Steith, J. & Fizet, C. (1977). *Tetrahedron Lett.* **37**, 3297–3300.
Stoe & Cie (1988). *DIF4. Diffractometer Control Program.* Version 7.04. Stoe & Cie, Darmstadt, Germany.

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C—H···π_{arene}, Csp^3—H···O=C and O—H···O intermolecular interactions in (2*R*/2*S*)-3-(3-hydroxyphenyl)-2-(1-oxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoic acid: a *meta*-tyrosine derivative

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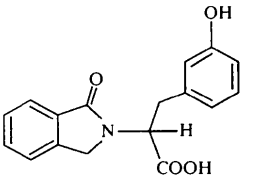
Abstract

The title compound, $C_{17}H_{15}NO_4$, a DL-*meta*-tyrosine derivative forms a hydrogen-bonded network in the solid state which consists of O_{acid}—H···O_{phenyl}—H···O=$C_{isoindole}$ chains [O···O 2.668 (2) and 2.653 (2) Å], Csp^3—H···O=C_{acid} [C···O 3.225 (3) Å] and two C—H···π_{arene} intermolecular interactions. The C_{arene}—H···π_{phenyl} interaction is short, C···*Cg* 3.542 (3) Å, where *Cg* is the phenyl ring centroid (H···*Cg* 2.64 Å and C—H···*Cg* 165°). The interplanar angle between the five- and six-membered rings of the isoindole system is 0.95 (13)° with the carbonyl-O atom 0.096 (3) Å from the C_4N ring plane. π–π stacking involving inversion symmetry-related isoindole groups occurs with *RS* pairs (interplanar distance of 3.43 Å).

Comment

Amino acid derivatives are a major class of chiral compounds with diverse applications in asymmetric synthesis and medicinal chemistry. DL-*meta*-Tyrosine (Byrkjedal *et al.*, 1974) and related compounds have attracted much interest, *e.g.* in biological studies (Kawai *et al.*, 1999), not least due to the close structural relationship with L-dopa (Howard *et al.*, 1995). The title compound, (I), a phthalimidine (isoindolin-1-one) derivative (Allin *et al.*, 1996; McNab *et al.*, 1997) is synthesized as a racemic mixture from DL-*meta*-tyrosine and forms part of a study of the hydrogen-bonding interactions and anion-recognition properties of a series of unnatural amino acid compounds (Dalton *et al.*, 1999; Gallagher *et al.*, 1999*a*,*b*).



(I)

A view of molecule (I) (*S* configuration) with our numbering scheme is given in Fig. 1 and selected dimensions are in Table 1. The bond lengths and angles in the heterocyclic ring are similar to those reported previously (Brady *et al.*, 1998) and in agreement with expected values (Orpen *et al.*, 1994). The angle between the five- and six-membered rings of the isoindole system is 0.95 (13)° and the maximum deviation from planarity for an atom in either ring plane is 0.0179 (12) Å for C3, with the carbonyl O3 atom 0.096 (3) Å from the C_4N ring plane. This ring is almost perpendicular to both the carboxylic acid CCO_2 plane, 83.12 (8)° and the 3-phenyl ring plane, 87.15 (7)°. Stacking arises involving the π–π systems of inversion symmetry-related isoindole groups (*RS* pairs), with an interplanar distance of 3.43 Å [3.35 Å in the DL-phenylalanine derivative (2*R*/2*S*)-2-(1-oxo-1,3-dihydro-2*H*-isoindol-2-yl)-3-phenylpropanoic acid, (II), which has a similar molecular geometry (Brady *et al.*, 1998)]. Examination of (I) with *PLATON* (Spek, 1998) revealed voids in the crystal lattice of volume 7 Å^3 (×4) which are too small to accommodate a solvent molecule.

