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trans-2-[(Dispiro[2.0.2.1]hept-7-yl)-carbonyl]-3-methyl- β -propiolactone

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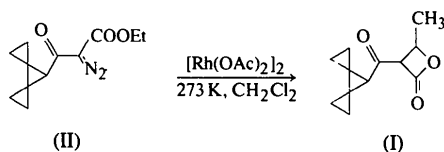
Abstract

The title compound, C₁₂H₁₄O₃, has a *trans* configuration of substituents in the β -lactone ring and an *exo* orientation of the carbonyl group with respect to the dispiroheptane moiety. The presence of a π -accepting carbonyl group causes elongation of the vicinal bonds and contraction of the distal one in the central three-membered ring. The difference in vicinal bond lengths is possibly a result of an asymmetric orientation of the carbonyl group.

Comment

The present work is part of our structural study of a relatively new class of hydrocarbons, *i.e.* polyspirocyclopropanes (triangulanes; Zefirov *et al.*, 1990) and their derivatives. Standard bond lengths for different kinds of bond in the triangulanes were calculated and found to be predictable on the basis of a simple scheme of substituent-effect addition (Lukin, Kozhushkov, Zefirov, Yufit & Struchkov, 1993). A similar conclusion was reached previously on the basis of a detailed study of the derivatives of the smallest triangulane, *i.e.* spiropentane (Irgartinger, Grieg, Klans & Gleiter, 1992). Recently, we have published (Yufit, Antipin, Lukin, Struchkov & Zefirov, 1993) the results of a charge-density study of dispiro[2.0.2.1]heptane-1-carboxylic acid, the first triangulane with a π -acceptor substituent, and discussed the

effect of the carboxy group on the molecular geometry. For a comparison of the effect of carbonyl-containing substituents in the 1- and 7-positions on the geometrical parameters of the dispiro[2.0.2.1]heptane skeleton, the X-ray crystallographic study of the title compound (I) was performed. The compound is a product of an unexpected intramolecular cyclization of (II), and its configuration was unknown.



Atoms C(8) and C(12) are located on opposite sides of the four-membered β -lactone ring plane (planar within 0.015 Å), which means that (I) has a *trans* configuration. The antiperiplanar (*ap*) orientation of the carbonyl group on the triangulane moiety is rather uncommon for triangulane, as well as for cyclopropane derivatives where the carbonyl group prefers the synperiplanar orientation (Allen, 1980). The bond lengths in the terminal three-membered rings are in good agreement with standard values (1.528 Å for terminal and 1.480 Å for central bonds). As in the previously studied triangulanes, the effect of the π -accepting carbonyl group is seen in contraction of the distal C(3)—C(4) bond and elongation of the vicinal C(3)—C(7) and C(4)—C(7) bonds. Using the standard values for bond lengths in triangulanes and Allen's (Allen, 1980) distal bond-lengthening parameter ($\delta_{\bar{C}=\text{O}} = 0.026$ Å), one can calculate the expected interatomic distances in the central ring of (I); 1.437 Å for the distal bond and 1.513 Å for the vicinal bonds. The observed values for the C(3)—C(4) and C(7)—C(4) bond lengths correspond well with those calculated, but the C(3)—C(7) distance of 1.530 (2) Å is elongated. There are no close intramolecular non-bonded contacts with C(3) and the

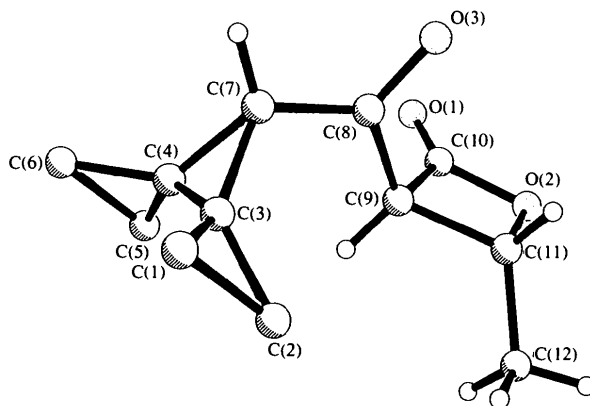


Fig. 1. The geometry and atom-labelling scheme of molecule (I) (H atoms of the triangulane CH₂ groups are omitted for clarity).

