

## Photoelectron Energy Spectra of Molecules having Classically Non-conjugated $\pi$ -Systems

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**Summary** Photoelectron spectroscopy has been used to investigate conjugative interaction between two aromatic rings which are classically non-conjugated.

However, since diphenylmethane and diphenylethane do not show additional bands with respect to toluene, we may

THE experimental observation that the 9.40 eV photoelectron band in benzene is broadened or split into two components in mono-substituted derivatives, has been taken as an experimental demonstration that the degeneracy of the upper  $\pi$ -levels in benzene is removed upon substitution.<sup>1</sup> Furthermore, in the photoelectron spectra of halogenobenzenes there are two bands which were assigned to halogen lone pairs having different amounts of interaction with the benzene  $\pi$ -electron system.<sup>1</sup> Photoelectron spectroscopy is, therefore, a suitable method for revealing conjugative interactions between different electronic groups in a molecule.

We report the photoelectron spectra of the classically non-conjugated systems, diphenylmethane, diphenylethane, and [2,2]-paracyclophane, and for comparison, biphenyl, in order to study the interaction<sup>2-5</sup> between the two aromatic rings in such molecules. The spectra (Figure) were obtained with a Perkin-Elmer PS 16 Photoelectron Spectrometer equipped with a heated probe. Diphenylmethane, diphenylethane, and biphenyl were purified commercial products while [2,2]-paracyclophane was prepared as in ref. 5. The mass spectra of the samples did not show any detectable impurity. The spectra of diphenylmethane and diphenylethane had broad and asymmetric first bands, indicating unresolved separation of two components, and four unresolved bands starting at ca. 11, 13, 15, and 16 eV (see Table). These features had also been found in the photoelectron spectrum of toluene.<sup>2</sup>

[2,2]-Paracyclophane and biphenyl had very low first ionisation potentials suggesting large  $\pi$ -delocalization. At about 11 eV, both gave complex spectra, indicating interactions between the  $\pi$ -systems. [2,2]-Paracyclophane shows a particularly broad first peak starting at ca. 7.8 eV; this is probably due to two contributions. This peak is followed by two sharper ones at ca. 9.4 and 10 eV. Biphenyl shows three sharp bands at ca. 7.9, 8.8, and 9.4 eV, the second of which is twice as intense as the other two and is again probably due to the contribution of two degenerate orbitals.

The results show that transannular effects<sup>2-5</sup> are operative in these systems, so that the fourfold degeneracy of the two pairs of doubly degenerate  $\pi$ -orbitals of the two benzenic rings is removed. The extent of the perturbation effects of the interacting  $\pi$ -systems seems greater in the [2,2]-paracyclophane since the first molecular orbitals spread in a higher energy range.

It is difficult, however, to draw any information on the relative contribution of the two resonance structures.<sup>5</sup> A comparison of the spectrum with those of other [m,n]-paracyclophanes is of crucial importance for this.

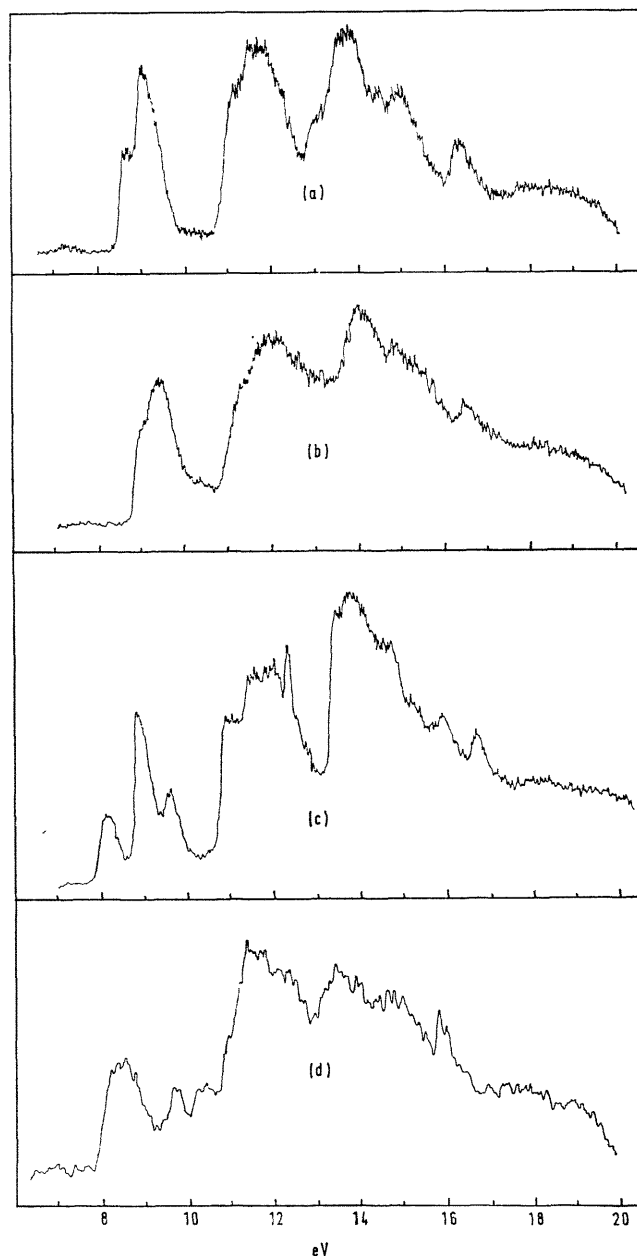


FIGURE. Gas phase photoelectron energy spectra of molecular systems containing two different benzenic rings excited by helium 584 Å radiation ( $h\nu = 21.921$  eV). (a) diphenylmethane, (b) diphenylethane, (c) biphenyl, (d) [2,2]-paracyclophane.

conclude that, if any† non-classical conjugation effect exists in the molecule, it is not strong enough to remove the diphenylmethane and diphenylethane spectra at *ca.* 11 and 13 eV appear unshifted in both the biphenyl and the

*Energy values of the pronounced maxima in the photoelectron spectra of some classically non-conjugated molecules (eV)*

Diphenylmethane .. ..	9.1			11.8	13.85	15.05	16.4
Diphenylethane .. ..	9.1			11.9	13.95	14.75	16.35
Biphenyl .. ..	8.3	9.1	9.75	11.8	14.05		16.9
[2,2]-Paracyclophane ..	8.4	9.7	10.3	11.7			

degeneracy of the two  $\pi$ -molecular orbitals of the second ring. In addition, *m*-aminobibenzyl shows a spectrum very similar to the *p*-amino toluene with the first three bands having vertical I.P.'s equal to  $7.9 \pm 0.1$ ,  $9.0 \pm 0.1$ , and  $10.5 \pm 0.1$  eV.

The two intense broad bands, which appeared in the

[2,2]-paracyclophane spectra. Interannular effects do not seem to have strongly influenced these bands; a high contribution from the electrons of the  $\sigma$ -framework is therefore likely.

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† We are now using mass spectrometry to investigate this. Homoconjugative effects in solution reactions have recently been studied.<sup>6</sup>

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