SHORT INTERACTIONS BETWEEN HETEROCYCLIC SULFUR ATOMS AND THIOCARBONYL SULFUR OR CARBONYL OXYGEN ATOMS

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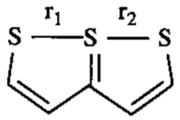
Abstract - Short intramolecular S---S=C contacts in *N*-(2-thiazolylidene)-benzenecarbothioamides (**11** and **12**), 0.60Å less than the corresponding separation predicted by Van der Waals radii, are accounted for by Coulombic interactions and 3d orbital participation as a result of electron delocalisation within each molecule. Similar considerations apply to S---O=C contacts, however short S---S intermolecular interactions between sulfides are due to the asymmetric electron distribution about the bonded sulfide atoms.

The structure of 1,6,6aλ^4 trithiapentalenes (thiathiophthenes) has been widely investigated[1] since their discovery in 1958. They are now described as 3-centred hypervalent molecules with a 10π aromatic system. The symmetrical structure (**1**) has S---S bond lengths of 2.35Å, but substitution modifies this by *ca.* ± 0.15Å. In all these molecules[2], $r_1 + r_2 = 4.7$Å. Interestingly, the Σ-delocalisation extends[3] to 5 collinear sulfur atoms, e.g. in **2**, with $r_1 = 2.17$Å, $r_2 = 2.58$Å, $r_3 = 2.58$Å and $r_4 = 2.18$Å. However, with four sulfur atoms in contact[4], e.g. in **3**, the bonds remain localised with S-S bond lengths, r_1 and r_3, of 2.06Å. Moreover, the central S---S bond, r_2, is 2.86Å, i.e. well within the Van der Waals distance (*vide infra*).

Trithiapentalenes are members of a general class of compound (**4**). For X, Y and Y^1 = S, i.e. compounds of type (**1**), a minimum value of $r_1 = 2.22$Å and a maximum value of $r_2 = 2.50$Å have been recorded! For X and Y^1 = S, and Y = O, i.e. when one terminal sulfur atom of **1** is replaced by oxygen, the minimum value of r_1 found so far is 2.18Å and the maximum value 2.44Å. As discussed later, a greater value for the S---O distance has been found in a case with a S-S---O interaction ((**14**): 2.62Å).



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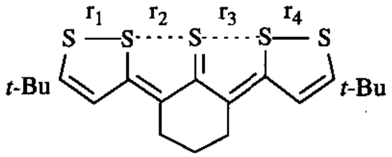

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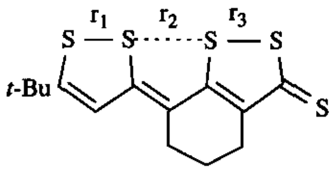

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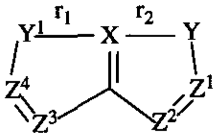

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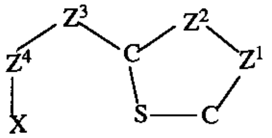
X = S, Se, Te
Y,Y^1 = O, S, Se, NR
Z^1, Z^2, Z^3, Z^4 = N or CR'

We are interested in a series of sulfur heterocycles (**5**) related to the trithiapentalenes which involve a linear arrangements of two sulfur and one carbon atoms. However, before the structures of these compounds can be discussed adequately, it is necessary to examine the contact distances of non-bonded atoms.



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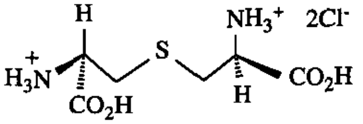
X = O, S
Z^1,Z^2,Z^3,Z^4 = CR, CR_2, NR, N, S

Van der Waals Distances. The Van der Waals radii most widely used are derived from X-ray studies of metals and ionic solids with spherical force fields. In his early work,[5] Pauling stated clearly that bonded atoms are not, in general, spherical, because the polarisability along a covalent bond is greater (*ca.* 3 times for halides) than along a vector at right angles to the bond. This conclusion has been largely overlooked although Bondi[6] in particular has given further examples of reduced radii along valency bonds. More recently extensive computerised searches of X-ray and neutron diffraction data using the Cambridge Structural Database have shown that, with the exception of nitrogen and oxygen, terminal atoms are generally spheroidal.[7] In the case of organic halides the difference between the major and minor radii of the halogen atoms increases regularly with the radius and with bond polarisability. Moreover, hydrogen atoms bonded to carbon are also spheroidal. Nyburg[8] gives effective radii of 1.01 and 1.26Å for hydrogen bonded to sp^3 carbon, and 0.94 and 1.32Å for hydrogen bonded to sp^2 carbon, the smaller radius extending along the valency bond.

