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Captodative Substitution and Cyclopropane Geometry. VI. Structure of Dimethyl *cis*-1,2-Bis(phenylthio)-1,2-cyclopropanedicarboxylate

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Abstract. $C_{19}H_{18}O_4S_2$, $M_r = 374{\cdot}48$, monoclinic, $P2_1/a$, $a = 8{\cdot}159\,(5)$, $b = 21{\cdot}093\,(17)$, $c = 11{\cdot}153\,(11)$ Å, $\beta = 105{\cdot}63\,(6)°$, $V = 1848\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}35$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}05$ cm^{-1}, $F(000) = 784$, $T = 291$ K, $R = 0{\cdot}038$ for 1975 observed reflections. One of the methoxycarbonyl groups bisects the cyclopropyl ring while the other adopts the less favorable perpendicular conformation. The effects of the substituents on the ring bond lengths are clearly dependent on the orientation of the π-acceptor groups: in the bisecting position they shorten the distal bond while, when perpendicular, the effects are negligible. The values of the distal-bond shortenings observed for the S—*R* and COOMe groups agree very well with literature data.

Introduction. In the course of our work on polar-substituent effects on cyclopropane geometry (Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1985, 1987), we have determined the X-ray structure of the title compound. This derivative was chosen because it is the only one in the series of bis(captodative)-substituted cyclopropanes for which the *cis* isomer was more stable than the *trans* isomer (Masamba, 1986). Moreover, the *cis* configuration of the methoxycarbonyl groups should force each one to adopt a different orientation towards the cyclopropyl ring. It offers thus the opportunity to estimate the effect of the orientation of the π-acceptor group on the ring bond-length pattern.

Experimental. Crystals obtained by evaporation from ether–petroleum ether. D_m not measured. Parallelepiped crystal with dimensions $0{\cdot}15 \times 0{\cdot}18 \times 0{\cdot}3$ mm. Lattice parameters refined using 15 reflections in the range $5 \le 2\theta \le 25°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 2737 $hk\pm l$ independent reflections with $(\sin\theta)/\lambda \le 0{\cdot}561$ Å^{-1}; $0 \le h \le 9$, $0 \le k \le 23$, $-12 \le l \le 12$; 1975 with $I \ge 2{\cdot}5\sigma(I)$. Standard reflection 401 checked every 50 reflections: no significant deviation. Structure solved by *SHELXS*86 (Sheldrick, 1985). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using F; H isotropic with common refined temperature factor. $w = 1/(\sigma^2 + 0{\cdot}00067F^2)$. $R = 0{\cdot}038$, $wR = 0{\cdot}041$ for 1975 observed reflections. Final maximum shift to e.s.d. $= 0{\cdot}31$ (y of C7). $S = 1{\cdot}28$. Maximum and minimum heights in final difference Fourier synthesis $= 0{\cdot}21$ and $-0{\cdot}20$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The 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 are given in Table 2. As a consequence of the steric conflict resulting from their *cis* configuration, the two methoxycarbonyl groups adopt a completely different orientation towards the cyclopropyl ring. The torsion angles $M23$—C1—C4—O5 = −76° and $M13$—C2—C8—O9 = 2° ($M13$ and $M23$ being respectively the midpoints of the C1—C3 and C2—C3 bonds), indicate that the methoxycarbonyl at C1 is in the perpendicular position while that at C2 adopts the preferred *s-cis* bisected orientation (Korp, Bernal & Fuchs, 1983). The phenyl groups of the two thiophenyl substituents are perpendicular to each other (dihedral angle between

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44222 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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mean planes = 77°) and each one is also nearly perpendicular to its geminal methoxycarbonyl (dihedral angles 92 and 103° respectively for the substituents at C1 and C2).

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

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

	x	*y*	*z*	$B_{\rm eq}$
C1	7952 (4)	1473 (1)	2277 (3)	3·36 (5)
C2	6721 (4)	1732 (1)	1064 (3)	3·44 (6)
C3	7223 (5)	2123 (2)	2248 (3)	4·15 (7)
C4	7327 (4)	976 (2)	3003 (3)	4·11 (7)
O5	7059 (3)	1066 (1)	3994 (2)	5·70 (6)
O6	7172 (4)	419 (1)	2438 (3)	6·08 (6)
C7	6594 (10)	−91 (3)	3111 (6)	9·26 (16)
C8	4940 (4)	1475 (2)	767 (3)	3·86 (6)
O9	4244 (3)	1342 (2)	1548 (2)	6·36 (6)
O10	4220 (3)	1430 (1)	−428 (2)	4·53 (5)
C11	2470 (5)	1212 (3)	−763 (4)	6·09 (10)
S12	10120 (1)	1367 (1)	2264 (1)	3·92 (2)
C13	11267 (4)	1538 (1)	3813 (3)	3·25 (6)
C14	10625 (4)	1852 (2)	4687 (3)	4·13 (6)
C15	11695 (5)	1972 (2)	5863 (3)	4·49 (7)
C16	13359 (5)	1790 (2)	6173 (3)	4·46 (7)
C17	13995 (5)	1488 (2)	5304 (3)	4·64 (7)
C18	12962 (4)	1359 (2)	4137 (3)	4·06 (7)
S19	7517 (1)	2031 (1)	−158 (1)	4·27 (2)
C20	7818 (4)	1364 (2)	−1026 (3)	3·55 (6)
C21	7833 (5)	741 (2)	−648 (3)	4·73 (7)
C22	8151 (6)	259 (2)	−1399 (4)	5·88 (9)
C23	8470 (5)	392 (2)	−2516 (4)	5·53 (9)
C24	8454 (5)	1003 (2)	−2898 (3)	5·27 (8)
C25	8142 (4)	1487 (2)	−2168 (3)	4·63 (7)

