Inorg. Chem. **2008**, *47*, 9085−9089

Inorganic Chemistry

Article

Synthesis and Characterization of Bis[bis(pentafluoroethyl)phosphinyl]imides, $M^+N[(C_2F_5)_2P(O)]_2^-$, M = H, Na, K, Cs, Ag, Me_4N[†]

Dana Bejan,[‡] Helge Willner,[*,‡] Nikolai Ignatiev,[*,§] and Christian W. Lehmann[||]

Bergische Universität Wuppertal, FB C − Anorganische Chemie, Gauss Strasse 20, D-42097 Wuppertal, Germany, Merck KGaA Company, Frankfurter Strasse 250, D-64293 Darmstadt, Germany, and Max Planck Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Received June 12, 2008

A convenient synthesis and a full characterization of the strong acid bis[bis(pentafluoroethyl)phosphinyl]imide and some of its salts $M^+N[(C_2F_5)_2P(O)]_2^-$, M = Na, K, Cs, Ag, Me_4N, are presented. Their thermal (mp, $T_{dec.}$) and spectroscopic (IR, Raman, NMR) properties are discussed. A single crystal structure of $[Me_4N][N\{P(O)(C_2F_5)_2\}_2]$ has been obtained, and the structural parameters of the anion are compared with the results of quantum-chemical calculations. The observed properties are comparable to those of bis((trifluoromethyl)sulfonyl)imide and their derivatives.

Introduction

The NH-Brønsted acidity of imides, HNR_2, is highly dependent on the nature of the subsitutent R. If R is strongly electron-withdrawing and charge delocalizing, then the resulting imides are strong acids.[1,2] Prominent examples are bis((perfluoroalkyl)-sulfonyl)imides,[3−7] in particular $HN(SO_2CF_3)_2$. Bis((trifluoromethyl)sulfonyl)imide was first reported by Foropoulos and DesMarteau,[8] and it shows a rich chemistry.[9,10] Salts containing the $(CF_3SO_2)_2N^-$ anion attracted much attention as electrolytes in batteries,[11−13] room temperature ionic liquids,[14,15] Lewis acid catalysts,[7,16−18] as well as in spectroscopic[19−22] and structural studies.[14,21,23,24] All $(R_FSO_2)_2N^-$ anions are chemically very robust and therefore they are not readily degradable in the environment. In this respect the derivatives, surfactants having a perfluorinated moiety, are of environmental concern. As possible replacements, the less stable but chemically related bis(bis(perfluoroalkyl)phosphinyl)imides, $[(R_F)_2P(O)]_2N^-$, can be considered as more environmentally friendly compounds. There are only two members known: $[(C_3F_7)_2P(O)]_2N^-$[25] and salts containing the $[(C_2F_5)_2P(O)]_2N^-$ anion (FPI), recently

---

[†] Dedicated to Dr. Sieghard Neufeldt on the occasion of his 80th birthday.

[*] To whom correspondence should be addressed. E-mail: willner@uni-wuppertal.de (H.W.), nikolai.ignatiev@merck.de (N.I.). Phone: +49(0)202-439-2517. Fax +49(0)202-439-3053.

[‡] Universität Wuppertal.

[§] Merck KGaA.

[||] Max Planck Institut für Kohlenforschung.

