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The conformation of some *N,N*-disubstituted arylamines

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The conformation of some *N,N*-disubstituted arylamines has been studied by X-ray crystallography.

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Aromatic amines form mono and diacyl derivatives.[1,2] Whereas the former are reactive towards electrophilic aromatic substitution, the latter are much less so.[3,4] In this paper we report the X-ray crystal structures of a series of *N,N*-disubstituted arylamines to shed some light on this difference. In studies on the crystal structures of some acetanilides, we examined the consequences of steric crowding on the plane of rotation of the arylamino group relative to the aromatic ring.[5] This rotation is reflected in the reactivity of the aromatic ring towards electrophiles. We have shown[6] that the nitrogen atom of some *N*-monomethyl-sulfonamides retained some pyramidal character compared to the acetanilides in which the amide resonance leads to an almost planar nitrogen. However, the N–S bond length was shorter than the sum of the covalent radii suggesting that there was some conjugation involving the sulfur d orbitals and the nitrogen lone pair. The aromatic Ar(C)–N bond length was longer than that of acetanilide.

We now report the geometry of two aryl *N,N*-dimethanesulfonamides, 2-methoxy-4-nitroaniline *N,N*-dimethanesulfonamide and 2-methyl-6-nitroaniline *N,N*-dimethanesulfonamide (Figs 1 and 2), a ditoluene-*p*-sulfonamide, 4-chloroaniline ditoluene-*p*-sulfonamide (Fig. 3), the mixed methylsulfonylacetyl derivative of 4-chloroaniline (Fig. 4) and the diacetyl derivative of 2,6-dichloroacetanilide (Fig. 5).

In the disulfonamide derivatives the N–S bond lengths are still shorter than the sum of the covalent radii (average 1.6895 Å versus 1.78 Å) (see Table 1) although this is marginally longer than the monomethanesulfonaamides. The amide N–C(O) bond lengths fall close to that in acetanilide (average 1.413 Å versus 1.35 Å).

The aryl (C(1)–N bond length (average 1.444 Å) in all the derivatives is longer than that of acetanilide (1.417 Å) or of an aromatic amine such as *p*-chloroaniline (1.386 Å) but it is not as long as an aliphatic C–N bond (1.47 Å). The planes of the sulfonamides and amide groups [S(1)–N–S(2)–C(1); S(1)–N–C(7)–C(1) and C(1)–N–C(7)–C(9)] are rotated to almost 90° relative to the plane of the aromatic ring (see Table 2). This implies very little conjugation between the nitrogen lone pair and the aromatic ring in the ground state.

The nitrogen atoms in the sulfonamide deviate little from the plane of their three substituents (see Table 1) and they are no longer significantly pyramidal implying some conjugation with the sulfur. Examination of the torsional angles around the N–S(O) and N–C(O) bonds (see Table 2) suggests that there may be a cross-conjugated system involving the nitrogen and each of the sulfonyl or amide groups rather than linear conjugation involving both sets of substituents. As would be expected, the carbonyl groups of the amide possess a *trans* relationship. In the case of the sulfonyl groups the sulfur is more nearly tetrahedral and the torsional angles involving the N–S(O) bonds are substantially less than 180° implying less conjugation of an amide type and possible the intervention of the sulfur d orbitals. The methanesulfonamides take up a geometry which allowes the methyl groups to be staggered along the S(1)–N–S(2) axis.

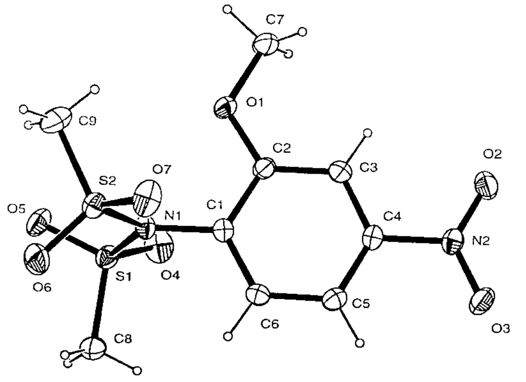

Fig. 1 Crystal structure of 2-methoxy-4-nitroaniline dimethanesulfonamide **1**.

