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Photoelectron Spectra and Molecular Properties V [1)]

THE PERTURBATION OF THE BENZENE π SYSTEM BY METHYLTHIO SUBSTITUENTS

Hans Bock and Gerhard Wagner [2)]
University of Frankfurt/Germany
Jürgen Kroner
University of Munich/Germany

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In alkylthio substituted aromatic compounds the extension of the π system by the sulphur electron pair can be rationalized within a "p-model". Neglecting contributions from unoccupied sulphur 3d orbitals [3)] reasonable correlations are achieved between HMO eigenvalues and half wave potentials [4)] or charge transfer absorption maxima [4)] as well as between the results of PPP calculations and ultraviolet excitation energies [5)].

We now wish to report the comparison of the photoelectron (PE) spectra of the corresponding mono- and 1,4-disubstituted methylthio and methoxy [6)] derivatives of benzene. Interpreted in terms of Koopmans' [7)] theorem, the experimental results confirm the orbital sequences deducible by perturbation arguments on the basis of the "p-model".

Qualitative πMO-schemes for thioanisole and anisole (Figure 1) suggest that the manner in which the degeneracy of the benzene e_{1g} molecular orbitals will be removed if a p-electron pair extends the π system, depends upon the ionization energy of the lone pairs relative to benzene (IE_{1}, C_6H_6 = 9.24 eV) [8)]. The symmetric e_{1g} orbital, Ψ_s, should be lowered in thioanisole (IE_{1}, CH_3SCH_3 = 8.67 eV)[2)], but raised in anisole

