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Captodative Substitution and Cyclopropane Geometry. III. Methyl 2-*tert*-Butylthio-1-*t*-chloro-2-*r*-cyano-1-cyclopropanecarboxylate, $C_{10}H_{14}ClNO_2S$

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Abstract. $M_r = 247 \cdot 75$, monoclinic, $P2_1/n$, $a = 8 \cdot 953$ (2), $b = 23 \cdot 338$ (8), $c = 6 \cdot 041$ (2) Å, $\beta = 99 \cdot 66$ (2)°, $V = 1244 \cdot 3$ (6) Å^3, $Z = 4$, $D_x = 1 \cdot 32$ g cm^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 4 \cdot 54$ cm^{-1}, $F(000) = 520$, $T = 291$ K, $R = 0 \cdot 044$ for 1313 observed reflections. The cyclopropyl ring bond lengths are significantly different: C(1)—C(2) = $1 \cdot 545$ (5), C(1)—C(3) = $1 \cdot 477$ (6) and C(2)—C(3) = $1 \cdot 506$ (5) Å. These variations resulted from the substitutent effects; captodative substitution (here CN, *tert*-butylthio), as π-acceptor groups, shortens the distal bond and lengthens the vicinal bonds of the cyclopropyl ring.

Introduction. The crystal structure of the title compound has been investigated as part of a programme of studies of captodative substituent effects on the cyclopropane geometry (Tinant, Declercq & Van Meerssche, 1984; Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1984). It is a well established fact that the cyclopropane ring undergoes significant geometrical changes under the influence of neighbouring π centres. For electron-withdrawing substituents the distal ring bond is shortened and vicinal bonds are lengthened (Allen, 1980; Ramasubbu, Rajaram & Venkatesan, 1982). Data for electron-donor and mixed donor–acceptor substituents are more sparse but results for *gem*-halogeno substitution indicate distal-bond lengthening (Allen, 1980; Deakyne, Allen & Craig, 1977).

Our objective is to analyse the effects of *gem*-donor–acceptor or captodative (*cd*) substitution ($c = \text{CN,COOCH}_3, \ldots$; $d = \text{SR,OR}, \ldots$) on the ring bond pattern of the cyclopropyl ring. In previous papers we have reported the crystal structures of *cis*- and *trans*-2-*tert*-butyl- (or 2-phenyl-)thio-1,2-dicyano-cyclopropanes. Now we wish to examine the effects of a Cl atom combined with *cd* substituents.

Experimental. Crystals obtained by evaporation from ether–petroleum ether. D_m not measured. Parallelepiped crystal with dimensions $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 4$ mm. Lattice parameters refined using 15 reflections in range $5 \leq 2\theta \leq 25°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 1830 $\pm hkl$ independent reflections with $\sin\theta/\lambda \leq 0 \cdot 561$ Å^{-1}; $-10 \leq h \leq 10$, $0 \leq k \leq 24$, $0 \leq l \leq 6$; 1313 with $I \geq 2 \cdot 5\sigma(I)$. Standard reflection (002) checked every 50 reflections: no significant deviation. No absorption correction. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Cyclopropyl H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using F. Cyclopropyl H isotropic with common fixed temperature factor, $B = 3 \cdot 95$ Å^2; other H computed with C—H = $1 \cdot 08$ Å. $w = 1/(\sigma^2 + 0 \cdot 00033F^2)$, $R = 0 \cdot 044$, $R_w = 0 \cdot 045$ for 1313 observed reflections, $S = 2 \cdot 27$. Final max. Δ/σ $0 \cdot 78$. Max. and min. heights in final difference Fourier

synthesis 0·18 and −0·30 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters are given in Table 1.* Fig. 1 is a stereoscopic view of the molecule, showing the numbering of the atoms (program *PLUTO*, Motherwell & Clegg, 1978). Bond distances and angles and selected torsion angles are given Table 2.

The average C—C distance (*Δ*) in the cyclopropyl ring, 1·509 (3) Å, is in perfect agreement with the mean over 115 structures [1·509 (2) Å] computed by Allen (1980). However, the individual bond lengths within the ring show remarkable differences. These bond-length variations result from the substituent effects and they can be explained very well using the formalism of substituent parameters as described by Allen (1980). Compared with the average ring bond length *Δ*, the CN and CO groups shorten the opposite bond to the substituted carbon, *i.e.* the distal bond, by respectively $\delta = -0.017$ (2) and $\delta = -0.026$ (5) Å. Each vicinal bond is lengthened by $\frac{\delta}{2}$. For Cl the reverse effect has been observed and $\delta = +0.012$ (7) Å (Allen, 1980). If we assume additivity of the substituent effects, the average value for δ of the *tert*-butylthio group to fit the observed ring bond pattern is −0·02 (1) Å. This value is the same as that estimated for three other *tert*-butylthiocyclopropanes (Tinant, Declercq & Van Meerssche, 1984; Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1984). This confirms that the *gem*-CN,S*R* *cd* substitution has a similar effect to that of π-acceptor groups and that electron density is transferred from the ring to the substituents.

