An INDO-MO study of the spectral properties and transannular interaction in [6]-helicene

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The INDO-MO calculations on [6]-helicene reported here enable one to classify the four HOMO's as predominantly π, in contrast to other occupied MO's. A linear adjustment of these four HOMO's correlates well with the experimental photoelectron and optical spectra. Viewed through Mulliken's overlap population between overlapping rings, the transannular interaction in [6]-helicene appears to be unfavourable and therefore minimised. The use of a skeleton representation of the molecule is considered and found inadvisable.

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Les calculs des orbitales moléculaires INDO de l'hélicène-[6] que l'on rapporte ici permettent de confirmer que les 4 orbitales moléculaires HO sont d'une façon prédominante de type π, ce qui est à l'opposé des autres orbitales moléculaires occupées. Un ajustement linéaire de ces 4 orbitales moléculaires s'harmonise bien avec les spectres photoélectronique et optique expérimentaux. En se basant sur la population de recouvrement de Mulliken entre les deux cycles qui chevauchent, l'interaction transannulaire dans l'hélicène-[6] semble être défavorisé et de ce fait est minimisée. On a envisagé l'emploi d'un modèle pour représenter la molécule mais l'expérience montre que c'est à déconseiller.

[Traduit par le journal]

Introduction

In recent years, a number of experimental and theoretical studies have been reported on [5]- to [14]-helicenes (1–3). The main objectives of the present INDO-MO calculations (4) are the following: (*1*) to examine the INDO-MO energy levels of [6]-helicene (X-ray geometry (5)) in relation to its experimental photoelectron (PE) and optical spectra; (*2*) to compare the agreement between INDO and PE and optical spectra of [6]-helicene with that for its constituent unit benzene (experimental geometry (6)); (*3*) to obtain a semi-quantitative account of transannular interaction (TI), i.e., secondary π delocalisation, between overlapping rings in the molecule; (*4*) to study the consequences of employing a skeleton model upon PE and optical spectra, σ–π mixing and TI in the molecule (see Fig. 1). The broad conclusions reached here might remain valid for higher members of the helicene series.

Results and Discussion

(*1*) *Energy Levels of Benzene and* [6]*-Helicene (X-ray Geometry)*

A comparison (Table 1) of INDO-MO energy levels of benzene with those from *ab initio* (7) and PE (8) spectral data[2] shows that the INDO ordering of the $a_{2u}\pi$ level (π_{11} in Table 1) is incorrect. Since the σ and π AO's do not mix in any benzene MO, Fig. 2 clearly indicates two separate dependences of the σ and π MO's instead of a collective dependence (9). The four π levels show a least-squares linear fit (in eV),

$$[1] \quad -(\mathrm{IP})_i = 0.276\varepsilon_i - 5.72$$

with an rms error of 0.07 eV (Fig. 2). The π–π* transition energies, calculated from INDO-MO levels adjusted by eq. [1], compare well with the corresponding experimental (10) results (Table 1).

The INDO lowering, $|\varepsilon_{\mathrm{INDO}}| - \mathrm{IP}$, of the HOMO (π) energy for benzene is quite high, 4.02 eV (Table 1). The calculated occupied π levels of benzene clearly reflect an exaggerated delocalisation energy which seems to be an artefact of INDO calculations on such planar systems. In contrast, the INDO lowering of the HOMO energy in [6]-helicene is 1.98 eV (Table 2), since extensive σ–π mixing[3] in this non-planar molecule raises the π orbitals in energy; in other words, non-planarity causes a loss in delocalisation energy. One therefore concludes that in planar aromatics where no mixing of σ and π AO's occurs, with increasing delocalisation the INDO method is likely to provide increasingly exaggerated delocalisation energies, whereas for non-planar molecules where extensive σ–π mixing occurs the INDO method would provide a more realistic description.

(*2*) *Nature of the MO's in* [6]*-Helicene*

In spite of extensive σ–π mixing it is possible to study the MO's of [6]-helicene in a manner which

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[2]Used in conjunction with the Koopmans theorem, viz. $-(\mathrm{IP})_i = \varepsilon_i$, where $(\mathrm{IP})_i$ and ε_i are experimental ionisation potential and energy, respectively, of the *i*th MO.