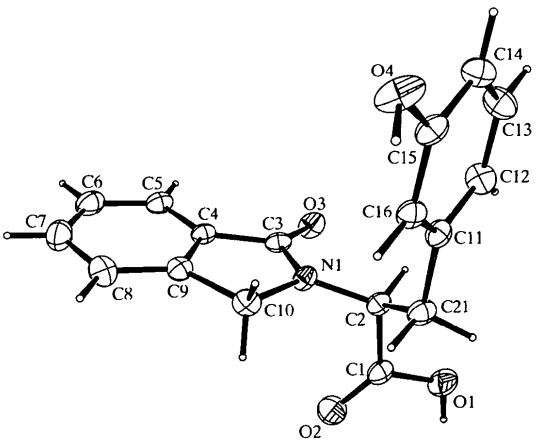


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The hydrogen bonding in (I) is dominated by O—H···O, C—H···O and C—H···π_{phenyl} interactions, detailed in Table 2 and depicted in Fig. 2. Conventional carboxylic acid O—H···O hydrogen bonding between pairs of carboxylic acid groups with graph set $R_2^2(8)$ is not observed (Ferguson *et al.*, 1995). Hydrogen bonding arises involving (i) the carboxylic acid O—H, phenolic O—H and phthalimidine carbonyl acceptor as O_{acid}—H···O_{phenyl}—H···O=$C_{isoindole}$ systems with (ii)

Csp^3—H···O=C_{acid} and (iii) C—H···π_{arene} interactions completing the intermolecular association. The crystal structure can be interpreted by considering *RS* pairs to associate through aromatic C—H···π interactions and π–π stacking about inversion centres. These *RS* dimers are linked through pairs of O_{phenyl}—H···O=$C_{isoindole}$ hydrogen bonds forming a one-dimensional chain in the direction of the *b* axis (Fig. 2). The O—H···O—H···O=C systems link the one-dimensional chains with weaker Csp^3—H···O=C_{acid} and Csp^3—H···π_{arene} interactions forming a three-dimensional network.

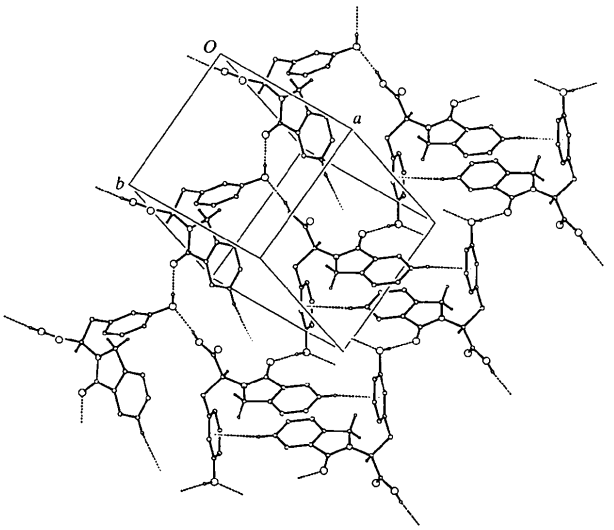


Fig. 2. A view of the intermolecular hydrogen bonding in the crystal structure of (I) highlighting the π–π stacking and the C—H···π_{phenyl} interactions.

Molecule (I) contains an extra O—H donor/acceptor in comparison to (II) which facilitates a shorter hydrogen bond along the O—H···O—H···O=C chain. In (II) the carboxylic acid O—H···O=$C_{isoindole}$ hydrogen bond dominates in combination with a C—H···O=C_{acid} and two C—H···π interactions. The aromatic C6—H6···π interaction is present in both (I) and (II) with similar π–π stacking. The structure of (2*S*)-2-{[(2*R*)-2-hydroxy-2-phenylethanoyl]amino}-4-methylpentanoic acid, (III), (Dalton *et al.*, 1999) has a similar donor/acceptor set taking part in intermolecular interactions as (I) with two O—H···O=C hydrogen bonds, a Csp^3—H···O=C_{acid} and an aromatic C—H···π interaction present in (III). However, there are considerable structural and packing differences between (I) and (III).