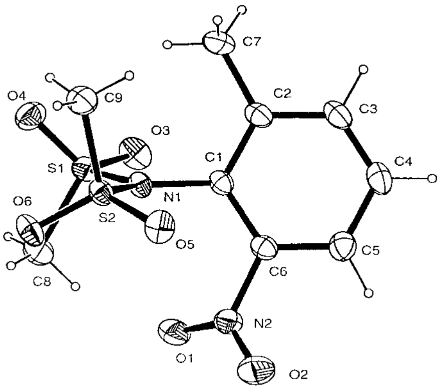

Fig. 2 Crystal structure of 2-methoxy-6-nitroaniline dimethanesulfonamide **2**.

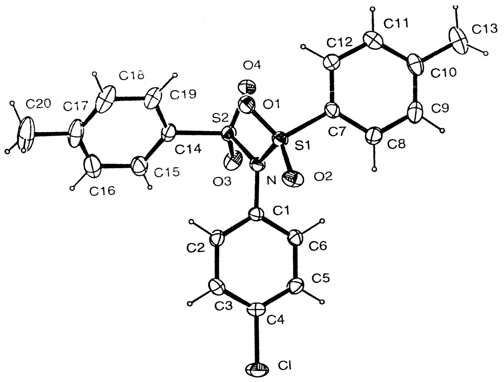

Fig. 3 Crystal structure of 4-chloroaniline ditoluene-*p*-sulfonamide **3**.

In conclusion we have shown that in the crystalline state these *N,N*-disubstituted arylamines show less evidence for conjugation between the nitrogen atom and the aromatic ring compared to the acetanilides. Whilst these results are commensurate with the predicted diminished reactivity of diacylanilides towards electrophilic aromatic substitution,

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Table 1 Bond lengths and nitrogen out of plane distances (/Å)

Compound	ArC(1)–N	N–S(1)	N–S(2)	Out of plane
1	1.4403(17)	1.6869(12)	1.6832(12)	0.0747(0.0013)
2	1.4480(17)	1.6974(12)	1.6872(12)	0.0644(0.0013)
3	1.4499(19)	1.6987(13)	1.6809(13)	0.0933(0.0014)
			N–C(8)	
4	1.447(2)	1.6922(4)	1.405(2)	0.0516(0.0017)
		N–C(7)	N–C(9)	
5	1.436(3)	1.423(3)	1.408(3)	0.0242(0.0022)

Table 2 Angles between the plane of the amides and the phenyl ring and selected torsion angles (°)

Compound	Angle between planes	Torsion angles	
		S(1)–N(1)–S(2)–O(4)	S(2)–N(1)–S(1)–O(4)
1	86.11	167.17	161.28
2	76.06	164.21	169.93
3	83.39	156.82	168.24
		C(8)–N–S–O(1)	C(1)–N–C(8)–O(3)
4	83.02	178.97	173.56
		C(9)–N–C(7)–O(1)	C(1)–N–C(9)–O(2)
5	89.3	178.12	174.82

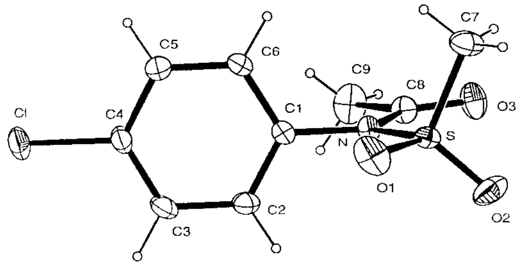

Fig. 4 Crystal structure of 4-chloroacetanilide methanesulfonamide **4**.