(1) DesMarteau, D. D. *Science* **2000**, *289*, 72–73.
(2) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S. Z.; Hu, L. Q.; Sung, K. S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignatiev, N.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, M. V.; Notario, R.; Maria, P. C. *J. Am. Chem. Soc.* **1994**, *116*, 3047–3057.
(3) Foropoulos, J. J.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 4260–4261.
(4) Zhang, J.; DesMarteau, D. D. *J. Fluorine Chem.* **2001**, *111*, 253–257.
(5) DesMarteau, D. D.; Zhu, S. Z.; Pennington, W. T.; Gotoh, Y.; Wtz, M.; Zuberi, S. S. S. *J. Fluorine Chem.* **1989**, *45*, 24.
(6) Hu, L. Q.; DesMarteau, D. D. *Inorg. Chem.* **1993**, *32*, 5007–5010.
(7) Hao, X.; Yoshida, A.; Nishikido, J. *Tetrahedron Lett.* **2005**, *46*, 2697–2700.
(8) Foropoulos, J. J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723.
(9) DesMarteau, D. D.; Witz, M. *J. Fluorine Chem.* **1991**, *52*, 7–12.
(10) Favier, I.; Dunach, E. *Tetrahedron Lett.* **2004**, *45*, 3393–3395.
(11) Geiculescu, O. E.; Xie, Y.; Rajagopal, R.; Creager, S. E.; DesMarteau, D. D. *J. Fluorine Chem.* **2004**, *125*, 1179–1185.
(12) DesMarteau, D. D. *J. Fluorine Chem.* **1995**, 72.
(13) Thomas, H. B.; Shafer, G.; Ma, J. J.; Tu, M. H.; DesMarteau, D. D. *J. Fluorine Chem.* **2004**, *125*, 1231–1240.
(14) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Dalton Trans.* **2004**, 2267–2271.
(15) Dzyba, S. V.; Bartsch, R. A. *ChemPhysChem.* **2002**, *3*, 161–166.
(16) Kobazashi, H.; Nie, J.; Sonoda, T. *Chem. Lett.* **1995**, 307–308.
(17) Wabnitz, T. C.; Spencer, J. B. *Org. Lett.* **2003**, *5*, 2141–2144.
(18) Xue, L.; Padgett, C. W.; DesMarteau, D. D.; Pennington, W. T. *Solid State Sci.* **2002**, *4*, 1535–1545.
(19) Tu, M.-H.; DesMarteau, D. D. *Spectrochim. Acta, Part A* **2005**, *61*, 1701–1705.
(20) Herstedt, M.; Smirnov, M.; Jahansson, P.; Chami, M.; Grondin, J.; Servant, L.; Lasseques, J. C. *J. Raman Spectrosc.* **2005**, *36*, 762–770.
(21) Fujii, K.; Fujimori, T.; Takamuku, T.; Kanzaki, R.; Umebayashi, Y.; Ishiguro, S.-I. *J. Phys. Chem. B* **2006**, *110*, 8179–8183.
(22) Rey, I.; Johansson, P.; Lindengren, J.; Lasseques, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249–3258.
(23) Hass, A.; Klare, C.; Betz, P.; Bruckmann, J.; Kruger, C.; Tsay, Y. H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1918–1925.
(24) Garlyauskayte, R.; Chernega, A. N.; Michot, C.; Armand, M.; Yagupolskii, Y. L.; Yagupolskii, L. M. *Org. Biomol. Chem.* **2005**, *3*, 2239–2243.

10.1021/ic801088q CCC: $40.75

Table 1. NMR Data of Related $C_2F_5{-}P$ Compounds

		CF$_2$			PCF$_2$			CF$_3$
compound	$\delta(^1H)$ [ppm]	$\delta(^{19}F_A)$ [ppm]	$\delta(^{19}F_B)$ [ppm]	$\delta(^{31}P)$ [ppm]	$^2J_{P,FA}$ [Hz]	$^2J_{P,FB}$ [Hz]	$^2J_{FA,FB}$ [Hz]	$\delta(^{19}F)$ [ppm]
$(C_2F_5)_2P(O)Cl$		−120.1 (m)	−124.4 (m)	+20.7 (q)	99.0	106.0	319.2	−82.0
$(C_2F_5)_2P(O)NH_2$	5.26 (s. br)	−124.9 (m)	−127.7 (m)	+12.9 (q)	78.6	84.3	335.1	−81.2
$C_2F_5P(O)(NH_2)_2$	4.03 (s. br)	−127.7 (d)		10.8 (t)		76.8		−81.7
$[NH_4]^+[(C_2F_5)_2PO_2]^-$	6.39 (t)	−126.7 (d)		−0.5 (q)		69.3		−82.0
$[NH_4]^+[(C_2F_5)_2P(O)]_2N^-$	3.15 (q)	−124.4 (m)	−127.1 (m)	−5.9 (q)	79.4	88.5	332.6	−81.7

reported by us.[26] In this publication we describe details of their syntheses and properties.

