

F–H···F hydrogen bond in diphenylguanidinium hydrogen bifluoride

Manuela Ramos Silva^{*}, José A. Paixão, Ana Matos Beja, Luiz Alte da Veiga

CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal

Received 23 August 2000; accepted 20 September 2000

Abstract

The crystal structure of $C_{13}H_{14}N_3^+FHF^-$ is reported. The structure contains the strong hydrogen-bonded system, the bifluoride anion $F-H\cdots F^-$. The geometry of this anion deviates significantly from linearity but has the H atom in an approximate centered position. The $F\cdots F$ distance is 2.293(3) Å, considerably less than twice the van der Waals radius of fluorine, as expected from a very strong hydrogen bond.

One of the phenyl rings of the diphenylguanidinium counter ion of the bifluoride anion is oriented *syn* to the unsubstituted N atom of the guanidine group, the other adopts an *anti* conformation.

The anions and cations are held together by a layered two-dimensional network of hydrogen bonds. Both NH and NH_2 groups of the cation are donors towards the fluoride ions, exhausting the potential of diphenylguanidine for hydrogen bonding. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diphenylguanidinium fluoride hydrogen fluoride; Diphenylguanidinium bifluoride; Hydrogen bond; X-ray structure determination

1. Introduction

The hydrogen bifluoride anion, $F-H\cdots F^-$, is of significant structural and theoretical interest. It is a classic example of semi-ionic, three-center, four-electron bonding [1] and exhibits the strongest known hydrogen bonds [2] which depending on the symmetry of the surrounding crystal field, can either be symmetric or asymmetric [3]. The most recent experimental and theoretical values of the dissociation energy of the bifluoride anion converge on a value of 46 kcal/mol (1 cal = 4.184 J) [4,5]. Good quality ab initio calculations of hydrogen fluoride systems using extended basis-sets have been reported [5], aiming at establishing models for multiple hydrogen exchange. According to these calculations, the isolated bifluoride anion has a $D_{\infty h}$ geometry with the shared proton exactly half-way between the two fluorine ions at a distance of 1.149 Å to each ion. Depending on the completeness of the basis-set and on the different models accounting for electron correlation, a range of values (2.256–2.298 Å) has been reported for the $F\cdots F$ distance in the ground state of the isolated symmetric anion. The best accuracy for the $F\cdots F$ distance in the

bifluoride anion is achieved from infrared diode laser spectroscopy, which gives a value of 2.27771(7) Å for the isolated ion in the gas phase [6].

Structural studies have shown that when the bifluoride ion is under the influence of a highly symmetrical crystal field as in the alkali metal bifluorides [7] or in tetramethylammonium bifluoride [8] the FHF^- anion keeps its linear and symmetric geometry. When the crystal field is of low symmetry the shared proton appears to have a preference to occupy an off-centered position and the anion is no longer linear [2,9,10]. A survey of the most recent release of the Cambridge Structural Database (April 2000) found 21 crystal structures containing the FHF^- ion as counter ion of organic or organometallic cations, the range of reported $F\cdots F$ distances is 2.233–2.342 Å. The smallest deviation from linearity is found in 1,3,5,7-tetramethyl-8-(propane-1,3-dioxy)-1-azonia-adamantane hydrogen difluoride [11], for which the $F-H\cdots F$ valence angle and $F\cdots F$ distance are 177.9° and 2.247 Å, respectively. The largest deviation from linearity is found in *p*-tolidinium bifluoride [9] where the valence angle and distance are 162.2° and 2.276 Å. The shortest $F\cdots F$ distance reported for an asymmetric, non-linear bifluoride anion is 2.233(2) Å in L-argininium fluoride hydrogen fluoride [12]. Recent calculations for the $(HF)_3$ molecule [5] which may be partitioned into the two theoretical subunits FH_2^+ and F_2H^- , show that the bifluoride anion deviates 27.7° from the linear geometry and the $F\cdots F$ distance is 2.255 Å.

^{*} Corresponding author. Tel.: +351-239-410600;
fax: +351-239-829158.
E-mail address: manuela@pollux.fis.uc.pt (M.R. Silva).