[3]σ and π refer separately to each ring in [6]-helicene, and not to the whole molecule.

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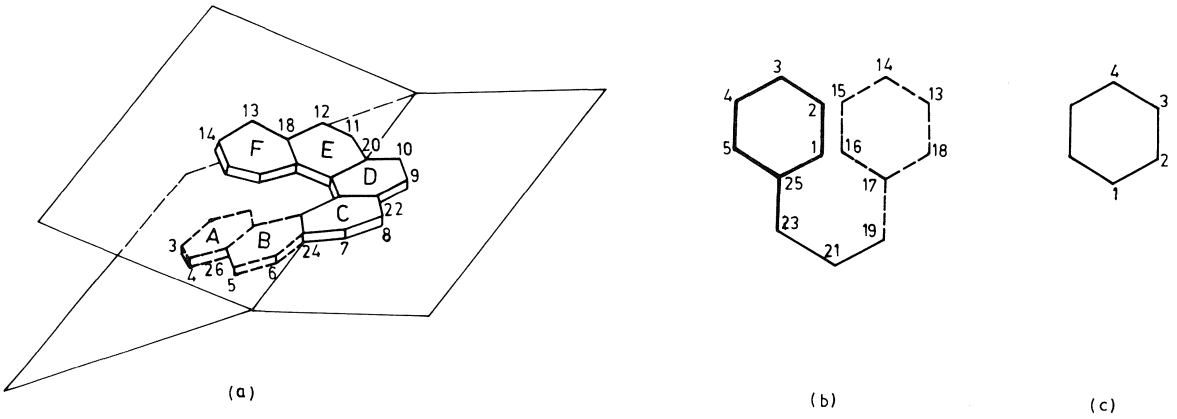

FIG. 1. (*a*) [6]-Helicence, (*b*) skeleton model of [6]-helicene, and (*c*) benzene. The same atom numbering is used for both (*a*) and (*b*) and hence some of those in (*b*) are not repeated in (*a*) for clarity. The H-atom numbering is the same as that of the C atom to which H is bonded. (*a*) is drawn after ref. 5. (*b*) is of C_2 symmetry with the two phenyl fragments, thick and dotted, respectively, above and below the plane of paper by 29.25°. In (*b*), the C—C and C—H bond lengths are taken as arithmetic means of the corresponding values in X-ray geometry, viz., 1.41 and 1.08 Å respectively, while all CCC angles are taken as 120°.

TABLE 1. INDO-MO and *ab initio* (7) MO energies compared with experimental ionisation potentials (8) of benzene. The "virtual orbital IP's" are *calculated* from PE and optical spectra (Koopmans theorem). The calculated and experimental (10) transition energies are given only for the first three bands. All values are in eV

MO type	INDO energy	*Ab initio* energy	−(IP)	α, *p*, β transition energies in ascending order	
				Calcd.	Expt.
π_{18}^*	9.71	—	−3.16	4.88	4.80
π_{16}^*, π_{17}^*	4.55	—	−4.56	6.29	6.14
π_{14}, π_{15}	−13.32	−9.25	−9.30	7.47	6.75
σ_{12}, σ_{13}	−13.63	−13.41	−11.40		
π_{11}	−22.81	−13.74	−12.1		
σ_9, σ_{10}	−18.63	−16.10	−13.8		
σ_8	−19.58	−16.95	−14.7		
σ_7	−20.80	−17.46	−15.4		
σ_6	−28.60	−19.48	−16.9		
σ_4, σ_5	−30.10	−22.50	−19.2		
σ_2, σ_3	−38.20	−27.79	−22.5		
σ_1	−51.60	−31.56	−25.9		

permits one to characterise the four HOMO's of the molecule as predominantly π, as follows. The orientation of the resultant *p* AO on a carbon atom with respect to the *X*-axis which is approximately perpendicular to the planes of the rings C, D (Fig. 1), together with an idea of the torsional angle of the planes[4] of A, B and E, F makes it possible to classify the resultant *p* AO in an MO as predominantly σ, π, or just σ–π. This permits classification of the four HOMO's as predominantly π, *in contrast to* the other occupied MO's whose σ character increases as one goes to higher binding energy. It may be noted that Obenland and Schmidt (3) empirically assign the π levels to be above 10 eV in the PE spectrum, thereby designating the first eight PE bands as π.

