Study of Sulfur-Sulfur Nonbonded Interactions in Substituted Diphosphine Disulfides by Gas-Phase UV Photoelectron Spectroscopy

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Ultraviolet photoelectron spectra (UPS) of tetrasubstituted diphosphine disulfides RR′P(S)-P(S)RR′ exhibit peculiar 1 : 2 : 1 splitting patterns in the region 7.5–9.5 eV for which a through-bond coupling mechanism between the sulfur lone pairs lying in the PPS planes is proposed. Further bond orbitals are related to bands at higher I. E. in the UP spectra.

Introduction

Structural studies of substituted diphosphine disulfides, RR′P(S)–P(S)RR′, (R=R′=CH_3, C_2H_5, n–C_3H_7, n–C_4H_9, C_6H_5; R=CH_3, R′=t–C_4H_9) are mainly concerned with their conformations and the nature of the interactions between the –P(S)RR′ moieties, and have been carried out until now mainly by nmr methods [1, 2]. We have employed ultraviolet photoelectron spectroscopy (UPS) in the gas phase, a technique which has proven useful in the study of nonbonded interactions, as in dicarbonyls and tricarbonyls (3–9), in diazodienes [10], diazobicycloalkenes [11, 12], azoderivatives [13, 14], and thiocyclohexanes [15], and of conformational equilibria in diphosphines [16–18], halomethanes [19], and hydrazines [20].

In this work the information yielded by UPS regarding conformations is not conclusive but provides evidence for a through-bond S–S interaction in symmetrically substituted tetraalkyldiphophine-disulfides.

Experimental

UPS gas-phase spectra were measured with a Perkin Elmer PS 18 photoelectron spectrometer (HeI radiation (21.22 eV), Ar and CH_3I calibration). Some of the alkyl compounds were prepared according to Hägele [21]. Commercial $[(CH_3)_2P(S)]_2$ and $[(C_2H_5)_2P(S)]_2$ were also used after purification. $[(C_6H_5)_2P(S)]_2$ was prepared according to Kuchen and Buchwald [22]; for comparison the UP spectra of $[(C_6H_5)_2P]_2$ (commercial Strem Chemical product) and of $[(C_6H_5)_2P(O)]_2$ prepared according to Ref. [22], were also measured.

Results and Discussion

The five diphosphine disulfides of the type RR′P(S)–P(S)RR′ (R=R′=CH_3, C_2H_5, n–C_3H_4, n–C_4H_9; R=CH_3, R′=t–C_4H_9), whose molecular model is shown in Fig. 1), exhibit in their UP spectra (Figs. 2, 3, Table 1) a group of three bands,

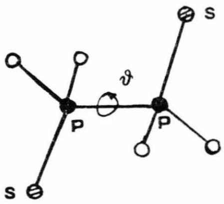

Fig. 1. Molecular model of tetraalkyldiphosphinedisulphides.

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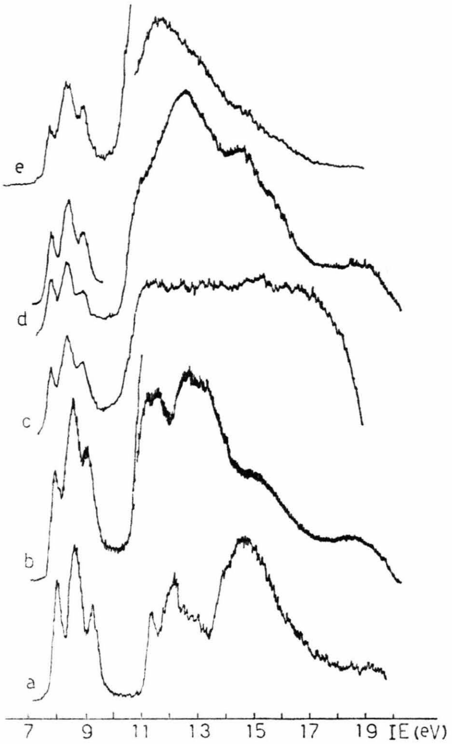

Fig. 2. He(I) gas-phase p.e. spectra of
(a) $[(CH_3)_2P(S)]_2$;
(b) $[(C_2H_5)_2P(S)]_2$;
(c) $[(CH_3)(t\text{-}C_4H_9)P(S)]_2$;
(d) $[(n\text{-}C_3H_7)_2P(S)]_2$;
(e) $[(n\text{-}C_4H_9)_2P(S)]_2$.