Table 2. *Bond distances* (Å) *and angles* (°)

C2—C1	1·551 (4)	C3—C1	1·491 (4)
C4—C1	1·496 (4)	S12—C1	1·787 (3)
C3—C2	1·517 (4)	C8—C2	1·502 (4)
S19—C2	1·776 (3)	O5—C4	1·197 (4)
O6—C4	1·325 (4)	C7—O6	1·460 (5)
O9—C8	1·194 (4)	O10—C8	1·307 (4)
C11—O10	1·450 (5)	C13—S12	1·766 (3)
C14—C13	1·394 (4)	C18—C13	1·384 (4)
C15—C14	1·389 (4)	C16—C15	1·363 (5)
C17—C16	1·372 (5)	C18—C17	1·374 (5)
C20—S19	1·762 (3)	C21—C20	1·379 (5)
C25—C20	1·393 (5)	C22—C21	1·385 (5)
C23—C22	1·369 (5)	C24—C23	1·356 (5)
C25—C24	1·372 (5)		
C3—C1—C2	59·8 (2)	C4—C1—C2	118·9 (3)
C4—C1—C3	117·6 (3)	S12—C1—C2	116·5 (2)
S12—C1—C3	120·3 (2)	S12—C1—C4	113·5 (2)
C3—C2—C1	58·2 (2)	C8—C2—C1	115·2 (3)
C8—C2—C3	114·0 (3)	S19—C2—C1	120·6 (2)
S19—C2—C3	114·0 (2)	S19—C2—C8	119·4 (2)
C2—C3—C1	62·1 (2)	O5—C4—C1	124·3 (3)
O6—C4—C1	111·5 (3)	O6—C4—O5	124·1 (3)
C7—O6—C4	114·3 (3)	O9—C8—C2	123·0 (3)
O10—C8—C2	113·2 (3)	O10—C8—O9	123·8 (3)
C11—O10—C8	115·2 (3)	C13—S12—C1	103·4 (1)
C14—C13—S12	125·5 (2)	C18—C13—S12	115·4 (2)
C18—C13—C14	119·0 (3)	C15—C14—C13	119·2 (3)
C16—C15—C14	121·2 (3)	C17—C16—C15	119·5 (3)
C18—C17—C16	120·6 (3)	C17—C18—C13	120·6 (3)
C20—S19—C2	105·8 (1)	C21—C20—S19	125·7 (2)
C25—C20—S19	116·2 (3)	C25—C20—C21	118·0 (3)
C22—C21—C20	120·1 (3)	C23—C22—C21	120·9 (4)
C24—C23—C22	119·5 (4)	C25—C24—C23	120·6 (4)
C24—C25—C20	121·0 (4)		

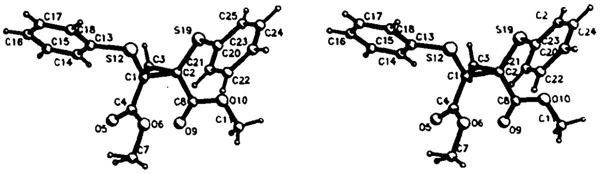

Fig. 1. Stereoscopic view of the molecule and atom numbering.

