X-Ray and Infrared Structural Studies on the Methyl Ester of Dithiocarbazic Acid and its *N*-Substituted Derivatives

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I.r. spectral and *X*-ray diffraction studies were carried out on the methyl ester of dithiocarbazic acid, $NH_2\cdot NH\cdot C(:S)\text{-}SMe$ (I), and of its *N*-substituted derivatives, $NMe_2\cdot NH\cdot C(:S)SMe$ (II), and $NH_2\cdot NMe\cdot C(:S)SMe$ (III). Crystals of (I) are monoclinic, space group $C2/c$, $Z = 8$, unit cell dimensions: $a = 14.018(5)$, $b = 5.518(3)$, $c = 14.079(4)$ Å, $\beta = 98.4(1)°$; (II) monoclinic, space group $P2_1/c$, $Z = 4$, unit cell dimensions: $a = 8.487(8)$, $b = 9.920(9)$, $c = 10.611(9)$ Å, $\beta = 117.1(1)°$; (III), monoclinic, space group $P2_1/c$, $Z = 4$, unit cell dimensions: $a = 7.071(5)$, $b = 9.815(6)$, $c = 10.142(7)$ Å, $\beta = 114.0(1)°$. The structures were solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to R 0.028 (I), 0.036 (II), and 0.029 (III) for 1 256, 1 132, and 917 reflections. The basic units of these structures are centrosymmetric dimers formed by $NH\cdots N$ hydrogen bonds in (I), and by $N{-}H\cdots S$ hydrogen bonds in (II) and (III). The component monomers are in the *cis, trans*-conformation, *i.e.* with the group $-NH\cdot NH_2$ bent toward C–S and the SMe towards the opposite side in (I) and in the *trans, cis*-conformation in (II) and (III). Change of conformation or of substituents does not significantly alter bond distances in the molecules.

THE methyl ester of dithiocarbazic acid (I), and its *N*-substituted derivatives has been studied in recent years, and their behaviour as ligands with transition metals is currently of interest; we have already prepared complexes [1,2] containing the ligand as a neutral molecule and as a deprotonated anion.

ESCA studies [3] carried out on (I) and its *N*-substituted derivatives have shown that the binding energy for N-3 is influenced by the substituents, while the same energy for N-2 is almost constant. Theoretical [4] and n.m.r.[5] studies agree in indicating the most stable conformations which these molecules can assume in solution.

We report here i.r. spectral and *X*-ray diffraction studies of the methyl ester of dithiocarbazic acid $NH_2\cdot NH\cdot C(:S)SMe$ (I), and its 3,3-dimethyl- (II) and 2-methyl- (III) derivatives, carried out in order to determine the influence of the substituents on the solid-state conformation.

EXPERIMENTAL

The esters were prepared as in refs. 6 and 7. I.r. spectra were measured with a Beckmann IR 7 spectrophotometer in the range 4 000—250 cm^{-1} as Nujol or polychlorotrifluoroethylene mulls, as solid films, or in hexachlorobutadiene solution.

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[1] C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 981.

[2] A. Monaci, F. Tarli, and A. M. Giuliani, to be published.

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[4] M. V. Andreocci, M. Bossa, G. Ramunni, M. Scazzocchio, D. Gattegno, and A. M. Giuliani, *J.C.S. Dalton*, 1974, 41.

[5] D. Gattegno and A. M. Giuliani, *Tetrahedron*, 1974, **30**, 701.

[6] G. Bahr and G. Schleitzer, *Z. anorg. Chem.*, 1955, **280**, 161.

[7] K. A. Jensen, V. Anthoni, and A. Holm, *Acta Chem. Scand.*, 1969, **23**, 1916.

Crystal Data.—*Compound* (I). $C_2H_6N_2S_2$, $M = 122.20$, Monoclinic, $a = 14.018(5)$, $b = 5.518(3)$, $c = 14.079(4)$ Å, $\beta = 98.4(1)°$, $U = 1\,077.4$ Å^3, $Z = 8$, $D_c = 1.51$, $F(000) = 512$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 8.07 cm^{-1}. Space group $C2/c$ from systematic absences and structure determination.

Compound (II). $C_4H_{10}N_2S_2$, $M = 150.26$, Monoclinic, $a = 8.487(8)$, $b = 9.920(9)$, $c = 10.611(9)$ Å, $\beta = 117.1(1)°$, $U = 795.9$ Å^3, $Z = 4$, $D_c = 1.25$, $F(000) = 320$. μ(Mo-K_α) = 5.73 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Compound (III). $C_3H_8N_2S_2$, $M = 136.23$, Monoclinic, $a = 7.071(5)$, $b = 9.815(6)$, $c = 10.142(7)$ Å, $\beta = 114.0(1)°$, $U = 642.8$ Å^3, $Z = 4$, $D_c = 1.41$, $F(000) = 288$. μ(Mo-K_α) = 6.85 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs, and refined by a least-squares procedure applied to the diffractometer measurements of several reflections.

