Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

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Boc–Phe–Aminomalonaldehyde

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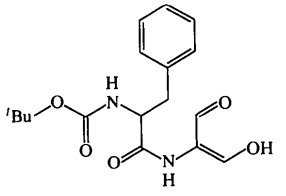
Abstract

The crystal structure of the title compound, (*N-tert*-butoxycarbonylphenylalanyl)aminomalonaldehyde {*tert*-butyl [1-(diformylmethylaminocarbonyl)-2-phenyl-1-ethyl]carbamate, $C_{17}H_{22}N_2O_5$}, was determined in order to examine the aminomalonaldehyde group in a peptide chain. The planarity constraints of the peptide bond and the aminomalonaldehyde group result in the formation of a pseudo-seven-membered ring through one intramolecular hydrogen bond (O17—H17···O11). The bond lengths in this ring indicate delocalization of the π electrons and the formation of a weak conjugated π-electron system.

Comment

Aminomalonaldehyde (Ama) contains both a primary amino group and an acidic group, namely an enolized malonaldehyde moiety, with acidity comparable to that of a carboxylic acid group; it can thus be considered as an anomalous amino acid. Following the idea of Ama incorporation into the peptide chain, we have condensed Boc–Phe–OSu with an alkaline solution of Ama (Arnold, Šauliová & Krchňák, 1973) and obtained the title compound, (I).



(I)

The molecular structure of Boc–Phe–aminomalonaldehyde, together with the atom-numbering scheme, is shown in Fig. 1. In the molecule, there are several potentially planar groups, of which we are interested mainly in the spatial arrangement of the peptide and Ama groups. The planarity constraints induced by these groups result in the eight non-H atoms C9, C10, O11, N12, C13, C14, O15, C16 and O17 lying in the same plane. The structure determination shows that they form a pseudo-seven-membered ring (comprising atoms O11, C10, N12, C13, C16, O17 and H17) through the creation of an intramolecular hydrogen bond between the O11 atom as a proton acceptor and O17 as a proton donor. The observed parameters indicate a relatively strong hydrogen bond (O11···O17 2.51 Å and O11···H17—O17 164.7°) in comparison with published values (Glusker, Lewis & Rossi, 1994). The closure of the chain to form the ring provoked some deviations from the predicted planar arrangement of the participating groups. The five atoms pertaining to the C13=C16 double bond (N12, C13, C16, O17 and C14) are not perfectly coplanar (the r.m.s. deviation of the fitted least-squares plane through these atoms is about 0.014 Å). The peptide group also deviates from a planar arrangement (r.m.s. deviation of about 0.018 Å). This non-planarity is formed by a twist about the C—N bond ($\Delta\omega = -3°$) and by a pyramidal deformation about the N atom ($\tau_N = 1.5°$) (Ramachandran & Kolaskar, 1973). Furthermore, in the seven-membered ring, the observed lengths of the single bonds are shorter and those of the double bonds and the peptide bond are longer than theoretical lengths (Glusker, Lewis & Rossi, 1994), which indicates the formation of a weak conjugated π-electron system. The phenyl ring and the seven-membered ring are approximately parallel to one another; the dihedral angle between them is 5.3 (1)°.

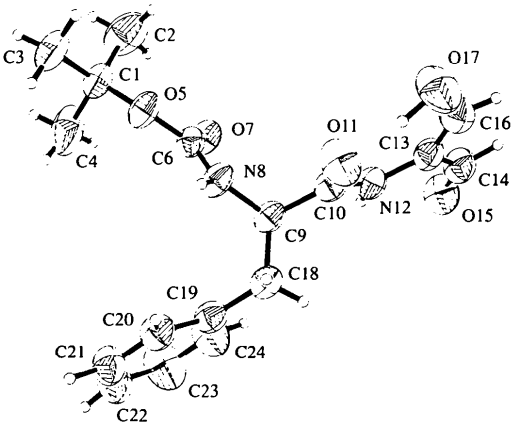


Fig. 1. A view of Boc–Phe–Ama showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The crystal packing is realised by a number of intermolecular hydrogen bonds: N8—H8···O15($\frac{3}{2}-y$, $\frac{1}{2}+x$, $\frac{1}{4}+z$) with N8···O15 3.19 Å and N8—H8···O15 175.6°; N12—H12···O7(y, x, $-z$) with N12···O7 3.06 Å and N12—H12···O7 160.0°. Furthermore, the

intermolecular distance between the pseudo-seven-membered ring and the neighbouring phenyl group suggests that some stacking interactions occur in the crystal. The pseudo-seven-membered ring is enclosed by three neighbouring rings (see Fig. 2): one parallel phenyl ring (the distance, d, between the centres of mass is 4.5 Å and the angle, σ, between the planes of the rings is 9.5°), one parallel pseudo-seven-membered ring (d = 4.6 Å and σ = 4.2°) and one perpendicular phenyl ring (d = 5.4 Å and σ = 88.7°). The observed distances indicate that the stacking probably results from intermolecular interactions of the ring π-electron systems (Glusker, Lewis & Rossi, 1994).