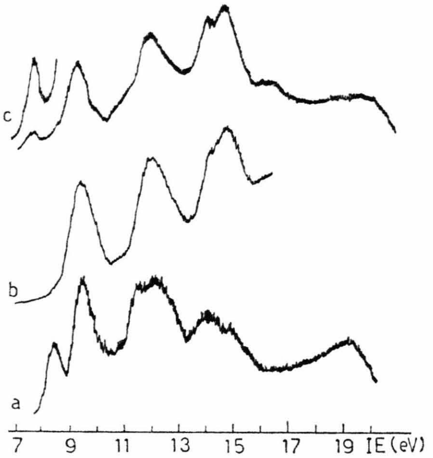

Fig. 3. He(I) gas phase p.e. spectra of:
(a) $[(C_6H_5)_2P(S)]_2$;
(b) $[(C_6H_5)_2P(O)]_2$;
(c) $[(C_6H_5)_2P]_2$.

with a characteristic intensity ratio 1 : 2 : 1, in the region of 8–9 eV, well separated from the following bands at I.E.s > 10 eV. From a comparison of the band system centers (8.66 to 8.35 eV) with the known I.E.s of other phosphine sulfides (8.53 eV in $(CH_3)_3P(S)$ [23] or 9.10 eV in $(CH_3)_2P(S)Br$ [24]), the whole band system is assigned to the ionization of the lone pairs of the two sulfur atoms. Experimentally, it turns out that the band profiles, relative intensities and the splitting between the components are completely independent of the temperature (the spectra were recorded at temperatures ranging from 77 °C for $[(CH_3)(t\text{–}C_4H_9)P(S)]_2$ to 127 °C for $[(CH_3)_2P(S)]_2$) and of the nature of the substituents. This suggests that the splitting mechanism is independent of the torsion angle around the P–P bond, and therefore the only explanation consistent with the experimental observations is that interaction occurs between the sulfur lone pairs which extend in the

Table 1. Ionization energies (eV) for some diphosphine disulphides.

Compound	σ_{SPPS}	π_S	σ^*_{SPPS}								
$[(CH_3)_2P(S)]_2$ calculat.[a]	9.62	10.51 10.60	11.15								
exper.	8.07	8.65	9.27	11.34		12.08	13.00		13.90		14.65
$[(C_2H_5)_2P(S)]_2$	7.96	8.56	9.09	11.30		11.66	12.75				
$[(n\text{-}C_3H_7)_2P(S)]_2$	7.84	8.41	8.96	11.50							
$[(n\text{-}C_4H_9)_2P(S)]_2$	7.80	8.34	8.94								
$[(CH_3)(t\text{-}C_4H_9)P(S)]_2$	7.79	8.34	8.94								
$[(C_6H_5)_2P(S)]_2$		8.45	9.50[b]	11.40		11.95			14.11		
$[(C_6H_5)_2P(O)]_2$			9.50[c]		11.70			14.04		14.45	
$[(C_6H_5)_2P]_2$		7.42[d]	9.08[d]		11.62			13.66		14.35	

[a] CNDO/2 non-d calculations assuming anti-planar configuration. The I.E. values calculated for other conformers of $[(CH_3)_2P(S)]_2$ are not reported but are available on request.
[b] $n_S^{-1} + \pi^{-1}$ of phenyl rings. [c] $n_O^{-1} + \pi^{-1}$ of phenyl rings. [d] n_P^{-1} (7.42), or ($n_P^{-1} + \pi^{-1}$ of phenyl rings) (9.08).

PPS planes via the σ-type orbitals of the P–P bond, whereas the out-of-plane pairs are not conjugated and remain nearly degenerate. The fact that the two split orbitals lie symmetrically in energy above and below the central unsplit energy level (see Fig. 4), despite of their mixing with the lower-lying σ_{P-P} orbitals, could be explained in terms of: i) an interaction occurring also with the higher-lying σ^*_{P-P} orbitals; ii) a small contribution of phosphorus-based orbitals. Therefore the energy of the two split levels is determined mainly by the energy of the 3p sulfur orbitals. This situation, as schematically depicted in Fig. 4, receives support from CNDO/2 calculations, which confirm the nature of the interaction and the independence of the splitting pattern on the torsion angle. Experimentally, the resonance integral for the bonding/antibonding interaction of the in-plane sulfur lone pairs turns out to be 0.58 ± 0.06 eV or ca 13.3 ± 1.4 kcal/mol.

It is interesting that a similar splitting effect has already been observed in several dicarbonyls (3—9), where a through-bond interaction occurs between the in-plane oxygen lone pairs via the skeletal σ_{C-C} orbitals, even if the carbon in the α-dicarbonyls and the phosphorus atoms give rise to different local bond geometry, trigonal planar, and tetrahedral, respectively.