Although the nine HOMO's of [6]-helicene, for which PE spectral bands have been reported, apparently show a fairly good linear correlation (Fig. 3), such a correlation yields transition energies which are three to four times the corresponding experimental values. In accordance with the above observations on the π MO's of benzene and [6]-helicene, the four HOMO's and two LUMO's (Table 2) of the latter have been gathered into a

[4]It should be noted, however, that no two rings in the molecule are strictly coplanar.

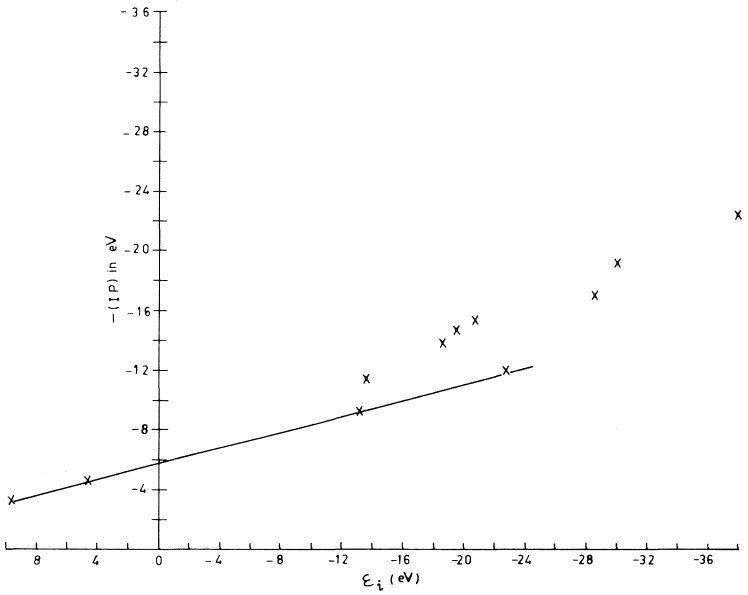

FIG. 2. Plot of experimental ionisation potentials $(IP)_i$ vs. INDO-MO energies (ε_i) of benzene. The "virtual orbital IP's" are calculated from observed PE and optical spectra (Koopmans theorem).

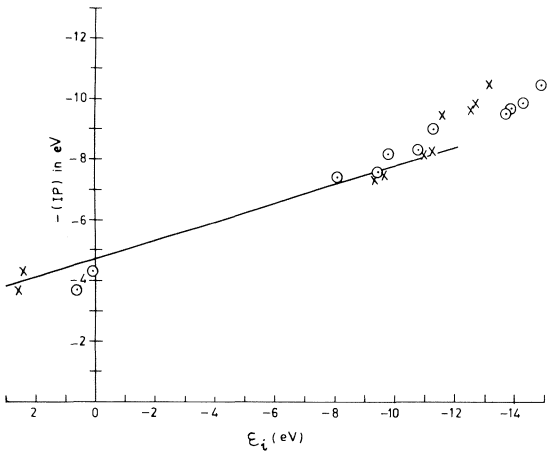

FIG. 3. Plot of experimental ionisation potentials $(IP)_i$ vs. INDO-MO energies (ε_i) of [6]-helicene in X-ray geometry (×) and skeleton model (○). The "virtual orbital IP's" are calculated from observed PE and optical spectra (Koopmans theorem).

least-squares linear (Fig. 3) expression,

$$[2] \quad -(IP)_i = 0.300\varepsilon_i - 4.74$$

with a slightly high rms error of 0.22 eV; this is due to a lack of perfect correlation between the MO's because of their differing π character, unlike benzene where the four MO levels are purely π. The close similarity between the slopes in eqs. [1] and [2] is quite significant, indicating that our characterisation of the four HOMO's as predominantly π is justified and a similar slope ($\sim$0.3) is likely to be encountered in INDO calculations on other helicenes. Since the agreement between the experimental and calculated (after adjustment according to eq. [2]) electronic transition energies is fairly good (Table 2), the identification of the α, p, and β bands as π–π^* transitions (2, 3, 11) is adequate.[5] In view of these observations, the skepticism (3) regarding INDO calculations on such molecules seems unjustified.

