Concerted Formation of *S*-Methyldithizonium and 2,3-Diphenyl-5-methylthiotetrazolium Cations in the Reaction of *S*-Methyldithizone and Iodine in Chloroform. Part 8.[1] Crystal Structures of *S*-Methyldithizone Hydrogen Tri-iodide and 2,3-Diphenyl-5-methyltetrazolium Tri-iodide–Chloroform[1,**]

Frank H. Herbstein* and Willi Schwotzer†
Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

S-Methyldithizone reacts with iodine in chloroform solution giving, in a single reaction, the cations *S*-methyldithizonium and 2,3-diphenyl-5-methylthiotetrazolium, which have been identified *via* X-ray structure analysis of the crystalline reaction products *S*-methyldithizone hydrogen tri-iodide (**3**) and 2,3-diphenyl-5-methylthiotetrazolium tri-iodide–chloroform (**4**). Compound (**3**) is triclinic [$a = 12.367(8)$, $b = 10.084(7)$, $c = 8.451(6)$ Å, $\alpha = 109.9(1)$, $\beta = 97.5(1)$, $\gamma = 96.9(1)^\circ$, $Z = 2$, space group $P\bar{1}$]. Stacks of antiparallel protonated *S*-methyldithizone cations are interleaved by isolated I_3^- ions, directed parallel to the normals to the cation planes. Compound (**4**) is monoclinic [$a = 15.923(8)$, $b = 10.218(7)$, $c = 16.118(8)$ Å, $\beta = 109.91(1)^\circ$, $Z = 4$, space group *Cc*]. There are two sets of interacting I_3^- ions directed along [110] and [1$\bar{1}$0], respectively; the distance between the terminal iodines of adjacent I_3^- ions is 3.608(1) Å, indicating appreciable interaction.

Irving and Ramakrishna[2] obtained black crystalline needles with a metallic lustre (m.p. 118 °C) from the reaction of *S*-methyldithizone [3-methylthio-1,5-diphenylformazan,‡ (**1**), where R = Ph and X = Me] and iodine in chloroform. The product was described as a non-stoicheiometric compound of *S*-methyldithizone and iodine (ratio 1 *ca.* 1.4) but was not further defined. Formulation as *S*-methyldithizone·HI_3 also gives acceptable agreement with the C,H analysis (Found: C, 26.6; H, 2.6. $C_{14}H_{15}I_3N_4S$ requires C, 27.8; H, 2.3%).

The redox system in equation (i) was noted as a possible

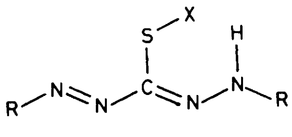
$$\text{formazan} \longrightarrow \text{tetrazolium ion} + H^+ + e \qquad (i)$$

proton–electron source.[2] We now show that the Irving–Ramakrishna reaction gives two crystalline products, which are identified by single-crystal *X*-ray structure analysis as *S*-methyldithizone·HI_3 (**3**) and the chloroform solvate of 2,3-diphenyl-5-methylthiotetrazolium·I_3 (**4**).

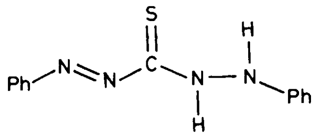
Experimental

Preparation of Crystals.—200 mg (0.74 mmol) of *S*-methyldithizone in 10 ml of $CHCl_3$ were added to 300 mg (1.18 mmol) of I_2 in $CHCl_3$, as described in reference 2. No precautions were taken to remove moisture or exclude atmospheric oxygen. After 2 d in a refrigerator at 5 °C, black prismatic crystals of (**3**) appeared and were separated. The mother liquors were left in the refrigerator and after 2 weeks a second crop of crystals (**4**) had appeared. Compound (**4**) crystallizes as approximately square bipyramids, which rapidly become covered with a brownish powder if exposed to the air.

