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Structures of Linear Multisulfur Systems. VII. The Crystal and Molecular Structure of 3,5-Bis(*N*,*N*-diisopropylthiocarbamoylimino)-4-methyl-1,2,4-dithiazolidine, $C_{17}H_{31}N_5S_4$

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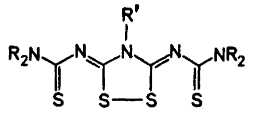
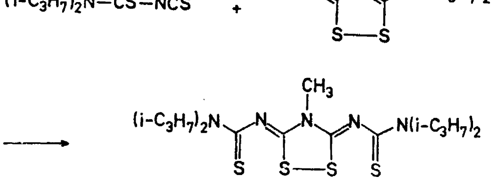
Crystals of the title compound, $C_{17}H_{31}N_5S_4$, are orthorhombic, space group *Pbcn*, with a unit cell of dimensions $a = 25.097(4)$ Å, $b = 8.451(2)$ Å, $c = 10.679(4)$ Å. X-Ray data were collected on an off-line four-circle diffractometer. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares to a final *R* factor of 0.048. The molecule lies on a two-fold axis. The four sulfur atoms are almost collinearly arranged at distances in the region between single bond and van der Waals distance, the central S – S being 2.167 Å and the terminal S – S distances, related by the two-fold axis, are 2.763 Å.

By autoxidation in solution several 1,1,5-trisubstituted dithiobiurets form orange compounds which have been identified as 3,5-bis(*N*,*N*-thiocarbamoylimino)-1,2,4-dithiazolidines (I).[1,2]

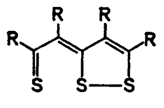


(I)

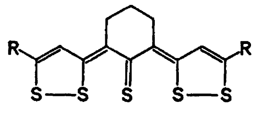
The present compound, however, has been synthesized according to another method recently published.[1]



This type of compounds may possibly possess partial bonding between all four sulfur atoms in the row. Such a bonding scheme would be in analogy with the S – S bonding in thiathiophthenes (II)[3] and in linear five-sulfur systems (III).[4,5] The present structure determination was undertaken primarily to study the sulfur bonding system.



(II)



(III)

EXPERIMENTAL

A crystalline sample of the compound was provided by Dr. J. Goerdeler, University of Bonn. A single crystal of dimensions 0.20 mm × 0.30 mm × 0.55 mm was mounted along the largest dimension, parallel to the crystallographic *c*-axis, and was used for all X-ray experiments. The space group was determined from Weissenberg and precession photographs. Cell dimensions were calculated from diffractometer measurements of setting angles for 12 reflections. 2589 independent reflections with $2\theta \leq 55°$ were recorded on a four-circle diffractometer using $\theta - 2\theta$ scan and niobium filtered Mo$K\alpha$ radiation. Scan ranges were calculated according to the relationship $\Delta\theta = A + B \tan \theta$,[6] with constants evaluated after scanning a few reflections manually and recording the widths of the peaks. Two standard reflections monitored throughout the data collection indicated no deterioration of the crystal. S.d. in the intensities were evaluated as $\sigma_I = [\sigma_c^2 + (0.03N_{\text{net}})^2]^{\frac{1}{2}}$, where σ_c is the error due to counting statistics. Standard deviations in structure factors were calculated as $\sigma_F = \sigma_I / 2(ILp)^{\frac{1}{2}}$. 609 reflections had net counts less than $2\sigma_c$. These reflections were assigned the threshold value $2\sigma_c$ and were given zero weight in the refinement unless $|F_c| > |F_{\text{threshold}}|$. Data were corrected for Lorentz and polarization effects according to standard procedures, and for absorption by the method described by Coppens *et al.*[7]

CRYSTAL DATA

$C_{17}H_{31}N_5S_4$; *M.W.* = 433.73; crystal system orthorhombic; space group *Pbcn*; cell dimensions:

$a = 25.097(4)$ Å, $b = 8.451(2)$ Å, $c = 10.670(4)$ Å. $V = 2263(1)$ Å^3; $D_x = 1.273$ g cm^{-3}; $D_m = 1.268$ g cm^{-3}; $Z = 4$; $F_{000} = 928$; $\mu_{(\text{Mo}K\alpha)} = 4.2$ cm^{-1}.

