Steric Inhibition of Resonance in Ortho-substituted Diphenylsulphides Studied by Photoelectron (He I) Spectroscopy

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(Z. Naturforsch. **30 a**, 1213–1214 [1975]; received July 14, 1975)

The analysis of the four lowest ionization energy values related to π MO's in diphenylsulphide and its o-o′-dimethyl and o-o-o′-o′-tetramethyl derivatives indicates that the conformation of the unsubstituted compound largely deviates from planarity, that this deviation increases with *ortho*-substitution and that the two phenyl rings in the tetramethyl derivative are nearly orthogonal to each other.

Recent charge transfer (CT) measurements on diphenylsulphide (DPS) derivatives indicate that two methyl groups in *ortho* position do not exert a sizable steric effect, but instead increase, with respect to the unbustituted compound, the availability of the sulphur lone pair to form CT complexes as it is evident from both the λ_{CT} and the K_{CT} values (see Table 1), this effect being similar to that observed for the p-p′ derivative [1, 2].

The effect of the steric hindrance is quite evident in the o-o-o′-o′-tetramethyl DPS from the values of K_{CT} with iodine [1] and λ_{CT} with π acceptors [2], while the λ_{CT} value with iodine would indicate that the electron density on sulphur is higher than in the unsubstituted and dimethyl derivatives [1].

The *ortho* groups rise the MO's energy, and could sterically hinder the interaction of the phenyl rings *via* the sulphur bridge and the interaction of the donor orbitals with the CT acceptors.

To have an independent estimation of the electronic effects of the methyl and of the reduction of conjugation due to the steric hindrance, we measured by photoelectron (He I) spectroscopy, the ionization energy (IE) values of the outer π MO's of DPS and its o-o′ and o-o-o′-o′ methyl derivatives. This technique is, indeed, very powerful in studying the steric inhibition of resonance [3, 4].

In Table 1 the IE values lower than 10.5 eV are reported. I_1, I_3 and I_4 correspond to the three combinations (anti-bonding, non bonding and bonding respectively) of the sulphur lone pair with the π_S rings orbitals [5]. The $\Delta(I_4 - I_1)$, then, gives a measure of the mesomeric interaction between the sulphur and the two rings. For its energy and intensity, I_2 is ascribed to the ionization from the degenerated π_A ring orbitals.

The Δ value for DPS (2.23 eV) is similar to the splitting of the π MO's deriving from the sulphur-ring interaction in thiophenol and thioanisole (Δ = 2.15 [6] and 2.08 [7] eV respectively). For a completely planar conformation, a much larger interaction (splitting) would be expected in DPS. The present result, in agreement with theoretical [8] and electron diffraction [9] studies, indicates that in this molecule a large deviation from planarity occurs.

In the o-o′ dimethyl DPS, the electron releasing effect of the methyl groups rises the energy of the rings π orbitals as it is evident from the reduction of the I_2 and I_3 values. The constancy of I_1 suggest that the inductive effect is balanced by the reduction of conjugation with respect to the unsubstituted compound. The decrease of the Δ value confirms this interpretation. This reduction is, however, small so that the presence of two methyls does not greatly influence the geometry of the compound, probably because the two substituents assume an *anti* conformation.

In o-o-o′-o′-tetramethyl DPS, the methyl effcets are enhanced: I_2 is lowered by about 0.25 eV with respect to the dimethyl derivative; moreover, the presence of four ortho-substituents forces the two phenyl rings to rotate through a wider angle, greatly reducing the conjugation. In fact, the first IE *increases* by 0.2 eV and the Δ value decreases by about 1 eV.

The IE value related to the bonding $S_{3p} - \pi_S$ combination (I_4 = 9.17 eV) does not greatly differ

Table 1. Outer π MO's IE values (eV)* and CT data **.

	I_1	I_2	I_3	I_4	$\Delta(I_4-I_1)$	$K_{CT}(I_2)$	$\lambda_{CT}(I_2)$	λ_{CT}(TCNE)
Diphenylsulphide (DPS)	7.88	9.20	9.5 (sh) ***	10.11	2.23	3.9	350	585
o-o′-dimethyl-DPS	7.85	8.95	9.3 (sh)	9.98	2.12	5.8	357	610
o-o-o′-o′-tetramethyl-DNS	8.08	8.69		9.17 (sh)	1.09	3.7	~360	520

* The IE data have been obtained with a Perkin-Elmer PS 18 photoelectron spectrometer. Reproducibility was ±0.05 eV. The samples were synthetized for previous works [1, 2].