Crystal Structure Determination.—Essentially similar methods were used for both structure analyses. After preliminary diffraction photography to check crystal quality,



(1)



(2)

crystal data (Table 1) were determined with a Philips PW 1100/20 four-circle diffractometer (graphite-monochromated Mo-K_α radiation), which was also used for intensity measurements (Table 2). Structure analysis and refinement were carried out using the SHELX-77[3] suite of programs; in addition the direct methods program MULTAN-77[4] and the plotting program ORTEP[5] were used. All calculations were made on the IBM 370/168 computer at Technion-Israel.

Although neither space group ($P\bar{1}$ nor *Cc*) is unequivocally determined by the systematic absences, the correctness of the choices is demonstrated by the successful structure determinations. In particular, we note that, as there are four asymmetric units in the unit cell of $(4)_s$, the cation (see below) would be required to have C_i-$\bar{1}$ or C_2-2 symmetry if the space group were *C*2/*c* but neither requirement is compatible with the structure found.

The positions of the heavy atoms were found by Patterson methods for (**3**) and by a combination of Patterson and direct methods for $(4)_s$. No difficulties were experienced with the refinement of (**3**), but difference syntheses indicated residual electron density in $(4)_s$, which was accounted for in terms of chloroform of solvation. Satisfactory agreement between observed and calculated crystal densities was obtained for one $CHCl_3$ molecule per asymmetric unit. It appeared that the $CHCl_3$ molecule had one major orientation (50% of the electron density) and many minor orientations; only the major orientation was refined. No hydrogen atoms were detected in difference syntheses, presumably due to the presence of heavy atoms and the neglect of absorption corrections. Phenyl hydrogens were introduced into both structures at calculated positions but were not refined.

The structure analyses show that compound (**3**) is *S*-methyldithizone·HI_3 and compound $(4)_s$ is 2,3-diphenyl-5-methyl-

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** This paper can also be regarded as Part 8 of the series 'Crystal Structures of Polyiodide Salts and Molecular Complexes.' For Part 7, see ref. 1.

† *Present address:* Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

‡ Conventional chemical numbering is used for chemical formulae. Crystallographic numbering is given in Figure 2 for compound (**3**) and in Figure 3(*a*) for compound (**4**).

Table 1. Crystal data; cell dimensions measured on Philips PW1100/20 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å)

Parameter	(*S*-Methyldithizone)$\cdot$ HI_3	2,3-Diphenyl-5-methylthiotetrazolium tri-iodide chloroform
Formula	$C_{14}H_{15}I_3N_4S$	$C_{15}H_{14}Cl_3I_3N_4S$
Relative molecular mass	652.08	769.44
F(000)	604	1 432
a (Å)	12.367(8)[a]	15.923(8)
b (Å)	10.084(7)	10.218(7)
c (Å)	8.451(6)	16.118(8)
α (°)	109.1(1)	90
β (°)	97.5(1)	109.91(8)
γ (°)	96.9(1)	90
V (Å^3)	972.0	2 465.7
D_m (g cm^{-3})	2.23[b]	2.11[c]
D_c (g cm^{-3})	2.22	2.08
Z	2	4
Space group	$P\bar{1}$	*Cc*
μ(Mo-K_α) (cm^{-1})	23.0	39.4

[a] This is the Delaunay reduced cell. [b] Flotational method; Nessler's reagent–H_2O. [c] Flotation method, *sym*-tetrabromoethane–toluene. The accuracy of the measurement is limited by slow decomposition.

thiotetrazolium tri-iodide–chloroform. Final non-hydrogen parameters are given in Tables 3 and 4, while structure factors, hydrogen parameters, and anisotropic temperature factors have been deposited in Supplementary Publication No. SUP 56067 (32 pp.).*

