Capto-dative Substitution and Cyclopropane Geometry. Part 1. Comparison between Capto-dative and Di-capto Substitution Effects on Cyclopropane Geometry; an *X*-Ray Diffraction Study[†][1]

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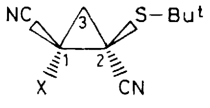
To study capto-dative (*cd*) and di-capto (*cc'*) substitution effects on cyclopropane geometry the crystal and molecular structures of the following three cyclopropane derivatives have been determined from *X*-ray diffraction data: 2-t-butylthio-1-*r*,2-*t*-dicyano-1-methoxycarbonylcyclopropane (**I**); 2-t-butylthio-1-*r*, 2-*t*-dicyano-1-phenylthiocyclopropane (**II**); and 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylcyclopropane (**III**). These structures have been solved by direct methods and refined by least-squares using 1 572, 3 729, and 1 768 reflections, respectively, to R = 4.7, 6.4, and 4.0%. In both capto-dative and di-capto substitution, the distal ring bond is shortened, but the vicinal bonds are lengthened. Although a long C(1)–C(2) ring bond is observed in each compound, this bond is the most stretched one in molecule (**I**) for which the highest activation energy of thermal *cis–trans* isomerisation was determined.

Substituent-induced bond-length variations in cyclopropane derivatives are well documented.[2] The *X*-ray diffraction data afford an important contribution to an interesting subject that is: what is the ability of cyclopropane to conjugate with adjacent substituents?

Allen[2] has shown that π-acceptor substituents shorten the distal ring bond but lengthen the vicinal bonds. For donor and mixed donor–acceptor substituents data are sparse and conclusions less clear; results for *gem* halogeno substitution indicate distal bond lengthening. To our knowledge there are no data available for *gem* donor–acceptor-substituted molecules [(**I**)—(**III**) carrying CN and SR].

It is our objective to determine these data and to compare the geometries of some of these new *cd*-, or *cc'*-, substituted cyclopropanes. Another point of interest is to answer the question of whether the easy isomerisation of the *cd*-substituted cyclopropanes is the result of a longer (weaker) C(1)–C(2) bond. Kinetic results for the thermal *cis–trans* isomerisation of *cd*- and *cc'*-substituted cyclopropanes have recently been reported.[3,4] Replacement of the di-capto substitution by a capto-dative[5] one decreases the activation energy of isomerisation by *ca.* 5 kcal mol^{-1}. This result can be attributed to the stabilisation of the diradical transition state[6,7] by the *cd*-substitution.

In the present study we report the structures of 2-t-butylthio-1-*r*,2-*t*-dicyano-1-methoxycarbonylcyclopropane (**I**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane (**II**), and 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylcyclopropane (**III**).



X
(**I**) CO$_2$Me
(**II**) SPh
(**III**) Ph

Experimental

The syntheses of the new cyclopropanes will be reported later.[8] These compounds were recrystallised from ether–petroleum ether to afford colourless crystals. Crystallographic data are presented in Table 1. The unit-cell parameters and their standard deviations were obtained by least-squares best fit to the setting angles of 15 reflections. Single-crystal *X*-ray diffraction data were collected with a Syntex P2$_1$ diffractometer using scan mode and radiation as described in Table 1. Lorentz and polarization corrections were applied but no absorption corrections were made.

The three structures were solved by direct methods. For (**I**) and (**II**), the application of MULTAN[9] revealed, respectively, 11/16 and 16/38 atoms of the asymmetric units. The remaining atoms were subsequently located by Fourier difference synthesis. For compound (**III**), normalized structure factors indicate $P1$ as the most probable space group and MULTAN gives the positions of the two sulphur atoms (one per independent molecule) in the asymmetric unit. These positions, confirmed by a Patterson synthesis, were correct but, because of an enantiomorph fixation problem, it was not possible to locate other atoms with the DIRDIF procedure.[10] Finally a fragment of six atoms (2S and 4C) was found using a program of tangent refinement of random phases. This fragment was introduced in DIRDIF and 32 atoms of the two independent molecules were located. The remaining six atoms were found on a Fourier difference map.