STRUCTURE DETERMINATION, REFINEMENT AND THERMAL ANALYSIS

The structure was solved by application of the symbolic addition procedure using a computer program written by Long.[8] Signs for 148 reflections were derived. An E-map calculated from the most probable set of signs revealed all non-hydrogen atoms. The structure was refined by full-matrix least-squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. At an R of 0.15, $(R = \sum||F_o| - |F_c||/\sum|F_o|)$, anisotropic temperature factors were introduced. The hydrogen atoms were localized from a difference Fourier map; positional and isotropic thermal parameters were refined. The molecule is lying on a crystallographic two-fold axis; the axis going through C(9), N(3) and the middle of the S(2) – S(2)′ bond (Fig. 1). Thus, the hydrogen atoms on the methyl group C(9) are disordered. In the difference map six methyl hydrogen sites could be distinguished. The three fractional hydrogen atoms in one asymmetric unit were included with occupancy factors of 0.5 and successfully refined. The refinement converged at an R of 0.048, the weighted R factor is 0.056, and the s.d. of an observation of unit weight $(s = |\sum w(|F_o| - |F_c|)^2 (m-n)|^{\frac{1}{2}})$, is 2.86. At this stage all shifts in non-hydrogen parameters were less than 0.2σ, and in hydrogen parameters less than 0.7σ. By comparing observed and calculated structure factors, no evidence of extinction was found.

A residual difference map calculated at the end of the refinement revealed a region of electron density 0.32 e Å^{-3} between S(1) and S(2) and another peak of density 0.56 e Å^{-3} between S(2) and S(2)′. The data included

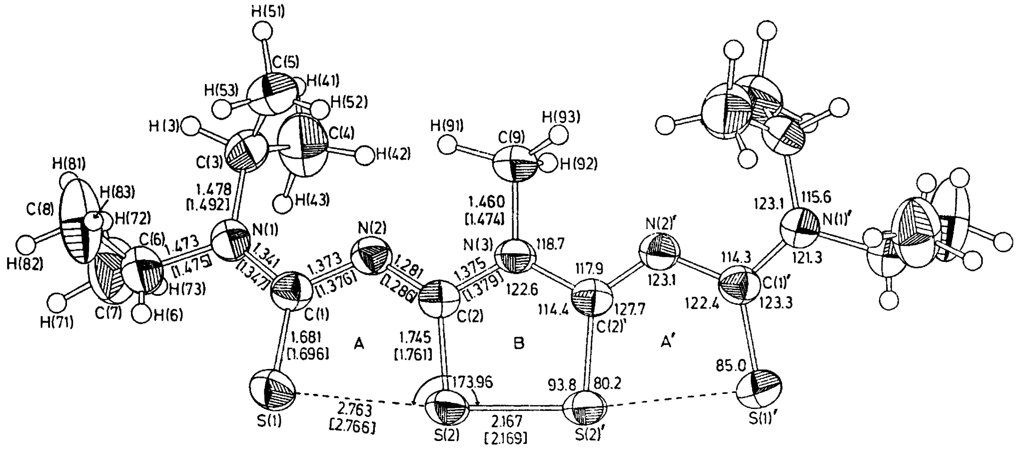


Fig. 1. Selected intramolecular distances and angles. Distances corrected for rigid body motion are shown in brackets. Standard deviations in S – S, S – C and C – N bonds as calculated from the least-squares inverse matrix are 0.001, 0.003, and 0.003 Å, respectively. Standard deviations in S···S – S and C – S – S angles are 0.03 and 0.1°; and 0.2° in angles at carbon and nitrogen. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50 % probability level. Only one set of the disordered hydrogen atoms on C(9) are included; the other set is obtained by a two-fold rotation around the N(3) – C(9) bond.

