Crystal and Molecular Structure of 3-Mercapto-1,3-diphenylprop-2-en-1-one by *X*-ray and Neutron Diffraction

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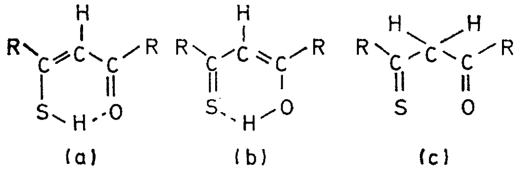
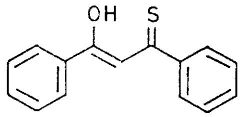
The crystal and molecular structure of the title compound has been solved by both *X*-ray and neutron diffraction methods. It has been shown to exist in the enolic form, with the enolic hydrogen atom located in a clearly asymmetric position. An alternation of short and long bond lengths about the monothio-β-diketone ring is also observed. The structure is compared with those of analogous β-diketone structures. Crystals are monoclinic, space group $P2_1/c$, with $a = 12.549(5)$, $b = 7.416(4)$, $c = 13.290(5)$ Å, $\beta = 98.289(12)°$, $Z = 4$.

THE monothio-β-diketones are well known as ligands in co-ordination compounds, and have recently been the subject of two extensive reviews.[1,2] They are generally formulated in the thioenolic form. Although it was agreed that they exist in either this or the enolic form, their actual structure was not clear.[1] Because of similarities between the monothio-β-diketones and the β-diketones,[3-6] and especially in view of the uncertainty of the enolic–thioenolic proton position it was decided to investigate the structure of a representative monothio-β-diketone by both *X*-ray and neutron-diffraction methods. 3-Mercapto-1,3-diphenylprop-2-en-1-one (thiodibenzoylmethane) (I) was chosen since it was the only monothio-β-diketone examined which was stable to *X*-rays.



Tautomeric forms of monothio-β-diketones:
(a) thioenol, (b) enol, and (c) thioxo



(I)

EXPERIMENTAL

Single crystals suitable for *X*-ray and neutron diffraction were grown by the very slow evaporation of an acetone solution of (I). Preliminary monoclinic cell dimensions, which were later refined by use of neutron-diffractometer measurements, were obtained from Weissenberg and oscillation *X*-ray photographs.

Crystal Data.—$C_{15}H_{12}SO$, $M = 240$. Monoclinic; $a = 12.549(5)$, $b = 7.416(4)$, $c = 13.290(5)$ Å, $\beta = 98.289(12)°$, D_m (flotation) $= 1.23$, $Z = 4$, $D_c = 1.31$, $U = 1\,223.9$ Å^3; μ_x (the linear absorption coefficient for Mo-K_α radiation) $= 2.41$ cm^{-1}; μ_N (the measured linear absorption coefficient for a neutron wavelength of 0.9831 Å) $= 1.44 \pm 0.40$ cm^{-1}. Space group $P2_1/c$ (No. 14) from systematic absences: $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$.

Data Collection.—(a) X-*Ray*. A suitable single crystal was mounted with the *b* axis approximately parallel to the ϕ axis of the Australian Atomic Energy Commission's *X*-ray diffractometer equipped with a solid-state detector. Two sets of crystallographically equivalent reflections, totalling 2 374 observations, were measured by use of the ω-scan technique for $\sin^2\theta/\lambda^2 \leq 0.372$. Considerable mechanical problems were encountered during data collection and only data collected with $\sin^2\theta/\lambda^2 \leq 0.25$ were reliable. In addition, peak overlap occurred for some of the remaining reflections. These unreliable reflections were deleted from the data set, absorption and Lorentz-polarisation corrections applied and equivalent reflections averaged to yield a unique set of 855 reflections. Estimated standard deviations were assigned to individual reflections on the basis of a least-squares polynomial regression of the form $\sigma_m{}^2(I) = \sum_{n=1}^{N} A_n I^{n-1}$ to determine A_n, where $\sigma_m{}^2(I)$ is the variance of the mean obtained for each pair of equivalent reflections. The analysis was performed on the absorption-corrected intensities before application of the Lorentz-polarisation correction. This approach was adopted in order to estimate non-counting errors in the data set.