Of particular interest is the ring bond-length pattern because of the different orientation of the two methoxycarbonyl groups. As the observed bond lengths C1—C3 and C2—C3 differ significantly [respectively 1·491 (4) and 1·517 (4) Å] for this symmetrically substituted derivative, it is clear that the effects of the substituents at C1 and C2 are not equal. It has been shown that the cyclopropane π-acceptor interactions are dependent on the orientation of the π system (Allen, 1980). Due to better orbital mixing, a maximum interaction occurs when the substituent bisects the cyclopropane ring, while the effect is minimal in the perpendicular conformation (Allen, 1980; Tinant, De Block, Declercq, Germain, Van Meerssche, Leroy & Weiler, 1982). There is ample evidence that π-acceptor groups shorten the distal bond and lengthen the vicinal bonds; mean distal-bond shortenings of −0·026 (Allen, 1980) and −0·022 Å (Tinant *et al.*, 1987) have been proposed for δCOO*R*. In a preceding work on captodative-substituted cyclopropanes, we have estimated the effect of an S—*R* group δS*R* to be approximately −0·020 Å (Tinant *et al.*, 1987). The ring bond pattern calculated for the title derivative using these increments is in perfect agreement with the observed bond lengths as long as the effect of the perpendicular methoxycarbonyl group on C1 is neglected; indeed the calculated values of the bond lengths are then 1·551, 1·488 and 1·521 Å for C1—C2, C1—C3, and C2—C3, respectively, as compared to the observed values of 1·551, 1·491 and 1·517 Å.

In conclusion, it appears clearly that a π-acceptor group has a negligible effect on the ring bond lengths when it is in the perpendicular orientation. It is also confirmed that captodative and dicapto substitution have similar effects on the cyclopropane geometry.

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Structure of Pyridoxal Homocysteine Thiolactone Enamine

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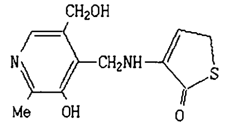
Abstract. 3-{[3-Hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl]methylamino}-2(5*H*)-thiophenone, abbreviated name 2,5-dihydro-2-oxo-3-pyridoxaminothiophene, $C_{12}H_{14}N_2O_3S$, $M_r = 266{\cdot}3$, monoclinic, $P2_1/c$, $a = 10{\cdot}029\,(2)$, $b = 11{\cdot}472\,(4)$, $c = 11{\cdot}760\,(2)$ Å, $\beta = 112{\cdot}80\,(2)°$, $V = 1247{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}42$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}6$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}044$ and $wR = 0{\cdot}054$ for 1537 unique observed reflections with $I > \sigma(I)$. The thiophene and pyridine rings are each planar with a dihedral angle of 95·0 (4)° between these planes. The C(O)—S and H_2C—S bonds are different [1·758 (3) and 1·784 (3) Å, respectively]. The CH_2OH group is disordered. The molecules are linked together by O—H···O and O—H···N hydrogen bonds.

Introduction. The title compound is one of a series prepared and investigated by McCully and co-workers for antineoplastic activity. Although high doses of the hydrochloride decreased growth of transplanted rhabdomyosarcoma in mice (McCully & Clopath, 1977), the free base was found to be inactive (McCully & Vezeridis, 1985). The structure of the free base was determined to verify the expected structure and to see the conformation of this rather crowded molecule.



Experimental. Pyridoxal homocysteine thiolactone enamine hydrochloride synthesized by the method of Okumura *et al.* (1971) from pyridoxal.HCl and homocysteine thiolactone (Sigma Chemical Co.). Free base crystallized from 0·07 *M* NaOH in methanol. Pale-yellow prismatic single crystal, 0·25 × 0·28 × 0·36 mm, mounted with epoxy cement. Nicolet *R*3*m* diffractometer, graphite monochromator; unit-cell parameters by least-squares refinement of 25 reflections ($26 \leq 2\theta \leq 28°$); θ–2θ scans at variable rates; $2\theta_{\max} = 45°$ for the range $0 \leq h \leq 10$, $0 \leq k \leq 12$, $-12 \leq l \leq 11$; three reflections monitored every 97 reflections with negligible change in intensity over the course of data collection; 1636 measured unique intensities, 1537 unique observed reflections (not including space-group absences) with $I > \sigma(I)$ used for refinement; absorption correction based on indexed and measured faces (max. and min. transmission factors 0·941, 0·925). Structure by direct methods; 10 of 14 H atoms found on difference map; for refinement, all C—H bond lengths fixed at 0·96 Å and refined with ideal geometry; anisotropic thermal parameters for all non-H atoms and fixed isotropic parameters for H atoms (20% greater than that of carrying atom). Refined by cascade block-diagonal least squares on *F* with max. $(\sin\theta)/\lambda = 0{\cdot}54$ Å^{-1}; refinement of 185 parameters converged to $R = 0{\cdot}044$, $wR = 0{\cdot}054$; $w = 1/[\sigma^2(F) + 0{\cdot}00040F^2]$ where $\sigma^2(F)$ is from counting statistics; goodness of fit = 1·791; $(\Delta/\sigma)_{\max} = -0{\cdot}05$ in final cycle; highest peak in final difference map 0·19, deepest hole, $-0{\cdot}23$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on a Data General Eclipse S140 computer using the *SHELXTL* 4.1 program package (Sheldrick, 1984).

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