Substituent Effects on the Electronic Structure of Some Styryl Methyl Sulphones studied by Ultraviolet Photoelectron Spectroscopy

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A gas-phase u.v. photoelectron spectroscopic study is reported on some *para*-substituted styryl methyl sulphones in which the *para*-substituent varies in electronegativity and conjugating ability. The main purpose was to observe the substituent effect on electronic structure. The spectral analysis and the trends in ionization energies relative to the highest MOs show that the substituent has both short- and long-range effects, influencing even the orbitals of the $-SO_2Me$ group. Satisfactory linear relationships were found between the spectral data for the three highest MOs and the Hammett σ_p values, the wavenumbers of the SO_2 stretching vibrations, and the ^{13}C n.m.r. shifts for C-1 of the styryl group.

Several photoelectron (p.e.) spectroscopic studies have revealed substituent effects on the electronic structure of aromatic systems; correlations have been made between ionization energies from gas-phase p.e. spectroscopic measurements and various chemicophysical parameters, such as Hammett and Taft constants.[1-4] Linear relationships have usually been found, indicating a strict connection between the energy of the highest MOs and chemical reactivity in aromatic systems.

Our investigation dealt with a series of disubstituted benzene derivatives (I) containing as a fixed substituent a methylsulphonylvinyl group. This study forms part of a more general investigation of the photochemical isomerization of donor-acceptor systems.[5,6] The sulphones (I) may be represented by the mesomeric formulae (A) and (B).

In previous investigations we have found a relatively strong electronic interaction between the SO_2Me group and the substituents R, directly by i.r. studies,[7] and indirectly by ^{13}C n.m.r.[8] and dipole moment[9] measurements and by quantum chemical calculations.[10] The results show that styryl methyl sulphones may be considered as polymethine-like compounds.[11] The aim of this work was to support these views by p.e. measurements, and to obtain new information on the structure of styrenes.

Experimental

The compounds were prepared by reactions of substituted aromatic aldehydes with diethyl methylsulphonylmethyl-phosphonate.[12,13] The gas-phase p.e. spectra (both He[I] and He[II], with excitation energies of 21.22 and 40.81 eV, respectively) were obtained with a Perkin-Elmer PS-18 spectrometer equipped with dual He-I/He-II lamp (Helectros Development), at temperatures ranging from 107 to 200 °C. Argon, methyl iodide, and self-ionizing helium were used as internal standards.

Results and Discussion

Representative spectra are reproduced in Figure 1, and ionization energies are reported in the Table, which also gives detailed assignments.

The spectra were interpreted by means of a fragment analysis, consisting of the construction of qualitative MO schemes starting from the energy levels of simpler parent molecules deduced from their known p.e. spectra. For instance, Figure 2 shows two diagrams in which the molecular orbitals of the simplest styryl methyl sulphone (R = H) are correlated with those of (a) methyl vinyl sulphone[14] and benzene,[15] and (b) dimethyl sulphone[14] and styrene.[16] The most relevant points emerging are as follows.

(i) The vinylsulphonyl substituent exerts a stabilizing effect on the $e_{1g}(\pi)$ orbital of benzene, and the degeneracy of this level is removed by interaction with the π-electrons of the ethylene system (we assume that the phenyl ring is coplanar with the C=C group).

(ii) The three highest molecular orbitals associated with the SO_2 group ($\pi^+_{SO_2}$, n^-_O, and $\sigma^+_{SO_2}$) are destabilized in styryl methyl sulphone with respect to both $CH_2=CH-SO_2Me$ and Me_2SO_2 by the electron-donating power of the phenyl ring. Furthermore they are closer in energy because of the destabilizing interaction of the $\sigma^+_{SO_2}$ orbital with the $e_{2g}(\sigma)$ level of benzene, which is split into two components, one of them at lower energy than in benzene.

