Diisopropyl 1-(methylsulfonyl)hydrazine-1,2-dicarboxylate

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Key indicators

Single-crystal X-ray study

$T = 200\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.030

wR factor = 0.089

Data-to-parameter ratio = 15.1

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

The title compound, $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_6\text{S}$, is the first example of a simple monosulfonamide derivative of a hydrazine-1,2-dicarboxylate. The molecule adopts an *s-cis* conformation about the amide bond bearing the methylsulfonyl group.

Received 13 March 2007

Accepted 13 March 2007

Comment

During attempts to effect a Mitsunobu reaction (Kürti & Czako, 2005) on an alcohol embedded within a complex and nitrogen-containing framework, the substrate was treated with a mixture of diisopropyl diazenedicarboxylate and triphenylphosphine, then heated at 323 K. The cooled reaction mixture was then quenched with water, worked up, and the material obtained reacted with methanesulfonyl chloride in the presence of triethylamine. Processing of this second reaction mixture in the usual fashion afforded small quantities of a crystalline product that was subjected to single-crystal X-ray analysis and thus shown to be the title compound, (I).

This outcome clearly suggested that the production of compound (I) by the means just described has nothing to do with the presence of the substrate alcohol. To establish that this was so, a tetrahydrofuran (THF) solution of bis-(1-methylethyl) diazenedicarboxylate was treated with triphenylphosphine in THF at 323 K then cooled, and water added to the reaction mixture. As a result, the previously reported (Muñiz & Nieger, 2006) reduction product diisopropyl 1,2-hydrazinedicarboxylate was obtained after chromatographic purification, although only in 15% yield. This material was immediately treated with a mixture of methanesulfonyl chloride and triethylamine (Crossland & Servis, 1970) and, after workup, the title compound, (I), was again obtained, this time in 82% yield. Compound (I) has been reported previously (Hunter & Barrows, 1975, 1976), but only in rather old patents, details of which are not available to us. The mechanism associated with the first step of the reaction sequence leading to (I) remains unclear and will be the subject of further study.

Compound (I) represents the first example of a simple monosulfonamide derivative of a hydrazine-1,2-dicarboxylate. All of the bond lengths and angles of (I) not involving H atoms fall within the expected ranges (Allen *et al.*, 1992).

Figure 1

The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of small radius.

A weak intermolecular hydrogen-bonding interaction (Table 1) is observed between the N—H group and the nominally sterically less hindered carbonyl atom O5 of an adjacent molecule. Intriguingly, the molecule adopts an *s-cis* conformation about the amide-type bond bearing the methanesulfonyl group. The same arrangement is also observed about the second and less substituted C(O)—N bond. The N2—C6 bond is shorter than its N1—C2 counterpart, presumably because of the reduced interaction between the N and CO in the latter case and as a result of the conjugation of this N atom with the attached SO₂Me residue.

Experimental

A solution of diisopropyl diazenedicarboxylate (1.04 ml, 5.5 mmol) and triphenylphosphine (1.39 g, 5.3 mmol) in tetrahydrofuran (16 ml) was heated at 323 K for 2 h and then water (0.8 ml) was added. The cooled reaction mixture was concentrated under reduced pressure and the residue subjected to flash chromatography (silica gel, eluted with 99:1 *v/v* hexane/propan-2-ol containing 0.1% triethylamine). Concentration of the relevant fractions ($R_f = 0.4$ in 9:1 *v/v* hexane/propan-2-ol containing 0.2% triethylamine) then afforded diisopropyl 1,2-hydrazinedicarboxylate (139 mg, 15%) as a clear colourless oil. A magnetically stirred solution of this material in dichloromethane (1.0 ml) maintained under nitrogen was cooled to 273 K and then treated, dropwise, with triethylamine (146 μ l, 1.05 mmol, 1.3 equivalents), followed by methanesulfonyl chloride (75 μ l, 1.0 mmol, 1.2 equivalents). After 2 h, the reaction mixture was warmed to 291 K, quenched with water (1.0 ml) and extracted with dichloromethane (2 $\times$ 1.0 ml). The combined organic phases were dried (MgSO₄), filtered and concentrated under reduced pressure and the residue subjected to flash chromatography (silica gel, eluted with 3:2 *v/v* hexane—ethyl acetate). Concentration of the relevant fractions ($R_f = 0.3$) afforded compound (I) as a white crystalline solid (165 mg, 82%; m.p. 375–377 K. Analysis, found: C 38.42, H 6.50, N 9.64%; C₉H₁₈N₂O₆S requires: C 38.29, H 6.43, N 9.92%.

Crystal data

C₉H₁₈N₂O₆S
 $M_r = 282.32$
 Monoclinic, $P2_1/c$
 $a = 9.0845$ (2) Å
 $b = 17.1465$ (4) Å
 $c = 9.9094$ (2) Å
 $\beta = 110.9720$ (13)°

$V = 1441.31$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 200$ K
 $0.43 \times 0.40 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: integration [Gaussian method (Coppens, 1970) implemented in *maxus* (Mackay *et al.*, 1999)]
 $T_{\min} = 0.908$, $T_{\max} = 0.976$

28645 measured reflections
 3280 independent reflections
 2459 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.089$
 $S = 0.94$
 3280 reflections
 217 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H1...O5 ⁱ	0.83 (2)	1.99 (2)	2.806 (2)	168 (2)

Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

All H atoms were observed in a difference electron-density map. They were then repositioned geometrically and their coordinates refined, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Restraints were imposed on distances and angles involving H atoms about C4.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN* (Molecular Structure Corporation, 1997); software used to prepare material for publication: *CRYSTALS*.

The authors thank the Australian Research Council for financial support.

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