Ultraviolet Photoelectron and *Ab Initio* Study of the Conformation of Some *p*-Substituted α-Phenylthioacetonitriles

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The analysis of the He^I photoelectron spectra of some *p*-substituted α-phenylthioacetonitriles (X-$C_6H_4SCH_2CN$; X = NO_2, Cl, H, CH_3, OCH_3, NH_2) shows evidence, in agreement with *ab initio* calculations, regarding the preferred conformation around the CC(ring)–S–C dihedral angle, ψ. By preference, ψ assumes large values; that is, the S–CH_2CN bond is significantly out of the ring plane. When the electron-releasing capability of X decreases, conformers with smaller ψ values have new features in the spectra. The dependence of the conformer distribution on steric and electronic factors is discussed.

The inductive effect of sulphur and steric effects have been found to be inadequate to explain the low basicity of some α-alkylthionitriles. It seemed reasonable to invoke an interaction between the cyano group and the sulphur atom, but it has been impossible to establish whether it occurs through space or through the bonds, and which orbitals contribute most to it.[1,2] Similarly, from analysis of the i.r. spectra of some *p*-substituted α-phenylthioacetonitriles it has been impossible to decide whether the electronic effect of the *para*-substituent is inductively or hyperconjugatively transmitted to the cyano group, or if both effects are operative.[3]

In order to improve our knowledge on the electronic interactions between the X, S, and CN groups in *para*-substituted α-phenylthioacetonitriles we present here analysis of the u.v. photoelectron spectra (p.e.s.) of compounds (**1**)—(**6**).

It is known from p.e.s. investigations that the conformation of alkyl aryl sulphides depends on the size of the alkyl group[4] and on the temperature[5] which determine the value of the angle ψ. In compounds (**1**)—(**6**) the rotation around the torsion angle χ should also be taken into account. For this reason, analysis of the p.e. spectra has been carried out with the help of *ab initio* computations. The aim was to obtain the energy-minimum conformation and the MO energies and localization properties for selected derivatives.

Experimental and Calculations

The He^I p.e. spectra were recorded by means of a Perkin-Elmer PS 18 photoelectron spectrometer. The spectra were calibrated with noble gas lines. The error in the quoted ionization energy (IE) values is ±0.05 eV.

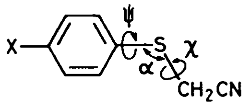
The samples, prepared as previously described,[3] were introduced in the collision chamber at the lowest temperature which gave suitable spectral intensity (50—90 °C). In particular, the spectra of the nitro- and amino-nitriles were recorded at the same temperature (*ca.* 90 °C).

Ab initio STO-3G[6] calculations on the derivative (**1**), (**3**), and (**6**) were carried out using the Gaussian 80 series of programs.[7] Sulphur 3*d* orbitals were not included in the basis set because they have little effect on the conformation of similar derivatives.[8]

Starting geometries were taken from *X*-ray structures of related diaryl sulphides.[9,10]

Results and Discussion

The He^I p.e. spectra of compounds (**1**)—(**6**) are shown in Figure 1. The uppermost IE values are presented in diagrammatic form in Figure 2.



(**1**) X = NO_2
(**2**) X = Cl
(**3**) X = H
(**4**) X = CH_3
(**5**) X = OCH_3
(**6**) X = NH_2

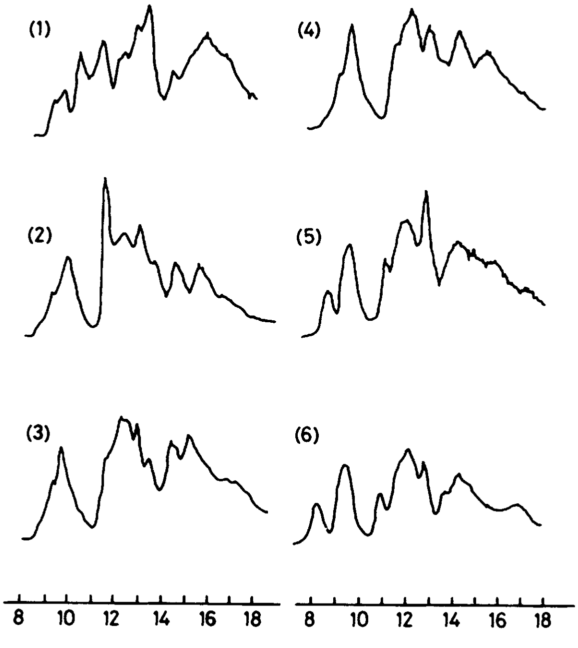


Figure 1. He^I photoelectron spectra of *p*-substituted α-phenylthioacetonitriles $XC_6H_4SCH_2CN$ (**1**)—(**6**)