(b) *Neutron*. A crystal of 45 mm^3 volume was mounted with the *b* axis approximately parallel to the ϕ axis of the Australian Institute of Nuclear Science and Engineering's four-circle computer-controlled diffractometer, 2TanA. Two sets of crystallographically independent reflections, totalling 3 222 observations, were collected by use of the ω—2θ scan technique. A standard reflection, monitored every 25 observations, showed no systematic variation during data collection.

Data were corrected for absorption and Lorentz effects and averaged to yield a unique set of 1 407 reflections, all of which were included in the least-squares refinement. Reflections were assigned individual estimated standard deviations as already outlined.

Structure Solution and Refinement.—(a) X-*Ray*. The *X*-ray structure was solved by means of direct methods. Using the symbolic addition procedure phases were assigned to 153 reflections. An *E* map based on these 153 phases allowed unambiguous location of all non-hydrogen atoms.

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[1] M. Cox and J. Darken, *Co-ordination Chem. Rev.*, 1971, **7**, 29.

[2] S. Livingstone, *Co-ordination Chem. Rev.*, 1971, **7**, 59.

[3] L. F. Power and R. D. G. Jones, *Acta Cryst.*, 1971, **B27**, 181.

[4] L. F. Power and R. D. G. Jones, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 35.

[5] L. F. Power and R. D. G. Jones, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 887.

[6] L. F. Power, K. E. Turner, and F. H. Moore, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 313; *J. Cryst. Mol. Structure*, 1975, **5**, 59.

TABLE 1

Final agreement factors for (I)

	X-Ray	Neutron
$R(F_o^2)$	0.047	0.044
$R'(F_o^2)$	0.051	0.070
$R(F_o)$	0.053	0.053
S	1.20	0.80
$(m-n)$	701	1 252

Where $R(F_o^2) = \Sigma||F_o^2|-|F_c^2||/\Sigma|F_o^2|$, $R'(F_o^2) = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^4|]^{\frac{1}{2}}$, $R(F_o) = \Sigma|F_o|-|F_c||/\Sigma|F_o|$, $S = [\Sigma w(|F_o^2|-|F_c^2|)^2/(m-n)]^{\frac{1}{2}}$, m = no. of observations in data set, n = no. of parameters varied in the refinement.

All phases assigned were later shown to be correct. Refinement was carried out in the usual manner by use of block-diagonal least-squares with an empirical weighting scheme. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and the scattering factor for sulphur was corrected for the real, but not the imaginary, part of the anomalous dispersion correction. Expected positions for all hydrogen atoms, except the enolic hydrogen (Figure 1), were calculated and included in the refinement with the individual isotropic temperature parameters of the atoms to which they were attached. A difference Fourier map was calculated and the position of the remaining hydrogen was

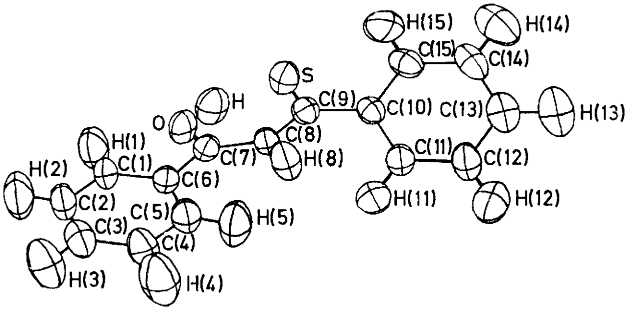

FIGURE 1 Notation for (I) showing 50% probability thermal ellipsoids

TABLE 2

Positional (fractional co-ordinates × 10^4) and thermal * parameters for (I). The first line of each entry contains X-ray, the second line the neutron parameters. Only neutron hydrogen atom parameters are quoted