Intensity Data.—These were collected on a Siemens AED single-crystal diffractometer, by use of Zr-filtered Mo-K_α radiation and the ω—2θ scan technique. All crystals were aligned with their b axis along the ϕ axis of the diffractometer and all reflections with $2\theta < 58°$ for (I) and with $2\theta < 50°$ for (II) and (III) were measured. Of 1 435 (I), 1 407 (II), and 1 132 (III) independent reflections, 1 256 (I), 1 132 (II), and 917 (III) having $I > 2\sigma(I)$ were considered observed and used in the analyses. Some evidence of decomposition of the samples during X-ray exposure was shown by the decreasing intensity of a standard reflection. Corrections for crystal decay were applied, taking the intensity of the standard reflection as internal scaling for the data set.

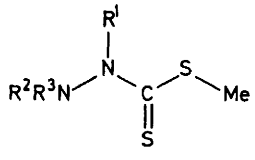
Data were corrected for Lorentz and polarization factors, but not for absorption in view of the low absorbance of the samples. The absolute scale was determined first by Wilson's method and then by correlating observed and calculated values.

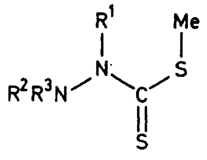
Structure Determination and Refinement.—The structures were solved by Patterson and Fourier methods and refined by block-diagonal least-squares, at first with isotropic, then with anisotropic thermal parameters. All hydrogen atoms were located directly from difference syntheses calculated after several cycles of least-squares. Further least-squares cycles were computed, hydrogen atoms being included with isotropic thermal parameters. Unit weights were chosen at every stage of the refinement by analysing the variation of $|\Delta F|$ with respect to $|F|$. Final R values were 0.028 (I), 0.036 (II), and 0.029 (III). Atomic scattering factors for non-hydrogen atoms were taken from ref. 8 and for hydrogen from ref. 9. Final atomic co-ordinates are given in Tables 1—3. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21883 (28 pp., 1 microfiche).*

All calculations were performed on a CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) with programs written by Immirzi.[10]

RESULTS AND DISCUSSION

The possible conformations for the compounds studied are: *cis,cis*, *cis,trans*, *trans,cis*, and *trans,trans*. Of these the *cis,trans*-conformation is present in the unsubstituted ester (I) (Figure 1), while the ***trans,cis*** is observed for both substituted esters (II) and (III) (Figures 2 and 3). The structural parameters for these molecules are quoted in Tables 4—6.


cis,cis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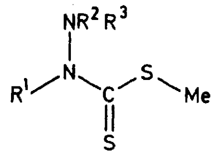
trans, cis

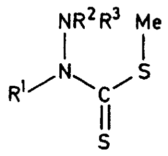
trans, trans

TABLE 1

Fractional atomic co-ordinates for (I), non-hydrogen (× 10^4) and hydrogen atoms (× 10^3), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
S(1)	2 825(1)	1 674(1)	1 686(1)
S(2)	779(1)	2 780(1)	1 353(1)
N(1)	2 109(1)	5 552(3)	734(1)
N(2)	1 407(1)	7 188(3)	284(1)
C(1)	3 922(1)	3 152(4)	1 461(2)
C(2)	1 899(1)	3 598(3)	1 196(1)
H(11)	398(1)	472(4)	180(1)
H(12)	393(1)	340(4)	74(1)
H(13)	441(1)	194(4)	170(1)
H(1)	269(1)	574(4)	59(1)
H(21)	87(1)	623(4)	9(1)
H(22)	121(2)	825(4)	76(2)

TABLE 2

Fractional atomic co-ordinates for (II), non-hydrogen (× 10^4) and hydrogen atoms (× 10^3), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
S(1)	1 643(1)	1 342(1)	2 044(1)
S(2)	−1 354(1)	3 073(1)	−26(1)
N(1)	2 020(3)	3 652(2)	1 115(2)
N(2)	3 833(3)	3 374(2)	2 036(2)
C(1)	−328(4)	402(3)	1 697(4)
C(2)	792(3)	2 775(3)	1 012(3)
C(3)	4 478(4)	4 327(4)	3 212(3)
C(4)	4 851(4)	3 425(4)	1 230(4)
H(1)	169(3)	452(3)	64(3)
H(11)	−100(3)	20(3)	75(3)
H(12)	−97(3)	89(3)	200(3)
H(13)	8(4)	−42(3)	227(3)
H(31)	369(3)	419(3)	375(3)
H(32)	563(3)	406(3)	381(3)
H(33)	438(3)	532(3)	286(3)
H(41)	427(3)	286(3)	38(3)
H(42)	469(3)	439(3)	72(3)
H(43)	616(3)	321(3)	195(3)

Theoretical studies [4] supported by the n.m.r. spectra [5] for compound (I) are consistent with the presence in solution of the conformers *cis,cis*, *cis,trans*, and *trans,cis*,

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

the first two being in rapid equilibrium owing to the low-energy barrier to rotation of the methyl group bound to sulphur. Similar studies on compound (III) show that the *cis,trans*-conformation is not allowed because of its high energy. In any case the *trans,trans*-conformation is excluded.