Table 1. Fractional coordinates and thermal parameters for non-hydrogen atoms with standard deviations. Thermal parameters are of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$, and the values are multiplied by a factor of 10^4.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	0.39859(3)	0.13653(8)	−.01841(8)	638(5)	412(4)	672(4)	−35(4)	137(4)	−109(4)
S(2)	0.47181(3)	0.17027(7)	0.17311(8)	475(4)	310(3)	712(5)	−17(3)	49(3)	−94(4)
N(1)	0.35798(9)	−.15455(25)	−.01178(22)	499(13)	437(12)	553(14)	−37(10)	54(11)	−119(11)
N(2)	0.43194(8)	−.11831(24)	0.10891(22)	410(12)	367(11)	517(14)	−22(9)	26(10)	−20(11)
N(3)	0.50000(0)	−.11336(32)	0.25000(0)	381(16)	295(14)	571(20)	0(0)	0(0)	−30(15)
C(1)	0.39563(10)	−.05350(29)	0.02745(26)	399(14)	396(13)	482(15)	−9(11)	1(12)	25(13)
C(2)	0.46507(9)	−.03521(27)	0.17232(24)	357(13)	369(13)	417(14)	−19(10)	6(11)	67(12)
C(3)	0.35774(13)	−.32432(34)	0.02133(33)	614(19)	436(16)	745(23)	−152(14)	51(16)	−199(17)
C(4)	0.34686(18)	−.35313(60)	0.15951(43)	799(27)	946(32)	871(30)	−331(26)	387(26)	−164(24)
C(5)	0.40535(19)	−.41291(47)	−.03095(48)	856(29)	494(20)	1059(34)	33(20)	−168(21)	−273(27)
C(6)	0.31409(15)	−.10184(46)	−.09335(39)	637(22)	572(21)	789(27)	−25(17)	77(19)	−253(19)
C(7)	0.26029(18)	−.12161(86)	−.03179(57)	609(25)	1226(46)	967(37)	231(28)	−225(35)	−144(24)
C(8)	0.31587(25)	−.18117(99)	−.22016(46)	743(33)	1908(72)	527(26)	123(40)	108(33)	−179(23)
C(9)	0.50000(0)	−.28611(51)	0.25000(0)	652(34)	327(21)	873(46)	0(0)	0(0)	−209(34)

Table 2. Fractional atomic coordinates and thermal parameters for hydrogen atoms with the corresponding standard deviations. Thermal parameters are of the form: $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$ and are multiplied by 10^3.

Atom	X/a	Y/b	Z/c	U	Atom	X/a	Y/b	Z/c	U
H(3)	0.3293(12)	−.3741(34)	−.0276(30)	65(9)	H(71)	0.2291(19)	−.0660(50)	−.0770(43)	130(17)
H(41)	0.3372(18)	−.4643(62)	0.1673(47)	136(18)	H(72)	0.2553(21)	−.2145(59)	−.0406(51)	119(23)
H(42)	0.3793(13)	−.3300(35)	0.2130(32)	66(10)	H(73)	0.2612(17)	−.1027(51)	0.0548(48)	113(18)
H(43)	0.3174(23)	−.2535(77)	0.1809(54)	183(24)	H(81)	0.3066(33)	−.2521(98)	−.2209(79)	220(53)
H(51)	0.3927(16)	−.5336(61)	−.0234(41)	122(15)	H(82)	0.2902(16)	−.1368(41)	−.2717(37)	77(11)
H(52)	0.4351(13)	−.3793(36)	−.0008(30)	59(10)	H(83)	0.3442(23)	−.1692(62)	−.2594(51)	134(22)
H(53)	0.4033(18)	−.3754(47)	−.1289(46)	114(15)	H(91)	0.4636(27)	−.3259(78)	0.1886(70)	105(22)
H(6)	0.3201(16)	−.0183(52)	−.1076(45)	107(17)	H(92)	0.4920(28)	−.2997(68)	0.3311(53)	59(21)
					H(93)	0.5405(35)	−.3301(80)	0.2510(79)	101(28)

extend slightly beyond the limit of the copper sphere, and in similar compounds where comparable or less amounts of data are used, the residual electron density near the sulfur atoms is less than 0.2 e Å^{-3}. Hence it is unlikely that the peaks in this case are due to Fourier series termination errors. One possible explanation could be that not only the methyl group, but the whole molecule is disordered around the two-fold axis. Such a disorder may also explain the fairly large thermal parameters observed. Any deviation from exact two-fold symmetry is too small, however, to be resolved by ordinary refinement methods.

Atomic scattering factors used were for sulfur, nitrogen, and carbon those of Hanson *et al.*[9] and for hydrogen those of Stewart *et al.*[10]

Final coordinates and thermal parameters are listed in Tables 1 and 2. Lists of observed and calculated structure factors may be obtained from the author.

