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trans-1-Cyano-2-phenylcyclopropanecarboxamide

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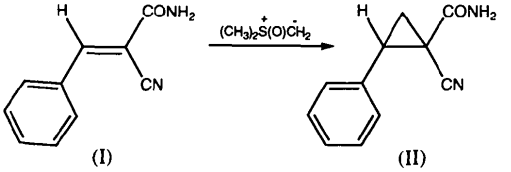
Abstract

In the title compound, $C_{11}H_{10}N_2O$, the carboxamide group adopts a bisected conformation with the carbonyl O atom eclipsing the cyclopropane ring, while the phenyl ring adopts an eclipsed conformation with respect to the C2—C3 bond of the cyclopropane ring. The crystal structure consists of cyclic $-CONH_2$ hydrogen-bonded dimers, wherein the hydrogen-bonded molecules are related by an inversion centre. These dimers are arranged along the crystallographic *x* axis.

Comment

Active research directed towards the synthesis of 1-aminocyclopropanecarboxylic acid and its alkylated analogs has been developed during recent years (Stammer, 1990; Burgess, Ho & Moge-Sherman, 1994) because of the potential applicability of these compounds as plant-growth and fruit-ripening regulators (Hoffman, Yang, Ichiara & Sakamura, 1982), as well as their use in conformationally restricted peptides (Burgess, Ho & Pettitt, 1994; Campbell, Horwell, Mahon, Pritchard & Walford, 1993).

Our interest in the synthesis of cyclopropyl amino acids (Cativiela, Díaz-de-Villegas & Jiménez, 1994, 1995) prompted us to test the behaviour of (*E*)-2-cyanocinnamamide, (I), as a precursor in the synthesis of 1-amino-2-phenylcyclopropanecarboxylic acid. When compound (I) was treated with Corey ylide, *i.e.* dimethyloxosulfonium methylide, a high yield of *trans*-1-cyano-2-phenylcyclopropanecarboxamide, (II), was obtained. In order to establish unambiguously the relative stereochemistry of the phenyl and amide groups, the crystal structure of this cyclopropane derivative has been determined.



(I) (II)

A perspective view of the title molecule, (II), together with atomic numbering is shown in Fig. 1. The values of the bond angles C5—C1—C4, C5—C1—C2 and C3—C1—C4 of 117.3 (2), 117.3 (2) and 117.2 (2)°, respectively, have been observed in other cyclopropane derivatives (Aitken, Royer, Husson, Chiaroni & Riche, 1990) and are related to the narrowing of the C3—C1—C2 bond angle to 57.09 (13)°. Significant nonlinearity in the cyano group (N2—C5—C1 bond angle of 178.3°) was observed.

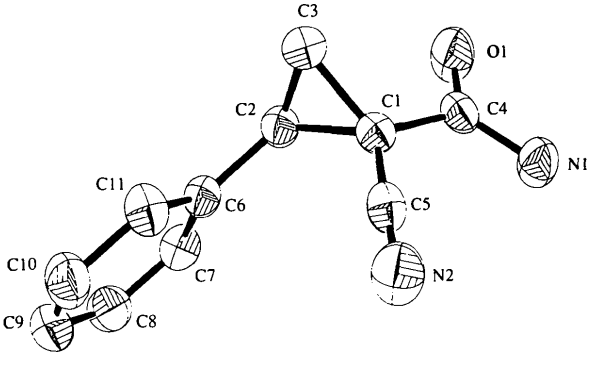


Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The C5—C1—C2—C6 torsion angle is twisted by −7.3° from the theoretical value (0°) for a *cis*-disubstituted cyclopropane. The amide group adopts a bisected conformation with the carbonyl O atom eclipsing the cyclopropane ring, with a torsion angle O1—C4—C1—*M*1 of 4.5° (where *M*1 is the midpoint of C2—C3 bond). This conformation allows optimum conjugation between the C=O moiety of the amide group and the cyclopropane ring. The C3—C2—C6—C11 torsion angle of −9.2 (3)° indicates that the aromatic ring