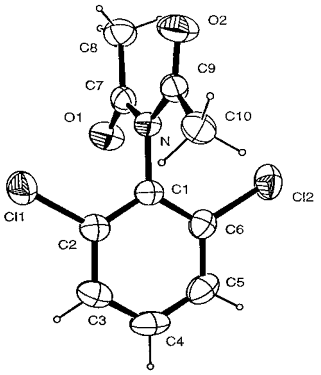

Fig. 5 Crystal structure of *N,N*-diacetyl-2,6-dichloroaniline **5**.

they may contain unquantified contributions from crystal packing effects and they do, of course, only give information about the ground state of the molecule.

Experimental

The *N,N*-dimethanesulfonamides of 2-methoxy-4-nitroaniline and 2-methyl-6-nitroaniline and the diacetyl derivative of 2,6-dichloroaniline, have been described previously. The *N,N*-ditoluene-*p*-sulfonamide of 4-chloroaniline, prepared with excess toluene-*p*-sulfonyl chloride, had m.p. 220–222°C (Found: M^+ 458.028 $C_{20}H_{18}ClNO_4S_2Na$ requires M^+ 458.026), ν_{max}/cm^{-1} 1595, 1189, 1170, 1086; δ_H 2.27 (6H, s, Ar-Me), 6.83 (2H, d, *J*=8.4 Hz), 7.32 (6H, multiplet), 7.50 (4H, br.d, *J*= 8.0 Hz). The *N*-methanesulfonyl derivative of 4-chloroacetanilide, prepared with methanesulfonyl chloride in pyridine, had. m.p. 140°, (Found: M^+ 269.995 $C_9H_{10}ClNO_3SNa$ requires M^+ 269.996), ν_{max}/cm^{-1} 1700, 1268, 1168, 1092; δ_H 1.90 (3H, s, Ac), 3.53 (3H, s, SO_2Me), 7.50 (1H, d, *J*=8.7 Hz), 7.57 (2H, d, *J*=8.7 Hz).

X-Ray crystal data and structure determinations (a) 2-methoxy-4-nitroaniline dimethanesulfonamide (Fig. 1), $C_9H_{12}N_2O_7S_2$, M_r 324.33, triclinic, space group $P\bar{1}$ (No.2), a = 7.6428(2), b = 9.6341(2), c = 9.7222(3) Å, α = 77.331(2)°, β = 71.439(1)°, γ = 79.801(2)°, V = 657.64(3) Å^3, Z = 2, D_{calc} = 1.64 g cm^{-3}, μ= 0.44 mm^{-1}, F(000) = 336, λ = 0.71073 Å. Data were collected using a crystal of size 0.3 × 0.3 × 0.2 mm^3 on a KappaCCD diffractometer. A total of 11161 reflections were collected for 3.77 < θ < 27.50° and $-9 \le h \le 9$, $-12 \le k \le 12$, $-12 \le l \le 12$. There were 3005 independent reflections and 2770 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were [$I > 2\sigma(I)$] R_1 = 0.030, wR_2 = 0.079 and (all data), R_1 = 0.033, wR_2 = 0.081. The goodness-of-fit on F^2 was 1.058 and the largest difference peak and hole was 0.35 and –0.38 e Å^{-3}.

(b) 2-methyl-6-nitroaniline dimethanesulfonamide (Fig. 2), $C_9H_{12}N_2O_6S_2$, M_r 308.33, monoclinic, space group $P2_1/n$ (No.14), a = 12.5178(4), b = 8.1955(2), c = 13.6268(3) Å, $\alpha = \gamma$ = 90°, β = 114.678(2)°, V = 1270.29(6) Å^3, Z = 4, D_{calc} = 1.61 g cm^{-3}, μ = 0.44 mm^{-1}, F(000) = 640, λ = 0.71073 Å. Data were collected using a crystal of size 0.4 × 0.3 × 0.3 mm^3 on a KappaCCD diffractometer. A total of 20109 reflections were collected for 3.82 < θ < 27.47° and $-15 \le h \le 16$, $-10 \le k \le 10$, $-17 \le l \le 16$. There were 2905 independent reflections and 2678 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were [$I > 2\sigma(I)$] R_1 = 0.029, wR_2 = 0.080 and (all data), R_1 = 0.033, wR_2 = 0.082. The goodness-of-fit on F^2 was 1.065 and the largest difference peak and hole was 0.34 and –0.36 e Å^{-3}.