Poly-hydrogen fluorides $[\text{H}_n\text{F}_{n+1}]^-$ have also been reported [13] in structures where the counter ion has a small positive charge, large size and symmetrical shape. In such structures the FHF^- subunits display off-centered linear and non-linear geometries. For these systems the $\text{F}\cdots\text{F}$ distances range from 2.255(1) to 2.484(1) Å for the linear geometry while for the non-linear geometry the distances range from 2.302(3) to 2.357(3) Å and the angles from 162(3) to 175(3)°. An interesting feature of these compounds is that many of them have been found to undergo solid-solid phase transitions at low temperature [13].

The title compound contains as counter ion of the bifluoride anion the diphenylguanidinium cation, $\text{C}_{13}\text{H}_{14}\text{N}_3^+$, which has several stable atropisomers at room temperature due to the low potential barrier of rotation of the phenyl rings around the C–N bonds. The two phenyl rings may be positioned either *syn-syn*, *syn-anti* or *anti-anti* to the unsubstituted N atom of the guanidine group. These atropisomers have been identified in solution, at room temperature, by NMR spectroscopy [14] and the three types of molecular conformations could also be stabilized in the solid state as shown by X-ray diffraction studies of several diphenylguanidinium salts [15–17]. Thus, from a structural point of view, diphenylguanidinium salts are interesting because different conformations of the cation may occur in the crystal. Note that although, the diphenylguanidine molecule lacks a chiral C atom, it may exhibit in a crystalline environment, a chiral conformation due to a propeller-like arrangement of the guanidine substituents [18]. It is worth mentioning that substituted guanidines, e.g. diarylguanidines have been reported to exhibit neuroprotective properties [19] and have been considered of potential value in the field of medicinal chemistry. Neuroleptic and antihypersensitive activities of *N,N'*-di-*o*-tolylguanidine and its congeners have been reported [20]. In itself, the guanidinium cation, $\text{C}(\text{NH}_2)_3^+$, is particularly interesting because of its high symmetry, planarity and Y aromatic character [21]. Its ability to establish hydrogen bonds to various proton acceptors play an important role in bioactive substances, e.g. in L-arginine as a substance for nitrogen oxide synthesis [22] or in the active sites of various proteins [23].

2. Crystal structure of $\text{C}_{13}\text{H}_{14}\text{N}_3^+\text{FHF}^-$

The title compound (1) crystallizes in the space group $P2_1/c$ with four formula units per cell and unit cell parameters given in Table 1. The guanidinium group of the cation is planar, as shown by the sum of the valence angles around C1 which is equal to 359.9(2)°. The N1–C1 and N3–C1 bond lengths are 1.340(3) and 1.336(3) Å close to the expected value for a delocalized C=N double bond (1.339 Å), the N2–C1 is slightly shorter (1.311(3) Å) but still larger than the expected value for a $\text{Csp}^2=\text{N}$ bond (1.295 Å) [24]. A comparison of these bond lengths with those of the neutral diphenylguanidine molecule [25] shows that some charge

Table 1
Crystal data and structure refinement of the title compound

Empirical formula	$\text{C}_{13}\text{H}_{14}\text{N}_3\text{F}_2$
Formula weight	251.28
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	$0.37 \times 0.20 \times 0.10$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (hexagonal axes)	
<i>a</i> (Å)	6.911(2)
<i>b</i> (Å)	17.044(5)
<i>c</i> (Å)	11.553(2)
β (Å)	106.08(2)
<i>V</i> (Å ³)	1307.5(6)
<i>Z</i>	4
Final <i>R</i> indices ($I > 2\sigma(I)$)	$R = 0.0462$, $wR = 0.0988$
<i>R</i> indices all data	$R = 0.1176$, $wR = 0.1248$

delocalization occurs on the guanidine fragment upon protonation. The N–C_{aryl} bond lengths N1–C2 and N3–C8 (1.418(3) and 1.418(3) Å), compare well with other diphenylguanidinium salts. The dihedral angles between the central planar guanidine moiety and the least-squares planes of the two phenyl rings are 45.53(12) and 57.06(8)° for rings C2–C7 and C8–C13, respectively, (C1–N1–C2–C3, 145.4(3) and C1–N1–C8–C9, 146.1(3)°). One of the phenyl rings is oriented *syn*, the other *anti* to the unsubstituted N atom of the guanidine group as shown by the torsion angles N2–C1–N1–C2, $\varphi_1 = 166.6(3)^\circ$ and N2–C1–N3–C8, $\varphi_2 = -26.8(4)^\circ$. The angle between the least-squares planes of the two phenyl rings is 77.18(8)°, a value intermediate between those found for a similar *syn-anti* conformation in the perchlorate (63.6(2)°) and dihydrogenphosphate (80.86(16)°) salts of *N,N'*-diphenylguanidinium [17,26].