TABLE 3

Fractional atomic co-ordinates for (III), non-hydrogen ($\times 10^4$) and hydrogen atoms ($\times 10^3$), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
S(1)	8 201(1)	2 874(1)	2 078(1)
S(2)	4 114(1)	2 129(1)	−385(1)
N(1)	4 737(3)	4 147(2)	1 454(2)
N(2)	6 089(4)	4 931(2)	2 625(2)
C(1)	8 813(5)	1 455(3)	1 190(3)
C(2)	5 537(4)	3 110(3)	1 017(3)
C(3)	2 524(4)	4 481(3)	834(3)
H(11)	876(4)	172(3)	22(3)
H(12)	792(4)	61(3)	116(3)
H(13)	1 023(5)	116(3)	188(3)
H(21)	596(4)	582(3)	235(3)
H(22)	571(4)	482(3)	334(3)
H(31)	177(5)	403(4)	−3(4)
H(32)	240(5)	543(3)	89(3)
H(33)	177(5)	413(3)	139(4)

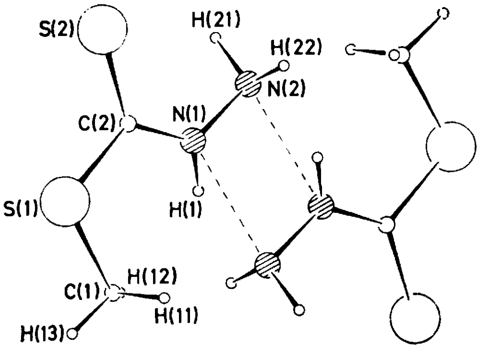

FIGURE 1 Dimer of compound (I) in the *cis,trans*-conformation

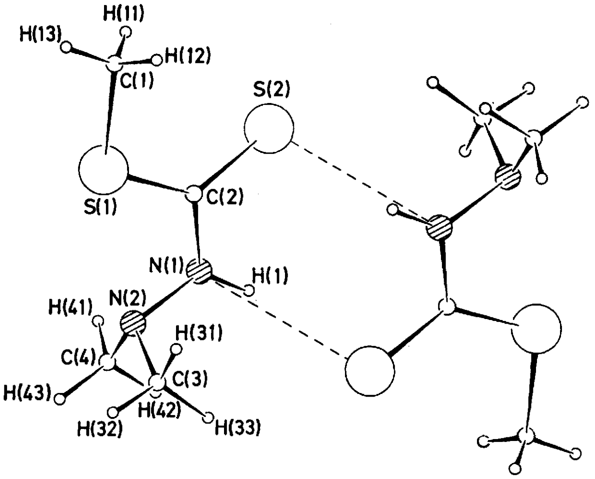

FIGURE 2 Dimer of compound (II) in the *trans,cis*-conformation

A comparison of the structural results obtained for these esters with those for thiosemicarbazide[11] and thiocarbonohydrazide[12] suggests that the conformation

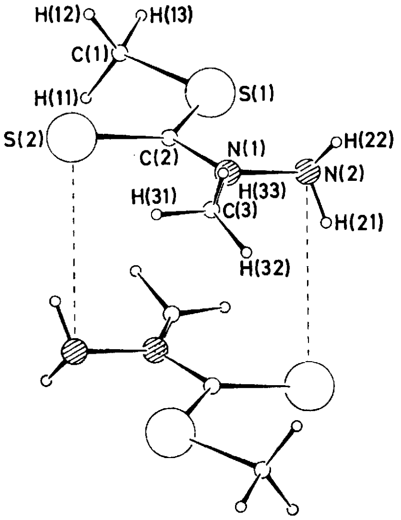

FIGURE 3 Dimer of compound (III) in the *trans,cis*-conformation

TABLE 4

Bond distances (Å) and angles (°) in (I)

(*a*) Distances

S(1)–C(1)	1.809(4)	C(1)–H(12)	1.03(1)
S(1)–C(2)	1.740(3)	C(1)–H(13)	0.98(2)
S(2)–C(2)	1.679(4)	N(1)–H(1)	0.87(1)
C(2)–N(1)	1.315(2)	N(2)–H(21)	0.93(2)
N(1)–N(2)	1.415(3)	N(2)–H(22)	0.96(3)
C(1)–H(11)	0.99(2)		

