

Orbital Interactions. Part 13.¹ The Observation of Through-bond Orbital Interactions between Benzene and Double Bonds in Some Dimethanoanthracenes

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The He^I photoelectron spectra of the structurally rigid dimethanoanthracenes (5)–(8) have been measured and their spectra have been assigned on the basis of band intensities, ionization energy correlations with related molecules, and *ab initio* SCF molecular orbital calculations. The results reveal the presence of large through-bond orbital interactions in (7) and (8) which destabilize the symmetric aromatic π -based orbital to a greater extent in the all-*trans* configuration (7) and the ethylenic π -based orbital more in the *trans-cis* configuration (8). This last result reveals yet another example which demonstrates the existence of a novel laticyclic through-bond orbital interaction which is relayed through methylene groups. The antisymmetric aromatic π -based orbitals in (7) and (8) appear not to be affected by any orbital interactions.

The long-range nature of orbital interactions through σ -bonds has recently been demonstrated^{2,3,†} by u.v. photoelectron (p.e.) spectroscopic^{4,5} and electron transmission⁶ studies on the dimethanonaphthalenes (1)–(4). In these compounds the π -systems are linked through four σ -bonds. As an extension of this work, we report here the u.v. photoelectron spectra of isomers of octahydrodimethanoanthracene (5) and (6) and hexahydrodimethanoanthracene (7) and (8) and demonstrate that the replacement of one of the ethylenic π -type bonds (10) by a benzene group which contains two π -based orbitals, the symmetric Ph_S (11) and the antisymmetric Ph_A (12), results in similarly large interactions through four bonds.

An analysis of the orbital interactions in compounds (5)–(8) can be described in terms of an appropriate selection of reference orbitals, in which the interactions are absent, after which a semi-quantitative assessment of the relative through-bond orbital interactions can then be made. The chosen reference orbitals and associated energies for (5)–(8) are based on orbitals and ionization energies (13)–(15) obtained for compounds (1)–(4). It is more usual with this type of reference orbital selection to refer to experimental data for the monosubstituted compounds. The proposal here however is that for compounds (5)–(8), the symmetric $\pi + \pi$ (13)–(15) ionization energies measured for the symmetric four-bond systems of diene (3) and dibenzo-substituted compound (9) form a more suitable reference orbital set. The reasons for this selection have been presented by Paddon-Row³ and by Paddon-Row *et al.*⁴ who have demonstrated that the high

symmetry of (3) results in a smaller through-bond destabilization of the symmetric $\pi + \pi$ symmetry-adapted orbital than is observed for the related antisymmetric combination or for the single π -based orbital in (1).

The inductive and through-space orbital interactions in the related two-bond benzonorbornadiene system have been discussed by Haselbach and Rossi⁷ and Domelsmith *et al.*⁸ However, it is most difficult to unscramble the inductive and resonance orbital interactions because it is not possible to obtain simple unperturbed reference orbitals. Further, we present some evidence later which indicates that the $\pi_s + \lambda\text{Ph}_s$ ionization energy has not been correctly assigned by both of the above groups.^{7,8}

Experimental

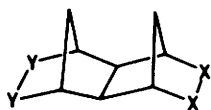
The details of the synthesis of compounds (5)–(8) will be reported elsewhere. The He^I p.e. spectra were measured on an instrument consisting of separately pumped ionization and analyser chambers. The electron analyser is a 150° double hemispherical electrostatic focusing type. The spectrometer is controlled by an on-line PDP 11/20 minicomputer which provides a repetitive 512 point analyser sweep voltage over any chosen range, and counts and stores the pulses from the detection and amplification system. Spectra can also be obtained in a single-sweep analogue output mode of operation.





The solid samples were introduced into the spectrometer *via* a stainless steel, water-cooled, solid insertion probe. The heater element consists of a bifilar coil formed from a double-wired 0.1 mm insulated tungsten element in a 1 mm outer diameter steel jacket.⁹ Thermocouples located close to the sample ampoule indicated that the temperatures required to volatilize the samples (5)–(8) were *ca.* 40–60 °C. The sample consumption rate was 2–4 mg h⁻¹.

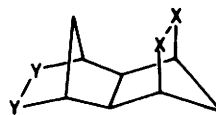
Accurate calibration of the spectra was achieved with a mixture of nitrogen (15.581 eV) and methyl iodide (9.538, 10.165 eV). The instrumental resolution was measured at *ca.* 30 meV for argon.



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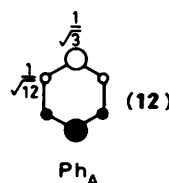
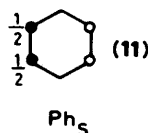
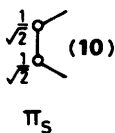
[‡] We draw attention to the nomenclature of interactions between localized orbitals and the intervening σ -framework. The mixing of symmetry-adapted combinations of μ orbitals with σ orbitals is called orbital interactions through bonds whereas the mixing of a single μ orbital with a σ -bond is called hyperconjugation. All such interactions, however, are simply related to the off-diagonal elements of a secular determinant.



