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S---S AND S---O INTERACTIONS IN SOME 4-THIAZOLINE DERIVATIVES

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Abstract—Structural data have been obtained by X-ray crystallography for three 4-thiazoline derivatives, 2-benzoylimino-3,4-diphenyl-4-thiazoline, 3-methyl-4-phenyl-2-thiobenzoylimino-4-thiazoline, and 3,4-diphenyl-4-thiazolin-2-ylidene thioacetophenone. In these compounds the separations between the sulphur atoms of the thiazoline rings and the adjacent oxygen or sulphur atoms of the carbonyl or thiocarbonyl groups approximate to the Huggins "constant energy" distances, suggesting that there is little or no bonding between them.

Many studies have been reported on compounds containing the structural unit 1 in which a divalent sulphur atom is conjugated with an electron-attracting Y=Z group. The resulting polarisation, expressed by canonical form 2a, suggests a further modification to the cyclic form 2b or an equivalent.

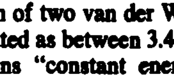
The best known examples of such systems are the thiathiophthens (trithiapentalenes),[1,2a,2b] usually represented by structure 3, which have been intensively studied by X-ray crystallography.[2c] The S–S bonds in these compounds are, judging from their lengths, weaker than other bonds in the molecule and therefore more liable to changes in bond length if the molecule is perturbed to some degree. The two S–S bond lengths can be equal or unequal, varying between 2.16 and 2.56 Å, but their sum always falls between 4.6 and 4.8 Å. The average S–S bond length of about 2.35 Å in these compounds should be compared (a) with the normal S–S single bond length of 2.10 Å in a *cis* planar disulphide group,[2d] (b) with the sum of two van der Waals radii for sulphur, variously estimated as between 3.40 and 3.70 Å,[3] and (c) with the Huggins "constant energy" distance 2.92 Å.[4–6] This last value corresponds to the distances reported between presumably non-bonded but adjacent sulphur atoms in, for example, isothiathiophthens (the 1,3-dithiole analogues of the thiathiophthens)[7] and in certain extended systems.[4,5]

1,2-Dithiol-3-ylidene ketones 4 have also been much studied,[1,2a,2b] both by the X-ray method and spectroscopically. The S–O distances reported range between 2.184 and 2.443 Å,[2c,4] much less than van der Waals separation of 3.10–3.25 Å,[3] and significantly less than the Huggins constant energy distance, 2.58 Å.[6] These values, and the absence of normal carbonyl-stretching bands in the infrared spectra,[8] indicate an "interaction" or partial bonding between sulphur and oxygen.

This kind of interaction is fully developed in the essentially symmetric structures 5,[9] 6,[10a] and 7[10b] which provide a lower limit of *ca.* 1.85 Å for S–O distances in systems of type 1 (Z=O). The upper limit may be of the order 2.90 Å, derived from data reported for compounds 8[11] and 9.[12]

Between these limits, and excluding the dithiolylidene ketones noted above, S–O distances of 2.034, 2.255, 2.294, 2.305, 2.373, 2.509, 2.515, 2.517, 2.553, 2.567, 2.571, 2.577, 2.604, 2.63, 2.64, 2.64, 2.67 and 2.70 Å have been found[2c,4,13,14] in a range of compounds which differ widely in structure but have in common the unit 1 (Z=O) or a related system.

The four longest of these values for S–O distances relate to compounds which, like 8 and 9, have sp^2 or sp^3 hybridised carbon atoms in the A-position in structure 1. The five shortest values, on the other hand, are found in compounds which have a heteroatom at position A. Most of the other values intermediate between these two groups, i.e. with S–O separations in the range 2.5–2.6 Å, also relate to compounds in which A is a heteroatom; the unusual betaine structure 10,[14] with sp^2 carbon in the



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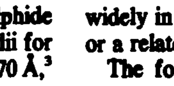

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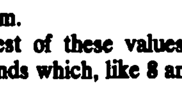

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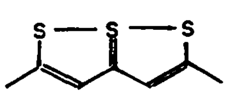

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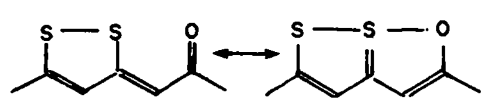

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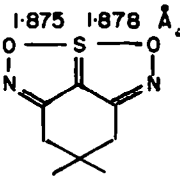

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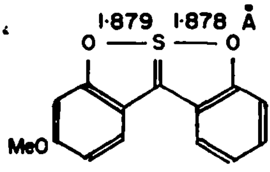

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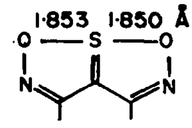