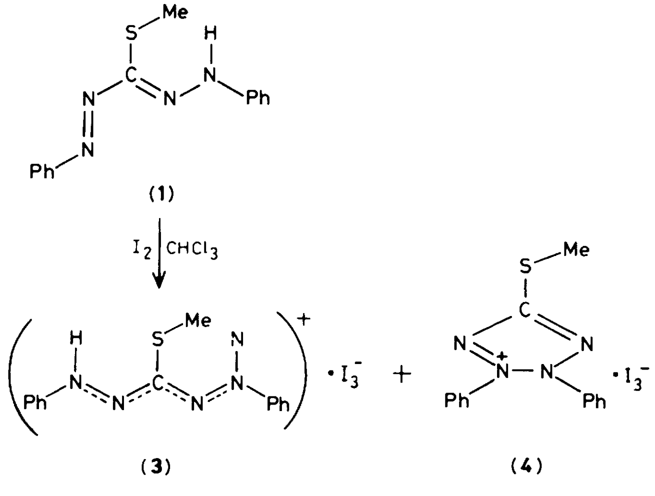
Results

Overall Chemical Reaction.—This can be formulated as in the Scheme.

S-*Methyldithizone Hydrogen Tri-iodide.*—1. *The cation.* This is in the *anti*, *s-trans* configuration,* and dimensions are given in Figure 1. Deviations from the mean plane through the formazan portion are less than 0.2 Å for all atoms (including those of the phenyl groups), except for those of the methyl group. The torsion angle C(19)–S(6)–C(3)–N(4) is 96(1.5)°, indicating that the plane through C(8), S(6), and C(19) is almost orthogonal to the formazan mean plane. The polar cation has the shape of a garden rake with a short handle; the prongs are represented by the formazan portion and the thiomethyl group is the handle. Charge balance requires protonation of the *S*-methyldithizone moiety but, as noted above, no hydrogens could be located experimentally. This point is referred to later (see Discussion section).

2. *The tri-iodide anion.* The essentially isolated tri-iodide anion has an asymmetrical bond length distribution, [I(1)–I(2) = 2.841(2) Å, I(2)–I(3) = 3.025(2) Å, and ∢ I(1)–I(2)–I(3) = 177.21(6)°] and hence is polar.

3. *Crystal structure.* There are alternate sheets of cations and anions parallel to (010) (Figure 2). In the cation layer there are pairs of cations arranged about centres of symmetry such that respective C–S and S–CH_3 dipoles are antiparallel; these pairs are stacked, in an offset manner, to form columns along [001]. The cation layer is formed by such columns related by translation along [100].



Scheme

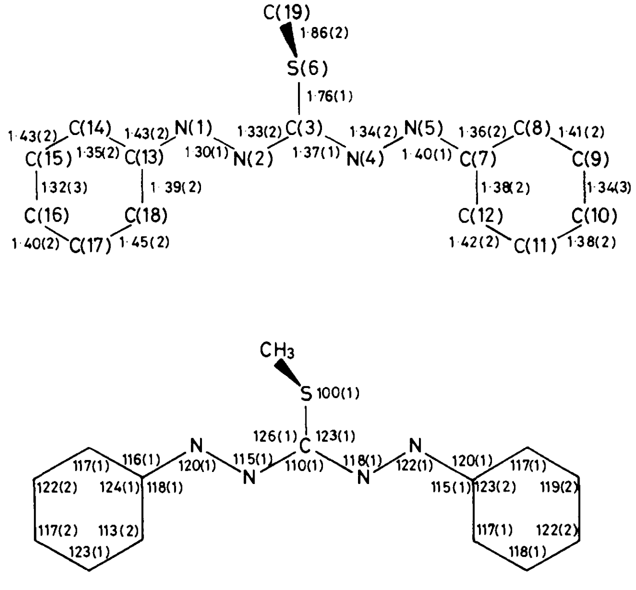


Figure 1. *S*-Methyldithizone cation (protonated): dimensions of the moiety; the crystallographic numbering scheme is shown. The position of C(19) is denoted schematically

The interleaving anionic layers contain oppositely aligned tri-iodide ions related by centres of inversion. The I_3^- ions lie approximately along [104] and are aligned parallel to the S–CH_3 vectors of the cations. There are no intermoiety distances shorter than van der Waals distances.

