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Ethyl (*Z*)-3-bromo-2-[(*tert*-butoxycarbonyl)-amino]-3-phenylacrylate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.034
wR factor = 0.050
Data-to-parameter ratio = 14.7

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

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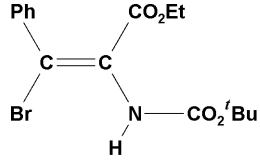
The title compound, $C_{16}H_{20}BrNO_4$, displays almost planar coordination at the enamine N atom, which thus has a stereochemically inactive lone pair. There is no indication of delocalized charge within the didehydrogenated amino acid, as shown by the bond lengths. The molecules are linked in pairs by two hydrogen bonds (N—H···O and C—H···O), and then by a longer C—H···O contact to form columns parallel to the *a* axis.

Comment

Imino acids and enamines, their stable tautomers, are used as synthons for structurally diversified α-amino acids, which are of interest because of their potential biological activity (Miossec *et al.*, 1994). Though several structures of α,β-unsaturated amino acids have been published, no β-halogenated didehydroamino acids have been structurally characterized so far. We present here the crystal structure of ethyl (*Z*)-3-bromo-2-[(*tert*-butoxycarbonyl)amino]-3-phenylacrylate, (I).



(I)

The central element in the structure of (I) (Fig. 1) is the didehydroamino acid, with the double bond between the α- and β-C atoms. These atoms and the four atoms connected to them (Br1, C11, C3 and N1) show an almost planar arrangement (r.m.s. deviation 0.042 Å). The coordination geometry at the N atom is slightly distorted planar (atoms N1, H1, C2 and C6; r.m.s. deviation 0.022 Å). The lone pair of nitrogen is thus stereochemically inactive. Nevertheless, in contrast to ethyl (*Z*)-2-[(benzoylcarbonyl)amino]-3-phenylacrylate (Nitz *et al.*, 1981), there is no evidence for charge delocalization, as shown by the bond lengths among atoms C1, C2, N1, C6 and O4. Two molecules of the compound are linked by a classical hydrogen bond (N1—H1···O1^{i}, see Table 2 for symmetry codes) and a 'weak' hydrogen bond (C16—H16···O3^{i}) to form a dimer, whose stability is indicated by its detection in the mass spectrum. A third, but longer and presumably weaker, 'weak' hydrogen bond (C4—H4*B*···O1^{ii}) forms a column of molecules parallel to the *a* axis (Fig. 2).

Experimental

A solution of 3.20 g protected L-phenylalanine and excess *N*-bromosuccinimide (NBS) in CCl_4 was refluxed for 6 h. After

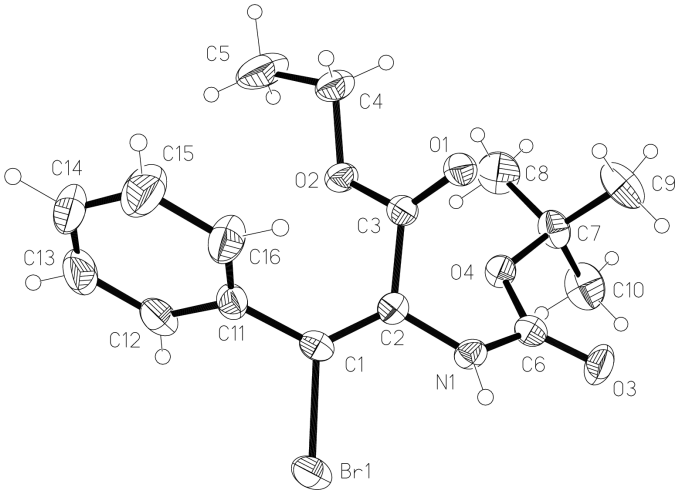


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary.

