Photoelectron Spectrum and Electronic Structure of Indigo

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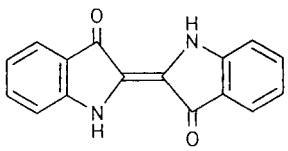
Received March 31, 1992

Key Words: Photoelectron spectrum / Electronic structure / Indigo / Calculations, AM1, HAM/3, MNDO, PM3

The He(I) photoelectron spectrum of indigo has been obtained by evaporating the compound at ca. 400°C. The ionization potentials are related to orbital energies or electronic states of the radical cation with the aid of semi-empirical SCF-MO calculations. A satisfactory interpretation of the spectrum up to 18 eV is obtained according to the HAM/3 method.

Indigo (**1**) is one of the oldest and still most important organic dyes. Compared with other mesomeric systems of similar size, the light absorption of indigo occurs at a remarkably long wavelength. This has stimulated many investigations on the relation between color and constitution[1-4]. We have studied the electronic structure of indigo by UV photoelectron spectroscopy and quantum chemical calculations.



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Results

The PE spectrum of indigo is shown in Figure 1, the ionization potentials are summarized in Table 1.

In the low-energy region (<12 eV) the spectrum shows four bands of approximately similar intensity. These are marked in the spectrum as 1, 2, 3 and 8. Between ca. 9.0 and 10.0 eV a broad and very strong band is found, which, according to its intensity, corresponds to four ionizations, numbered 4–7. The rather low first *IP* of ca. 7.0 eV (adiabatic) is reflected in the ability of indigo to be readily oxidized.

Table 1. Observed and calculated ionization potentials [eV] of indigo

Obsd.	Calcd.[a]	Assignment
7.31	7.80	$\pi_{11}\ 6A_u$
8.26	8.56	$\pi_{10}\ 5B_g$
8.85	8.75	$n_O\ A_g$
9.2 sh	9.17	$n_O\ B_u$
9.37	9.17	$\pi_9\ 5A_u$
9.5 sh	9.19	$\pi_8\ 4B_g$
9.7 sh	9.44	$\pi_7\ 4A_u$
11.00	10.80	$\pi_6\ 3B_g$

[a] HAM/3 results.

An interpretation of the PE spectrum should be possible with the aid of quantum chemical calculations. On the basis of Koopmans' theorem[5] orbital energies ε_i are related to vertical ionization potentials IP_i. Many investigations have shown that there is a linear correlation of the form shown in eq. (1)[6].

$$IP_i = a \cdot (-\varepsilon_i) + b. \qquad (1)$$

In the HAM/3 method orbital energies cannot be used, but *IP* values are calculated directly[7].

Semi-empirical SCF-MO calculations on indigo with full geometric optimization have been performed by the MNDO[8], AM1[9],