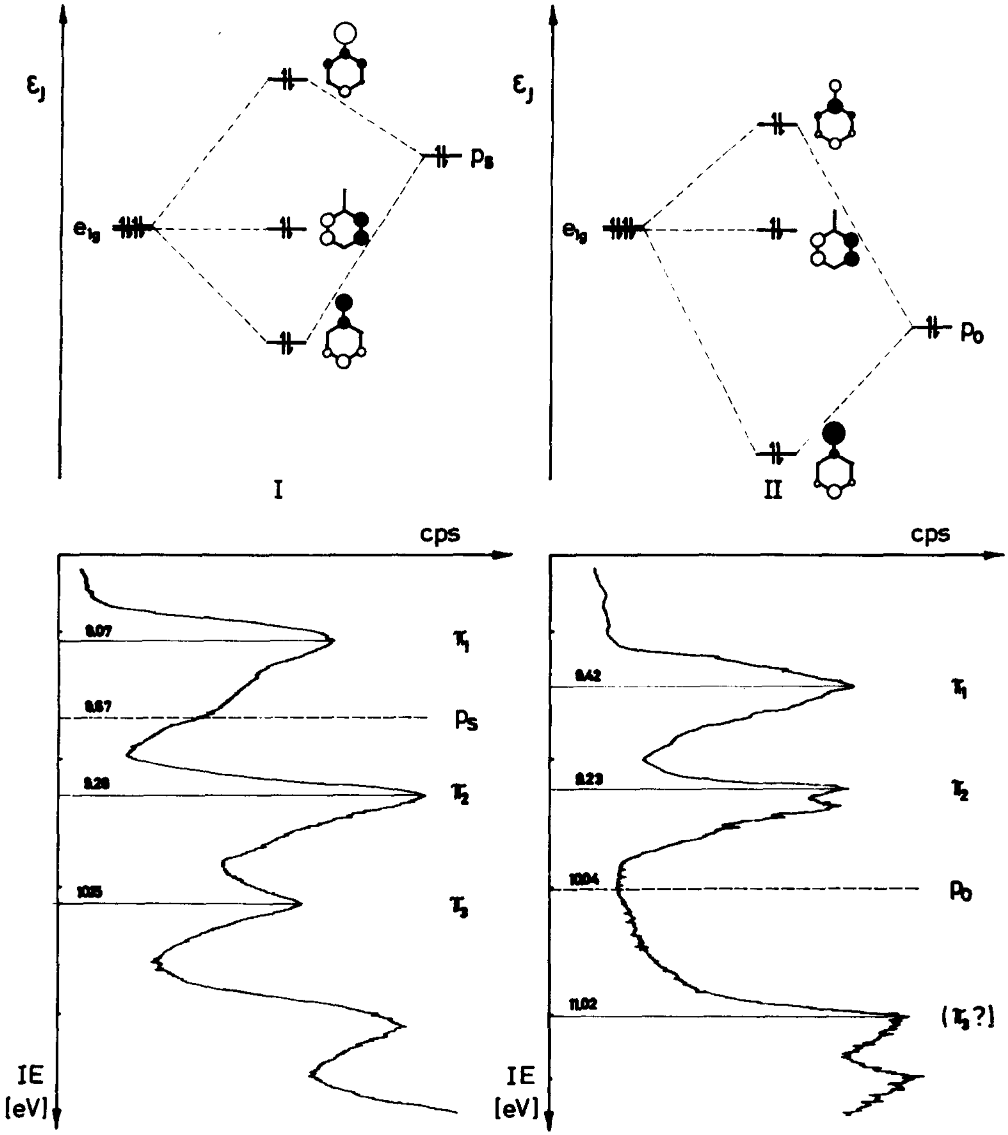


Figure 1. Qualitative πMO schemes for thioanisole (I) and anisole (II) in comparison to their PE spectra

(IE_{1}, CH_3OCH_3 = 10.04 eV) 2), whereas the antisymmetric one, Ψ_{as}, should remain approximately constant.

The PE spectra9) (Figure 1) strongly support the above conclusions. The slight deviations from equal splitting are probably due to inductive effects. Nevertheless the magnitudes of the energy differences, $\Delta IE\ (p_S - \pi_1) < \Delta IE\ (\pi_3 - p_O)$, are in accordance with the general expectation that (2p/2p)π-interactions should be stronger than (2p/3p)π-type.

The splitting patterns for 1,4-disubstitution (Figure 2) are derived starting from the two combinations of the heteroatom p orbitals $n_X^+ = \frac{1}{\sqrt{2}}(p_X + p_X)$ and $n_X^- = \frac{1}{\sqrt{2}}(p_X - p_X)$, which due to the large distance d_{XX} should remain (nearly) degenerate. Mixing of these combinations with the benzene molecular orbitals of suitable symmetry - i.e., $n_X^-/\Psi_S(e_{1g})$, and to comparable but opposite amounts, n_X^+/a_{2u} and n_X^+/e_{2u} - leads to four π energy levels (Figure 2).

The essential features of the qualitative splitting patterns are reflected in the low energy region of the PE spectra9) (Figure 2). Preceding the ionizations from the σ skeleton there are four distinguishable π bands in the methylthio derivative (III) and three in the methoxy compound (IV); the π_4 ionization energy of which is roughly estimated to be at least 10.25 + (9.25 - 7.90) = 11.6 eV. Again the antisymmetric e_{1g} benzene orbitals Ψ_{as} at 9.28 eV and 9.25 eV, respectively, remain unaffected. The ionization energies π_2 and π_3 correspond to the CH_3XCH_3 reference levels p_S and p_O - the observed deviations may be attributed to inductive effects or a slight lowering in energy of the n^+ combination due to n^-/n^+ splitting - and thus confirm the qualitative prediction of negligible delocalization of the n_X^+ substituent electron pair orbitals. Again the energy differences $\pi_2 - \pi_1$ are greater in the methoxy compound IV demonstrating the better overlap between 2p/2p relative to 2p/3p orbitals.

The "p-model" for interactions involving sulphur and oxygen electron pairs, as corroborated by the PE data, contributes as well to the understanding for other molecular properties as illustrated by the following examples.