(*b*) Angles

C(1)–S(1)–C(2)	105.0(1)	H(11)–C(1)–H(12)	110(2)
S(1)–C(2)–S(2)	116.2(1)	H(11)–C(1)–H(13)	115(1)
S(1)–C(2)–N(1)	119.3(1)	H(12)–C(1)–H(13)	109(1)
S(2)–C(2)–N(1)	124.5(1)	H(1)–N(1)–C(2)	120(1)
C(2)–N(1)–N(2)	123.6(1)	H(1)–N(1)–N(2)	116(1)
H(11)–C(1)–S(1)	109(1)	H(21)–N(2)–N(1)	104(1)
H(12)–C(1)–S(1)	111(1)	H(22)–N(2)–N(1)	109(2)
H(13)–C(1)–S(1)	102(1)	H(21)–N(2)–H(22)	104(2)

TABLE 5

Bond distances (Å) and angles (°) in (II)

(*a*) Distances

S(1)–C(1)	1.801(8)	C(1)–H(12)	0.89(3)
S(1)–C(2)	1.738(3)	C(1)–H(13)	0.98(3)
S(2)–C(2)	1.670(6)	C(3)–H(31)	1.07(3)
C(2)–N(1)	1.323(5)	C(3)–H(32)	0.93(3)
N(1)–N(2)	1.424(6)	C(3)–H(33)	1.04(3)
N(2)–C(3)	1.459(4)	C(4)–H(41)	0.98(3)
N(2)–C(4)	1.468(7)	C(4)–H(42)	1.08(3)
N(1)–H(1)	0.97(3)	C(4)–H(43)	1.04(3)
C(1)–H(11)	0.92(3)		

(*b*) Angles

C(1)–S(1)–C(2)	102.4(2)	H(31)–C(3)–N(2)	107(2)
S(1)–C(2)–S(2)	125.1(2)	H(32)–C(3)–N(2)	106(2)
S(1)–C(2)–N(1)	113.6(2)	H(33)–C(3)–N(2)	112(2)
S(2)–C(2)–N(1)	121.3(2)	H(31)–C(3)–H(32)	109(2)
C(2)–N(1)–N(2)	119.6(2)	H(31)–C(3)–H(33)	110(2)
N(1)–N(2)–C(3)	109.2(2)	H(32)–C(3)–H(33)	114(2)
N(1)–N(2)–C(4)	109.4(2)	H(41)–C(4)–N(2)	109(2)
C(3)–N(2)–C(4)	112.6(3)	H(42)–C(4)–N(2)	110(2)
H(11)–C(1)–S(1)	113(2)	H(43)–C(4)–N(2)	106(2)
H(12)–C(1)–S(1)	108(2)	H(41)–C(4)–H(42)	99(2)
H(13)–C(1)–S(1)	106(2)	H(41)–C(4)–H(43)	118(2)
H(11)–C(1)–H(12)	110(3)	H(42)–C(4)–H(43)	113(2)
H(11)–C(1)–H(13)	111(3)	H(1)–N(1)–C(2)	121(2)
H(12)–C(1)–H(13)	109(3)	H(1)–N(1)–N(2)	119(2)

[11] G. D. Andreetti, P. Domiano, G. Fava Gasparri, M. Nardelli, and P. Sgarabotto, *Acta Cryst.*, 1970, **B26**, 1005.

[12] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1969, **B25**, 2286.

TABLE 6

Bond distances (Å) and angles (°) in (III)

(*a*) Distances

S(1)–C(2)	1.764(3)	C(1)–H(12)	1.04(3)
S(2)–C(2)	1.673(3)	C(1)–H(13)	1.00(3)
S(1)–C(1)	1.804(4)	N(2)–H(21)	0.91(3)
C(2)–N(1)	1.325(4)	N(2)–H(22)	0.88(3)
N(1)–N(2)	1.412(3)	C(3)–H(31)	0.93(4)
N(1)–C(3)	1.467(4)	C(3)–H(32)	0.94(3)
C(1)–H(11)	1.00(3)	C(3)–H(33)	0.98(3)

(*b*) Angles

C(1)–S(1)–C(2)	102.1(2)	H(12)–C(1)–S(1)	111(2)
S(1)–C(2)–S(2)	124.5(2)	H(13)–C(1)–S(1)	104(2)
S(1)–C(2)–N(1)	113.1(2)	H(21)–N(2)–H(22)	110(3)
S(2)–C(2)–N(1)	122.4(2)	H(21)–N(2)–N(1)	108(2)
C(2)–N(1)–N(2)	117.7(2)	H(22)–N(2)–N(1)	107(2)
C(2)–N(1)–C(3)	123.7(2)	H(31)–C(3)–H(32)	120(3)
N(2)–N(1)–C(3)	118.6(2)	H(31)–C(3)–H(33)	98(3)
H(11)–C(1)–H(12)	114(2)	H(31)–C(3)–N(1)	114(2)
H(11)–C(1)–H(13)	113(3)	H(32)–C(3)–H(33)	103(3)
H(11)–C(1)–S(1)	112(2)	H(32)–C(3)–N(1)	108(2)
H(12)–C(1)–H(13)	102(2)	H(33)–C(3)–N(1)	114(2)