The anion FHF^- deviates significantly from linearity as seen from the F–H \cdots F angle (166(3)°). However, F–H and H \cdots F distances (1.14(3) and 1.17(3) Å) are equal within experimental error which is an unusual occurrence in asymmetric bifluoride anions. Nevertheless, one should always bear in mind the limited accuracy of X-ray scattering in determining the position of the inner shared proton. The F \cdots F distance is 2.293(3) Å which is considerably less than twice the van der Waals radius of fluorine (1.4 Å), as expected from a very strong hydrogen bond, but compares well with the values found in other organic bifluoride salts.

The hydrogen bonds link together anions and cations in layers parallel to the (0 1 0) plane (Fig. 1). Both F atoms accept two protons each, in addition to the shared inner proton. Each guanidine moiety donates two of its hydrogen atoms to the fluorine atoms of the same FHF^- anion, establishing relatively strong hydrogen bonds (N2 \cdots F2, 2.739(3) and N1 \cdots F1, 2.852(3) Å) in a herring-bone type conformation, helped by the fact that the distance between atoms N1 and N2 is close to that between F1 and F2. The remaining guanidine protons are oriented towards fluorine

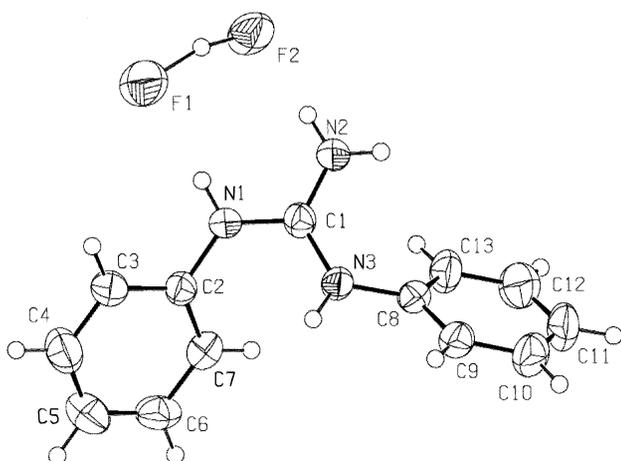


Fig. 1. ORTEP plot of the anion and cation of the title compound. Displacement ellipsoids are drawn at the 50% level.

atoms of symmetry related anions, fully exhausting the diphenylguanidine potential for hydrogen bonding.

A search for voids in the crystal structure that might be occupied by solvent molecules was conducted using the computer program PLATON [27] and none was found.

Table 2
Selected bond distances and angles (A°)

N1–C1	1.340(3)	C1–N1–C2	127.2(2)
N3–C1	1.336(3)	C1–N3–C8	125.3(2)
N2–C1	1.311(3)	N1–C1–N2	119.0(2)
N3–C8	1.418(3)	N3–C1–N2	121.5(2)
N1–C2	1.418(3)	C2–N1–C1–N2	166.6(3)
F1...F2	2.293(3)	C8–N3–C1–N2	–26.8(4)

3. Experimental

3.1. Synthesis

The title compound was obtained in an unsuccessful attempt to obtain a nickel complex. Pure nickel (Aldrich, 99.99%) was dissolved in concentrated hydrofluoric acid (Merck, 40%), in a plastic flask. An ethanolic solution of diphenylguanidine (Aldrich, 98%) was then added to the flask and left at room pressure and temperature. After a few months an inhomogeneous white-green solid was deposited at the bottom of the recipient. The solid was filtered and white crystals were separated by successive selective recrystallization from ethanol.

