An Examination of the Structures of Iodosylbenzene (PhIO) and the Related Imido Compound, PhINSO₂-4-Me-C₆H₄, by X-Ray Powder Diffraction and EXAFS (Extended X-Ray Absorption Fine Structure) Spectroscopy

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Structural data derived from X-ray powder diffraction and EXAFS spectroscopy are presented for iodosylbenzene (PhIO) and the imido analogue, PhINSO₂-4-Me-C₆H₄, which indicate that these compounds are polymeric in the solid state.

Poly- or hyper-coordinate iodine compounds are used extensively as reagents in organic synthesis,[1] amongst these being iodosylbenzene, PhIO 1, and the imido analogues, PhINR, which are employed as oxygen and imido transfer agents respectively.[1,2] Despite the extensive use of these compounds, however, very little is known about their solid-state structures except that they are most likely polymeric in view of their insolubility in many common organic solvents.† For iodosylbenzene, the only structural information of which we are aware comprises studies by IR–Raman[3] and Mössbauer spectroscopy,[4] both of which are consistent with a polymeric O–I–O backbone; there are apparently no structural data for any PhINR compounds. Herein, we describe some preliminary structural results for this class of compound derived from X-ray powder diffraction and iodine EXAFS spectroscopy which establish their polymeric nature.

Samples of 1, prepared according to ref. 5, were completely amorphous as judged by X-ray powder diffraction data, but a sample of PhINSO₂-4-Me-C₆H₄ 2[6] showed a high degree of crystallinity. A partial structure was determined from the powder diffraction data,‡ in a manner similar to that described previously,[7] from which the positions of the iodine and sulfur atoms were established and, as can be seen from the Rietveld profile shown in Fig. 1, these atoms account for most of the scattering. Although the remaining atoms were not directly located, the derived I···I distance of 3.95 Å clearly establishes the polymeric nature of 2 (parallel to the crystallographic 2₁ axis). A nitrogen atom was subsequently placed in a bridging site between the iodine atoms in a calculated position on the basis of EXAFS spectroscopic data (see below) but this made little difference to the refinement; a view of part of the crystal structure showing the iodine, sulfur and nitrogen (calculated position) atoms indicating the polymeric structure is shown in Fig. 2.

In order to obtain further structural information, iodine K-edge EXAFS measurements§ were made on both 1 and 2 as well as on two compounds of better known structure, viz. KIO₄ 3 (the neutron diffraction structure[8] of ND₄IO₄ was used as the source of data on the I–O distance) and PhI(O₂CMe)₂

4.[9] The expected structures were well reproduced with the caveat that for 4 it was not possible to distinguish between the bonded I–O and I–C contacts. In this case, and for 1 and 2, the short contacts were modelled simply as carbon atoms rather than the actual mixture of carbon and oxygen or carbon and nitrogen atoms. The Fourier transforms of the iodine EXAFS spectra of 1 [Fig. 3(a)] and 2 each showed a substantial peak at ca. 3.8 Å corresponding to a neighbouring iodine atom linked to the central iodine by a bridging oxygen (for 1) or nitrogen (for 2). Subsequent model fitting [Fig. 3(b)] confirmed the presence of these neighbouring iodines, although it did not allow for a clear assignment of the number of iodines at this distance, fits of similar quality being obtained with coordination numbers of one or two. Furthermore, for both 1 and 2, improved fits were obtained by assuming a degree of asymmetry in the two I–O (or I–N) bonded contacts. Thus for 1 the longer of the I–O contacts refined to 2.377(12) Å (cf. the averaged shorter I–O and I–C distance of 2.04 Å) and for 2 the longer I–N contact to 2.49 Å (cf. the averaged shorter I–N and I–C distance of 2.06 Å). These distances imply angles at oxygen (I–O–I) and nitrogen (I–N–I) of 114 and 120° respectively as illustrated in Fig. 4.

A comparison of the EXAFS and X-ray powder diffraction data for 2 shows that they are reasonably consistent. Thus the X-ray diffraction data reveal I···I contacts of 3.95 Å and I···S contacts of 2.94 and 4.21 Å, while the EXAFS analysis indicates an I···S distance of 3.14 Å (the discrepancy may be a consequence of this shell overlapping with a shell consisting of ortho carbons and sulfonyl oxygens). Assumption of a standard N–SO₂R distance (1.62 Å)[10] allows estimation of the location of the nitrogen in the crystal structure. Optimised coordinates for nitrogen which give N–I and N–S distances of 2.06 and 1.62 Å and have the nitrogen coplanar with I, I′ and S (i.e. assuming sp² hybridisation at N) give the N···I′ distance as 2.77 Å and valance angles at nitrogen (I–N–S 105, I′–N–S 146, I–N···I′ 109°) and iodine (N–I–N′ 171°) in line with expectation.

While the fine details of the molecular dimensions should be treated with some caution, the structural evidence presented here is clearly consistent with linear polymeric, asymmetrically bridged structures for 1 and 2 in the solid state having the
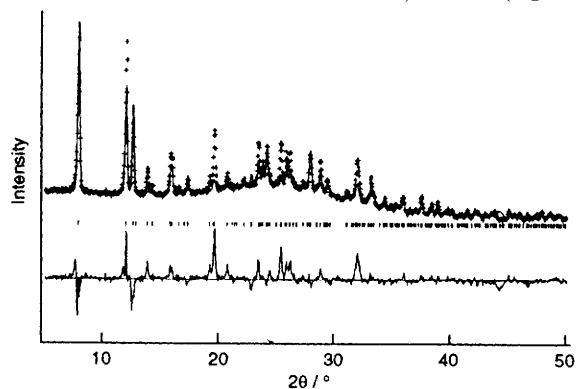

Fig. 1 A Rietveld profile for 2 showing the fit between the observed data and that calculated for the iodine and sulfur atoms only
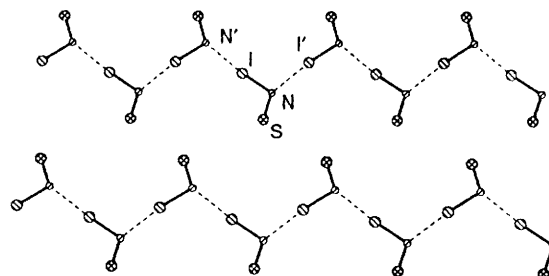

Fig. 2 A view of part of the crystal structure of 2 derived from the X-ray powder diffraction data showing several monomeric units in two polymer chains (parallel to the crystallographic 2₁ axis). Only the iodine, sulfur and nitrogen (calculated) atoms are shown.
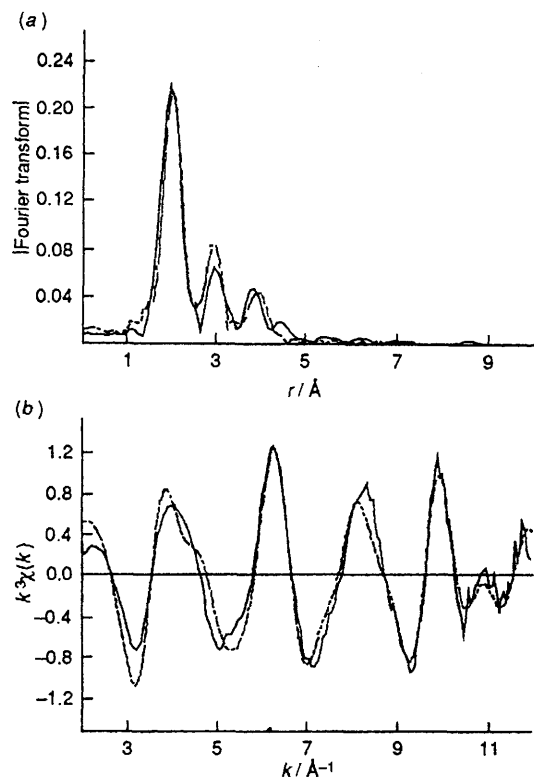
Fig. 3 (*a*) Observed (——) and calculated (------) Fourier transform magnitudes (quasi-radial distribution function, arbitrary units) of the k^3-weighted iodine K-edge EXAFS spectrum for solid **1**. (*b*) Observed (——) and calculated (------) k^3-weighted iodine K-edge EXAFS spectrum for solid **1**.
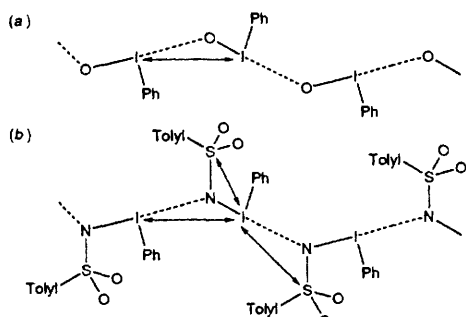

Fig. 4 Schematic solid state structures of **1** (*a*) and **2** (*b*) showing the nonbonded I⋯I and (for **2**) I⋯S distances discussed in the text. The phenyl groups have been placed in illustrative but chemically reasonable positions.

expected T-shaped geometry around the iodine(III) centres. Further studies on related solid compounds are in progress together with an iodine K-edge EXAFS study of **1**, **2** and related compounds which have been dissolved in the presence of BF_3, an important class of reagent in organic chemistry.[1]

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Footnotes

† For solvents in which these compounds dissolve, a reaction generally occurs. Thus PhIO dissolves in MeOH to give $PhI(OMe)_2$.

‡ *Crystal data* for **2**: $C_{13}H_{12}INO_2S$, monoclinic, space group $P2_1/c$, $a =$ 11.575(4), $b =$ 7.784(2), $c =$ 15.214(6) Å, $\beta =$ 104.49(3)°, $Z =$ 4. A partial structure was obtained from X-ray powder diffraction data

collected on a Stoe STADI/P transmission system using Cu-$K_{\alpha 1}$ radiation ($\lambda =$ 1.54056 Å). A polycrystalline sample was well ground and loaded into a 0.2 mm diameter Lindemann tube. Data were collected over the range $5 < 2\theta < 85°$ in 0.02° steps for a period of about 15 hours. Data were indexed on the basis of the first 22 observable lines using the program TREOR[11] (figure of merit, $M_{22} =$ 13.5). The pattern decomposition[12] option of the Rietveld program GSAS[13] was used to extract the first 165 integrated intensities from the powder pattern (in the region $5 < 2\theta < 45°$). These were used as imput to the direct methods program SIR88[14] from which the iodine position was located. The sulfur atom was found from a difference Fourier map after a Rietveld refinement of the whole diffraction profile ($5 < 2\theta < 55°$). Agreement factors for this partial model were $R_{wp} =$ 9.9%, $R_p =$ 6.5% using 2500 observations (313 reflections). A plausible nitrogen atom position was proposed geometrically (based on EXAFS data) although this made little difference to the agreement factors.

§ All EXAFS data were collected at the Daresbury synchrotron radiation source (SRS) on station 9.3 in transmission mode, to 18 Å^{-1} in k-space at the iodine K-edge. The solid samples were diluted with boron nitride in order to achieve changes in log (I_0/I) in the range 1–1.5 at the absorption edge. Raw data were corrected for dark currents and converted to k-space (with EXCALIB[15]), and backgrounds subtracted (with EXBACK[15]) to yield EXAFS functions $\chi^{obs}{}_i(k)$ and truncated to remove noisy data at high k. These were Fourier-filtered to remove features at distances below *ca.* 1.2 Å, but not to remove long-distance features of the quasi-radial distribution function (*i.e.* no further noise removal was attempted). Model fitting was carried out with EXCURV92,[15] using curved wave theory. Only shells significant[16] at the 95% level were included in the final models, *i.e.* shells added to the model were only retained if they caused a reduction in the R index of $> 4\%$ of the previous value. *Ab initio* phase shifts and back-scattering factors using spherical wave theory were used throughout. The values used throughout for the proportion of absorption leading to EXAFS ('AFAC' = 0.72) and the magnitude of inelastic effects modelled by an imaginary potential ('VPI' = -6.1 eV), were confirmed by fits to data for KIO_4 and $PhI(O_2CMe)_2$. Final $R(R')$ indices for **1–4** were 0.119 (0.112), 0.114 (0.094), 0.156 (0.131), and 0.051 (0.040) respectively. Residual index R was calculated as below:

$$R = \sum_i \{k^3(\chi^{obs}{}_i - \chi^{calc}{}_i)\}^2 / \sum_i \{k^3\chi^{obs}{}_i\}^2$$

R' was calculated as for R, with final model parameters, but with data Fourier-filtered with $r_{max} = ca.$ 6 Å to remove noise. Details of the final models, which gives interatomic distances (r), Debye–Waller factors (a) and the 'coordination' numbers, *i.e.* the number of atoms in a given shell, are available on request from the authors.

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