$C_{14}H_{15}NO$

5-Phenyl-3-oxa-4-azatricyclo[5.2.1.0²,⁶]-dec-4-ene

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Abstract

A molecule of the title compound, $C_{14}H_{15}NO$, consists of an isoxazole ring fused to norbornane. The conformation of the five-membered isoxazole ring is nearly planar and its fusion onto the norbornane moiety is *exo*.

Comment

Isoxazolines have become versatile intermediates in the synthesis of a variety of complex biomolecules as a result of their relatively facile ring cleavage to afford β-hydroxy ketones and γ-amino alcohols (Curran, 1988; Torssell, 1988; Caramella & Grunanger, 1984; Lang & Lin, 1984). Nitrile oxide cycloaddition with alkenes is a simple method of obtaining isoxazolines (Grundmann & Grunanger, 1971). A view of the title compound, (I), is given in Fig. 1.
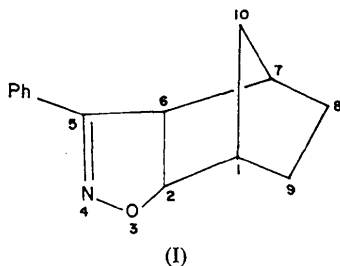
5-Phenyl-3-oxa-4-azatricyclo[5.2.1.0²,⁶]dec-4-ene forms a special type of compound since the bicyclic moiety (norbornane unit) can be fused to the isoxazole ring in two different ways, either in an *exo* or an *endo* fashion. In order to know which type of fusion has taken place, proton NMR spectra for the title compound were obtained.

The title compound was found to possess an *exo*-fused isoxazoline ring from analysis of the coupling
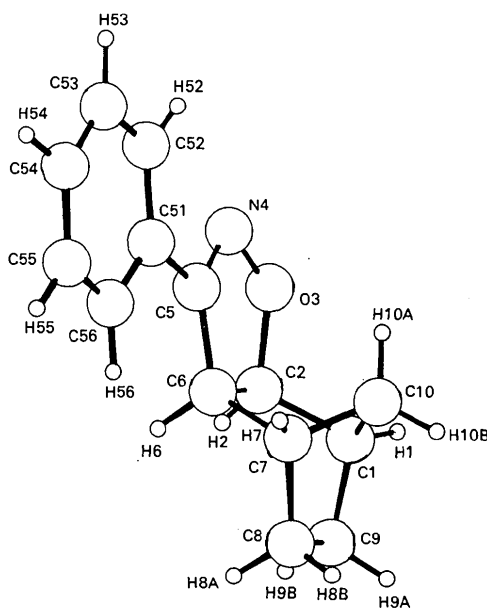

Fig. 1. Structure of the molecule showing the atomic numbering scheme.

constants of the H2 and H6 protons (Fig. 1); the signals were found to be doublets with $J_{2,6} = 8.2$ Hz. The value for *exo–exo* vicinal coupling in the norbornane moiety is 12 Hz, while the value for *endo–endo* vicinal coupling is 9 Hz. This serves to indicate that the fusion of the isoxazoline ring onto norbornane is *exo*, leading to an *endo* orientation of the H2 and H6 protons. According to the Karplus relationship (Kemp, 1986), the dihedral angle corresponding to 8.2 Hz is near 0°. From the X-ray structure analysis of the title compound, the dihedral angle for H2—C2—C6—H6 is found to be 5.6 (4)°, thereby the *exo* orientation of the isoxazole to norbornane is confirmed.

From the ^{13}C NMR data, it was found that the $C=N$ values were shifted upfield (~4 p.p.m.) when the substituent attached to the $C=N$ double bond was changed from methyl to phenyl (Nagarajan & Krishna Pillay, 1993*a*). This means that when an aryl group is present at the oximino linkage, there is an effective conjugation. This would require the phenyl ring to be coplanar with the isoxazole ring. The phenyl ring makes an angle of 4.6 (1)° with the isoxazole ring and this enables both groups to establish conjugation. It was found that a weak C—H···N intramolecular interaction exists between the proton on C52 of the phenyl and atom N4 [H···N = 2.504 (3) Å], which contributes to the stabilization of the planar conformation. Dapporto, Paoli, Brandi, De Sarlo, Goti & Guarna (1992) have also reported the presence of conjugation in a similar situation.

Although the isoxazoline ring has been shown to possess a puckered conformation analogous to pyra-

zoline and 2,3-dihydrofuran on the basis of NMR spectral characteristics (Nagarajan & Krishna Pillay, 1993*b*), it adopts a nearly planar conformation in the title compound [puckering parameters: $q_2 =$ 0.044 (3) Å, $\varphi_2 = 145$ (4)°; C2 deviates 0.072 (3) Å from the least-squares plane formed by O3, N4, C5, C6]. The fusion of the isoxazole to norbornane prevents it from achieving a puckered conformation.