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elongation of the bond may be the result of an asymmetric orientation of the carbonyl group about the triangulane moiety [torsion angles O(3)—C(8)—C(7)—C(3) and O(3)—C(8)—C(7)—C(4) are -126.9 and 167.7° , respectively] which makes the interaction of the carbonyl π system more effective with one of the vicinal bent bonds rather than with another. We could not find any analogy of this feature among carbonyl-containing cyclopropanes and triangulanes, and only the further study of other triangulanes will help to determine whether it is an artefact or an effect specific to triangulanes.

Experimental

The title compound was crystallized from a hexane–diethyl ether solution (1:1).

Compound (I): yield 40%, m.p. 347–348 K, $^1\text{H NMR}$: 0.62–0.88 (*m*, 5H), 0.88–1.00 (*m*, 2H), 1.1–1.21 (*m*, 1H), 1.44 (*d*, 3H, $J = 5.8$ Hz), 2.48 (*s*, 1H), 4.40 (*d*, 1H, $J = 4.6$), 4.75 (*p*, 1H, $J = 5.8$ Hz); $^{13}\text{C NMR}$: 4.67, 4.90, 5.2–5.33 (CH_2); 23.98, 25.08, 163.82, 199.32 (C); 19.27 (CH_3); 34.66, 65.80, 70.43 (CH).

Crystal data

$\text{C}_{12}\text{H}_{14}\text{O}_3$
 $M_r = 206.2$
 Triclinic
 $P\bar{1}$
 $a = 8.000$ (4) Å
 $b = 10.162$ (4) Å
 $c = 7.198$ (2) Å
 $\alpha = 107.69$ (3) $^\circ$
 $\beta = 100.23$ (3) $^\circ$
 $\gamma = 73.48$ (3) $^\circ$
 $V = 531.8$ (4) Å 3
 $Z = 2$
 $D_x = 1.29$ Mg m $^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 20 reflections
 $\theta = 12$ – 13°
 $\mu = 0.092$ mm $^{-1}$
 $T = 123$ K
 Prism
 $0.3 \times 0.3 \times 0.2$ mm
 Colourless

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3000 measured reflections
 2799 independent reflections
 2267 observed reflections
 $[F \geq 4\sigma(F)]$
 $R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 30^\circ$
 $h = 0 \rightarrow 10$
 $k = -13 \rightarrow 14$
 $l = -10 \rightarrow 9$
 3 standard reflections monitored every 97 reflections
 intensity decay: not significant

Refinement

Refinement on F
 $R = 0.038$
 $wR = 0.037$
 $S = 2.78$
 2267 reflections
 192 parameters
 All H-atom parameters refined

$w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.34$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.21$ e Å $^{-3}$
 Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	0.8502 (1)	0.6188 (1)	0.1221 (1)	0.029 (1)
O(2)	0.8237 (1)	0.6871 (1)	−0.1582 (1)	0.026 (1)
O(3)	0.9248 (1)	0.9567 (1)	0.2259 (1)	0.026 (1)
C(1)	1.4980 (2)	0.9369 (2)	0.2193 (2)	0.026 (1)
C(2)	1.4177 (2)	0.8508 (2)	0.0288 (2)	0.024 (1)
C(3)	1.3839 (2)	0.8463 (1)	0.2227 (2)	0.018 (1)
C(4)	1.3787 (2)	0.7436 (1)	0.3209 (2)	0.019 (1)
C(5)	1.4134 (2)	0.5866 (1)	0.2827 (2)	0.027 (1)
C(6)	1.4938 (2)	0.6763 (2)	0.4691 (2)	0.028 (1)
C(7)	1.2217 (2)	0.8703 (1)	0.3253 (2)	0.018 (1)
C(8)	1.0582 (2)	0.8611 (1)	0.1982 (2)	0.018 (1)
C(9)	1.0535 (2)	0.7316 (1)	0.0239 (2)	0.018 (1)
C(10)	0.9015 (2)	0.6676 (1)	0.0183 (2)	0.021 (1)
C(11)	0.9592 (2)	0.7590 (1)	−0.1716 (2)	0.022 (1)
C(12)	1.0497 (2)	0.6867 (2)	−0.3544 (2)	0.031 (1)