TABLE 7

Internal rotation angles ψ (°) of the SMe group

	(I)	(II)	(III)
C(2)–S(1)–C(1)–H(11)	−62.4	−58.9	−69.8
C(2)–S(1)–C(1)–H(12)	59.7	62.4	58.4
C(2)–S(1)–C(1)–H(13)	175.5	179.2	168.1
$\Delta\psi_{\mathrm{av.}}$ from gauche conformation	2.4	1.4	7.7

TABLE 8

Details of least-squares planes through atoms S(1),C(2),N(1),S(2) for the three compounds. Equations are in the form: $mX + nY + pZ = d$ where X,Y,Z are co-ordinates in Å referred to orthogonal axes and Z is perpendicular to X,Y. Deviations (Å) of relevant atoms from the planes are in square brackets

Compound (I): $0.0285X - 0.5186Y - 0.8545Z = -2.3830$

[S(1) 0.001(1), C(2) −0.001(1), N(1) 0.001(2), S(2) 0.001(1), N(2) 0.043(2), C(1) −0.110(3)]

Compound (II): $0.4666X - 0.4487Y - 0.7622Z = -1.8793$

[S(1) −0.001(1), C(2) 0.001(3), N(1) −0.001(2), S(2) −0.001(1), N(2) −0.030(2), C(1) −0.034(4)]

Compound (III): $0.5084X + 0.6061Y - 0.6117Z = 3.0452$

[S(1) −0.001(1), C(2) 0.006(3), N(1) −0.004(2), S(2) −0.001(1), N(2) 0.069(2), C(1) 0.065(3), C(3) −0.120(3)]

TABLE 9

ν(C–N) bands (cm^{-1}) correlated with C–N bond distances (Å)

Compound	C–N	ν(C–N)
(MeS)$_2$C⁚N·N⁚C(SMe)$_2$	1.281(9) [a]	1 520 [b]
NH$_2$·NH·C(⁚S)SMe	1.315(2)	1 515—1 520
Me$_2$N·NH·C(⁚S)SMe	1.323(5)	1 515, 1 540
NH$_2$·N(Me)·C(⁚S)SMe	1.325(4)	<1 500
Ph$_2$N·NH·C(⁚S)SMe	1.337(6) [c]	1 500
[NH$_2$·NH·C(⁚S)S]N$_2$H$_5$	1.330(8) [d]	1 520

[a] A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Cryst. Struct. Comm.*, 1975, **4**, 141. [b] Ref. 2. [c] Ref. 13. [d] Ref. 14.

of this type of molecule is essentially determined by their ability to form N–H···N and N–H···S hydrogen bonds, which enable the molecules to be joined in centrosymmetric dimers. These dimers have bifurcated intra- and inter-molecular N–H···N hydrogen bonds in thiosemicarbazide [11] where they are responsible for the *trans*-conformation of the hydrazine NH$_2$ group with respect to the thione sulphur atom.

Centrosymmetric dimers with N–H···N hydrogen bonds, involving both the imino- and the amino-nitrogen atoms, are present in compound (I) (Figure 1), with the hydrogen atom of the $>$N–H group pointing in the direction of the lone pair of the NH$_2$ group [H(1)···N(2$^{\mathrm{III}}$)–N(1$^{\mathrm{III}}$) 99°, H(1)···N(2$^{\mathrm{III}}$)–H(21$^{\mathrm{III}}$) 129°, H(1)···N(2$^{\mathrm{III}}$)–H(22$^{\mathrm{III}}$) 109°]. In this case, however, there is no possibility of bifurcation and the NH$_2$ group is *cis* with respect to the thione sulphur. The methyl group is *trans* with respect to the same sulphur atom.

TABLE 10

Hydrogen bonds and short intermolecular contacts (distances Å, angles °)

(*a*) Hydrogen bonds

(i) Compound (I)

N(2)···S(2$^{\mathrm{I}}$)	3.555(5)	N(2)–H(21)···S(2$^{\mathrm{I}}$)	129(1)
H(21)···S(2$^{\mathrm{I}}$)	2.90(1)	H(21)–N(2)···S(2$^{\mathrm{I}}$)	39(1)
N(2)···S(2$^{\mathrm{II}}$)	3.598(2)	N(2)–H(22)···S(2$^{\mathrm{II}}$)	151(2)
H(22)···S(2$^{\mathrm{II}}$)	2.73(2)	H(22)–N(2)···S(2$^{\mathrm{II}}$)	22(1)
N(1)···N(2$^{\mathrm{III}}$)	2.968(4)	N(1)–H(1)···N(2$^{\mathrm{III}}$)	145(2)
H(1)···N(2$^{\mathrm{III}}$)	2.21(2)	H(1)–N(1)···N(2$^{\mathrm{III}}$)	25(1)

(ii) Compound (II)