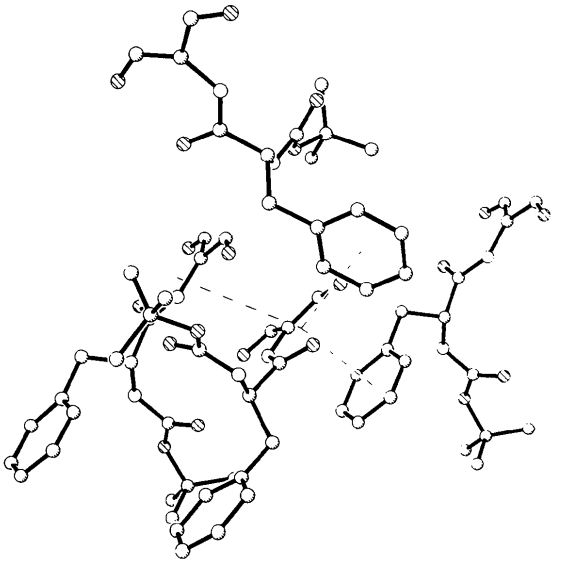


Fig. 2. View of the packing of Boc–Phe–Ama molecules in the crystal. Dashed lines indicate the distances between the centres of mass of the interacting aromatic rings.

Experimental

Colourless crystals of the title compound were grown by slow evaporation from a methanol/water solution at room temperature.

Crystal data

$C_{17}H_{22}N_2O_5$
M_r = 334.37
Tetragonal
$P4_12_12$
a = 10.790 (1) Å
c = 30.688 (3) Å
V = 3572.8 (6) Å^3
Z = 8
D_x = 1.243 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13–15°
μ = 0.092 mm^{-1}
T = 293 (2) K
Prism
0.6 × 0.5 × 0.4 mm
Colourless

Data collection

Enraf–Nonius CAD-4 MACHIII four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4306 measured reflections
3882 independent reflections
3113 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0179
θ_{max} = 26.97°
h = 0 → 13
k = 0 → 13
l = 0 → 39
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0347
$wR(F^2)$ = 0.0987
S = 1.033
3877 reflections
306 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.4513P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.007
$\Delta\rho_{max}$ = 0.102 e Å^{-3}
$\Delta\rho_{min}$ = −0.139 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0039 (6)
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)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	1.0835 (2)	0.8205 (2)	0.14179 (5)	0.0539 (4)
C2	1.0926 (4)	0.6870 (3)	0.12794 (10)	0.0947 (9)
C3	1.0845 (2)	0.8305 (3)	0.19121 (6)	0.0675 (5)
C4	1.1801 (3)	0.9062 (4)	0.12281 (10)	0.1051 (12)
O5	0.96062 (11)	0.87145 (12)	0.13105 (3)	0.0515 (3)
C6	0.92379 (14)	0.88239 (15)	0.08911 (4)	0.0426 (3)
O7	0.96812 (11)	0.82765 (12)	0.05843 (3)	0.0537 (3)
N8	0.83042 (14)	0.96303 (14)	0.08637 (4)	0.0498 (3)
C9	0.7697 (2)	0.9889 (2)	0.04541 (5)	0.0460 (4)
C10	0.6544 (2)	0.9090 (2)	0.04120 (5)	0.0484 (4)
O11	0.58212 (14)	0.9002 (2)	0.07224 (4)	0.0758 (4)
N12	0.63758 (13)	0.85166 (13)	0.00306 (4)	0.0474 (3)
C13	0.5429 (2)	0.7677 (2)	−0.00849 (5)	0.0520 (4)
C14	0.5423 (2)	0.7304 (2)	−0.05370 (6)	0.0629 (5)
O15	0.6153 (2)	0.7644 (2)	−0.08093 (4)	0.0767 (4)
C16	0.4567 (2)	0.7138 (2)	0.01683 (7)	0.0683 (5)
O17	0.4356 (2)	0.7233 (2)	0.05909 (5)	0.0969 (6)
C18	0.7355 (2)	1.1269 (2)	0.04309 (6)	0.0530 (4)
C19	0.8469 (2)	1.2093 (2)	0.04184 (5)	0.0510 (4)
C20	0.8801 (2)	1.2822 (2)	0.07711 (6)	0.0576 (4)
C21	0.9798 (2)	1.3614 (2)	0.07493 (7)	0.0691 (5)
C22	1.0490 (2)	1.3688 (2)	0.03762 (8)	0.0787 (6)
C23	1.0188 (3)	1.2948 (3)	0.00273 (9)	0.0938 (9)
C24	0.9195 (2)	1.2159 (2)	0.00484 (7)	0.0790 (7)