The thermal parameters of the 11 atoms in rings A + B + A′ (Fig. 1) were analyzed in terms of rigid body motion according to the method of Schomaker and Trueblood.[11] The r.m.s. difference between observed U_{ij}'s and those calculated from the derived **T**, **L**, **S** molecular tensors is 0.0026 Å^2. The maximum angle of vibration is 7.8°; the principal axis of libration being approximately parallel to the S(2) – S(2)′ direction. Bond distances corrected according to this model using the method of Cruickshank[12] are shown in brackets in Fig. 1. Corrections of bond lengths involving the atoms in the isopropyl groups are probably underestimated as these atoms presumably have additional riding motion.

All calculations were carried out on a UNIVAC 1110 computer. The programs, except when otherwise noted, have been made available by the Chemistry Department, Weizmann Institute of Science, Rehovoth, Israel; or have been written by K. Maartmann-Moe of this Department.

RESULTS AND DISCUSSION

In Fig. 1 intramolecular distances and angles except those involving the methyl and isopropyl groups, are shown. The remaining bond distances and angles are listed in Tables 3 and 4.

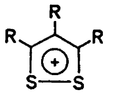
The four sulfur atoms are approximately collinear, the angle S(1) – S(2) – S(2)′ being 173.96(3)°. The terminal S···S distances of 2.763(1) Å are appreciably shorter than van der Waals contact of 3.40 Å,[13] and also shorter than Huggin's constant energy distance of 2.94 Å.[14] In comparison the longest S – S distance observed in any of the unsymmetrically substituted thiathiophthenes (II) determined so far, is 2.56 Å.[15] The central sulfur-sulfur bond distance, S(2) – S(2)′ in the dithiazolidine ring, of 2.167(1) Å is significantly longer than corresponding distances in unsaturated five-membered cyclic disulfides like, *e.g.*, the dithiolium ion (IV), the thiuret ion (V), rhodan hydrate and xanthan hydride (VI), where bond lengths in the range 2.00 – 2.08 Å have been found.[16] S(2) – S(2)′ is also significantly longer than the accepted single bond distance of 2.10 Å.[16]

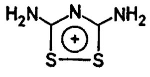
Table 3. C – C and C – H bond distances with the corresponding standard deviations in parentheses. C – C bond lengths corrected for rigid body motion are listed in brackets.

	(Å)		(Å)
C(3) – C(4)	1.519(6)[1.531]	C(6) – H(6)	0.74(5)
C(3) – C(5)	1.516(6)[1.530]	C(7) – H(71)	1.03(5)
C(6) – C(7)	1.511(6)[1.524]	C(7) – H(72)	0.80(5)
C(6) – C(8)	1.511(8)[1.521]	C(7) – H(73)	0.94(5)
C(3) – H(3)	0.98(3)	C(8) – H(81)	0.65(9)
C(4) – H(41)	0.97(5)	C(8) – H(82)	0.92(5)
C(4) – H(42)	1.01(4)	C(8) – H(83)	0.83(6)
C(4) – H(43)	1.14(6)	C(9) – H(91)	1.17(10)
C(5) – H(51)	1.07(5)	C(9) – H(92)	0.90(10)
C(5) – H(52)	0.86(4)	C(9) – H(93)	1.07(10)
C(5) – H(53)	1.09(5)		

Table 4. Bond angles in the methyl group and isopropyl groups. Standard deviations in parentheses.