The orientation of the methoxycarbonyl substituent towards the cyclopropyl ring is given by the torsion angle O(1)—C(5)—C(1)—*M*23 = 26 (1)° with *M*23 the midpoint of the C(2)—C(3) bond. This *s-cis* conformation of the carbonyl enables overlapping of the cyclopropane 3*e'* orbital with that of an adjacent *p* orbital of the substituent. It is predominant in carbonyl-substituted cyclopropanes (Kusuyama, 1979). However, the bond lengths C(1)—C(5) = 1·510 (5) and C(5)=O(1) = 1·195 (4) Å are closer to the mean values computed for unconjugated carbonyl-substituted cyclopropanes [1·504 (6) and 1·203 (5) Å] than to those of derivatives with a bisected conformation for the C=O group [1·484 (5) and 1·209 (3) Å (Allen, 1981)]. The C(2)—C(4) distance [1·452 (5) Å] is also slightly longer than the mean observed for cyanocyclopropanes [1·441 (4) Å (Allen, 1981)].

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39869 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å^2)*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Cl	3589 (1)	4690 (1)	1117 (2)	4·00
S	5075 (1)	3880·2 (0·4)	5391 (2)	3·51
O(1)	−220 (3)	4339 (2)	2966 (6)	5·58
O(2)	636 (3)	4222 (2)	−243 (5)	4·43
N	1374 (4)	3242 (2)	5949 (9)	5·86
C(1)	2406 (4)	4450 (2)	2964 (7)	2·94
C(2)	3104 (3)	4048 (2)	4895 (6)	3·06
C(3)	2690 (4)	4659 (2)	5304 (7)	3·35
C(4)	2124 (4)	3599 (2)	5503 (7)	3·62
C(5)	786 (4)	4335 (2)	1893 (7)	3·18
C(6)	−886 (4)	4064 (2)	−1372 (9)	5·20
C(7)	5304 (4)	3210 (2)	3823 (8)	3·73
C(8)	5084 (7)	2692 (2)	5292 (12)	6·49
C(9)	4227 (5)	3174 (3)	1621 (10)	5·68
C(10)	6934 (5)	3227 (3)	3481 (13)	7·27

Table 2. *Bond distances (Å) and angles (°) and selected torsion angles (°, σ = 1°)*

Cl–C(1)	1·754 (3)	C(1)–C(3)	1·477 (6)
S–C(2)	1·783 (3)	C(1)–C(5)	1·510 (5)
S–C(7)	1·857 (4)	C(2)–C(3)	1·506 (5)
O(1)–C(5)	1·195 (4)	C(2)–C(4)	1·452 (5)
O(2)–C(5)	1·301 (5)	C(7)–C(8)	1·532 (7)
O(2)–C(6)	1·465 (5)	C(7)–C(9)	1·509 (7)
N–C(4)	1·131 (5)	C(7)–C(10)	1·508 (5)
C(1)–C(2)	1·545 (5)		
C(2)–S–C(7)	106·8 (2)	C(3)–C(2)–C(4)	117·8 (3)
C(5)–O(2)–C(6)	116·5 (3)	C(1)–C(3)–C(2)	62·4 (3)
Cl–C(1)–C(2)	117·6 (2)	N–C(4)–C(2)	178·5 (4)
Cl–C(1)–C(3)	118·5 (3)	O(1)–C(5)–O(2)	125·3 (3)
C(2)–C(1)–C(3)	59·7 (3)	O(1)–C(5)–C(1)	121·6 (4)
Cl–C(1)–C(5)	115·0 (3)	O(2)–C(5)–C(1)	113·1 (3)
C(2)–C(1)–C(5)	117·0 (3)	S–C(7)–C(8)	109·4 (3)
C(3)–C(1)–C(5)	117·9 (3)	S–C(7)–C(9)	112·8 (3)
S–C(2)–C(1)	121·5 (2)	C(8)–C(7)–C(9)	109·9 (4)
S–C(2)–C(3)	116·4 (3)	S–C(7)–C(10)	103·9 (3)
C(1)–C(2)–C(3)	57·9 (3)	C(8)–C(7)–C(10)	108·8 (4)
S–C(2)–C(4)	115·0 (3)	C(9)–C(7)–C(10)	111·8 (4)
C(1)–C(2)–C(4)	116·3 (3)		

