

The Role of Non-Bonded Interactions Involving Sulphur in the Crystal Engineering of 4 Å Short Axis Structures. Unusual Topochemical Reactivity of 4-(4-Chlorophenyl)thiazole-2(1H)-thione

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Directionally specific interstack S···S and S···Cl contacts may be employed to engineer crystal structures such that a 4 Å short axis is obtained; a representative compound, the crystal structure of which has been determined, and which additionally exhibits unusual solid-state reactivity, is the title thione (**1**).

When planar aromatic molecules are translated in the crystal along a short axis (SA), two broad classifications arise depending on whether $3.7 < SA < 4.2 \text{ \AA}$ (β -structure) or $SA > 4.7 \text{ \AA}$ (non- β -structure). The pronounced paucity of structures with $4.2 < SA < 4.7 \text{ \AA}$ is indicative of important differences between β and non- β packings. In the former, a molecule is mostly stabilised by its two 4 Å translated (and therefore parallel) neighbours. In the latter, more uniform

stabilisation is obtained from a larger number of non-parallel neighbours. Crystallographically, the non- β -structure is achieved for aromatic compounds by the use of glide planes and screw axes and by optimising C···H interactions which are most effective between inclined molecules. Conversely, the β -structure may be engineered through in-plane interstack interactions (Cl···Cl, C–H···O) which are responsible for the formation of two-dimensional molecular motifs

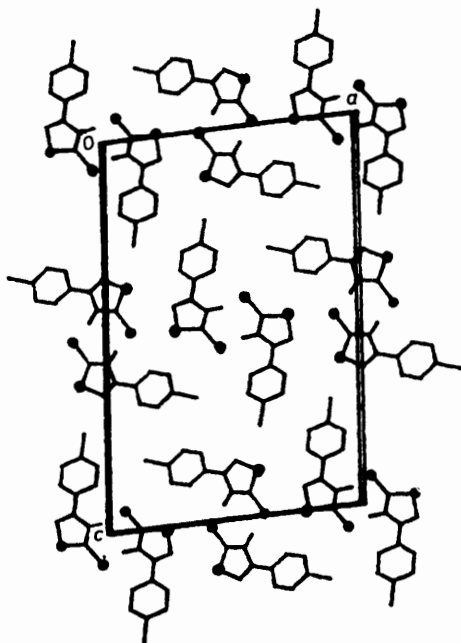
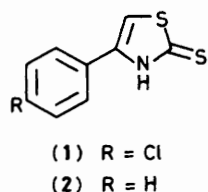
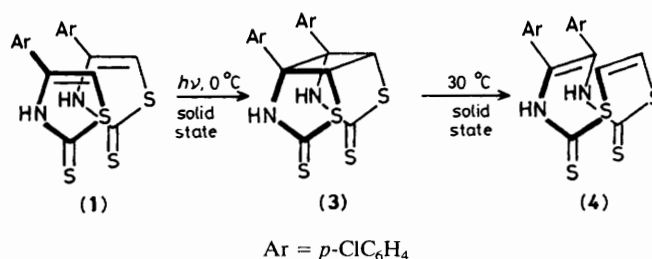


Figure 1. Unit cell in the crystal structure of the thione (1). Sulphur atoms are indicated as filled circles. (N-H) atoms are included. Symmetry-independent molecules are nearly along the page horizontal and vertical.

(sheets, ribbons).^{1,2} Since van der Waals stacking of such motifs to optimise C...C contacts is the only manner of extending the structure into the third dimension, these interactions are directly responsible for β -structure adoption and account for the so-called β -steering ability of groups such as chloro³ or methylenedioxy.⁴

We report here a novel method of crystal engineering⁵ a β -structure by the introduction of a sulphur atom into the molecular framework of an aromatic compound. Sulphur has a distinct β -steering propensity for three reasons: (a) it may have *inter*-stack non-bonded contacts to other hetero atoms (S, N, Cl, O); (b) as an in-plane C-H...S or N-H...S bond acceptor, it reduces the number of 'free' H atoms which must be stabilised by non- β -steering C...H interactions; (c) as a hetero atom, it changes the C/H stoichiometric ratio so as to enhance the role of C...C *vis-à-vis* C...H interactions. These features are exemplified in this communication by the title compound (1), which additionally shows unusual topochemical solid-state reactivity.

In the course of the crystal structure determination of the thione (2) (SA 6.210 Å), it was noted that hydrogen bonded molecules form corrugated sheets (interplanar dihedral angle 35°).⁶ However, these sheets cannot be stacked to form a β -structure since the peripheral H atoms on the phenyl group must dovetail with C atoms on neighbouring molecules through C...H interactions, thereby implying a non- β -packing. Nevertheless, because of the sheet-like character of the crystal structure, it was felt that the molecules of (2)



tended towards the β -motif. Accordingly, the 4-phenylthiazole-2-(1*H*)-thione system was tentatively identified as one which could lead to the β -structure and a chloro substituent was introduced to give the thione (1).[†] This was sufficient to achieve a β -structure.