N(1)···S(2$^{\mathrm{I}}$)	3.480(4)	N(1)–H(1)···S(2$^{\mathrm{I}}$)	166(2)
H(1)···S(2$^{\mathrm{I}}$)	2.46(3)	H(1)–N(1)···S(2$^{\mathrm{I}}$)	10(2)

(iii) Compound (III)

N(2)···S(2$^{\mathrm{IV}}$)	3.522(3)	N(2)–H(22)···S(2$^{\mathrm{IV}}$)	142(2)
H(22)···S(2$^{\mathrm{IV}}$)	2.79(3)	H(22)–N(2)···S(2$^{\mathrm{IV}}$)	29(2)
N(2)···S(2$^{\mathrm{V}}$)	3.639(3)	N(2)–H(21)···S(2$^{\mathrm{V}}$)	151(2)
H(21)···S(2$^{\mathrm{V}}$)	2.82(3)	H(21)–N(2)···S(2$^{\mathrm{V}}$)	22(2)

(*b*) Short intermolecular contacts

(i) Compound (I)

N(2)···S(1$^{\mathrm{II}}$)	3.582(3)	N(1)···S(1$^{\mathrm{VII}}$)	3.673(2)
N(1)···S(1$^{\mathrm{VI}}$)	3.636(2)		

(ii) Compound (II)

N(1)···C(1$^{\mathrm{VIII}}$)	3.675(6)

(iii) Compound (III)

N(2)···S(2$^{\mathrm{IX}}$)	3.583(3)

Roman numeral superscripts denote the following equivalent positions:

I	$-x, 1 - y, -z$	VI	$\frac{1}{2} - x, \frac{1}{2} - y, -z$
II	$x, 1 + y, z$	VII	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
III	$\frac{1}{2} - x, \frac{3}{2} - y, -z$	VIII	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
IV	$x, \frac{1}{2} - y, \frac{1}{2} + z$	IX	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
V	$1 - x, 1 - y, -z$		

In the case of thiocarbonohydrazide [12] the molecule assumes a *cis,trans*-conformation which allows the formation of centrosymmetric dimers bound by N–H···S hydrogen bonds. Hydrogen bonds of the same N–H···S type are present in compound (II) (Figure 2), where the presence of the methyl groups at the terminal nitrogen does not allow the formation of N–H···N hydrogen bonds. In order for the observed dimerization to occur the NMe$_2$ group must be *trans* with respect to C=S. The same molecular conformation with the same kind of dimers is also present in Ph$_2$N·NH·C(⁚S)SMe.[13]

In compound (III) methylation of the imino-nitrogen atom reduces the possibility of hydrogen bonding, but

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[13] L. Gastaldi and P. Porta, *Cryst. Struct. Comm.*, 1975, **4**, 721.

nevertheless this does occur, between the terminal NH$_2$ group and the thione sulphur (Figure 3), because the NH$_2$ group is *trans* with respect to C=S.

These differences in conformation in the esters are not accompanied by significant differences in bond distances, and similarly the presence of substituents does not influence these parameters. Only the angles N(1)–C(2)–S(1) and S(1)–C(2)–S(2) differ significantly probably as a consequence of steric effects involving the SMe methyl group. In all these compounds the hydrogen atoms of the SMe group are gauche with respect to the S(1)–C(1) bond, irrespective of the position of the methyl group relative to C=S (Table 7).