The structure of the norbornane moiety may be viewed as two interlocked five-membered rings. C10 deviates -0.851 (3) and -0.853 (3) Å from the least-squares planes of C7, C8, C9 and C1 and C1, C2, C6 and C7, respectively, thus constituting the common flap of the two envelopes. Similar values of this deviation [0.86 (1) and 0.84 (1) Å] have been reported for the norbornane moiety in 6,6-dimethyl-1-phenyl-7-thiatricyclo[3.2.1.1^{3,8}]nonane 7,7-dioxide (Estienne, Pepe, Siri, Baldy & Samat, 1992). In the title compound, the norbornane moiety is found to be rigid, as expected.

Experimental

The title compound was obtained, employing Torssell's one-pot synthesis (Larsen & Torssell, 1984), by the cycloaddition of norbornene with benzonitrile oxide. *N*-Chlorosuccinimide (2.66 g, 0.02 mol) and dichloromethane (75 ml) were added to a round-bottomed flask, fitted with a reflux condenser. To the suspension, pyridine (1 ml) and benzaldoxime (2.42 g, 0.02 mol) were added. The mixture was heated under reflux for 1 h and allowed to cool. Norbornene (1.88 g, 0.02 mol), in 10 ml of CH_2Cl_2, and triethylamine (2 ml in 5 ml of CH_2Cl_2) were added and heated under reflux for 1 h. The mixture, after being allowed to cool, was washed with water (to remove succinimide, pyridine.HCl) and dried over anhydrous Na_2SO_4. Concentration *in vacuo* yielded the title compound (70%). Recrystallization from ethanol afforded colourless crystals, m.p. 382 K. Density D_m was measured by flotation in aqueous KBr.

Crystal data

$C_{14}H_{15}NO$
$M_r = 213.3$
Monoclinic
$P2_1/n$
$a = 12.456$ (8) Å
$b = 6.279$ (2) Å
$c = 14.409$ (3) Å
$\beta = 92.19$ (3)°
$V = 1126.1$ (8) Å^3
$Z = 4$
$D_x = 1.26$ Mg m^{-3}
$D_m = 1.27$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 22 reflections
$\theta = 10.1–18.6°$
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Plate
$0.3 \times 0.25 \times 0.1$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none

$R_{int} = 0.04$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 7$
$l = -17 \rightarrow 17$

2328 measured reflections
1488 independent reflections
1368 observed reflections
$[F > 6\sigma(F)]$

2 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.076$
$wR = 0.073$
$S = 2.49$
1368 reflections
145 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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}
C1	0.3484 (2)	−0.0519 (5)	1.0109 (2)	0.060 (1)
C2	0.2337 (2)	−0.0282 (5)	0.9764 (2)	0.050 (1)
O3	0.2068 (2)	0.1926 (3)	0.9547 (1)	0.064 (1)
N4	0.1262 (2)	0.2636 (4)	1.0129 (2)	0.055 (1)
C5	0.1043 (2)	0.1157 (4)	1.0706 (2)	0.042 (1)
C6	0.1676 (2)	−0.0831 (4)	1.0605 (2)	0.041 (1)
C7	0.2564 (2)	−0.1239 (4)	1.1369 (2)	0.051 (1)
C8	0.3073 (3)	−0.3364 (5)	1.1153 (2)	0.065 (1)
C9	0.3683 (3)	−0.2896 (6)	1.0269 (3)	0.072 (1)
C10	0.3429 (2)	0.0317 (5)	1.1100 (2)	0.061 (1)
C51	0.0224 (2)	0.1526 (4)	1.1402 (2)	0.044 (1)
C52	−0.0263 (3)	0.3501 (5)	1.1494 (2)	0.062 (1)
C53	−0.1024 (3)	0.3822 (6)	1.2142 (3)	0.077 (1)
C54	−0.1305 (3)	0.2181 (8)	1.2717 (3)	0.082 (1)
C55	−0.0853 (3)	0.0217 (7)	1.2633 (2)	0.072 (1)
C56	−0.0076 (2)	−0.0128 (5)	1.1976 (2)	0.055 (1)