- (1) Y-Y≡CH=CH, X-X≡CH₂-CH₂
 (3) Y-Y≡CH=CH, X-X≡CH=CH
 (5) Y-Y≡, X-X≡CH₂-CH₂
 (7) Y-Y≡, X-X≡CH=CH
 (9) Y-Y≡, X-X≡



- (2a) Y-Y≡CH₂-CH₂, X-X≡CH=CH
 (2b) Y-Y≡CH=CH, X-X≡CH₂-CH₂
 (4) Y-Y≡CH=CH, X-X≡CH=CH
 (6) Y-Y≡, X-X≡CH₂-CH₂
 (8) Y-Y≡, X-X≡CH=CH



$\pi_S + \pi_S$
9.35 eV
(13)



$\text{Ph}_S + \text{Ph}_S$
8.66 eV
(14)



$\text{Ph}_A + \text{Ph}_A$
8.94 eV
(15)

Table. Assignment of π_S - and Ph-based experimental vertical ionization energies (IE) and molecular orbital compositions based on STO-3G *ab initio* eigenvalues (ϵ)

Compound	IE ^a		MO Symmetry	Orbital composition ^b
(5)	8.33	-6.95	<i>a'</i>	0.89 Ph_S , 0.11 σ_{CH}
	8.83	-7.42	<i>a''</i>	0.95 Ph_A , 0.05 σ_{CH}
(6)	8.34	-6.93	<i>a'</i>	0.89 Ph_S , 0.11 σ_{CH}
	8.83	-7.43	<i>a''</i>	0.96 Ph_A , 0.04 σ_{CH}
(7)	8.22	-6.86	<i>a'</i>	0.78 Ph_S , 0.10 π_S , 0.12 σ_{CH}
	8.79	-7.45	<i>a''</i>	0.97 Ph_A , 0.03 σ_{CH}
	9.19	-7.84	<i>a'</i>	0.71 π_S , 0.11 Ph_S , 0.18 σ_{CH}
(8)	8.28	-6.92	<i>a'</i>	0.86 Ph_S , 0.14 σ_{CH}
	8.78	-7.40	<i>a''</i>	0.96 Ph_A , 0.04 σ_{CH}
	8.78	-7.43	<i>a'</i>	0.74 π_S , 0.04 Ph_S , 0.22 σ_{CH}

^a Accuracy is 0.02 eV. ^b Summed and normalized.

Results and Calculations

Figure 1 shows the He^I p.e. spectra of some octahydro- and hexahydro-anthracene isomers (5)–(8) with the low-energy regions of each spectrum (Ph^{-1} and π^{-1} bands) shown as inserts. The measured vertical ionization energies, together with calculated eigenvalues and assignments, are in the Table.

The first band of each compound (5)–(8), similarly to that of many other substituted benzenes,^{8,10,11} exhibits vibrational fine structure with a mean effective frequency of *ca.* 1 000 cm⁻¹. In this present study, the second line was assigned as the vertical ionization energy. In some substituted benzenes (*e.g.* toluene and *o*-xylene) the first line of the vibronic structure is so intense that it is usually assumed that the vertical and adiabatic ionization energies are indistinguishable. As the size and number of substituent groups is increased however, the relative intensity of this first vibrational component rapidly decreases and its energy is taken to approximate that of the adiabatic ionization. While a detailed vibronic analysis would be very desirable, the maximum resolution of the photoelectron experiment is too low to permit this except in the case of highly symmetric molecules.

The full spectra in Figure 1 show the first component of each

lowest energy band as a small shoulder with intensity well below that of the band maximum. On the other hand, when the spectra are recorded on an expanded scale (inserts in Figure 1), this first line appears to have almost the same intensity as the second and most intense component. It is thus difficult owing to problems associated with sweep rates and time constants chosen for the spectrometer operation to interpret vibrational structure for these molecules. This is further illustrated by the full time-averaged digitized spectrum shown in Figure 1c. The time constant used to record this spectrum was substantially smaller than for the single-sweep spectra of Figure 1a, b, and d; the enhanced relative intensity of the first component of the lowest energy band observed for compound (7) is a result of this.