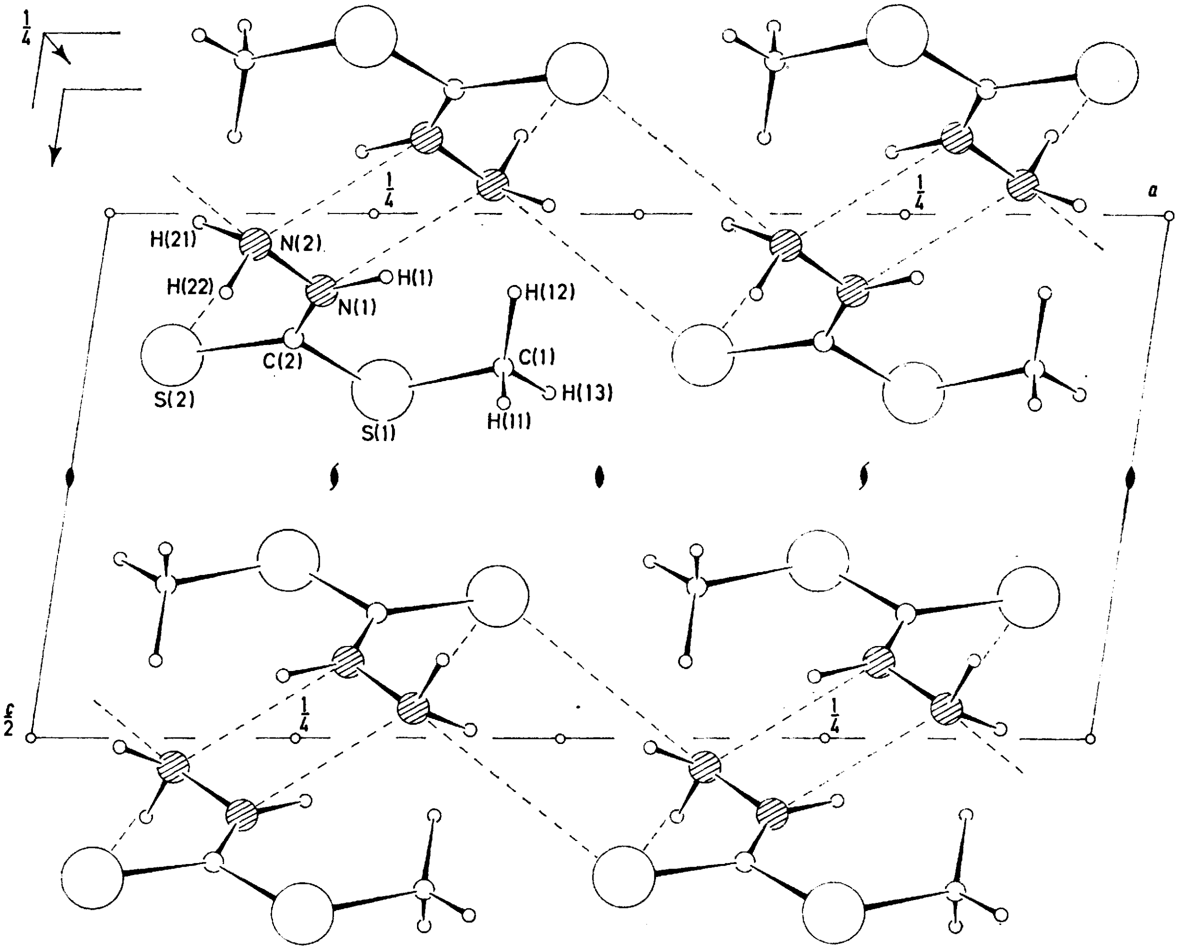

FIGURE 4 Packing of (I): zig-zag chains run along [100] due to N–H · · · S hydrogen bonds formed by the terminal NH$_2$ groups

The N(1),C(2),S(1),S(2) system is planar in all these compounds, even where there are significant differences in the values of the angles around C(2). An analysis of planarity (Table 8) shows that the plane running through NCSS leaves the terminal nitrogen atom and the carbon atom of the SMe group on opposite sides in compound (I), and on the same side in (II) and (III). The structure analysis confirms the conjugation already observed [14] in the NCSS group and suggested also by the i.r. spectra, as can be seen from the data of Table 9 where stretching ν(C–N) bands are correlated with the C–N bond distances. The esters containing the NH·C(:S)SMe moiety [(I) and (II)] have higher values of ν(C–N) with respect to compound (III), as a consequence of the coupling of ν(C–N) with δ(N–H).

The values of the stretching frequencies ν(N–N) for (I)—(III) and for Ph$_2$N·NH·C(:S)SMe are 975, 950, 975, and 960 cm^{-1}, corresponding N–N distances being 1.415(3), 1.424(6), 1.412(3), and 1.410(7) Å.[13] These frequencies and distances are higher than those observed for hydrazine in the solid state: [ν(N–N) 885 cm^{-1} (ref. 15), N–N 1.46 Å (ref. 16)] indicating a reduction of the repulsion between the lone pairs at the nitrogen atoms, the lone pair at the imino-nitrogen being now involved in conjugation with the C(:S)S group. The ν(N–N) frequency is not influenced by substitution at the terminal nitrogen, and the stretching frequencies ν(N–H)-(imino) for compound (II) and for Ph$_2$N·NH·C(:S)SMe are equal (3 125 cm^{-1}). These facts are consistent with

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[14] A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and F. Logiudice, *Acta Cryst.*, 1969, **B25**, 93.

[15] J. Goubeau and U. Kull, *Z. anorg. Chem.*, 1962, **316**, 182.

[16] R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, 1951, **4**, 10.

