Non Linear Dependence of the First Ionization Energy of Diphenylsulphides and Diphenylethers on σ_P^+ Constants

G. Buemi and S. Pignataro

Istituto di Chimica Fisica dell'Univesità di Catania, Italy

and G. Spunta

Laboratorio dei Composti del Carbonio contenenti Eteroatomi del C.N.R.,
Ozzano Emilia (Bologna), Italy

(Z. Naturforsch. **32 a**, 292—294 [1977]; received February 6, 1977)

The first ionization energy of several mono and bisubstituted diphenylsulphides and diphenylethers have been measured by photoelectron spectroscopy and plotted against σ substituent constants. A sinusoidal dependence has been found in all cases. Such finding has been interpreted as probably due to conformational variations of the diphenylsulphide and diphenylether systems with the substituent.

The correlation of the first ionization energy (IE) with the substituent constants is an old matter of study. It was first shown that for aromatic compounds Brown's σ_P^+ is the most appropriate type of σ and that, in gas phase correlations, the solution values have to be changed for substituents heavily affected by solvation [1].

Since then, in the majority of the reported cases, linear correlations of the IE's with the σ_P^+ were found by using either electron impact [1, 2] or photoelectron spectroscopy values [3, 4].

In the diphenylmethane and diphenylethane cases, the IE's vs. σ_P^+ plots show [5] a break at the hydrogen point. This was interpreted as the consequence of the variation of the nature of the highest occupied molecular orbital (HOMO).

In this paper we would like to report the cases of diphenylsulphides (DPS) and diphenylethers (DPO) for which an even more complex dependence of the IE values on the σ_P^+'s is found.

Results and Discussion

Table 1 lists the first IE values of the studied compounds. Figure 1 shows the plot of the IE's of the para-monosubstituted DPS's (Y = H) vs. σ_F^+. The same plots for some pp′-disubstituted DPS series are also reported.

Considering the monosubstituted compounds, a clear departure from a linear correlation is observed. This, in our opinion, could be ascribed to conformational variations of the system with the substituents.

Table 1. First IE values (eV) of p,p′ diphenylsulphides and diphenylethers [*].

p-p′-Substituents p	 p′	Diphenyloxides	Diphenylsulphides
H	H	8.32	7.88
H	OH	8.19	7.83
H	OCH_3	8.04	7.79
H	NH_2	7.71	7.69
H	$N(CH_3)_2$	7.30	7.28
H	SO_2CH_3	—	8.30
H	NO_2	8.87	8.40
NH_2	OCH_3	7.56	—
NH_2	NH_2	7.41	7.23
NH_2	$N(CH_3)_2$	7.18	7.03
NH_2	SO_2CH_3	—	8.15
NH_2	NO_2	8.13	8.22
$N(CH_3)_2$	$N(CH_3)_2$	7.05	6.87
$N(CH_3)_2$	NO_2	7.56	7.58
NO_2	OCH_3	8.46	—
NO_2	NO_2	9.27	8.81

In DPS the two phenyl rings are equally rotated (in opposite directions) by about 38° with respect to the C-S-C plane [7]. The HOMO results to be about 70% localized on the sulphur atom and the rest equally distributed between the two rings [**].

In the p-NO_2 derivative, however, the angle between the C-S-C plane and the plane of the substituted ring is very small while the unsubstituted ring is rotated [9] by about 84° with respect to the

---

[*] These data were obtained by using a Perkin-Elmer PS18 Photoelectron Spectrometer. The estimated error is ± 0.05 eV.

[**] Calculations were performed at CNDO/2 level [8] on some DPS's and DPO. — The molecular geometries for the calculations on DPS and DPO were taken from Ref. 7. For the latter compound no important changes of percentage or energy of the HOMO were found by using 37° or 50° for the angle of twist of the rings with respect to the C-O-C plane. The geometries for p-NO_2 [9] and p-$N(CH_3)_2$ [10] DPS were taken from reported X-ray studies.

C-S-C plane. Sulphur is therefore preferentially conjugated with the nitro-substituted ring, which, bearing a strong electron withdrawing substituent, forces the IE of the HOMO to rise abruptly. The rotation of the unsubstituted ring prevents the conjugation with sulphur and therefore further stabilizes the HOMO. This orbital is now mainly localized on sulphur (about 75%) and the substituted ring (about 20%).

However, on going from DPS to its p-$N(CH_3)_2$ derivative, the conformation changes in the contrary manner. In this compound the substituted ring is largely rotated (about 82°, s. [10]) with respect to the C-S-C plane.

The HOMO is mainly localized on sulphur ($\sim 34\%$) and on the $C_6H_4N(CH_3)_2$ part of the molecule ($\sim 50\%$)***. This explains the strong influence of the $-N(CH_3)_2$ group on the experimental IE.

The conformation is however unfavorable for the occurrence of the strongest interaction between the $C_6H_4N(CH_3)_2$ group and the rest of the molecule. Therefore the IE of the p-$N(CH_3)_2$ DPS is higher than predicted by extrapolating the NO_2 and the H points in the IE/σ_P^+ plot to the $N(CH_3)_2$ σ_p^+ value.

The situation for the other mono substituted compounds here reported is now rather obvious and explains the non-linear trends observed in Figure 1.

