Molecular structure of 1-phenyl-2-trifluoromethyl-3-benzoylaziridine

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1-Phenyl-2-trifluoromethyl-3-benzoylaziridine has been studied by X-ray structural analysis. Protons of the aziridine cycle are in *trans* positions. The C(1)—N(1) bond is the shortest of the corresponding bonds in aziridine derivatives, which have been studied by X-ray structural analysis previously.

Key words: molecular structure, aziridines, 1-phenyl-2-trifluoromethyl-3-benzoylaziridine.

Crystals of 1-phenyl-2-trifluoromethyl-3-benzoylaziridine (**1**) have been studied by X-ray structural analysis with the aim of unambiguously establishing the mutual arrangement of substituents in the molecule. The overall view of the molecule is shown in Fig. 1; the bond lengths and bond angles are given in Tables 1 and 2, respectively.

Figure 1 clearly shows that the CF_3 group is in the *trans* position with respect to the two other substituents in the three-membered cycle, which are in mutually *cis* positions. The Ph ring at the N atom is in a perpendicular conformation (p)[1] (the plane of the Ph ring is perpendicular to the bisector plane of the endocyclic C(1)—N(1)—C(2) angle); the carbonyl group has a *cis-gauche* conformation (*cg*) (the O(1)—C(4)—C(2)—C(1) torsion angle is 6.5°); the CF_3 group is in a staggered conformation with respect to the C(1)—C(3) bond. The dihedral angle between the planes of the carbonyl group and the C(5)—C(10) benzene ring is 17.8°. The most interesting feature of molecule **1** is the substantial shortening of the N(1)—C(1) bond to 1.438(3) Å. Apparently, this value is the smallest of the N—C bond lenghts in the derivatives of aziridine studied by X-ray structural analysis. Note that bond lengths in the aziridine cycle are very labile and vary within wide limits with the electronic nature and mutual arrangement of substituents:

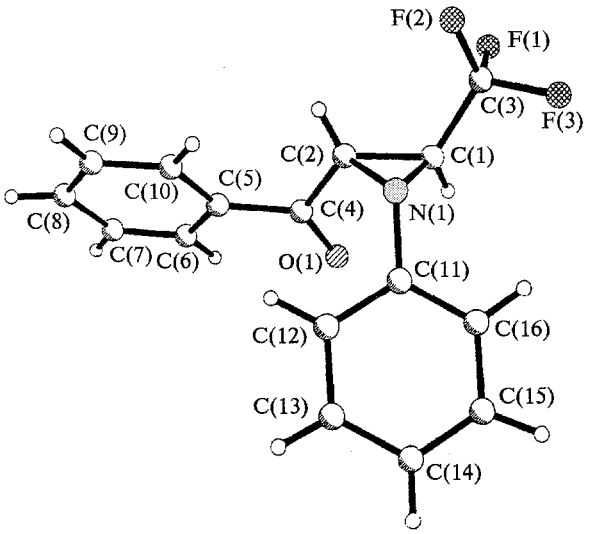

Fig. 1. Overall view of the molecule of 1-phenyl-2-trifluoromethyl-3-benzoylaziridine.

Table 1. Bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(4)	1.213(3)	C(1)—C(3)	1.477(5)	C(9)—C(10)	1.382(5)
N(1)—C(1)	1.438(3)	C(2)—C(4)	1.502(4)	C(11)—C(12)	1.386(4)
N(1)—C(2)	1.482(3)	C(4)—C(5)	1.483(4)	C(11)—C(16)	1.383(4)
N(1)—C(11)	1.430(3)	C(5)—C(6)	1.388(4)	C(12)—C(13)	1.387(4)
F(1)—C(3)	1.321(4)	C(5)—C(10)	1.390(4)	C(13)—C(14)	1.378(5)
F(2)—C(3)	1.327(4)	C(6)—C(7)	1.376(5)	C(14)—C(15)	1.368(5)
F(3)—C(3)	1.342(4)	C(7)—C(8)	1.375(5)	C(15)—C(16)	1.381(4)
C(1)—C(2)	1.484(4)	C(8)—C(9)	1.367(4)		