We are particularly interested in the minimum contact distances between non-bonded sulfur atoms, and between non-bonded sulfur and oxygen atoms. In a detailed analysis of mono-coordinated sulfur compounds ($>$ C=S), Nyburg[7] established a minor radius of 1.6Å and a major radius of 2.0Å. In contrast, the corresponding radii of carbonyl oxygen were both found to be 1.54Å, close to the Pauling value of 1.50Å. In the case of sulfur the value for the major radius (2.0Å) is larger than the Pauling radius (1.87Å), but unlike the value for the halides it is based on few measurements rendering the extrapolation difficult. For the alkyl chlorides, bromides and iodides, the major radius is almost equal to the Pauling value. This finding is particularly important because it shows that the Van der Waals radius is insensitive to the negative charge on the atom (*vide infra*). Dicoordinated sulfur compounds have also been analysed in a similar manner.[9] In an important paper Rosenfeld and Parathasarathy[10] found the two sulfur atoms of adjacent *meso*-lanthionine molecules in **6** to be only 3.25Å apart. The pair of molecules adopt C_{2h} symmetry with two carbon atoms and two sulfur atoms collinear (*Figure 1a*). This orientation is very common and in their detailed study Dunitz and Parathasarathy[9] showed that many dialkyl sulfides had contact distances between 3.25Å and 3.50Å, i.e. *well within* the traditional Van der Waals distance (3.7Å, Pauling; 4.0Å, Nyburg). The value of 3.25Å is close to the minimum contact distance (3.2Å) found for thiocarbonyl compounds. It is interesting to note that the S---S distance[11] in *N,N'-bis*(phenylthio)sulfurdiimide (7) is 3.29Å, i.e. close to the value for lanthionine. This



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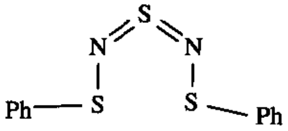

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molecule is held in the Z/Z conformation by lone-pair interactions[12] in the NSN group. The small difference (3.29 and 3.25Å) could be due to the different orientations of the a_1 orbitals (*vide infra*).

There are two general explanations for these short contact distances. The first[7] recognises that the equilibrium distance is determined by the balance of dispersion forces and closed shell repulsions. Consequently, a fixed Van der Waals distance cannot be assigned (*vide infra*). The spheroidal form of most peripheral atoms is then explained by the increased polarisability *and* by the reduced electronic repulsion along the valency bond. The second explanation[9] invokes orbital combination of lone-pair orbitals and unoccupied orbitals of correct symmetry, usually σ^* and d-orbitals. This will be discussed later.

In a theoretical study, Boyd[13] considered the approach of two dimethyl sulfide molecules. The correct orientation (C_{2h}) was predicted by Extended Hückel theory with a contact distance within the Van der Waals region, although the method fails at smaller distances. Alternative methods failed completely. For example, CNDO/2 predicts a stable complex at the Van der Waals distance with an energy of -140 kcal/mol! On the other hand, MINDO/3 predicts a complex with a reasonable energy of -6 kcal/mole, but at a distance close to the S-S covalent bond length. Semi-empirical methods of this kind cannot tackle the problem, more advanced theories of weak interactions have to be used.[14] The relative success of the Extended Hückel method is due to the influence of the overlap integral which determines the exclusion repulsion of closed shell orbitals. It is clear that the preferred orientation reduces the repulsion between the two a_1 orbitals which is maximum in the D_{2h} form (*Figure 1b*). The overlap of the two a_1 orbitals, which are *antiperiplanar*, is thus minimised. The two p_σ (C-S) orbitals produce a spherically symmetrical field at sulfur as the overlap integral of the two

