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Acta Cryst. (1996). C**52**, 3104-3105

(*E*)-3-(4-Chlorophenyl)-3-cyclopropyl-2-(phenylthio)acrylonitrile

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(*Received 11 March 1996; accepted 30 May 1996*)

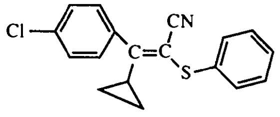
Abstract

The unambiguous identification of the *E* configuration of the title compound, $C_{18}H_{14}ClNS$, confirms a previous tentative assignment from NMR spectroscopic data. Bond lengths and angles are normal. The plane containing the acrylyl group makes angles of 98.0 (1) and 87.6 (3)° with the planes of the *p*-chlorophenyl and cyclopropyl rings, respectively, preventing conjugation.

Comment

The versatility of vinyl sulfides makes them highly valued synthetic intermediates. In addition, certain unsaturated sulfides, particularly vinyl sulfides, have been found to have significant negative inotropic activities (Gautier, Roche, Métin, Carpy & Madesclaire, 1995) and have also displayed useful biological activities as pesticides, bactericides (Erhardt, Ertel, Mildenberger, Sachse & Hartz, 1979) and oxygen-radical scavengers (Duroux, Roche & Madesclaire, 1991). Knowledge of the exact configuration of the *Z* and *E* diastereoisomers was required to conduct a pharmacological study and establish structure–activity relationships. Also, these readily accessible *gem*-functionalized vinyl sulfides are useful intermediates in the synthesis of sulfonamides, which are of great interest in cardiovascular pharmacology.

We report here the X-ray crystal structure determination of the title compound, (1). The results confirm the *E* configuration of this diastereoisomer, as already suggested by NMR spectroscopic data (Roche & Madesclaire, 1996).



(1)

Bond lengths and angles are consistent with previous results. In particular, values for S—C bond lengths [S(13)—C(2) 1.766 (4) and S(13)—C(14) 1.769 (3) Å] and C=C—S and C—S—C angles [C(3)=C(2)—S(13) 123.6 (3) and C(2)—S(13)—C(14) 103.7 (2)°] are consistent with published values for other vinyl sulfides; respective corresponding values are 1.752 (10) and 1.794 (12) Å, and 127.0 (2) and 102.5 (2)° (Derissen & Bijen, 1973), 1.759 (8) and 1.795 (8) Å, and 127.5 (7) and 102.1 (5)° (Samdal, Seip & Torgrimsen, 1979), 1.752 (2) and 1.793 (3) Å, and 124.9 (2) and 100.1 (1)° (Métin, Roche, Veschambre & Madesclaire, 1992), and 1.755 (2) and 1.768 (2) Å, and 123.2 (1) and 103.0 (1)° (Gautier *et al.*, 1995).

The length of the C≡N triple bond [1.143 (5) Å] is in the normal range [1.133 (6)–1.152 (7) Å; Rabinovich & Shakked, 1978]. Also, the length of the C(1)—C(2) bond [1.438 (5) Å] shows it to be a single σ bond, excluding any π delocalization between the vinyl C(2)=C(3) double bond and the nitrile C(1)≡N(20) triple bond.

The central C(2)=C(3) vinyl group and atoms S(13), C(1), C(4) and C(10) are nearly coplanar, the maximum deviation from the best plane being 0.070 (4) Å. As expected, the N(20) atom lies in this plane, with a deviation of 0.024 (4) Å.

The plane defined by the vinyl group forms an angle of 98.0 (1)° with the plane of the *p*-chlorophenyl ring, which prevents π-electron conjugation, and an angle of 87.6 (3)° with the cyclopropane ring.

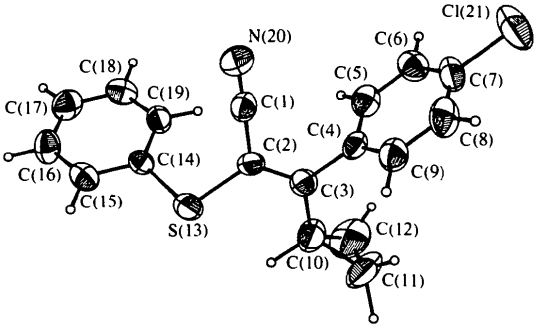


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

There is no evidence for the formation of intra- or intermolecular hydrogen bonds. The crystal packing is stabilized by π–π (about 3.8 Å) and σ–π (about 4.3 Å) charge-transfer interactions, and by van der Waals contacts.