All three structures were refined by full-matrix least-squares analysis first with isotropic and then anisotropic temperature factors using SHELX-76.[11] Some hydrogen atoms (the numbers of which are indicated in Table 1 for each structure) were then located from a Fourier difference synthesis. Only the positions of these atoms have been included in three further refinement cycles with fixed isotropic temperature factors, B =

[†] Part of these results was presented at the 8th European Crystallographic Meeting (1983), Eighth European Crystallographic Meeting Abstracts, p. 134.

Table 1. Crystal data

Compound	**(I)**	**(II)**	**(III)**
Formula	$C_{11}H_{14}N_2O_2S$	$C_{15}H_{16}N_2S_2$	$C_{15}H_{16}N_2S$
M	238.31	288.44	256.37
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P1$
a (Å)	8.551(1)	11.821(3)	8.910(5)
b (Å)	24.940(6)	10.479(4)	13.703(9)
c (Å)	6.124(1)	25.605(7)	6.252(4)
α (°)			93.18(5)
β (°)	101.77(2)	99.80(2)	80.29(10)
γ (°)			102.92(10)
U (Å^3)	1 278.6(5)	3 125.5(5)	733.2(14)
Z	4	8	2
D_x (g cm^{-3})	1.24	1.23	1.16
$F(000)$	504	1 216	272
X-ray radiation (graphite monochromatized)	Mo-K_α	Cu-K_α	Mo-K_α
λ (Å)	0.710 69	1.5418	0.710 69
Crystal dimensions (mm^3)	0.3 × 0.3 × 0.16	0.25 × 0.28 × 0.20	0.45 × 0.18 × 0.10
μ (cm^{-1})	2.4	28.8	2.0
Scan mode	ω	θ—2θ	ω
2θ range (°)	3—47	3—114	3—47
No. of reflections measured	1 876	4 195	2 154
No. of reflections with $I > 2.5\sigma(I)$ used in structure refinement	1 572	3 729	1 768
No. of observed H	2	14	13
No. of calculated H	12	18	19
R (= $\Sigma\Delta/\Sigma F_o$)	0.047	0.064	0.040
R_w	0.052	0.064	0.041
w	$1/[\sigma^2(F_o) + 0.000\,19F_o^2]$	$1/\sigma^2(F_o)$	$1/[\sigma^2(F_o) + 0.000\,51F_o^2]$

Table 2. Atomic co-ordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2) for (**I**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-methoxycarbonylcyclopropane

	x	y	z	B_{eq}
C(1)	7 883(3)	619(1)	10 184(5)	3.27
C(2)	7 183(3)	1 042(1)	8 319(5)	3.14
C(3)	7 471(4)	467(1)	7 780(5)	3.48
C(4)	6 791(4)	446(1)	11 583(5)	3.85
C(5)	9 593(4)	675(1)	11 280(5)	3.43
C(6)	11 418(4)	848(2)	14 658(6)	5.06
C(7)	8 308(4)	1 434(1)	7 871(5)	3.75
C(8)	5 073(4)	1 841(1)	9 638(5)	3.67
C(9)	6 177(5)	1 798(2)	11 917(6)	5.65
C(10)	5 466(5)	2 338(2)	8 429(7)	5.99
C(11)	3 341(5)	1 859(2)	9 865(9)	6.41
N(1)	5 951(4)	298(1)	12 684(5)	5.41
N(2)	9 151(4)	1 754(1)	7 483(6)	5.63
O(1)	10 656(3)	676(1)	10 254(4)	5.21
O(2)	9 791(3)	730(1)	13 450(4)	4.84
S(2)	5 151(1)	1 236(0)	7 907(1)	3.37

3.95 Å^2. The other hydrogen atoms were calculated at a C–H distance of 1.08 Å from the carbon atom to which they are bonded. In the structure factor calculations these atoms are affected by the same temperature factor, B = 3.95 Å^2. Final R and R_w values are given in Table 1. Atomic co-ordinates for the three compounds are presented in Tables 2, 3, and 4, respectively.