The second ionization bands of compounds (5) and (6) (which do not exhibit any resolved vibrational fine structure) have the same total intensity as the lowest energy bands. By contrast, the total intensity of the second bands for compounds (7) and (8) is twice that of the first. This observation is not unexpected in that these molecules contain an additional π_S -type bond the energy of which appears to be approximately degenerate with the Ph_A based orbital. A further observation is that this second band for compound (7) exhibits strong vibrational fine structure with three clearly resolved maxima observed at 8.79, 9.00, and 9.19 eV. This results makes the

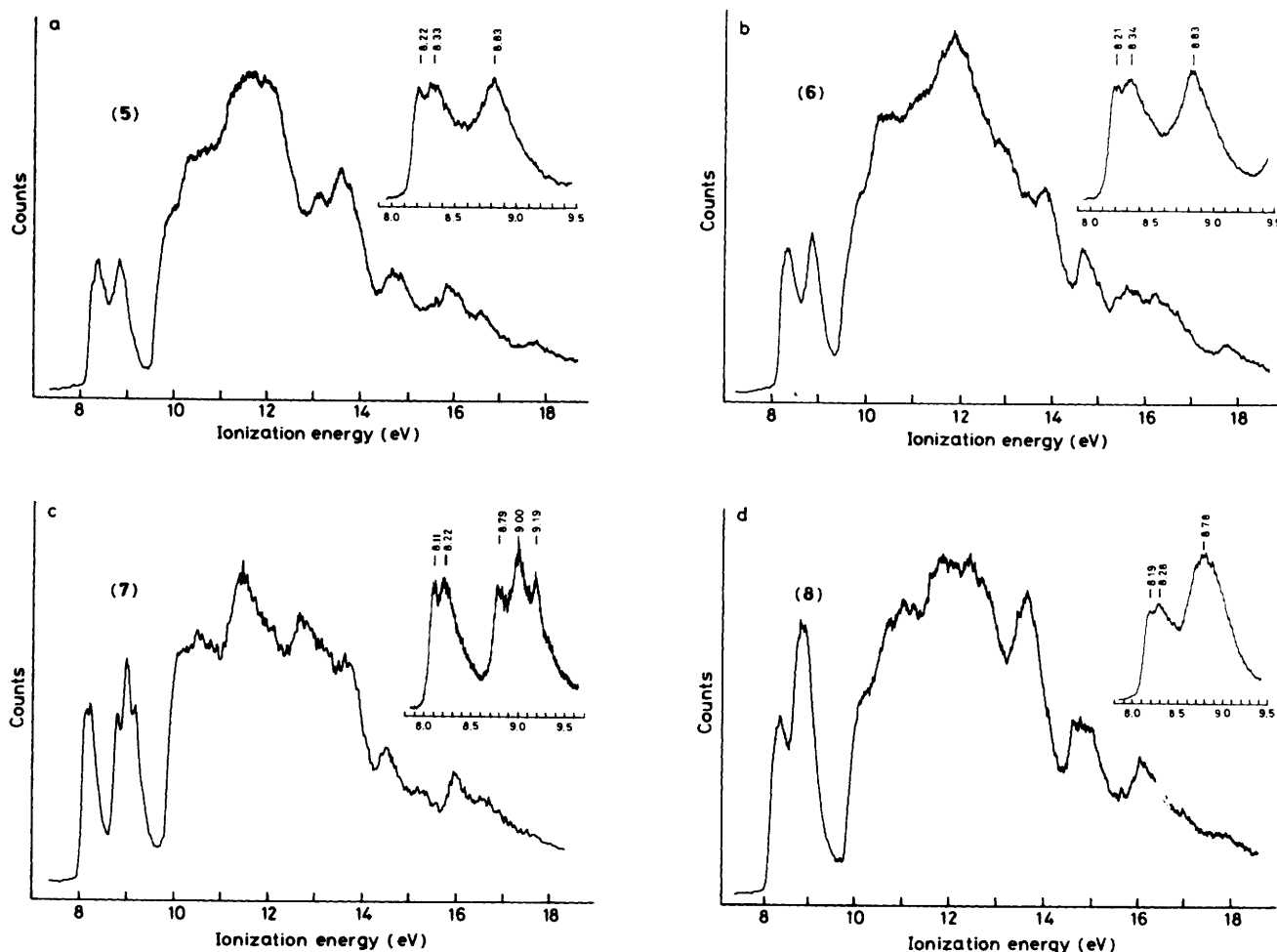


Figure 1. He^I p.e. spectra of the dimethanoanthracenes (5)–(8). Spectra a, b, and d are single-sweep spectra whilst spectrum c is a time-averaged spectrum. All inserts are single-sweep spectra

assignment of the two vertical ionization energies for this pair of overlapping bands more difficult. A band-fitting procedure might allow the vertical energies to be resolved, but since neither of the basis band shapes are known, such an analysis is non-unique. A more promising result is obtained by taking into account a detailed analysis of the SCF eigenvalues.

Ab initio SCF molecular orbital (MO) calculations¹² have been used to assist in the assignment of the photoelectron spectra of compounds (5)–(8). The calculated MO eigenvalues obtained from STO-3G basis set calculations* are compared with the experimental ionization energies of compounds (5)–(8) in Figure 2 and the Table.

