# 3-Oxo-4-thioxo-1,2,5,6-tetrathiapentalene (OTTP): a Novel Thiocarbon with an Unusual Chalcogen Network in its Solid State Structure

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The novel title heterocycle, which was prepared in three steps and is the last possible isomer of the $C_4X_6$ (X = chalcogen) group, exhibits unusual $^{13}C$ n.m.r. line broadening and a short intramolecular nonbonded S–O distance as well as extremely short intermolecular contacts in the solid state, as determined by *X*-ray crystallography.

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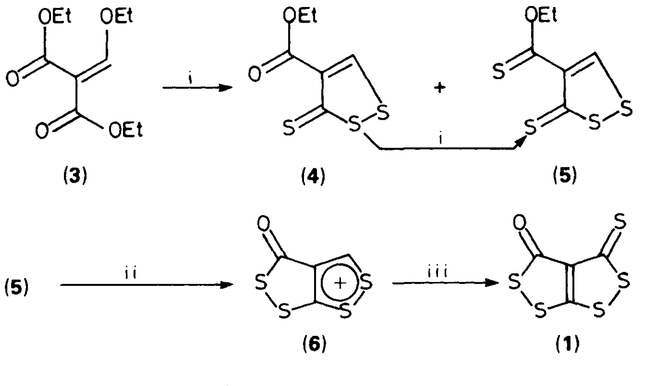
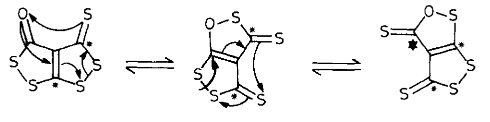
Of the four possible isomers of the $C_4X_6$ family (X = chalcogen), the title compound OTTP, (**1**), and its analogue $C_4S_6$, (**2**), are the only isomers which have not been synthesized previously.[1] Earlier attempts, by us[2a] and by others,[2b] to prepare (**2**) have been unsuccessful. Here we report the preparation, isolation, and characterization of (**1**), a presumed precursor of (**2**). The synthesis of OTTP is outlined in Scheme 1.

The unoptimized yields of (**4**) and (**5**) are 15 and 10%, respectively, and the conversion of (**4**) to (**5**) proceeds in 50% yield. The oxidative cyclization, with presumed loss of chloroethane and/or iodoethane, affords crude salt (**6**), the counterion of which is assumed to be a mixture of chloride and iodide ($C_4HCl_{0.72}I_{0.28}OS_4$); insolubility and lability precluded further characterization.† The unoptimized yield of the oxidative sulphuration from (**6**) to (**1**) proceeds in 30—50% yield. Attempts to obtain (**1**) or $C_4S_6$ directly from triformylmethane, triethyl methanetricarboxylate, tris(*N*,*N*-dimethyl)methanetricarboxamide, ethyl 2-carboxyethyl-3-dimethylaminoacrylate or ethyldithiocarboxyethyl-3-dimethylaminoacrylate, under diverse conditions, led to intractable tars or very low yields of variously substituted 1,2-dithiole-3-thiones.[3]

OTTP is a lustrous red crystalline solid. It is insoluble in alcohols but sparingly soluble in carbon disulphide and slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulphoxide (DMSO), anisole, hot benzene, and toluene. OTTP affords the best crystals from the latter solvent. Spectroscopic and analytical data for (**1**) are in agreement with the proposed structure.‡ The solution $^{13}C$ n.m.r. spectrum (DMSO) is unusual in that the resonances due to the thione (thioxo) carbon (δ 205.5) and the $sp^2$ carbon atom bearing the two sulphur substituents (δ 194.0) are very broad (*ca.* 1 p.p.m. at 20 °C), whereas the remaining two carbon resonances [δ C=O 182.32, C(C=O)(C=S) 136.18] are



**Scheme 1.** *Reagents and conditions:* i, Lawesson's Reagent/toluene, reflux; ii, IC̄/MeCN, room temp.; iii, $S_8$/pyridine, reflux.