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

C10—O11	1.235 (2)	C13—C16	1.344 (3)
C10—N12	1.336 (2)	C13—C14	1.444 (2)
N12—C13	1.411 (2)	C16—O17	1.321 (3)
O11—C10—N12	123.6 (2)	C16—C13—N12	129.3 (2)
C10—N12—C13	128.03 (15)	O17—C16—C13	130.8 (2)
O11—C10—N12—C13	−3.8 (3)	C9—C10—N12—C13	176.27 (15)

Data collection: Enraf–Nonius diffractometer software. Cell refinement: Enraf–Nonius diffractometer software. Data reduction: Enraf–Nonius diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s)

used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *O* (Jones & Kjeldgaard, 1993). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arnold, Z., Šauliová, J. & Krchňák, V. (1973). *Collect. Czech. Chem. Commun.* **38**, 2633–2640.

Glusker, J. P., Lewis, M. & Rossi, M. (1994). In *Crystal Structure Analysis for Chemists and Biologists*. New York: VCH.

Jones, T. A. & Kjeldgaard, M. (1993). *O*. Version 5.9.1. University of Uppsala, Sweden.

Ramachandran, G. N. & Kolaskar, A. S. (1973). *Biochem. Biophys. Acta*, **303**, 385–388.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Methyl 7α,12α-Dihydroxy-3α-methacryloylamino-5β-cholan-24-oate

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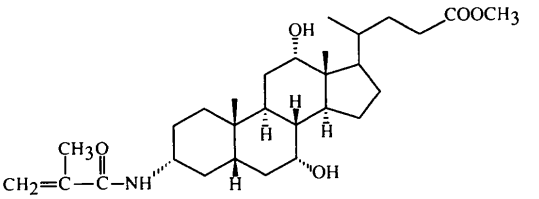
Abstract

In the title compound, $C_{29}H_{47}NO_5$, the methacryloylamino group is confirmed to be attached on position 3 of the steroid skeleton of cholic acid methyl ester as a 3α-epimer. The crystal structure of the title compound, recrystallized from acetone, contains two molecules in the asymmetric unit and is stabilized by intermolecular hydrogen bonds.

Comment

Natural compounds are used in the preparation of organic polymer materials with biomedical and pharmaceutical applications. The title compound, (I), was one of the epimers synthesized as a monomer in the preparation of such polymers (Denike & Zhu, 1994). It was readily polymerized by a free-radical polymerization in solution, despite the presence of the bulky cholic acid side group (Denike & Zhu, 1994). It also copolymerized easily with methacrylic monomers (Zhu, Moskova & Denike, 1996). The title compound can be recrystallized from a variety of solvents such as acetone, methanol or toluene. The compound crystallized from acetone was used for this X-ray diffraction study as part of an attempt to elucidate the characteristics of polymers prepared from the title compound and other related methacrylic monomers.



(I)

The title compound crystallizes in the monoclinic space group $P2_1$, with two molecules in an asymmetric unit (Figs. 1 and 2). Molecules 1 (C1–C29) and 2 (C31–C59/C59′) have the same overall configuration for the principal molecular framework, but the methacryloylamino group attached in an α configuration at position 3 of the steroid skeleton differs with respect to the orientation of the methacryloyl side chain. If the torsion angles C*m*2—C*m*3—N*mp*—C*nq* are compared, we find −111.7 (2)° for molecule 1 (m = 0, n = 2, p = 3 and q = 6), −123.4 (17)° for molecule 2*A* (m = 3, n = 5, p = 3 and q = 6) and −125.0 (14)° for molecule 2*B* (m = 3, n = 5, p = 3′ and q = 6′). In molecule 2, we find that the methacryloylamino group could not be described without the introduction of a disorder model, therefore, two sets of atoms were defined for this group for molecule 2. The occupancy in both molecules (2*A* and 2*B*) was initially refined and the occupancy factor fixed at 0.50 for each in the final cycles of refinement.

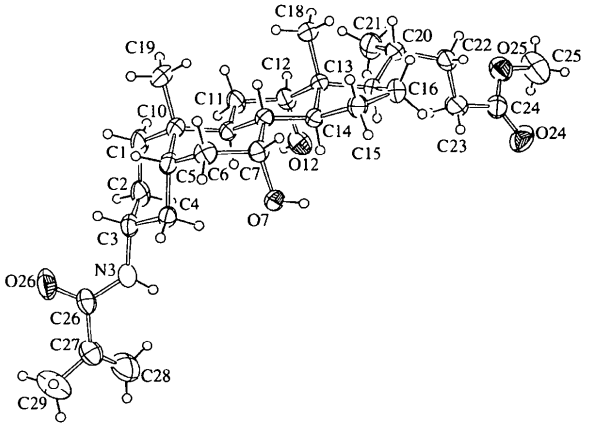


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of molecule 1 of (I). Ellipsoids correspond to the 40% probability level and H atoms are represented by spheres of arbitrary size.