Anistropic thermal parameters are given in Supplementary Publication SUP 56222 (8 pp.).*

Results and Discussion

Interatomic distances and bond angles together with their standard deviations are given in Tables 5 and 6 for the three structures. For compounds (**II**) and (**III**), with two independent molecules per asymmetric unit, we have reported mean bond lengths and angles, because in each case these two molecules have very similar geometries (maximum deviation between individual parameters < 2σ). The numbering of atoms is the same for the three compounds, except for the substituent X. The stereoviews of these structures[12] are given in Figures 1—3 and confirm the *trans* configuration of the nitrile groups.

Except for the cyclopropane ring bonds, to be discussed in detail later, all bond lengths and angles are consistent within the series. Moreover, they are in almost perfect agreement with published values. The mean interatomic distances $C_{(ring)}$–CN and C≡N are 1.445(2) and 1.136(2) Å. These values agree with those reported by Allen[13] for 14 cyanocyclopropanes 1.441(4) and 1.143(3) Å respectively. The distances $C_{(ring)}$–CO_2Me of 1.486(4) and C=O 1.206(4) Å observed for (**I**) are also similar to the means calculated for carbonyl-substituted cyclopropanes, 1.484(4) and 1.209(3) Å.[13]

To the best of our knowledge, there are no structural data available for t-butylthio- or phenylthiocyclo-propanes.[14] The average values of C(2)–S(2) and S(2)–C(8) distances and C(2)–S(2)–C(8) bond angle were determined to be 1.778(2) and 1.853(2) Å and 106.9(1)°, respectively.

For the phenylthio substituent in (**II**), we observed the distances C(1)–S(1) 1.798(4) and S(1)–C(12) 1.778(4) Å and the valence angle C(1)–S(1)–C(12) 101.5(1)°.

Molecular conformations do not present any special feature (Figures 1—3) except that the orientations of the planar ester group in (**I**) or the phenyl group in (**III**) towards the cyclopropyl ring must be described. Indeed cyclopropane–π-acceptor interactions are dependent on the orientation of the π-system. A better orbital mixing, thus a maximum interaction, occurs when the substituent bisects the cyclopropane ring[2] (τ = 0°). The methoxycarbonyl group is nearly in the bisected conformation in (**I**); the value of τ O(1)–C(5)–C(1)–M(1) with M(1) the midpoint of the distal C(2)–C(3) bond is −24°. In molecule (**III**). the phenyl group cannot adopt the bisected conformation; τ

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* For details of the Supplementary Publications Scheme, see Instructions for Authors (1985), section 4.0 (January Issue). Structure factor tables are available from the editorial office on request.

Table 3. Atomic co-ordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2) for (**II**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane

	x	*y*	*z*	B_{eq}	*x*	*y*	*z*	B_{eq}
C(1)	1 094(5)	823(5)	4 064(2)	3.75	3 871(4)	−3 434(5)	5 994(2)	3.55
C(2)	1 766(4)	1 143(5)	3 610(2)	3.60	3 221(4)	−3 108(5)	6 459(2)	3.38
C(3)	1 465(5)	2 169(5)	3 976(3)	4.29	3 542(5)	−2 079(5)	6 098(2)	4.09
C(4)	−101(5)	517(5)	3 918(2)	4.13	5 070(5)	−3 788(5)	6 128(2)	3.76
C(7)	2 949(5)	733(6)	3 686(3)	4.71	2 040(5)	−3 487(5)	6 388(2)	4.02
C(8)	1 442(4)	2 227(5)	2 549(2)	4.16	3 584(5)	−2 044(5)	7 523(2)	4.20
C(9)	671(5)	2 014(7)	2 019(2)	6.11	4 374(5)	−2 246(7)	8 042(2)	6.06
C(10)	1 237(5)	3 543(5)	2 766(3)	5.37	3 760(5)	−741(6)	7 301(3)	5.50
C(11)	2 698(5)	2 070(7)	2 503(3)	5.87	2 342(5)	−2 210(7)	7 580(3)	5.83
C(12)	1 478(5)	−1 589(5)	4 492(2)	4.14	3 381(5)	−5 814(5)	5 530(2)	3.97
C(13)	2 144(6)	−2 273(6)	4 196(2)	5.28	4 131(7)	−6 447(7)	5 262(3)	7.99
C(14)	1 879(9)	−3 556(7)	4 087(3)	6.77	4 349(8)	−7 727(9)	5 343(4)	9.59
C(15)	982(9)	−4 108(8)	4 262(4)	7.69	3 762(8)	−8 374(7)	5 683(4)	7.60
C(16)	303(7)	−3 445(8)	4 560(4)	7.65	3 002(8)	−7 762(8)	5 944(3)	6.99
C(17)	559(6)	−2 174(7)	4 675(3)	6.08	2 817(6)	−6 488(7)	5 865(3)	5.92
N(1)	−1 049(5)	257(5)	3 824(2)	5.69	5 998(4)	−4 079(5)	6 205(2)	5.28
N(2)	3 897(4)	432(5)	3 753(3)	6.55	1 101(4)	−3 779(5)	6 333(2)	5.70
S(1)	1 788(1)	33(2)	4 659(1)	4.90	3 127(1)	−4 159(2)	5 399(1)	4.79
S(2)	978(1)	942(1)	2 957(1)	4.01	4 030(1)	−3 339(1)	7 106(1)	3.70

