Capto-dative Substitution and Cyclopropane Geometry. Part 2.[1] *X*-Ray Structure of *cis*-1,2-Dicyano-1,2-bis(phenylthio)cyclopropane, $C_{17}H_{12}N_2S_2$

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The crystal and molecular structure of the title compound has been determined from *X*-ray diffraction data using direct methods and least-squares refinement. The crystals are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 17.775(9)$, $b = 6.965(4)$, $c = 12.994(5)$ Å, $\beta = 101.57(4)°$. Using 1 507 independent reflections with $I \geqslant 2.5\sigma(I)$ the structure was refined to $R = 0.046$ and $R_w = 0.054$. The ring bond-lengths are very similar to those observed in 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane. This confirms electron-density transfer from cyclopropyl to the substituents in capto-dative substituted cyclopropanes. The structure of the *trans* isomer has been also determined but it appears to be disordered.

The structure of the title compound has been investigated as part of a study of capto-dative (*cd*) (here *c* =CN, *d* = SR) substituent effects on cyclopropane geometry. Recently we have reported the structures of three *cd*- or *cc*-substituted cyclopropanes. We have shown that in these derivatives the distal ring bond, opposite to the substituted carbon atom, is shortened and vicinal bonds lengthened.[1] In order to see how the configuration of the substituents can influence the ring bond-length pattern, we decided to compare the geometries of *cis*- and *trans*-1,2-dicyano-1,2-bis(phenylthio)cyclopropane. Unfortunately, we found a disordered structure for the *trans* isomer and the ring bond-distances that we determined are of too poor a precision to be useful in a comparative analysis.† Nevertheless, we compared the structure of the *cis* isomer with that 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane for which the configuration of the bulky SR groups was *trans* and for which the electronic effects of t-butylthio- and phenylthio-substituents are similar.[1]

Experimental

The compound was recrystallized from ether–light petroleum to give colourless parallelepipeds. Crystal data: $C_{17}H_{12}N_2S_2$, $M = 308.43$, monoclinic, space group $P2_1/n$, $a = 17.775(9)$, $b = 6.965(4)$, $c = 12.994(5)$ Å, $\beta = 101.57°$, $U = 1\ 576.1$ Å^3, $D_c = 1.30$ g cm^{-3}, $Z = 4$. Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, $\mu = 3.25$ cm^{-1}.

The unit cell parameters and their standard deviations were obtained by a least-squares best fit to the setting angles of 15 reflections with values of 2θ between 5 and 20°; 2 340 independent reflections were collected on a Syntex $P2_1$ diffractometer using the ω scan mode and graphite-monochromatized Mo-K_α radiation. Only 1 507 reflections with $I \geqslant 2.5\sigma(I)$ were conserved for the refinement of the structure. Lorentz and polarization corrections were applied but no absorption corrections were made.

The structure was solved by the direct MULTAN-80 method and refined by full-matrix least-squares analysis first with isotropic and then with anisotropic temperature factors using SHELX-76.[3] Hydrogen atoms were located from a difference Fourier synthesis after the sixth refinement cycle at $R = 0.057$. Three further cycles with common isotropic temperature factors, $B = 3.95$ Å^2, for the hydrogen atoms were performed. In this final stage a weighting scheme $w = 1/(\sigma^2 + 0.011\ 14F^2)$ was applied. The final R value was 0.046 and R_w 0.054, for 1 507 reflections. Positional co-ordinates and equivalent isotropic thermal parameters ‡ are given in Table 1.

Table 1. Atomic co-ordinates (× 10^4) and equivalent temperature factors (Å^2)

$$B_{eq} = \tfrac{8}{3}\pi^2\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$$

Atom	*x*	*y*	*z*	B_{eq}
S(1)	4 865(1)	2 003(2)	8 725(1)	4.14
S(2)	5 075(1)	−2 687(2)	8 048(1)	4.14
C(1)	4 903(2)	1 315(6)	7 411(3)	3.43
C(2)	5 021(2)	−814(6)	7 102(3)	3.47
C(3)	5 657(3)	636(7)	7 209(4)	3.88
C(4)	4 415(3)	2 423(7)	6 593(4)	4.35
N(1)	4 025(3)	3 240(8)	5 954(4)	6.59
C(5)	4 626(3)	−1 317(7)	6 060(4)	4.17
N(2)	4 295(3)	−1 737(8)	5 250(4)	6.04
C(6)	3 868(2)	1 789(7)	8 733(3)	3.82
C(7)	3 588(3)	164(8)	9 136(4)	4.54
C(8)	2 829(3)	71(10)	9 201(5)	5.70
C(9)	2 353(3)	1 565(11)	8 872(4)	5.77
C(10)	2 627(3)	3 174(10)	8 472(4)	5.60
C(11)	3 386(3)	3 310(9)	8 405(4)	4.67
C(12)	5 924(2)	−3 844(6)	7 869(3)	3.53
C(13)	6 045(3)	−4 437(8)	6 898(4)	4.68
C(14)	6 716(3)	−5 340(8)	6 808(5)	5.28
C(15)	7 251(3)	−5 725(8)	7 694(6)	5.56
C(16)	7 148(4)	−5 190(9)	8 644(5)	5.65
C(17)	6 486(3)	−4 211(7)	8 746(4)	4.82

Discussion

Figure 1 is a stereoscopic view of the molecule, showing the numbering of the atoms; Figure 2 shows the packing in the unit cell.[5] Bond distances, angles, and selected torsion angles are given in Tables 2—4.