Figure 1 shows the arrangement of molecules as viewed down the SA. Both molecules in the asymmetric unit (interplanar dihedral angles 27 and 31°) exist as the thione tautomer and are C=S...H-N hydrogen bonded around distinct inversion centres (N...S 3.29 and 3.33 Å). Symmetry-independent hydrogen-bonded dimers are further held together by short S...S contacts of 3.41 Å to generate linear ribbons of molecules which extend along [120]. These contacts are between a thione and a heterocyclic S atom. Adjacent screw-related ribbons are additionally linked through short S...Cl contacts of 3.54 Å to generate the two-dimensional array shown in Figure 1. The β -crystal structure arises from a 4 Å stacking of this array. It may be noted that both the S...S and S...Cl contacts are significantly shorter than the van der Waals values (radii: S, 1.85 Å; Cl, 1.80 Å) and that their angular preferences are almost exactly that predicted by a nucleophile-electrophile model.⁹ Since these preferred directions are nearly in the heterocyclic ring planes, such *inter*-stack contacts may be ribbon-generating (S...S) as well as ribbon-linking (S...Cl) and therefore important from the viewpoint of crystal engineering.

A significant question is whether the β -steering arises merely because of the presence of the chlorine atom.^{1,3} Curiously, no short Cl...Cl contacts are observed in the structure of (1). So the role of Cl in directing the packing of (1) is unlike its behaviour in simpler chloro-aromatic molecules and suggests perhaps that Cl...S and S...S interactions are of greater significance energetically than Cl...Cl ones. Further, in all β -structures arising from Cl...Cl interactions, more than one Cl atom per molecule is usually present.¹ These observations suggest that S, Cl, and perhaps N, atoms are all required for the β -packing to be adopted here.

For the relatively small number of heterocycles where solid-state 2 + 2 cycloadditions have been reported, the heterocyclic group usually plays only an incidental role.¹⁰ However, the C=C bond in (1) is actually part of such a group and it was therefore of interest to examine the material further. Irradiation at 0°C (Pyrex) of crystalline (1) [m.p. 212°C; i.r.(KBr) 1455 and 1060 cm⁻¹ (C=S). δ (¹H, CD₃COCD₃) 7.4 (s, 1H, heterocyclic-H); δ (¹³C) 191.1 (C=S),

[†] *Crystal data for (1):* C₉H₆ClNS₂, *M* = 277.5, monoclinic, space group *P*2₁/*n*, *a* = 17.327(4), *b* = 3.950(2), *c* = 27.877(6) Å, β = 93.88(2)°, *U* = 1903(2) Å³, *F*(000) = 928, *Z* = 8, *D*_c = 1.46 g cm⁻³, *D*_m = 1.49 g cm⁻³, μ (Mo-K α) = 7.12 cm⁻¹. The crystals are extremely light-sensitive and the data, collected on an Enraf Nonius CAD-4 diffractometer, gave 2271 independent reflections of which 783 had *I* > 2.0 σ (*I*). The structure was solved with MULTAN 80⁷ and refined anisotropically using block-diagonal procedures with SHELX 76⁸ with the H atoms placed in calculated positions. The final *R* value was 0.050 (*R*_w 0.044). 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, 1986.

130.1 and 110.6 (heterocyclic)] using sunlight or an Hg lamp led to rapid reaction with all starting material consumed. Spectral data for the product [i.r. 1480, 1060 (C=S), 935 cm^{-1} (cyclobutane C-H bend); δ (^1H) 5.85 (s, 2H, cyclobutane); δ (^{13}C) 198.9 (C=S), 101.2, and 72.1] confirmed that the topochemical dimer (3) was formed quantitatively. Such solid-state transformations involving heterocyclic rings are unusual and have been reported only for thymine and coumarin derivatives and related compounds.¹¹

Dimer (3) was isolated by t.l.c. [silica gel, hexane-EtOAc (80:20)] and careful removal of solvent at low temperatures. These precautions were necessary since (3) is extremely reactive and collapses to a more stable compound, m.p. 118 °C, which was unequivocally characterised as the novel ten-membered unsaturated heterocycle [i.r. 1475, 1090, 1040, 825, and 640 cm^{-1} ; δ (^1H , CDCl_3) 7.8–7.5 (q, 8H, AA'BB') and 7.4 (s, 2H); δ (^{13}C , CDCl_3) 191.6 (C=S), 134.5, 132.2, 129.1, 127.6 (aromatic), 156.1, and 116.0 (ten-membered ring); m/z 452(8.9%), 454(7.7), and 456(2.1), all ($M - 2\text{H}$)⁺, 227(100) and 229(42.5), both ($M/2$)⁺]. Compound (4) was also obtained in the solid state when (1) was irradiated at room temperature but always together with (3). Though (4) is more stable than (3) it still decomposes slowly in solution to uncharacterised products. It is, however, stable to solid-state irradiation at 0 or 30 °C. These experiments indicate that (4) must arise thermally from (3) and this is understandable in view of the strained ring structure in (3).

The β -crystal structure of the thione (1) does not seem to be a stray observation and a survey of the crystallographic literature indicates that several sulphur heterocycles adopt this mode. Some representative examples are benzo-2,1,3-thiadiazole, benzothienobenzothiophene, benzothiopyrone, 2-thienylacrylic acid, thioindigo, and tetrathiafulvalene-tetracyanoquinodimethane.¹² A consideration of these and other compounds shows that the ambit of crystal engineering of 4 Å β -structures may be significantly enlarged to include heterocyclic compounds and that novel physical properties and solid-state reactivity patterns may emerge as a consequence. The role of *inter*-rather than *intra*-stack contacts may well be the dominant theme in all these crystal structures and the ramifications of this fact could extend to other chalcogen heterocycles, notably 'organic metals'.

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