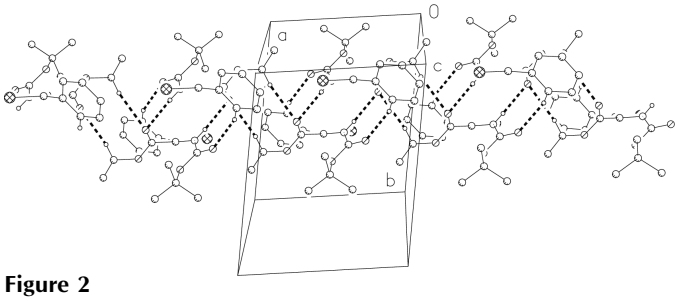


Figure 2
Packing diagram of the title compound, viewed perpendicular to the *ab* plane. Hydrogen bonds are indicated by dashed lines. Only those H atoms participating in hydrogen bonds are shown.

cooling, the solvent was removed in vacuo, the residue taken up in diethyl ether, filtered and finally the product was purified by chromatographic work-up on silica gel. The main product could be identified as 3-bromo-2-(*tert*-butoxycarbonylimino)-3-phenylpropionic acid, which underwent enamine–tautomerization upon crystallization from Et_2O/hexane to form the title compound. Yield: 2.80 g (69%), m.p. 377 K; ^{1}H NMR (DRX 400 Bruker at 400.1 MHz): 7.36–7.27 (*m*, 5H, C_6H_5), 6.48 (*s*, *br*, 1H, NH), 3.98 (*q*, $^3J_{HH}$ = 7.15 Hz, 2H, CH_2), 1.47 [*s*, 9H, $C(CH_3)_3$], 0.87 (*t*, $^3J_{HH}$ = 7.15 Hz, 3H, CH_3); ^{13}C NMR (DRX 400 Bruker at 100.6 MHz): 162.91 [*s*, *C*(O)OEt], 151.98 [*s*, *C*(O)O^{t}Bu], 137.70 (*s*, NH*C*═CBr), 129.75 (*s, ipso*-C_6H_5), 129.16 (*s, p*-C_6H_5), 129.12 (*s*, *m*-C_6H_5), 128.26 (*s, o*-C_6H_5), 104.42 (*s*, C═*C*BrPh), 82.09 [*s*, *C*$(CH_3)_3$], 61.78 (*s*, *C*H_2CH_3), 28.15 [*s*, C(*C*$H_3)_3$], 13.38 (*s*, CH_2*C*H_3); MS (Finnigan MAT 8430, CI-pos., NH_3, *m*/*z*): 756 [$2M + NH_4^+$], 739 [$2M + H^+$], 387 [$M + NH_4^+$], 370 [$M + H^+$]. Calculated for $C_{16}H_{20}BrNO_4$ (370.24): C 51.91, H 5.44, N 3.78%; found: C 51.80, H 5.39, N 3.73%.

Crystal data

$C_{16}H_{20}BrNO_4$
M_r = 370.24
Triclinic, $P\overline{1}$
a = 8.5554 (12) Å
b = 10.1468 (18) Å
c = 10.7086 (16) Å
α = 71.729 (10)°
β = 87.445 (10)°
γ = 81.861 (10)°
V = 873.9 (2) Å^3
Z = 2
D_x = 1.407 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 62 reflections
θ = 2–11°
μ = 2.37 mm^{-1}
T = 173 (2) K
Prism, colourless
0.26 × 0.20 × 0.20 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1990)
T_{min} = 0.793, T_{max} = 0.881
6090 measured reflections
3046 independent reflections
2016 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.050
S = 0.79
3046 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.918 (3)	C2—C3	1.512 (4)
C1—C2	1.321 (3)	N1—C6	1.372 (3)
C1—C11	1.485 (4)	C6—O4	1.341 (3)
C2—N1	1.401 (3)		
C2—C1—C11	127.2 (3)	N1—C2—C3	114.8 (2)
C2—C1—Br1	117.9 (2)	C6—N1—C2	125.6 (3)
C11—C1—Br1	114.69 (18)	C6—N1—H1	115.8 (17)
C1—C2—N1	124.1 (3)	C2—N1—H1	117.9 (17)
C1—C2—C3	120.9 (3)	O4—C6—N1	110.1 (3)
C1—C2—N1—C6	145.0 (3)	C2—N1—C6—O4	−11.3 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.87 (2)	2.19 (3)	3.035 (3)	162 (2)
C4—H4*B*···O1^{ii}	0.99	2.58	3.561 (4)	170
C16—H16···O3^{i}	0.95	2.33	3.204 (4)	152

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $-x, 1-y, -z$.

H1 (at nitrogen) was refined freely. Methyl H atoms were located in difference syntheses, idealized (C—H = 0.98 Å and H—C—H = 109.5°) and refined on the basis of rigid groups allowed to rotate but not to tip. Other H atoms were included using a riding model, with fixed C—H bond lengths of 0.95 Å; U_{iso}(H) values were fixed at 1.2U_{eq} of the parent atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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