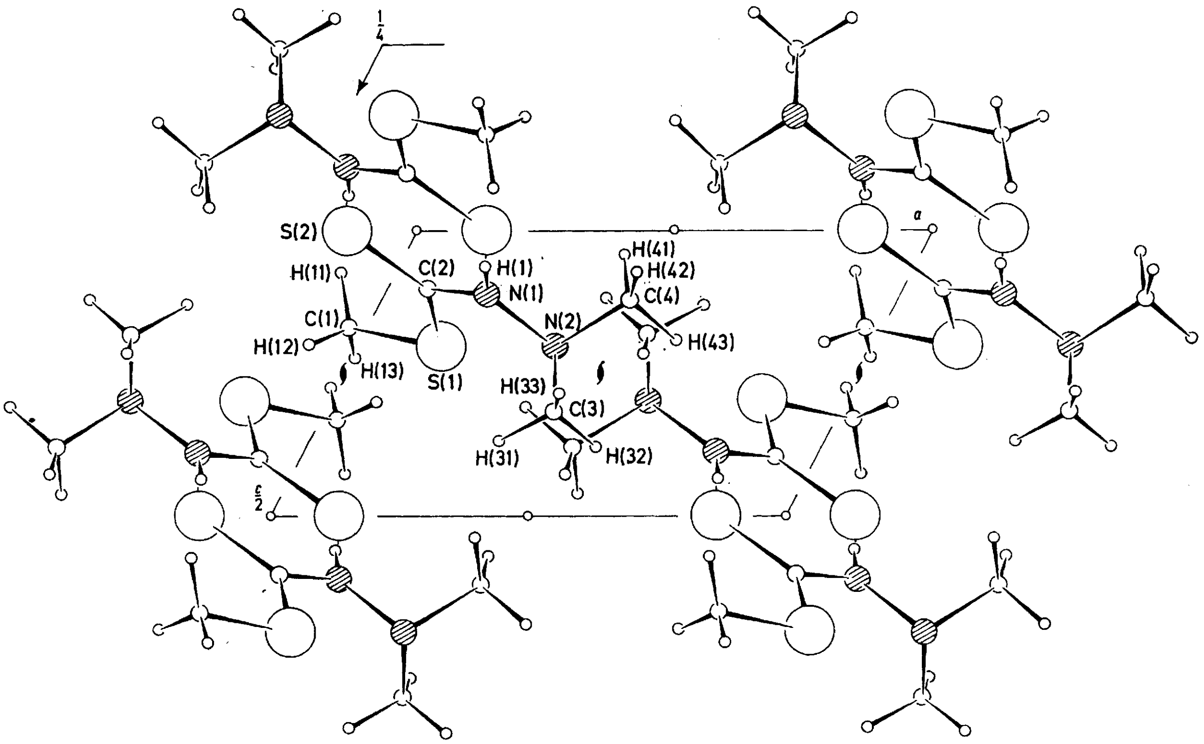

FIGURE 5 Packing of (II): van der Waals contacts between dimers

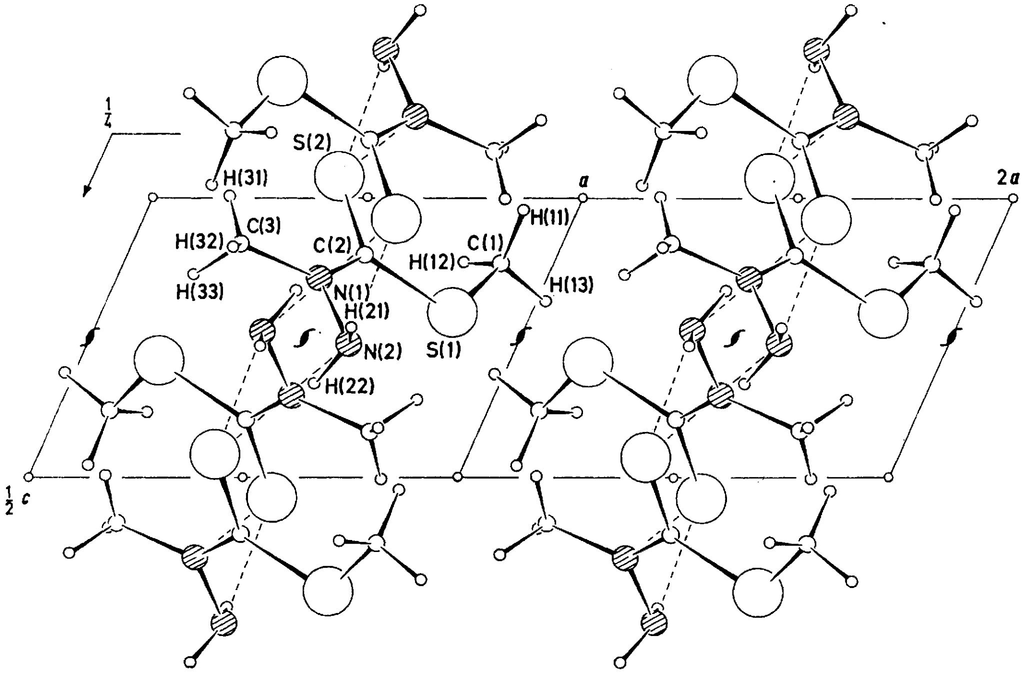

FIGURE 6 Packing of (III): chains of dimers joined together by N–H · · · S hydrogen bonds

a low electron transmission along N–N as already observed for these compounds from ESCA measurements.[3] The packing of the hydrogen-bonded dimers of (I) and (III) is due to hydrogen-bond interactions N–H · · · S involving the terminal nitrogen and sulphur, while for (II) it is due to van der Waals contacts (Figures 4—6, Table 10).

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