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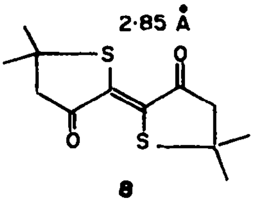

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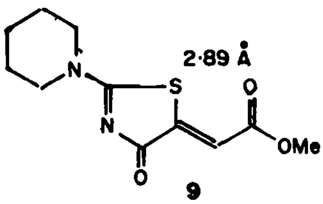

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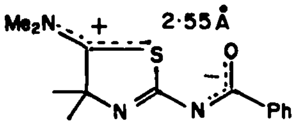

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A-position and an S–O distance of 2.553 Å is an interesting exception.

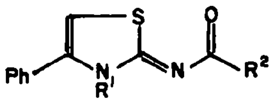
We have investigated a series of compounds represented by general structures 11, 12, 14 and 15, which contain the structural unit 1 with A = sp^2 carbon. Compounds of type 11 were prepared both by acylation of 2-imino-3,4-diphenyl-4-thiazoline and 2-imino-3-methyl-4-phenyl-4-thiazoline, and by cyclisation of S-phenacyl derivatives of the appropriate N-acylthioureas. Sulphurisation of the products gave the corresponding thioamides 12. Thiazolin-2-ylidene ketones 14 and the related thiones 15 were obtained by the route shown. Similar reaction sequences have been used previously for the preparation of analogous benzothiazoline derivatives[15] and of 1,2-dithiol-3-ylidene ketones.[16]

Of the various compounds prepared, three proved suitable for crystallographic study. Data were recorded on a CAD4 diffractometer using graphite monochromatized MOKα radiation and a θ/2θ scan. The structure of compound 15 (R^1=R^2=Ph) was solved by the heavy atom (S) method, and the structures of compounds 11(R^1=R^2=Ph) and 12 (R^1=Me, R^2=Ph) by direct methods (MULTAN).[17] The structure refinements were carried out according to full matrix least squares techniques.

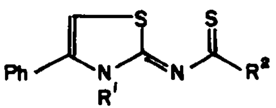
Crystallographic data are summarised in Table 1 and a selection of the derived bond lengths are collected in Table 2.[18]

Compound 11 (R^1=R^2=Ph) thus has a sulphur–oxygen separation of 2.614 Å, slightly larger than the Huggins constant energy distance of 2.58 Å. The values for the sequence of bonds N–C–N–C (g, e, d in Table 2) are in accord with the classical structure, allowing for some delocalisation of electrons, and we conclude that there is very little or no bonding between sulphur and oxygen in this compound.

The N–C–N–C sequence in compound 12



11



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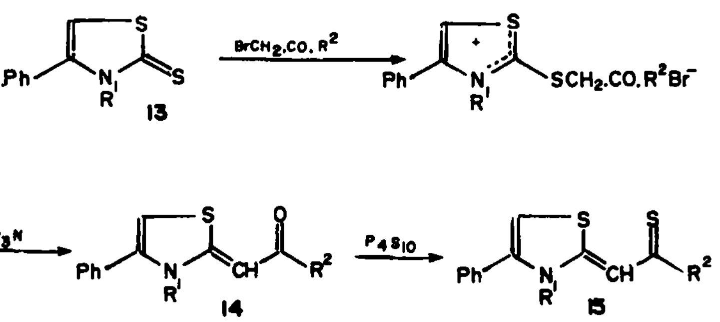
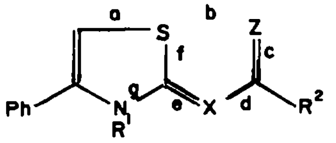


Table 1. Crystallographic data

Compound	11 ($R^1=R^2=Ph$) $C_{22}H_{16}N_2OS$	12 ($R^1=Me,R^2=Ph$) $C_{17}H_{14}N_2S_2$	15 ($R^1=R^2=Ph$) $C_{23}H_{17}NS_2$
Colour	Yellow	Orange	Red
a	11.726(2) Å	10.830(2) Å	8.239(2) Å
b	15.237(3) "	11.328(2) "	10.274(2) "
c	10.485(2) "	12.842(2) "	12.550(2) "
α	90°	100.22(1)°	75.70(2)°
β	101.42(2)°	95.70(1)°	80.75(3)°
γ	90°	90.24(1)°	66.28(2)°
Spacegroup	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2
D	1.244g/cm^3	1.290g/cm^3	1.266g/cm^3