The geometry of the molecule is very similar to that observed for 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane.[1]

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† The structure was solved by MULTAN-80[2] and refined by SHELX-76 program[3] on the basis of 1 181 reflections for which $I \geqslant 2.5\sigma(I)$. Data were collected in the same way as the *cis* isomer. Two positions, with occupation factors 0.53 and 0.47, nearly perpendicular to each other, were found for the cyclopropane ring. The final *R* value is 0.046. Standard deviations of the bond lengths are in the range 0.015—0.022 Å. Crystal data: $C_{17}H_{12}N_2S_2$, $M = 308.43$, orthorhombic, space group $P2_12_12_1$; cell dimensions $a = 9.175(4)$, $b = 14.044(7)$, $c = 12.126(5)$ Å, $U = 1\ 562.5$ Å^3, $Z = 4$. Co-ordinates and geometrical parameters are available from the editorial office.

‡ Lists of structure factors are available from the editorial office on request.

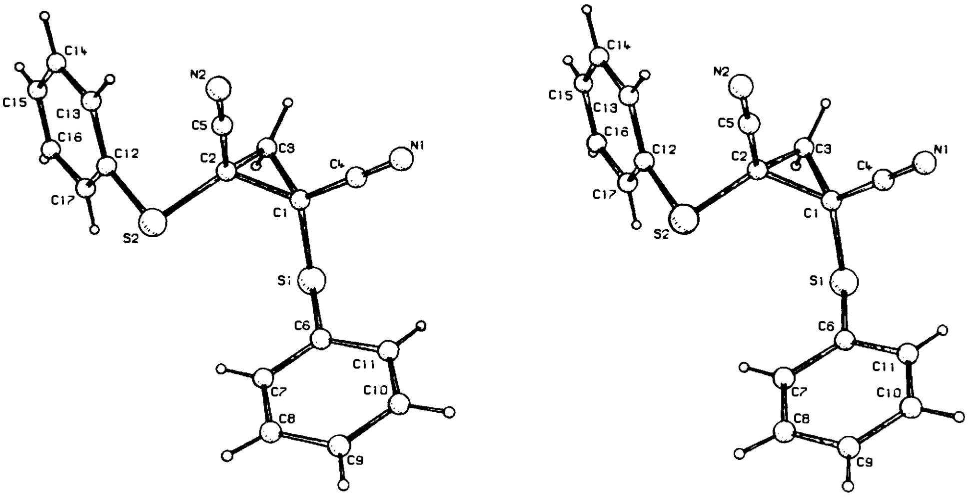

Figure 1. Stereoscopic view of the compound *cis*-1,2-dicyano-1,2-bis(phenylthio)cyclopropane[4]

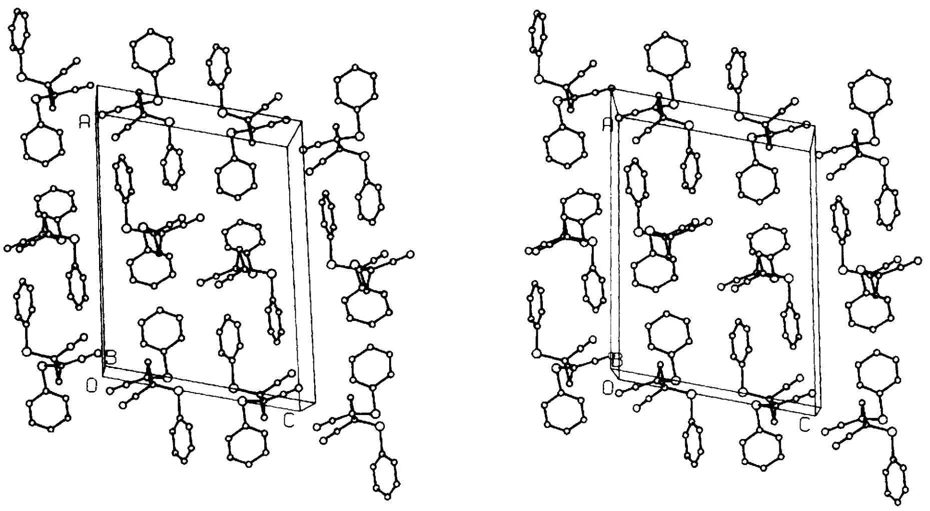

Figure 2. Stereoscopic view showing the unit-cell packing[4]