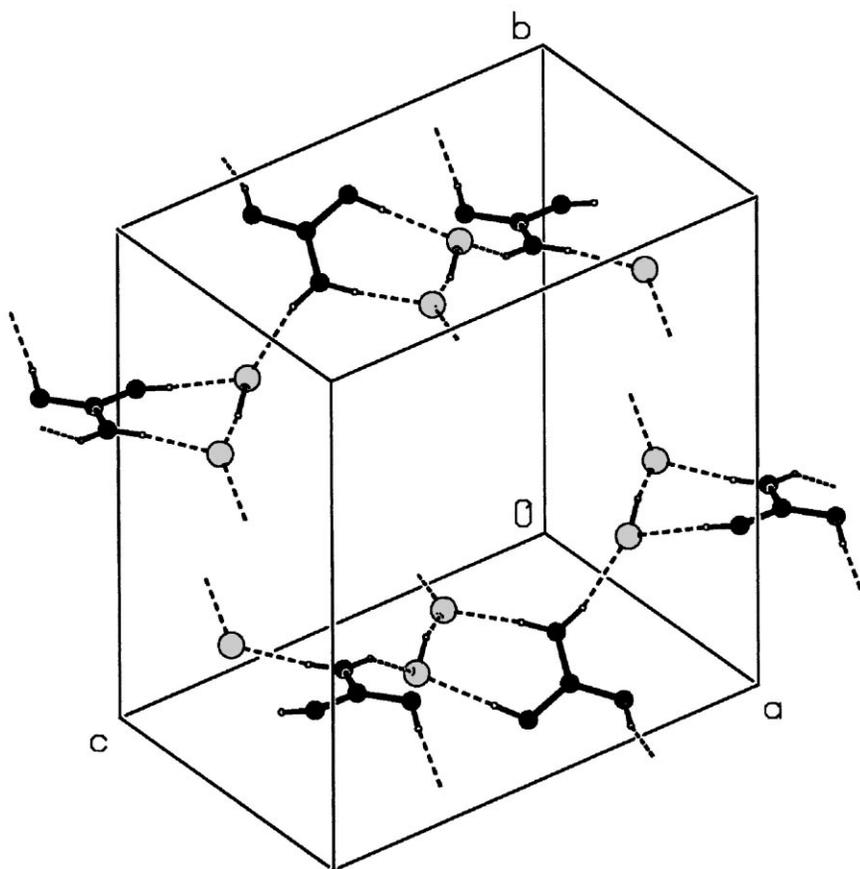


Fig. 2. Hydrogen bonding network. Phenyl rings were omitted for clarity.

3.2. Structure determination of the title compound

A single crystal was selected and tested by photographic methods prior to data collection. The diffraction data were collected at room temperature, using a CAD-4 ENRAF-NONIUS diffractometer [28] with Mo K α radiation up to a θ limit of 25°. The 2318 independent intensity values for a half hemisphere of data were collected, from which a total of 1303 had $I > 2\sigma(I)$. Three intensity and orientation control reflections measured every 3 h of X-ray exposure time showed a continuous intensity decay of 3.3% during the data-collection, which was compensated using a linear decay correction.

The structure was solved by direct methods using SHELXS97 [29], which gave the positions of all non-hydrogen atoms. All hydrogen atoms except that of the FHF⁻ anion were placed at calculated idealized positions and refined as riding with an isotropic temperature factor of 1.2 U_{eq} of the parent atoms. The bifluoride hydrogen atom was then located from a difference-Fourier map and freely refined with an isotropic displacement factor. The structure was refined by SHELXL97 [30] by full-matrix least-squares to a final agreement factor of 4.6%, allowing anisotropic displacement factors to all non-hydrogen atoms. The crystal data and structure refinement details and selected bond distances and angles are summarized in Tables 1 and 2, respectively. An ORTEPII [31] drawing of the anion and cation is depicted in Fig. 2. The hydrogen bond network is shown in Fig. 1. All calculations were performed on a Pentium 333 MHz PC running LINUX.

CCDC 150505

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (FCT).