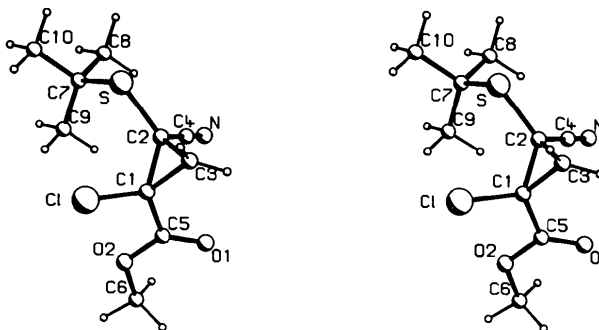|			
C(7)–S–C(2)–C(1)	−93	C(5)–C(1)–C(2)–C(4)	0
C(7)–S–C(2)–C(3)	−160	Cl–C(1)–C(5)–O(1)	−157
C(7)–S–C(2)–C(4)	57	Cl–C(1)–C(5)–O(2)	24
C(6)–O(2)–C(5)–O(1)	−3	C(2)–C(1)–C(5)–O(1)	58
C(6)–O(2)–C(5)–C(1)	176	C(2)–C(1)–C(5)–O(2)	−120
Cl–C(1)–C(2)–S	5	C(3)–C(1)–C(5)–O(1)	−10
Cl–C(1)–C(2)–C(4)	−144	C(3)–C(1)–C(5)–O(2)	172
C(5)–C(1)–C(2)–S	149		

Fig. 1. Stereoscopic view of the molecule and atom numbering (program *PLUTO*, Motherwell & Clegg, 1978).

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Structure of 3-Methylcytidinium Chloride, $C_{10}H_{16}N_3O_5{}^+.Cl^-$

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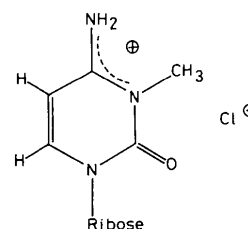
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Abstract. $M_r = 293.7$, orthorhombic, $P2_12_12_1$, $a = 7.225$ (1), $b = 11.639$ (1), $c = 14.921$ (1) Å, $V = 1254.7$ (3) Å^3, $Z = 4$, $D_x = 1.56$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 2.79$ mm^{-1}, $F(000) = 616$, $T = 290$ K, $R = 0.030$ for 1959 observed reflexions. The dimensions and conformation of the 3-methyl-cytidinium cation ($\chi = 45.2$, $P = 163.0$, $\tau_m = 40.3$, $\psi = 55.2°$) are very similar to those characterizing the cytidinium cation in cytidine hydrochloride. The pyrimidine ring shows deviations of up to 0.03 Å from planarity and N(4) is 0.118 Å from the pyrimidine plane. There is a two-dimensional network of H bonds in which all available proton donors are utilized: NH···O(2) 2.89, NH···Cl$^-$ 3.20, OH···Cl$^-$ 3.07, 3.25, 3.27 Å.

Introduction. In our previous studies of the factors influencing dimensions and molecular interactions of nucleosides we have investigated the effects of base modification and protonation (Jaskólski, Krzyżosiak, Sierzputowska-Gracz & Wiewiórowski, 1981; Krzyżosiak, Jaskólski, Sierzputowska-Gracz & Wiewiórowski, 1982; Kozerski, Sierzputowska-Gracz, Krzyżosiak, Bratek-Wiewiórowska, Jaskólski & Wiewiórowski, 1984; Jaskólski, 1982a, b, 1984a). The present paper reports the structure of a cytidinium cation which has a methyl group instead of a proton at the N(3) site. It is of interest to investigate the

differences between the N-protonated and N-methylated cations. There has been a structural report on the 3-methylcytidinium cation in the literature (3-methylcytidine methyl sulphate monohydrate; Shefter, Singh, Brennan & Sackman, 1974) but the accuracy is low and therefore not suitable for detailed comparative studies.

Experimental. Suitable crystals obtained from methanol–ethyl acetate, crystal 0.3 × 0.4 × 0.4 mm, Syntex $P2_1$ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions, $\pm h \pm k \pm l$ measured up to $2\theta = 115°$ and hkl up to $2\theta = 132°$, θ:2θ scan, background–peak–background, 8810 reflexions collected, 1981 unique ($R_{int} = 0.030$), 1970 observed with $I \geq 1.96\sigma(I)$, no significant variation for two standard reflexions, no absorption correction; structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain,