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DISCOVERY AND X-RAY CRYSTAL STRUCTURE OF A NEW HOST COMPOUND: 1,3,4-TRIS (PHENYLTHIO) [1] BENZOTHIENO [3,2-c] PYRIDINE

By Christopher J. Gilmore, David D. MacNicol, Anthony Murphy, and Marie A. Russell Department of Chemistry, University of Glasgow, Glasgow G12 800, Scotland

Summary. In 1,3-dimethyl-2-imidazolidinone (DMEU) as solvent, pentafluoropyridine reacts with PhSNa to give an essentially quantitative yield of pentakis (phenylthio) pyridine (1); however, analogous reaction with pentachloro-pyridine leads to the unexpected co-formation of the title compound (2), a new host whose crystal structure has been elucidated by X-ray methods for both the unsolvated crystal and for the chlorobenzene inclusion compound.

We have recently shown that hexakis(arylthio)benzenes,¹ hexakis(aryloxy)benzenes,² and octakis(arylthio)naphthalenes,^{3,4} classes of molecule of great interest owing to their ability to form inclusion compounds, can be readily synthesised by exploiting the remarkable ability of the polar aprotic solvent 1,3dimethyl-2-imidazolidinone (DMEU) to promote complete substitution of an appropriate perhalo carbocyclic precursor. In view of this, extension of the method to the synthesis of heterocyclic systems appeared attractive and pentakis-(phenylthio)pyridine (1), previously uncharacterised, was selected as initial target. Indeed, in line with expectation, reaction of pentafluoropyridine with 10 molar equivalents of PhSNa in DMEU for 6 days at ambient temperature leads to



(1)

(2)

complete halogen replacement, pentakis(phenylthio)pyridine (1), m.p. 133-133.5° C, being isolated in near quantitative yield.⁵ Of more immediate concern, however, treatment of pentachloropyridine under similar substitution conditions (in normal daylight) gave an unexpected co-product, m.p. 176-177°C (unsolvated), exhibiting an ABMX pattern in its 360 MHz 1 H n.m.r. spectrum. This feature strongly suggested a benzothienopyridine, a structure requiring the formation of a carbon-carbon bond. The structure (2) was firmly established by an X-ray analysis of the unsolvated crystal (from CCl_A), vide infra. The formation of

(2) is of mechanistic interest: significantly (2) was formed in reduced quantity when the reaction was carried out in the dark⁶ (t.l.c. monitoring), while irradiation with tungsten lamps increased the yield (to <u>ca</u>. 30%). These findings, and the complete absence of (2) for a run carried out in the dark with added <u>m</u>-dinitrobenzene, are consistent with an S_{RN}^{-1} mechanism⁷ involving loss of a Cl⁻ ion from a radical anion thereby generating a radical centre at a β -carbon of the pyridine; following cyclisation with the previously-introduced phenylthio group on the pyridine's γ -carbon, subsequent hydrogen loss may then give (2). Most interestingly, 1,3,4-tris(phenylthio)[1]benzothieno[3,2-c]pyridine (2) exhibits the ability to form crystalline inclusion compounds. Typical guests are toluene, chlorobenzene, bromobenzene, and 1,4-dioxan, the host-guest ratio being 2:1 in each case. The chlorobenzene adduct was selected for X-ray study.

Diffraction intensities for both crystals were measured with an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo- \underline{K}_{α} radiation. 2918 and 1982 independent reflections [I > 2.5 σ I] were recorded for the unsolvated form and the chlorobenzene adduct respectively.^{*,†} The structures were solved by the direct methods package MITHRIL.⁸ The unsolvated form was refined to $\underline{R} = 0.036$ ($\underline{R}_{w} = 0.046$). The hydrogen atoms were located by Fourier methods and refined with isotropic thermal parameters. The solvated form was refined to $\underline{R} = 0.058$ ($\underline{R}_{w} = 0.070$). The chlorobenzene guest is disordered around a centre of symmetry, and was refined as a rigid body with idealised geometry and an overall, isotropic temperature factor. All the other hydrogen atoms were included with idealised geometry, and given isotropic thermal parameters 10% greater than the equivalent isotropic temperature factors of their attached carbon atoms.

Figure 1 shows corresponding general views of $\binom{2}{n}$ in the unsolvated crystal and in the chlorobenzene inclusion compound; while no significant differences between corresponding bond lengths are found for the two cases, it is interesting to note that perceptible changes in host conformation do occur on complexation-particularly marked in the torsion angle C(2) - S(2) - C(21) - C(26) which

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

[†]Structure factor tables available as supplementary data. See Announcement to authors, <u>Tetrahedron Letters</u>, <u>47</u>, 5154 (1983).



Figure 1. Corresponding general views for 1,3,4-tris(phenylthio)[1]benzothieno[3,2-c]pyridine (2), (a) in the unsolvated crystal; and (b) in the chlorobenzene adduct. The non-hydrogen atoms are represented by 50% probability ellipsoids. The labelling is the same for both molecules.

changes from 107.0(3)° to 66.8(8)° on guest inclusion. Incorporation of chlorobenzene also causes a marked attenuation of the thermal motion (or positional disorder) of the phenyl ring attached to S(6).

A comparison of the molecular packing in unsolvated (2) and the chlorobenzene adduct of (2), illustrated in Figures 2 and 3 respectively, reveals a denser packing of benzothienopyridine molecules in the former. In the chlorobenzene inclusion compound the guest molecules are accommodated, round centres of symmetry at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, in continuous voids that run along the <u>a</u>-direction. Because of its location close to a centre of inversion the chlorobenzene exhibits statistical disorder,⁹ this corresponding to the two equally



Figure 2. A stereodiagram illustrating the molecular packing in the unsolvated form of $\binom{2}{2}$.



Figure 3. A stereoview, approximately normal to the \underline{bc} plane, illustrating the host-guest packing in the chlorobenzene adduct of $\binom{2}{2}$.

populated orientations shown in Figure 4. Reflecting a loose guest fit, the chlorobenzene molecule undergoes pronounced thermal motion, and there are no host-guest contacts less than the sum of the appropriate van der Waals radii.

Figure 4. Representation of the disorder of the chlorobenzene guest (principal orientations) around the centre of symmetry (i).

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- 5. Compound (1) gave a satisfactory microanalysis and had spectroscopic properties (¹H and ¹³C n.m.r., i.r., and m.s.) fully in accord with its formulated structure.
- The formation of (2) in the dark contrasts with the <u>photochemical</u> generation of other benzothieno[3,2-c]pyridines and related systems (J. Bratt, B. Iddon, A.G. Mack, H. Suschitzky, J.A. Taylor, and B.J. Wakefield, <u>J. Chem. Soc</u>., Perkin Trans. 1, 1980, 648).
- 7. See, for example, R.A. Rossi, <u>Acc. Chem. Res</u>., 1982, <u>15</u>, 164; and references therein.
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- 9. There is crystallographic evidence for a second guest orientation, corresponding to <u>ca</u>. 20% of the chlorobenzene molecules.

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