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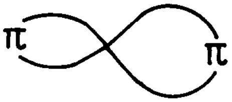
EVIDENCE FOR THROUGH-BOND INTERACTION BETWEEN MUTUALLY PERPENDICULAR PI SYSTEMS

Rolf Gleiter,* Rudolf Haider,
Jens Spanget-Larsen and Peter Bischof

Institut für Organische Chemie der Universität,
Im Neuenheimer Feld 270, D-6900 Heidelberg 1,
West-Germany

Summary: Comparison of the photoelectron (PE) spectra of tetravinylmethane (1) and trans, trans, trans-1,2,3,4-tetravinylcyclobutane (2) indicates that through-bond interaction in 2 is comparable in magnitude to the through-space spiro interaction in 1. A similar result is obtained by comparison of the UV absorption spectra of 9,9'-spirobifluorene (3) and 8b,8c,16b,16c -tetrahydrocyclobuta[1,3-1:2,4-1']diphenanthrene (4).

On the basis of model calculations we have previously postulated1) that the through-bond interaction between two π systems linked via a cyclobutane ring as in system B should be similar in magnitude to the spiro interaction in the corresponding system A. Simple model systems to test this hypothesis are tetravinylmethane (1)2) and the tetravinylcyclobutane 23), as well as spirobifluorene (3)4) and the phenanthrene dimer 45). In this communication we discuss the PE data for 1 and 2 and the UV absorption data for 3 and 4.



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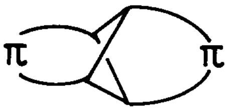

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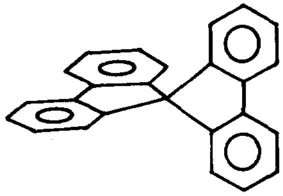

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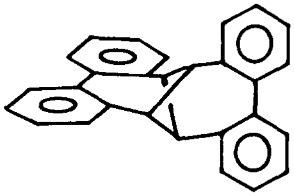

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The positions of the lowest PE bands of 1[2b,6] and 2[7] are indicated in Fig. 1. The orbital assignment is based on the results of MO calculations[8]. The

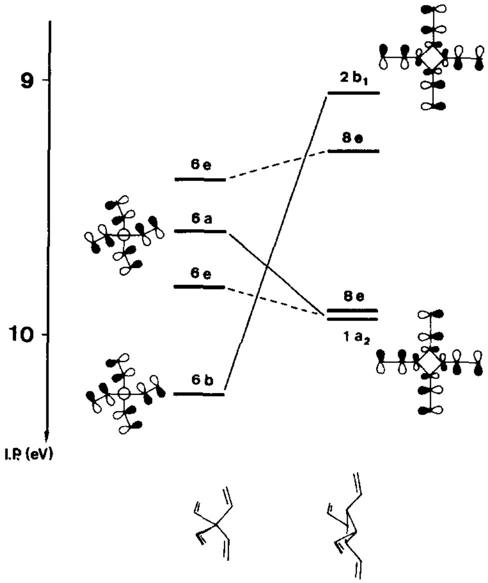

Fig. 1 Correlation between the first bands in the PE spectra of 1 and 2.

energy difference between the a_2 and b_1 levels for 2 is similar in magnitude (but different in sign) to the splitting of the corresponding levels for 1, in agreement with our general predictions[1].

Comparison of the PE data for 3[9] and 4 is complicated by the poor spectral resolution in the case of 4[11]. However, the similarity of the near-UV absorption spectra of these compounds is consistent with the assumption that long-range conjugative effects (i.e., spiro interaction in 3, through-bond interaction in 4) play a similar role in both cases. Wavenumber, polarization and relative intensity of the first five singlet transitions for 3[10,11] and 4[11] in stretched polyethylene at 77 K is indicated in Fig. 2. According to the results of simple model calculations, the fourth transition D which has no obvious counterpart in the spectrum of biphenyl or fluorene can be assigned to a state with large charge resonance character[11] (this result is in contrast to the interpretation of Sagiv et al.[10]). The considerable intensity of the observed D band (f $\sim$ 0.5) can be explained in part by long-range conjugative effects and configuration interaction[11].

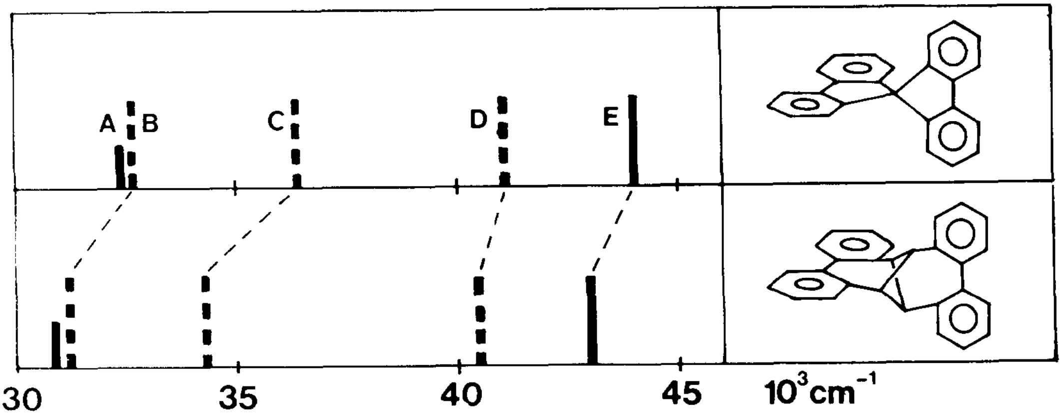

Fig. 2 Correlation between the first bands in the electronic absorption spectra of 3 and 4. Broken (solid) bars indicate polarization direction perpendicular (parallel) to the long-axis of the molecule.

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7) The gas phase He(I_α) PE spectrum of 2 shows three bands below 10 eV with relative integrated intensities 1:1:2. The band maxima are at ① 9.01 eV, ② 9.30 eV, and ③④ 9.96 eV[3b].

8) The assignment of the PE bands is based on the assumption of S_4 symmetry for 1[2b] and D_{2d} symmetry for 2[3b]; it is assumed that the doubly degenerate e levels are split by 0.4 - 0.5 eV as a result of Jahn-Teller effects in the radical cations.

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