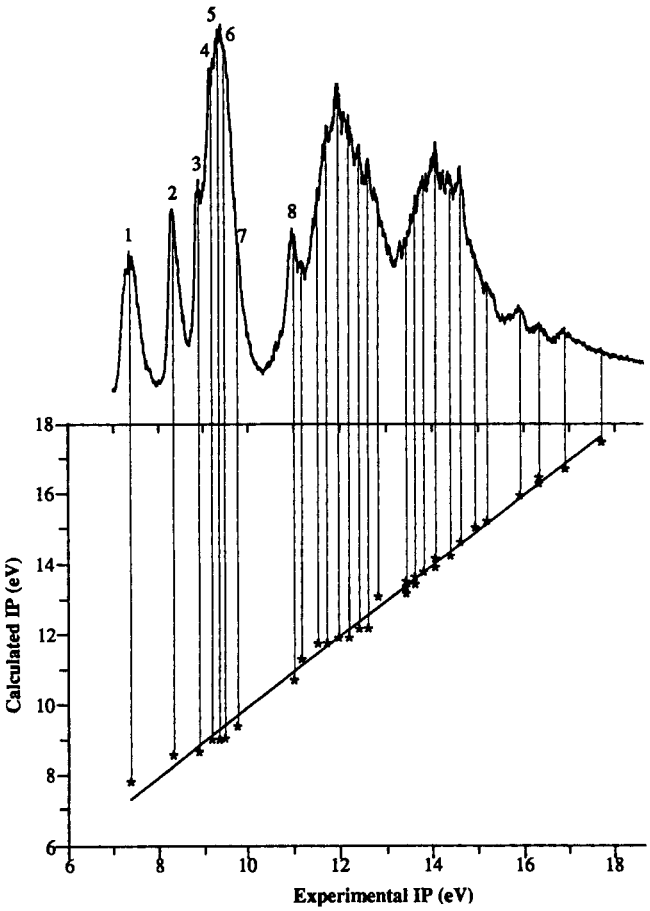

Figure 1. PE spectrum of indigo and correlation with HAM/3 results

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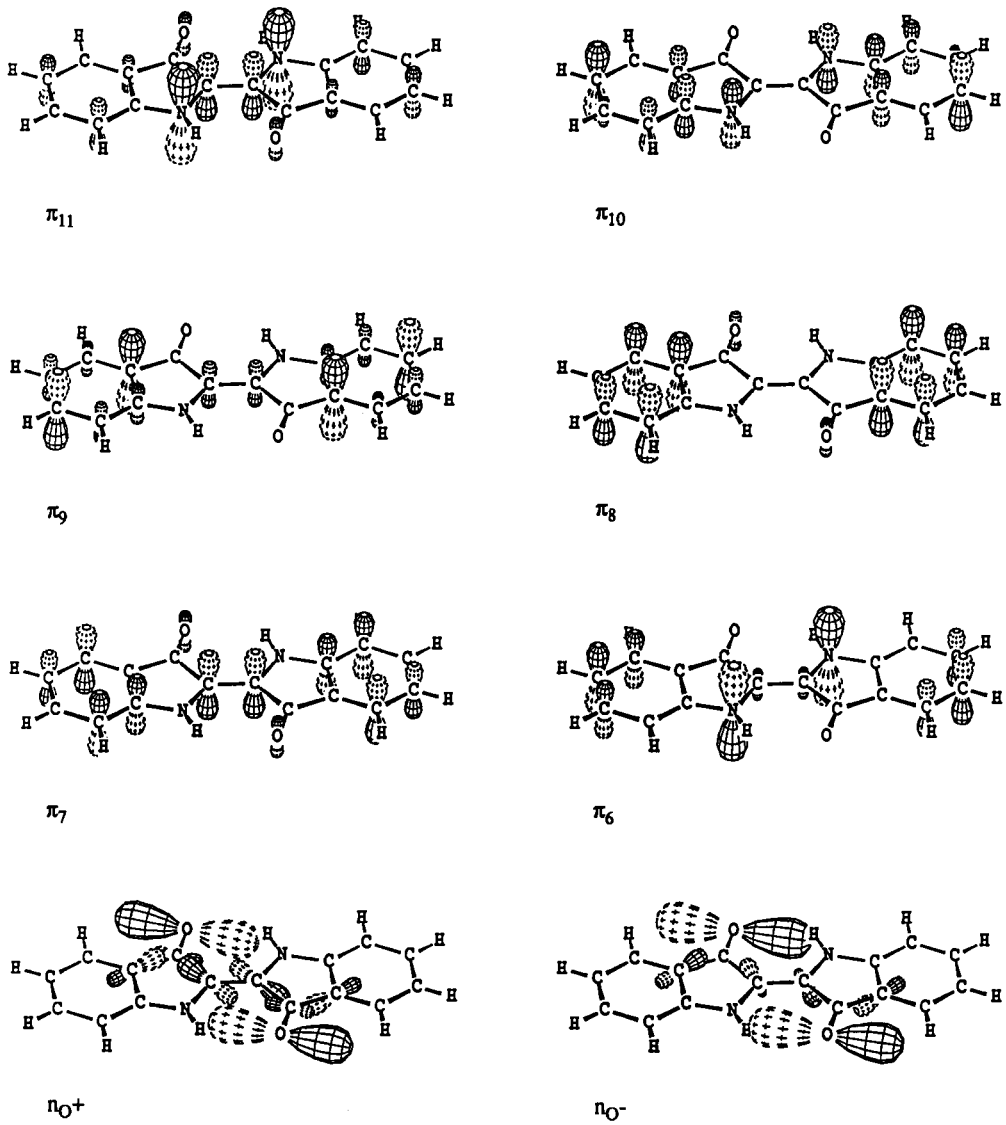

Figure 2. π and n_O MOs of indigo (AM1 results)

PM3[10], and HAM/3[7] method. The most relevant results of the former three methods are given in Table 2, while some results of the latter method are included in Table 1, more are displayed graphically in Figure 1.

In a qualitative manner the MOs of indigo can be derived from those of benzene, ethylene, formaldehyde, and ammonia[11]. With respect to the PE spectrum the higher occupied MOs are of prominent interest. According to the molecular symmetry C_{2h} of indigo, the 11 occupied π MOs factorize as 6 × A_u and 5 × B_g; σ MOs are of A_g or B_u symmetry.

All calculations by the methods MNDO, AM1, and PM3 lead to the same sequence of MOs, and the MO energies vary only slightly (less than 0.35 eV for the upper occupied MOs given in Table 2). Some MOs of indigo are depicted in Figure 2 and are characterized here briefly; π_{11} (HOMO) has large coefficients on the central C atoms and on the neighboring N atoms. It is C–C-bonding and C–N-antibonding and can be interpreted as an antisymmetric combination of the $\pi_{C=C}$ with the $2p_z$ AOs of the N atoms; $\pi_6-\pi_{10}$ are mainly localized in the benzene rings. They resemble the MOs π_2 and π_3 of benzene[13]. However, π_9 and π_7 have contributions of the central $\pi_{C=C}$, whereas π_{10} and π_6 show sizable coefficients on the N atoms. The two remaining MOs in Figure 2 belong to σ-type orbitals. They are symmetric to the molecular plane and have no $2p_z$ coefficients. According to their large coefficients on the O atoms they are easily identified as n_O MOs.