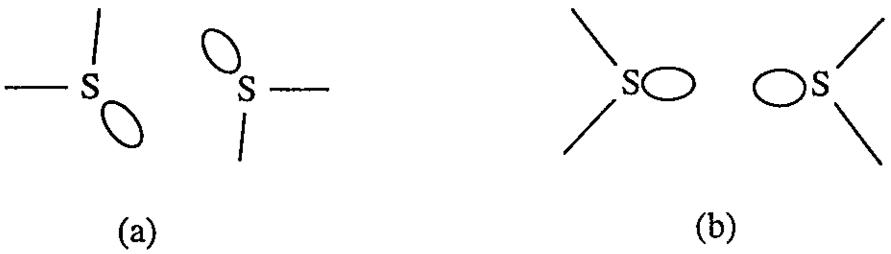


Figure 1. Orientations of sulfide groups: (a) C_{2h}, (b) D_{2h}.

orthogonal, in plane, p orbitals is independent of orientation. The close approach cannot be due to $p\pi$-σ^*_{sc} combination as the two orbitals are orthogonal in this configuration. If one of the S-C bonds is at 90° to the other S-C bond (*Figure* 2), the p_π orbital has maximum overlap with the σ_{cs} and σ^*_{cs} orbitals, and hence p_π- σ^* overlap is possible to reduce the contact distance. However, the S---S distance[9] increases to 3.5Å showing

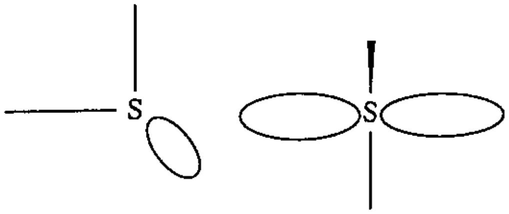
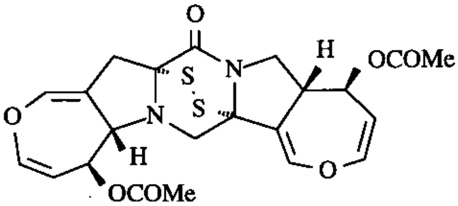


Figure 2. Perpendicular orientation of sulfide groups.

that the repulsion due to p-σ_{cs} perturbation is greater than the stabilisation due to the p-σ^*_{cs} combination, as is usually the case in stereo-electronic effects. This distance (3.5Å) is characteristic of S_8, disulfides[15] and polysulfides.[15] The spiral conformation in the latter allows the sulfur atoms to align themselves as shown in

Figure 2. When the disulfide bond is constrained in a ring,[16] as in **8** with small dihedral angles of 18° and 15° about the S-S bonds for the two distinct molecules, the contact distance is reduced to 3.25Å since the contact now involves σ_{cs}---σ_{cs} interaction. Furthermore, short S---S distances are claimed to be important in promoting electrical conductivity in radical cation salts of tetrathiafulvalene derivatives,[17] e.g. **9**, where in-plane intermolecular contacts of the order of 3.3Å are observed whose orientations are similar to that in *Figure 1(a)*. Coulombic repulsion between the adjacent cations does not prevent these close contacts, as anticipated by Pauling's work.



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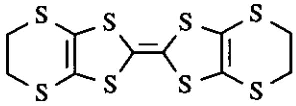

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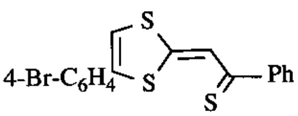
We can at this point recognise three Van der Waals distances of 3.7Å (~ 4.0Å), 3.5Å and 3.2Å corresponding to the predominant p-p, p-σ and σ-σ interactions (repulsions) respectively.

Results and Discussion.



