

Solid-State Reactivity of Thiazinones: Structure of Ethyl 6-Oxo-2-phenyl-1,3-thiazine-4-carboxylate

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Abstract. (I), $C_{13}H_{11}NO_3S$, $M_r = 261.3$, monoclinic, $P2_1/a$, $a = 8.760$ (3), $b = 19.553$ (15), $c = 7.081$ (3) Å, $\beta = 97.18$ (4)°, $V = 1203$ (2) Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.19$ cm⁻¹, $F(000) = 544$, $T = 120$ K, $R = 0.037$ for 2219 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The molecule is approximately planar; the maximum deviation from the least-squares plane is 0.221 (3) Å [C(16)]. Molecules lie in layers which mark the limits of channels in which amine molecules can diffuse and react with (I) by nucleophilic attack.

Introduction. The title compound (I) belongs to the class of 6*H*-1,3-thiazin-6-one compounds which have been described as useful tools for synthetic applications (Schroth, Spitzner, Freitag, Richter & Dobner, 1986; Tea, Chehna, Pradere, Duguay & Toupet, 1986) and particularly for preparing penicillic derivatives (Chehna, Pradere, Vicens, Toupet & Quiniou, 1988). These molecules contain electrophilic centers at the C(2), C(4) and C(6) positions. The reactivity of each center depends on the basic and acidic conditions of reaction. The title compound reacts with *N,N*-dimethylamine, HNMe₂, at the C(6) position, with ring contraction, opening a new route to thiazolinic compounds as part of penam (4-thia-1-azabicyclo[3.2.0]heptan-2-one) skeletons (Morin & Gorman, 1982) and to precursors of substituted thiazoles (Metzger, 1979). In the course of a study of the reactivity of single crystals of (I) with gaseous HNMe₂, we noticed anisotropic behaviour of the reaction (Chehna, Pradere, Perrin, Lecocq, Baert & Vicens, 1988): the nucleophilic amine attack starts at

both ends of the single needle-like crystals of (I) and proceeds along the long axis of the crystals. In order to clarify this effect and the results from investigations of the molecular packing of (I) by theoretical means (Decoret, Bayard, Baert, Chehna, Pradere & Vicens, 1990), the low-temperature X-ray structure of (I) has been determined.

Experimental. Compound (I) was prepared according to a described procedure (Tea *et al.*, 1986) and crystallized from 80:20 hexane–ethyl acetate at room temperature to yield thin yellow needle-like crystals. A crystal with dimensions 0.5 × 0.4 × 0.25 mm mounted on a PW1100 four-circle diffractometer, Mo *K*α graphite-monochromated radiation ($\lambda = 0.71069$ Å), ω - 2θ scan, low temperature. Lattice parameters from 25 reflections with $20 \leq \theta \leq 27^\circ$. 3795 reflections ($\sin\theta/\lambda \leq 0.703$ Å⁻¹) of which 3429 were unique ($R_{\text{int}} = 0.025$), measured in the range $-12 \leq h \leq 12$, $k \leq 23$, $l \leq 9$; 2219 satisfied $I \geq 3\sigma(I)$. The intensities of three reference reflections showed no significant variation. Lorentz-polarization corrections applied but absorption and extinction ignored. Structure solved using direct methods (Germain, Main & Woolfson, 1971), and Fourier methods, anisotropic full-matrix least-squares refinement of 163 parameters based on F (SHELX76; Sheldrick, 1976), with anisotropic thermal parameters applied to all non-H atoms. H atoms located from successive Fourier difference maps with U values equal to the values of the isotropic U of their carriers, and not refined. Final $R = 0.037$, unit weights, $S = 4.35$ and $(\Delta/\sigma)_{\text{max}} = 0.002$. The largest peaks in the final difference map were 0.28 and -0.27 e Å⁻³. Atomic scattering factors were taken from *International*