For large hydrocarbon molecules, one may expect that the Koopmans' approximation¹³ ($IE = -\epsilon_{SCF}$) will provide a reasonable approximation to differences of ionization energies for the highest lying levels. This is because the orbital relaxation and correlation effects which contribute to the Koopmans' defect are sensitive to the degree of localization of each MO. These defects for the various π -based orbitals in compounds (5)–(8) and other polymethanopentacenes (2a–c)⁵ are ex-

pected to be similar. The excellent correlation that is observed between 18 calculated orbital eigenvalues of the above mentioned compounds and the π_s , Ph_s , and Ph_A ionization energies lends support to the assignment of the low-energy bands as suggested by the MO calculations.

As experimental geometries are not available for compounds (5)–(8), and standard parameters are unlikely to be accurate, the molecular geometries used in the *ab initio* calculations become an important consideration. In this study, the (BIGSTRN-2) molecular mechanics program (run with default parameters)¹⁴ was used to provide optimized molecular geometries of compounds (5)–(8).† The resulting co-ordinates were then used as input for the single point MO calculations. For the class of compounds considered here this procedure appears to give geometries which are reliable as input to MO calculations. A complete STO-3G optimum geometry for the dibenzo analogue of norbornadiene produced negligibly different orbital eigenvalues to those obtained with a BIGSTRN-2 optimized geometry in a single-point STO-3G calculation.⁵

As mentioned earlier, the unscrambling of the Ph_A and π_s vertical ionization energies from the second band in the spectrum of compound (7) (Figure 1c) has been made on the basis of the MO calculations which predict the energy split to be 0.39 eV. The only combination of the three maxima at 8.79,

* Because of limitations in available disk storage, the calculations were carried out with an integral cut-off criterion of 10^{-5} hartree instead of the usual 10^{-7} hartree limit. Selected test runs on smaller molecules demonstrated that this limit must be increased to 10^{-4} to show a significant effect on calculated π -type MO eigenvalues.

† Details of structures will be supplied upon request to the authors.

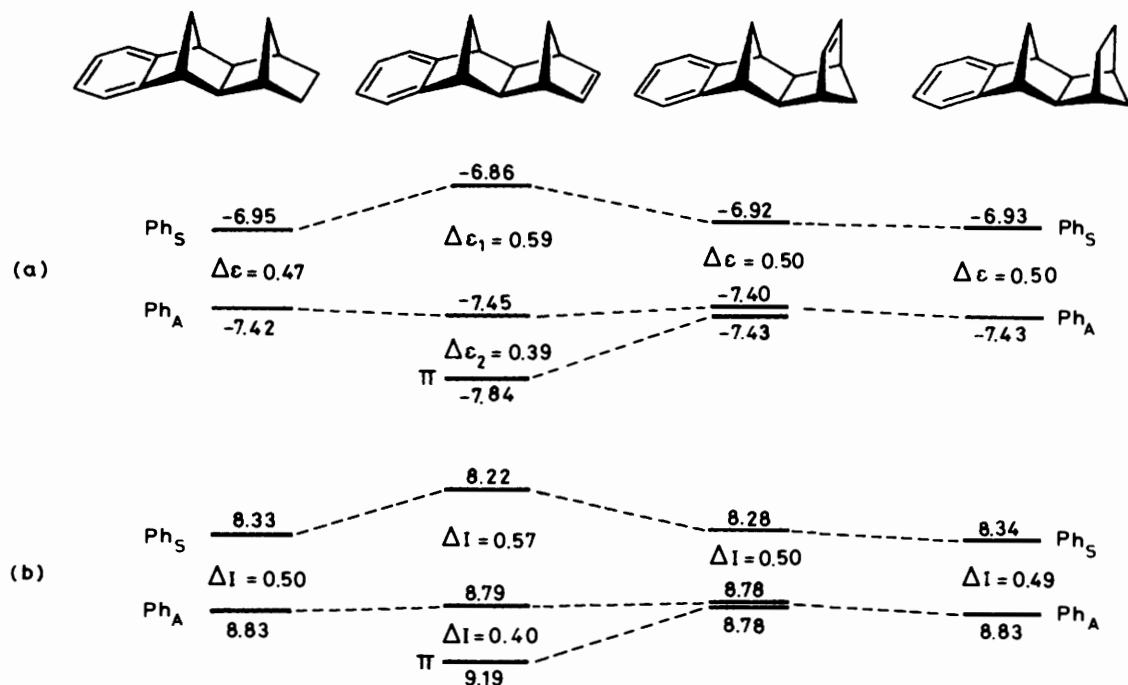


Figure 2. Correlation diagram for the Ph_S , Ph_A , and π_S ionization energies of compounds (5)–(8) based on: a, STO-3G *ab initio* orbital eigenvalues (in eV); b, Experimental vertical IEs (in eV, accuracy ± 0.02 eV)