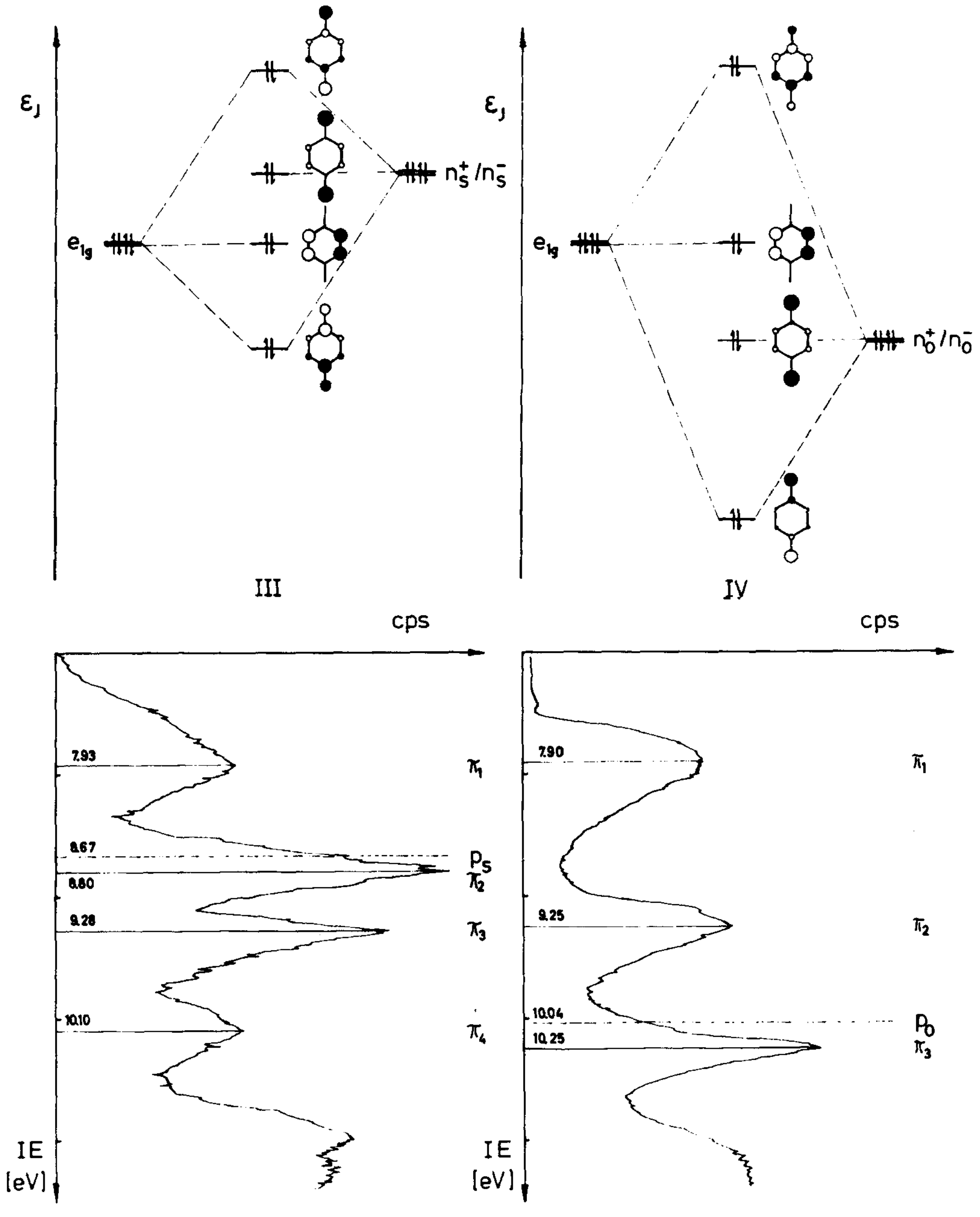


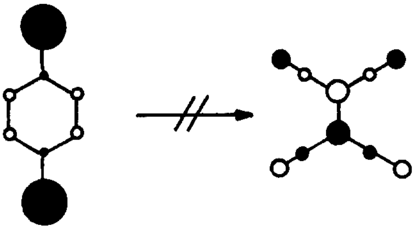
Figure 2. Qualitative πMO schemes for 1,4-bismethylthio (III) and dimethoxy benzene (IV) in comparison to their PE spectra