Table 4. Atomic co-ordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2) for (**III**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylcyclopropane

	x	*y*	*z*	B_{eq}	*x*	*y*	*z*	B_{eq}
S(2)	−1 246(8)	5 743(5)	1 962(11)	4.33	2 216(8)	1 221(5)	6 711(11)	4.56
N(1)	197(9)	7 703(6)	−2 403(14)	4.73	2 329(10)	−543(6)	1 898(14)	4.98
N(2)	2 430(0)	4 824(0)	2 100(0)	6.49	6 479(11)	2 107(7)	7 034(16)	7.13
C(1)	1 736(9)	6 989(6)	22(13)	3.26	4 338(10)	13(6)	4 486(14)	4.48
C(2)	831(10)	6 118(6)	1 568(13)	3.54	4 014(11)	815(6)	6 229(14)	4.71
C(3)	1 411(11)	7 166(6)	2 439(14)	4.13	3 866(12)	−246(6)	6 836(14)	4.61
C(4)	820(10)	7 377(6)	−1 271(14)	3.49	3 154(10)	−278(6)	3 111(15)	3.79
C(7)	1 727(10)	5 396(6)	1 869(14)	4.32	5 417(12)	1 529(7)	6 674(15)	4.81
C(8)	−1 752(10)	4 640(6)	153(14)	4.30	2 456(10)	2 341(6)	5 055(14)	4.34
C(9)	−3 464(11)	4 596(7)	115(17)	6.50	799(12)	2 403(8)	4 999(20)	8.04
C(10)	−1 532(13)	3 698(7)	1 119(17)	6.65	3 340(12)	2 253(7)	2 811(15)	5.96
C(11)	−797(12)	4 792(7)	−2 116(15)	5.97	3 276(14)	3 264(7)	6 239(18)	7.84
C(12)	3 380(10)	6 971(6)	−1 133(13)	3.28	5 990(10)	26(6)	3 382(14)	4.04
C(13)	3 589(11)	6 452(7)	−3 058(14)	4.45	6 898(12)	−534(8)	4 050(16)	6.16
C(14)	5 039(11)	6 439(8)	−4 167(16)	5.67	8 335(12)	−558(8)	2 919(20)	8.26
C(15)	6 337(11)	6 944(7)	−3 324(16)	5.27	8 848(13)	−31(8)	1 058(19)	7.56
C(16)	6 159(11)	7 457(7)	−1 415(16)	5.54	8 020(11)	529(8)	334(16)	5.83
C(17)	4 665(10)	7 477(6)	−286(15)	4.34	6 556(11)	562(7)	1 493(15)	5.13