**Scheme 2**

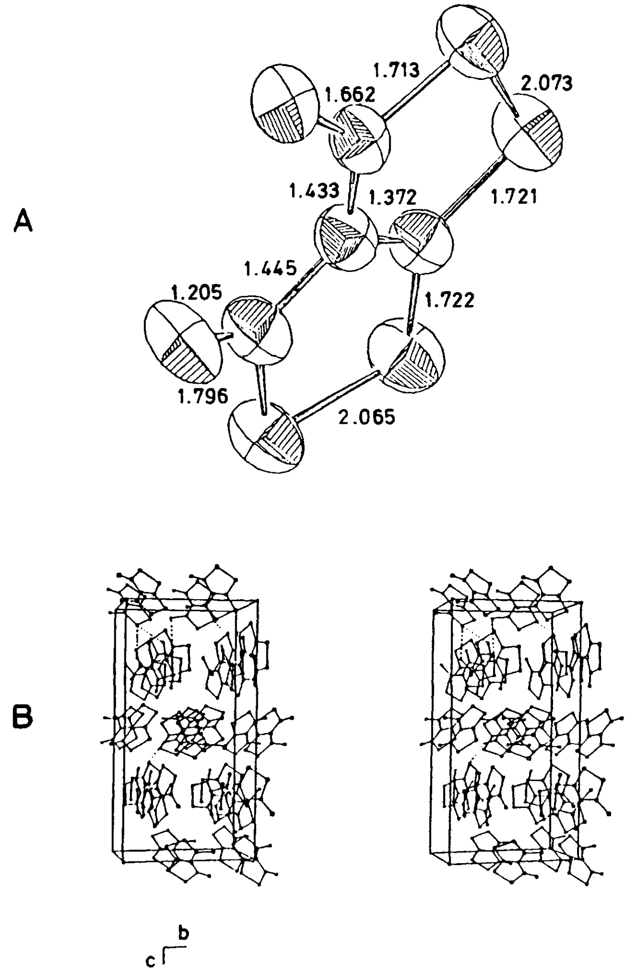


**Figure 1.** A, Ortep plot of one molecule showing thermal ellipsoids and intramolecular bond lengths; B, stereoview of several unit cells showing the two types of molecular sheets.

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† A small sample was converted to a hexafluorophosphate which could be characterized spectroscopically.

‡ I.r.(KBr, ν $cm^{-1}$) 1645, 1418, 1322, 1119, 980, 940; u.v.-vis (THF, $\lambda_{max}$ nm) 260, 282, 321, 354, 410.

of normal sharpness.§ Cyclic voltammetry in nitrobenzene at 40 °C [$Bu_4NPF_6$ (0.05 M), scan rate 100 mV $s^{-1}$] showed an irreversible oxidation peak at +1.33 V ('reverse' oxidation wave peak at +0.6 V) and an irreversible reduction peak at −0.60 V *vs.* Ag/AgCl ('reverse' oxidation wave at +0.13 V). This behaviour is typical of follow-up reactions; in this case, possible formation of a transannular S–O bond following removal of an electron, and rupture of an S–S bond following addition of an electron.

The crystal structure¶ of OTTP is shown in Figure 1. The bond distances and angles (Figure 1A) are normal, and the intramolecular O–S separation is 3.16 Å, which is 0.16 Å shorter than the sum of O and S van der Waals (vdW) radii, yet the molecule is not distorted (planar molecule, no unusual bond angles); this implies an attractive rather than repulsive transannular S–O interaction.

The molecules form two types of sheets in their packing motif. In one sheet the molecules align in such a way as to minimize the net bulk dipole moment, *i.e.*, with the carbonyl bonds pointing in opposite directions (*ca.* 180° relative to each other), and in the second sheet they pack with the carbonyls at *ca.* 140° relative to each other (Figure 1B). The sheets are interconnected by very short intermolecular contacts in all directions; of these the shortest intermolecular S–O contact is 2.88 Å and the shortest S–S contact is 3.087 Å (0.44 and 0.51 Å shorter than the sum of the vdW radii of S–O and S–S, respectively), as shown by broken lines in Figure 1. These remarkably short intermolecular contacts create an unprecedented three-dimensional chalcogen network.

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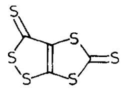
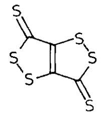
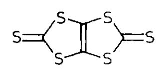
## References

1 Tetrathiapentalenes (**i**), (**ii**), and (**iii**) have been prepared: G. C. Papavassiliou, *Chem. Scr.*, 1985, **25**, 167; A. M. Richter and E. Fanghänel, *Tetrahedron Lett.*, 1983, **24**, 3577; and R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, 1977, **99**, 5521, respectively. The structure of (**i**) was recently established by *X*-ray crystallography: F. L. Lu, M. Keshavarz-K., G. Srdanov, R. H. Jacobson, and F. Wudl, *J. Org. Chem.*, 1989, **54**, 2165.


(i)


(ii)


(iii)

2 (a) F. Wudl, *Pure Appl. Chem.*, 1982, **54**, 1051; (b) F. Closs, W. Breimaier, W. Frank, R. Gompper, and A. Hohenester, *Synth. Met.*, 1989, **29**, E537.

3 F. Closs, M. Keshavarz-K., and R. H. Jacobson, unpublished work.

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§ The simplest explanation would be that (**1**) is a fluctional molecule [suggested for (**2**) by G. Calzaferri and R. Gleiter, *J. Chem. Soc., Perkin Trans. 2*, 1975, 559] where the two broad carbon atoms are interconverting on the n.m.r. time scale. If this were the case, there should be three broad resonances, as shown in Scheme 2; the broad resonances are assigned to the groups indicated by asterisks. The star indicates that the carbon should also be broad, which is not observed.

¶ *Crystal data* for (**1**): $C_4S_5O$, $M$ = 224.36, orthorhombic, *Pbca*, $a$ = 9.691(1), $b$ = 12.802(2), $c$ = 24.316(4) Å, $U$ = 3016.74 $Å^3$, $Z$ = 16, $D_c$ = 1.98 g $cm^{-3}$, $D_m$ = 1.97 g $cm^{-3}$, $\lambda(\text{Mo } K_\alpha)$ = 0.71069 Å, $\mu$ = 13.98 $cm^{-1}$, $F(000)$ = 4352, $T$ = 295 K. For 2301 observed unique reflections with $I \geqslant 3\sigma(I)$, full-matrix least-squares anisotropic refinement gave $R$ = 0.073 and $R_w$ = 0.079. 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.