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^2$) with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	3003 (1)	4805 (1)	9183 (1)	28 (1)
C(1)	3060 (2)	3901 (1)	8882 (4)	29 (2)
O(2)	4255 (2)	3610 (1)	9488 (3)	39 (2)
C(3)	1681 (2)	3578 (1)	7956 (3)	25 (2)
C(4)	359 (2)	3919 (1)	7380 (3)	20 (2)
N(5)	98 (2)	4611 (1)	7437 (3)	19 (1)
C(6)	1147 (2)	5033 (1)	8150 (3)	20 (1)
C(7)	809 (2)	5774 (1)	8166 (3)	18 (1)
C(8)	1891 (2)	6249 (1)	8994 (3)	20 (2)
C(9)	1522 (3)	6938 (1)	9014 (3)	21 (2)
C(10)	91 (3)	7167 (1)	8200 (3)	24 (2)
C(11)	-983 (3)	6699 (1)	7352 (3)	24 (2)
C(12)	-634 (2)	6007 (1)	7332 (3)	19 (2)
C(13)	-1011 (3)	3484 (1)	6592 (3)	21 (2)
O(14)	-943 (2)	2874 (1)	6424 (3)	29 (1)
O(15)	-2275 (2)	3861 (1)	6181 (2)	20 (1)
C(16)	-3669 (3)	3476 (1)	5551 (4)	25 (2)
C(17)	-4873 (3)	3992 (2)	4801 (5)	37 (3)

Tables for X-ray Crystallography (1974, Vol. IV) and from Stewart, Davidson & Simpson (1965) for H atoms. All calculations were performed on a Micro-VAXII.

Discussion. Atomic fractional coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1,* selected interatomic distances and bond angles are listed in Table 2. The conformation of the molecule and the atomic numbering are depicted in Fig. 1.

There is no hydrogen bonding; some intermolecular distances are less than the sum of the van der Waals radii [C(4)—C(12) 3.378, C(8)—C(13) 3.355 and C(9)—C(13) 3.239 Å].

The least-squares plane shows that the molecule is approximately planar, the largest deviation from the plane being 0.221 Å for the C(16) atom in the ethyl group.

The view of the packing arrangement (Fig. 2) shows that the molecules lie in layers which delimit channels parallel to the needle axes. The radius of these channels is about 2.6 Å. The ketone functions which undergo nucleophilic amine attack are perpendicular to the needle axes and lie in the walls of the channels. One can assume that gaseous molecules of HNMe₂ penetrate these channels during the course of the reaction leading to an anisotropic destruction of the crystals of (I) along the needle axes.

* Lists of structure factors, anisotropic thermal parameters, atomic deviations from the least-squares plane and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54702 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances (Å) and bond angles (°) with *e.s.d.*'s in parentheses

S—C(1)	1.782 (2)	C(7)—C(12)	1.403 (3)
S—C(2)	1.754 (2)	C(8)—C(9)	1.387 (3)
C(1)—O(2)	1.221 (3)	C(9)—C(10)	1.387 (4)
C(1)—C(3)	1.446 (3)	C(10)—C(11)	1.394 (3)
C(3)—C(4)	1.354 (3)	C(11)—C(12)	1.386 (3)
C(4)—N(5)	1.374 (3)	C(13)—O(14)	1.201 (3)
C(4)—C(13)	1.519 (3)	C(13)—O(15)	1.333 (3)
N(5)—C(6)	1.291 (3)	O(15)—C(16)	1.456 (3)
C(6)—C(7)	1.479 (3)	C(16)—C(17)	1.507 (4)
C(7)—C(8)	1.402 (3)		
C(1)—S—C(6)	103.9 (1)	C(6)—C(7)—C(12)	119.1 (2)
S—C(1)—O(2)	117.1 (2)	C(8)—C(7)—C(12)	119.2 (2)
S—C(1)—C(3)	117.0 (2)	C(7)—C(8)—C(9)	120.1 (2)
O(2)—C(1)—C(3)	125.9 (2)	C(8)—C(9)—C(10)	120.6 (2)
C(1)—C(3)—C(4)	123.8 (2)	C(9)—C(10)—C(11)	119.7 (2)
C(3)—C(4)—N(5)	127.9 (2)	C(10)—C(11)—C(12)	120.5 (2)
C(3)—C(4)—C(13)	116.2 (2)	C(7)—C(12)—C(11)	120.1 (2)
N(5)—C(4)—C(13)	115.8 (2)	C(4)—C(13)—O(14)	123.1 (2)
C(4)—N(5)—C(6)	121.9 (2)	C(4)—C(13)—O(15)	111.5 (2)
S—C(6)—N(5)	125.3 (2)	O(14)—C(13)—O(15)	125.3 (2)
S—C(6)—C(7)	114.7 (2)	C(13)—O(15)—C(16)	115.0 (2)
N(5)—C(6)—C(7)	119.7 (2)	O(15)—C(16)—C(17)	106.6 (2)
C(6)—C(7)—C(8)	121.8 (2)		