The studied compounds are derived from the corresponding thioanisole $XC_6N_4SCH_3$ by substitution of a CN group for a hydrogen atom. The close similarity of the electronic structures should give rise to similar photoelectron spectra, apart from bands related to MOs mainly localized at the CN group.

The three lowest IE values of thioanisoles have been related[11,12] to MOs deriving from the in-phase and out-of-phase combinations of the sulphur lone pair (n_S) and the

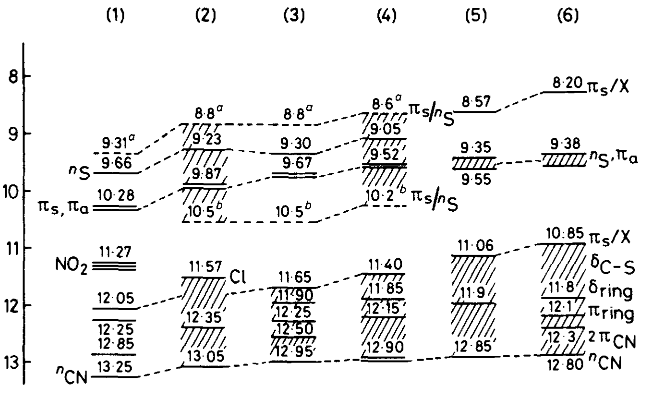


Figure 2. Experimental (p.e.s.) partial energy level diagrams (eV) for α-phenylthioacetonitriles (**1**)—(**6**). a, b, Out-of-phase and in-phase combinations, respectively, of the sulphur lone pair (n_S) and the symmetric component (π_S) of the phenyl e_{1g} orbital in 'planar' rotamers (see text)

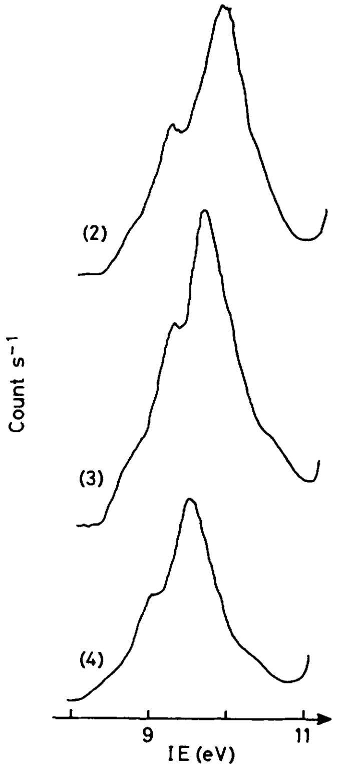
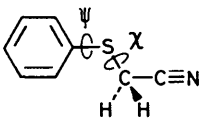


Figure 3. Low IE region of the He^I photoelectron spectra of compounds (**2**)—(**4**) in expanded scale

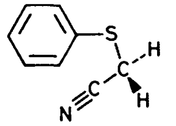
symmetric component (π_S) of the phenyl e_{1g} oribital and to the anti-symmetric (π_A) e_{1g} orbital. The bands in the spectra at slightly higher IE values (10—12 eV) have been related to orbitals localized at the X substituent or to MOs resulting from their interaction with the thioanisole group orbitals and to the σ(C–S)MO.

