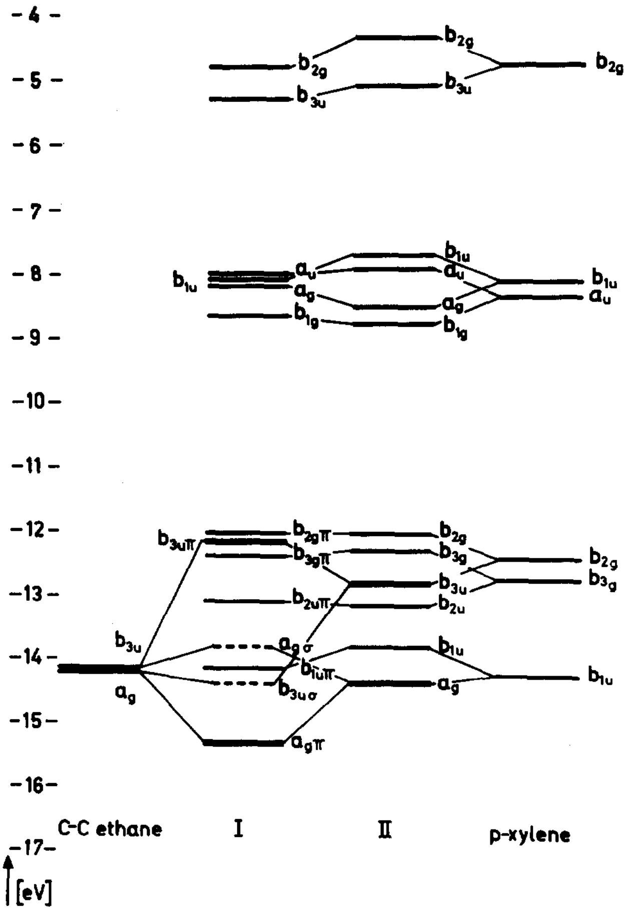


fig. 1 (The σ^*-orbitals of ethane are not included)

In II we consider a system consisting of two parallel undistorted p-xylene molecules held at a distance of 3 Å. This system corresponds in essence to the models which have been used so far as a representation for the electronic situation in [2. 2]-paracyclophane.

The coordinates of the carbon atoms in I were taken from X-ray data (5) and the position of the hydrogen atoms calculated under the assumption of R (C-H) = 1,10 Å, $\widehat{HCH}$ = 109 1/2° (c.f. standard tables (6)). Both II and I have D_{2h} symmetry. The orbital energies were obtained from an extended Hückel calculation (4). Our results are summarized in fig. 1. The split of the orbitals in II is due entirely to σ-π-interaction. The results for I show a strong interaction between the two σ-orbitals a_g and b_{3u} of the carbon bonds 7-7' and 8-8' with the π-orbitals belonging to the same irreducible representation.

As can be seen from fig. 1 the σ and π-orbitals of II and ethane are bunched close together favoring σ-π-interaction in I. This situation does not seem peculiar to I since more accurate calculations on small molecules (7) show a similar ordering of σand π-levels. This suggests that our picture is reasonable, at least on a qualitative scale.

A predicted consequence of the σ-π-interaction is the shift of the b_{3u} level towards higher, and of the a_g level towards lower energy. From this one expects, qualitatively, a strong bathochromic shift (0. 65 ev) of the B_{2u} band in the electronic spectrum of I relative to the position of the band of the same label in the spectrum of system II, and thus relative to that of the electronic spectrum of p-xylene. This conclusion should still be valid in a more sophisticated treatment.

The other transitions occuring in the near UV should be only slightly affected by σ-π-interaction, and the results derived from considerations of π-interactions only (model system II) should therefore give a satisfactory interpretation.

Thus, our treatment suggests that one of the strongly overlapping longwave bands observed in the region 280-300 nm of the spectrum of I corresponds to the shifted B_{2u} band of p-xylene (265 nm). In contrast, calculations based on model system II assign a forbidden B_{1u} state to the longwave band, while the B_{2u} band should still occur at the same position as in p-xylene (2, 3).

It is to be noted that A. Ron and O. Schnepp (8) found from crystal spectra at 20. 4°K that the lowest transition of [2. 2]-paracyclophane has B_{2u} symmetry and occurs at 329. 37 nm, in essential agreement with our conclusions.

The recently published ESR spectrum (9) of the radical anion of I indicates that the lowest antibonding orbital is b_{1g} rather than a_g in contrast to calculations carried out for model II which yields the reverse order (10). Moreover the coupling constant observed for the ring protons in the radical anion of I suggests that the thermal and vibronic mixing between the two lowest antibonding orbitals is smaller, i. e. the energy splitting is larger than in p-xylene. This coupling constant (2.97 gauss) is closer to that for the occupancy of b_{1g} alone (ca. 3.1 gauss) than the corresponding value for the ring proton in p-xylene radical anion (5.34/2 = 2.67 gauss).

From the light induced reaction of [2.2]-paracyclophane (11) one has deduced that the primary step following excitation consists in the breaking of one of the C-C carbon bonds (7-7' or 8-8').

As seen from our model, a transition $b_{3u} \longrightarrow b_{1g}$ will weaken the bonds 7-7' and 8-8' and strengthen the transannular bonds at the same time.

In the case of I the weakening seems to dominate the situation. In related molecules like [2.2]-paracyclonaphtane (11) and tetrabenzo-[2.2]-paracyclophane (12) a bond forming between the rings is preferred.

To conclude, inclusion of σ-π-interaction in the model described here, the electron structure of paracyclophanes (which could be considered as a special case of hyperconjugation) yields, even on a qualitative level, a satisfactory explanation of the electronic spectra, the ESR spectrum and the photochemical behaviour of such compounds.

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