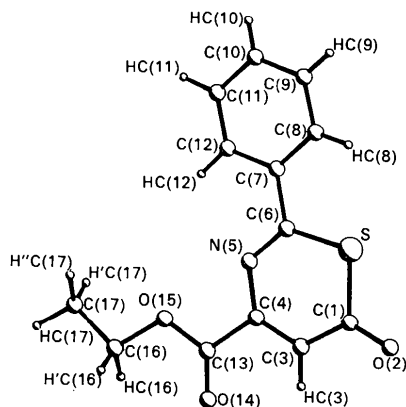


Fig. 1. View of the molecule (PLUTO; Motherwell & Clegg, 1978).

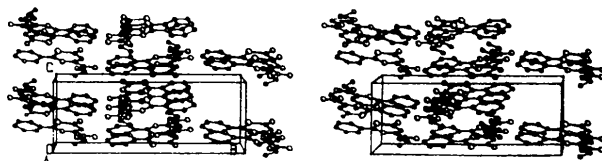


Fig. 2. Stereoscopic view along the (010) axis (PLUTO; Motherwell & Clegg, 1978).

The observation that compound (I) crystallizes in a centrosymmetric space group should offer convenient routes through topochemical solid-state reactions to chiral products from achiral precursors.

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Structure of Potassium Strontium Cuprate, $K_{0.95}Sr_{0.05}CuO_2$

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Abstract. $K_{0.95}Sr_{0.05}CuO_2$, $M_r = 137.07$, orthorhombic, $Cmcm$, $a = 4.3727$ (1), $b = 11.6794$ (4), $c = 5.4112$ (1) Å, $V = 276.35$ (2) Å³, $Z = 4$, $D_x = 3.296$ g cm⁻³, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $\mu = 231.85$ cm⁻¹, $F(000) = 259.8$, $T = 298$ K, $R_{wp} = 14.57\%$, $R_{ex} = 10.48\%$, $\chi^2 = 1.93$ for 22 basic variables with 4900 observations corresponding to 115 reflections. The structure of the title compound has been refined by Rietveld analysis of X-ray powder diffraction data. Cu is surrounded by four O atoms in a rectangular configuration. These CuO₄ units share edges to form infinite chains, which are separated from each other by K⁺/Sr²⁺ ions in trigonal prismatic sites formed by the oxide ions. $K_{0.95}Sr_{0.05}CuO_2$ is a solid solution based on the stoichiometric end member KCuO₂ and represents a mixed-valence compound rich in copper(III).

Experimental. $K_{0.95}Sr_{0.05}CuO_2$ was prepared as a polycrystalline powder by solid-state reaction

between KO₂, SrO₂ and CuO. Because of the air-sensitive nature of the materials all manipulations were carried out in a Miller–Howe high-integrity argon-filled glove box. Appropriate quantities of the starting materials were ground together in an agate mortar and pestle for 15 min. The resulting mixture was then formed into pellets and placed in a Pt boat which was located within a silica tube fitted with two gas breakthroughs and taps. The tube was removed from the glove box, connected to an oxygen supply, and placed within a cylindrical furnace. The sample was heated under flowing oxygen at 673 K for 6 d. Weight-loss measurements confirmed the loss of only O₂ from the reaction mixture. Phase purity was determined by X-ray powder diffraction photographs using a Stoe Guinier camera with Cu K α radiation. Solid-solution formation was confirmed by shifts in lattice parameters away from those of stoichiometric KCuO₂ ($a = 4.3857$, $b = 11.6878$, $c = 5.4135$ Å) (Pienkowski, Bruce, Abrahams, Janes &