Photoelectron Spectra of Some Decahydrotrimethanoanthracenes: Observation of Large π Orbital Interactions through Six Bonds and an Apparent Violation of the *trans* Rule

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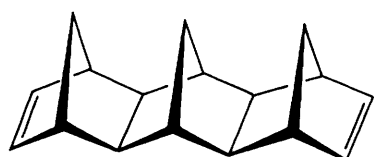[b] Chemistry Department, New South Wales Institute of Technology, P.O. Box 123, Broadway, NSW 2007, Australia

Photoelectron spectroscopic studies of the trimethanoanthracenes have revealed a large π orbital interaction through six bonds, an apparent violation of the *trans* rule and a new and effective way by which a CH_2 group can act as a through-bond relay.
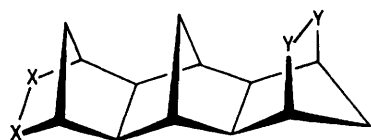
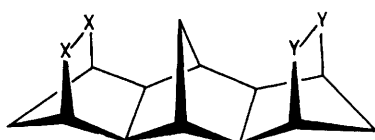Calculations have led to the following two important predictions concerning the dependence of orbital interactions

through bonds[1] (OITB) on the conformation and length of the relaying σ framework. (i) OITB are maximized for an all-
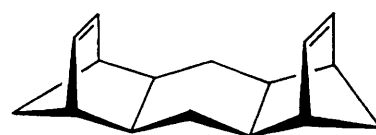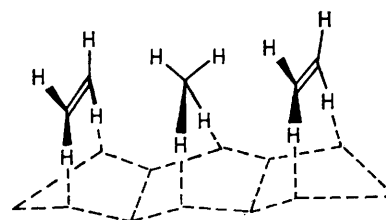
(1)

(2)

(3)

a; X-X; Y-Y = CH=CH
b; X-X = CH=CH; Y-Y = CH_2-CH_2
c; X-X = CH_2-CH_2; Y-Y = CH=CH

(4)

(5)

(6)

Table 1. Vertical π I_p's (eV) and PRDDO assignments and splitting energies ΔE(PRDDO).

Compound	π I_p	Assignment	ΔI_p	ΔE(PRDDO) /eV
(1)	8.58	$\pi - \pi$	0.32	0.17
	8.90	$\pi + \pi$		
(2a)	8.36	$\pi - \pi$	0.38	0.23
	8.74	$\pi + \pi$		
(2b)	8.68	π	—	—
(2c)	8.47	π	—	—
(3a)	8.24	$\pi - \pi$	0.52	0.49
	8.76	$\pi + \pi$		
(3b)	8.51	π	—	—
(4)	8.48[a]	$\pi - \pi$	0.87	0.75
	9.35[a]	$\pi + \pi$		

[a] Ref. 3.

trans (*i.e.* staggered) arrangement of σ bonds (the *trans* rule).[1-4] (ii) Interactions through *n* bonds (OIT-*n*-B) are attenuated only mildly with increasing *n* such that OIT-6-B and OIT-8-B could be as large as 0.2 and 0.1 eV, respectively.[1,3,4] The exiguity of experimental data has made the generality of these predictions difficult to assess. Thus only three studies, two on OIT-4-B[3,5] and one on OIT-5-B,[6] have provided supportive evidence for the *trans* rule. From a photoelectron study of a series of di-iodopolyethynes it seemed that OIT-*n*-B are attenuated with increasing *n* more rapidly than predicted, being 0.3 eV for OIT-5-B and negligible for OIT-7-B.[7] We now report the results of the first experimental study of OIT-6-B which reveal not only that such interactions can be large but also an apparent violation of the *trans* rule.

The He I photoelectron spectra of the trimethanoanthracenes (1),[8] (2),[8] and (3),[8,9] have been measured and the vertical π I_p's are given in Table 1.

The π ΔI_p of 0.32 eV for (1) is a direct measure of πOIT-6-B in this compound and is the largest value so far reported for orbitals interacting through more than 4 bonds. Indeed this result, together with that observed for OIT-4-B in (4)[3] (Table

1), suggests that OIT-8-B in the next higher 'norbornylogue' of (1) *i.e.* the corresponding tetramethanonaphthacene, should be 0.1—0.15 eV and therefore measurable. PRDDO MO[10] (PRDDO = partial retention of diatomic differential overlap) calculations on (1) gave the level ordering $\pi - \pi > \pi + \pi$ in agreement with the parity rule.

Surprisingly the π ΔI_p's increase along the series (1), (2a), (3a), reaching a maximum of 0.52 eV for (3a). This trend, which is also qualitatively reproduced by PRDDO calculations, violates the *trans* rule since on going from (1) to (3a) the number of *trans* arrangements of vicinal σ bonds progressively decreases. However this violation is only apparent and is due to the presence of additional orbital interactions mediated by the central bridging CH_2 group in (3a) and, to a lesser extent, in (2a) but which are virtually absent in (1). Supportive of this view is the observation that the measured π ΔI_p of (5), whose geometry is expected to resemble that of (3a) minus the central CH_2 group, is only *ca.* 0.2 eV.[11] This value may be taken as a measure of the magnitude of OIT-6-B in both (5) and (3a). It then follows that interactions involving the CH_2 group in (3a) amount to 0.32 eV (= 0.52−0.20 eV). A direct estimate of the magnitude of the mediating effect of the CH_2 group on the π interactions in (3a) was obtained from an STO-3G *ab initio* calculation on a model ethene–methane–ethene system, (6), whose configuration mimics that expected of the corresponding groups in (3a).† The calculated π,π splitting energy of 0.38 eV (which disappeared when the CH_4 molecule was removed) is in good agreement with the value of 0.32 eV obtained above by indirect means. A similar calculation on the ethene–methane–ethene system whose configuration now mimics that of the corresponding groups in (2a) gave a splitting energy of 0.1 eV. Thus OIT-6-B in (2a) are estimated to be 0.28 eV, *i.e.* 0.1 eV *larger* than those predicted for (3a). Therefore the *trans* rule *is* satisfied for the series (1), (2a), and (3a) *provided* that OIT-6-B alone are considered.

The lowering of the π I_p's of (2c) and (3b) by, respectively, 0.21 and 0.17 eV compared to (2b) is due to interactions between the central CH_2 group and the double bond in the former two molecules. PMO theory then tells us that the mixing of the CH_2 group with *two* double bonds, as in (3a), should be double the above interaction *i.e.* 0.34—0.42 eV. This value is in excellent agreement with that calculated for (6) (*vide supra*).

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