Table 2. Selected bond lengths



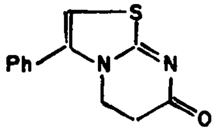
Compound	X	Z	Bond lengths in Å						
			a	b	c	d	e	f	g
(11, $R^1=R^2=Ph$)	N	O	1.738(3)	2.614(2)	1.237(3)	1.373(3)	1.312(3)	1.748(2)	1.363(3)
(12, $R^1=Me,R^2=Ph$)	N	S	*1.728(9)	2.88(1)	1.676(5)	1.340(8)	1.328(8)	1.740(6)	1.356(8)
			1.736(8)	2.96(1)	1.675(9)	1.346(7)	1.335(8)	1.736(9)	1.359(7)
(15, $R^1=R^2=Ph$)	CH	S	1.735(4)	2.937(3)	1.677(4)	1.395(5)	1.394(5)	1.731(4)	1.376(4)

* Two independent molecules in the asymmetric unit

(R^1=Me, R^2=Ph) shows less disparity between the C–N bond lengths, implying a higher degree of delocalisation than in compound 11 (R^1=R^2=Ph) but the S–S distances of 2.88 or 2.96 Å approximate to the constant energy distance, 2.92 Å, indicating virtually no bonding between the adjacent sulphur atoms.

The same conclusion must apply to compound 15 (R^1=R^2=Ph), with a S–S distance of 2.94 Å, despite extensive electron delocalisation as indicated by the equality of the two C–C bonds (d and e in Table 2) in the conjugated system.

Infrared data (presumed carbonyl stretching frequencies) for the ketones and amides prepared in this study are collected in Table 3. The six compounds all show strong absorption bands in the 1590 cm^{-1} region, but in view of the X-ray data reported, we do not interpret these low values as implying bonding interactions between sulphur and oxygen atoms. Nevertheless, the geometry of the compounds is important, since the



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bicyclic compound 16, a "trans" analogue of 11 (R^1=R^2=Me) with similar conjugation of the thiazoline residue and an amide carbonyl group, shows an infrared absorption band at 1650 cm^{-1} (KBr disk) or 1655 cm^{-1} ($CHCl_3$ solution).[19]

Our results suggest that, in systems 11, 12, 14 and 15, all of type 1 (with A = sp^{2}C), a balance of attractive electrostatic forces (arising from contributions of canonical forms 2a) and *repulsive* interactions (between the adjacent heteroatoms) leads to separations which correspond fairly closely to the Huggins constant energy distances.

Table 3. Infrared data: presumed C=O stretching frequencies

Compound	cm.$^{-1}$
11 (R^1=R^2=Ph)	1594^a, 1597^b
11 (R^1=Ph,R^2=Me)	1590^a, 1595^b
11 (R^1=Me,R^2=Ph)	1592^a, 1599^b
11 (R^1=R^2=Me)	1590^a, 1593^b
14 (R^1=R^2=Ph)	1591^c
14 (R^1=Me,R^2=Ph)	1590^c

a KBr disk; b $CHCl_3$ solution; c nujol

EXPERIMENTAL

2-*Acetylimino-3,4-diphenyl-4-thiazoline* (11; R^1=Ph, R^2=Me)

Prepared by acetylation of 2-imino-3,4-diphenyl-4-thiazoline,[20] and by treatment of N-Acetyl-N'-phenyl thiourea[21] with phenacyl bromide in hot ethanol,[22] this compound formed pale yellow rhombs from ethyl acetate, m.p. 210° (lit.[22] m.p. 209.5–210.5°), ν_{max} (KBr) 1590 cm^{-1} ($CHCl_3$) 1595 cm^{-1}; λ_{max} (EtOH) 226, 265, 310 nm (ϵ 12,100, 5100, 12,100); δ ($CDCl_3$), 2.15 (3H, s), 6.60 (1H, s), 7.00–7.40 (10H, m).

2-*Benzoylimino-3,4-diphenyl-4-thiazoline* (11; R^1=R^2=Ph)

Prepared by benzoylation of 2-imino-3,4-diphenyl-4-thiazoline,[20] and from N-benzoyl-N'-phenylthiourea[21] by treatment with phenacyl bromide,[22] this compound formed pale yellow rhombs from ethanol m.p. 207–8° (lit.[22] m.p. 203–4°), ν_{max}. (KBr) 1594 cm^{-1} ($CHCl_3$) 1597 cm^{-1}; λ_{max} (EtOH) 245, 275, 336 nm (ϵ 13,400, 6600, 13,200); δ ($CDCl_3$) 6.96 (1H, s), 7.00–7.54 (13H, m), 8.00–8.15 (2H, m).

