X-Ray Crystal Structure of an *N*-Sulphinyl Derivative of a Primary Amine: *N*-Sulphinyl-*p*-bromoaniline

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The first *X*-ray crystal structure of an unstable *N*-sulphinyl derivative of a primary amine, *N*-sulphinyl-*p*-bromoaniline, is described.

N-Sulphinyl derivatives of primary amines, $R-N=S^{+}-O^{-}$, which are nitrogen analogues of sulphur dioxide (**4**), are important synthetic substrates which undergo a wide range of cycloaddition reactions.[1—5] The compounds are obtained by treatment of a primary amine with thionyl chloride. They are highly moisture sensitive and quickly revert to the parent amine on exposure to the atmosphere. Most derivatives are liquids but even the more stable low-melting solid compounds, such as *N*-sulphinyl-*para*-substituted anilines, show i.r. N–H bands after 15—30 min exposure to the atmosphere, indicating that moisture has begun to penetrate the crystal.

Despite the wide interest in these compounds, the detailed structure has not been established unequivocally. In papers up to the early 1980s they have been represented with the *E*-structure (**1**), with the undefined structure $-N=S^{+}O^{-}$, or with the *Z*-structure (**2**). Earlier attempts to distinguish between *E*-(**1**), *Z*-(**2**) and a linear-type structure, drawn as in (**3**), using i.r. spectra[6] and dipole moments[7,8] were not successful. Extensive theoretical calculations have been carried out on the *N*-sulphinyl amine structure.[9—13] Since the mid-1980s the weight of opinion has favoured the *Z*-structure (**2**), which is now the more usual representation. An *X*-ray crystal structure[14] of *N*′-sulphinyl-*N*-phenylhydrazine (**5**) lent support for the *Z*-structure, but the hydrazine derivative (**5**) is a stable material which can be recrystallised from ethanol and in which the *Z*-structure is facilitated by an intramolecular hydrogen bond. We now report the first *X*-ray crystal structure† of an unstable *N*-sulphinyl derivative of a primary amine, *N*-sulphinyl-*p*-bromoaniline (**6**) (Figure 1).

Compound (**6**) is an unstable yellow solid which reverts to *p*-bromoaniline rapidly at ambient temperatures. Absorptions due to N–H vibrations appear in the i.r. spectrum after about 30 min exposure to the atmosphere. Extensive attempts to prolong the life of the crystals by various sealing methods and using low temperature *X*-ray techniques were unsuccessful, but it was found that crystals could be readily grown in Nujol and that when wet they retained a protective film of Nujol which allowed sufficient time for data collection. Nujol-wet crystals were mounted in a capillary tube but secondary difficulties of crystal movement and/or partial melting were also encountered during the eight or more hours necessary for

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† *Crystal data*: for (**6**); C_6H_4BrNOS, monoclinic, space group $P2_1/n$, $a = 7.752(1)$, $b = 6.119(1)$, $c = 15.876(1)$ Å, $\beta = 90.10(2)°$, $U = 753.03$ Å^3, $\mu = 55.17$ cm^{-1}, $F(000) = 424$, $Z = 4$. 640 Reflections observed with $I > 2\sigma I$, using a CAD4 diffractometer and Mo-K_α radiation; $2\theta_{max.} = 45°$. The structure was solved by Patterson methods, SHELX86,[15] and refined with 56 variable parameters using SHELX76.[16] After full matrix refinement, $R = 6.02\%$ and $R_w = 5.42\%$. The maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.20 and −0.63 e/Å.[17] The ORTEP program was used to obtain the drawing.[17] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

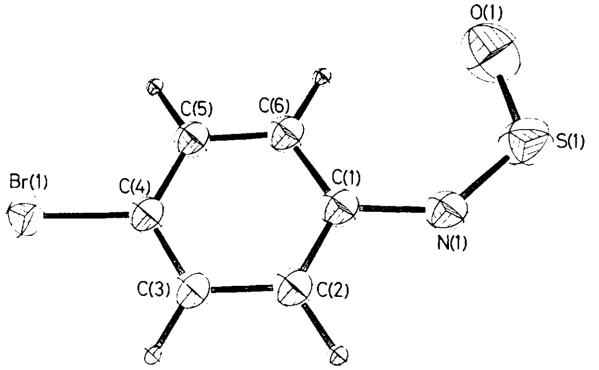
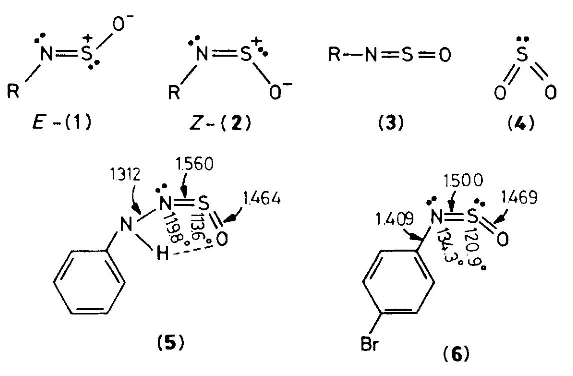


Figure 1. The *Z*-structure of *N*-sulphinyl-*p*-bromoaniline, (**6**).



Scheme 1. Bond lengths in Å.

data collection. However, these secondary problems were finely balanced, and with repeated attempts using different crystals eventually a crystal survived long enough for the structure to be solved. The compound was fully planar and had the *Z*-structure shown in Figure 1. A comparison of the bond distances in molecules (**5**) and (**6**) shows that the $-N{=}S^+{-}O^-$ dimensions in (**5**) do not represent the normal sulphinyl amine structure because of distortion due to conjugation along the N–N bond, which at 1.312 Å is shortened almost to a double bond while the N=S bond is lengthened[18] (Scheme 1). In compound (**6**) the double bond character of the N=S bond is evident, with a bond length 1.500 Å, (the N–S single bond length in the structure $>C{=}N{-}S{-}X$ is 1.656 Å[18]) and this is fully in agreement with the strong dienophile character of aromatic *N*-sulphinylamines in cycloaddition reactions.[1—5] The $S^+{-}O^-$ bond length of 1.469 Å suggests a double bond in this linkage and structure (**6**) with expanded valency on sulphur is the best representation of the molecule. The *Z*-structure then is due to the greater repulsive interaction between the nitrogen lone pair and the π-bond of the S=O moiety. The planar NSO structure in compound (**6**) is more open than in (**5**), with a bond angle at N of 134.3° compared to 119.8° and a bond angle at S of 120.9° compared to 113.6° for (**5**). This opening of the angles separates the O atom from the *N*-substituent, the reverse situation occurs with structure (**5**) where the intramolecular hydrogen bond is favoured by smaller angles.

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