2,3-*Diphenyl-5-methylthiotetrazolium Tri-iodide–Chloroform.*—1. *The cation.* The tetrazolium ring [Figure 3(*a*)] is essentially planar [deviations from the mean plane through the atoms of the ring and S(6) are less than 0.06 Å]. The methyl group is rotated somewhat out of this plane {τ[N(4)–C(3)–S(6)–C(19)] = $-9(1.5)$°}, while the dihedral angles between the mean planes of the phenyl rings and the tetrazolium ring are 58(2)° [phenyl C(7) to C(12)] and 69(2)° [phenyl C(13) to C(18)]. Thus the two phenyls are related by an approximate two-fold axis.

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* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

* We follow the authors of reference 14 in using 'configuration' to describe the arrangement of substituents about a formal double bond and 'conformation' for that about a formal single bond. Isomerism about the C=N double bond is designated *syn-anti* and that about the C–N single bond *s-cis* and *s-trans*.

Table 2. Experimental details

	(*S*-Methyldithizone)·HI_3	2,3-Diphenyl-5-methylthiotetrazolium tri-iodide–chloroform
1. Crystal shape	Black tablets	Black square bipyramids
2. Scan method	$\omega/2\theta$	$\omega/2\theta$
3. Max (sin θ/λ) (Å^{-1})	0.5947	0.5947
4. Limits on indices	$-14 \leq h \leq 14$; $-11 \leq k \leqslant 11$; $l \leq 9$	$-17 \leq h \leq 17$; $k \leq 12$; $l \leq 18$
5. Standards	Stable	Stable
6. Absorption correction	None	None
7. No. of reflections		
(i) measured	3 326	2 378
(ii) observed	2 902	2 234
(iii) in final refinement cycle	2 438	2 165
(iv) acceptance criterion	$F^2 \geq \sigma(F^2)$	$F^2 \geq 1.4\sigma(F^2)$
8. Refinement scheme	Full matrix	Full matrix
9. Weighting scheme	$1.6905/[\sigma^2(F) + 0.0014F^2]$	$0.8046/[\sigma^2(F) + 0.0053F^2]$
10. σ(I-I) (Å)	0.002	0.001
σ(C-C) (Å)	0.030	0.025
(C-C-C) (°)	2	1.5
11. Final $R_F = \dfrac{\Sigma\lvert F_0 - F_c\rvert}{\Sigma\lvert F_0\rvert}$	0.0815	0.0510
$R_w = \dfrac{\Sigma\sqrt{w}\lvert F_0 - F_c\rvert}{\Sigma\sqrt{w}F_0}$	0.0823	0.0575

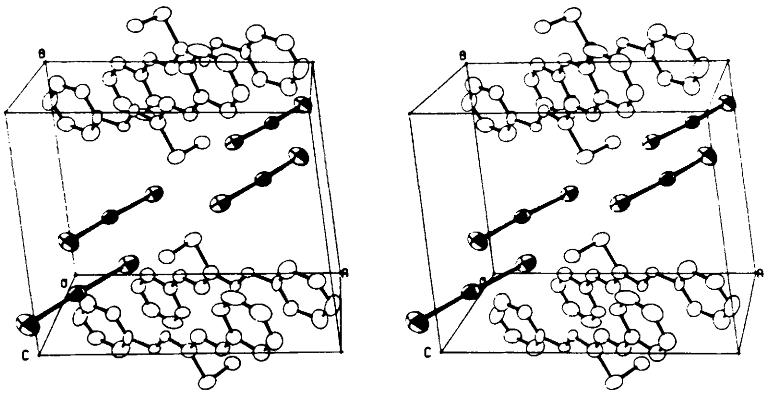

Figure 2. *S*-Methyldithizone·HI_3. ORTEP stereodiagram. The ellipsoids are 50% probability ellipsoids

2. *The tri-iodide anion.* The tri-iodide anion is fully ordered, is nearly symmetrical [Figure 3(*b*)] and shows strong interaction with its neighbours.

3. *Crystal structure.* The structure (Figure 4) can be described in terms of *C* face-centred layers parallel to (001), with cations and anions segregated on alternate layers. Successive layers of a particular type are related by the *c* glide plans.

Discussion

The Cations.—The *S*-methyldithizone cation has the *anti, s-trans* configuration, which is also found in the yellow isomers of *S*-isopropyldithizone[6] and 3-methylthio-1,5-di-(*o*-tolyl)-formazan[7] (1 with R = *o*-tolyl, X = Me) and in dithizone (2) itself.[1,8] The *syn, s-trans* configurational isomer is found in *S*-methyldithizone (1) itself[9] and in 3-carboxymethylthio-1,5-diphenylformazan[10] (2 with R = Ph, X = CH_2CO_2H). These three neutral *S*-methyldithizone derivatives have similar bond lengths, despite the configurational differences. They can all be represented by structure (1), although it is clear from the actual bond lengths that some delocalization must occur.

The protonation site in the *S*-methyldithizone cation has not been located directly. Three tautomeric structures (each accompanied by its symmetrical counterpart) can be written for the protonated *S*-methyldithizone cation. Bond length differences would be expected to be small; the measured values, which are not especially accurate because of the presence of the iodines, do not match the structures very well even with allowance for delocalization. Although formula (3) can be used as a convenient working hypothesis, the prudent conclusion would seem to be that direct location of the proton is needed.

The cation found in the structure of $(4)_S$ can be represented by a conventional covalent bond structure (4) (Scheme) and is thus not mesoionic.[11-13] The crystal of the parent neutral mesoionic molecule, dehydrodithizone, has been determined[14] and also that of its dimeric complex with $HgCl_2$;[15] the dimensions of a closely related cationic ring system were obtained during the structure analysis of 5-(1,5-diphenyl-3-formazanyl)-1,3-diphenyltetrazolium chloride[16] (earlier results for some other related tetrazolium ring systems are summarized in ref. 14). The accuracy of the present results is not high enough to warrant detailed discussions of the relatively small

Table 3. Atomic co-ordinates and U_{eq} for *S*-methyldithizone•HI$_3$ × 10^4. E.s.d.s are given in brackets in units of the last significant figure (U_{eq} = 1/3 trace *U*; × 10^4 for I, S and × 10^3 for other atoms). The hydrogen parameters have been deposited in Supplementary Publication No. SUP 56067 (32 pp.)

Atom	*x*	*y*	*z*	U_{eq}
I(1)	6 577(1)	6 010(1)	9 250(2)	611(8)
I(2)	7 966(1)	6 298(1)	6 651(2)	466(7)
I(3)	9 184(1)	6 612(2)	4 131(2)	704(10)
N(1)	3 033(12)	−2 135(15)	3 723(18)	30(8)
N(2)	3 627(12)	−1 107(16)	5 031(20)	35(8)
C(3)	4 502(14)	−1 425(17)	5 803(22)	44(10)
N(4)	5 038(12)	−318(15)	7 208(19)	49(9)
N(5)	5 904(11)	−506(14)	8 187(18)	41(8)
S(6)	4 929(4)	−3 117(5)	5 177(6)	522(28)
C(7)	6 474(14)	562(16)	9 700(19)	35(9)
C(8)	6 204(15)	1 892(18)	10 186(23)	51(11)
C(9)	6 804(20)	2 907(19)	11 731(28)	62(13)
C(10)	7 677(19)	2 595(20)	12 569(25)	58(12)
C(11)	7 965(14)	1 263(19)	12 074(23)	49(11)
C(12)	7 371(15)	211(18)	10 530(24)	51(11)
C(13)	2 017(12)	−1 938(17)	2 883(21)	37(9)
C(14)	1 507(16)	−3 001(20)	1 431(24)	54(11)
C(15)	516(16)	−2 804(20)	530(25)	55(12)
C(16)	116(15)	−1 608(23)	998(25)	60(12)
C(17)	685(16)	−505(21)	2 474(28)	62(12)
C(18)	1 693(15)	−617(19)	3 484(26)	54(12)
C(19)	5 762(14)	−2 899(16)	3 572(21)	41(10)

