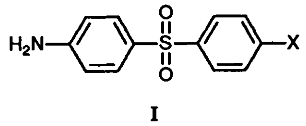
Molecular Structure and Crystal Packing of five 4-Aminophenyl (4-Substituted Phenyl) Sulfones. Correlations between Structural Distortions, Spectroscopic Parameters and Electronic Substituent Effects

Valerio Bertolasi,*[,a] **Valeria Ferretti,**[a] **Paola Gilli**[a] **and Pier G. De Benedetti**[b]
[a] *Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy*
[b] *Dipartimento di Chimica, Università di Modena, 41100 Modena, Italy*

The crystal structures of five 4-aminophenyl 4-X-phenyl sulfones (X = NO_2, CN, F, OCH_3, NH_2) are reported. The molecules present a relevant degree of charge redistribution where electronic charge transfer mainly occurs from the amino to the sulfonyl group with consequent shortening of C–N and C–S distances and increase of the quinoid character of the phenylene group. The *p*-aminophenylsulfonyl moiety is characterized by a substantial geometrical constancy in spite of the fact that the *p*-X-phenyl group is able to modulate the properties of the whole molecule as shown by the strict intercorrelation between the Hammett constant σ_p of the substituent X on one side and the proton NMR chemical shift of the *p*-amino group on the other side. The electronic effects of X are transmitted without increasing the quinoid character of the attached phenylene, and change only its S–C distance. This suggests an inductive charge transfer, without resonance components, from X to the SO_2 sulfur, whose partial charge can modulate the properties of the terminal aminic group through the almost constant π-delocalization of the *p*-aminophenylsulfonyl moiety. A detailed analysis of the hydrogen bonds present in the packing of the five crystals has been carried out. It is shown that the hydrogen bond scheme is mainly controlled by *p*-aminophenylsulfonyl moieties forming linear chains or bidimensional networks of π-resonant hydrogen bonds linking the molecules by means of N–H···O=S interactions. The N···O distances and the IR frequencies show that these hydrogen bonds are rather weak and similar to those found in *p*-nitroaniline derivatives.

p-Aminophenyl sulfones are a class of molecules which contain electron donor and acceptor functional groups, as well as hydrogen bond acceptors and donors. These features can give rise to a molecular redistribution of charge by means of intra- and inter-molecular interactions with consequent interesting structural and electronic properties.[1,2] The biological and pharmacological activities of this class of molecules as antibacterial and antileprotic agents have been widely described[3,4] and, more recently, their non-linear optical (NLO) properties have been investigated in view of their analogies with *p*-nitroaniline (PNA) derivatives.[5,6] They differ from PNAs only in one respect: the NO_2 group is replaced by the sulfonyl one which possesses similar electron-withdrawing character and has the advantage of being bifunctional, a feature which permits modification of its electronic properties by substitution. In particular, the biological activities of the 4-aminophenyl (4-substituted phenyl) sulfones have been shown to be related to the electronic structure of the common p-NH_2–$C_6H_4SO_2$– moiety modulated by the 4′-substituents *via* intramolecular interactions.[1,4]

Substituent effects on the electronic structure of sulfones (I) have been investigated by means of ^1H NMR, ^{13}C NMR and IR spectroscopy, and semiempirical quantum-mechanical calculations,[1,4] and the generally good linear intercorrelations among spectral data, computed electronic charges and Hammett constants of the *para* substituents $\sigma_p(X)$, have been shown to be interpretable in terms of intramolecular redistribution of charge from the donor to the acceptor group.[1] The present paper is devoted to ascertaining whether the intramolecular distortions determined by X-ray crystallography are, likewise, intercorrelated with the electronic properties of the substituents. At the same time a crystal packing analysis is carried out to establish whether these compounds form typical patterns of hydrogen bonds which are to be related to their characteristic electronic structures. For this purpose, a series of five crystal structures of such compounds (**1**–**5**) having substituents with different electronic properties has been accurately determined and analysed.



I

1; X = NO_2 **4**; X = OCH_3
2; X = CN **5**; X = NH_2
3; X = F

Results and Discussion

Crystal data, experimental details, structure determinations and refinement of the five compounds are reported in Table 1, and final coordinates in Tables 2–6. Bond distances are given in Table 7 and a selection of bond and torsion angles in Tables 8 and 9. ORTEP[12] views of the molecules are shown in Fig. 1.† Crystal structures show that all the molecules have similar conformations with the two phenyl rings approximately perpendicular to the C(1)–S–C(1′) plane as shown by the values of

---

† Tables of thermal parameters, hydrogen atom co-ordinates and bond angles have been deposited at the Cambridge Crystallographic Data Centre. For details, see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 2*, 1993, in the January issue.

Table 1 Crystal data[a]

Compound	**1**	**2**	**3**	**4**	**5**[b]
Name	4-Aminophenyl 4-nitrophenyl sulfone	4-Aminophenyl 4-cyanophenyl sulfone	4-Aminophenyl 4-fluorophenyl sulfone	4-Aminophenyl 4-methoxyphenyl sulfone	4-Aminophenyl 4-aminophenyl sulfone
Formula	$C_{12}H_{10}SO_4N_2$	$C_{13}H_{10}SO_2N_2$	$C_{12}H_{10}SO_2FN$	$C_{13}H_{13}SO_3N$	$C_{12}H_{12}SO_2N_2$
M	278.3	258.3	251.3	263.3	248.3
Space group	$C2/c$	$P2_1/n$	$Pbcn$	$Pna2_1$	$P2_12_12_1$
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Cell parameters,					
a/Å	20.994(4)	10.971(2)	15.058(2)	20.073(6)	5.758(1)
b/Å	7.805(1)	8.122(2)	10.431(2)	7.712(2)	8.058(1)
c/Å	15.590(3)	14.201(3)	15.222(2)	8.258(5)	25.529(3)
β/°	99.38(2)	102.36(5)			
V/Å^3	2520.4(8)	1236.1(5)	2390.9(6)	1278.4(9)	1184.5(3)
Z	8	4	8	4	4
D_c/g cm^{-3}	1.47	1.39	1.40	1.37	1.39
F(000)	1152	536	1040	552	520
μ(Mo-Kα)/mm^{-1}	0.26	0.24	0.26	0.24	0.25
Crystal size/mm^3	0.15 × 0.24 × 0.38	0.21 × 0.38 × 0.40	0.17 × 0.48 × 0.50	0.20 × 0.26 × 0.48	0.19 × 0.31 × 0.54
Independent reflections	3653	3597	3468	1496	1528
Observed $[I > n\sigma(I)]$	1780 ($n = 3$)	1654 ($n = 3$)	1513 ($n = 3$)	974 ($n = 2$)	1312 ($n = 3$)
Θ_{min}–Θ_{max}/°	2–30	2–30	2–30	2–27	2–27
Refinement					
H atoms	isotropic	isotropic	isotropic	isotropic	isotropic
non-H atoms	anisotropic	anisotropic	anisotropic	anisotropic	anisotropic
R,R_w	0.046, 0.060	0.040, 0.048	0.042, 0.052	0.036, 0.042	0.032, 0.042
Max shift/error	0.04	0.07	0.03	0.03	0.08
Largest ΔF peak/e Å^{-3}	0.37	0.19	0.26	0.18	0.20
S	1.18	1.25	1.63	1.18	1.18
No. of variables (last cycle)	212	203	194	215	202