(iii) The $\pi_{C=C}$ orbital, already stabilized in methyl vinyl sulphone in comparison with ethylene (ionization energy 10.51 eV[17]) owing to the presence of the SO_2Me moiety, is not shifted much on passing to styryl methyl sulphone despite the stabilizing interaction with the $e_{1g}(\pi)$ orbital of benzene, because of the opposing inductive effect of the phenyl group; the same is observed on passing from ethylene to styrene.

A few comments are necessary on the assignments reported in the Table. The conjugative interaction between the substituents and the $e_{1g}(\pi)$ level of benzene leads to a destabiliz-

(A)   (B)

(1)
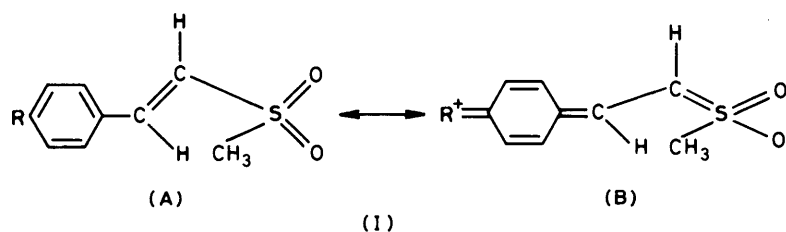
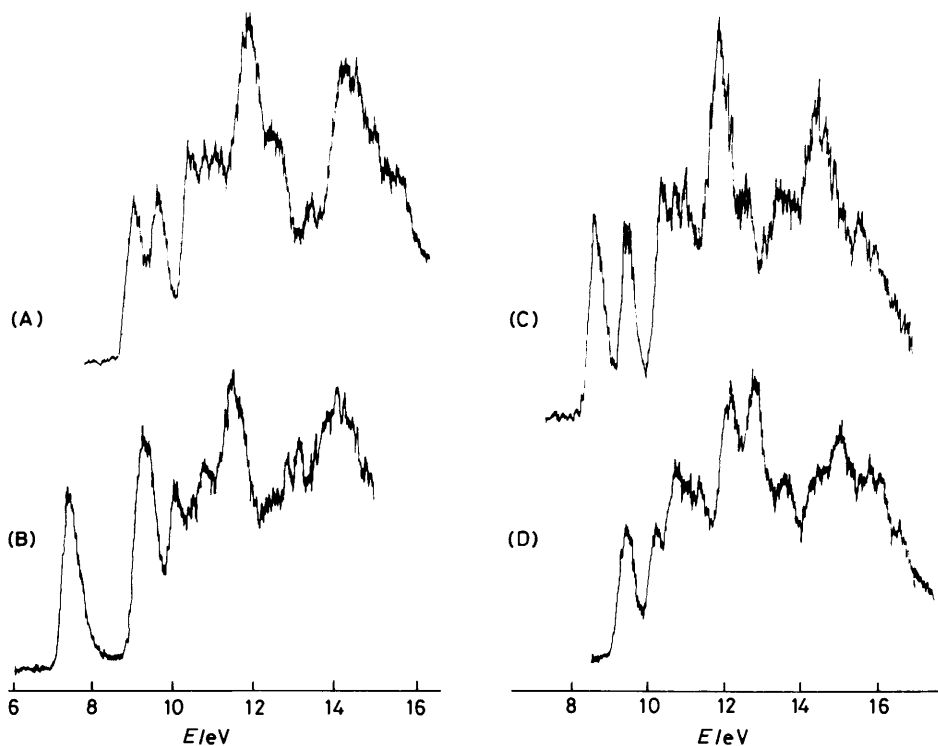R = H, *p*-Me, *p*-F, *p*-Cl, *p*-Br, *p*-NO₂, *p*-Me₂N, *p*-CN, or *p*-OMe

Figure 1. He[1] gas-phase photoelectron spectra of styryl methyl sulphones (I): (A) R = H, (B) R = 4-Me$_2$N, (C) R = 4-Me, (D) R = 4-CN

Table. Ionization energies (E/eV) for substituted styryl methyl sulphones (I) [a]

