The Observation of Long-range Benzene–Benzene Interactions

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The linear polymethanoaromatic compounds, (**2a**—**c**), (**4a**), (**5a**), and (**6**) have been synthesized and their photoelectron spectra measured, which revealed the presence of large π orbital interactions through bonds, for (**2b,c**), and laticyclic hyperconjugative interactions in (**4a**).

Recent studies on the dienes (**1b,c**) and (**3**), using mainly photoelectron (p.e.) spectroscopy, have demonstrated[1—3] the long-range nature of orbital interactions through *m* bonds,[4] (OIT-*m*-B), in (**1b,c**) and the existence of a novel kind of hyperconjugation, called laticyclic hyperconjugation,†[3b] in which the interactions are relayed through one or more methylene groups, in (**3a**)[2] and (**3b**).[3] Because both kinds of interactions could play a significant role in electron transfer processes[3b] it seemed appropriate to investigate them between groups other than double bonds, such as aromatic and heterocyclic systems. In this respect we have synthesized the hitherto unknown compounds (**2b,c**), (**4a**), and (**5a**) and measured their p.e. spectra together with those of (**2a**),[5a] (**6**),[5c] and (**7**).[5b]

The synthesis of (**2b,c**) followed that developed for (**1b**).[6] Bromination of (**8a**)[7] gave rearranged (**9a**) which was readily converted into (**10a**) (KOBu^t, Me$_2$SO followed by Na, EtOH). Benzene annelation[8] of (**10a**) produced (**2b**).‡ Reaction of (**10a**) with hexachlorocyclopentadiene followed by reductive dechlorination of the adduct gave (**8b**), which was then converted into (**2c**) *via* (**9b**) and (**10b**).‡ Double benzene annelation[8] of (**3a**) gave (**4a**). In a similar fashion (**5a**) was synthesized from the corresponding diene.‡

The π I_p's of (**2**), (**4a**), (**5a**), (**6**), and (**7**) are given in Table 1, together with their (STO-3G) calculated[9] orbital energies and assignments.§ Two pairs of π I_p bands should be observed for (**2**), (**4**)—(**6**); that pair containing the lowest π I_p band results from mixing of the π_s orbitals [see (**11**)] of the two aromatic rings, to give MOs of a_1 and b_1 symmetries,¶ and the other pair is due to the mixing of the π_a orbitals [see (**12**)] to give a_2 and b_2 MOs.¶ Only three π I_p bands were observed for (**2a**), (**2c**), and (**4a**) due to the merging of two bands. Assignments in these cases were deduced from the relative band intensities and MO calculations.

Analysis of the data in Table 1 leads to the following conclusions.

(i) Excellent correlations exist between the calculated orbital energies and the π I_p's for the dienes (**1a**—**c**) and monoenes[1a]

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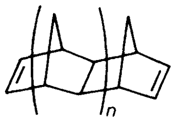
† In this type of hyperconjugation, the interacting π MOs and the $_\psi\pi$ ribbons of the methylene groups display the laticyclic topology (see M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1971, **93**, 6193) as shown by structure (7) of ref. 3a.

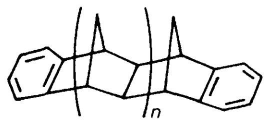
‡ All new compounds gave satisfactory combustion and spectral data.

§ A full (C_{2v} symmetry constraint) STO-3G geometry optimization on (**2a**) was performed. All other calculations were carried out on MM2 optimized geometries: D. J. Iverson and K. Mislow, *Quantum Chemistry Program Exchange*, 1980, **13**, 410.

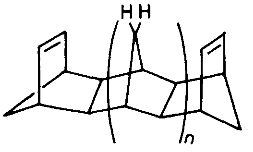
¶ $a_1 = \pi_s + \pi_s$; $a_2 = \pi_a - \pi_a$; $b_1 = \pi_s - \pi_s$; $b_2 = \pi_a + \pi_a$



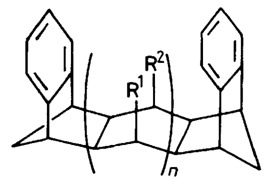
(1) a; $n = 0$
b; $n = 1$
c; $n = 2$



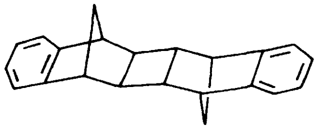
(2) a; $n = 0$
b; $n = 1$
c; $n = 2$



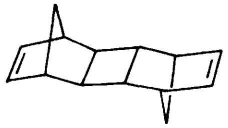
(3) a; $n = 1$
b; $n = 2$



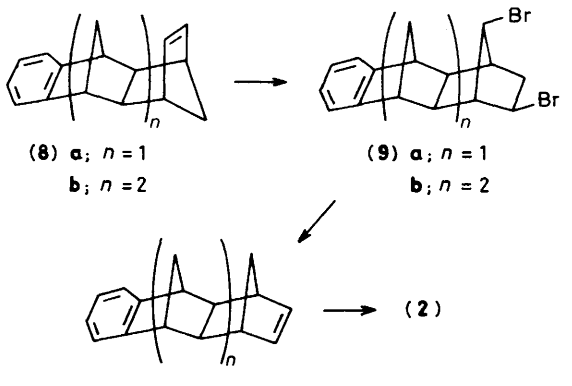
(4) $R^1,R^2 = CH_2$ } **a**; $n = 1$
(5) $R^1 = H$, $R^2 = H$ } **b**; $n = 2$



(6)



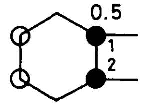
(7)



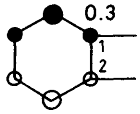
(8) a; $n = 1$
b; $n = 2$

(9) a; $n = 1$
b; $n = 2$

(10) a; $n = 1$
b; $n = 2$



π_s
(11)



π_a
(12)

($I_p = -0.97\varepsilon_\pi + 1.28$; $r = 0.95$) and for the aromatic compounds (**2a,b**) ($I_p = -1.04\varepsilon_\pi + 1.07$; $r = 0.99$). These correlations justify the application of Koopmans' theorem[10] to the data and reinforce our confidence in the assignment of π levels using STO-3G calculations.