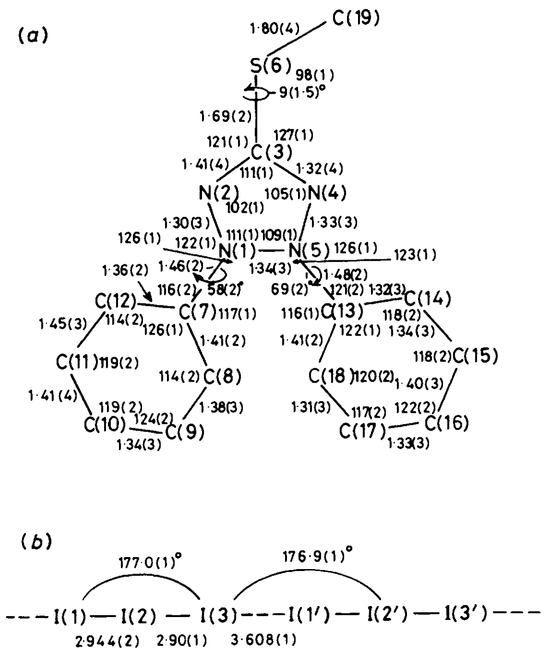

Figure 3. 2,3-Diphenyl-5-methylthiotetrazolium tri-iodide–chloroform. (*a*) Dimensions of the cation. The crystallographic numbering used is shown. The orientation of the phenyls is *schematic* only; they are, in fact, almost normal to the plane of the diagram. (*b*) Dimensions of tri-iodide anion.

differences found in the geometries of these compounds. The phenyl substituents in the tetrazolium ring are always inclined at a large angle to the ring plane; this is for steric reasons as the distance between C(8) and C(18) in the hypothetical planar cation [Figure 3(*a*)] would be *ca.* 1.75 Å. Consequently, delocalization is not possible over both tetrazolium and phenyl ring systems.

Table 4. Atomic co-ordinates and U_{eq} for 2,3-diphenyl-5-methylthiotetrazolium tri-iodide–chloroform; for details see caption to Table 3. The *x,z* co-ordinates of I(1) were held fixed in order to define the origin of the unit cell. The chlorine occupancies were fixed at 0.5. The hydrogen parameters have been deposited in Supplementary Publication No. SUP 56067 (32 pp.)

Atom	*x*	*y*	*z*	U_{eq}
I(1)	7 939	1 763(2)	6 266	642(7)
I(2)	9 403(1)	178(1)	6 067(1)	548(6)
I(3)	10 834(1)	−1 478(2)	5 939(1)	727(9)
N(1)	9 159(11)	7 461(14)	3 675(9)	45(7)
N(2)	8 789(11)	8 548(16)	3 734(11)	56(8)
C(3)	9 359(14)	9 446(16)	3 561(14)	62(9)
N(4)	10 014(11)	8 860(13)	3 389(11)	52(8)
N(5)	9 885(10)	7 629(16)	3 460(10)	45(7)
S(6)	9 142(5)	11 101(5)	3 522(5)	873(30)
C(7)	8 798(12)	6 207(16)	3 834(10)	50(8)
C(8)	7 905(13)	5 919(22)	3 320(12)	59(10)
C(9)	7 576(15)	4 775(27)	3 551(11)	80(13)
C(10)	8 053(20)	3 957(25)	4 182(22)	97(17)
C(11)	8 963(24)	4 233(19)	4 647(20)	97(18)
C(12)	9 342(18)	5 471(19)	4 506(17)	58(12)
C(13)	10 389(13)	6 538(16)	3 249(14)	42(8)
C(14)	10 043(15)	5 826(20)	2 529(12)	62(10)
C(15)	10 550(19)	4 898(23)	2 352(18)	75(13)
C(16)	11 429(21)	4 738(24)	2 933(22)	66(16)
C(17)	11 768(14)	5 435(25)	3 670(15)	69(11)
C(18)	11 271(13)	6 359(20)	3 824(15)	64(10)
C(19)	10 163(30)	11 670(25)	3 368(32)	127(24)
				U_{iso}
Cl(1)	7 398(13)	7 546(19)	5 020(13)	119(4)
Cl(2)	6 567(15)	7 507(22)	6 363(14)	139(5)
Cl(3)	8 233(17)	6 399(22)	6 664(17)	129(6)