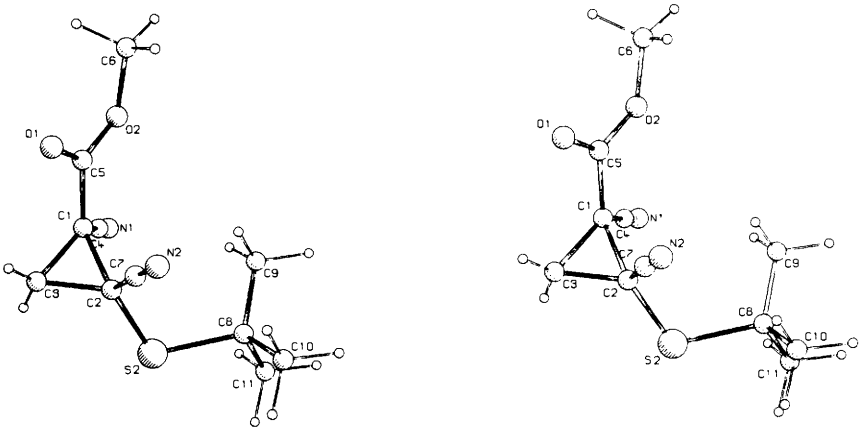


Figure 1. Stereoscopic view of compound (I), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-methoxycarbonylcyclopropane [12]

Table 5. Bond lengths (Å)

	(I)	(II)[a]	(III)[a]
C(1)–C(2)	1.580(4)	1.557(5)	1.555(5)
C(1)–C(3)	1.491(4)	1.507(6)	1.503(6)
C(2)–C(3)	1.503(4)	1.510(5)	1.505(6)
C(1)–C(4)	1.455(4)	1.442(5)	1.442(6)
C(2)–C(7)	1.438(5)	1.438(5)	1.450(7)
C(2)–S(2)	1.772(3)	1.782(4)	1.784(4)
N(1)–C(4)	1.142(4)	1.130(5)	1.134(5)
N(2)–C(7)	1.131(4)	1.142(5)	1.136(6)
S(2)–C(8)	1.854(3)	1.851(4)	1.853(4)
C(8)–C(9)	1.521(5)	1.510(6)	1.511(7)
C(8)–C(10)	1.516(5)	1.514(6)	1.510(6)
C(8)–C(11)	1.515(5)	1.514(5)	1.528(6)
C(1)–S(1)		1.798(4)	
C(1)–C(5)	1.486(4)		
O(1)–C(5)	1.206(4)		
O(2)–C(5)	1.312(4)		
O(2)–C(6)	1.466(4)		
S(1)–C(12)		1.778(4)	
C(1)–C(12)			1.519(5)
C(12)–C(13)		1.381(6)	1.365(6)
C(12)–C(17)		1.380(6)	1.378(6)
C(13)–C(14)		1.387(7)	1.362(7)
C(14)–C(15)		1.365(8)	1.371(7)
C(15)–C(16)		1.376(8)	1.339(7)
C(16)–C(17)		1.374(7)	1.397(6)

[a] Mean values for the two independent molecules in the asymmetric unit.

C(17)–C(12)–C(1)–M(1) = 62°. This conformation of the phenyl ring in phenylcyclopropane derivatives is common[2,15] and probably results from the steric repulsion between the CN group and the *ortho* hydrogen atom.

The cyclopropane ring bond lengths are in the range 1.491—1.580 Å with a standard deviation of 0.005 Å. Substituent-induced bond length asymmetries are therefore significant and again indicate conjugative interaction between the cyclopropyl ring and the adjacent substituents. For the three molecules in question the most substituted C(1)–C(2) bond is always the longest one. In (**I**), the C(1)–C(2) distance of 1.580(4) Å is, as far as we know, the longest ring bond ever observed in a monocyclic cyclopropane system.[2] The average $C–C_{(ring)}$ distances are 1.525(2), 1.525(3), and 1.521(3) Å for (**I**), (**II**), and (**III**), respectively. These values are slightly greater than the expected mean

Table 6. Valence angles (°)