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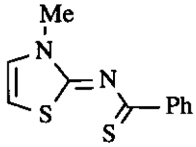

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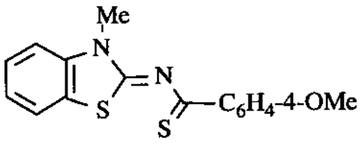

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As mentioned above, we are particularly concerned with a series of heterocycles (**5**) which involve a linear contact of a sulfur atom and a C-S bond. Since p_π and σ orbitals are in contact, the anticipated Van der Waals distance is 3.5 Å as for polysulfides. We have recently measured the ambient temperature X-ray crystal structures of the *N*-(2-thiazolylidene)thioamides (**11** and **12**). The structures of **11** and **12** are shown in *Figures 3* and *4*, and relevant molecular geometry is given in *Table 1*. The most important feature of both molecules is a short intramolecular S(1)---S(2) contact of *ca.* 2.9Å (**11**: 2.926(1), **12**: 2.906(1)Å), *ca.* 0.6Å within the expected van der Waals distance but 0.4Å longer than the trithiapentalene with the longest recorded bond (see, however, **14**). Despite this, the thioamide groups remain almost coplanar with the thiazoline rings (torsion angles: S(1)-C(1)-N(2)-C(5), **11**: 3.1(3)°, **12**: 1.7(3)°; C(1)-N(2)-C(5)-S(2), **11**: 3.1(3)°, **12**: 3.0(3)°). The S(2)---S(1)-C(1) angles are 76.4(1)° and 77.9(1)°, and the C(5)-S(2)---S(1) angles are 83.4(1)° and 83.4(1)°.

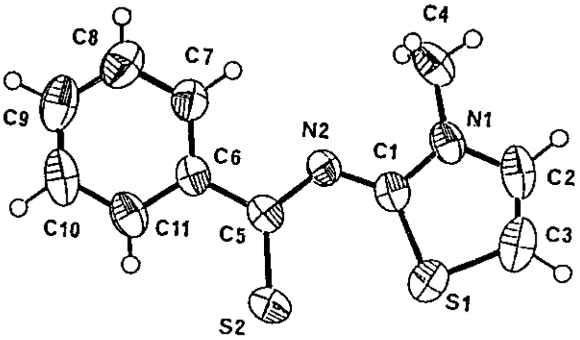


*Figure 3. Molecular structure of **11** with atomic displacement parameters drawn at the 50% level.*[18]

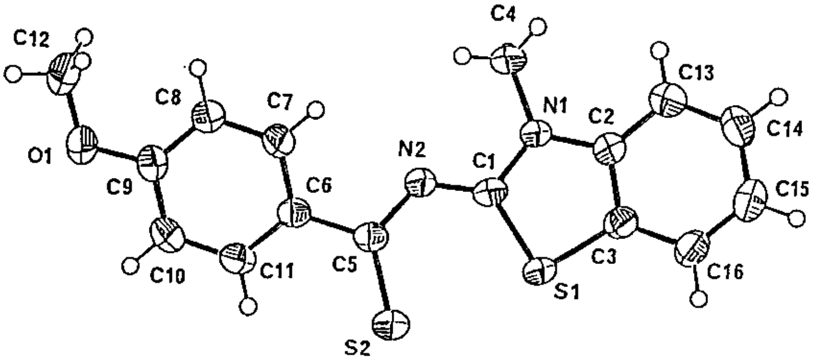


*Figure 4. Molecular structure of **12** with atomic displacement parameters drawn at the 50% level.*[18]

The bond angles at C(1), N(2) and C(5) are distorted to increase the S(1)---S(2) separation (and decrease the S(2)---S(1)-C(1) angle). Bond lengths in the moiety C(1)-N(2)-C(5)-S(2) suggest considerable delocalisation of electron density from the heterocyclic ring towards S(2), thus the two C,N bonds involving N(2) are of similar lengths (N(2)-C(1) & N(2)-C(5), **11**: 1.328(2) & 1.331(2), **12**: 1.311(3) & 1.351(3)Å respectively).