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	3 143(3)	3 616(6)	787(3)	57(4)	286(14)	68(3)	21(7)	10(3)	20(6)
	3 124(2)	3 630(3)	792(2)	46(1)	244(5)	75(2)	25(2)	13(1)	21(2)
C(2)	2 261(3)	3 268(7)	65(4)	44(4)	317(17)	117(4)	22(6)	16(4)	26(7)
	2 239(2)	3 269(3)	58(2)	47(2)	273(6)	93(2)	15(2)	5(1)	21(3)
C(3)	2 391(3)	2 507(6)	−853(4)	62(4)	234(15)	98(4)	−4(6)	−8(3)	−13(7)
	2 377(2)	2 507(3)	−875(2)	60(2)	231(5)	91(2)	4(2)	−5(2)	3(3)
C(4)	3 407(4)	2 111(6)	−1 047(3)	75(4)	290(15)	71(3)	0(7)	−1(3)	−29(6)
	3 411(2)	2 107(3)	−1 064(2)	63(2)	253(5)	75(2)	7(2)	−8(1)	−17(2)
C(5)	4 291(3)	2 432(6)	−330(3)	57(4)	219(13)	63(3)	6(6)	8(3)	−20(6)
	4 299(2)	2 442(3)	−336(2)	56(2)	221(5)	60(2)	7(2)	6(1)	−13(2)
C(6)	4 170(3)	3 193(5)	606(3)	45(4)	116(12)	60(3)	8(5)	10(3)	22(5)
	4 165(1)	3 199(3)	600(1)	49(1)	154(4)	53(1)	3(2)	9(1)	9(2)
C(7)	5 095(3)	3 508(6)	1 408(3)	66(4)	171(14)	52(3)	−13(6)	15(3)	5(5)
	5 076(1)	3 519(3)	1 403(1)	53(1)	159(4)	52(1)	3(2)	12(1)	4(2)
C(8)	6 112(3)	2 848(5)	1 381(3)	60(4)	160(13)	53(3)	2(6)	12(3)	−8(5)
	6 103(1)	2 814(3)	1 379(2)	46(1)	160(4)	49(1)	9(2)	5(1)	−4(2)
C(9)	7 001(3)	3 005(5)	2 143(3)	60(4)	147(12)	49(3)	−10(5)	5(3)	13(5)
	6 995(1)	3 017(3)	2 147(1)	52(1)	158(4)	52(1)	−2(2)	3(1)	−3(2)
C(10)	8 031(3)	2 243(5)	1 943(3)	49(3)	149(12)	56(3)	12(6)	−7(3)	−4(5)
	8 036(1)	2 237(3)	1 949(1)	48(1)	158(4)	52(1)	0(2)	−2(1)	2(2)
C(11)	8 349(3)	2 271(5)	979(3)	56(4)	162(12)	58(3)	15(6)	−1(3)	2(5)
	8 322(1)	2 276(3)	966(2)	53(1)	202(5)	58(1)	11(2)	7(1)	−8(2)
C(12)	9 330(3)	1 627(6)	814(3)	82(4)	231(15)	84(4)	39(7)	20(3)	−10(6)
	9 322(2)	1 637(3)	792(2)	58(2)	249(6)	81(2)	31(2)	10(2)	−14(3)
C(13)	10 037(3)	939(7)	1 597(4)	50(3)	245(15)	105(4)	28(7)	−5(4)	−20(8)
	10 042(2)	911(3)	1 581(2)	61(2)	233(6)	96(2)	19(3)	5(2)	−17(3)
C(14)	9 739(3)	830(6)	2 552(4)	69(4)	221(14)	86(4)	23(7)	−15(3)	10(7)
	9 750(2)	808(3)	2 557(2)	57(2)	201(5)	97(2)	16(2)	−17(1)	6(2)
C(15)	8 770(3)	1 528(6)	2 719(3)	65(3)	191(15)	67(3)	−8(6)	0(3)	−2(5)
	8 758(2)	1 501(3)	2 740(2)	66(2)	191(5)	63(2)	−7(2)	−12(1)	14(2)
O	4 845(2)	4 477(4)	2 174(2)	66(2)	343(10)	65(2)	21(4)	11(2)	−41(4)
	4 847(3)	4 508(4)	2 170(2)	68(2)	274(7)	63(2)	17(3)	20(2)	−34(3)
S	6 965(1)	4 081(2)	3 251(1)	85(1)	352(4)	67(1)	−13(2)	10(1)	−30(2)
	6 977(4)	4 085(8)	3 255(4)	65(4)	284(14)	59(3)	−16(6)	7(3)	−34(6)
H	5 521(5)	4 585(7)	2 705(4)	96(4)	343(14)	79(4)	4(6)	27(3)	−42(6)
H(1)	3 025(4)	4 204(9)	1 495(4)	77(3)	505(18)	98(4)	64(6)	15(3)	−21(7)
H(2)	1 444(4)	3 590(10)	223(5)	64(4)	548(20)	140(5)	42(7)	13(4)	−4(8)
H(3)	1 701(4)	2 238(9)	−1 436(5)	86(4)	420(16)	123(5)	7(7)	−25(4)	−29(7)
H(4)	3 536(4)	1 567(9)	−1 773(4)	95(4)	538(19)	102(4)	35(7)	−11(3)	−82(8)
H(5)	5 094(4)	2 149(8)	−518(4)	66(3)	507(18)	79(3)	23(6)	12(3)	−62(6)
H(8)	6 209(3)	2 018(7)	739(4)	64(3)	300(12)	75(3)	34(5)	−3(2)	−38(6)
H(11)	7 790(3)	2 845(7)	353(3)	89(3)	344(12)	61(3)	36(5)	16(2)	8(5)
H(12)	9 541(4)	1 700(9)	37(5)	95(4)	455(17)	96(4)	44(6)	33(3)	0(7)
H(13)	10 811(5)	404(8)	1 459(5)	80(4)	383(16)	142(5)	53(7)	11(4)	−23(7)
H(14)	10 281(4)	229(8)	3 160(5)	104(4)	349(14)	132(5)	25(6)	−23(4)	37(7)
H(15)	8 528(4)	1 452(8)	3 491(4)	101(4)	369(14)	71(4)	−1(6)	2(3)	35(6)