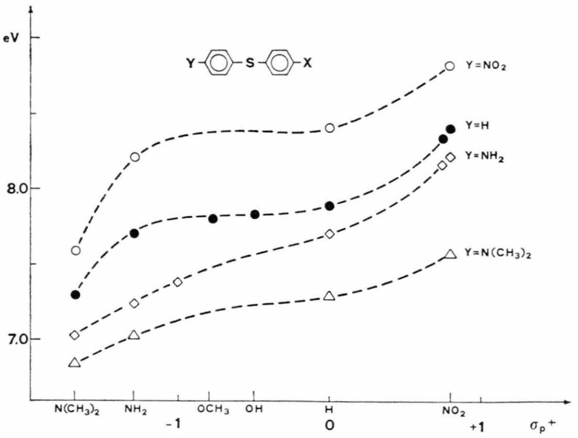

Fig. 1. Plot of the first IE values of p and p,p′ substituted diphenylsulphides ($Y\text{-}C_6H_4\text{-}S\text{-}C_6H_4\text{-}X$) vs. σ_p^+ of the substituent. The σ_p^+ values were taken from Ref. 6 except that of the OH group which was taken from Ref. 1.

In fact, the substituent effect on the energy of the HOMO is much smaller than that found in other series of compounds (e. g. benzenes [3, 4]), in agreement with the increased energy gap between the HOMO and the substituent orbitals and with the reduced MO coefficient on the substituted carbon atom.

The similarity of the behaviour shown by p-Y, p′-X disubstituted compounds, confirms that the observed non linear trends of the monosubstituted derivatives is real. This trend is almost unchanged for the p-NO_2, p′-X derivatives, while it is smoothed for the p-NH_2, p′-X and expecially for the p-$N(CH_3)_2$, p′-X compounds (see Figure 1). For this last series the HOMO has the largest Y character and is therefore less influenced by the p′-X substituent.

On the other hand for the DPO system, whose HOMO has mainly ring character (about 75%), a less evident departure from a linear correlation can be easily predicted. This is confirmed by the plots reported in Fig. 2: without having seen the DPS correlations, one would have probably drawn linear regressions.

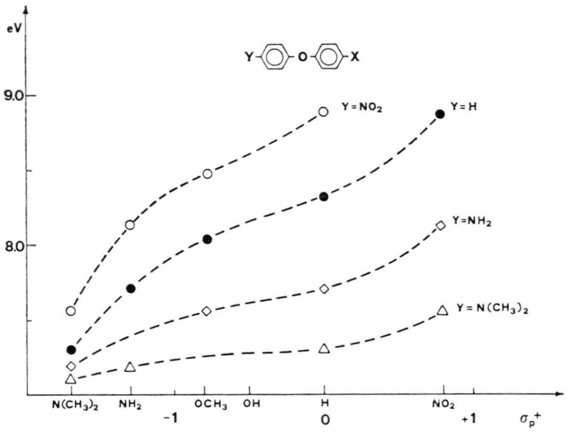

Fig. 2. Plot of the first IE values of p- and p,p′ substituted diphenylethers ($Y\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}X$) vs. Brown's σ_p^+.

If one compares the monosubstituted DPS and DPO correlations, another effect is observed: the *ΔIE* between the p-$N(CH_3)_2$-DPO and DPO is larger than that found for the corresponding DPS compounds. The larger substituent effect in the DPO is in agreement with what we have recently found in

---

*** It is important to notice that, while sulphur contributes to the HOMO mainly from its p_z orbital, the contribution from the $C_6H_4N(CH_3)_2$ part of the molecule arises mainly from p_x and p_y atomic orbitals.

the anisole and thioanisole series [11] and can again be ascribed to the stronger ring character in the oxygen derivatives.

Acknowledgement

S. P. would like to thank C. N. R. for financial support.

---

[1] S. Pignataro, A. Foffani, G. Innorta, and G. Distefano, Z. Physik. Chem. N. F. **49,** 291 [1966]; P. Linda, G. Marino, and S. Pignataro, J. Chem. Soc. (B) **1971,** 1585 and references therein.

[2] F. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, J. Amer. Chem. Soc. **92,** 6867 [1970].

[3] A. D. Baker, D. P. May, and D. W. Turner, J. Chem. Soc. (B) **1968,** 22.

[4] R. Egdell, J. C. Green, and C. N. R. Rao, Chem. Phys. Letters **33,** 600 [1975].

[5] S. Pignataro, V. Mancini, G. Innorta, and G. Distefano, Z. Naturforsch. **27 a,** 534 [1972].

[6] H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc. **80,** 4979 [1958].

[7] M. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, J. Chem. Soc. **1963,** 1167; V. Galasso, G. De Alti, and A. Bigotto, Tetrah. **27,** 6151 [1971].

[8] J. A. Pople and D. L. Beveridge, Approximate M. O. Theory, McGraw-Hill Co, New York 1970.

[9] A. Krajewski, L. Riva di Sanseverino, A. Dondoni, and A. Mangini, J. Cryst. Mol. Struct. **5,** 345 [1975].

[10] G. Bandoli, D. A. Clemente, E. Tondello, and A. Dondoni, J. Chem. Soc. Perkin Trans. **II,** 157 [1974].

[11] F. Bernardi, G. Distefano, A. Mangini, S. Pignataro, and G. Spunta, J. Electr. Spectr. **7,** 457 [1975].