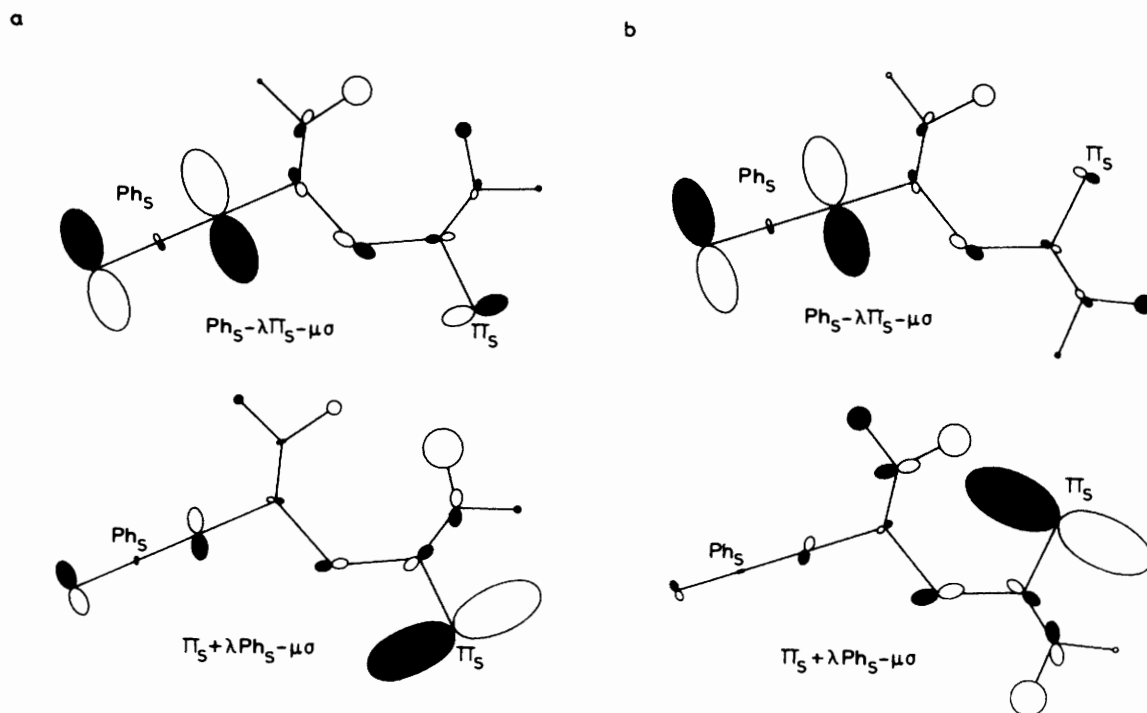


Figure 3. The Ph_S - and π_S -based molecular orbitals of: a, compound (7); b, compound (8). Each molecule orbital is represented by its projection in the molecular symmetry plane. The size of each carbon 2p and hydrogen 1s orbital indicates its contribution to the MO

9.00, and 9.19 eV in this band that comes close to the calculated result is the first and the third.

It is interesting to note that the related $\text{Ph}_A/\pi_S + \lambda\text{Ph}_S$ band in benzonornadiene as reported by Haselbach and Rossi⁷ is

also overlapped and has three resolved components at 9.05, 9.34, and *ca.* 9.5 eV. A lower ionization band associated with the $\text{Ph}_S - \lambda\pi_S$ orbital appears at 8.34 eV. Similar ionization energies have been reported by Domelsmith *et al.*,⁸ although their