Table 2. Bond distances (Å)

S(1)–C(1)	1.787(4)	C(6)–C(11)	1.375(7)
S(1)–C(6)	1.781(4)	C(7)–C(8)	1.370(7)
S(2)–C(2)	1.782(4)	C(8)–C(9)	1.355(9)
S(2)–C(12)	1.767(4)	C(9)–C(10)	1.365(9)
C(1)–C(2)	1.561(6)	C(10)–C(11)	1.372(7)
C(1)–C(3)	1.493(6)	C(12)–C(13)	1.385(6)
C(1)–C(4)	1.453(6)	C(12)–C(17)	1.380(7)
C(2)–C(3)	1.501(6)	C(13)–C(14)	1.374(8)
C(2)–C(5)	1.439(7)	C(14)–C(15)	1.364(8)
C(4)–N(1)	1.123(6)	C(15)–C(16)	1.336(8)
C(5)–N(2)	1.136(6)	C(16)–C(17)	1.388(8)
C(6)–C(7)	1.381(7)		

Table 3. Bond angles (°)

C(1)–S(1)–C(6)	102.3(2)	S(1)–C(6)–C(7)	120.3(4)
C(2)–S(2)–C(12)	100.0(2)	S(1)–C(6)–C(11)	119.5(4)
S(1)–C(1)–C(2)	122.2(3)	C(7)–C(6)–C(11)	120.0(5)
S(1)–C(1)–C(3)	117.4(3)	C(6)–C(7)–C(8)	119.7(5)
C(2)–C(1)–C(3)	58.9(3)	C(7)–C(8)–C(9)	120.3(6)
S(1)–C(1)–C(4)	115.1(3)	C(8)–C(9)–C(10)	120.2(5)
C(2)–C(1)–C(4)	114.1(4)	C(9)–C(10)–C(11)	120.7(5)
C(3)–C(1)–C(4)	117.7(4)	C(6)–C(11)–C(10)	119.1(6)
S(2)–C(2)–C(1)	120.6(3)	S(2)–C(12)–C(13)	123.3(4)
S(2)–C(2)–C(3)	119.5(3)	S(2)–C(12)–C(17)	118.1(4)
C(1)–C(2)–C(3)	58.3(3)	C(13)–C(12)–C(17)	118.6(4)
S(2)–C(2)–C(5)	114.8(3)	C(12)–C(13)–C(14)	120.7(5)
C(1)–C(2)–C(5)	114.1(3)	C(13)–C(14)–C(15)	119.2(5)
C(3)–C(2)–C(5)	117.8(4)	C(14)–C(15)–C(16)	121.6(6)
C(1)–C(3)–C(2)	62.8(3)	C(15)–C(16)–C(17)	120.0(6)
C(1)–C(4)–N(1)	178.2(6)	C(12)–C(17)–C(16)	119.9(5)
C(2)–C(5)–N(2)	177.7(5)		

Table 4. Selected torsion angles (°)

C(6)–S(1)–C(1)–C(2)	−90
C(6)–S(1)–C(1)–C(3)	−158
C(6)–S(1)–C(1)–C(4)	56
C(1)–S(1)–C(6)–C(7)	98
C(1)–S(1)–C(6)–C(11)	−86
C(12)–S(2)–C(2)–C(1)	−130
C(12)–S(2)–C(2)–C(3)	−61
C(12)–S(2)–C(2)–C(5)	87
C(2)–S(2)–C(12)–C(13)	−52
C(2)–S(2)–C(12)–C(17)	130
S(1)–C(1)–C(2)–S(2)	3
S(1)–C(1)–C(2)–C(5)	146
C(4)–C(1)–C(2)–S(2)	−143
C(4)–C(1)–C(2)–C(5)	0

Of particular interest is the cyclopropyl ring-bond pattern: all bond lengths agree to within 2σ (Table 5). The distances C(ring)–S and C(phenyl)–S and the angle C(ring)–S–C(phenyl) are also in perfect agreement with the values found in 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane. It can thus be concluded that the configuration of the bulky SR substituents has no effect on the ring bond-lengths.

As for other *cd*-substituted cyclopropanes, we observe a very long C(1)–C(2) bond. In fact it results from distal bond shortening and vicinal bond lengthening. This situation is the same as that observed for π-acceptor substituents.[5,6] Electron density is transfered from the cyclopropyl ring to the substituents.

Table 5. Comparison of ring bond-lengths (Å) between *cis*-1,2-dicyano-1,2-bis(phenylthio)cyclopropane (I) (this work) and 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane (II)[1]

Bond	(I)	(II)
C(1)–C(2)	1.561(6)	1.557(5)
C(1)–C(3)	1.493(6)	1.507(6)
C(2)–C(3)	1.501(6)	1.510(5)
Mean	1.518(4)	1.525(3)

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