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

C1—C2	1.502 (4)	C7—C8	1.515 (4)
C1—C9	1.529 (5)	C7—C10	1.516 (4)
C1—C10	1.525 (4)	C8—C9	1.536 (5)
C2—O3	1.457 (4)	C51—C52	1.389 (4)
C2—C6	1.530 (4)	C51—C56	1.388 (4)
O3—N4	1.405 (4)	C52—C53	1.371 (5)
N4—C5	1.283 (4)	C53—C54	1.376 (6)
C5—C6	1.487 (4)	C54—C55	1.363 (7)
C5—C51	1.476 (4)	C55—C56	1.396 (4)
C6—C7	1.552 (4)		
C9—C1—C10	102.0 (3)	C6—C7—C10	101.9 (2)
C2—C1—C10	101.5 (2)	C6—C7—C8	107.0 (2)
C2—C1—C9	107.1 (3)	C8—C7—C10	102.0 (2)
C1—C2—C6	104.4 (2)	C7—C8—C9	103.1 (3)
C1—C2—O3	111.9 (2)	C1—C9—C8	103.3 (3)
O3—C2—C6	104.9 (2)	C1—C10—C7	94.3 (2)
C2—O3—N4	109.7 (2)	C5—C51—C56	119.8 (3)
O3—N4—C5	109.4 (2)	C5—C51—C52	121.4 (3)
N4—C5—C51	119.8 (2)	C52—C51—C56	118.9 (3)
N4—C5—C6	114.7 (3)	C51—C52—C53	120.8 (3)
C6—C5—C51	125.5 (2)	C52—C53—C54	119.9 (4)
C2—C6—C5	101.1 (2)	C53—C54—C55	120.6 (4)
C5—C6—C7	115.8 (2)	C54—C55—C56	120.0 (4)
C2—C6—C7	102.0 (2)	C51—C56—C55	119.8 (3)
C9—C1—C10—C7	−54.2 (3)	C51—C5—C6—C2	177.9 (3)
C2—C1—C10—C7	56.2 (3)	C6—C5—C51—C52	174.5 (3)
C10—C1—C9—C8	32.9 (3)	C6—C5—C51—C56	−5.9 (4)
C2—C1—C9—C8	−73.2 (3)	C51—C5—C6—C7	−72.8 (4)
C9—C1—C2—C6	69.6 (3)	C5—C6—C7—C8	177.9 (2)
C9—C1—C2—O3	−177.4 (3)	C2—C6—C7—C8	−73.4 (3)
C10—C1—C2—C6	−36.9 (3)	C5—C6—C7—C10	−75.4 (3)
C10—C1—C2—O3	76.0 (3)	C2—C6—C7—C10	33.3 (3)

C14H15NO

C1—C2—C6—C7	2.3 (3)	C6—C7—C10—C1	−54.5 (2)
C1—C2—C6—C5	122.0 (2)	C8—C7—C10—C1	56.0 (3)
C1—C2—O3—N4	−117.3 (3)	C6—C7—C8—C9	69.6 (3)
O3—C2—C6—C7	−115.5 (2)	C10—C7—C8—C9	−37.0 (3)
O3—C2—C6—C5	4.2 (3)	C7—C8—C9—C1	2.2 (3)
C6—C2—O3—N4	−4.6 (3)	C5—C51—C56—C55	−179.8 (3)
C2—O3—N4—C5	3.1 (3)	C5—C51—C52—C53	179.9 (3)
O3—N4—C5—C6	−0.1 (3)	C52—C51—C56—C55	−0.2 (5)
O3—N4—C5—C51	179.3 (2)	C56—C51—C52—C53	0.3 (5)
N4—C5—C6—C2	−2.7 (3)	C51—C52—C53—C54	0.7 (6)
N4—C5—C51—C52	−4.8 (4)	C52—C53—C54—C55	−1.7 (6)
N4—C5—C51—C56	174.8 (3)	C53—C54—C55—C56	1.8 (6)
N4—C5—C6—C7	106.6 (3)	C54—C55—C56—C51	−0.8 (5)

Structure solution was by direct methods using *DIRDIF* (Beurskens *et al.*, 1990). Non-H atoms were located with *DIRDIF* using the *ORIENT* option with the norbornane rigid group, taken from *DIRDIF ORBASE*, as an input model. Refinement was performed by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). All the non-H atoms were refined with anisotropic displacement parameters. H atoms were located from a difference Fourier map and fixed at a distance of 0.95 Å from their parent atom. H atoms were included in the structure-factor calculations and given displacement parameters equal to $1.1U_{eq}$ of their parent atom, but their parameters were not refined. *PARST* (Nardelli, 1983) was used for molecular geometry calculations and molecular graphics were prepared using *PLUTO* (Motherwell & Clegg, 1978).

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Influence of Crystal Environment on Molecular Conformation: p-Bromo-N-(p-dimethylaminobenzylidene)aniline

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Abstract

p-Bromo-N-(p-dimethylaminobenzylidene)aniline, $C_{15}H_{15}BrN_2$, (1), comprises two independent molecules with markedly different conformations. Molecule *A* is essentially planar along its entire length (including the dimethylamino group) whereas molecule *B* deviates considerably from planarity with an interplanar angle of 145.8 (3)° between the two phenyl rings and the NMe₂ group twisted by 10 (2)° out of the plane of the phenyl ring to which it is bound. While polymorphism and crystal packing effects are well documented for benzylidene derivatives, this is an interesting example with two quite distinct conformations in the same crystal phase. The differences are accounted for in terms of crystal-packing effects. The structure highlights the ability of particular molecular arrangements to stabilize a less favourable molecular conformation.

Comment

Recently, we embarked on a programme to develop molecular materials which exhibit non-linear optical properties (Houlton, Jassim, Roberts, Silver, McArdle, Cunningham & Higgins, 1992; Houlton, Miller, Silver, Jassim, Ahmet, Axon, Bloor & Cross, 1993). Two classes of compound have been considered: organometallic and organic derivatives.