Results and Discussion

Synthetic Aspects. The synthesis of $HN[P(O)(C_2F_5)_2]_2$ is a modification of the procedure described by Yagupolskii et al. for $HN[P(O)(C_3F_7)_2]_2$[25] and in our patent application for $HN[P(O)(C_2F_5)_2]_2$.[26] In both cases three synthetic steps were required. First, the amide is generated and isolated according to eq 1:

$$(C_2F_5)_2P(O)Cl + 2NH_3 \rightarrow (C_2F_5)_2P(O)NH_2 + NH_4Cl \tag{1}$$

In a second step, the imide is formed under strongly basic conditions:

$$(C_2F_5)_2P(O)NH_2 + (C_2F_5)_2P(O)Cl + 2Et_3N \rightarrow [Et_3NH][N\{P(O)(C_2F_5)_2\}_2] + [Et_3NH]Cl \tag{2}$$

Finally, the pure acid is isolated by heating the imide with concentrated sulfuric acid in vacuum.

$$[Et_3NH][N\{P(O)(C_2F_5)_2\}_2] + H_2SO_4 \rightarrow HN[P(O)(C_2F_5)_2]_2 + [Et_3NH]HSO_4 \tag{3}$$

We have now developed a one pot procedure. In a pre-reaction, $(C_2F_5)_2P(O)Cl$ diluted in ether was treated with ammonia at −78 °C. Subsequently, a sample of the products was analyzed by NMR spectroscopy. According to the NMR-spectra of authentic samples of phosphinic and phosphonic acid derivatives (see Table 1), the products $(C_2F_5)_2P(O)NH_2$, $[NH_4][(C_2F_5)_2PO_2]$, $[NH_4][N\{P(O)(C_2F_5)_2\}_2]$, and traces of $C_2F_5P(O)(NH_2)_2$ were detected. These products were not worked up because otherwise unreacted ammonia will decompose $(C_2F_5)_2P(O)NH_2$ according to

$$(C_2F_5)_2P(O)NH_2 + NH_3 \rightarrow C_2F_5P(O)(NH_2)_2 + C_2F_5H \tag{4}$$

This undesired reaction would reduce the yield considerably. The reaction was terminated by adding Et_3N and the calculated amount of $(C_2F_5)_2P(O)Cl$ and then slowly warming it up. The free acid was obtained as described above (eq 3).

Properties of $HN[P(O)(C_2F_5)_2]_2$. Bis(bis(pentafluoroethyl)phosphinyl)imide is a colorless, hygroscopic solid compound which melts at 47 °C and decomposes at $T_{onset} = 196$ °C (TGA). It is hydrolytically stable in aqueous solution for several weeks, and its acidic ionization constant was determined by titration, $pK_a = 1.9$. This value compares closely with a pK_a of 1.7 for $HN(SO_2CF_3)_2$.[8] To estimate the intrinsic acidic strength of the solid, an IR[27–29] spectroscopic method was applied. The acidic strength is based on the N−H stretching frequencies of tri-*n*-octylammonium salts in CCl_4 solution. For the contact ion pair

$$(C_8H_{17})_3N^+{-}H\cdots N[P(O)(C_2F_5)_2]_2^-$$

ν(N−H) is 3081 cm^{-1}. This is a little lower than that for $HN(SO_2CF_3)_2$ (3086 cm^{-1})[30] which also indicates a slightly lower acidity for neat $HN[P(O)(C_2F_5)_2]_2$.

The room temperature ionic liquid, $[(C_8H_{17})_3NH(D)][N\{P(O)(C_2F_5)_2\}_2]$, has $\nu(NH) = 3029$ and $\nu(ND) = 2213$ cm^{-1}.

Properties of the Salts $M^+N[P(O)(C_2F_5)_2]_2^-$, M = Na, K, Cs, Ag, [Me$_4$N]. Salts containing the $[(C_2F_5)_2P(O)]_2N^-$ anion (FPI) are conveniently prepared by reacting the aqueous acid with oxides, hydroxides, or carbonates. The neutral aqueous solutions are hydrolytically stable, but under basic conditions they decompose rapidly with evolution of C_2F_5H. Except for the [Me$_4$N] derivative, all of the above-mentioned salts are soluble in water. Their melting points increase in the series M[FPI]: [Me$_4$N][FPI] (98 °C) < Cs[FPI] (107 °C) < K[FPI] (223 °C) < Na[FPI] (230 °C). The increase appears to follow their lattice energy. Ag[FPI] (211 °C) does not fit in this series because Ag$^+$ is more covalently bonded. The thermal stabilities (T_{onset}, TGA) of the salts are dependent on the strength of the interionic interaction and therefore there is a decrease observed in the series M[FPI]: [Me$_4$N][FPI] (440 °C) < Cs[FPI] (380 °C) < K[FPI] (250 °C) < Na[FPI] (210 °C). Again Ag[FPI] (220 °C) does not fit this trend.

