N1—C8	1.458 (4)	C9—C12	1.528 (4)
N2—C13	1.263 (3)	C13—C14	1.458 (4)
C7—N1—C8	119.9 (3)	C8—C9—C12	108.6 (3)
C13—N2—C12	120.2 (3)	C10—C9—C11	109.2 (3)
O1—C1—C6	120.2 (4)	N2—C12—C9	112.0 (3)
N1—C7—C6	121.6 (3)	N2—C13—C14	122.2 (3)
N1—C8—C9	112.1 (3)	O2—C19—C14	121.7 (3)
O1—C1—C6—C7	1.8 (5)	C8—C9—C12—N2	−174.0 (3)
C1—C6—C7—N1	−3.9 (5)	N2—C13—C14—C19	−2.2 (5)
N1—C8—C9—C12	62.9 (4)	C13—C14—C19—O2	−0.1 (5)

H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl and hydroxyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. Refinement was on all reflections except for one flagged by the user for potential systematic errors.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1992). Cell refinement: *MADNES*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1029). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Cyano-6-(3-methoxyphenyl)-4-methylthio-2-pyranone†

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Abstract

In the crystal structure of the title compound, $C_{14}H_{11}NO_3S$, the asymmetric unit consists of two molecules having different conformations. The main difference involves the orientation of the methoxy groups, but the angles between the two six-membered rings also differ slightly. This is the first reported structure of a δ-lactone with methylthio and cyano substituents.

Comment

Substituted δ-lactones are useful intermediates in the synthesis of various biologically active naturally occurring pyrones such as anibine, phenylcoumalin, paracotoin and xangonin (Tominaga, Ushirogochi & Matsuda, 1987; Tominaga, Ushirogochi, Matsuda & Kobayashi, 1977). They are also well known for their medicinal (Tominaga, Ushirogochi, Matsuda & Kobayashi, 1984) and synthetic applications (Ram, Hussaini, Singh & Shoeb, 1993). We have synthesized several lactones and subjected them to antibacterial and antifungal activity screening. In this context, the title phenyl-substituted δ-lactone, (I), has been prepared and its X-ray structure is reported here. It would appear to be the first reported structure of a δ-lactone with methylthio and cyano substituents.

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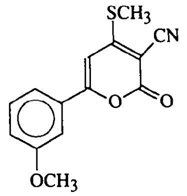
† Alternative nomenclature: 6-(3-methoxyphenyl)-4-methylthio-2-oxo-3-pyrancarbonitrile.



(I)

The asymmetric unit contains two molecules of the title compound and one of these is illustrated in Fig. 1. These two molecules have the same bond lengths and angles within experimental error, but have different conformations. These differences are illustrated in Fig. 2, in which the two molecules have been superimposed at the labelled atoms. Clearly the major difference involves the orientation of the methoxy groups; this is quantified by the C14—O3—C12—C11 torsion angles of 180.0 (6) and −3.3 (11)° in the two molecules. A smaller effect involves the relative orientations of the six-membered rings; this can be gauged from the O2—C4—C8—C9 torsion angles of 170.1 (6) and 173.1 (5)°.

The bond angles and distances are unexceptional (Allen *et al.*, 1987). The average C_{sp^2}—S distance [1.735 (6) Å] is shorter than the average C_{sp^3}—S distance [1.781 (6) Å]; this observation is consistent with some double bonding in the sp^2 case. The C2—C6—N1 cyanide units are linear within experimental error.

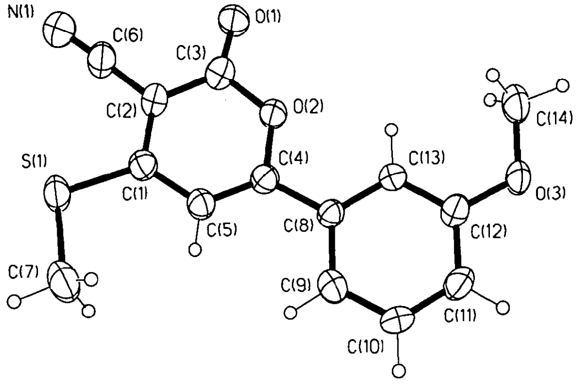


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

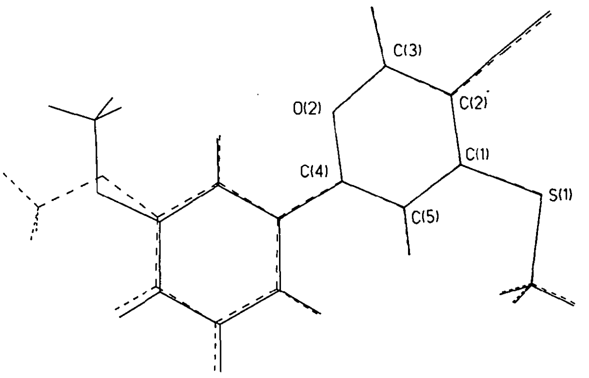


Fig. 2. Superposition of the two molecules in the asymmetric unit.