* Thermal parameters (× 10^4) are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

clearly in an enolic position. The structure was briefly reported[7] at this stage.

Final refinement was carried out, allowing all positional parameters and the non-hydrogen atom anisotropic thermal parameters to vary, by use of the Brookhaven full-matrix least-squares programme LINUS. The function minimised was $\Sigma w(|F_o|^2 - |F_c^2|)^2$, where $w^{-1} = \sigma^2(F_o^2)$. Observed and calculated structure factors are (*X*-ray and neutron) listed in Supplementary Publication No. SUP 21487 (15 pp., 1 microfiche),* while final agreement factors are shown in Table 1. The *X*-ray scattering factors used were taken from ref. 8.

(ii) *Neutron*. The *X*-ray parameters were used as the starting point for the neutron structure-refinement. Anisotropic thermal parameters were assigned to all atoms and together with positional parameters and an isotropic extinction parameter were varied in the final full-matrix least-square cycles. Because of computer storage limitations, it was necessary to carry out the final refinement with overlapping blocks of parameters. Neutron scattering lengths used were C 0.665, O 0.577, S 0.280, and H −0.372. A final difference-Fourier map, computed at the convergence of the least-squares refinement, did not show any significant peaks.

TABLE 3

Bond lengths (Å) for (I)

	X-Ray	Neutron
C(1)–C(2)	1.381(5)	1.394(2)
C(1)–C(6)	1.381(5)	1.404(2)
C(2)–C(3)	1.375(6)	1.396(3)
C(3)–C(4)	1.368(6)	1.390(3)
C(4)–C(5)	1.375(5)	1.388(3)
C(5)–C(6)	1.394(5)	1.397(3)
C(6)–C(7)	1.477(5)	1.467(2)
C(7)–C(8)	1.373(5)	1.396(2)
C(8)–C(9)	1.400(5)	1.410(2)
C(9)–C(10)	1.470(5)	1.487(2)
C(10)–C(11)	1.396(5)	1.404(3)
C(10)–C(15)	1.389(5)	1.396(3)
C(11)–C(12)	1.367(5)	1.392(3)
C(12)–C(13)	1.365(5)	1.390(3)
C(13)–C(14)	1.376(5)	1.400(3)
C(14)–C(15)	1.369(5)	1.400(3)
C(7)–O	1.321(4)	1.321(3)
O · · · S	2.849(3)	2.865(5)
C(9)–S	1.681(4)	1.675(5)
O–H	0.78(4)	1.024(8)
S–H	2.13(4)	1.904(7)
C(1)–H(1)	0.94(3)	1.051(5)
C(2)–H(2)	0.79(3)	1.079(6)
C(3)–H(3)	0.95(4)	1.064(6)
C(4)–H(4)	0.84(3)	1.056(6)
C(5)–H(5)	0.93(3)	1.082(6)
C(8)–H(8)	0.89(3)	1.059(6)
C(11)–H(11)	0.92(3)	1.063(7)
C(12)–H(12)	0.94(3)	1.079(7)
C(13)–H(13)	0.88(3)	1.069(7)
C(14)–H(14)	0.88(3)	1.056(7)
C(15)–H(15)	0.90(3)	1.079(7)

Final agreement factors are shown in Table 1 while observed and calculated structure factors are listed in the Supplementary Publication (see earlier). Positional and thermal parameters for the two refinements are shown in Table 2.