The absorption maxima of the charge transfer complexes between TCNE and I[4,10,11], II[10,11,12], IV[10,11,12] fit into a linear regression with the vertical PE ionization energies obtained from alkyl and halogen substituted benzene derivatives

$$\nu_m^{CT} = - 4.183 \cdot 10^4 + 0.733 \cdot 10^4 \ IE_v \qquad (1)$$

Because this correlation is not valid for the n_X charge transfer complexes of aliphatic sulfides[13] and ethers[2], the molecular orbitals involved must be of π symmetry (cf. Figure 1 and 2).

The 1,4-bis(methylthio) derivative III exhibits only two CT-bands[4,11]; according to the above correlation the one corresponding to the π_2 level is missing[2]. This can be explained by the forbidden charge transfer between the π_2 donator orbital and the Ψ_{-1} acceptor orbital of TCNE:



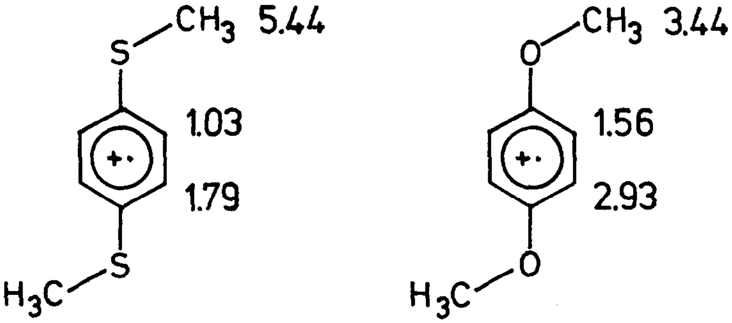
(2)

The long wavelength CT maximum of III (ν_m^{CT} = 14 800 cm^{-1}), deviating slightly from correlation (1), corresponds to an ionization potential IE_v^{corr} = 7.74 eV. The higher experimental value (Figure 2: 7.93 eV) could be explained by a not fully planar conformation of the hardly volatile III under measurement conditions[9]. Besides the PE bandshape (Figure 2) and the unexpected small energy difference between mono and disubstitution (IE_1^{I} = 8.07 eV; IE_1^{III} = 7.93 eV) this assumption is further supported by the ionization potential $IE_v \sim 7.6$ eV calculated from another linear correlation[2] with half wave oxidation potentials[4,14]

$$E_{1/2}^{ox} = -3.545 + 0.629 \ IE_v \qquad (3)$$

inserting the value $E^{ox}_{1/2}$ = 1.19 V for 1,4-bis(methylthio)-benzene[4].

Information on the nature of the highest filled molecular orbital in the 1,4-disubstituted derivatives III and IV are supplied by the esr spectra of their radical cations[15]. According to the McConnell equation $a_{H\mu} = |Q|(c^{HMO}_{J\mu})^2$ the proton coupling constants $a_{H\mu}$ are proportional ($|Q| \sim 24$ Gauss) to the square of the HMO-coefficient $c^{HMO}_{J\mu}$ at the centers μ; the expected value for the benzene e_{1g} orbital Ψ_s is $a_{H\mu} = 24\cdot(\frac{1}{\sqrt{12}})^2 = 2$ Gauss. The experimental finding[15]



(4)

clearly demonstrates that the Ψ_s contribution to the highest filled molecular orbital predominates in the oxygen compound, whereas the higher spin density in the SCH_3 group points to the prevailing n_x^- electron pair character in the 1,4-bis(methylthio)-benzene (Figure 2).

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