*Table 1. Selected Molecular Geometry for **11** and **12**.*

Interatomic distances (Å)	**11**	**12**
S(1)-C(1)	1.737(2)	1.753(2)
S(1)...S(2)	2.926(1)	2.906(1)
S(2)-C(5)	1.677(2)	1.673(2)
N(1)-C(1)	1.346(2)	1.353(3)
N(2)-C(1)	1.328(2)	1.311(3)
N(2)-C(5)	1.331(2)	1.351(3)
Interatomic angles (°)		
S(2)...S(1)-C(1)	76.4(1)	77.9(1)
S(1)...S(2)-C(5)	83.4(1)	83.4(1)
C(1)-N(2)-C(5)	122.4(2)	123.1(2)
S(1)-C(1)-N(2)	131.7(1)	129.7(2)
S(2)-C(5)-N(2)	125.8(1)	125.9(2)
N(2)-C(5)-C(6)	113.3(1)	113.1(2)

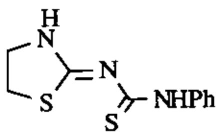
The development of opposite charges on the sulfur atoms must play an important role in this short S,S contact. Comparable results are found in **10** which has similar angular distortions and S---S distance. The phenyl ring in **11** lies at 16.0(1)° to the best plane of the heterocyclic ring, and the 4-methoxyphenyl ring in **12** lies similarly at 23.2(1)° to its heterocyclic ring, in both cases to increase the contact distance of S(2) to the *ortho* hydrogen atom (S(2)---H(11), **11**: 2.74(2), **12**: 2.75(3)Å). There are no short intermolecular contacts.

It is quite remarkable that in compounds of type **10** *and* **11** *the* S---S distances are the same irrespective of bond length and bond angle changes. This suggests strongly that an attraction exists between the sulfur atoms. Examples of similar S---S contacts are given in *Table 2*, and again non-bonded distances are close to 2.9Å.

Table 2. Compounds with short S---S and S---O Contact Distances

	r_{S-S}	Δ		r_{S-O}	Δ
10(19)	2.91	0.59	**15**(22)	2.68	0.46
11*	2.93	0.57	**16**(23)†	2.68	0.46
12*	2.90	0.60	**17**(24)	2.70	0.44
13(20)	2.90	0.60	**18**(25)	2.64	0.50
14(21)	2.96	0.54	**19**(26)	2.64	0.50

*this work; †see next page.



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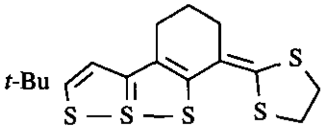

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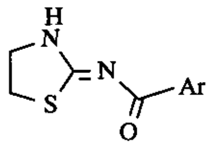

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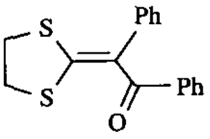

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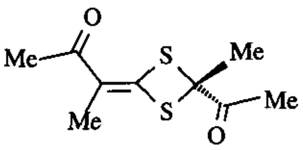

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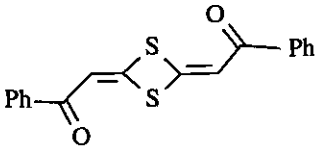

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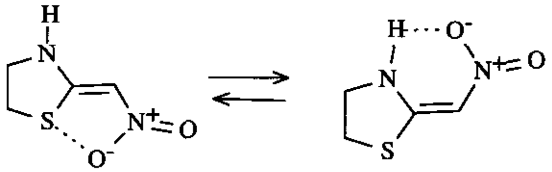
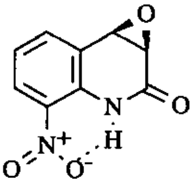
This distance appears to be characteristic of a particular kind of interaction discussed later. A similar contact distance is observed in the disulfide (**3**), which has two normal S-S bonds and a non-bonded distance of 2.86Å. More information is available on the carbonyl analogues (*Table 2*). All these molecules can be regarded as highly conjugated heterodienes with exocyclic bond angles greater than 120° due to the S---O interaction. As the C, S and X (X = O,S) atoms are approximately collinear the σ_{cs} and p_x orbitals have maximum overlap. According to the above discussion, the appropriate Van der Waals distances are 3.50Å for the S---S and 3.15Å for the S...O contacts respectively. The data of *Table 2* show differences (Δ) of ca. 0.60 and ca. 0.45Å respectively between the Van der Waals and observed distances for S---S and S---O contacts.