Experimental

For the preparation of (I), ethyl 2-cyano-3,3-bis(methylthio)propenoate (4.34 g, 0.02 mol) (Söderbäck, 1963) was dissolved in *N*,*N*-dimethylformamide (40 ml). KOH (2.24 g, 0.04 mol) was added and the solution stirred for 10 min. 3-Methoxyacetophenone (2.75 ml, 0.02 mol) was added and the contents stirred for 6 h at 301–303 K. The reddish-brown liquid supernatant was poured onto crushed ice (200 g) and the contents stirred for 4 h, when a yellow solid precipitated out. It was filtered, dried and recrystallized from acetone as yellow needles (2.5 g, 46% yield; m.p. 463 K).

Crystal data

$C_{14}H_{11}NO_3S$
$M_r = 273.30$
Orthorhombic
$Pna2_1$
$a = 29.321\ (23)$ Å
$b = 18.671\ (17)$ Å
$c = 4.693\ (3)$ Å
$V = 2569\ (3)$ Å^3
$Z = 8$
$D_x = 1.413$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 8$–$10°$
$\mu = 0.254$ mm^{-1}
$T = 220\ (2)$ K
Needle
0.70 × 0.25 × 0.07 mm
Yellow

Data collection

Siemens *P*3*R*3 diffractometer
ω–2θ scans
Absorption correction: analytical
$T_{min} = 0.94$, $T_{max} = 0.98$
2659 measured reflections
2556 independent reflections
1859 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0316$
$\theta_{max} = 25.05°$
$h = -34 \rightarrow 1$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 5$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0513$
$wR(F^2) = 0.1666$
$S = 1.105$
2544 reflections
347 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.7503P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.14 (19)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.23631 (5)	0.89517 (8)	0.2746 (4)	0.0463 (4)
O1	0.10556 (13)	0.7251 (2)	0.4521 (11)	0.0459 (11)
O2	0.16879 (12)	0.7070 (2)	0.6970 (9)	0.0348 (10)
O3	0.19917 (13)	0.5303 (2)	1.4656 (11)	0.0466 (12)