DISCUSSION

TABLE 4

Bond angles (°) for (II)

	X-Ray	Neutron
C(6)–C(1)–C(2)	120.8(4)	119.8(2)
C(6)–C(1)–H(1)		119.1(2)
H(1)–C(1)–C(2)		121.1(3)
C(1)–C(2)–C(3)	120.5(5)	120.8(2)
C(1)–C(2)–H(2)		118.9(4)
H(2)–C(2)–C(3)		120.4(3)
C(2)–C(3)–C(4)	119.3(5)	119.0(2)
C(2)–C(3)–H(3)		120.7(4)
H(3)–C(3)–C(4)		120.3(4)
C(3)–C(4)–C(5)	120.9(4)	120.9(2)
C(3)–C(4)–H(4)		120.3(2)
H(4)–C(4)–C(5)		118.8(3)
C(4)–C(5)–C(6)	120.5(4)	120.3(2)
C(4)–C(5)–H(5)		118.8(3)
H(5)–C(5)–C(6)		120.8(3)
C(5)–C(6)–C(1)	118.1(4)	119.2(2)
C(5)–C(6)–C(7)	122.2(4)	122.1(2)
C(1)–C(6)–C(7)	119.6(4)	118.7(2)
C(6)–C(7)–O	113.2(4)	114.7(2)
C(6)–C(7)–C(8)	124.2(4)	123.3(2)
O–C(7)–C(8)	122.6(4)	122.0(2)
C(7)–C(8)–C(9)	126.8(4)	125.6(2)
C(7)–C(8)–H(8)		116.7(2)
H(8)–C(8)–C(9)		117.6(2)
C(8)–C(9)–S	123.7(2)	125.2(2)
C(8)–C(9)–C(10)	117.8(4)	117.1(2)
S–C(9)–C(10)	118.5(3)	117.6(2)
C(9)–C(10)–C(15)	121.5(4)	120.7(2)
C(9)–C(10)–C(11)	122.4(4)	120.4(2)
C(11)–C(10)–C(15)	116.0(4)	118.9(2)
C(10)–C(11)–C(12)	121.7(4)	120.3(2)
C(10)–C(11)–H(11)		120.3(3)
H(11)–C(11)–C(12)		119.4(3)
C(11)–C(12)–C(13)	120.6(4)	120.7(2)
C(11)–C(12)–H(12)		119.7(3)
H(12)–C(12)–C(13)		119.6(3)
C(12)–C(13)–C(14)	119.5(4)	119.4(2)
C(12)–C(13)–H(13)		121.6(2)
H(13)–C(13)–C(14)		119.0(3)
C(13)–C(14)–C(15)	119.6(4)	120.0(2)
C(13)–C(14)–H(14)		120.3(3)
H(14)–C(14)–C(15)		119.8(3)
C(14)–C(15)–C(10)	122.5(4)	120.6(2)
C(14)–C(15)–H(15)		120.8(2)
H(15)–C(15)–C(10)		118.6(3)
C(7)–O–H	109.6(37)	108.5(3)
C(9)–S–H	84.5(19)	83.5(3)
O–H–S	152.5(55)	155.0(3)

Bond lengths and angles for the neutron and *X*-ray determinations are compared in Tables **3** and **4**. The bond lengths determined from the *X*-ray study are systematically shorter than those determined from the neutron study, and this is especially pronounced in the two phenyl rings. The aromatic bond lengths observed in the neutron determination are in the range **1.388—1.404(3)** Å. This compares favourably with the expected[9] value of **1.395(3)** Å. Corresponding bond lengths determined from the *X*-ray study lie in the range **1.365—1.396(5)** Å. It is felt that the poor agreement of the *X*-ray results with both the published and neutron-determined values is a reflection of the poor quality of the *X*-ray data. Hence in the following

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] L. F. Power, K. E. Turner, and F. H. Moore, *Tetrahedron Letters*, 1974, 875.

[8] D. T. Cromer, and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] O. Kennard, ‘Handbook of Chemistry and Physics,’ Chemical Rubber Company, Ohio, 1967, p. F145.

discussion parameters derived from the neutron data will be used.