The presence of C—H···O and C—H···π_{arene} interactions with stronger hydrogen bonds *e.g.* O—H···O has been commented on previously (Steiner, 1997). The role of C—H···π_{arene} interactions in controlling self-inclusion processes in calixarenes has been addressed (Ferguson *et al.*, 1996). Theoretical calculations on the nature of C—H···π_{arene} interactions have been reported in several organic systems with an estimation of the binding energy between the C—H donor and aromatic π cloud (Samanta *et al.*, 1998), as well as with database studies (Malone *et al.*, 1997). The role which these interactions play in protein structures has also been detailed (Umezawa & Nishio, 1998). However, a thorough understanding of the control and exploitation of *X*—H···π_{arene} interactions (*X* = C, N, O) still remains an elusive goal in crystal-engineering studies (Braga *et al.*, 1998). Further studies are in progress on related phthalimidine derivatives.

Experimental

The title compound was prepared by the overnight reaction of DL-*m*-tyrosine and *o*-phthalaldehyde in refluxing acetonitrile (Allin *et al.*, 1996). Filtration of the hot solution and subsequent slow cooling of the filtrate allowed the isolation of large, colourless crystals. IR ($\nu_{C=O}$ cm^{-1}): 1732, 1650 (KBr). Melting point 462–464 K (uncorrected). ^1H NMR data (400 MHz) (δ, d_6 DMSO, p.p.m.), 3.11 (*m*, 2H, CH_2), 4.41 (*br s*, 2H, CH_2), 5.07 (*m*, 1H, CH), 6.52–6.66, 6.98–7.02 (*m*, 4H, C_6H_4), 7.44–7.48, 7.56–7.65 (*m*, 4H, *m*-C_6H_4), 9.30 (*s*, 1H, O—H).

Crystal data

$C_{17}H_{15}NO_4$
M_r = 297.30
Monoclinic
$P2_1/n$
a = 11.3483 (15) Å
b = 8.9413 (10) Å
c = 14.705 (3) Å
β = 104.586 (13)°
V = 1444.0 (4) Å^3
Z = 4
D_x = 1.368 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.77–19.87°
μ = 0.098 mm^{-1}
T = 294 (1) K
Plate
0.35 × 0.28 × 0.09 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2786 measured reflections
2684 independent reflections
1452 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 25.4°
h = −13 → 13
k = 0 → 10
l = 0 → 17
3 standard reflections
frequency: 240 min
intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.085
S = 0.941
2684 reflections
202 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0111 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.328 (2)	N1—C3	1.351 (2)
O2—C1	1.196 (2)	N1—C10	1.462 (2)
O3—C3	1.236 (2)	C1—C2	1.523 (3)
O4—C15	1.378 (2)	C2—C21	1.533 (3)
N1—C2	1.448 (2)	C3—C4	1.471 (3)
C2—N1—C3	121.71 (16)	N1—C2—C21	113.20 (16)
C2—N1—C10	124.49 (16)	C1—C2—C21	109.97 (17)
C3—N1—C10	112.88 (16)	O3—C3—N1	124.18 (19)
O1—C1—O2	124.3 (2)	O3—C3—C4	128.72 (19)
O1 C1 C2	110.17 (18)	N1 C3—C4	107.07 (18)
O2—C1—C2	125.55 (19)	O4—C15—C14	117.2 (2)
N1—C2—C1	110.12 (16)	O4—C15—C16	122.2 (2)
C3—N1—C2—C1	−86.6 (2)	C2—N1—C3—O3	−5.7 (3)
O2—C1—C2—N1	−19.9 (3)	C1—C2—C21—C11	170.0 (2)
O2—C1—C2—C21	105.5 (2)	C2—C21—C11—C16	122.7 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.82	1.88	2.668 (2)	160
O4—H4···O3^{ii}	0.82	1.86	2.653 (2)	164
C6—H6···*Cg*1^{iii}	0.93	2.64	3.542 (3)	165
C10—H10*A*···O2^{iv}	0.97	2.43	3.225 (3)	139
C21—H21*A*···*Cg*2^{iv}	0.97	2.86	3.553 (3)	129

