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Benzyl *N*,*N*-bis[2-(pentafluoroanilino)ethyl]carbamate

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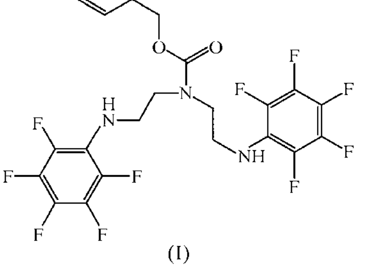
The title compound, $C_{24}H_{17}F_{10}N_3O_2$, exhibits intramolecular N—H···O hydrogen bonding, as well as intramolecular Ar···Ar^F face-to-face interactions. The molecules are linked together by N—H···F—C hydrogen bonds, forming chains parallel to the *a* axis. Adjacent symmetry-related chains are combined in double zipper-like ribbons by parallel Ar^F···Ar^F offset π-stacking interactions.

Comment

Interest in tris-amine derivatives, RN(CH_2CH_2NHR')$_2$, has grown steadily over the past two decades. These ligands are widely used to stabilize unusual metal oxidation states and coordination geometry around various metal centres (Fauré *et al.*, 1999; Ward *et al.*, 2002; Gade & Mountford, 2001). Their complexes were applied in several catalytic processes (Gade & Mountford, 2001; Schrodi *et al.*, 2001). Particular attention has been paid to the complexes of fluorinated tris-amine ligands due to the electron-withdrawing properties of the C_6F_5 group and additional secondary Ar—F···*M* interactions (Schrock *et al.*, 1998; Cochran *et al.*, 2000). We report here the structure of the title mixed aryl/pentafluoroaryl substituted bis(aminoethyl)carbamate, (I).



(I)

As expected for carbamate derivatives, the C11—N1 and C11—O2 bond lengths of (I) are almost equal [1.356 (2) and 1.351 (2) Å, respectively] due to strong conjugation effects (Fig. 1). This causes the central carbamate group (N1/O1/O2/C11), together with the adjacent α-C atoms (C12/C21/C31), to be planar within 0.110 (1) Å. Compound (I) contains three outward aryl substituents. One of them, fluorinated ring C23–C28, is linked to the carbamate fragment by an N—H···O hydrogen bond [2.07 (2) Å]. To the best of our knowledge, similar hydrogen bonding has been observed only once before, in the structure of 2-(pentafluorophenylamino)-pent-2-en-4-one, $C_6F_5NHC(Me){=}CHCOMe$ (Gordon *et al.*, 2002). The rotation of the C23–C28 aryl ring around the N2—C23 bond seems to be restricted due to noticeable conjugation with neighbouring amine atom N2. This is confirmed by the C24—C23—N2—H2 torsion angle [−5.6 (17)°] and by sufficient shortening of the N2—C23 bond distance [1.375 (2) Å]. The other two aryl groups, C13–C18 and C33–C38, are nearly parallel [dihedral angle = 11.56 (6)°] and are bonded by the well known Ar···Ar^F face-to-face interaction (Dunitz, 2004), with a centroid-to-centroid separation of 3.749 Å and a displacement angle (Janiak, 2000) of 15.0°. Thus, the conformation of the molecule of (I) is completely predetermined by the aforementioned intramolecular interactions.

In the crystal structure of (I), translationally related molecules are linked together by N—H···F—C hydrogen bonds [2.17 (2) Å], forming chains parallel to the *a* axis (Fig. 2). The low propensity of organic fluorine to participate in hydrogen bonding has been the subject of several reports (Howard *et al.*,

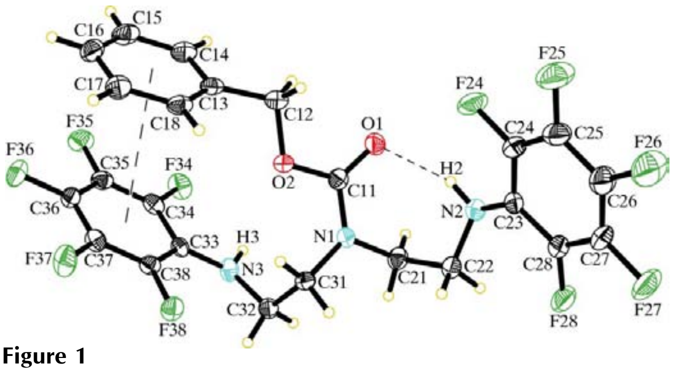


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds and the Ar···Ar^F face-to-face interaction.

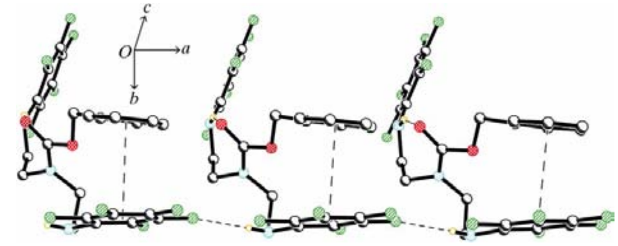


Figure 2
The hydrogen-bonded (dashed lines) chains in (I) parallel to the *a* axis. H atoms not involved in hydrogen bonds have been omitted.

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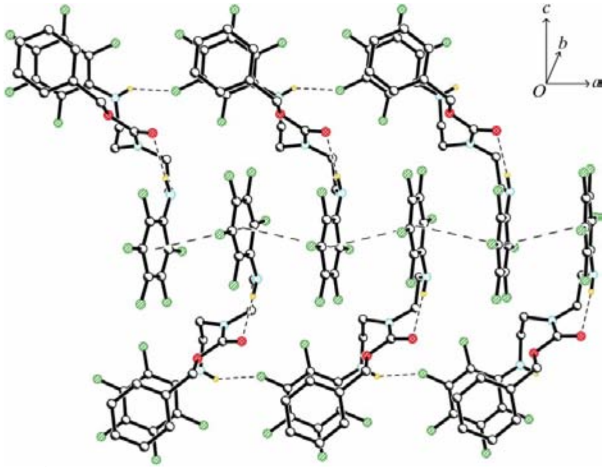

Figure 3
Double zipper-like chains parallel to the *a* axis. Dashed lines indicate hydrogen bonds and $Ar^F\cdots Ar^F$ offset π-stacking interactions. H atoms not involved in hydrogen bonds have been omitted.

1996; Dunitz & Taylor, 1997). However, in this case, this unusual hydrogen bonding may result from the high acidity of atom H3 caused by the neighbouring highly electron-withdrawing C_6F_5 group. Adjacent symmetry-related chains are combined in double zipper-like ribbons by parallel $Ar^F\cdots Ar^F$ offset π-stacking interactions (Fig. 3). The interplanar $Ar^F\cdots Ar^F$ distance is 3.8191 (4) Å, the centroid-to-centroid separation is 3.902 Å and the displacement angle is 25.0°. Finally, these chains are linked by intermolecular $Ar\cdots Ar^F$ interactions, forming a complex three-dimensional network.

In conclusion, the molecular geometry and crystal packing of (I) are determined by the different types of secondary bonding formed by the penafluoroanilino groups.

Experimental

The title compound was obtained as a side product from an alkylation reaction of $HN(CH_2CH_2NHC_6F_5)_2$ with benzyl chloride in the presence of K_2CO_3, according to the general method described by Cochran *et al.* (2000). Crystals were obtained by recrystallization from toluene.

Crystal data

$C_{24}H_{17}F_{10}N_3O_2$
$M_r = 569.41$
Orthorhombic, *Pbca*
$a = 7.6382$ (7) Å
$b = 14.9272$ (15) Å
$c = 40.857$ (4) Å
$V = 4658.4$ (8) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.16$ mm^{-1}
$T = 120$ (2) K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1K diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.925$, $T_{\max} = 1.000$ (expected range = 0.896–0.969)
25323 measured reflections
5603 independent reflections
4174 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.102$
$S = 1.04$
5603 reflections
420 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C11	1.355 (2)	O1—C11	1.224 (2)
N2—C23	1.375 (2)	O2—C11	1.351 (2)
N3—C33	1.379 (2)		
C11—N1—C31	124.19 (15)	C11—O2—C12	113.69 (14)
C11—N1—C21	117.67 (15)	O1—C11—O2	123.02 (16)
C31—N1—C21	118.13 (14)	O1—C11—N1	124.25 (17)
C23—N2—C22	121.97 (16)	O2—C11—N1	112.72 (15)
C33—N3—C32	125.41 (16)		
C24—C23—N2—H2	−5.6 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O1	0.86 (2)	2.07 (2)	2.886 (2)	157 (2)
N3—H3$\cdots$F37$^{\rm i}$	0.86 (2)	2.17 (2)	2.9282 (19)	147 (2)

Symmetry code: (i) $x - 1, y, z$.

H atoms were located in a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3060). Services for accessing these data are described at the back of the journal.

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