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Acta Cryst. (1997). C**53**, 1973–1975

(*S*)-3-(*O*$^{\gamma}$-Methyl-*N*$^{\alpha}$-triphenylmethylglutamyl)benzotriazole 1-Oxide

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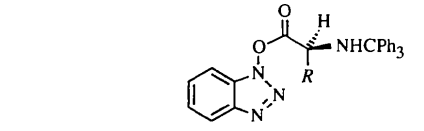
(*Received 10 June 1997; accepted 28 August 1997*)

Abstract

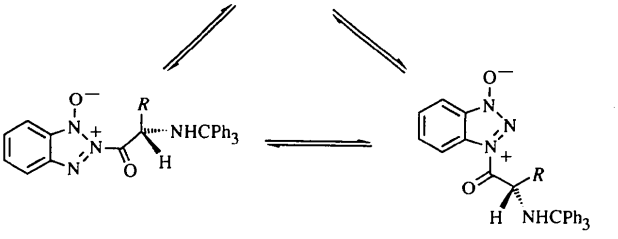
The title compound, $C_{31}H_{28}N_4O_4$, is the product of the condensation of γ-methyl (*S*)-*N*$^{\alpha}$-triphenylmethylglutamate with 1-hydroxybenzotriazole in the presence of *N*,*N*′-dicyclohexylcarbodiimide. The crystal structure determination unambiguously shows that the acyl moiety is attached to the N3 atom of the benzotriazole ring.

Comment

Condensation of *N*$^{\alpha}$-triphenylmethylamino acids with 1-hydroxybenzotriazole (HOBt) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) results in equilibrium mixtures of an ester form (1) and two amide forms (2) and (3), which are suitable for use in peptide synthesis (Barlos, Papaioannou & Theodoropoulos, 1984). An IR investigation of these mixtures has shown the presence of three carbonyl bands at 1810–1820, 1730–1740 and 1670–1680 cm^{-1}. Subsequently, the pure ester (1*a*) (Vlassi *et al.*, 1990) and amide (3*a*) (Barlos *et al.*, 1985) forms were isolated and unambiguously characterized by X-ray crystallographic analyses. The related studies showed that the carbonyl bands at 1810–1820 and 1730–1740 cm^{-1} are associated with the carbonyl functions of the ester (1) and the amide (3) forms, respectively. Although the title compound has been obtained in an oily form, as an intermediate in the synthesis of (*S*)-4-amino-5-hydroxypentanoic acid (Barlos *et al.*, 1987), it has only quite recently been obtained in a crystalline form, during the course of an independent study on the application of the benzotriazolyl esters of *N*$^{\alpha}$-triphenylmethylamino acids to the synthesis of amides using concentrated aqueous amines (Mamos *et al.*, 1997). The recrystallized compound showed two IR carbonyl bands at 1736 and 1722 cm^{-1}, one of which is obviously due to its γ-methyl ester function. Accordingly, we decided to determine the structure of this compound by X-ray analysis and compare it with the structure already obtained for the amide form (3*a*). The crystal structure determination of the title compound, (3*b*), unambiguously shows that the acyl moiety is also attached to the N3 atom of the benzotriazolyl ring.



(1*a*) R=$CH_2CH(CH_3)_2$



(2)

(3*a*) R=$CH_2CH_2SCH_3$
(3*b*) R=$CH_2CH_2CO_2CH_3$

A comparison of the most interesting acyl part of the crystal structures of amides (3*a*) and (3*b*) shows that the bond lengths and angles are similar (Table 1). Amides (3*a*) and (3*b*) differ, however, in the orientation of the side chain. In the former structure, the side chain is directed away from the benzotriazolyl ring, whereas in the latter, the side chain is directed towards it. It is worth noting that the bond lengths of the two carbonyl functions in amide (3*b*) are 1.200 (3) and 1.186 (4) Å, the bond length of the amide carbonyl function being the longer. For comparison, the corresponding bond length of the ester carbonyl function of (1*a*) is 1.179 (5) Å (Vlassi *et al.*, 1990). The triphenylmethyl moiety adopts the usual propeller-like conformation, which is the established means of reducing steric interaction between the phenyl rings in this group (Destro, Pilati & Simonetta, 1980). The acyl moiety of (3*b*) adopts an overall planar geometry, which is in sharp contrast to the structure of ester (1*a*), in which the ester function is perpendicular [92.9 (4)°] to the benzotriazolyl plane. This

latter conformation appears to make the carbonyl C atom more accessible to external nucleophiles and might account, at least in part, for the fact that the ester form (1) reacts much faster than the amide forms (2) and (3) (Barlos, Papaioannou & Theodoropoulos, 1984).