(I) clearly exists in the enol form, with strong intramolecular hydrogen bonding between the oxygen and sulphur atoms. An alternation of short and long bonds is also observed about the monothio-β-diketone ring, a situation analogous to that found in the β-diketones.[5,6]

The monothio-β-diketone ring is essentially planar, although the sulphur deviates considerably from the plane. The phenyl rings are also approximately planar, although the C(10)—(15) ring deviates from a true plane significantly more than does the C(1)—(6) ring. The planes, and deviations from them, are listed in Table 5.

TABLE 5

Deviations (Å) from mean planes for (I) and equations * of planes

Plane (1): C(1)—(6)
$0.1379X + 0.9140Y - 0.3816Z = 2.5761$
[C(1) 0.007(2), C(2) −0.004(3), C(3) −0.003(3), C(4) 0.004(2), C(5) 0.001(2), C(6) −0.004(2)]

Plane (2): C(10)—(15)
$0.3820X + 0.9031Y + 0.1961Z = 5.7043$
[C(10) −0.007(2), C(11) 0.012(2), C(12) −0.007(2), C(13) −0.012(3), C(14) 0.016(2), C(15) −0.006(2)]

Plane (3): C(7)—(9), O, S
$0.3326X + 0.8353Y - 0.4378Z = 3.4089$
[C(7) −0.002(8), C(8) 0.000(2), C(9) 0.007(2), O 0.019(3), S −0.048(6), H 0.006(6)]

* X, Y, and Z are orthogonal (Å) co-ordinates, where $X = ax$, $Y = by$, and $Z = cz$.

The C(9)–S bond [1.675(5) Å] is quite short and is of the same magnitude as the double bond [1.73(2) Å] in ethylenethiourea.[9] The C(7)–O, C(7)–C(8), and C(8)–C(9) bond lengths are also shorter than expected for single bonds and hence may be inferred to show partial double-bond character. The C(7)–C(8) and C(8)–C(9) bond lengths are in fact close to those found in the aromatic rings. There is also some evidence to suggest partial conjugation of the monothio-β-diketone ring with the attached phenyl rings, the C(6)–C(7) and C(9)–C(10) bond lengths being significantly shorter than expected for carbon–carbon single bonds. The molecule, as a whole, is not planar. The dihedral angle between the two phenyl rings is 17.4°. Each phenyl ring makes a dihedral angle of *ca.* 38.5° with the approximately planar monothio-β-diketone ring. Hence the amount of conjugation expected to occur between the phenyl rings and the monothio-β-diketone ring will be small. The deviation of the molecule from planarity is mainly due to the interaction of H(8) with H(5) and H(11) [H(5) ··· H(8) 2.02, H(11) ··· H(8) 2.21 Å].

The value of the C(9)–S bond is very similar to that found[10] for the monothio-β-diketone co-ordination compound bis-(1,1,1-trifluoro-4-mercaptopent-3-en-2-one)nickel(II). The C(7)–O, C(7)–C(8), and C(8)–C(9) bond lengths, however, are appreciably shorter in the complex.

The molecules pack approximately parallel to the *ac* crystallographic plane. An *ac* projection is shown in Figure 2. There are no interactions between the molecules other than van der Waals and crystal packing forces. The only hydrogen bond present is the strong intramolecular one between the oxygen and sulphur atoms *via* the enolic hydrogen.

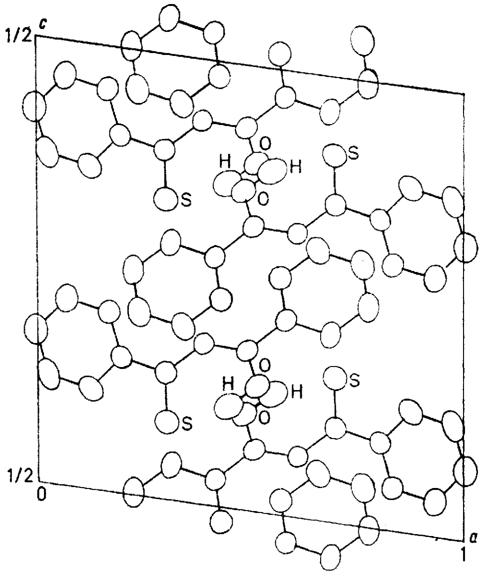

FIGURE 2 *ac* Projection for (I)

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