In CD_3CN solution, the salts are nearly completely dissociated, and their NMR spectra are almost identical. The ^{19}F NMR spectrum of the C_2F_5 group shows a singlet at −81 ppm and a multiplet at −125 ppm in a relative intensity ratio of 3:2. The sharp signal at −81 ppm of the CF_3 group does not couple with the CF_2-group, but the ^{13}C satellites ($^1J_{CF} = 95.3$ Hz) are split by coupling with the CF_2 group. As will be discussed below, the free anion exhibits no symmetry. As a consequence the F atoms in the CF_2 group are not equivalent and the $-CF_2-P$ moiety gives an AA′X spin system. The observed and simulated AA′ part of the ^{19}F

---

(25) Pavlenko, N. V.; Matyushecheva, G. I.; Semenii, V. Y.; Yagupol' skii, L. M. *Journal of General Chemistry of the USSR* **1985**, *55*, 1586–1590.

(26) Ignatiev, N.; Weltz-Biermann, U.; Heckmeier, M.; Bissky, G.; Willner, H. Patent Application No. DE 10 2005 025 31 5A, Germany, 2005.

(27) Keder, W. E.; Burger, L. L. *J. Phys. Chem.* **1965**, *69*, 3075–3080.

(28) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *116*, 5466–5469.

(29) Reed, C. A. *Chem. Commun.* **2005**, 1669–1677.

(30) Stayanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 8500–8508.

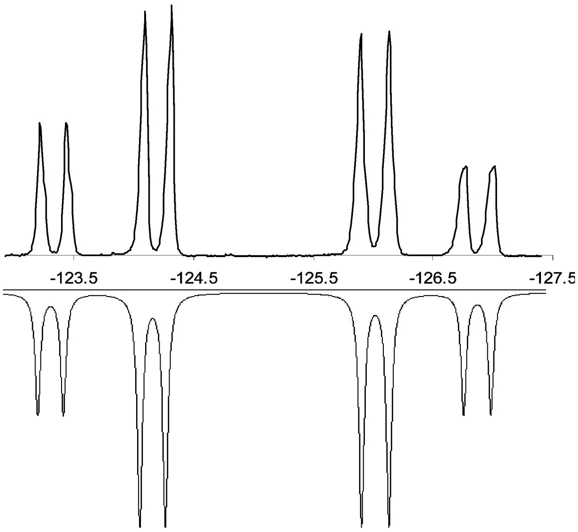


Figure 1. Observed (top) and simulated (bottom) spectrum of the CF_2 resonances in acetonitrile−D_3.

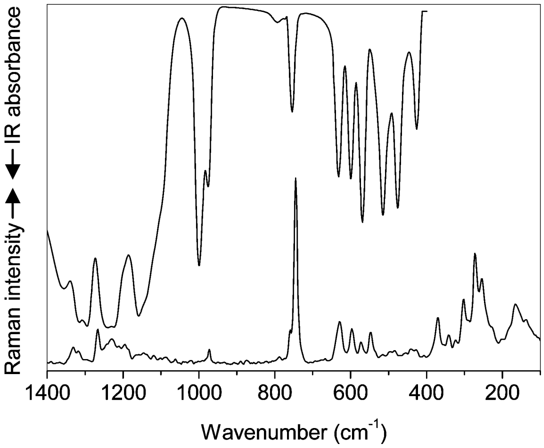


Figure 2. Infrared and Raman spectra of solid $Cs^+[N\{P(O)(C_2F_5)_2\}_2]^-$ recorded as a KBr pellet and as a solid compound, respectively.

NMR spectrum is depicted in Figure 1, and the NMR parameters are collected in Table 1. The additional unresolved splitting in the experimental spectrum may be due to different rotamers of the anion. In the ^{31}P NMR spectrum, only one broad quintet is observed between −6 and −8 ppm (depending on the solvent) because of coupling with the four nearly identical ^{19}F nuclei of the two CF_2 groups.