[a] Data collection instrument: Enraf–Nonius CAD4; $T = 295$ K; radiation: Mo-Kα ($\lambda = 0.710\,69$ Å) graphite monochromated; $w/2\theta$ scan; 25 centring reflections in the range 9–14° θ range; 3 monitored reflections every 2 h; solution by MULTAN82;[7] full matrix refinement; $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$; weights $w = 4F_o^2/\sigma^2(F_o^2) + (pF_o^2)^2$, $p = 0.05, 0.05, 0.04, 0.05, 0.06$ for compounds **1**, **2**, **3**, **4** and **5**, respectively. All calculations performed by the CAD4 SDP[8] and PARST[9] systems of programs; scattering factors from ref. 10. [b] This structure has been independently determined,[11] with very similar results. Our crystal structure redetermination is included for sake of homogeneity of the data.

Table 2 Positional parameters with esds in parentheses for compound **1**

Atom	x	y	z
S	0.128 55(3)	0.114 84(9)	0.603 29(4)
O(1)	0.166 67(9)	0.058 9(3)	0.540 6(1)
O(2)	0.097 1(1)	0.278 8(2)	0.590 4(1)
C(1)	0.175 2(1)	0.106 1(3)	0.706 3(2)
C(2)	0.150 0(1)	0.163 7(3)	0.778 1(2)
C(3)	0.185 2(1)	0.147 9(4)	0.859 7(2)
C(4)	0.246 7(1)	0.074 1(3)	0.870 9(2)
C(5)	0.272 5(1)	0.026 2(4)	0.798 3(2)
C(6)	0.237 1(1)	0.039 8(4)	0.716 4(2)
N(1)	0.282 1(1)	0.056 0(4)	0.953 5(2)
C(1′)	0.067 6(1)	−0.041 0(3)	0.608 3(2)
C(2′)	0.006 6(1)	0.006 9(4)	0.621 7(2)
C(3′)	−0.038 9(1)	−0.118 2(4)	0.627 8(2)
C(4′)	−0.022 5(1)	−0.284 9(4)	0.620 1(2)
C(5′)	0.037 2(2)	−0.334 0(4)	0.604 8(2)
C(6′)	0.082 7(1)	−0.211 3(4)	0.598 9(2)
N(1′)	−0.071 9(1)	−0.416 9(4)	0.625 5(2)
O(3′)	−0.123 9(1)	−0.376 3(4)	0.636 2(2)
O(4′)	−0.058 0(1)	−0.563 3(4)	0.615 5(3)
H(1N)	0.262(2)	0.039(4)	0.998(2)
H(2N)	0.310(2)	−0.023(5)	0.960(2)

Table 3 Positional parameters with esds in parentheses for compound **2**

Atom	x	y	z
S	0.630 92(6)	0.295 39(8)	0.349 84(4)
O(1)	0.757 3(2)	0.344 1(3)	0.388 9(1)
O(2)	0.582 4(2)	0.150 0(2)	0.385 6(1)
C(1)	0.609 6(2)	0.281 7(3)	0.225 3(2)
C(2)	0.519 7(2)	0.176 7(3)	0.173 6(2)
C(3)	0.497 4(2)	0.173 5(3)	0.075 0(2)
C(4)	0.564 1(2)	0.274 9(3)	0.024 9(2)
C(5)	0.653 6(2)	0.380 6(3)	0.077 6(2)
C(6)	0.676 1(2)	0.384 3(3)	0.176 4(2)
N(1)	0.544 5(2)	0.265 7(3)	−0.073 3(2)
C(1′)	0.534 4(2)	0.462 6(3)	0.366 4(2)
C(2′)	0.413 5(2)	0.436 5(3)	0.373 2(2)
C(3′)	0.337 2(2)	0.569 3(4)	0.378 5(2)
C(4′)	0.383 1(3)	0.727 0(3)	0.376 0(2)
C(5′)	0.505 9(3)	0.752 5(3)	0.372 0(2)
C(6′)	0.582 2(3)	0.619 2(3)	0.367 2(2)
C(7′)	0.302 9(3)	0.868 6(4)	0.374 7(2)
N(1′)	0.240 5(3)	0.980 1(4)	0.370 4(2)
H(1N)	0.474(2)	0.223(3)	−0.103(2)
H(2N)	0.588(2)	0.327(3)	−0.096(2)

the $w1$ and $w2$ parameters used to define the dihedral angles by a linear combination of torsion angles (Table 9). In such a way all molecules are seen to adopt a typical arrangement intermediate between 'butterfly' and 'propeller' conformations.

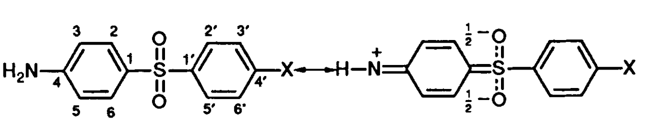
In analogy with *p*-nitroaniline derivatives *p*-aminophenylsulfonyls show a high degree of charge redistribution and the parameters which may be of interest in analysing this are summarized in Table 10.

Table 4 Positional parameters with esds in parentheses for compound **3**

Atom	*x*	*y*	*z*
S	0.659 44(5)	0.302 44(7)	0.098 31(4)
O(1)	0.619 4(2)	0.222 4(2)	0.033 2(1)
O(2)	0.748 6(1)	0.351 3(2)	0.083 0(1)
C(1)	0.659 5(3)	0.219 9(2)	0.197 7(2)
C(2)	0.616 3(2)	0.103 3(3)	0.204 4(2)
C(3)	0.618 7(2)	0.037 0(3)	0.281 6(2)
C(4)	0.662 9(2)	0.083 9(2)	0.354 5(2)
C(5)	0.705 6(2)	0.202 0(3)	0.347 0(2)
C(6)	0.704 5(2)	0.267 9(2)	0.269 7(2)
N(1)	0.667 4(2)	0.016 6(3)	0.430 8(2)
C(1′)	0.590 4(2)	0.436 6(2)	0.113 3(1)
C(2′)	0.627 1(2)	0.556 5(3)	0.119 2(2)
C(3′)	0.573 4(2)	0.662 1(2)	0.131 0(2)
C(4′)	0.484 9(2)	0.642 6(2)	0.137 5(2)
C(5′)	0.446 0(2)	0.526 1(3)	0.132 0(2)
C(6′)	0.499 5(2)	0.420 7(2)	0.119 4(2)
F	0.432 2(1)	0.746 1(2)	0.153 1(1)
H(1N)	0.690(2)	0.050(3)	0.477(2)
H(2N)	0.635(2)	−0.047(3)	0.437(2)

Table 5 Positional and thermal parameters with esds in parentheses for compound **4**

Atom	*x*	*y*	*z*
S	0.129 84(4)	0.044 2(1)	0
O(1)	0.095 9(1)	0.209 1(3)	−0.009 4(5)
O(2)	0.170 2(1)	0.009 6(5)	0.140 3(3)
C(1)	0.178 8(2)	0.023 4(5)	−0.172 6(5)
C(2)	0.242 1(2)	−0.045 0(5)	−0.165 3(5)
C(3)	0.279 2(2)	−0.057 9(5)	−0.303 9(6)
C(4)	0.254 1(2)	−0.005 0(5)	−0.452 9(4)
C(5)	0.190 7(2)	0.063 4(6)	−0.458 2(4)
C(6)	0.153 8(2)	0.080 0(6)	−0.320 3(5)
N(1)	0.292 0(2)	−0.015 6(6)	−0.590 2(4)
C(1′)	0.068 0(2)	−0.115 8(5)	−0.007 6(5)
C(2′)	0.073 9(2)	−0.266 2(6)	0.081 5(5)
C(3′)	0.024 3(2)	−0.390 9(5)	0.077 3(6)
C(4′)	−0.030 4(2)	−0.365 7(5)	−0.021 1(5)
C(5′)	−0.035 6(2)	−0.217 0(6)	−0.112 8(5)
C(6′)	0.012 8(2)	−0.093 9(5)	−0.105 8(5)
O(3′)	−0.082 2(1)	−0.478 5(4)	−0.035 6(4)
C(7′)	−0.081 3(2)	−0.632 0(7)	0.063 7(8)
H(1N)	0.276(1)	0.000(5)	−0.671(5)
H(2N)	0.324(2)	−0.097(5)	−0.591(6)



IIa **IIb**

An important parameter is the degree of the quinoid structural distortion (**IIb**) contributing to the ground state of the molecule. Such quinoid character can be measured by the parameter $Q = (d_{1-2} + d_{1-6} + d_{3-4} + d_{4-5})/4 - (d_{2-3} + d_{5-6})/2$ which is zero for a perfect hexagonal benzene structure, and 0.138 for a perfect quinoid structure, where $d_{1-2} = d_{1-6} = d_{3-4} = d_{4-5} = 1.455$ Å and $d_{2-3} = d_{5-6} = 1.317$ Å.[13] A parallel Q' parameter can be defined for the second phenylene bearing the X substituent. Other geometrical quantities are the two S–C distances, the C–NH$_2$ lengths and the degrees of pyramidality, $\langle\alpha\rangle$, of the aminic nitrogen (measured as the average of the two C–N–H and of the H–N–H angles).

Table 10 includes some additional spectroscopic parameters, in particular the NMR chemical shifts $\delta(\mathrm{NH_2})$, $\delta[^{13}\mathrm{C}(1)]$ and $\delta[^{13}\mathrm{C}(1')]$ taken from ref. 1 and the IR symmetrical and asymmetrical stretching frequencies of the NH$_2$ group (ν_a and ν_s). All these parameters are liable to be intercorrelated with Hammett's σ_p(X) constants[14,15] reported in the last line of

Table 6 Positional parameters with esds in parentheses for compound **5**

Atom	*x*	*y*	*z*
S	0.125 7(1)	0.081 19(6)	0.875 56(2)
O(1)	−0.122 8(3)	0.063 0(2)	0.880 50(7)
O(2)	0.269 5(4)	−0.053 7(2)	0.893 69(7)
C(1)	0.212 0(4)	0.263 0(3)	0.907 82(8)
C(2)	0.078 9(4)	0.405 2(3)	0.902 60(8)
C(3)	0.153 8(4)	0.551 8(3)	0.924 27(8)
C(4)	0.363 8(4)	0.558 0(3)	0.952 05(7)
C(5)	0.491 5(4)	0.413 0(3)	0.958 54(8)
C(6)	0.419 5(4)	0.266 5(3)	0.936 02(9)
N(1)	0.435 8(4)	0.708 3(3)	0.972 89(8)
C(1′)	0.186 8(4)	0.113 4(2)	0.809 19(8)
C(2′)	0.026 8(4)	0.195 3(3)	0.777 72(9)
C(3′)	0.076 4(4)	0.220 7(3)	0.725 52(9)
C(4′)	0.283 1(4)	0.166 9(3)	0.703 99(8)
C(5′)	0.440 7(4)	0.082 0(3)	0.735 33(9)
C(6′)	0.394 4(4)	0.057 8(3)	0.788 01(9)
N(1′)	0.327 2(4)	0.194 2(3)	0.651 36(8)
H(1N)	0.385(4)	0.801(3)	0.956 0(9)
H(2N)	0.578(5)	0.709(4)	0.982(1)
H(1′N)	0.269(9)	0.289(6)	0.640(2)
H(2′N)	0.480(7)	0.173(5)	0.640(1)

Table 7 Bond distances (Å) with esds in parentheses

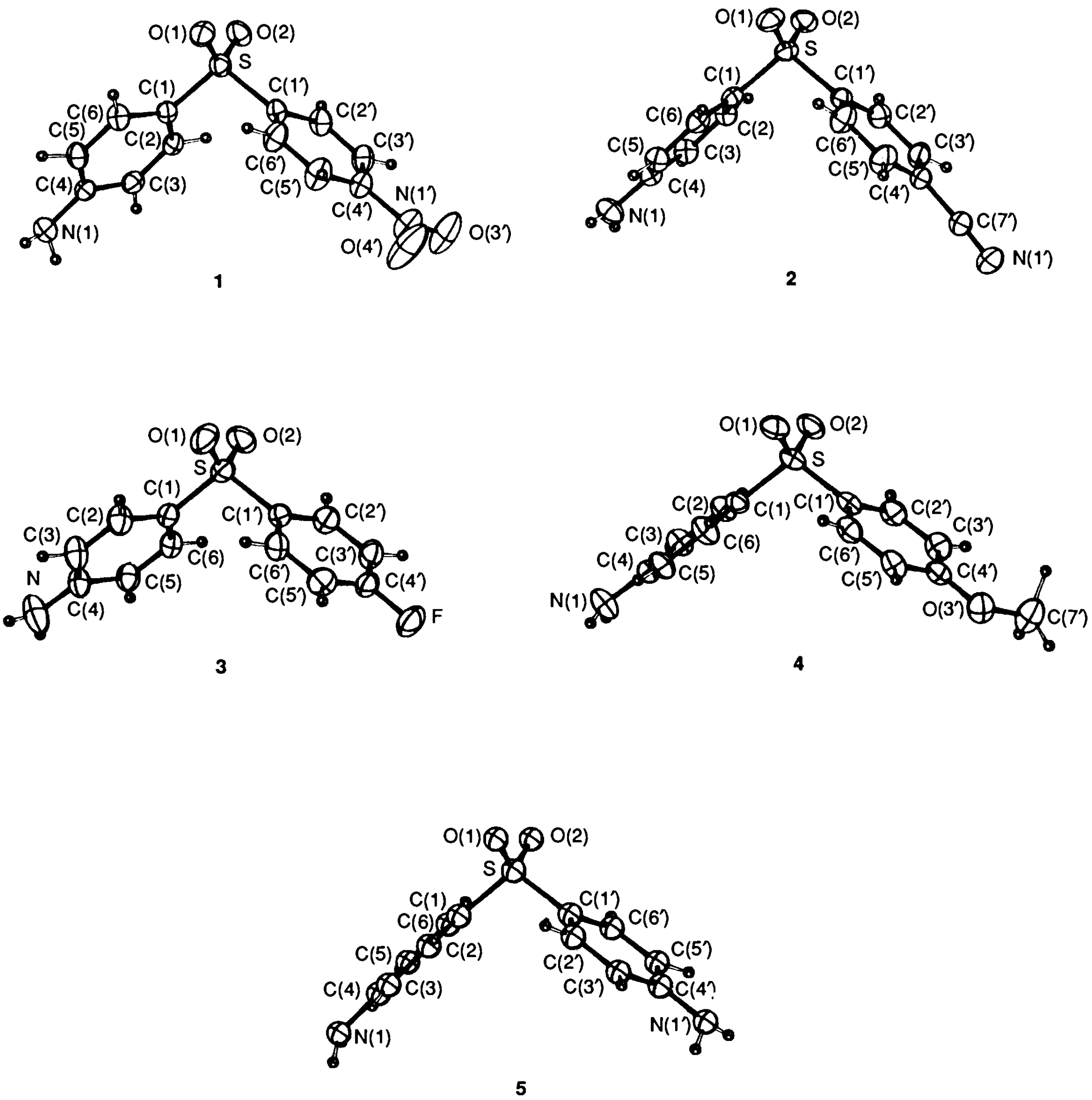
	1	**2**	**3**	**4**	**5**
S–O(1)	1.429(2)	1.434(2)	1.429(2)	1.445(2)	1.444(2)
S–O(2)	1.439(2)	1.432(2)	1.455(2)	1.439(2)	1.443(2)
S–C(1)	1.741(3)	1.737(2)	1.741(3)	1.739(4)	1.753(2)
S–C(1′)	1.776(2)	1.768(2)	1.758(3)	1.751(4)	1.750(2)
C(1)–C(2)	1.388(4)	1.389(3)	1.383(4)	1.377(6)	1.385(3)
C(1)–C(6)	1.384(3)	1.388(4)	1.382(4)	1.389(6)	1.395(3)
C(2)–C(3)	1.369(4)	1.369(4)	1.364(4)	1.369(6)	1.374(3)
C(3)-C(4)	1.398(3)	1.394(4)	1.383(4)	1.391(6)	1.403(3)
C(4)–C(5)	1.384(4)	1.395(3)	1.394(4)	1.378(6)	1.390(3)
C(5)–C(6)	1.373(4)	1.372(4)	1.363(4)	1.364(5)	1.377(3)
N(1)–C(4)	1.385(4)	1.367(4)	1.359(4)	1.368(5)	1.386(3)
C(1′)–C(2′)	1.382(3)	1.367(3)	1.370(4)	1.379(6)	1.389(3)
C(1′)–C(6′)	1.380(4)	1.375(3)	1.382(4)	1.383(6)	1.386(3)
C(2′)–C(3′)	1.380(4)	1.377(4)	1.378(4)	1.385(6)	1.378(3)
C(3′)–C(4′)	1.356(4)	1.380(4)	1.352(4)	1.380(6)	1.381(3)
C(4′)–C(5′)	1.368(5)	1.376(5)	1.352(4)	1.378(6)	1.390(3)
C(5′)–C(6′)	1.366(5)	1.379(4)	1.376(4)	1.360(6)	1.385(3)
C(4′)–N(1′)	1.474(4)				1.385(3)
N(1′)–O(3′)	1.174(3)				
N(1′)–O(4′)	1.196(4)				
C(4′)–C(7′)		1.446(4)			
N(1′)–C(7′)		1.129(5)			
C(4′)–F			1.361(3)		
C(4′)–O(3′)				1.361(5)	
C(7′)–O(3′)				1.440(7)	

Table 8 A selection of bond angles (°) with esds in parentheses

	1	**2**	**3**	**4**	**5**
C(2)–C(1)–C(6)	120.2(3)	119.6(2)	119.4(2)	119.5(4)	120.4(2)
C(3)–C(4)–C(5)	119.1(2)	118.4(2)	118.0(2)	118.4(3)	119.1(2)
C(2′)–C(1′)–C(6′)	120.7(2)	121.1(2)	120.3(2)	119.0(4)	120.0(2)
C(3′)–C(4′)–C(5′)	122.5(3)	120.4(2)	123.9(3)	120.1(4)	119.2(2)
C(1)–S–C(1′)	103.5(1)	103.3(1)	106.3(1)	107.8(2)	105.9(1)
O(1)–S–O(2)	118.1(1)	119.5(1)	118.9(1)	118.2(2)	117.7(1)
C(1)–S–O(1)	109.0(1)	108.6(1)	108.3(1)	107.7(2)	109.0(1)
C(1)–S–O(2)	110.0(1)	109.2(1)	108.2(1)	109.0(2)	108.4(1)
C(1′)–S–O(1)	108.0(1)	107.1(1)	107.8(1)	106.5(2)	107.4(1)
C(1′)–S–O(2)	107.3(1)	107.9(1)	106.7(1)	107.3(2)	107.9(1)

Table 9 A selection of torsion angles (°) with esds in parentheses

		1	2	3	4	5
C(2)–C(1)–S–C(1′)	*T1*	−69.0(2)	−93.3(2)	109.1(2)	−106.2(4)	73.5(2)
C(6)–C(1)–S–C(1′)	*T2*	110.3(2)	82.1(2)	−72.8(2)	75.0(4)	−103.0(2)
C(2′)–C(1′)–S–C(1)	*T3*	100.2(3)	91.6(2)	107.8(2)	100.9(4)	−84.9(2)
C(6′)–C(1′)–S–C(1)	*T4*	−79.5(2)	−85.1(2)	−72.0(2)	−78.0(4)	94.9(2)
(*T1* + *T2* + 180)/2	*w*1	110.6	84.4	108.2	74.4	75.2
(*T3* + *T4* + 180)/2	*w*2	100.4	93.2	107.9	101.4	95.0



1 2 3 4 5

Fig. 1 ORTEP[12] views of the molecules **1**–**5** showing the thermal ellipsoids at 30% probability

Table 10. It has been already shown for a larger set of substituents[1] that $\delta(NH_2)$ and the two $\delta[^{13}C(1)]$ are strictly intercorrelated with $\sigma_p(X)$; the corresponding linear regressions for the present five compounds are as follows:

$$\delta(NH_2) = 6.152(6) + 0.25(1)\sigma_p(X) \quad r = 0.997;$$

$$\delta[^{13}C(1)] = 125.7(2) - 3.4(4)\sigma_p(X) \quad r = -0.994;$$

$$\delta[^{13}C(1')] = 137.7(6) + 14(1)\sigma_p(X) \quad r = 0.992.$$

What has to be ascertained now is whether similar correlations can be established with the structural parameters determined by X-ray diffraction.

The values found for Q are 0.018 for **1**, 0.021 for **2**, 0.022 for **3**, 0.018 for **4**, and 0.018 and 0.005 Å for the two *p*-aminophenylsulfonyl groups present in **5**. Because of its molecular symmetry, in this last compound it must be decided whether the ring having the greater Q is the modulated *p*-aminophenylsulfonyl group or the modulating *p*-X-phenyl moiety, the first hypothesis seeming much more reasonable by analogy with the other four compounds. On this assumption, the average Q value is 0.019(4) Å showing that the quinoid character is essentially constant for all the compounds investigated. In this respect the *p*-aminophenylsulfonyls are similar to *p*-nitroanilines (which have Q values in the range 0.020–0.032 Å, *e.g.* Q = 0.032 in *p*-nitroaniline,[16] 0.031 in 2-methyl-4-nitroaniline[17] and 0.023 Å in 2-methoxy-4-nitroaniline[18]) and other conjugated aniline

Table 10 Structural, extra thermodynamic and spectroscopic data for compounds **1**–**5**[a]

	1	**2**	**3**	**4**	**5**	**5′**
Q	0.018	0.021	0.022	0.018	0.018	—
Q'	−0.002	−0.004	−0.013	0.008	—	0.005
d[S–C(1)]	1.741(3)	1.737(3)	1.741(3)	1.739(4)	1.753(2)	—
d[S–C(1′)]	1.776(2)	1.768(3)	1.758(3)	1.751(4)	—	1.750(2)
d(C–N)	1.385(4)	1.367(4)	1.359(4)	1.368(5)	1.386(3)	1.385(3)
⟨α⟩	113(3)	119(2)	119(2)	116(3)	115(3)	114(3)
$\nu_a(NH_2)$	3453	3461	3476	3470	3397	3457
$\nu_s(NH_2)$	3370	3364	3378	3372	3337	3368
$\delta(NH_2)$	6.33	6.34	6.17	6.08	6.01	
$\delta[^{13}C(1)]$	123.19	123.41	125.05	126.31	128.08	
$\delta[^{13}C(1')]$	148.65	147.19	139.65	134.82	128.08	
X	NO_2	CN	F	OMe	NH_2	
$\sigma_p(X)$	0.78	0.70	0.06	−0.28	−0.57	

[a] ^1H and ^{13}C chemical shifts in ppm relative to Me_4Si; measured in $(CD_3)_2SO$. $\nu_a(NH_2)$ and $\nu_s(NH_2)$ in cm^{-1}; measured as CsI pellets on a Nicolet 510P FT–IR spectrometer. Bond distances in Å and angles in degrees with esds in parentheses. Q, as defined in text. ⟨α⟩, average bond angle at N(1). Hammett constants from refs. 14 and 15.

Table 11 Hydrogen bond parameters, distances in Å and angles in degrees

Compound	D–H···A	Symmetry op.[a]	D–H	D···A	H···A	D–H···A
1	N(1)–H(1N)···O(1)	I	0.88(4)	3.097(3)	2.34(4)	145(3)
	N(1)–H(2N)···O(2)	II	0.84(4)	3.485(3)	2.70(4)	154(3)
2	N(1)–H(1N)···O(1)	I	0.87(2)	3.207(3)	2.42(2)	151(2)
	N(1)–H(2N)···N(2)	II	0.80(3)	3.203(4)	2.41(2)	168(3)
3	N(1)–H(1H)···O(2)	I	0.86(3)	2.978(3)	2.13(3)	174(3)
	N(1)–H(2N)···O(1)	II	0.83(3)	3.028(4)	2.36(3)	139(3)
4	N(1)–H(1N)···O(2)	I	0.75(4)	3.312(4)	2.64(3)	151(3)
	N(1)–H(2N)···O(1)	II	0.90(4)	3.165(5)	2.30(4)	162(4)
5	N(1)–H(1N)···O(2)	I	0.91(2)	2.947(3)	2.08(2)	158(2)
	N(1)–H(2N)···N(1)	II	0.85(3)	3.264(3)	2.45(3)	160(3)
	N(1′)–H(1′N)···O(1)	III	0.88(5)	3.298(3)	2.42(5)	173(4)
	N(1′)–H(2′N)···O(2)	IV	0.94(4)	3.293(3)	2.77(4)	116(3)

[a] Compound **1**: I = $x, y, z + \frac{1}{2}$; II = $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - Z$. Compound **2**: I = $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; II = $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$. Compound **3**: I = $\frac{3}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; II = $x, -y, \frac{1}{2} + z$. Compound **4**: I = $x, y, z - 1$; II = $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$. Compound **5**: I = $x, y + 1, z$; II = $\frac{1}{2} + x, \frac{3}{2} - y, 2 - z$; III = $-x, \frac{1}{2} + y, \frac{3}{2} - z$; IV = $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

derivatives (*e.g.* $Q = 0.009$ in *p*-amino-*p*′-nitrobiphenyl, 0.22 in *p*-amino-*p*′-nitrodiphenylacetylene, 0.017 in *p*-amino-*p*′-nitrodiphenylbutadiyne and 0.018 Å in *p*-amino-*p*′-nitrodiphenylhexatriyne[19]). On the other hand the relationship between quinoid character and intramolecular ground-state charge transfer is confirmed by the low Q value (0.07 Å) in both *p*-diaminobenzene[20] and *N*,*N*-dimethyl-1,4-phenylenediamine[21] and by the Q value of zero in *p*-nitroaniline hydrochloride[22] where resonance is made impossible.

The quinoid distortion is paralleled by the shortening of C–N(1) and S–C(1) distances according to **IIb**. The average d(C–N) value in **1**–**5** [1.37(1) Å] is definitely shorter than the commonly accepted value for a single $C(sp^2)$–$N(sp^3)$ bond of 1.44–1.45[23] and compares well with that observed in *p*-nitroaniline [1.355(3) Å].[16] The actual d(C–N) values (ranging from 1.359 to 1.386 Å) do not show any correlation with $\sigma_p(X)$ but appear to be mostly dependent on the degree of pyramidalization, ⟨α⟩, of the amino nitrogen ($r = -0.88$), in good agreement with what was reported in previous papers.[20,23] Likewise, the average S–C(1) distance of 1.742(2) Å is shorter than the accepted value of 1.763 Å[13] for the C(aromatic)–SO_2 bond and than the other S–C(1′) distance [on average 1.761(9) Å]. It seems of interest that the S–C(1′) lengths are strictly correlated with $\sigma_p(X)$ values [$r = 0.967$; Fig. 2(*a*)] while the S–C(1) ones are not ($r = -0.666$), being essentially constant irrespective of the X substituent. All data admit a reasonable general explanation. The *p*-aminophenylsulfonyl group is characterized by a substantial geometrical constancy irrespective of X [$Q = 0.019(4)$, d[S–C(1)] = 1.742(2) Å, on average; d(C–N) = 1.36–1.39 Å, according to the different N pyramidalization]. The other *p*-X-phenyl group modulates the properties of the whole molecule as shown by the very strict relationship between $\sigma_p(X)$ and proton NMR chemical shift of the *p*-amino group, $\delta(NH_2)$ [$r = 0.997$, Fig. 2(*b*)]. The effect of X is transmitted without substantial modification of the quinoid character of the attached phenylene and by changing only the S–C(1′) distance. This seems to imply a purely inductive transmission without significant resonance components where what is essentially modified by X is the partial charge of the SO_2 sulfur which, in turn, modulates the properties of the terminal aminic substituent through the almost constant π-delocalization of the modulated *p*-aminophenylsulfonyl group.

As far as the essentially constant overall molecular shape is concerned (Table 9), the conformation of the 4′-substituted phenyl moiety seems to be determined by exchange repulsions more than by a π contribution to the S–C(1′) bond while that of the *p*-aminophenyl group should be affected by a bonding interaction between the *p*-orbitals on sulfur and the benzene ring. The spreading of the *w*1 angle (from 74.4 to 110.6°) corresponds to a range of the angle Φ between such *p* orbitals of −15.6–20.6°. However, the overlap between these orbitals changes with Φ according to the expression $S_\pi \alpha \cos(\Phi)$ and

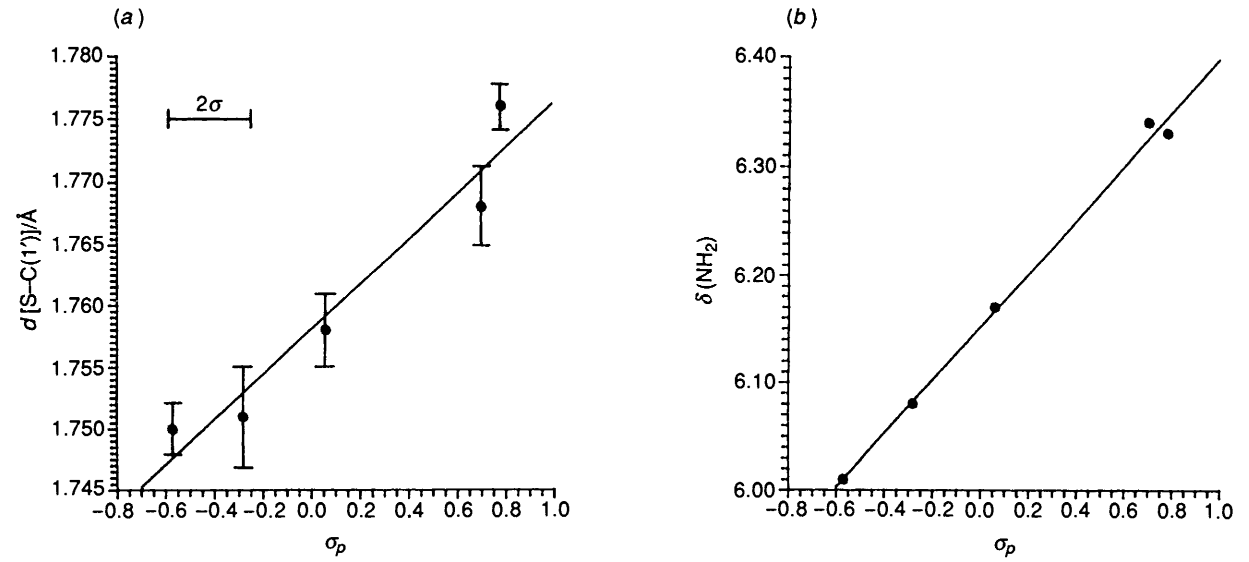


Fig. 2 (*a*) Scatter plot of the S–C(1') bond distance *vs.* Hammett constant σ_p(X) for compounds **1–5**, (r = 0.967); (*b*) scatter plot of the proton NMR chemical shift of the *p*-amino group, $\delta(NH_2)$ *vs.* σ_p(X), (r = 0.997)

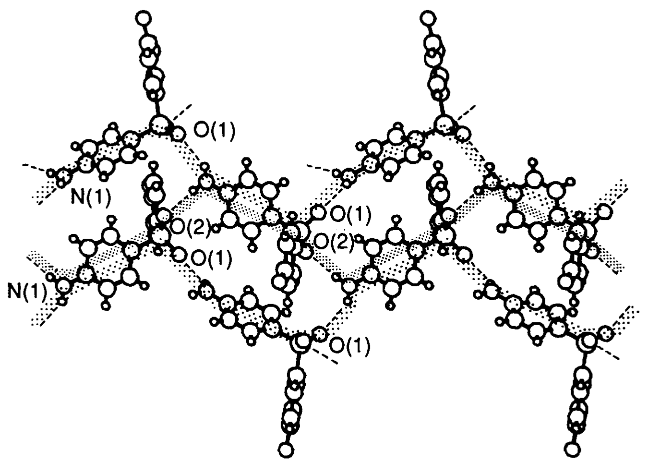


Fig. 3 Hydrogen bonding bidimensional network for compound **3**. The two systems of π-conjugated resonant chains are indicated by the different shadings.

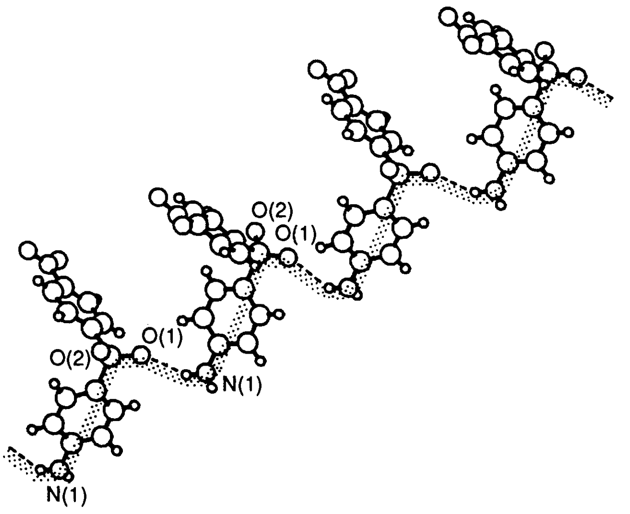
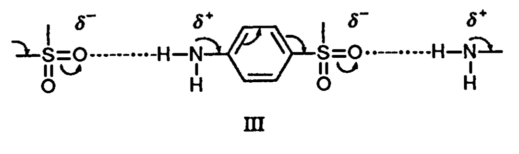


Fig. 4 Single π-conjugated resonant chain formed by the strongest hydrogen bond of compound **1** (see Table 11)

decreases only as 1, 0.96, 0.94, while Φ assumes the values of 0, −15.6, 20.6°.

Another interesting feature of the *p*-aminophenylsulfonyl moiety is that it generally controls the hydrogen bonding network within the crystal (Table 11). In its most general form the network leitmotif is represented by the packing of compound **3** (Fig. 3). Each NH_2 donates two hydrogen bonds to SO_2 oxygens located on different molecules and each SO_2 group accepts, through its oxygens, two hydrogen bonds donated by NH_2 groups lying on two distinct molecular entities, resulting in the formation of a bidimensional network. It has been previously shown that more efficient hydrogen bonds can be established whenever the donor and acceptor groups are connected by a π-conjugated system (RAHB = resonance assisted hydrogen bond)[24–26] as actually happens in the present case for the two systems of resonant chains indicated by the different shadings in Fig. 3. Within each chain the resonance form **III** generates partial charges which have the correct sign for strengthening the hydrogen bond.



III

Different factors (crystal packing, presence of other substituents which can or cannot form other hydrogen bonds by themselves) appear to produce either two chains of comparable strength (**3** of Fig. 3, **4**) or one chain much stronger than the other (**1** of Fig. 4, **5**). Also when the hydrogen bonding network is more complicated because of other substituents (CN in **2** and another NH_2 in **5**) the chain of resonant *p*-aminophenylsulfonyl moieties remains distinguishable. In spite of the resonance the N–H···O=S=O hydrogen bond appears to be intrinsically rather weak. The average N···O distance on the five shortest hydrogen bonds of compounds **1–5** (Table 11) is 3.08(9) Å while the average value on 1357 intermolecular N–H···O hydrogen bonds is reported[27] to be 2.892(3) Å. Also in this respect the *p*-aminophenylsulfonyl group mimics *p*-nitroanilines and, in fact, the average N···O distance for 29 such compounds[28] amounts to 3.06(9) Å. Similar conclusions can be drawn from the values of the IR frequencies of the NH_2 group (Table 10) which are known to be decreased because of hydrogen bond formation from their values of ν_a = 3550–3500 and ν_s = 3450–3400 cm^{-1} [28,29] in the absence of interactions. Average values for structures **1–4** are only slightly smaller [ν_a = 3465(9) and ν_s = 3371(5) cm^{-1}]. Only in **5** is a group of frequencies more shifted (ν_a = 3397, ν_s = 3337

cm^{-1}) and this is attributed to the NH_2 vibrations of the modulated *p*-aminophenylsulfonyl (see Table 10) which is donating the strongest hydrogen bond [N(1)–H(1N)•••O(2); N(1)•••O(2) = 2.947 Å] and accepting a further weak hydrogen bond from its second proton [N(1)–H(2N)•••N(1); N(1)•••N(1) = 3.264(3) Å].

Acknowledgements

We thank Prof. G. Gilli, University of Ferrara, for useful discussion and *Ministero Università e Ricerca Scientifica e Tecnologica*, Italy, for financial support.

References

1 P. G. De Benedetti, U. Folli, D. Iarossi and C. Frassineti, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1527.
2 P. G. De Benedetti and C. Frassineti, *J. Mol. Struct., Theochem.*, 1983, **92**, 191.
3 J. L. McCullough and T. H. Maren, *Antimicrob. Agents Chemother.*, 1973, **3**, 665.
4 P. G. De Benedetti, *J. Mol. Struct., Theochem.*, 1992, **256**, 231.
5 A. Ulman, C. S. Willand , W. Kohler, D. R. Robello, D. J. Williams and L. Handley, *J. Am. Chem. Soc.*, 1990, **112**, 7083.
6 J. F. Nicoud and R. J. Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, eds. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987, vol. 2, p. 221.
7 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York and Louvain, 1980.
8 B. A. Frenz, Structure Determination Package, College Station, Texas and Enraf–Nonius, Delft, 1978.
9 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
10 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, vol. 4.
11 G. Bocelli and A. Cantoni, *Acta Crystallogr., Sect. C*, 1990, **46**, 2257.
12 C. K. Johnson, ORTEP II. A Fortran Thermal-Ellipsoids Plot Program for Crystal Structures Illustrations; Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
13 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, 21.
14 O. Exner, in *Correlation Analysis in Chemistry: Recent Advances*, eds. N. B. Chapman and J. Shorter, Plenum, New York, 1978, ch. 10.
15 J. Shorter, in *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*, eds. R. I. Zalewski, T. M. Krygowski and J. Shorter, Elsevier, Amsterdam, 1991, ch. 2.
16 M. Colapietro, A. Domenicano, C. Marciante and G. Portalone, *Z. Naturforsch., Teil B*, 1982, **37**, 1309.
17 G. F. Lipscomb, A. F. Garito and R. S. Narang, *J. Chem. Phys.*, 1981, **75**, 1509.
18 S. Mehdi, *Acta Crystallogr., Sect. C*, 1992, **48**, 749.
19 E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 1989, **111**, 8771.
20 M. Colapietro, A. Domenicano, G. Portalone, G. Schultz and I. Hargittai, *J. Phys. Chem.*, 1987, **91**, 1728.
21 H. Nakai, T. Saito and M. Yamakawa, *Acta Crystallogr., Sect. C*, 1988, **44**, 1057.
22 G. Ploug-Sorensen and E. Krogh Andersen, *Acta Crystallogr., Sect. B*, 1982, **38**, 671.
23 G. Gilli, V. Bertolasi, F. Bellucci and V. Ferretti, *J. Am. Chem. Soc.*, 1986, **108**, 2420.
24 G. Gilli, F. Bellucci, V. Ferretti and V. Bertolasi, *J. Am. Chem. Soc.*, 1989, **111**, 1023.
25 G. Gilli and V. Bertolasi, in *The Chemistry of Enols*, ed. Z. Rappoport, J. Wiley & Sons, New York, 1990, ch. 13.
26 V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1991, **113**, 4917.
27 R. Taylor, O. Kennard and W. Versichel, *Acta Crystallogr., Sect. B*, 1984, **40**, 280.
28 T. W. Panunto, Z. Urbanczyk-Lipkowska, R. Johnson and M. C. Etter, *J. Am. Chem. Soc.*, 1987, **109**, 7786.
29 N. B. Colthup, L. H. Daly and S. E. Wiberley in *Introduction to Infrared and Raman Spectroscopy*, third edn., Academic Press, 1990, p. 339.

Paper 2/04091C
Received 30*th July* 1992
Accepted 20*th October* 1992