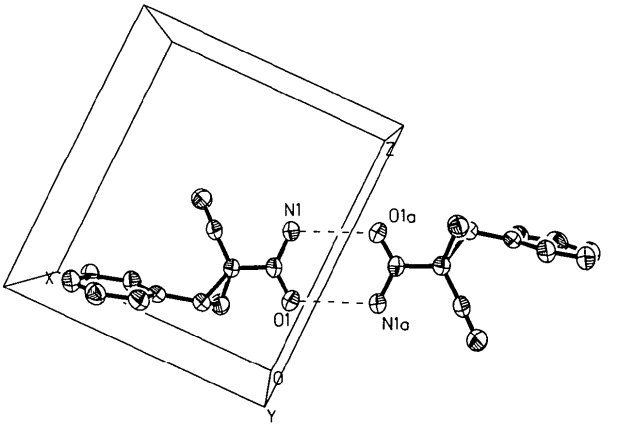


Fig. 2. View of the title compound along the crystallographic *y* axis showing hydrogen bonds between two molecules related by an inversion centre.

is in an eclipsed conformation with respect to the C2—C3 bond. This conformation complicates the conjugation between the phenyl group and the cyclopropane ring and is probably due to an added steric effect between the phenyl group and the substituents on the C1 atom of the cyclopropane ring.

The crystal structure of *trans*-1-cyano-2-phenylcyclopropanecarboxamide consists of cyclic $-CONH_2$ hydrogen-bonded dimers. The amide H atom is hydrogen bonded to the amide O atom of the nearest $(-x, -y+2, -z+1)$ symmetry-related molecule. A dimer is formed which consists of the *RS* and *SR* enantiomers of the racemic mixture related by an inversion centre (Fig. 2). Dimers in the unit cell are arranged in two separate infinite chains along the crystallographic x axis.

Experimental

The synthesis of *trans*-1-cyano-2-phenylcyclopropanecarboxamide was carried out under an argon atmosphere by reaction of (*E*)-2-cyanocinnamamide, (I), and freshly prepared NaH-derived dimethyloxosulfonium methylide (molar ratio 1:1.2) in dry dimethylformamide for 15 min at room temperature. Crystals were obtained by slow evaporation from chloroform solution.

Crystal data

$C_{11}H_{10}N_2O$
$M_r = 186.21$
Monoclinic
$P2_1/n$
$a = 9.292\ (2)$ Å
$b = 10.139\ (2)$ Å
$c = 10.095\ (2)$ Å
$\beta = 91.59\ (3)°$
$V = 950.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.301$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 4.5–12.5°$
$\mu = 0.086$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.26 × 0.26 × 0.24 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2206 measured reflections
1649 independent reflections
1170 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0181$
$\theta_{max} = 25°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 97 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0435$
$wR(F^2) = 0.1171$
$S = 1.071$
1649 reflections
128 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1576P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.028$
$\Delta\rho_{max} = 0.131$ e Å^{-3}
$\Delta\rho_{min} = -0.176$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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}
O1	0.08289 (15)	0.9678 (2)	0.34256 (14)	0.0639 (5)
N1	0.1893 (2)	0.9559 (2)	0.5446 (2)	0.0495 (5)
N2	0.5307 (2)	0.8237 (2)	0.5133 (2)	0.0549 (5)
C1	0.3220 (2)	0.8897 (2)	0.3525 (2)	0.0371 (5)
C2	0.3607 (2)	0.9479 (2)	0.2154 (2)	0.0398 (5)
C3	0.3032 (2)	0.8125 (2)	0.2227 (2)	0.0499 (6)
C4	0.1881 (2)	0.9414 (2)	0.4142 (2)	0.0391 (5)
C5	0.4395 (2)	0.8525 (2)	0.4406 (2)	0.0377 (5)
C6	0.5129 (2)	0.9792 (2)	0.1828 (2)	0.0365 (5)
C7	0.5492 (2)	1.1093 (2)	0.1553 (2)	0.0445 (5)
C8	0.6874 (2)	1.1418 (2)	0.1199 (2)	0.0520 (6)
C9	0.7917 (2)	1.0460 (3)	0.1125 (2)	0.0540 (6)
C10	0.7580 (2)	0.9177 (3)	0.1406 (2)	0.0525 (6)
C11	0.6188 (2)	0.8835 (2)	0.1745 (2)	0.0459 (5)