In order to explain the origin of these short contact distances the following equilibrium is pertinent:[23]



16a **16b**



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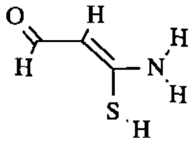
The hydrogen bonded form (**16b**) is the more stable isomer in dichloromethane, but the isomer (**16a**) is the more stable in DMSO. This facile equilibrium indicates that, in addition to non-bonded repulsions an attraction exists between the sulfur and oxygen atoms comparable to the NH...O hydrogen bond energy (3-5 kcal/mole). It should be noted that the distance between the (N)H and O atoms in **16b** (assuming 120° angles) is only *ca.* 1.7Å for a planar system. Such short intramolecular hydrogen bonds are however well known, as shown for example by **22**[26] in which the NHO angle is found to be 104° and the H---O distance 1.86Å.

In order to understand the origin of these close contact distances, it is necessary to consider the nature of the interactions involved as a sulfur or an oxygen atom approaches the sulfur atom combined with carbon. The equilibrium distance is determined by the balance of attractive and repulsive forces. According to theories of small interactions[27] the attractive forces involve 1) Coulombic attraction 2) Polarisation and 3) Charge Transfer.

These are balanced by the repulsive force due to the interpenetration of the closed electron shells (exclusion repulsion). All the molecules of interest here are highly polar and conjugated. The strong conjugation, as shown for example by the equivalent CN and NC bonds of compounds (**11** and **12**) and the short N-C and C-S bond lengths in the ring, leads to a highly polar structure with a formal partial positive charge on sulfur and corresponding negative charge on thiocarbonyl sulfur (or carbonyl oxygen). Extended-Hückel calculations on a model compound (**21**) give too large a negative charge (1.5e) on oxygen. An AMI calculation with geometry optimisation (see Experimental) gives a charge of +0.16 on sulfur and -0.31 on oxygen giving a Coulomb energy of -6.5 k.cal/mole. Moreover, these formal charges affect the orbitals, in particular by reducing the energies of polarisation orbitals, e.g. on sulfur and the σ^*_{cs} energy. The energies of the p_π(O) or (S) orbitals will be increased. These changes affect both the polarisation and charge transfer terms.



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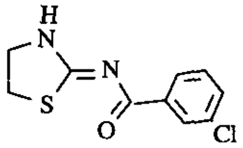

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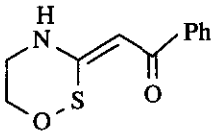

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It is noted that X-ray and neutron diffraction studies[28] at 122 K provide no evidence for $p_\pi(O)$-$\sigma^*_{s\text{-}c}$ stabilisation in compound (**22**). Electron density deformation maps show considerable concentration of electrons between S and O in compound (**23**) which is explained by strong $p_\pi(O)$-$\sigma^*_{s\text{-}o}$ perturbation. In contrast, no trace of electrons was found in the region between S and O in compound (**22**), all the deformation around the atoms could be attributed to lone pairs. We conclude therefore that the stabilisation in **22** and the molecules in *Table 2* is due largely to Coulombic forces, although 3d orbitals on sulfur also are involved.[28] In addition, the formal positive charge on the ring sulfur will draw the electrons closer to the nucleus thus reducing the overlap between the p_π and σ_{sc} orbitals. This will produce a reduction in the contact distance as observed. In an attempt to understand the small variations in these S...O and S...S contact distances with considerable changes in structure (*Table 2*) we undertook molecular modelling calculations using several standard procedures (*Table*

3). The various methods show large variations in the energies as a function of S---S distance, but a general trend is observed. In all cases the change in energy in the Van der Waals region is small (e.g. 3.0-4.0Å). However, in the 3.0 to 2.8Å region the energy rises sharply due to the dominance of the $1/r^{12}$ term.

