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3-Cyano-4-(*N*,*N*-dimethylamino)-6-phenyl-2*H*-pyran-2-one

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.114
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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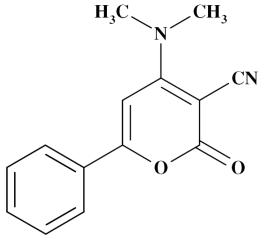
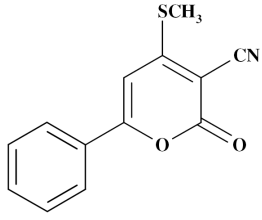
The isolation of the title compound, $C_{14}H_{12}N_2O_2$, as a by-product from the reaction of ethyl 2-cyano-3,3-bis(methylthio)acrylate with acetophenone is reported. There are two independent molecules, and the dihedral angles between the pyran ring and the attached phenyl group are 10.32 (8) and 26.34 (5)°.

Comment

The presence of carbonyl functionality and its position in conjugation with the double bond carrying bis(alkylthio) group at the β-position places ketene dithioacetal and its derivatives as versatile reagents for the preparation of different classes of heterocyclic compounds (Kumar *et al.*, 1976; Chauhan & Junjappa, 1976). We have reported the synthesis of a number of heterocyclic compounds by the application of ketene dithioacetals (Parmar *et al.*, 1997). Various 4-hydroxy-2*H*-pyran-2-ones and their derivatives have exhibited a variety of pharmacological properties (Israili & Smissman, 1976; Kretzschmar *et al.*, 1969); some of these pyrones were found to be useful intermediates in the synthesis of naturally occurring bioactive compounds such as phenylcoumalin, paracotoin, methoxyparacotoin and yangonin



(I)



(II)

derivatives (Tominaga *et al.*, 1977, 1984). In an attempt to synthesize 3-cyano-4-methylthio-6-phenyl-2*H*-pyran-2-one, (II), by treating ethyl 2-cyano-3,3-bis(methylthio)acrylate and acetophenone in DMF and potassium hydroxide, we obtained the title compound, (I), as a minor side product along with (II). Pyrones of the type (I) having an amino group at the C-4 position are of particular interest in that they have exhibited antibacterial and antifungal activities. Although the title compound has been previously reported (Tominaga *et al.*, 1984), its NMR and MS data have not been reported and the melting point (519 K) given earlier does not agree with that obtained for our sample (559–560 K). In order to characterize this compound unambiguously, we now report extensive spectral data and its X-ray crystallographic structure.

The asymmetric unit of the title compound, (I), contains two molecules, one of which is illustrated in Fig. 1. The bond

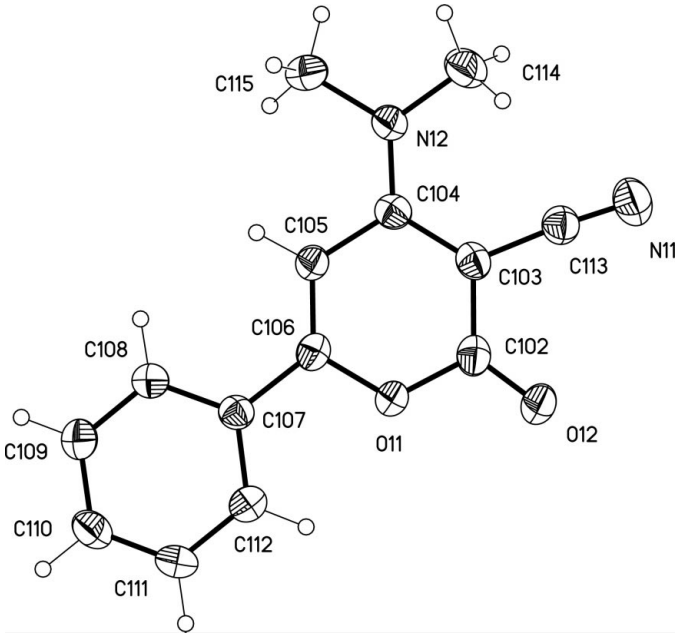


Figure 1
View of one of the two independent molecules in (I). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

lengths and angles are unexceptional and are essentially identical for both molecules. The conformations of these two molecules, however, do differ significantly. The angles between the least-squares planes through the pyran ring and the attached phenyl groups are 10.32 (8) and 26.34 (5)° for the two molecules; the comparative angles between the planes of the pyran rings and the C—N—C planes of the amino groups are 15.13 (15) and 7.00 (12)°, respectively. These differences are also illustrated by the torsion angles listed in Table 1.

The structure of the 3-cyano-2*H*-pyran-2-one fragment has been reported previously, but only in combination with a 4-methylthio substituent (five structures: Kumar *et al.*, 1999, and references therein). In all of these structures, the methylthio substituent is approximately coplanar with the pyran ring. Similarly, in (I), the dimethylamino group in the 4-position is almost coplanar (see angles quoted above) and this may be attributed, as in the methylthio case, to some π-bonding; this is manifest in the C_{ar}—N linkage which is much shorter than the N—Me distances (Table 1).

Experimental

A mixture of ethyl 2-cyano-3,3-bis(methylthio)acrylate (4.34 g, 0.02 mol), acetophenone (2.4 ml, 0.02 mol), powdered KOH (2.24 g, 0.04 mol) and DMF (30 ml) was stirred at 305 K for 7 h. The red–brown mixture was poured onto crushed ice (300 g) and stirred at room temperature for 2 h. The yellow solid that separated was filtered, washed with water, dried and treated with cold acetone (3 × 15 ml); the combined acetone solution was concentrated to yield (II) as yellow needles (1.94 g, 40% yield; m.p. 481 K) [*cf.* literature m.p. 474 K (Tominaga *et al.*, 1984)]. The cold acetone insoluble solid crystallized from hot acetone to yield (I) as pale yellow needles (0.96 g, 20% yield), m.p. 559–560 K (literature m.p. 519 K, Tominaga *et al.*, 1984).

Crystal data

$C_{14}H_{12}N_2O_2$
M_r = 240.26
Monoclinic, $P2_1/n$
a = 11.6587 (9) Å
b = 7.2783 (6) Å
c = 27.9741 (16) Å
β = 99.684 (3)°
V = 2339.9 (3) Å^3
Z = 8
D_x = 1.364 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4345 reflections
θ = 1.5–26.0°
μ = 0.09 mm^{-1}
T = 180 (2) K
Block, pale yellow
0.30 × 0.20 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.973, T_{max} = 0.982
12 607 measured reflections
4561 independent reflections
2864 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.0°
$h = -10 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -34 \rightarrow 34$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.114
S = 1.014
4561 reflections
329 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N12—C104	1.341 (2)	N22—C204	1.342 (2)
N12—C114	1.462 (3)	N22—C214	1.455 (2)
N12—C115	1.476 (2)	N22—C215	1.466 (2)
C114—N12—C104—C103	−14.6 (3)	C214—N22—C204—C203	7.7 (3)
O11—C106—C107—C108	−170.67 (17)	O21—C206—C207—C208	−153.68 (17)

H atoms were added at calculated positions and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL*/*PC* (Siemens, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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