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

O1—C4	1.229 (2)	C1—C3	1.531 (3)
N1—C4	1.324 (2)	C1—C2	1.555 (3)
N2—C5	1.143 (2)	C2—C3	1.475 (3)
C1—C5	1.440 (3)	C2—C6	1.495 (3)
C1—C4	1.502 (3)		
C5—C1—C4	117.3 (2)	C6—C2—C1	121.3 (2)
C4—C1—C3	117.2 (2)	C2—C3—C1	62.26 (13)
C5—C1—C2	117.3 (2)	O1—C4—N1	123.1 (2)
C4—C1—C2	116.8 (2)	O1—C4—C1	119.1 (2)
C3—C1—C2	57.09 (13)	N1—C4—C1	117.8 (2)
C3—C2—C1	60.65 (13)	N2—C5—C1	178.3 (2)
C5—C1—C2—C6	−7.3 (3)	C2—C1—C4—O1	36.6 (3)
C3—C1—C4—O1	−28.3 (3)	C3—C2—C6—C11	−9.2 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H···O1^i	0.91	2.00	2.908 (2)	175

Symmetry code: (i) $-x, 2-y, 1-z$.

The structure was refined by blocked full-matrix least squares, with anisotropic displacement parameters for all non-H atoms. H atoms were located from a difference Fourier map and refined using a riding model and with one overall isotropic displacement parameter.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-2-Fluorocyclohexyl *p*-Toluenesulfonate and *trans*-2-Fluorocycloheptyl *p*-Toluenesulfonate

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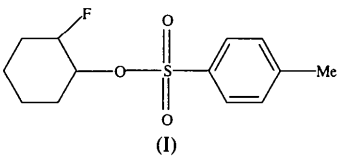
Abstract

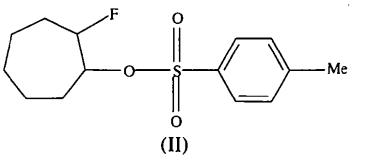
The title compounds, $C_{13}H_{17}FO_3S$ and $C_{14}H_{19}FO_3S$, have *trans* configurations with long distances between the F and sulfonyl O atoms. Some disorder was found in the cycloheptyl group.

Comment

Both title compounds, *trans*-2-fluorocyclohexyl *p*-toluenesulfonate, (I), and *trans*-2-fluorocycloheptyl *p*-toluenesulfonate, (II), are obtained by the action of tosyl chloride on *trans*-fluorohydrines (Baklouti & El-Gharbi, 1979). They constitute a class of compounds from which it is possible to synthesize quite a large variety of other monofluorinated products by substitution of the *p*-toluenesulfonate group (Toulgui, Chaabouni & Baklouti, 1990).



(I)



(II)

The identification of the two *trans*-2-fluorocycloalkyl *p*-toluenesulfonates, (I) and (II), was made from IR, ^{1}H NMR and ^{19}F NMR spectra, and mass spectroscopy measurements. From dynamic ^{19}F NMR, it was established that, in solution, the compounds adopt *trans* configurations; however, the spacial arrangement of the tosyl group relative to the fluorocycloalkyl moiety could not be determined without X-ray structure analysis. This investigation has shown that for the two title compounds, the more stable conformation is characterized by the longest distance between the F atoms and the O atoms of the sulfonyl moiety.

The average C—C distance is 1.378 (8) Å in the aromatic rings of the two compounds and 1.511 (5) Å in the cyclohexyl group of compound (I). As described elsewhere (Dupont *et al.*, 1991; Geetha & Rajan, 1991), some disorder was observed in the cycloheptyl group: one C—C bond distance (C6—C7) is 1.298 (15) Å, whereas the other six are comparable, in the range 1.487 (17)–1.521 (12) Å.

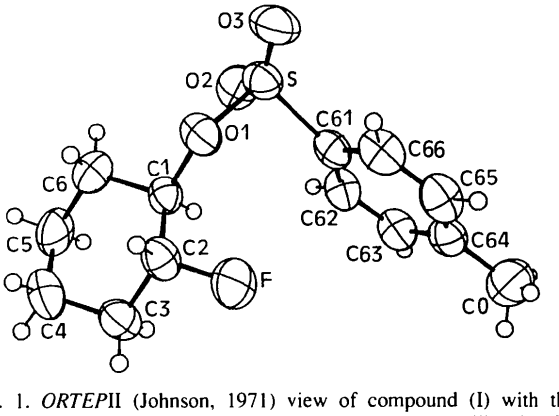


Fig. 1. *ORTEP*II (Johnson, 1971) view of compound (I) with the atomic numbering and 50% probability displacement ellipsoids for non-H atoms. H atoms are shown as small spheres of arbitrary radii.

† Deceased 24th October 1993.