Angle	(°)	Angle	(°)
N(1) – C(3) – C(4)	112.9(3)	N(1) – C(6) – H(6)	105(3)
N(1) – C(3) – C(5)	112.8(3)	C(7) – C(6) – H(6)	112(3)
C(4) – C(3) – C(5)	114.8(3)	C(8) – C(6) – H(6)	104(4)
N(1) – C(3) – H(3)	107(2)	C(6) – C(7) – H(71)	115(3)
C(4) – C(3) – H(3)	108(2)	C(6) – C(7) – H(72)	101(4)
C(5) – C(3) – H(3)	100(2)	C(6) – C(7) – H(73)	113(3)
C(3) – C(4) – H(41)	106(3)	H(71) – C(7) – H(72)	106(5)
C(3) – C(4) – H(42)	112(2)	H(71) – C(7) – H(73)	114(4)
C(3) – C(4) – H(43)	101(3)	H(72) – C(7) – H(73)	107(5)
H(41) – C(4) – H(42)	110(3)	C(6) – C(8) – H(81)	114(8)
H(41) – C(4) – H(43)	122(4)	C(6) – C(8) – H(82)	109(3)
H(42) – C(4) – H(43)	105(3)	C(6) – C(8) – H(83)	115(4)
C(3) – C(5) – H(51)	102(2)	H(81) – C(8) – H(82)	97(8)
C(3) – C(5) – H(52)	112(2)	H(81) – C(8) – H(83)	115(8)
C(3) – C(5) – H(53)	100(2)	H(82) – C(8) – H(83)	104(5)
H(51) – C(5) – H(52)	123(3)	N(3) – C(9) – H(91)	107(3)
H(51) – C(5) – H(53)	109(3)	N(3) – C(9) – H(92)	97(4)
H(52) – C(5) – H(53)	108(3)	N(3) – C(9) – H(93)	110(6)
N(1) – C(6) – C(7)	112.2(3)	H(91) – C(9) – H(92)	109(6)
N(1) – C(6) – C(8)	111.9(4)	H(91) – C(9) – H(93)	129(8)
C(7) – C(6) – C(8)	111.5(4)	H(92) – C(9) – H(93)	100(9)


(IV)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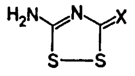
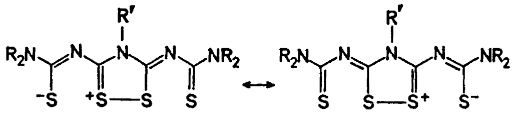
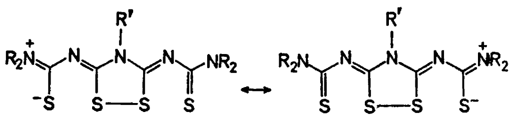

(VI)

X = O or S

Evidently, the interaction between S(1) and S(2) and between S(1)′ and S(2)′ is sufficiently strong to significantly influence the central S(2) – S(2)′ bond. Thus, one may envisage a sulfur-sulfur bonding scheme with delocalized σ-bonding across all four atoms in the row. It is possible that the interaction between the outer sulfur atoms, S(1)···S(2) and S(2)′···S(1)′, is partly caused by an electrostatic interaction.


(VIIa) (VIIb)


(VIIIa) (VIIIb)

In valence bond language this may be depicted by contribution of, *e.g.*, the following resonance forms in which the terminal sulfur atoms are negatively charged (VII a – b, and VIIIa – b).

This is consistent with the results from semiempirical molecular orbital calculations by the CNDO/2 method, in which the terminal sulfur atoms are found to carry a negative charge of 0.44 electrons.[17]

The S – S distances observed in the present compound agree well with those found in a closely related symmetrical dithiazolidine molecule studied by Flippen [2.784(3) Å, 2.171(3) Å, 2.784(3) Å].[18] In another symmetrically substituted compound where no crystallographic symmetry was imposed on the molecule, a slightly asymmetric arrangement was observed in the sulfur sequence, the bond distances being 2.742(5) Å, 2.161(5) Å, 2.785(5) Å.[18]

The $S-C_{sp^2}$ and $N-C_{sp^2}$ bond distances are all in the region between single bonds and double bonds; indicating π-conjugation throughout the system. This is also in good agreement with findings in the two structures mentioned above.[18] Rings A + B + A′ of the molecule may be considered as a delocalized π-system involving 14 electrons. As indicated by the short exocyclic $N-C_{sp^2}$ bond the two π-electrons on