** From Refs. 1 and 2 K_{CT}/l mol^{-1}; λ_{CT}/nm (±2) *** sh = shoulder.

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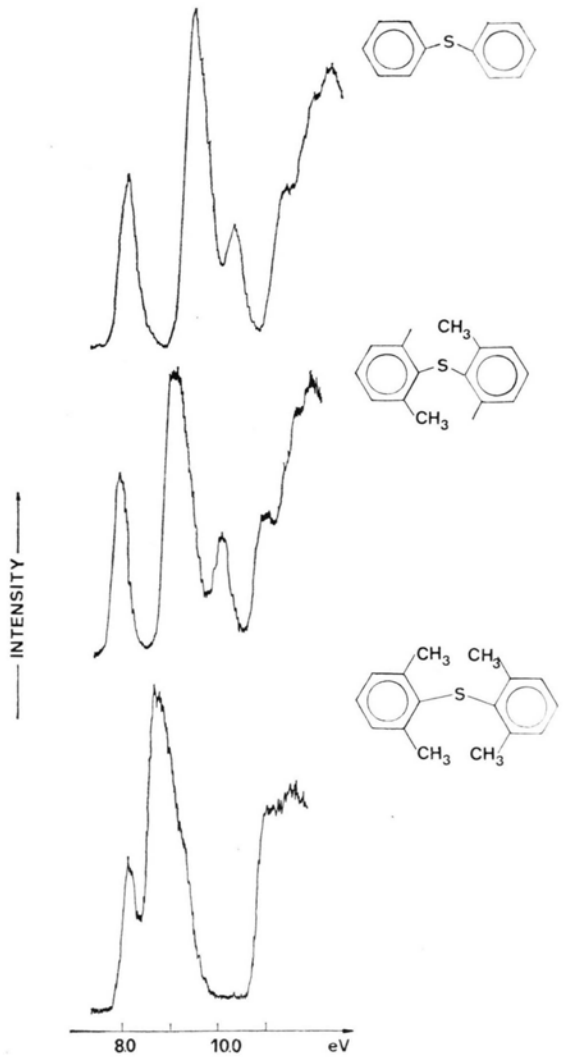

Fig. 1. Low IE part of the photoelectron (He I) spectra of diphenylsulphide, o-o′-dimethyldiphenylsulphide and o-o-o′-o′-tetramethyldiphenylsulphide.

from the value corresponding to the π_S MO of metaxilene (9.03 eV [10]) indicating that the ring orbitals experience only a small perturbation. So that, in this compound, the conformation is near to the most unfavorable one for mesomeric interaction: in other words, the two rings are nearly orthogonal to each-other.

The role of the steric hindrance effect is shown by the photoelectron spectra themselves as presented in Figure 1. The spectra of the unsubstituted compound and of the dimethyl derivative show three bands (corresponding to I_1, I_2 and I_4) and a shoulder on the high IE side of the second band (I_3). In the same energy range, the spectrum of the tetramethyl derivative shows only two, not completely resolved, bands; I_4 appearing as a shoulder of the second one.

A short comment on the comparison between the CT and the PES data is worthy to be done. By analogy with Thioanisole [6] and Thiophenole [11], the first IE of DPS is related to the ionization from a π MO with prevailing sulphur 3p character. In the dimethyl derivative, the small reduction of the conjugation increases the sulphur character of this MO so that the overlap with the virtual orbitals of the acceptors is favored despite the nearly constant I_1 value. In the tetramethyl derivative, I_1 is even more localized on sulphur, but the interaction with CT acceptors is strongly hindered by the presence of the four ortho substituents. The discrepancy between the λ_{CT} value with iodine and the other data (see Table 1) can be ascribed in part to the uncertainty of this measurement [1], and in part to the fact that I_3 and I_4 in the tetramethyl derivative are much lower than the corresponding values in the other compounds, so that these MO's could contribute more effectively to the formation of CT complexes. (With a σ acceptor the interaction should be less influenced by steric hindrance than with π acceptors.)

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Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Würzburg