TABLE 2. Several INDO-MO energies, experimental (3) ionisation potentials and the first three transition energies of [6]-helicene. The "virtual orbital IP's" are *calculated* from PE and optical spectra (Koopmans theorem). All values are in eV and values in parentheses refer to the skeleton model

		α, p, β transition energies in ascending order	
INDO energy	−(IP)	Calcd.	Expt.
2.62(0.66)	−3.69	3.53 (3.18)	3.04
2.42(0.21)	−4.33		
−9.35(−8.11)	−7.37	3.59 (3.36)	3.68
−9.64(−9.53)	−7.50	3.62 (3.72)	
−11.02(−9.81)	−8.18		
−11.31(−10.84)	−8.30	3.68 (3.90)	3.93
−11.43(−11.41)	−8.97		
−11.55(−13.71)	−9.53		
−12.57(−13.94)	−9.74		
−12.65(−14.26)	−9.94		
−13.19(−14.87)	−10.50		

[5]This prescription (12) is somewhat arbitrary. Negative bond orders occur inevitably in such MO calculations irrespective of which axial system is employed (see, e.g., ref. 13).

TABLE 3. $n(r,s)$, $d(r,s)$, and $d'(r,s)$ values in au calculated for a few non-bonded pairs of atoms in [6]-helicene, whose interatomic distances are relatively small (Fig. 1)

Distance between atoms (Å)	Non-bonded pair	$n(r,s)$	$d(r,s)$	$d'(r,s)$
3.09	$C_{16}C_{25}$	0.0006	0.0673	−0.0431
3.10	$C_{16}C_{23}$	0.0004	0.0765	−0.0073
3.15	$C_{17}C_{23}$	−0.0024	0.2476	−0.0506
3.22	C_1C_{16}	0.0008	0.0656	0.0082
3.22	C_1H_{16}	−0.0002	0.0183	0.0021
3.28	$C_{17}C_{25}$	0.0001	0.0449	0.0323
3.40	H_1H_{16}	0.0000	0.0008	0.0008

TABLE 4. Mulliken overlap populations, $n(r,s) \times 10^4$, in au between certain non-bonded atom pairs in [6]-helicene (Fig. 1). Values in parentheses refer to the skeleton model and are listed only where they differ from the X-ray geometry

Atom	C_1	C_2	C_3	C_4	C_{23}	C_{25}	C_{26}
C_{14}	0	0	0	0	0	0	0
C_{15}	−1	0	0	0	0	0	0
C_{16}	8(−4)	0(−1)	0	0	4(−13)	6(54)	0(−1)
C_{17}	0	0	0	0	−24(−65)	1(14)	0

(3) Transannular Interaction

By virtue of their greater flexibility the helicenes can minimise TI which would otherwise increase their total energy, if the interaction is of the Möbius-type (3). An indication of the electron density between overlapping rings in [6]-helicene would help to assess the nature and extent of this interaction. It was found that of the three quantities given below, the Mulliken overlap population (MOP) is the most suitable index of overall electron distribution between a pair of bonded or non-bonded atoms (14). These quantities are:

$$[3] \quad d'(r,s) = \sum_{\mu\varepsilon r} \sum_{\nu\varepsilon s} P_{\mu\nu}$$

$$[4] \quad d(r,s) = \sum_{\mu\varepsilon r} \sum_{\nu\varepsilon s} |P_{\mu\nu}| \quad \text{(ref. 12)}^5$$

$$[5a] \quad n(r,s) = \sum_{i} \sum_{\mu\varepsilon r} \sum_{\nu\varepsilon s} n(i,\mu,\nu)$$

$$[5b] \quad n(i,\mu,\nu) = 2N_i C_\mu(i) C_\nu(i) S_{\mu\nu}$$

where $P_{\mu\nu}$ is a density matrix element of INDO calculations with the AO's μ and ν centred on the atoms r and s respectively; N_i is the occupation number of the ith MO; $C_\mu(i)$ is the LCAO coefficient of the μth AO of atom r in the ith MO and $S_{\mu\nu}$ is the overlap integral. Table 3 shows that there is no correspondence between $n(r,s)$ and either $d(r,s)$ or $d'(r,s)$, and Table 5 shows that, for benzene, $n(r,s)$ is the most reliable index of electron distribution. Tables 3 and 4 list the MOP values for a few atom pairs from overlapping rings in [6]-helicene. The sign of MOP indicates the favourable (positive sign) or unfavourable (negative sign) nature of TI while its magnitude is a measure of the strength of this interaction.