N1	0.1231 (2)	0.8721 (3)	−0.0260 (15)	0.055 (2)
C1	0.2117 (2)	0.8213 (3)	0.4356 (14)	0.0341 (13)
C2	0.1671 (2)	0.8031 (3)	0.3615 (13)	0.0325 (14)
C3	0.1441 (2)	0.7443 (3)	0.4937 (14)	0.0348 (14)
C4	0.2135 (2)	0.7227 (3)	0.7593 (14)	0.0318 (13)
C5	0.2344 (2)	0.7785 (3)	0.6379 (14)	0.0342 (13)
C6	0.1424 (2)	0.8410 (3)	0.1507 (16)	0.043 (2)
C7	0.2921 (2)	0.8986 (4)	0.427 (2)	0.064 (2)
C8	0.2329 (2)	0.6732 (3)	0.9693 (14)	0.0301 (13)
C9	0.2798 (2)	0.6743 (3)	1.0243 (15)	0.045 (2)
C10	0.2973 (2)	0.6272 (3)	1.2202 (16)	0.048 (2)
C11	0.2709 (2)	0.5792 (3)	1.3627 (16)	0.044 (2)
C12	0.2242 (2)	0.5794 (3)	1.3116 (16)	0.0356 (14)
C13	0.2053 (2)	0.6245 (3)	1.1130 (13)	0.0318 (13)
C14	0.1509 (2)	0.5288 (3)	1.4193 (18)	0.049 (2)
S1′	0.48504 (5)	0.09602 (8)	0.2945 (5)	0.0479 (4)
O1′	0.64227 (13)	0.2002 (2)	0.3789 (12)	0.0560 (14)
O2′	0.58904 (13)	0.2474 (2)	0.6514 (10)	0.0392 (10)
O3′	0.61100 (15)	0.4330 (2)	1.3378 (13)	0.0596 (14)
N1′	0.5901 (2)	0.0686 (3)	−0.0737 (14)	0.0516 (15)
C1′	0.5239 (2)	0.1575 (3)	0.4300 (14)	0.0326 (13)
C2′	0.5675 (2)	0.1547 (3)	0.3286 (14)	0.0328 (13)
C3′	0.6026 (2)	0.1997 (3)	0.4428 (15)	0.0401 (15)
C4′	0.5450 (2)	0.2531 (3)	0.7416 (14)	0.0354 (14)
C5′	0.5125 (2)	0.2088 (3)	0.6410 (14)	0.0336 (13)
C6′	0.5801 (2)	0.1068 (3)	0.1088 (16)	0.0370 (14)
C7′	0.4341 (2)	0.1153 (3)	0.4831 (17)	0.050 (2)
C8′	0.5391 (2)	0.3104 (3)	0.9556 (14)	0.0344 (14)
C9′	0.4958 (2)	0.3295 (3)	1.0501 (14)	0.040 (2)
C10′	0.4910 (2)	0.3845 (3)	1.2446 (17)	0.048 (2)
C11′	0.5288 (2)	0.4212 (3)	1.3459 (17)	0.049 (2)
C12′	0.5711 (2)	0.4016 (3)	1.2553 (16)	0.042 (2)
C13′	0.5763 (2)	0.3462 (3)	1.0565 (14)	0.0375 (15)
C14′	0.6082 (2)	0.4942 (3)	1.5246 (19)	0.062 (2)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.731 (6)	S1′—C1′	1.738 (6)
S1—C7	1.788 (7)	S1′—C7′	1.774 (6)
O1—C3	1.203 (7)	O1′—C3′	1.201 (7)
O2—C4	1.375 (6)	O2′—C4′	1.364 (6)
O2—C3	1.385 (7)	O2′—C3′	1.382 (8)
O3—C12	1.379 (7)	O3′—C12′	1.364 (7)
O3—C14	1.433 (7)	O3′—C14′	1.442 (8)
N1—C6	1.158 (8)	N1′—C6′	1.152 (8)
C4—C8	1.465 (8)	C4′—C8′	1.478 (8)
C1—S1—C7	103.6 (3)	C1′—S1′—C7′	103.7 (3)
C4—O2—C3	122.5 (4)	C4′—O2′—C3′	122.9 (5)
C12—O3—C14	117.3 (5)	C12′—O3′—C14′	117.6 (5)
C2—C1—S1	118.4 (5)	C2′—C1′—S1′	117.5 (5)
C1—C2—C6	122.2 (5)	C1′—C2′—C6′	121.5 (5)
N1—C6—C2	178.3 (7)	N1′—C6′—C2′	178.8 (7)
C7—S1—C1—C2	−179.9 (5)	C7′—S1′—C1′—C2′	178.5 (5)
C5—C1—C2—C6	−177.0 (6)	C5′—C1′—C2′—C6′	−177.0 (5)
O2—C4—C8—C9	170.1 (6)	O2′—C4′—C8′—C9′	173.1 (5)
C14—O3—C12—C11	180.0 (6)	C14′—O3′—C12′—C11′	−3.3 (11)

The temperature of the crystal was controlled using an Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Refinement was on F^2 for all reflections except for 12 with very negative F^2 or flagged for potential systematic errors. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they were attached.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service (Allen *et al.*, 1991) at Daresbury. AK and NK thank the Council of Scientific and Industrial Research (CSIR, New Delhi, India) for the award of research fellowships.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 129–134

Disodium D-3-Phosphoglycerate (a Reinvestigation at 80 K) and Bis(cyclohexylammonium) D-3-Phosphoglycerate Dihydrate at 85 K

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Abstract

The structure of the D-3-phosphoglycerate dianion in the disodium salt $2Na^+.C_3H_5O_7P^{2-}$ [Na_2H(3-PGA), (I)] and the hydrated bis(cyclohexylammonium) salt $2C_6H_{14}N^+.C_3H_5O_7P^{2-}.2H_2O$ [(CHA)$_2$H(3-PGA).2H$_2$O, (II), where H(3-PGA) = $^-HO_3POCH_2CH(OH)COO^-$, CHA = $C_6H_{11}NH_3^+$] has been determined by X-ray analyses at 80 and 85 K, respectively. A room-temperature