In the spectra of (**1**)—(**6**) ionization from MOs mainly localized at the cyano group [2π(CN) and *n*(CN)] are expected to generate bands at *ca.* 12—13 eV, the *n*(CN) one (mainly localized at the nitrogen lone pair) producing an intense sharp peak.[13]



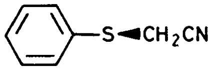
(**7**)

ψ = 0°, χ = 180°



(**8**)

ψ = 0°, χ = 0°



(**9**)

ψ = 90°

The spectra of (**5**) and (**6**) agree with this expectation. Weak shoulders appear in the spectra of (**2**)—(**4**) between 8 and 9 and between 10 and 11 eV, while in the spectrum of (**1**) the first band is split into two components of similar intensity (see Figure 1).

The initial part of the spectra of (**2**)—(**4**) is reported in expanded scale in Figure 3. The shoulders are more clearly seen, except that on the high-energy side of the main band in (**2**).

They seem to be a real feature. I.r. and mass spectra did not display the presence of impurities in the samples. Furthermore, the low-energy shoulder cannot be ascribed to the 1β satellite of the ionizing radiation because of energy and intensity reasons.

On the basis of the assignment of the spectrum of *p*-nitroanisole and cyano derivatives,[11–13] only one ionization is expected below the intense band at 10.28 eV in the spectrum of (**1**), and the energy separation (0.35 eV) between the two maxima observed is too large to be ascribed to vibrational fine structure.

P.e.s. investigations of thioanisole and related compounds[4,5] have shown that additional features in the spectra can be related to the presence of a mixture of conformers, owing to the steric hindrance between the relatively bulky alkyl groups and the *ortho* hydrogens.

This effect alone can hardly explain our experimental observations because, the most intense features in the spectra of compounds (**2**)—(**4**) appear to be related (see below) to the 'perpendicular conformer' as in the p.e. spectrum of phenyl isopropyl sulphide.[5] However, the steric hindrance of the SCH_2CN group is probably smaller than that of the SC_2H_5 groups, whose p.e. spectrum shows similar intensity of the 'planar' and 'perpendicular conformers'.[5]

A comparison with literature data[4,5] suggests, however, that in this case also, an electronic factor determines the conformational preference: the rotation around the S–ring bond reduces π-conjugation between the substituted ring and the sulphur lone pair.

Ab initio computations on compounds (**1**), (**3**), and (**6**) have been performed to determine conformational stabilities and to investigate the conformational dependence of the orbital energies. First, we have considered the effect on the total energy of (**3**) of varying χ between 0 and 180° mantaining ψ fixed at 0° or 90° [see (**7**)—(**9**)]. In both cases, the minimum occurs when χ = 180°. The total energy changes slightly with the χ value except when χ is close to 0°. The *syn* form (χ = 0°) is less stable (by *ca.* 29 kJ mol^{-1}, ψ = 90°) or much less stable (ψ = 0°) than the *anti* form. We have therefore assumed χ = 180° in the remaining calculations.

The computed total energy differences with respect to the most stable conformer for selected ψ values are presented in the Table. Optimization of the α bond angle and of the C–S bond distances (S–ring = r_1; S–CH_2 = r_2) slightly reduces the total energy. On going from ψ = 0° to ψ = 90°, α decreases by 6—7° and the C–S bond distances increase slightly ($\leqslant$0.01 Å).

Only one minimum, at ψ = 90°, is predicted for (**6**). For (**3**), the absolute minimum at ψ = 90° is accompanied by a second relative minimum (*ca.* 4 kJ mol^{-1} higher energy) at ψ = 0°. The relative conformational energy for internal rotation in (**1**) shows a slightly more involved trend. Two minima of nearly equal energy (ΔE 0.21 kJ mol^{-1}) are computed at ψ = 60° (absolute

Table. Relative energies with respect to the most stable conformer, and optimized C–S–C bond angle (α) and C–S bond distances (r_1 and r_2) for some *p*-substituted α-phenylthioacetonitriles at various ψ angles (χ = 180° in all cases)