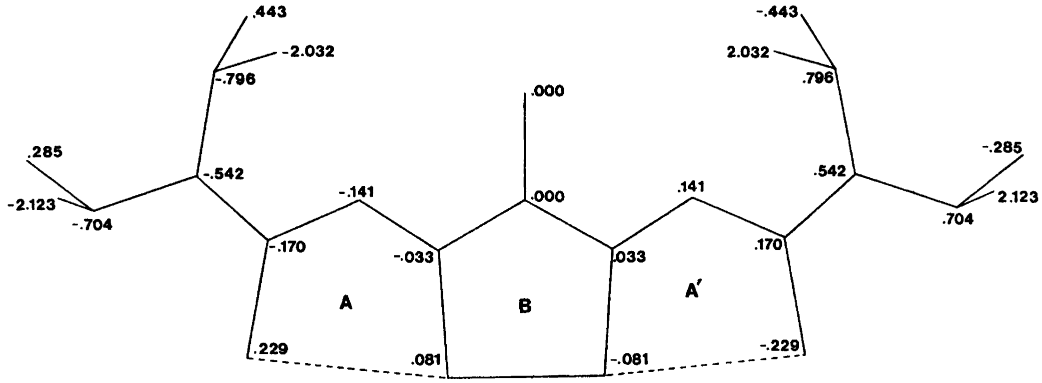


Fig. 2. Deviations from the best least-squares plane through the 11 atoms of rings A+B+A′.

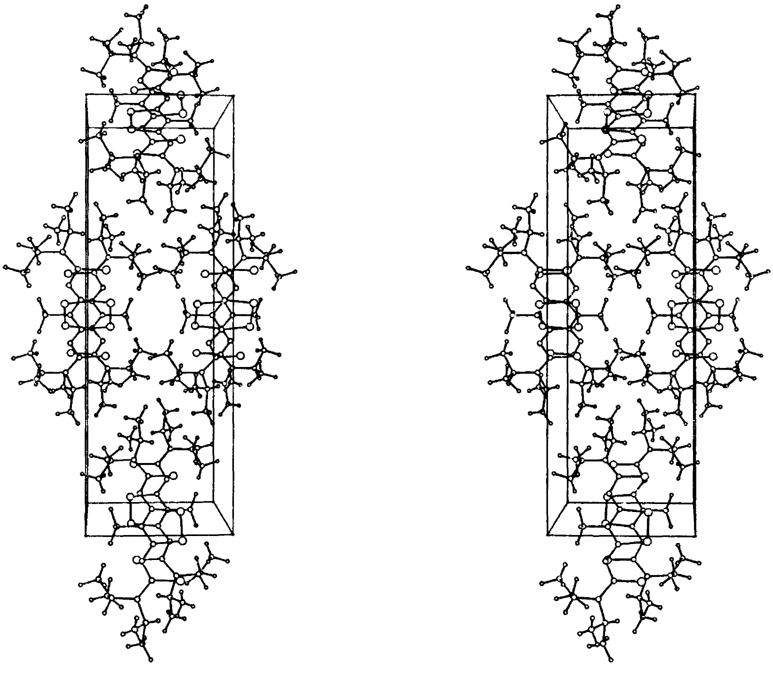


Fig. 3. Stereoscopic view of the molecular packing. The *a*-axis is vertical, top to bottom; the *b*-axis is horisontal, left to right; and the *c*-axis is pointing towards the viewer. Figs. 1 and 3 are drawn by computer using the ORTEP program.[19]

each of the atoms N(1) and N(1)′ also participate in the delocalized π-system giving a total of 18 π-electrons. The average $N-C_{sp^3}$ bond in the present structure is 1.470 Å (1.480 Å after correction for rigid body motion), and the average $C_{sp^3}-C_{sp^3}$ bond length is 1.514 Å (1.527 Å with RBM correction).

The bulky substituents introduce overcrowding in the molecule. A best least-squares plane fitted to the 11 atoms of ring A+B+A′ shows that this part of the molecule deviates significantly from planarity (Fig. 2). There is a twist of the molecule around the C(2)···C(2)′ direction; the dihedral angle between rings A and A′

being 15.5°. The substituent on C(1) is bent out of the plane of ring A; N(1), C(3) and C(6) deviating 0.362, 0.419, and 0.603 Å, respectively, from plane A. The double bond character of the C(1) – N(1) bond effectively prevents the group from being twisted around this bond. Despite the imposed molecular deformation there still remain some short intramolecular contacts; S(1)···H(6) = 2.55(4) Å, H(91)···H(42) = 2.13(8) Å, H(91)···H(52) = 2.19(8) Å and H(93)···H (42′ = 2.06(10) Å.

A stereo drawing of the molecular packing in the crystal is shown in Fig. 3. Molecules related by the crystallographic *c*-glide are stacked on top of one another; partially overlapping at an interplanar distance of 3.71 Å. There are no intermolecular contacts shorter than van der Waals distances.

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