2-*Imino-3-methyl-4-phenyl-4-thiazoline*

50% Aqueous hydrobromic acid (7.2 ml) was added to a solution of methylthiourea (4.7 g) in ethanol (100 ml), followed by phenacyl bromide (9.8 g). The solution obtained by heating the mixture under reflux for 3 h was concentrated and then allowed to cool, affording 2-imino-3-methyl-4-phenyl-4-thiazoline hydrobromide (3.0 g) m.p. 275° decomp. (lit.[23] 274°). Further concentration of the mother liquor gave material which proved to consist mainly of 2-methylamino-4-phenyl-4-thiazoline hydrobromide.

2 - *Acetylimino* - 3 - *methyl* - 4 - *phenyl* - 4 - *thiazoline* (11; R^1=R^2=Me)

Prepared by acetylation[24] of the imino-compound and from N-acetyl-N'-methylthiourea[25] by the action of phenacyl bromide, this compound formed colourless needles from ethanol m.p. 118° (lit.[24] 121°). ν_{max} (KBr) 1590 cm^{-1} ($CHCl_3$), 1593 cm^{-1}; λ_{max} (EtOH) 218, 260, 300 nm (ϵ 13,900, 2800, 15,200); δ (d_6 DMSO) 2.17 (3H, s), 3.53 (3H, s), 6.91 (1H, s), 7.52 (5H, m).

2 - *Benzoylimino* - 3 - *methyl* - 4 - *phenyl* - 4 - *thiazoline* (11; R^1 = Me, R^2 = Ph)

Benzoylation of the imino-compound and treatment of N-benzoyl-N'-methylthiourea with phenacyl bromide in acetone gave the same product which crystallised from ethanol in colourless needles m.p. 120–1°, ν_{max} (KBr) 1592 cm^{-1} ($CHCl_3$) 1599 cm^{-1}; λ_{max} (EtOH) 235, 276, 286, 331 nm (ϵ 15,000, 6100, 5900, 22,200); δ ($CDCl_3$) 3.72 (3H, s), 6.54 (1H, s), 7.24–7.60 (8H, m), 8.32–8.44 (2H, m) (Found: C 69.3; H, 5.1; N, 9.2; S, 11.0. $C_{17}H_{14}N_2OS$ requires: C, 69.4; H, 4.8; N, 9.5; S, 10.9%).

2-*Thioacylimino-4-thiazolines*

3,4-*Diphenyl-2-thioacetylimino-4-thiazoline* (12; R^1=Ph, R^2=Me) was prepared by heating together for 5 h, under reflux in pyridine (25 ml), 2-acetylimino-3,4-diphenyl-4-thiazoline (0.6 g) and phosphorus pentasulphide (2g). The resulting mixture was stirred with water (300 ml) for 1 h and the solid product crystallised from ethyl acetate-light petroleum (b.p. 60–80°) when it formed yellow rhombs (0.35 g) m.p. 212–214°; δ (d_6 DMSO) 3.50 (3H, s), 7.20–7.50 (11H, m); M$^+$, *m/e* 310 (Found: C, 66.0; H, 4.6; N, 8.9. $C_{17}H_{14}N_2S_2$ requires: C, 65.8; H, 4.5; N, 9.0%).

The following compounds were prepared similarly: 3,4-*Diphenyl-2-thiobenzoylimino-4-thiazoline* (12; R^1=R^2=Ph) crystallised from ethanol–ethyl acetate in orange needles (79.6% yield) m.p. 245°; δ ($CDCl_3$) 6.77 (1H, S), 7.10–7.50 (13H, m), 8.10–8.20 (2H, m); M$^+$, *m/e* 372 (Found: C, 71.0; H, 4.3; N, 7.3; S, 17.1. $C_{22}H_{16}N_2S_2$ requires: C, 71.0; H, 4.3; N, 7.5; S, 17.2%). 3-*Methyl-4-phenyl-2-thioacetylimino-4-thiazoline* (12; R^1=R^2=Me) crystallised from chloroform-light petroleum (b.p. 60–80°) in yellow rhombs (56.4%) m.p. 137°; δ ($CDCl_3$) 2.81 (3H, s), 3.75 (3H, s), 6.66 (1H, s), 7.40–7.60 (5H, m); M$^+$, *m/e* 248 (Found: C, 58.1; H, 5.0; N, 11.5. $C_{12}H_{12}N_2S_2$ requires: C, 58.1; H, 4.8; N, 11.3%). 3 - *Methyl* - 4 - *phenyl* - 2 - *thiobenzoylimino* - 4 - *thiazoline* (12; R^1=Me, R^2=Ph) crystallised from aqueous ethanol in orange needles (53.7%) m.p. 139–140°; ($CDCl_3$) 3.80 (3H, s), 6.60 (1H, s), 7.30–7.60 (8H, m), 8.40–8.60 (2H, m); M$^+$, *m/e* 310 (Found: C, 65.9; H, 4.6; N, 8.9. $C_{17}H_{14}N_2S_2$ requires: C, 65.8; H, 4.5; N, 9.0%).