R	E_1	E_2	E_3	E_4	E_5	E_6	E_7
4-Me$_2$N	7.52 $n_{NMe_2}(b_1)$ [b] + ring $\pi_3(b_1)$	9.41 ring $\pi_3(b_1)$ + $n_{NMe_2}(b_1)$, $\pi_2(a_2)$	10.07 $\pi^+_{SO_2}$	10.89 n^-_O, $\sigma^+_{SO_2}$	11.51 $\pi_{C=C}$, $\pi^-_{SO_2}$, σ_{ring}		
4-MeO	8.52 ring $\pi_3(b_1)$	9.59 ring $\pi_2(a_2)$	10.34 $\pi^+_{SO_2}$, n^-_O, n_{OMe}	10.97 $\sigma^+_{SO_2}$	11.55 $\pi_{C=C}$, $\pi^-_{SO_2}$, σ_{ring}		
4-Me	8.74 ring $\pi_3(b_1)$	9.55 ring $\pi_2(a_2)$	10.41 $\pi^+_{SO_2}$	10.76 n^-_O	11.01 $\sigma^+_{SO_2}$	11.70 $\pi_{C=C}$, σ_{SO_2}, σ_{ring}	12.35 σ_{ring}
H	9.08 ring $\pi_3(b_1)$	9.66 ring $\pi_2(a_2)$	10.44 $\pi^+_{SO_2}$	10.85 n^-_O	11.13 $\sigma^+_{SO_2}$	11.87 $\pi_{C=C}$, $\pi^-_{SO_2}$, σ_{ring}	12.54 σ_{ring}
4-F	9.05 ring $\pi_3(b_1)$	9.99 ring $\pi_2(a_2)$	10.51 $\pi^+_{SO_2}$	10.90 n^-_O	11.17 $\sigma^+_{SO_2}$	11.87 $\pi_{C=C}$, $\pi^-_{SO_2}$, σ_{ring}	12.26 σ_{ring}
4-Cl	8.94 ring $\pi_3(b_1)$	9.94 ring $\pi_2(a_2)$	10.53 $\pi^+_{SO_2}$	10.81 n^-_O	11.12 $\sigma^+_{SO_2}$	11.53 n_{Cl}, $\pi_{C=C}$, $\pi^-_{SO_2}$, σ_{ring}	12.39 σ_{ring}
4-Br	8.92 ring $\pi_3(b_1)$	9.88 ring $\pi_2(a_2)$	10.87 n_{Br}, $\pi^+_{SO_2}$, n^-_O, $\sigma^+_{SO_2}$	11.92 $\pi_{C=C}$, σ_{ring}	12.28 σ_{ring}		
4-CN	9.47 ring $\pi_3(b_1)$	10.24 ring $\pi_2(a_2)$	10.69 $\pi^+_{SO_2}$	11.12 n^-_O	11.30 $\sigma^+_{SO_2}$	12.09 $\pi^-_{SO_2}$, π_{CN}, $\pi_{C=C}$	12.69 2 × σ_{ring}, π_{CN}
4-NO$_2$	9.62 ring $\pi_3(b_1)$	10.31 ring $\pi_2(a_2)$	10.76 $\pi^+_{SO_2}$	11.31 π_{NO_2}, σ_{NO_2}, n^-_O, $\sigma^+_{SO_2}$	12.05 $\pi_{C=C}$, $\pi^-_{SO_2}$		