Table 2. Calculated orbital energies [eV] of indigo

MNDO	AM1	PM3	Orbital
−8.64	−8.37	−8.38	π_{11} $6A_u$
−9.24	−9.24	−9.27	π_{10} $5B_g$
−9.87	−10.10	−10.15	π_9 $5A_u$
−9.89	−10.19	−10.18	π_8 $4B_g$
−10.16	−10.40	−10.43	π_7 $4A_u$
−10.66	−10.60	−10.74	n_O A_g
−11.32	−11.43	−11.41	n_O B_u
−12.04	−12.31	−11.70	π_6 $3B_g$

For the lowest unoccupied MO (LUMO, π_{12}, $6B_g$) energies of −1.34 to −1.16 eV are calculated, which are in accord with the fact that indigo is easily reduced to its leuco form. The orbitals $\pi_7-\pi_{11}$ form the five highest occupied MOs, and below these the n_O MOs are found. Accordingly, the first five ionization bands in the PE spectrum should correspond to these π MOs and the next

two to the n_O orbitals. On the other hand, the HAM/3 method assigns only the first two ionizations to π MOs (π_{11} and π_{10}; Table 1), whereas the next two correspond to the n_O levels.

The HAM/3 results suggest that the strong ionization band centered at ca. 9.3 eV is formed by four ionization events, while according to the other methods it should be a superposition of only three bands. For MNDO, AM1, and PM3 calculations it is well-known that π and n MOs, relative to the respective ionizations, are calculated with different accuracy. Extensive studies on heterocyclic aromatic compounds suggest that n_N orbital energies should be corrected by ca. 0.9 (MNDO), 0.7 (AM1), and 0.3 eV (PM3) prior to correlation with ionization potentials[13], and it may well be possible that similar corrections should be applied to the n_O orbitals of carbonyl groups.

Of special interest is the energy split of the two n_O orbitals. Here only slight variations are found by the applied methods: 0.73 (AM1), 0.69 (PM3), and 0.64 eV (MNDO). It is difficult to assign ionization bands to these MOs by accepting a value of this size. The ionizations 6 and 7, which should be chosen from the calculated orbital sequence, are split by only ca. 0.2 eV, and the ionizations 7 and 8, as an alternative, are split by 1.5 eV, which is more than twice as large as the calculated values. The HAM/3 method calculates a split of 0.42 eV for the n_O *IP* values which fits well to the observed ionizations 3 and 4.

On the other hand, one might consider the shape of the ionization bands to be a criterion for their assignment. While the bands 1, 2, 3, and 8 appear to have rather similar intensities and widths, the strong band centered at 9.3 eV is a superposition of several bands, at least two of them should be rather broad. The latter could, therefore, be assigned as originating from the n_O orbitals, while the former sharper bands should belong to π ionizations. On the low energy side of the broad band the peaks of two sharp bands labeled 4 and 5 are discernible, which accordingly are assigned to π_8 and π_7. This leads to ionization 6 and 7 as originating from the two n_O orbitals. This would mean that their split should be rather small (ca. 0.2 eV) which again is only in accord with the HAM/3 results.

In Figure 1 a correlation of all ionization potentials up to 18 eV, which were calculated by the HAM/3 method, with the experimental values is shown. As is quite obvious, there is an excellent linear correlation ($IP_{calcd.} = 0.995 \cdot IP_{obs.} + 0.065$). The slope has a value very close to 1.00, the intercept is near zero and the correlation coefficient is $r^2 = 0.995$. Below 10 eV there are seven *IP*s (four forming the strong band at ca. 9.3 eV). This result seems to be more probable than that of the other three methods which – in a linear correlation according to eq. (1) – would place only six *IP*s below 10 eV.

This work was supported by the *Fonds der Chemischen Industrie*, Frankfurt a.M.

Experimental

Indigo was obtained from Riedel-de Haën A.G., Seelze/Hannover. The PE spectrum was recorded in the region 6–21 eV by using a Leybold-Heraeus UPG200 spectrometer with He(I) excitation (21.21 eV). The temperature of the inlet system was ca. 400 °C. The calibration of the energy scale was performed with an argon/xenon mixture. The accuracy of ionization potentials was ±0.03 eV for sharp peaks.

Most calculations were performed with the standard MOPAC program package, version 6.1[14]. MOs were plotted by using the program PERVAL[15] on a personal computer.

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