	(I)	(II)[a]	(III)[a]
C(3)–C(1)–C(2)	58.5(2)	59.0(2)	59.1(2)
C(4)–C(1)–C(2)	115.5(2)	117.5(3)	115.3(3)
C(4)–C(1)–C(3)	117.1(3)	118.0(4)	116.9(4)
C(5)–C(1)–C(2)	117.2(2)		
C(5)–C(1)–C(3)	118.8(3)		
C(5)–C(1)–C(4)	116.9(3)		
S(1)–C(1)–C(2)		120.6(2)	
S(1)–C(1)–C(3)		116.7(3)	
S(1)–C(1)–C(4)		114.0(3)	
C(12)–C(1)–C(2)			119.8(3)
C(12)–C(1)–C(3)			120.3(4)
C(12)–C(1)–C(4)			114.3(3)
C(3)–C(2)–C(1)	57.8(2)	58.8(2)	58.8(2)
C(7)–C(2)–C(1)	115.0(2)	116.0(3)	114.1(3)
C(7)–C(2)–C(3)	117.5(3)	117.2(3)	115.9(4)
S(2)–C(2)–C(1)	120.1(2)	115.1(2)	121.9(3)
S(2)–C(2)–C(3)	115.4(2)	121.3(3)	113.4(3)
S(2)–C(2)–C(7)	117.5(2)	115.8(3)	118.4(3)
C(2)–C(3)–C(1)	63.7(2)	62.2(2)	62.2(2)
N(1)–C(4)–C(1)	178.4(4)	176.8(4)	174.2(4)
O(1)–C(5)–C(1)	122.8(3)		
O(2)–C(5)–C(1)	112.3(3)		
O(2)–C(5)–O(1)	124.9(3)		
N(2)–C(7)–C(2)	177.6(3)	179.0(5)	179.5(3)
C(10)–C(8)–C(9)	110.4(3)	110.7(4)	111.3(4)
C(11)–C(8)–C(9)	110.7(3)	111.3(4)	110.7(4)
C(11)–C(8)–C(10)	109.8(3)	110.0(4)	110.0(4)
S(2)–C(8)–C(9)	112.3(2)	102.1(3)	102.2(3)
S(2)–C(8)–C(10)	110.4(2)	112.0(3)	112.0(3)
S(2)–C(8)–C(11)	103.1(2)	110.5(3)	110.5(3)
C(6)–O(2)–C(5)	116.4(3)		
C(8)–S(2)–C(2)	106.9(1)	106.3(1)	107.6(2)
C(12)–S(1)–C(1)		101.5(1)	
C(17)–C(12)–C(13)		119.7(4)	118.6(4)
S(1)–C(12)–C(13)		119.7(4)	
S(1)–C(12)–C(17)		120.6(4)	
C(13)–C(12)–C(1)			121.4(4)
C(17)–C(12)–C(1)			119.8(4)
C(14)–C(13)–C(12)		119.8(5)	121.5(5)
C(15)–C(14)–C(13)		119.3(6)	119.3(5)
C(16)–C(15)–C(14)		121.6(5)	120.8(5)
C(17)–C(16)–C(15)		118.8(5)	119.6(5)
C(16)–C(17)–C(12)		120.7(5)	119.9(4)

[a] Mean values for the two independent molecules in the asymmetric unit.

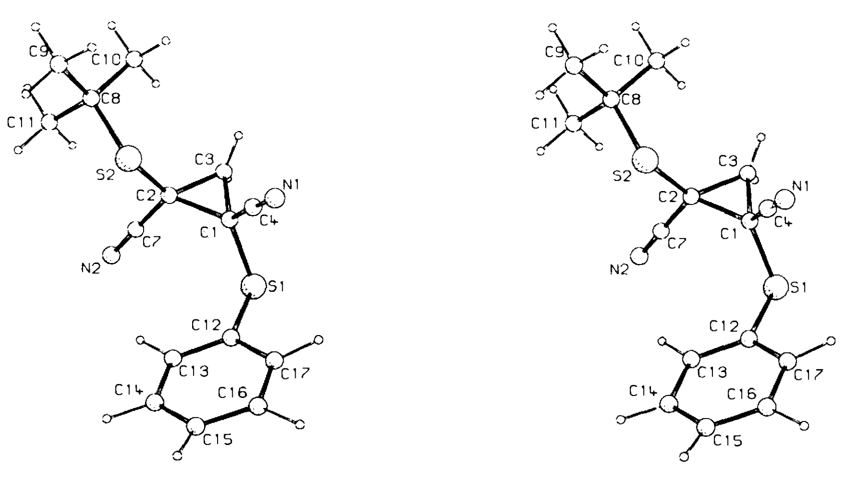


Figure 2. Stereoscopic view of compound (**II**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylthiocyclopropane[12]