The absolute configuration of (3*b*), which was chosen to agree with the known chirality of the commercially available γ-methyl (*S*)-glutamate from which (3*b*) was synthesized, is depicted in Fig. 1.

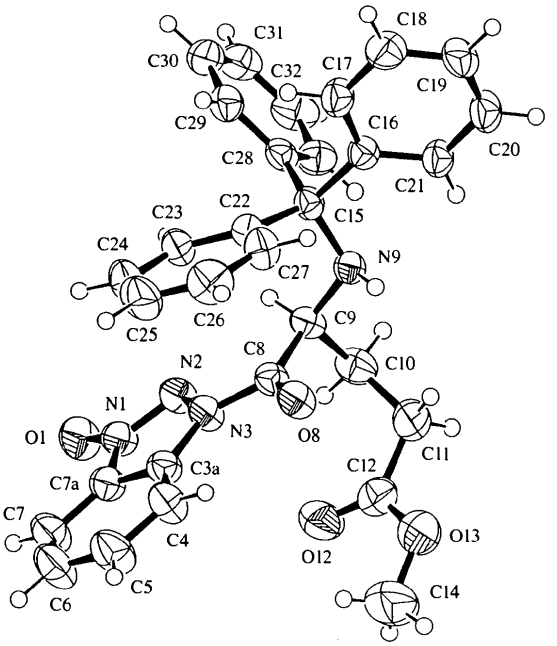


Fig. 1. View of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

HOBt.H_2O (4.59 g, 30 mmol) and DCC (4.54 g, 22 mmol) were added sequentially to an ice-cold solution of γ-methyl N^{α}-triphenylmethylglutamate (8.07 g, 20 mmol) in tetrahydrofuran (60 ml), and the resulting reaction mixture was stirred at 273 K for 30 min and at room temperature for 2 h. Then, a few drops of glacial AcOH and H_2O were added and after an additional 30 min of stirring at room temperature, the precipitated *N,N'*-dicyclohexylurea (DCU) was filtered off and washed with ethyl acetate (150 ml). The combined filtrates were washed sequentially with 5% aqueous citric acid, H_2O, 5% aqueous $NaHCO_3$ and H_2O. The organic phase was dried (Na_2SO_4) and the resulting solution was kept overnight in the refrigerator. Filtration of an additional precipitate of DCU and evaporation of the solvent left a residue, which on adding diethyl ether and refrigeration gave a crystalline product (9.37 g, 90%). Crystals suitable for X-ray analysis were obtained by recrystallization from ethyl acetate.

Crystal data

$C_{31}H_{28}N_4O_4$
M_r = 520.57
Orthorhombic
$P2_12_12_1$
a = 9.031 (1) Å
b = 14.262 (2) Å
c = 20.580 (2) Å
V = 2650.9 (5) Å^3
Z = 4
D_x = 1.304 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 49 reflections
θ = 15.08–20.57°
μ = 0.088 mm^{-1}
T = 293 (2) K
Prism
0.90 × 0.50 × 0.40 mm
Colourless

Data collection

Philips PW1100 diffractometer (updated by Stoe)
ω–2θ scans
Absorption correction: none
2660 measured reflections
2660 independent reflections
2499 reflections with $I > 2\sigma(I)$
θ_{max} = 25.03°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: 4.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.120
S = 1.079
2660 reflections
348 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 0.3966P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.245 e Å^{-3}
$\Delta\rho_{min}$ = −0.286 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0126 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—N1	1.262 (3)	N3—C8	1.420 (3)
N1—N2	1.309 (3)	C3a—C7a	1.383 (4)
N1—C7a	1.400 (3)	C8—O8	1.200 (3)
N2—N3	1.373 (3)	C12—O12	1.186 (4)
N3—C3a	1.380 (3)		
O1—N1—N2	122.6 (2)	C3a—N3—C8	127.5 (2)
O1—N1—C7a	125.5 (2)	N3—C3a—C7a	105.1 (2)
N2—N1—C7a	111.9 (2)	N3—C3a—C4	134.5 (2)
N1—N2—N3	105.3 (2)	C7—C7a—N1	130.0 (3)
N2—N3—C3a	111.6 (2)	C3a—C7a—N1	106.2 (2)
N2—N3—C8	120.9 (2)		

The data have not been corrected for absorption effects. An extinction correction was applied. H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C). The H atom on N9 was located from a difference map and refined isotropically.