Table 3. S...S Contact Energies (kcal/mole) from Various Molecular Modelling Programs.

r (Å)	Biosym[a]	COSMIC[b]	SYBYL[c]	MM2[d]	AMBER(3)
2.6	3.02	5.09	11.17	60.13	29.86
2.8	1.06	2.00	3.57	23.01	11.05
3.0	0.34	0.55	0.92	8.99	4.07
3.2	0.08	-0.09	0.02	3.46	1.38
3.4	-0.01	-0.33	-0.26	1.22	0.35
3.6	-0.04	-0.38	-0.31	0.31	-0.04
3.7	-0.04	-0.37	-0.31	0.09	-0.13
3.8	-0.04	-0.35	-0.29	-0.05	-0.17
3.9	-0.04	-0.33	-0.27	-0.13	-0.19
4.0	-0.04	-0.30	-0.25	-0.17	-0.20

[a] $E = 365906.4/r^{12} - 250.8/r^{6}$

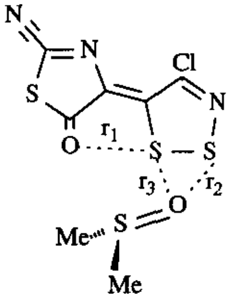
[b] $E = 0.38\,[\exp.\ 5.643\,(1-r/3.6) - 11.286\,(1-r/3.60)]$

[c] $E = 0.314(3.6/r)^{12} - 2(3.6/r)^{-6}$

[d] $E = 0.202\,(4.22/r)^{-12} - 2(4.22/r)^{-6}$

Consequently, changes in the attractive energies, in particular the dominant Coulombic form which varies as 1/r, are relatively small. At distances closer than *ca.* 2.9Å, therefore, the atoms behave as hard spheres, well within the classical Van der Waal distance.

Close contact distances are not just restricted to intramolecular cases. The X-ray structure of a remarkable complex (**24**) has been determined recently by Rees, Sivadasan and Williams (Imperial College, London). The S-S bond length of 2.056Å is normal for a disulfide, and the intramolecular S...O distance, r_1, is the longest recorded for this style of molecule (2.62Å) with a O...S-S grouping.



24

This value is slightly smaller than the values given in *Table 2*. The DMSO molecule is held at similar distances to the S atoms of disulfide bond (r_2 = 2.71Å; r_3 = 2.83Å). In this molecule, conjugation of the sulfur atoms with the nitrile group increases the charge on sulfur and decreases the charge on oxygen. This decreases the interaction between O and S and hence increases r_1. The increased positive charge on the sulfur atoms increases the electrostatic attraction of the DMSO oxygen atom. Assuming a point charge model, and a charge of +0.16 on each sulfur atom the Coulombic energy is found to be -5.6 kcal/mole, i.e. similar to the estimated value for the intramolecular S---O contact in **21**.

Other examples of close intermolecular contacts are known, and this interesting field requires further investigation.

EXPERIMENTAL

Preparation of 11

2-Aminothiazole was methylated on the ring N atom by reaction with iodomethane in ethanol[29], and the product was benzoylated on the exocyclic N atom by treatment with benzoyl chloride in pyridine. This material (0.28 g) was heated under reflux in benzene (10 ml) under nitrogen with Lawesson's reagent (0.84 g) for 3 h. The hot reaction mixture was filtered and evaporated, and the residue was crystallised to give **11**, *N-(3-methyl-2-(3H)-thiazolylidene)benzenecarbothioamide* (0.17 g, 57%) as thick orange plates (from benzene), mp 136-137°C, Anal. Calcd for $C_{11}H_{10}N_2S_2$ C: 56.4, H: 4.3, N: 11.9, S: 27.4: Found C: 56.1; H: 4.3; N: 11.9; S: 26.9. ^{13}C Nmr (δ, 67.8 MHz, DMSO-d_6) 203.3, 167.4, 144.1, 130.8, 128.8, 127.8, 127.2, 108.1 and 37.0.