It is perhaps surprising that tri-iodide *salts* rather than molecular compounds should be obtained from chloroform. However, it is clear that the methylthio group cannot form molecular compounds with iodine in the same way as thiones.[1] Furthermore, there are two reactions that take place in concert; this makes proton transfer possible and is a necessary and sufficient condition for formation of salts in a non-ionizing solvent such as chloroform. The reactions are similar to those suggested for the oxidation of dithizone to dehydrodithizone[14] and for reaction of dithizone and methyl iodide to give a tetrazolium salt.[17]

Formation of the tetrazolium ring requires isomerization about the C=N double bond and rotation about the C–N single bond in order to obtain the *syn*, *s-cis* isomer, which can then form the tetrazolium ring by elimination of hydrogen. The existence of both *syn* and *anti* isomers of *S*-methyldithizone derivatives[6–10] suggests that the energy barrier between them cannot be large, and this has been demonstrated in a comprehensive study of the interconversion of the isomers of 3-methylthio-1,5-diarylformazans in solution.[18] Differences in solubility of the two salts could account for their different times of appearance.

The Anions.—The degree of asymmetry in the tri-iodide anion of (3) [difference between the two I–I distances = Δ = 0.184(3) Å] is quite large but appreciably less than that found in NH_4I_3 [Δ = 0.322(6) Å].[19] The accepted explanation is that asymmetry in the bond lengths in the I_3^- anion results from an asymmetry in the electrostatic field operating on the anion in the crystal environment.[20] The I–I distances found

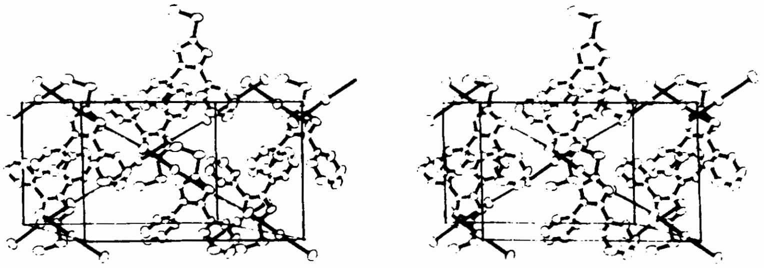

Figure 4. 2,3-Diphenyl-5-methylthiotetrazolium tri-iodide–chloroform. ORTEP stereodiagram. The axes are orientated as in Figure 2. The chloroform of solvation has been omitted from the diagram. The ellipsoids are 50% probability ellipsoids

here fit excellently into a correlation plot of interatomic distances in linear tri-iodide systems.[21]

In the tri-iodide ion of (**4**) asymmetry has almost vanished but the secondary interaction between the I_3^- units in a chain is the strongest on record, (*cf.* reference 22) as shown by the distance of 3.608(1) Å between adjacent I_3^-. Successive I_3^- units in a chain are related by C-centring and hence point in the same direction; thus the chains are polar, although the degree of polarity will be small because of the closeness of the two I–I bond lengths.

Acknowledgements

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