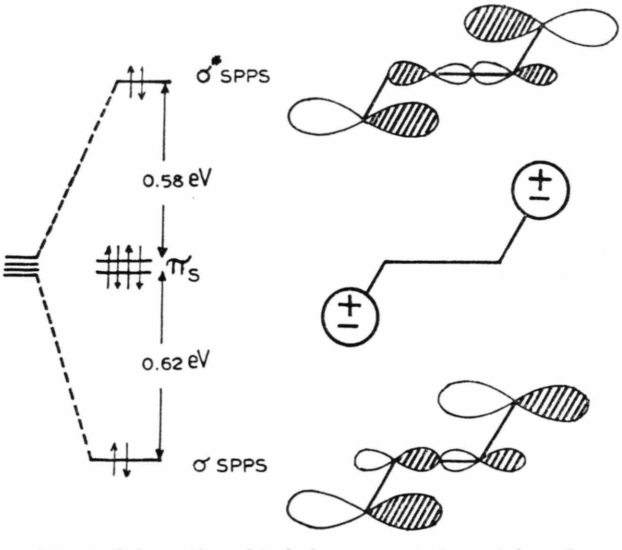

Fig. 4. Schematic orbital diagram of the sulphur lone-pairs interaction in tetramethyldiphosphinedisulphide (the reported values are experimental).

As for the actual conformers present in the gas phase, the above assignment implies that:

i) no conformational information can be derived from the splitting patterns of the UPS bands, the coupling mechanism being independent of the conformation.

ii) the out-of-plane sulfur lone pairs do not seem to interact appreciably in the whole series of compounds, any possible splitting being contained within the band-width of the second ionization. This indicates that through-space interactions are weak in the conformers which are more likely to occur in the gas phase, i.e. anti-planar and gauche by analogy with nmr and X-ray crystallographic data [1, 2, 25—29], supported by our computations.

Further data on the electronic structure of alkyl substituted diphosphine disulfides are supplied by the analysis of other features in the UP spectra. The band system centres of the n_S ionizations shift to lower I.E. with increasing size of the alkyl substituents, e.g. from 8.66 eV for the tetramethyl to 8.36 eV for the tetra-n-butyl derivative, in agreement with the known electron-releasing effect of alkyl groups.

The higher-energy region of the photoelectron spectrum is best interpreted for the tetramethyl-derivative, since with higher alkyl substituents σ(CH, CC) ionizations give rise to a broad, intense and unresolved band extending between ca. 10 and 16 eV, masking all other spectral features. In the spectrum of tetramethyldiphosphine disulfides the peaks are assigned, in order of increasing I.E., both by analogy with simpler phosphines and phosphine sulfides and by comparison with CNDO/2 calculations as follows: $\sigma_{(P-S)}$ at 11.34 eV, $\sigma_{(P-C)}$ at 12.01 eV, $\sigma_{(C-H)}$ at 14.65 eV (shoulder at 13.9 eV); no bands arising from σ_{pp}^{-1} ionization, expect in the region ca. 10—12 eV (compare $[(CH_3)_2P]_2$) [16, 17], can be identified.

In the case of phenyl substituents, such as tetraphenyldiphosphine disulfide, the UP spectrum displays broader and less resolved bands at 9.50, 11.40—11.85 and 14.11 eV. The n_S ionization yields a single, broad band peaked at 8.50 eV; lack of the triplet structure characteristic of the alkyl-substituted derivatives hints at a strong interaction of the π system of the phenyl rings with the sulfur lone pairs.

In order to obtain further data for empirical correlations, we also investigated the gas-phase UP spectrum of two related compounds, $[(C_6H_5)_2P]_2$ and $[(C_6H_5)_2P(O)]_2$. In both compounds the most intense bands are again of the benzenoid type, at 9.08, 11.62 and 13.66—14.35 eV in the diphosphine, and at 9.50, 11.76 and 14.04—14.45 eV in the dioxide, the shift being obviously related to the inductive effect of the oxygen atoms.

Several conformers of tetraphenyldiphosphine can exist, like in the case of the tetraalky-diphosphines and diarsines [16, 17].

The most interesting feature in the spectrum of $[(C_6H_5)_2P]_2$ is the band at low I.E. (7.42 eV) which can only be due to ionization of P Ione pair orbitals. Nothing is known about the conformation of the molecule in gas phase; for a gauche conformation, Ione pair ionizations are expected close to the value for $(C_6H_5)_2PH$ [8.28 eV [30]), whereas in anti-planar conformation an almost symmetrical splitting around the same value would be expected. Overlap with the intense benzenoid band at 9.08 eV prevents observation of the complete patterns of n_P ionizations in the diphosphine. We assign to the molecule a predominant anti-planar conformation in the gas phase, with one of the two Ione pair ionizations identified in the band at 7.42 eV, while the second one contributes to the strong band at 9.08 eV together with benzenoid ionizations. The shoulder at 8.20 eV at the foot of the benzenoid band is due to the presence of a small gauche component in the rotamer mixture. The overall splitting can be estimated as about 1.6 eV and is thus smaller than in simpler diphosphines ($\sim$ 2 eV), a fact which we attribute to coupling of the P Ione pairs to the π systems of the phenyl groups. This is the only case among the investigated molecules when UPS data supply direct, although still incomplete evidence on conformation around the P–P axis in the diphosphine systems.

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