Data collection: *DIF*4 (Stoe & Cie, 1987*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1987*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93. Other programs include: *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1017). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1975–1978

Bis(4-methoxyphenylsulfonyl)methane: a Three-Dimensional Network Generated by Short C—H···O Hydrogen Bonds

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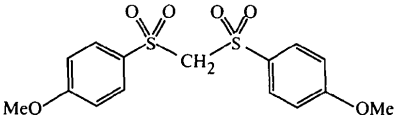
(*Received 19 May 1997; accepted 27 August 1997*)

Abstract

In the title compound, $C_{15}H_{16}O_6S_2$, each molecule utilizes CH_2, CH_3 and aromatic C—H bonds to form C—H···O hydrogen bonds to four other molecules, with C···O distances of 3.256 (4), 3.336 (4), 3.425 (3) and 3.431 (3) Å: the molecules are thereby linked into a continuous three-dimensional network.

Comment

In molecular solids which contain an excess of hard hydrogen-bond acceptors over hard hydrogen-bond donors (Braga *et al.*, 1995), it is to be expected that C—H bonds, particularly those in aromatic systems, will participate as donors in hydrogen bonds of C—H···O or C—H···N types (Hanton, Hunter & Purvis, 1992). Thus, in ferrocene-1,1′-diylbis(2-phenylethanedione), $[Fe(C_5H_4COCOPh)_2]$, which contains four carbonyl groups per molecule, but no hard hydrogen-bond donors, there is a three-dimensional network generated by short C—H···O hydrogen bonds in which C—H bonds from both the phenyl and the cyclopentadienyl groups participate (Ferguson, Glidewell, Royles & Smith, 1996): similarly, there is a two-dimensional network of C—H···N hydrogen-bonds in cyanoferrocene, $[(C_5H_5)Fe(C_5H_4CN)]$, where again there are no hard hydrogen-bond donors (Bell, Ferguson & Glidewell, 1996). We report here the structure of bis(4-methoxyphenylsulfonyl)methane, $(CH_3OC_6H_4SO_2)_2CH_2$, (I), which contains no hard hydrogen-bond donors, but even more hard hydrogen-bond acceptors per molecule than the ferrocenebisdione mentioned above: the crystal structure comprises a three-dimensional network of C—H···O hydrogen bonds, in which both methoxy and sulfonyl O atoms act as hydrogen-bond acceptors, while aromatic, methylene and methyl C atoms all act as hydrogen-bond donors.



(I)

The asymmetric unit (Fig. 1) consists of a single molecule and these molecules are connected into a continuous three-dimensional array by means of a variety of C—H···O hydrogen bonds. Both of the C—H bonds of the central methylene group act as donors, but to different types of O atom in different molecules as the corresponding acceptors. Atom C1 in the molecule at (x, y, z) acts as donor, *via* H1*A*, to the ether-type O23 atom in the molecule at (x, $1-y$, $-\frac{1}{2}+z$): the corresponding C—H bond at (x, $1-y$, $\frac{1}{2}+z$) acts as donor to O23 in the molecule at (x, y, $-1+z$), thus giving a $C(8)$ chain (Bernstein *et al.*, 1995) running parallel to the [001] direction and generated by the action of the c glide plane (Fig. 2). These [001] chains are linked by a second type of C—H···O hydrogen bond into sheets parallel to the (100) plane: the methoxy carbon atom C17 at (x, y, z) acts as donor, H17*A*, to the sulfone oxygen O12 in the molecule at (x, $-y$, $-\frac{1}{2}+z$), so linking two adjacent chains, and the carbon atom C17 in this latter molecule acts in turn as acceptor to O12 in the molecule at (x, y, $-1+z$). Hence, between any pair of chains running along [001] and related by translation along [010], there are zigzag $C(9)$ cross-links generated by the methoxy···sulfone hydrogen bonds. These cross-links generate a continuous two-dimensional net built from a single type of $R_4^4(36)$ ring, which is propagated in the [010] direction by translation and in the [001] direction by the c glide plane (Fig. 2).