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(1*H*)-thione

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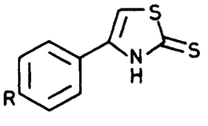
Directionally specific interstack S····S and S····Cl contacts may be employed to engineer crystal structures such that a 4 Å short axis is obtained; a representative compound, the crystal structure of which has been determined, and which additionally exhibits unusual solid-state reactivity, is the title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

When planar aromatic molecules are translated in the crystal along a short axis (SA), two broad classifications arise depending on whether $3.7 < \mathrm{SA} < 4.2$ Å (β-structure) or SA > 4.7 Å (non-β-structure). The pronounced paucity of structures with $4.2 < \mathrm{SA} < 4.7$ Å 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 *inter*-stack interactions (Cl····Cl, C–H····O) which are responsible for the formation of two-dimensional molecular motifs



(1) R = Cl
(2) R = H

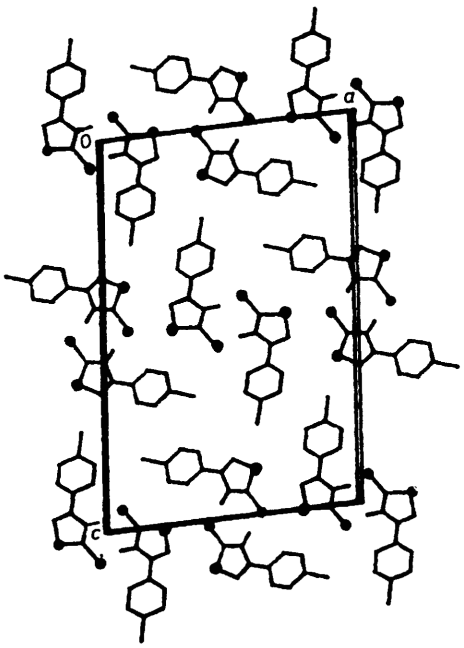
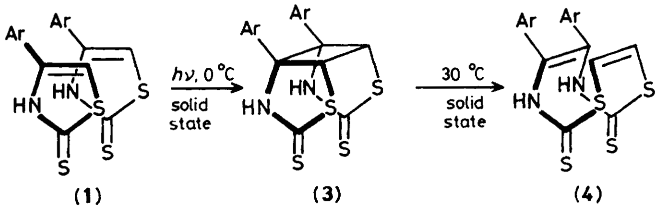


Figure 1. Unit cell in the crystal structure of the thione (**1**). Sulphur atoms are indicated as filled circles. (N–)H atoms are included. Symmetry-independent molecules are nearly along the page horizontal and vertical.

(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 chloro[3] or methylenedioxy.[4]

We report here a novel method of crystal engineering[5] 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 stoicheiometric 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.



Ar = p-ClC_6H_4

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, CD_3COCD_3) 7.4 (s, 1H, heterocyclic-H); δ(^{13}C) 191.1 (C=S),

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[†] *Crystal data for* (**1**): $C_9H_6ClNS_2$, $M = 277.5$, monoclinic, space group $P2_1/n$, $a = 17.327(4)$, $b = 3.950(2)$, $c = 27.877(6)$ Å, $\beta = 93.88(2)°$, $U = 1903(2)$ Å^3, $F(000) = 928$, $Z = 8$, $D_c = 1.46$ g cm^{-3}, $D_m = 1.49$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 7.12$ 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 $I > 2.0\sigma(I)$. The structure was solved with MULTAN 80[7] and refined anisotropically using block-diagonal procedures with SHELX 76[8] 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 (^{1}H) 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 (^{1}H, $CDCl_3$) 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 $(M - 2H)^{+\cdot}$, 227(100) and 229(42.5), both $(M/2)^{+\cdot}$]. 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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