References

- [1] G.C. Pimentel, *J. Chem. Phys.* 19 (1951) 446.
- [2] J.M. Williams, L.F. Schneemeyer, *J. Am. Chem. Soc.* 95 (1973) 5780.
- [3] A. Lautie, F. Romain, M.H. Limage, A. Novak, H. Prevost-Czeskleba, J. Moret, *J. Mol. Struct.* 118 (1984) 227.
- [4] P.G. Wenthold, R.R. Squires, *J. Phys. Chem.* 99 (1995) 2002.
- [5] D. Heidrich, N.J.R. Eikema Hommes, P.R. Scheleyer, *J. Comp. Chem.* 14 (1993) 1149.
- [6] K. Kawagushi, E. Hirota, *J. Chem. Phys.* 84 (1986) 2953.
- [7] J.J. Rush, L.W. Schroeder, A.J. Melveger, *J. Chem. Phys.* 56 (1972) 2793.
- [8] W.W. Wilson, K.O. Christie, J. Feng, R. Bau, *Can. J. Chem.* 67 (1989) 1898.
- [9] W.A. Denne, M.F. Mackay, *J. Cryst. Mol. Struct.* 1 (1971) 311.
- [10] M.K. Wittlesy, R.N. Perutz, B. Greener, M.H. Moore, *J. Chem. Soc., Chem. Commun.* 2 (1997) 187.
- [11] P.G. Jones, A.J. Kirby, I.V. Komarov, P.D. Wothers, *Chem. Commun.* 16 (1998) 1695.
- [12] M.R. Silva, J.A. Paixão, A.M. Beja, L.A. da Veiga, *Acta Cryst. C* 56 (2000) 104.
- [13] D. Mootz, D. Boenick, *Z. Anorg. Allg. Chem.* 544 (1987) 159.
- [14] G. Alagona, C. Ghio, P. Nagy, G. Durant, *J. Phys. Chem.* 98 (1994) 5422.
- [15] A.M. Beja, J.A. Paixão, M.R. Silva, L.A. da Veiga, E. de M. Gomes, J. Martín-Gil, *Z. Kristallogr. NCS* 213 (1998) 655.
- [16] J.A. Paixão, P.S.P. Silva, A.M. Beja, M.R. Silva, E. de M. Gomes, M. Belsley, *Acta Cryst. C* 55 (1999) 1287.
- [17] P.S.P. Silva, J.A. Paixão, A.M. Beja, M.R. Silva, L.A. da Veiga, *Acta Cryst. C* 55 (1999) 1096.
- [18] A. Tanatani, K. Yamaguchi, I. Azumaya, R. Fukutomi, K. Shudo, H. Kagechika, *J. Am. Chem. Soc.* 120 (1998) 6433.
- [19] J.W. Olney, J. Labruyere, M.T. Price, *Science* 244 (1989) 1360.
- [20] B.L. Largent, H. Wikstrom, A.L. Gundlach, S.H. Snyder, *Mol. Pharmacol.* 32 (1987) 772.
- [21] A. Gobbi, G. Frenking, *J. Am. Chem. Soc.* 115 (1993) 2362.
- [22] K.A. White, M.A. Marletta, *Biochemistry* 31 (1992) 6627.
- [23] M.M. Flocco, S.L. Mowbray, *J. Mol. Biol.* 235 (1994) 709.
- [24] G. Bergehoff, K. Brandenburg, *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, 1995, p. 683.
- [25] L.N. Zakharov, V.G. Andrianov, Y.T. Struchkov, *Sov. Phys. Crystallogr.* 25 (1980) 34.
- [26] J.A. Paixão, P.S.P. Silva, A.M. Beja, M.R. Silva, L.A. da Veiga, *Z. Kristallogr. NCS* 213 (1998) 419.
- [27] A.L. Spek, PLATON. Molecular Geometry Program, University of Utrecht, Utrecht, The Netherlands, 1995.
- [28] Enraf Nonius CAD-4 Software, Version 5.0, Enraf Nonius, Delft, The Netherlands, 1989.
- [29] G.M. Sheldrick, *Acta Cryst. A* 46 (1990) 467.
- [30] G.M. Sheldrick, SHELXL-97: a program for refining crystal structures, University of Göttingen, Germany, 1997.
- [31] C.K. Johnson, ORTEPII, Report ORNL-5138. Oak Ridge National Laboratory, TN, USA, 1976.