[a] As an assignment aid, p.e. data of monosubstituted benzenes were used from ref. 16 and A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 1968, 22; K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, 'Handbook of He[1] Photoelectron Spectra of Fundamental Organic Molecules,' Japan Scientific Societies Press, Tokyo, Helsted Press, New York, 1980; T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2536; J. W. Rabelais, *J. Chem. Phys.*, 1972, **57**, 960; A. W. Potts, M. L. Lyus, E. P. F. Lee, and G. H. Fattahallah, *J. Chem. Soc., Faraday Trans. 2*, 1980, 556. [b] The b_1 and a_2 labels, characters from C_{2v} point group, are used for purposes of identification although all these molecules have C_s symmetry.
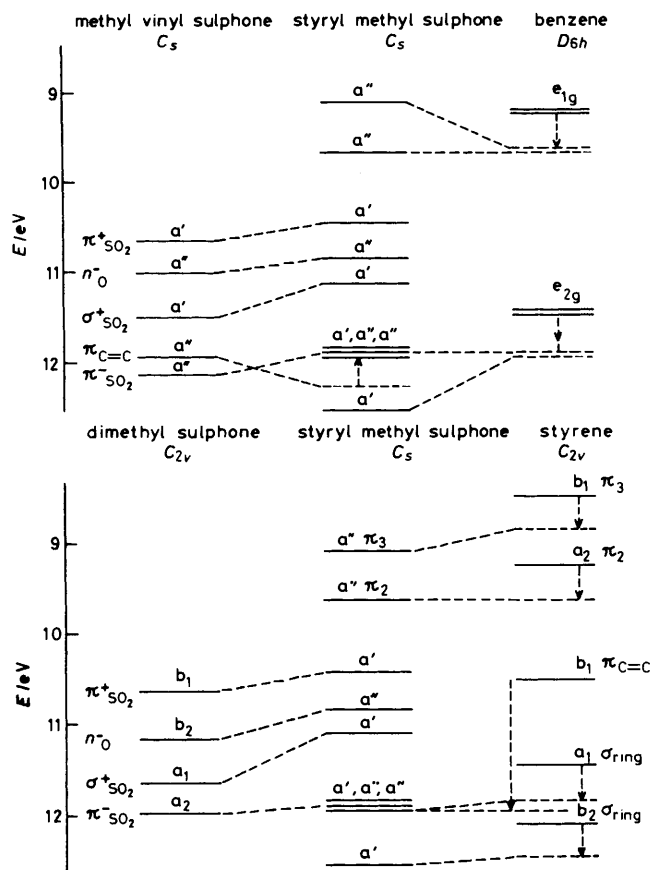
Figure 2. Energy level diagram for the outer MOs of styryl methyl sulphone and correlation with those of parent molecules. The arrows indicate shifts due to inductive effects
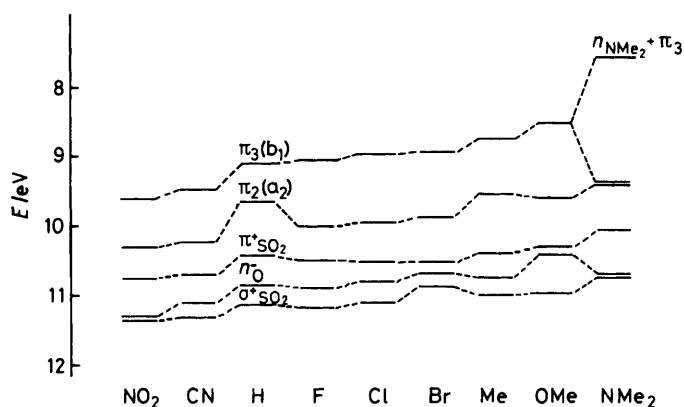

Figure 3. Correlation diagram for the p.e. bands of (1)

Figure 4. Plot of π_3 (A), π_2 (B) of the aromatic ring, and $\pi^+_{SO_2}$ (C) ionization energies against Hammett σ constants

ation of the b_1 component with respect to the a_2 component in all cases. The b_1 and a_2 orbitals have maximum and zero electron density, respectively, on the carbon atoms bearing the substituents.

In the compound with R = NMe$_2$ the orbitals $\pi_3(b_1)$ and $\pi_2(a_2)$, mainly localized on the ring and corresponding to the second p.e. band, are accidentally degenerate as a result of the stabilization of the b_1 level of the phenyl ring by interaction with the NMe$_2$ orbital.