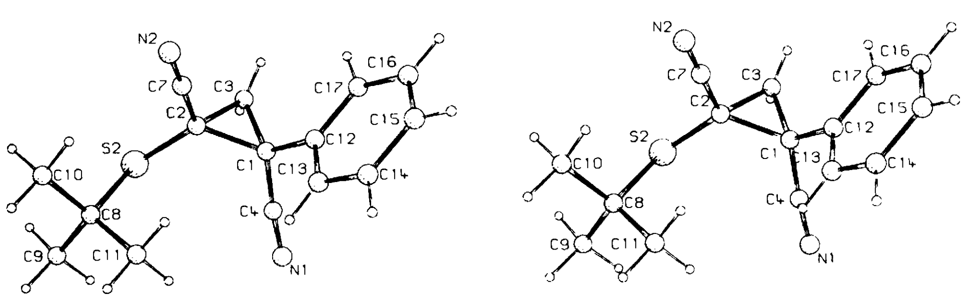
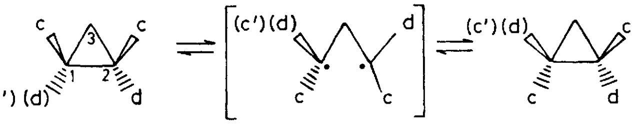


Figure 3. Stereoscopic view of compound (**III**), 2-t-butylthio-1-*r*,2-*t*-dicyano-1-phenylcyclopropane[12]



c = CN, CO_2R d = SR, OR, NR_2

Scheme.

of 1.510 Å[2] but are similar to that observed for 1,1,2,2-tetracyanocyclopropane[16] (1.523 Å).

Because there are no published structural data for alkylthio- or arylthio-substituted cyclopropanes, it is of interest to estimate the geometrical deformations of the ring induced by this kind of substituent. The bond lengths that we observed can be explained by the substituent parameters derived by Allen.[2]

There is now ample evidence that for π-acceptor substituents the distal ring bond is shortened and vicinal bonds lengthened because of electron-density transfer from cyclopropane 3*e*'-orbitals to the low lying π-orbitals of C=O, C=C, C≡N, • • •.[17–19]

Allen has established mean distal bond shortenings,[2] δ, related to the individual mean $C–C_{(ring)}$ distance, for these π-acceptors. They are −0.026, −0.017, and −0.018 Å for C=O, C≡N, and phenyl, respectively. Compared with the average ring bond length each vicinal bond is lengthened by δ/2. Thus, the only unknown substituent effect in (**I**)—(**III**) is that of the SR group. If we assume additivity of substituent effects,[20] as Allen does, the best result to fit the experimental bond lengths in each structure corresponds to a negative value for δ_{SR} (*ca.* −0.025 Å). In other words, thioalkyl or thioaryl substituent will cause, as does a π-acceptor group, a shortening of the distal bond and a lengthening of the vicinal bonds. However, the additivity of the substituent effects does not always explain the results of donor–acceptor substitution.[21] It would be necessary to determine the geometries of purely SR-substituted cyclopropanes in order to confirm our first deduction. Nevertheless, it can certainly be concluded that the capto-dative couple (SR, CN) as with the dicapto one, causes a shortening of the distal bond and a lengthening of the vicinal bonds. In both cases, electron density is transferred from the cyclopropyl ring to the substituents. The C(1)–C(2) bond is thus particularly weakened by *cd* and by *cc* substitutions on C(1) and C(2).