Symmetry codes: (i) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, 1+y, z$; (iii) $2-x, 1-y, 2-z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Molecule (I) as synthesized is a DL racemic mixture and crystallized in the monoclinic system with space group $P2_1/n$ determined from the systematic absences. H atoms were allowed for as riding atoms with C—H in the range 0.93 to 0.98 Å and O—H 0.82 Å. Fig. 3, a view of the C_{arene}—H···π_{arene} hydrogen bonding interactions, has been deposited as a supplementary diagram.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*III (Burnett & Johnson, 1996), *ORTEX* (McArdle, 1995) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1055). Services for accessing these data are described at the back of the journal.

References

Allin, S. M., Hodkinson, C. C. & Taj, N. (1996). *Synlett*, pp. 781–782.
Brady, F., Gallagher, J. F. & Kenny, P. T. M. (1998). *Acta Cryst.* C**54**, 1523–1525.
Braga, D., Grepioni, F. & Tedesco, E. (1998). *Organometallics*, **17**, 2669–2672.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Byrkjedal, A., Mostad, A. & Rømming, C. (1974). *Acta Chem. Scand. Ser. B*, **28**, 750–756.
Dalton, J. P., Gallagher, J. F., Kenny, P. T. M. & O'Donohoe, M. (1999). *Acta Cryst.* C**55**, 126–129.
Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Ferguson, G. (1998). *PREP*8. *A WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX*96 *and SHELXL*97 *Programs*. University of Guelph, Canada.
Ferguson, G., Gallagher, J. F., Li, Y., McKervey, M. A., Madigan, E. M., Malone, J. F., Moran, M. B. & Walker, A. (1996). *Supramol. Chem.* **7**, 223–228.
Ferguson, G., Gallagher, J. F. & McAlees, A. J. (1995). *Acta Cryst.* C**51**, 454–458.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gallagher, J. F., Kenny, P. T. M. & Sheehy, M. J. (1999*a*). *Acta Cryst.* C**55**, 1257–1260.
Gallagher, J. F., Kenny, P. T. M. & Sheehy, M. J. (1999*b*). *Inorg. Chem. Commun.* **2**, 200–202, 327–330.
Howard, S. T., Hursthouse, M. B., Lehmann, C. W. & Poyner E. A. (1995). *Acta Cryst.* B**51**, 328–337.
Kawai, K., Flores, L. G. II, Nakagawa, M., Shikano, N., Jinnouchi, S., Tamura, S. & Kubodera, A. (1999). *Nucl. Med. Commun.* **20**, 153–157.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
McNab, H., Parsons, S. & Shannon, D. A. (1997). *Acta Cryst.* C**53**, 1098–1099.
Malone, J. F., Murray, C. M., Charlton, M. H., Docherty, R. & Lavery, A. J. (1997). *J. Chem. Soc. Faraday Trans.* pp. 3429–3436.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G., & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, Appendix A. Weinheim: VCH Publishers.
Samanta, U., Chakrabarti, P. & Chandrasekhar, J. (1998). *J. Phys. Chem. A.* **102**, 8964–8969.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1998). *PLATON. Molecular Geometry Program*. Version of November 1998. University of Utrecht, The Netherlands.
Steiner, T. (1997). *Chem. Commun.* pp. 727–734.
Umezawa, Y. & Nishio, M. (1998). *Bioorg. Med. Chem.* **6**, 493–504.

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Decabromodiphenyl ether

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Abstract

Bis(pentabromophenyl) ether, $C_{12}Br_{10}O$, shows strange differences in the endocyclic angles between the two different rings, although they are both substituted in the same manner. Several short van der Waals contact