Experimental

The synthesis of the title compound was carried out by condensation of phenylthioacetonitrile and *p*-chlorophenyl cyclopropyl ketone (molar ratio 1:1) in the presence of ^{n}BuLi (1.2 mol, c = 1.4 *M*) in tetrahydrofuran solution for 1 h at 243 K under argon. It was crystallized from ethyl acetate. The density D_m was measured by flotation in xylene.

Crystal data

$C_{18}H_{14}ClNS$
$M_r = 311.828$
Orthorhombic
$P2_12_12_1$
$a = 5.739\ (1)$ Å
$b = 7.621\ (2)$ Å
$c = 36.561\ (5)$ Å
$V = 1599.1\ (6)$ Å^3
$Z = 4$
$D_x = 1.2953$ Mg m^{-3}
$D_m = 1.26$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–$12°$
$\mu = 0.362$ mm^{-1}
$T = 293$ K
Prismatic
0.23 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2755 measured reflections
2755 independent reflections
1466 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 30°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 51$
3 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.049$
$S = 1.34$
1462 reflections
191 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.11$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $g = 0.566 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	0.3500 (7)	−0.1711 (5)	0.89555 (9)	3.44 (8)
C(2)	0.3758 (7)	0.0165 (5)	0.89402 (9)	3.16 (8)
C(3)	0.5054 (7)	0.0909 (5)	0.86763 (9)	3.38 (9)
C(4)	0.6193 (7)	−0.0233 (5)	0.84008 (9)	3.11 (8)
C(5)	0.8248 (8)	−0.1084 (5)	0.84804 (9)	3.93 (9)
C(6)	0.9339 (9)	−0.2177 (6)	0.8227 (1)	4.3 (1)
C(7)	0.8314 (9)	−0.2386 (5)	0.7894 (1)	4.22 (9)
C(8)	0.6281 (9)	−0.1593 (6)	0.78073 (9)	4.8 (1)
C(9)	0.5190 (8)	−0.0502 (6)	0.8060 (1)	4.14 (9)
C(10)	0.540 (1)	0.2817 (5)	0.8655 (1)	5.3 (1)
C(11)	0.581 (1)	0.3773 (6)	0.8306 (1)	6.9 (1)
C(12)	0.770 (1)	0.3566 (7)	0.8555 (2)	7.8 (1)
S(13)	0.2015 (2)	0.1367 (1)	0.92493 (3)	4.09 (2)
C(14)	0.2813 (7)	0.0523 (4)	0.96822 (8)	2.67 (7)
C(15)	0.1241 (7)	0.0805 (5)	0.9961 (1)	3.56 (8)
C(16)	0.1772 (8)	0.0263 (6)	1.03148 (9)	4.3 (1)
C(17)	0.3841 (9)	−0.0562 (6)	1.0385 (1)	4.5 (1)
C(18)	0.5428 (8)	−0.0850 (5)	1.0108 (1)	3.93 (9)
C(19)	0.4933 (8)	−0.0290 (5)	0.97579 (9)	3.37 (8)
N(20)	0.3273 (7)	−0.3199 (4)	0.89710 (9)	4.91 (9)
Cl(21)	0.9698 (3)	−0.3748 (2)	0.75769 (3)	7.32 (3)

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

C(1)—C(2)	1.438 (5)	C(7)—Cl(21)	1.748 (4)
C(1)—N(20)	1.143 (5)	C(10)—C(11)	1.487 (6)
C(2)—C(3)	1.344 (5)	C(10)—C(12)	1.482 (9)
C(2)—S(13)	1.766 (4)	C(11)—C(12)	1.426 (9)
C(3)—C(4)	1.483 (5)	S(13)—C(14)	1.769 (3)
C(3)—C(10)	1.470 (5)		
C(2)—C(1)—N(20)	179.1 (4)	C(3)—C(10)—C(11)	123.5 (3)
C(1)—C(2)—C(3)	120.3 (3)	C(3)—C(10)—C(12)	121.0 (4)
C(1)—C(2)—S(13)	115.6 (3)	C(11)—C(10)—C(12)	57.4 (4)
C(3)—C(2)—S(13)	123.6 (3)	C(10)—C(11)—C(12)	61.1 (4)
C(2)—C(3)—C(4)	118.9 (3)	C(10)—C(12)—C(11)	61.5 (4)
C(2)—C(3)—C(10)	122.1 (3)	C(2)—S(13)—C(14)	103.7 (2)
C(4)—C(3)—C(10)	119.0 (3)		

C(1)—C(2)—C(3)—C(4)	0.5 (6)
C(1)—C(2)—C(3)—C(10)	−178.7 (4)
S(13)—C(2)—C(3)—C(4)	−171.7 (3)
C(3)—C(2)—S(13)—C(14)	−130.1 (4)
C(2)—C(3)—C(4)—C(5)	−80.6 (5)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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