The activation energies[3,4] for the *trans–cis* isomerisation of the three cyclopropane derivatives represent a measure of the ease of breaking the C(1)–C(2) cyclopropane ring bond. It is influenced by the substituents in the ground state and in the diradical transition state (Scheme). The activation energy of isomerisation of compound (**I**), *cc*'-substituted on C(1), (31.7 ± 0.7 kcal mol^{-1}) is greater than that of compound (**III**) (26.7 ± 0.7 kcal mol^{-1}) and of the bis *cd*-substituted cyclopropane (**II**) (26.9 ± 1.1 kcal mol^{-1}). The highest energy barrier is found for the longest C(1)–C(2) bond. At this stage we cannot conclude how these changes in the cyclopropane bond lengths are related to ground-state energy changes. However, it seems that the particularly easy isomerisation of bis-*cd*-substituted cyclopropane is not a consequence of a destabilised ground state but of an increased spin delocalisation in the transition state.

Conclusions

For the *cd*-, as well as *cc*-substituted cyclopropanes, we observe a long C(1)–C(2) bond, which can be explained by a transfer of electron density from the cyclopropyl ring to the substituents. This result is in agreement with the observed one for a series of 2,3-dimethyl-2,3-bis(*p*-X-phenyl)butane-1,4-dinitrile derivatives.[22] For these hexasubstituted ethanes we also found very long central C–C distances both for X = acceptor (CN, CO_2Me) and X = donor (SMe, NMe_2). Although a *cc*-substituted cyclopropane has a longer C(1)–C(2) ring bond than the *cd*-substituted one, the later one isomerises more readily because of a greater stabilisation of the corresponding diradical transition state.

References

1 See also: Capto-dative Substituent Effects, Part 18: F. Lahousse, R. Mérényi, J. R. Desmurs, H. Allaime, A. Borghese, and H. G. Viehe. *Tetrahedron Lett.*, in the press.
2 F. H. Allen, *Acta Crystallogr.*, 1980, **B36**, 81.
3 A. De Mesmaeker, L. Vertommen, R. Mérényi, and H. G. Viehe, *Tetrahedron Lett.*, 1982, **23**, 69.
4 R. Mérényi, A. De Mesmaeker, and H. G. Viehe, *Tetrahedron Lett.*, 1983, **24**, 2765.
5 H. G. Viehe, R. Mérényi, L. Stella, and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 917.
6 A. Chmurny and D. J. Cram, *J. Am. Chem. Soc.*, 1973, **95**, 4237.
7 W. von E. Doering, G. Horowitz, and K. Sachdev, *Tetrahedron*, 1977, **33**, 273.
8 A. De Mesmaeker, part of Ph.D. Thesis, University of Louvain-la-Neuve, Belgium, 1983.
9 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN-80, A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data, Universities of York and Louvain-la-Neuve, Belgium, 1980.
10 P. T. Beurkens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, and V. Parthasarathi, Direct Methods for Difference Structures, Technical Report 1981/2, Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, Netherlands.
11 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.
12 S. Motherwell and W. Clegg, PLUTO, University of Cambridge, 1978.
13 F. H. Allen, *Acta Crystallogr.*, 1981, **B37**, 890.
14 Cambridge Crystallographic Database, University of Cambridge.
15 B. Tinant, I. De Block, J. P. Declercq, G. Germain, M. Van Meerssche, G. Leroy, and J. Weiler, *Bull. Soc. Chim. Belg.*, 1982, **91**, 629.

16 Y. Wang and G. D. Stucky, *Acta Crystallogr.*, 1973, **B29**, 1255.
17 R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, 1971, **93**, 5699.
18 M. D. Harmony, R. N. Nandi, J. V. Tietz, J. I. Choe, S. J. Getty, and S. W. Staley, *J. Am. Chem. Soc.*, 1983, **105**, 3947.
19 N. Ramasubbu, J. Rajaram, and K. Venkatesan, *Acta Crystallogr.*, 1982, **B38**, 196.
20 C. A. Deakyne, E. C. Allen, and N. C. Craig. *J. Am. Chem. Soc.*, 1977, **99**, 3895.
21 M. E. Jason, J. C. Gallucci, and J. A. Ibers, *Isr. J. Chem.*, 1981, **21**, 95.
22 A. Parfonry, B. Tinant, J. P. Declercq, and M. Van Meerssche, presented at the Eighth European Crystallographic Meeting, Abstracts p. 135, 1983.

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