(c) 4-chloroaniline ditoluene-p-sulfonamide (Fig. 3), $C_{20}H_{18}ClNO_4S_2$, M_r 435.92, monoclinic, space group $P2_1/n$ (No.14), a = 12.1282(2), b = 10.8699(2), c = 15.6366(6) Å, $\alpha = \gamma$ = 90°, β = 104.610(1)°, V = 1994.75(6) Å^3, Z = 4, D_{calc} = 1.45 g cm^{-3}, μ = 0.43 mm^{-1}, F(000) = 904, λ = 0.71073 Å. Data were collected using a crystal of size 0.3 × 0.2 × 0.2 mm^3 on a KappaCCD diffractometer. A total of 35512 reflections were collected for 3.82 < θ < 28.22° and $-16 \le h \le 15$, $-14 \le k \le 14$, $-20 \le l \le 20$. There were 4887 independent reflections and 4109 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were [$I > 2\sigma(I)$] R_1 = 0.036, wR_2 = 0.085 and (all data), R_1 = 0.047, wR_2 = 0.089. The goodness-of-fit on F^2 was 1.056 and the largest difference peak and hole was 0.40 and –0.37 e Å^{-3}.

(d) 4-chloroacetanilide methanesulfonamide (Fig. 4), $C_9H_{10}ClNO_3S$, M_r 247.69, monoclinic, space group P2/c (No.15), a = 20.2275(5), b = 6.8315(1), c = 16.2897(4) Å, $\alpha = \gamma$ = 90°, β = 99.647(1)°, V = 2219.15(8) Å^3, Z = 8, D_{calc} = 1.48 g cm^{-3}, μ = 0.52 mm^{-1}, F(000) = 1024, λ = 0.71073 Å. Data were collected using a crystal of size 0.4 × 0.2 × 0.1 mm^3 on a KappaCCD diffractometer. A total of 15967 reflections were collected for 3.94 < θ < 27.86° and $-25 \le h \le 26$, $-8 \le k \le 8$, $-21 \le l \le 18$. There were 2597 independent reflections and 2307

reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I > 2\sigma(I)]$ $R_1 = 0.037$, $wR_2 = 0.084$ and (all data), $R_1 = 0.043$, $wR_2 = 0.088$. The goodness-of-fit on F^2 was 1.053 and the largest difference peak and hole was 0.70 and –0.76 e Å^{-3}.

(e) N,N-diacetyl-2,6-dichloroaniline (Fig. 5), $C_{12}H_9Cl_2NO_2$, M_r 270.10, orthorhombic, space group Pbca (No.61), a = 7.6675(2), b = 25.3232(8), c = 11.1748(4) Å, $\alpha = \beta = \gamma = 90°$, V = 2169.76(12) Å^3, Z = 8, D_{calc} = 1.65 g cm^{-3}, μ = 0.58 mm^{-1}, $F(000)$ = 1104, λ = 0.71073 Å. Data were collected using a crystal of size 0.20 × 0.10 × 0.05 mm^3 on a KappaCCD diffractometer. A total of 7454 reflections were collected for $3.99 < \theta < 24.73°$ and $-7 \le h \le 8$, $-29 \le k \le 29$, $-13 \le l \le 10$. There were 1815 independent reflections and 1433 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. Final R indices were $[I > 2\sigma(I)]$ $R_1 = 0.038$, $wR_2 = 0.089$ and (all data), $R_1 = 0.054$, $wR_2 = 0.096$. Goodness-of-fit on F^2 was 1.022 and the largest difference peak and hole was 0.22 and –0.26 e Å^{-3}.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (233606-9, 225990).

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