Table 2. Selected geometric parameters (Å, $^\circ$)

O(1)—C(10)	1.193 (2)	C(4)—C(5)	1.485 (2)
O(2)—C(10)	1.357 (2)	C(4)—C(6)	1.480 (2)
O(2)—C(11)	1.500 (2)	C(4)—C(7)	1.519 (2)
O(3)—C(8)	1.221 (1)	C(5)—C(6)	1.526 (2)
C(1)—C(2)	1.529 (2)	C(7)—C(8)	1.466 (2)
C(1)—C(3)	1.477 (2)	C(8)—C(9)	1.522 (2)
C(2)—C(3)	1.484 (2)	C(9)—C(10)	1.524 (2)
C(3)—C(4)	1.440 (2)	C(9)—C(11)	1.539 (2)
C(3)—C(7)	1.530 (2)	C(11)—C(12)	1.498 (2)
C(10)—O(2)—C(11)	91.3 (1)	C(2)—C(1)—C(3)	59.2 (1)
C(1)—C(2)—C(3)	58.7 (1)	C(1)—C(3)—C(2)	62.2 (1)
C(1)—C(3)—C(4)	139.5 (1)	C(2)—C(3)—C(4)	139.4 (1)
C(1)—C(3)—C(7)	134.5 (1)	C(2)—C(3)—C(7)	136.0 (1)
C(4)—C(3)—C(7)	61.4 (1)	C(3)—C(4)—C(5)	139.0 (1)
C(3)—C(4)—C(6)	136.4 (1)	C(5)—C(4)—C(6)	61.9 (1)
C(3)—C(4)—C(7)	62.2 (1)	C(5)—C(4)—C(7)	138.1 (1)
C(6)—C(4)—C(7)	135.4 (1)	C(4)—C(5)—C(6)	58.8 (1)
C(4)—C(6)—C(5)	59.2 (1)	C(3)—C(7)—C(4)	56.4 (1)
C(3)—C(7)—C(8)	116.3 (1)	C(4)—C(7)—C(8)	122.9 (1)
O(3)—C(8)—C(7)	121.6 (1)	O(3)—C(8)—C(9)	118.5 (1)
C(7)—C(8)—C(9)	119.9 (1)	C(8)—C(9)—C(10)	112.3 (1)
C(8)—C(9)—C(11)	117.3 (1)	C(10)—C(9)—C(11)	83.8 (1)
O(1)—C(10)—O(2)	127.0 (1)	O(1)—C(10)—C(9)	137.5 (1)
O(2)—C(10)—C(9)	95.5 (1)	O(2)—C(11)—C(9)	89.3 (1)
O(2)—C(11)—C(12)	111.8 (1)	C(9)—C(11)—C(12)	119.0 (1)

H atoms were located from a difference Fourier map and refined isotropically. The programs in *SHELXTL-Plus* (Sheldrick, 1990) were used for all calculations.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Benzyl-5-methoxycarbonylmethylthio-4-nitroimidazole

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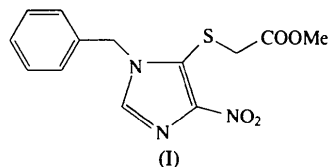
Abstract