ψ/°	ΔE/kJ mol^{-1}	r_1/Å	r_2/Å	α/°
p-$NO_2C_6H_4SCH_2CN$ (**1**)				
0	0.21	1.782	1.812	103.4
30	1.84	1.786	1.816	102.2
60	0.0	1.790	1.820	97.7
90	0.71	1.791	1.821	96.3
$HC_6H_4SCH_2CN$ (**3**)				
0	3.97	1.785	1.815	103.4
30	4.39	1.788	1.818	102.4
60	0.25	1.790	1.820	98.0
90	0.0	1.790	1.820	96.6
p-$NH_2C_6H_4SCH_2CN$ (**6**)				
0	10.16	1.787	1.817	103.5
30	8.90	1.788	1.818	102.7
60	1.72	1.789	1.819	98.3
90	0.0	1.789	1.819	97.0

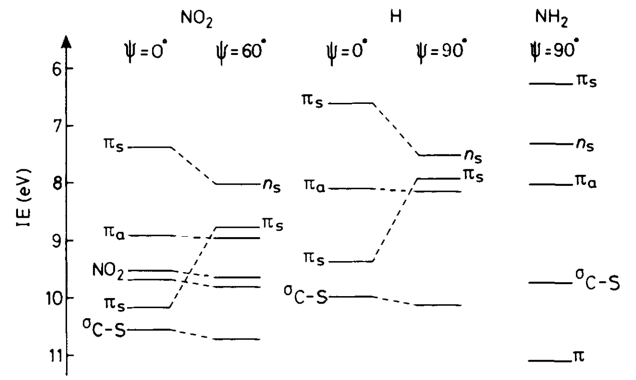


Figure 4. *Ab-initio* STO-3G partial energy level diagrams of some *p*-substituted α-phenylthioacetonitriles at selected ψ values

minimum) and ψ = 0°, and two maxima appear at ψ = 30° (absolute maximum) and 90°.

All the energy differences between the various conformers and the barriers to rotation are very small. The largest difference (10.16 kJ mol^{-1}) is computed between the planar (ψ = 0°) and perpendicular (ψ = 90°) conformer of (**6**), so that the relative energy minima are predicted to be extremely shallow. Thus it appears that the SCH_2CN group of the $XC_6H_4SCH_2CN$ derivatives rotates almost freely.

On the other hand, the p.e. spectra with two separate bands for only one ionization event [as in (1)] or with evident shoulders [as in (**2**)—(**4**)] strongly suggest the presence of two predominant conformers.

This could imply that calculations underestimate barriers to rotations. However, Heilbronner *et al.* have shown[14] that a double band can be observed even if internal rotation is nearly completely free as in divinylacetylene,[15] and that (for the numerical experiment chosen by the authors) it results more from the angular dependence of orbital energies than from the conformer distribution density.[14] These two factors can combine to give two band maxima each corresponding to a predominant group of conformers.

The computed uppermost oribital energies for (1) (ψ = 0° and 60°), (**3**) (ψ = 0 and 90°), and (**6**) (ψ = 90°) are presented in Figure 4. As expected, on going from small to large ψ values the interaction between the n_S and the uppermost ring orbital decreases reducing the splitting between their in-phase and out-of-phase combinations, while the antisymmetric e_{1g} (π_A) orbital remains unperturbed. Similarly, on increasing the ψ angle, only small energy changes are shown by the σ(C–S), π(CN), σ(ring), n(CN), and the low lying π MOs of all the derivatives.

The above analysis and the close similarity of the diagrams of Figure 4 with the corresponding data of Figures 2 and 3 allows one to assign the spectra of (**1**)—(**6**). They derive from the overlap of the spectra of two main groups of conformers: one with a large ψ value ('perpendicular conformer') and a second one, containing a smaller number of contributing rotamers with a smaller ψ value ('planar conformer'). The number of the latter conformers increases with the electron-withdrawing ability of X.