Preparation of 12

2-Aminobenzothiazoline was methylated on the ring N atom by reaction with iodomethane in ethanol and the product was acylated on its ring N atom with 4-methoxybenzoyl chloride in pyridine.[30] This material (0.90 g) was refluxed in benzene (10 ml) under nitrogen with Lawesson's reagent (1.00 g) for 3 h. The hot reaction mixture was filtered and evaporated and the residue was recrystallised to give **12** *4-methoxy-N-(3-methyl-2-(3H)-benzothiazolylidene)benzenecarbothioamide* (0.26 g, 27%) as red blocks (from pyridine), mp 217-219°, Anal. Calcd for $C_{16}H_{14}N_2OS_2$ C, 61.1; H, 4.5; N, 8.9; S 20.4: Found C, 61.0; H, 4.4; N, 9.0; S, 20.4. ^{13}C Nmr (δ, 67.8 MHz, DMSO-d_6) 203.1, 166.9, 162.3, 136.5-112.5 (8 resonances), 55.3 and 33.4.

X-Ray Crystallography. X-Ray diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer, equipped with MoKα radiation and a graphite monochromator, using ω-2Θ scans. No absorption corrections were applied. Structures were solved by direct methods with SHELXS-86[31] and refined on F by full-matrix least-squares analyses using SHELX 76.[32] Non-hydrogen atoms were assigned anisotropic displacement parameters, all hydrogen atoms were located in difference Fourier maps and refined with isotropic displacement parameters, and a weighting scheme applied in the final cycles of refinement. Details

Table 4. Crystallographic Data.

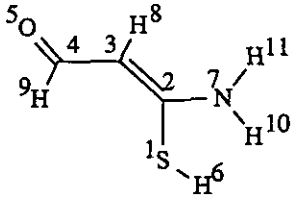
	11	**12**
Molecular formula	$C_{11}H_{10}N_2S_2$	$C_{16}H_{14}N_2OS_2$
Molecular weight	234.3	314.4
crystal form	thick orange plates	red blocks
crystal size (mm)	0.54 x 0.32 x 0.26	0.32 x 0.32 x 0.28
crystal system	monoclinic	monoclinic
a (Å)	17.944(4)	7.304(2)
b (Å)	7.713(1)	25.355(5)
c (Å)	8.052(2)	8.560(2)
β (°)	98.76(2)	113.36(3)
V (Å^3)	1101.1	1454.2
Z	4	4
calculated density (gcm^{-3})	1.41	1.44
space group	$P2_1/a$	$P2_1/n$
absorption coefficient (cm^{-1})	4.3	3.5

	11	**12**
max(sinΘ/λ) (Å^{-1})	0.62	0.62
F(000)	488	656
no. measured reflections	2404	3149
no. unique reflections	2156	2566
no. reflections observed ($I > 2.5\sigma(I)$)	1856	2251
No. of parameters refined	176	246
weighting scheme $w^{-1} = (\sigma^2(F) + gF^2)$, g:	0.0003	0.0005
final R, R_w	0.036, 0.037	0.036, 0.039
max. (Δ/σ) in final cycle	0.09	0.04
max. & min. electron density in final difference Fourier map (e Å^{-3})	0.25 & -0.36	0.22 & -0.34

of each crystal structure are given in *Table 4*. Fractional atomic coordinates and displacement parameters and structure factor tables have been deposited as Supplementary Data. Geometry calculations were made with PARST-91,[33] and molecular illustrations with PLATON-91.[18]

Results of Charge Density Calculation

Table 5. Charge Density Calculations for the Model Compound (d-orbitals excluded)



Atom	Charge[a]	Charge[b]
1	-0.1038	0.1570
2	0.6282	0.0017
3	-0.2307	-0.3793
4	0.7253	0.2340
5	-1.2170	-0.3091
6	0.1271	0.0098
7	-0.4439	-0.4022
8	0.0272	0.1674
9	0.0011	0.0588
10	0.2451	0.2348
11	0.2414	0.2269

[a] Extended Hückel: Hückel Constant = 1.75

[b] AMI: Fletcher-Reeves optimiser; Convergence limit = 0.0100000; Iteration limit 50; Optimisation algorithm = Fletcher-Reeves; RMS gradient 0.1000 kcal/mole; Max. cycles = 1.65; RHF Calculation

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