Table 3 indicates that the secondary π delocalisation between overlapping rings depends more sensitively on the relative orientations of the π orbitals concerned than on the interatomic distances. The values listed in Table 4 are quite small and confirm the earlier suggestion (3) that TI in [6]-helicene is unfavourable and therefore minimised. This is specifically reflected by the fact that the largest value of $n(r,s)$, viz., −0.0024, for the pair C_{17}, C_{23} is nearly equal in magnitude to the value of 0.0023 for C_1, H_3 in benzene.

(4) Effects of using a Skeleton Model for [6]-*Helicene*

Since the MO's of the skeleton model $C_{15}H_{10}$ (Fig. 1) show an overall linear correlation (Fig. 3), none of the occupied MO's can be classified as predominantly σ or π, in contrast to benzene or the X-ray geometry. Further, such a linear correlation embracing all the points does not reproduce the optical spectrum, although the five HOMO's of $C_{15}H_{10}$ have higher energies than the corresponding MO's of X-ray geometry because of an in-

TABLE 5. $n(r,s)$, $d(r,s)$, and $d'(r,s)$ values in au, calculated for non-bonded pairs of atoms in benzene (Fig. 1)

Interaction between	$n(r,s)$	$d(r,s)$	$d'(r,s)$
C_1C_4	−0.0115	0.4726	−0.3966
C_1H_1	0.6767	1.3461	−0.3067
C_1H_2	−0.0069	0.0605	−0.0605
C_1H_3	0.0023	0.1867	0.1867
C_1H_4	0.0001	0.0302	0.0302

creased $\sigma-\pi$ mixing in the former. Therefore, as with the X-ray geometry, a linear relationship was tested for only four HOMO's and two LUMO's, viz.

$$[6] \quad -(IP)_i = 0.382\varepsilon_i - 4.17$$

where the slope is considerably different from that in benzene or the X-ray geometry. Although eq. [6] well reproduces optical spectral results, such an agreement is superficial since there is no reason to differentiate the four HOMO's from other occupied MO's as far as $\sigma-\pi$ mixing is concerned. Furthermore, taken together, the skeleton energy levels show a worse agreement with experimental IP's and transition energies as compared with the unadjusted levels of X-ray geometry (Table 2).

The skeleton model also displays a different pattern of TI (Table 4) because of different orientations of the $p\pi$ AO's, as compared with the X-ray geometry. Except for two of the non-vanishing $n(r,s)$ values, the rest are negative, apparently indicating an unfavourable interaction. However, since the two largest $n(r,s)$ values, 0.0054 and -0.0065 for the atom pairs C_{16}, C_{25} and C_{17}, C_{23} respectively, are comparable in magnitude, one cannot conclude (*i*) whether TI in the skeleton is unfavourable or not, and (*ii*) if unfavourable, whether TI is minimised.

Thus we conclude that information and interpretations obtained from the skeleton model are not only quite different from those of the X-ray geometry, they are by and large unrealistic, although five skeleton HOMO's superficially show a "better" agreement with IP values (Table 2). Therefore in making semi-empirical MO calculations on large molecules, it is not always physically meaningful to replace the real molecules with certain skeleton ones.

Conclusion

The present INDO-MO calculations identify four HOMO's of [6]-helicene as predominantly π, in contrast to other occupied MO's. In a plot of $-(IP)_i$ of helicene against the corresponding ε_i(INDO), those MO's which are linearly correlated by a slope of ~ 0.3 should be predominantly π. Such a classification for [6]-helicene well reproduces its PE and optical spectra. The transannular interaction between overlapping rings in the molecule is examined by means of Mulliken overlap population. This confirms an earlier suggestion (3) that the TI in [6]-helicene is unfavourable and therefore minimised. The use of a skeleton model as a substitute for the real molecule was found to lead to unrealistic information and interpretation regarding $\sigma-\pi$ mixing, PE and optical spectra, and TI in the molecule. Therefore, one should be very careful in making such substitutions in semi-empirical calculations on large molecules.

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