Therefore, the intense bands below *ca.* 11 eV, are assigned to the π_S, π_A and n_S MOs of the 'perpendicular conformer', while the shoulders present in the spectra of (**2**)—(**4**) are assigned to the in-phase and out-of-phase combinations of the π_S and n_S oribitals of the 'planar conformer'. In the spectrum of (**1**), only the antibonding combination is visible, while the bonding one is hidden by the intense band (peaking at 11.27 eV) deriving from the ionization from three* MOs localized at the NO_2 group.[16] A characteristic sharp band related to chlorine AOs appears[17] at 11.57 eV in the spectrum of (**2**). The bands related to ionization from the σ(C–S), and the π(CN) MOs, contribute to the envelope of bands appearing between 11.5 and 13 eV, but they are in general not resolved from those related to σ and the inner π-ring orbitals. The last sharp component of this region, peaking from 13.25 to 12.80 eV on going from (**1**)—(**6**), is probably related to the n(CN) MO.[13]

The increasing importance of the 'planar conformer' with the electron-withdrawing properties of the X substituent could be explained by the following arguments. In the studied compounds, several π-electron-rich groups (X, benzene ring, S, and CN) are connected together. The resulting electronic repulsion can be relieved by distorsion from planarity or by introduction of a strong acceptor group such as NO_2.

In fact, the sulphur substituents (S–R, R = H or alkyl group) have σ and π electron-donor ability with respect to the phenyl ring.[18–20] Both are enhanced by a *p*-nitro-substituent which significantly lowers the energy of the lowest unoccupied MO (LUMO),[21] facilitating the sulphur $\longrightarrow$ ring charge-transfer (CT) interaction. This stabilizing interaction is maximized in the planar conformation, which could become the most stable. Conversely, an amino substituent increases the energy of the LUMO,[22,23] reducing the sulphur $\longrightarrow$ ring CT interaction. In the latter case electronic repulsion can prevail in determining the most stable conformation. The two effects balance each other when the X substituent is not strong.

This analysis is supported by the crystal structure of the *p*-dialkylamino- and *p*-nitro-diphenyl sulphides where the angle between the normals to the two phenyl rings is 82 and 84°, respectively.[9,10] However, the C–S–C plane is nearly coplanar with the substituted ring in the nitro-derivative,[9] and with the unsubstituted ring in the amino compound.[10]

The unusual variation of the HOMO energy of *p*-substituted diphenyl sulphides with the σ_p^+ values has been ascribed to these geometrical variations.[18]

Conclusions

The value of the CC(ring)–S–C dihedral angle, ψ, is the main geometrical parameter determining the π-conjugation in *para*-

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* The uppermost π-MO mainly localized at the nitro group [$\pi(O^-)$, $1a_2$] is wrongly predicted by the present calculations to be nearly degenerate with the HOMO (7.57 and 7.36 eV, respectively, ψ = 0°) rather than close to the pair of σ-MOs as found experimentally.[16] For clarity, the π-NO_2 MO has been omitted from the sketch of Figure 4.

substituted α-phenylthioacetonitriles. The distribution of ψ values, in turn, depends on the interplay of the steric hindrance between the S–CH_2CN group and the phenyl *ortho*-hydrogen atoms, the electronic repulsion between π-electron rich groups, and the CT interaction between sulphur and the LUMO of the substituted phenyl ring. In the amino derivative, where the energy of the ring HOMO is increased by the amino group, the repulsion between filled π-orbitals is maximized and the S $\longrightarrow$ LUMO (ring) CT interaction is made difficult. Under these conditions, the (small) barrier to rotation about the C(ring)–S bond reaches a maximum and only 'perpendicular' conformers are seen in the p.e. spectrum.

The other extreme behaviour is shown by the nitro derivative. The strong electron-withdrawing group reduces the π-electron density of the filled ring orbitals, and introduces a new low lying empty MO (also localized at the ring) which can easily accept charge from sulphur. The decreased repulsion and the stabilizing CT interaction favour the 'planar conformer', whose contribution to the p.e. spectrum increases accordingly.

The varying CT interaction creates a variable positive charge on sulphur which is inductively transmitted to the CN group, in agreement with the inductive mechanism proposed[3] for the transmission of the X substituent effect to the CN group in this class of compound.

On the other hand, the alternative explanation for the transmission of the substituent effect, *i.e.* the hyperconjugation between the S–CH_2 bond and the π(CN) orbitals, seems equally supported by the present calculations. In fact, the analysis of the σ(C–S) MO indicates that its localization at the CN group orbitals slightly increases on going from the NH_2 and H to the NO_2 derivative (from 5 to 10%), both for $\psi = 0$ and 90°, indicating an increased hyperconjugative interaction.

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