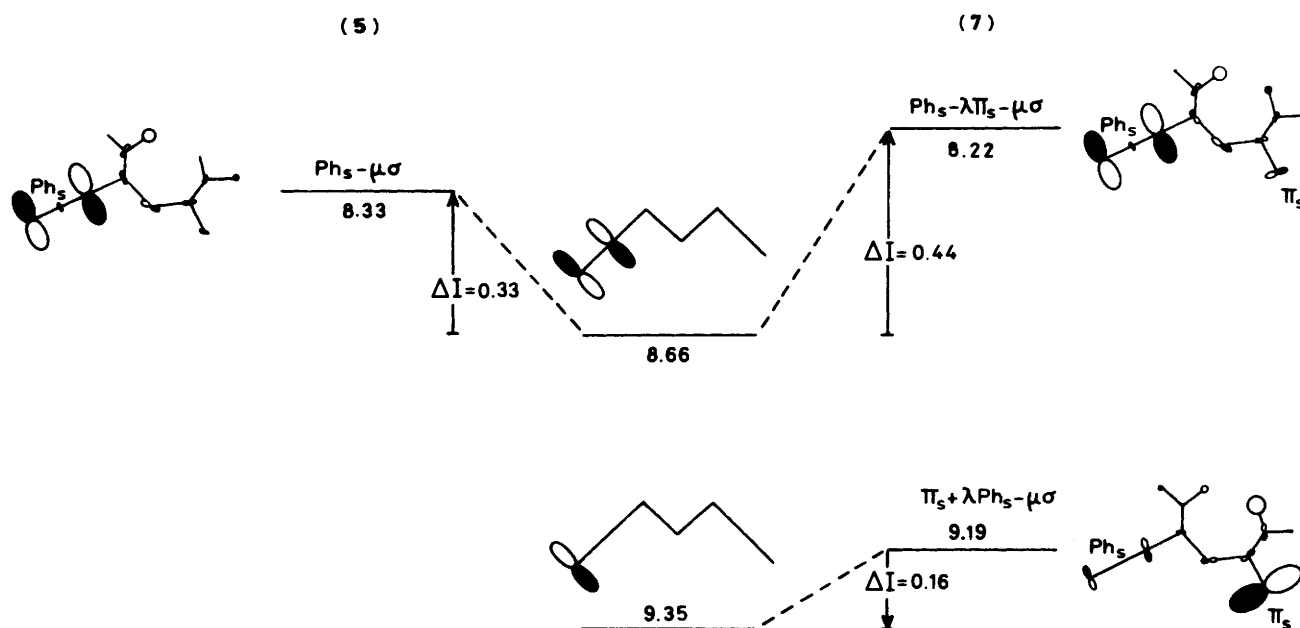


Figure 4. Correlation diagram for the ionization energies (in eV) of the π_s and Ph_s reference orbitals with the related orbitals observed for compounds (5) and (7)

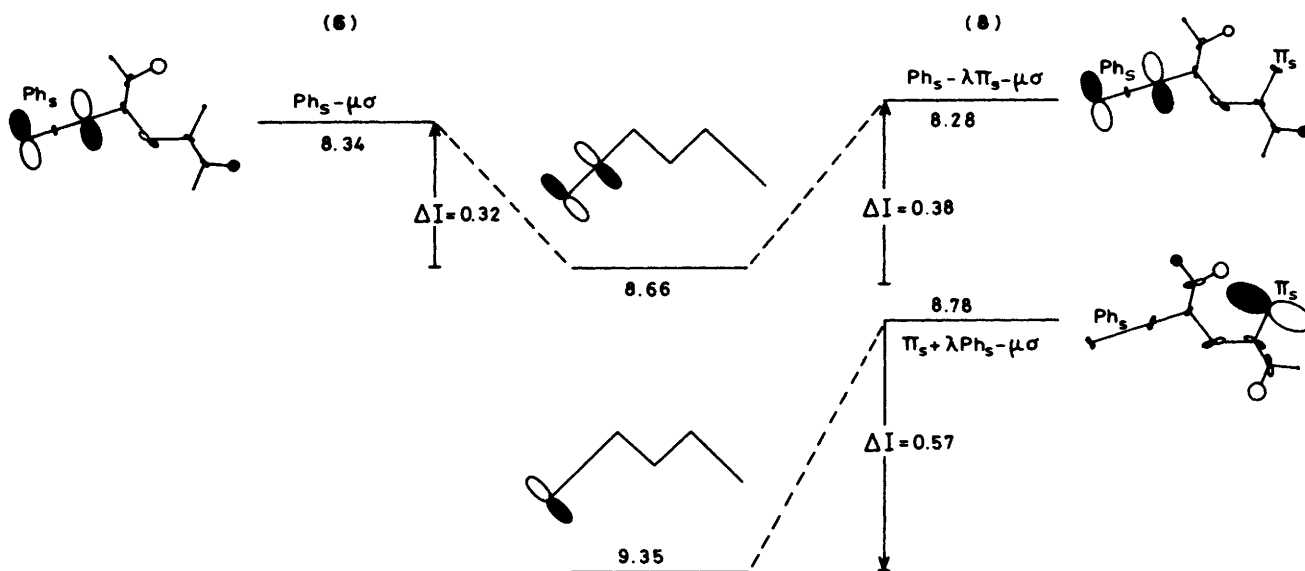


Figure 5. Correlation diagram for the ionization energies (in eV) of the π_s and Ph_s reference orbitals with the related orbitals observed for compounds (6) and (8)

spectrum was recorded at a lower resolution. Both groups have assigned the Ph_A and $\pi_s + \lambda\text{Ph}_s$ ionization energies at 9.05 and 9.34 eV respectively. A single-point 3-21G *ab initio* SCF calculation using a complete STO-3G optimized geometry for benzonornadiene yields calculated ionization energies for the $\text{Ph}_s - \lambda\pi_s$, Ph_A , and $\pi_s + \lambda\text{Ph}_s$ orbitals of 8.37, 9.02, and 9.66 eV, respectively. As with compound (7) then, it would appear that the $\text{Ph}_A/\pi_s + \lambda\text{Ph}_s$ ionization energies ought to be assigned to the first and third components of the second band rather than the first and second components. These above results lead us then to propose a revised ionization energy for the $\pi_s + \lambda\text{Ph}_s$ orbital in benzonornadiene of *ca.* 9.6 eV. This revision does not greatly affect the magnitude of the Ph_s/π_s

resonance integral and consequently the through-space orbital interaction of *ca.* 0.2 eV estimated by Haselbach and Rossi.⁷ Their neglect of the hyperconjugative interactions present in the reference orbitals is probably a more serious omission.