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Table 2. Bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg
C(1)—N(1)—C(2)	61.0(2)	C(2)—C(4)—C(5)	118.2(2)
C(1)—N(1)—C(11)	120.1(2)	C(4)—C(5)—C(6)	119.5(2)
C(2)—N(1)—C(11)	122.0(2)	C(4)—C(5)—C(10)	121.5(2)
N(1)—C(1)—C(2)	60.9(2)	C(6)—C(5)—C(10)	119.0(3)
N(1)—C(1)—C(3)	117.1(2)	C(5)—C(6)—C(7)	119.9(3)
C(2)—C(1)—C(3)	121.3(3)	C(6)—C(7)—C(8)	120.6(3)
N(1)—C(2)—C(1)	58.0(2)	C(7)—C(8)—C(9)	120.0(3)
N(1)—C(2)—C(4)	119.6(2)	C(8)—C(9)—C(10)	120.1(3)
C(1)—C(2)—C(4)	117.2(2)	C(5)—C(10)—C(9)	120.3(3)
F(1)—C(3)—F(2)	108.2(3)	N(1)—C(11)—C(12)	119.9(2)
F(1)—C(3)—F(3)	106.2(3)	N(1)—C(11)—C(16)	119.7(3)
F(2)—C(3)—F(3)	104.8(3)	C(12)—C(11)—C(16)	120.0(3)
F(1)—C(3)—C(1)	111.7(3)	C(11)—C(12)—C(13)	119.6(3)
F(2)—C(3)—C(1)	114.0(3)	C(12)—C(13)—C(14)	120.2(3)
F(3)—C(3)—C(1)	111.4(3)	C(13)—C(14)—C(15)	119.7(3)
O(1)—C(4)—C(2)	119.7(3)	C(14)—C(15)—C(16)	121.0(3)
O(1)—C(4)—C(5)	122.1(3)	C(11)—C(16)—C(15)	119.5(3)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors U ($\times 10^3$) for nonhydrogen atoms in the structure of **1**

Atom	x	y	z	U/Å^2
O(1)	3502(2)	8656(2)	2499(2)	61(1)
N(1)	376(2)	9736(2)	1810(2)	38(1)
F(1)	1144(3)	10632(3)	4370(2)	105(1)
F(2)	−252(3)	11507(2)	3077(2)	86(1)
F(3)	−909(2)	9828(2)	3592(2)	83(1)
C(1)	1010(3)	9702(3)	2865(2)	44(1)
C(2)	1834(3)	10314(2)	2244(2)	40(1)
C(3)	268(4)	10428(3)	3471(2)	59(1)
C(4)	3196(3)	9678(3)	2149(2)	41(1)
C(5)	4130(3)	10335(3)	1628(2)	40(1)
C(6)	556(3)	9941(3)	1750(2)	52(1)
C(7)	6439(3)	10544(3)	1268(3)	64(1)
C(8)	5899(3)	11523(3)	650(3)	64(1)
C(9)	4484(3)	11912(3)	515(2)	55(1)
C(10)	3595(3)	11326(3)	1003(2)	45(1)
C(11)	208(3)	8620(2)	1246(2)	39(1)
C(12)	663(3)	8573(3)	395(2)	44(1)
C(13)	330(3)	7545(3)	−216(2)	54(1)
C(14)	−455(3)	6579(3)	20(2)	61(1)
C(15)	−885(4)	6627(3)	868(3)	64(1)
C(16)	−563(3)	7641(3)	1486(2)	51(1)

1.441—1.510 Å for N—C bonds (see Refs. 2, 3) and 1.450—1.504 Å for C—C bonds (see Refs. 4, 5). In the case of molecule **1**, shortening of the N(1)—C(1) bond is primarily due to the interaction of the π acceptor carbonyl group with the Walsh-type orbitals of the three-membered cycle. By analogy with derivatives of cyclopropane, this should result in a shortening of the N(1)—C(1) bond and a slight lengthening of two other

Table 4. Atomic coordinates ($\times 10^3$) and isotropic temperature factors U ($\times 10^2$) for hydrogen atoms in the structure of **1**

Atom	x	y	z	U/Å^2
H(1)	149(1)	900(1)	318(1)	6(1)
H(2)	183(1)	1113(1)	220(1)	5(1)
H(6)	600(1)	925(1)	221(1)	6(1)
H(7)	738(1)	1026(1)	135(1)	4(1)
H(8)	661(1)	1187(1)	32(1)	9(1)
H(9)	400(1)	1257(1)	6(1)	7(1)
H(10)	261(1)	1158(1)	90(1)	4(1)
H(12)	131(1)	924(1)	26(1)	6(1)
H(13)	65(1)	757(1)	−26(1)	7(1)
H(14)	−80(1)	597(1)	−47(1)	6(1)
H(15)	−150(1)	603(1)	107(1)	5(1)
H(16)	−92(1)	774(1)	204(1)	5(1)

bonds in the aziridine cycle, which was observed previously, for example, in the structure of 1-phenyl-2,2-aziridinedicarboxamide.[2] The effect of the electron-withdrawing CF_3 group and π donor Ph ring at the nitrogen atom may be an additional factor, causing shortening of the endocyclic N(1)—C(1) bond. However, no substantial shortening of the endocyclic N—$C(CF_3)_2$ bond is observed in the structures of 1-alkoxy-2,2-bis(trifluoromethyl)aziridines[6] (1.490 and 1.483 Å for two diastereoisomers, respectively); the orientation of the C(11)—C(16) benzene ring in molecule **1** is typical of *N*-phenyl derivatives of aziridines and provides the most favorable conditions for interaction of its π system with the lone electron pair of the nitrogen atom; this orientation is highly unfavorable for interaction with MOs of the three-membered cycle. Therefore, the effect of the benzoyl group remains the major reason for asymmetry of the three-membered cycle of molecule **1**.

The remaining geometric parameters of the molecule have normal values; no shortened intermolecular contacts are observed in the crystal.

Experimental

Crystals of **1** are monoclinic (crystals were obtained according to a known procedure[7]), at 20 °C a = 9.478(3) Å, b = 10.822(2) Å, c = 14.093(4) Å, β = 106.43, Z = 4, $C_{16}H_{12}F_3NO$, space group $P2_1/n$. The unit-cell parameters and intensities of 2850 independent reflections, of which 2151 with $I \geq 2\sigma(I)$ were used for solving and refining the structure, were measured on a Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $\theta \leq 30°$). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms (Table 3). The H atoms were located from the difference series and were refined isotropically (Table 4). The final values of the R factors were as follows: R = 0.086, R_w = 0.083. All calculations were performed on an IBM PC/AT computer using the SHELX PLUS program package.

References

1. F. A. Allen, *Acta Crystallogr.*, 1980, **B36**, 81.
2. S. Brückner, L. Malpezzi, A. V. Prosyanik, and S. V. Bondarenko, *Acta. Crystallogr.*, 1985, **C41**, 215.
3. D. Delugeard, M. Vaultier, and J. Meinnel, *Acta. Crystallogr.*, 1975, **B31**, 2885.
4. A. B. Zolotoi, O. A. D'yachenko, L. O. Atovmyan, V. F. Rudchenko, I. I. Chervin, and R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.*, 1984, 48 [*Chem. Heterocycl. Compd.*, 1984 (Engl. Transl.)].
5. Z. Kaluski, E. Gzhesiak-Figas, V. D. Orlov, and F. G. Yaremenko, *Zh. Strukt. Khim.*, 1990, **31**, 155 [*J. Struct. Chem.*, 1990, **31** (Engl. Transl.)].
6. R. G. Kostyanovskii, G. K. Kadorkina, A. B. Zolotoi, O. A. D'yachenko, L. O. Atovmyan, I. I. Chervin, and Sh. S. Nasibov, *Dokl. Akad. Nauk SSSR*, 1983, **269**, 1103 [*Dokl. Chem.*, 1983, **269** (Engl. Transl.)].
7. O. G. Khomutov, V. I. Filyakova, and K. I. Pashkevich, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 282 [*Russ. Chem. Bull.*, 1994, **43**, 261 (Engl. Transl.)].

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