2-*Phenacylthio-3,4-diphenylthiazolium bromide*

Phenacyl bromide (0.5 g) was adhed to a stirred solution of 3,4-diphenyl-4-thiazolin-2-thione (0.5 g)[26] in acetone (15 ml). After 30 min, the white precipitate was collected and crystallised from ethanol–ether, yielding colourless prisms (0.6 g) m.p. 177–8°, ν_{max} (C=O) 1690 cm^{-1} (Found: C, 58.7; H, 4.0; N, 2.8. $C_{21}H_{18}BrNS_2O$ requires: C, 59.0; H, 3.8; N, 3.0%).

3,4 - *Diphenyl* - 4 - *thiazolin* - 2 - *ylidene acetophenone* (14; R=R^2=Ph)

Triethylamine (1.5 ml) was added to a solution of the 2-phenacylthiothiazolium bromide (0.2 g) in ethanol (10 ml) and the mixture was warmed briefly on the steam-bath. The product which separated on cooling crystallised from ethanol in yellow needles (113 mg) m.p. 227–8°, ν_{max} 1591 cm^{-1}; δ ($CDCl_3$) 6.52 (1H, s), 6.90–7.85 (16H, m) (Found: C, 77.9; H, 4.7; N, 3.8. $C_{23}H_{17}NSO$ requires: C, 77.7; H, 4.8; N, 3.9%).

3,4 - *Diphenyl* - 4 - *thiazolin* - 2 - *ylidene thioacetophenone* (15; R^1=R^2=Ph)

The foregoing ketone (0.4 g) was heated under reflux in pyridine (15 ml) with phosphorus pentasulphide (0.8 g) for 8 h. The red solid obtained when the cooled reaction mixture was treated with water was crystallised from ethyl acetate–petrol, forming red needles (0.29 g) m.p. 270–1°, δ ($CDCl_3$) 6.68 (1H, s), 6.90–7.70 (16H, m) (Found: C, 74.1; H, 4.5; N, 3.8. $C_{23}H_{17}NS_2$ requires: C, 74.4; H, 4.6; N, 3.8%).

3 - *Methyl* - 2 - *phenacylthio* - 4 - *phenylthiazolium bromide*

Prepared by the same method as for the 3-phenyl compound, the thiazolium bromide crystallised from ethanol–ether in colourless granules (85%) m.p. 182–3°, ν_{max} 1685 cm^{-1} (Found: C, 52.9; H, 3.9; N, 3.5. $C_{18}H_{16}BrNOS_2$ requires: C, 53.2; H, 3.9; N, 3.4%).

3 - *Methyl* - 4 - *phenyl* - 4 - *thiazolin* - 2 - *ylidene acetophenone* (14; R^1=Me, R^2=Ph).

A solution of 3-methyl-2-phenacylthio-4-phenylthiazolium bromide (1.5 g) in ethanol (20 ml) containing triethylamine (2 ml) was warmed on the steam-bath for 30 min. The product which separated on cooling crystallised from ethyl acetate–petrol in pale yellow needles (0.9 g) m.p. 179–181°, ν_{max} 1590 cm^{-1} δ ($CDCl_3$) 3.50 (3H, s), 6.47 (1H, s), 7.20–8.0 (11H, m) (Found: C, 73.8; H, 5.1; N, 4.5. $C_{18}H_{15}NOS$ requires: C, 73.7; H, 5.1; N, 4.8%).

3 - *Methyl* - 4 - *phenyl* - 4 - *thiazolin* - 2 - *ylidene thioacetophenone* (15; R^1=Me, R^2=Ph)

3 - Methyl - 4 - phenyl - 4 - thiazolin - 2 - ylidene acetophenone (0.2 g) was heated under reflux in pyridine (15 ml) with phosphorus pentasulphide (0.5) for 6 h. The red solid obtained by treatment of the reaction mixture with water crystallised from

ethyl acetate–petrol as orange-red rhombs (0.15 g) m.p. 169–170°, δ ($CDCl_3$), 3.50 (3H, s), 6.44 (1H, s), 7.10–7.90 (11H, m) (Found: C, 69.7; H, 4.7; N, 4.4. $C_{18}H_{15}NS_2$ requires: C, 69.9; H, 4.85; N, 4.5%).

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