Discussion

(A) Ph_A Energies in Compounds (5)–(8).—The observed ionization energy of the Ph_A level shows a steady decrease from *o*-xylene at 9.09 eV through benzonornane at 8.95 eV⁸ to compounds (7) and (8) at 8.83 eV. This result is consistent with increasing inductive and resonance interactions as the alkyl substituent increases in size.

The incorporation of the ethylenic π bond in compounds (7) and (8) decreases the ionization energy of the Ph_A orbitals by 0.05 eV from the value in (5) and (6). This slight destabilization which accompanies the replacement of two σ -CH bonds by an ethylenic π -bond may be viewed as the result of increased through-bond orbital interactions between the Ph_A and deeper lying σ -levels. The inductive interaction between the Ph and π_s orbitals in these four-bond linked systems is expected to be negligible as the ionization energies reported by Houk *et al.*⁸ for a related three-bond system indicate that the inductive effects on the Ph_A and Ph_S orbitals of an ethylenic π orbital in that system are very small (*ca.* 0.03 eV).

The *ab initio* SCF canonical orbital compositions of the Ph_A orbitals (shown in the Table) indicate that the amount of σ_{CH} admixture into the Ph_A orbital ranges between 3 and 5%. Although the calculated and experimental ionization energies do not correlate exactly, the calculated result does correctly predict that the Ph_A orbital energies should remain essentially constant for compounds (5)–(8). Inaccuracies in the calculated molecular geometries will contribute to small differences between theory and experiment here.

A comparison of the ionization energy of the Ph_A reference orbital approximated by the $\text{Ph}_A + \text{Ph}_A$ level (15) at 8.94 eV with those of the Ph_A -based orbitals in (5)–(8) at *ca.* 8.81 eV reveals that the hyperconjugative and through-bond interactions in (5)–(6) and (7)–(8) respectively are essentially constant and destabilize this reference orbital by *ca.* 0.13 eV. This result confirms that the change from the C_{2h} all-*trans* geometry in (9) to the C_s ethylene-substituted all-*trans* or *trans-cis* structures has little effect on the Ph_A energy level.

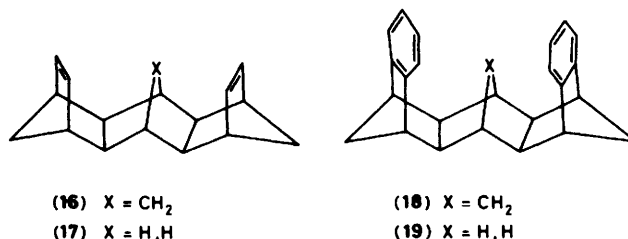
(B) Ph_S Energies in Compounds (5)–(8).—The observed ionization energy for the Ph_S orbital decreases from 8.57 eV in *o*-xylene through 8.45 eV in benzonorbornene⁸ to 8.33–8.34 eV in compounds (5) and (6), consistent with increase in the size of the alkyl framework and its associated inductive and resonance orbital interactions.

(i) Compound (7). Analysis of the MO coefficients (Table) for the Ph_S and π_s -based orbitals in (7) shows intermixing to the extent of 10%, though each of the Ph_S - and π_s -based orbitals contains an average of 15% σ_{CH} admixture.

Diagrams of these molecular orbitals (Figure 3a) show that the through-bond effect arises through admixture with a three-centre σ -orbital which is antibonding with respect to π_s in each case, but alternatively bonding and antibonding with respect to Ph_S in the $\pi_s + \lambda\text{Ph}_S - \mu\sigma$ and $\text{Ph}_S - \lambda\pi_s - \mu\sigma$ combinations, respectively. This effect is accentuated by the favourable *trans-trans* conformation of (7) and is similar to the result obtained for (3).⁴

A correlation of the π_s and Ph_S reference orbital ionization energies which are approximated by the $\pi_s + \pi_s$ (13) and $\text{Ph}_S + \text{Ph}_S$ (14) levels with those of related levels in (5) and (7) is shown in Figure 4. As for (1) and (3),⁴ the antisymmetric orbital $\text{Ph}_S - \lambda\pi_s - \mu\sigma$ in (7) undergoes the largest through-bond destabilization, at 0.44 eV [compared with 0.87 eV in (3)]. This is larger than either that observed for the $\pi_s - \mu\sigma$ orbital in (5) at 0.33 eV [compared with 0.50 eV in (1)] or for the symmetry-adapted orbital $\pi_s + \lambda\text{Ph}_S - \mu\sigma$ at 0.16 eV in (7) [compared with approximately zero eV in (3)]. The larger destabilization of the $\pi_s + \lambda\text{Ph}_S - \mu\sigma$ orbital in (7) compared with the related orbital (3) no doubt arises from the reduction in symmetry from C_{2h} (3) to C_s (7) which allows for more σ -orbital through-bond destabilization.