(ii) Through-space interactions are largely responsible for the observed splitting within both $\pi_s \pm \pi_s$ and $\pi_a \pm \pi_a$ levels in (**2a**). Such interactions were found to be larger in (**4**; $n = 0$)[11] because of the better orbital overlap which must exist between the parallel faces of the aromatic rings in this molecule. The different ΔI_p (or $\Delta\varepsilon_\pi$) values for the b_1, a_1 and b_2, a_2 splittings reflect the different magnitudes of the orbital coefficients of the interacting atoms, *i.e.* 1 and 2, in π_s, (**11**), and π_a, (**12**).

Table 1. π Ionization potentials, I_p (eV), SCF (STO-3G) orbital energies, ε_π (eV), and assignments.

Compound	$\pi\, I_p{}^{a}$	ε_π	Assignment	ΔI_p	$\Delta\varepsilon_\pi$
(**1a**)	8.69^{b}	−7.54	b_1	0.86	0.80
	9.55^{b}	−8.34	a_1		
(**1b**)	8.48^{c}	-7.46^{c}	b_1	0.87	0.89
	9.35^{c}	-8.35^{c}	a_1		
(**1c**)	8.58^{d}	−7.70	b_1	0.32	0.31
	8.90^{d}	−8.01	a_1		
(**2a**)	8.17	−6.76	b_1	0.60	0.68
	8.76^{e}	−7.44	a_1		
		−7.50	a_2		
	9.05^{f}	−7.65	b_2	0.29	0.15
(**2b**)	8.10	−6.77	b_1	0.56	0.47
	8.66	−7.24	a_1		
	8.80	−7.39	a_2	0.14	0.16
	8.94^{f}	−7.55	b_2		
(**2c**)	8.23^{f}		b_1	0.26	
	8.49^{f}		a_1		
	$8.81^{e,f}$		a_2,b_2	*ca.* 0^{g}	
(**3a**)	8.24^{d}	−7.13	b_1	0.52	0.51
	8.76^{d}	−7.64	a_1		
(**4a**)	7.98		b_1	0.38	
	8.36		a_1		
	8.81^{e}		a_2,b_2	*ca.* 0^{g}	
(**5a**)	8.33^{e}		b_1,a_1	*ca.* 0^{g}	
	8.75^{e}		a_2,b_2	*ca.* 0^{g}	
(**6**)	8.26		a_g	0.31	
	8.57		b_u		
	8.95^{e}		a_g,b_u	*ca.* 0^{g}	
(**7**)	8.60		a_g	0.43	
	9.03		b_u		

[a] Value taken at centroid of band; uncertainty ±0.02 eV. [b] Ref. 13. [c] Ref. 1a. [d] Ref. 2. [e] Superposition of two bands. [f] Uncertainty ±0.05 eV. [g] Uncertainty ±0.1 eV.

(iii) The sizeable b_1, a_1 splitting energies observed for (**2b**), (**6**), and (**2c**) are attributed to the presence of orbital interactions through four, five, and six bonds, respectively. The inverted sequence of levels for (**6**), *i.e.* $a_g > b_u$, is to be expected from the parity rule.[4] The π_a, π_a splitting energies for these compounds are considerably smaller and reflect the weaker ability of π_a, compared to π_s, to overlap with the σ MOs of the molecular framework.

(iv) No splitting within the a_1, b_1 and a_2, b_2 pairs of levels in (**5a**) could be detected experimentally. This is to be expected because of the unfavourable separation of the aromatic rings (for through space interactions) and the geometry of the connecting σ bonds[4] (for OIT-6-B). However (**4a**) shows a large a_1, b_1 splitting energy of 0.38 eV. As in the case of (**3a**)[2] and (**3b**)[3] this is due to laticyclic hyperconjugative interactions between the b_1 MO and the b_1 ($_\psi\pi$) MO of the methylene group.[3b] The a_1, a_2, and b_2 π MOs of (**4a**) are expected to be unaffected by these interactions, because of their symmetry, and their energies should be identical with those of corresponding MOs in (**5a**). This expectation is borne out by the π I_p data for (**4a**) and (**5a**).

(v) The ratio of the a_1, b_1 (or a_g, b_u) ΔI_p value for each of the dienes (**1a**—**c**), (**7**), and (**3a**) to that for the respective member of the aromatic series (**2a**—**c**), (**6**), and (**4a**) has a value around 1.4. This constancy is expected since the splitting energies depend on the square of the orbital coefficient of an interacting carbon atom. Using ethene and benzene as models the STO-3G computed value for the ratio is 1.8, in reasonable agreement with the experimental result.

(vi) The b_1 levels of (**1c**) and (**2c**) lie respectively 0.77 and 0.43 eV higher than the corresponding a_1 levels of (**1b**) and (**2b**). These values indicate that extensive σ, π hyperconjugative mixing is still present in (**1c**) and (**2c**) *even though OIT-6-B in these compounds* (as measured by the ΔI_p values) *are small.* We suggest that this mixing is substantial even when the π-systems are separated by more than eight σ bonds, when OITB (*i.e.* ΔI_p) is negligible, and that it could play a more important role in long-range electron transfer processes than is thought.[12]

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