Figure 3 is a correlation diagram for the ionization energies of all the molecules of the series. In a simple interpretation
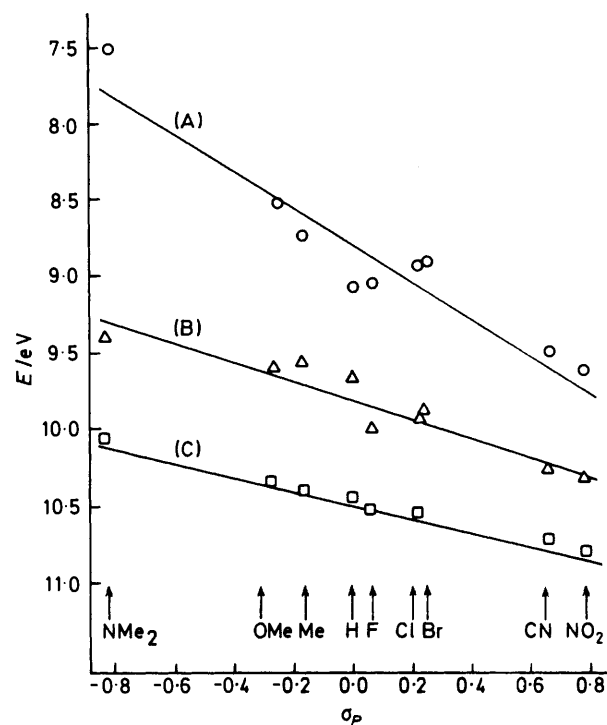
following current approximate concepts regarding the properties of substituents, it is of interest that electron-withdrawing substituents such as halogens can be viewed as exerting both inductive $(-I)$ and conjugative $(+R)$ effects; thus the $-I$ effect stabilizes the a_2 level to quite a large extent (ca. 0.3 eV), whereas the b_1 orbital, affected by opposite $-I$ and $+R$ effects, remains at essentially the same energy. In the case of the nitro and cyano derivatives the high electro-negativity of the substituents induces a partial positive charge on the ring, so that both b_1 and a_2 levels are higher in ioniz-ation energy than in the unsubstituted compound; the conjugative effect is on the contrary quite weak, not affecting the splitting between b_1 and a_2 because of the large energy difference between the two π systems.

In the compounds with R = Me, OMe, or NMe$_2$, the dominant effect appears to be the conjugative one $(+R)$; the inductive effect is almost negligible, as revealed by the invariant position of the a_2 level. The interaction between the π-symmetry orbitals of the ring and of the substituent is particularly important in the dimethylamino derivative, the highest MO of which has its main contribution from the nitrogen lone-pair, and some admixture with the π_3 orbital.

The ionization energies of the orbitals mainly localized on the SO$_2$Me group are also influenced by the para-substituents, although these are rather distant in the space, and not directly linked. The trends, in cases where the p.e. bands have been unambiguously identified, are analogous to those described for the upper MOs.

The treatment of substituent effects adopted in the above discussion is a simplified one, based on separate inductive and resonance effects. This does not mean, in principle, that the two effects are independent. More significant models for the interpretation of substituent effects can be considered, such as the ' substituent shell concept ' developed by Godfrey et al.[18]