(ii) Compound (8). Since the energies of the Ph_S and Ph_A levels in (8) are reduced by the same amount compared with their values in (6) (Figure 2), it is reasonable to conclude that any shifts arising from through-bond interactions of Ph_S with π_s are negligible. Figure 5 shows a correlation of the π_s and Ph_S



reference orbital ionization energies, which are approximated by (13) and (14), respectively, with those observed for the related levels of (6) and (8). Figure 5 illustrates the effect of through-bond interactions on the reference orbitals when there is a change from the *trans-trans* (*t-t*) to the *trans-cis* (*t-c*) conformation.

The *ab initio* ionization energies of (8) show the same energy difference of 0.50 eV for the Ph_S - and Ph_A -based orbitals as the experimental values. Analysis of the MO coefficients (Table 1) for the π_s - and Ph_S -based MOs in (8) shows that the intermixing of the π_s and Ph_S reference orbitals is considerably reduced (4%) compared with that in (7). Further, the π_s -based orbital is admixed with considerably more σ_{CH} (22%) than the Ph_S -based orbital (14%).

A comparison of the diagrams of the Ph_S - and π_s -based MOs in (8) (Figure 3b) shows that the *trans-cis* conformation does not allow for the same favourable disposition of the three-centre bonding σ -orbital with both the Ph_S and π_s reference orbitals as is present in the *trans-trans* conformation of (7). Consequently, the extent of destabilization of the Ph_S orbital is smaller in (8) at 0.38 eV than in (7) at 0.44 eV [compared with 0.45 eV in (4) to 0.87 eV in (3)]. By contrast, in the *t-c* conformation of (8) there is considerable destabilization of the π_s reference orbital (Figure 5) of 0.57 eV [compared with 0.19 eV in (7)] by through-bond interaction which results because of the change in conformation from *t-t* to *t-c* [compared with 0.70 eV in (2a), 0.89 eV in (4), and 0.57 eV in (2b)]. Recent photoelectron studies on some polymethanoanthracenes and pentenes (16)–(19) have demonstrated the existence of a novel 'laticyclic' through-bond interaction which is relayed through one or more methylene groups.^{5,15} Figure 3b shows that in the *t-c* conformation the methylene-based orbital contribution is orientated to provide strong antibonding overlap with the ethylenic π orbital and consequently contributes to the large destabilization the π_s reference orbital in (8).

In summary, Figure 3 shows that for the Ph_S -based orbital in the *t-t* conformation of (7), the carbon $2p$ orbitals in the intervening σ -structure are orientated to provide antibonding overlap with π_s and Ph_S reference orbitals. This occurs to a lesser extent for the π_s -based orbital in the *t-t* conformation. However, for the Ph_S -based orbital in the *t-c* conformation of (8), the intervening σ -structure overlaps with Ph_S but not with π_s . In the π_s -based orbital in the *t-c* conformation, the intervening σ -structure does not overlap with Ph_S but does with π_s .

Examination of the spectra of (5) and (6) in Figure 1 reveals that although the low-energy regions of the spectra are similar, this is not the case for the higher energy regions. In particular, the change from the *trans-trans* to the *trans-cis* conformation in (5) and (6) respectively appears to destabilize an orbital with an energy at *ca.* 12 eV in (5) *ca.* 13 eV in (6). Other distinctive differences in the higher energy regions for (5)–(8) exist, but they are not discussed further here.

Conclusion

The significance of this work is that it has allowed a dissection of the through-bond orbital interactions in a series of rigid

dimethanoanthracenes (5)–(8). Conformation is shown to determine which of the aromatic Ph and ethylenic π orbitals undergo the greatest interaction through four bonds and the importance of laticyclic interactions in which methylene groups relay through-bond interactions is observed. The aromatic Ph_A orbital is shown to be affected least by such interactions. The use of the molecular mechanics method to obtain optimized molecular geometries cheaply prior to *ab initio* MO calculations has been shown to work well. Finally, the SCF *ab initio* MO results reproduce the experimental energy splittings very well and provide a useful technique for the assignment of photoelectron spectra which includes the unscrambling of the complex orbital interactions present in compounds of this type.

Acknowledgements

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