Molecules of the title compound, methyl 1-benzyl-4-nitro-5-imidazolylthioacetate, C₁₃H₁₃N₃O₄S, can be viewed as an arrangement of three intersecting planes of atoms. The plane of the imidazole ring and its bonded atoms (r.m.s.d. = 0.030 Å) intersects the plane of the benzyl group (r.m.s.d. = 0.004 Å) at an angle of 89.0 (5)°. The plane of atoms extending from the S atom to the methyl group (r.m.s.d. = 0.004 Å) intersects the first two planes at angles of 85.9 (5) and 15.2 (5)°, respectively. The imidazole ring is twisted about the S—C3(ring) bond so that the C11—S—C3—N1(ring) torsion angle is obtuse. The conformation of the chain of atoms from the imidazole ring to the benzyl group is nominally *trans*, while that to the thioacetate is *gauche*.

Comment

The thioether-substituted nitroimidazole, (I), was intended to be a precursor, which should react *via* a cyclization pathway similar to that of a comparably substituted benzenoid compound (Sicker, Reifegerste, Hauptmann, Wilde & Mann, 1985), leading to a sulfur-containing purine analog. However, all attempts to cyclize (I) failed and its regiochemistry was in doubt, *i.e.* it was not known whether the S substituent was at the C1 or C3 position. Proton NMR chemical-shift differences between the C1 and C3 substituent patterns were insufficient for assignment, and convergent synthetic routes did not confirm a regioisomer. A diffraction study of crystals of (I) was thus undertaken and showed the molecule

to contain a benzyl group attached to the imidazole ring at position N1, a nitro group at C2 and a thio group at C3.



Details of the structure can be described in terms of three intersecting planes. A central plane composed of ten atoms (r.m.s.d. = 0.030 Å) contains the imidazole ring, nitro group and C4 and S atoms. A second plane contains the seven atoms of the benzyl group (r.m.s.d. = 0.004 Å) and intersects the central plane at an angle of 89.0 (5)°. The torsion angle involving atoms common to these two planes, C5—C4—N1—C3, is 102.7 (4)°. The third plane consists of six atoms and contains the S atom and the chain of atoms bonded to it (r.m.s.d. = 0.004 Å). It intersects the central plane at an angle of 85.9 (5)°. The C11—S—C3—N1 torsion angle is 117.4 (4)°. The benzyl and thio group planes intersect at an angle of 15.2 (5)°.

The benzyl and thio groups bonded to the imidazole ring have different conformations. Whereas the C10—C5 bond of the benzyl group is nominally *trans* to the C4—N1 bond [torsion angle 151.2 (4)°], the C12—C11 bond is *gauche* relative to the S—C3 bond [torsion angle -72.1 (4)°]. This molecular arrangement at the S atom results in closest and marginally favorable non-bonded distances from O1 to a C11 H atom [2.36 (1) Å], and from O4 to a C4 H atom [2.83 (1) Å].

Three related compounds have been reported that have the same arrangement of ten atoms as is present in the central plane of (I). All contain a methyl group bonded to the imidazole ring at position N1, a nitro group at C2 and a substituted S at C3. One compound contains a purine group at the S atom (Cook & Bugg, 1975), the second a hydroxypyridine group (Puig-Torres, Martin, Larson & Simonsen, 1984) and the third a triazole ring (Dupont, Dideberg & Jamouille, 1984).

Only minor geometrical differences are noted among the ten atoms common to all four compounds. However, two features present in structure (I) distinguish it from the other three. Firstly, the twist of the imidazole ring around the S—C3 bond in (I) results in a C11—S—C3—N1 torsion angle that is obtuse. In the three related structures, the ring is twisted in the opposite manner so that the comparable chains of atoms have an acute torsion angle. A change to this arrangement in structure (I) would move C4 too close to O4 and lead to steric destabilization. Secondly, the *gauche* conformation noted for the C12—C11—S—C3 linkage in structure (I) is *trans* for comparable linkages in all of the related structures. A change to this arrangement in (I) would eliminate the intramolecular, and presumably favorable, non-bonded contacts to atoms O1 and O4.