A better understanding of substituent effects in styryl methyl sulphones can be obtained by a series of correlations
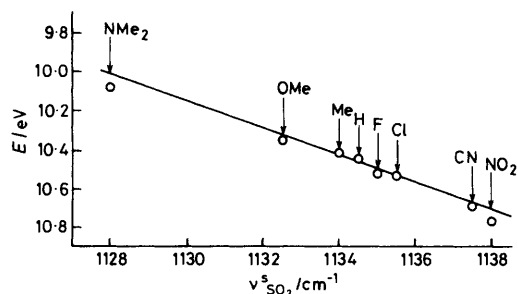
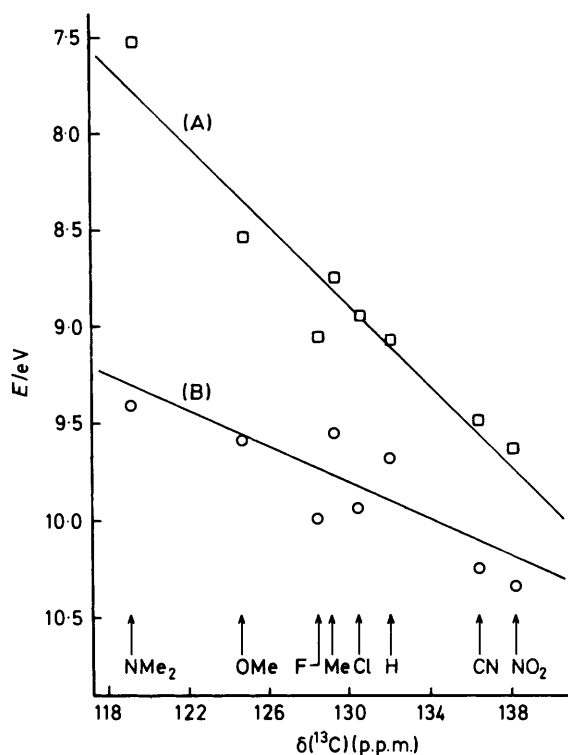**Figure 5.** Plot of $\pi^+_{SO_2}$ ionization energy against wavenumber of SO_2 symmetric stretching vibration

Figure 6. Plot of π_3 (A) and π_2 (B) ionization energies of the aromatic ring against ^{13}C n.m.r. shifts

between observed ionization energies and other chemico-physical parameters.

A satisfactory linear relationship between p.e. data for the three highest orbitals $(\pi_3, \pi_2, \pi^+_{SO_2})$ and Hammett σ_p constants [19] was found, as shown in Figure 4, except for deviations and inversions when R = halogen, as observed in similar free-energy relationships.[1] It should be remembered that p.e. measurements are performed in the gas phase, whilst the Hammett constants are obtained from pK_a measurements in solution. The deviations from linearity can be explained in terms of differential interactions of the solvent with the halogens, in addition to other more complex factors. The ionization energies generally increase with increasing electron-withdrawing power of the substituent. The slopes of the plots of the first three ionization energies are, respectively 1.19, 0.61, and 0.43 ($r = 0.95$, 0.94, and 0.88) suggesting different influences of the substituents on the three MOs. The $\pi_3(b_1)$ orbital is clearly the most sensitive, since it has an important

contribution from the carbon atom directly involved in the substitution.

We also attempted a correlation of ionization energy $(\pi^+_{SO_2})$ with the wavenumbers of the SO_2 stretching vibrations.[7] The relationship between $v^s_{SO_2}$ and ionization energy related to the SO_2 group is approximately linear (slope 0.067, $r = 0.99$; see Figure 5) as are those of both sets of spectrometric data with the Hammett constants (for the correlation of the i.r. data with these parameters see ref. 8). The existence of these linear correlations is not a trivial finding, in that in one case $[E(\pi^+_{SO_2})/v^s_{SO_2}]$ different properties of the same group are concerned, whilst in the other two cases $[E(\pi^+_{SO_2})/\sigma_p$ and $v^s_{SO_2}/\sigma_p]$ different properties of different groups are involved. This demonstrates that the stretching vibration of the SO_2 group, strictly depending on SO bond order, is influenced also by the overall electronic structure of the molecule and therefore indirectly by the substituents on the phenyl ring. The same applies to n.m.r. shifts which are, to a first-order approximation, dependent on electron densities of atoms, and are influenced only as a second-order effect by the π system. Good correlations can be obtained of $E(\pi_3)$ and $E(\pi_2)$ with n.m.r. data, e.g. $\delta(^{13}C)$ of the phenyl C-1. The relations found $[E(\pi_3)/\delta(^{13}C)$: slope 0.102, $r = 0.96$; $E(\pi_2)/\delta(^{13}C)$: slope 0.046, $r = 0.85$; see Figure 6] are of the same order of magnitude as in the case of E/σ or $\delta(^{13}C)/\sigma^8$ correlations.

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