The infrared and Raman spectra of the $[(C_2F_5)_2P(O)]_2N^-$ anion are similar in all salts and an example is presented in Figure 2.

The spectra are quite complicated because of the low symmetry of the anion (93 fundamentals are in principle allowed) and, in addition, several rotamers (P═O/P═O *cis* or *trans* and different C_2F_5 orientations) are possible, each giving its own spectrum. However, several of the C_2F_5 and stretching modes overlap as can be seen by comparison of observed and calculated band positions in Table 2. The highest mode is attributed to the ν_{as} PNP stretch followed by the C−C, P═O, C−F stretches, and below 1000 cm^{-1} by deformation modes. The strongest Raman band at 746 cm^{-1} is attributed to the symmetric CF_3 deformations. Altogether, the vibrational spectra are suitable for fingerprint identification. The possible rotamers could be assigned by recording spectra at different temperatures, which is not the aim of this work.

Table 2. Observed and Calculated Band Positions (cm^{-1}) and Infrared Band Intensities of the $[(C_2F_5)_2P(O)]_2N^-$ Anion

IR[a]	Raman[b]	ν_{calcd}[c]	assignment	
1322 vs	1328 (12)	1370 (1000)	ν_1	$\nu(PNP)$
1315 vs	1317 (10)	1315 (110)	ν_2	$\nu(CC)$
1295 vs		1300 (330)	ν_3	$\nu(CC)$
1246 vs	1262 (25)	1295(600)	ν_4/ν_5	$\nu(CC)$
1230 vs	1230 (16)	1255 (280)	ν_6	$\nu_s(PO)$
1207 s	1207 (12)	1215 (800)	$\nu_7/\nu_8/\nu_9$	$\nu_{as}(CF_3)$
1190 s	1190 (13)	1205 (250)	ν_{10}/ν_{11}	$\nu_{as}(CF_3)/\nu_s(PO)$
1160 vs	1160 (8)	1170 (700)	$\nu_{12}-\nu_{15}$	$\nu_{as}(CF_3)$
1146 s	1147 (8)	1142 (200)	ν_{16}	$\nu_s(CF_2)$
1136 vs	1136 (7)	1138 (500)	ν_{17}/ν_{18}	$\nu(PC)$
1100 vs	1100 (6)	1100 (330)	$\nu_{19}-\nu_{23}$	$\nu(CF_2)$
995 vs		965 (250)	$\nu_{24}-\nu_{26}$	$\nu(PC)$
970 s	970 (30)	950 (100)	ν_{27}	$\nu(PC)$
760 m	760 (19)	750 (10)	ν_{28}	$\nu_s(PNP)$
745 w	745 (100)	730 (25)	$\nu_{29}-\nu_{32}$	$\delta(CF_3)$
625 s	625 (23)	620 (30)	$\nu_{33}-\nu_{35}$	
600 s	600 (20)	600 (50)	ν_{36}/ν_{37}	
570 s	570 (14)	580 (40)	ν_{38}/ν_{39}	
	545 (20)	575 (0.5)	ν_{40}	
530 m		550 (200)	ν_{41}/ν_{42}	
515 s		520 (150)	$\nu_{43}-\nu_{46}$	
475 s		470 (130)	ν_{47}/ν_{48}	
425 m	425 (10)	420 (70)	$\nu_{49}-\nu_{52}$	
	370 (25)	360 (10)	$\nu_{53}-\nu_{56}$	
	340 (16)	340 (3)	ν_{57}	
	303 (35)	300 (4)	$\nu_{58}-\nu_{61}$	
	272 (50)	272 (4)	$\nu_{62}-\nu_{63}$	
	255 (42)	250 (7)	$\nu_{64}-\nu_{65}$	

[a] KBr pellet; s = strong, m = medium, w = weak, v = very. [b] Solid, Cs salt relative intensities in parenthesis. [c] B3LYP/6−31+G(d), IR intensities in parenthesis (km mol^{-1}).

Table 3. Crystallographic Data for $[(CH_3)_4N]^+[N\{P(O)(C_2F_5)_2\}_2]^-$ at 100 K

formula	$C_{12}H_{12}F_{20}N_2O_2P_2$
molecular weight [g mol^{-1}]	658.18 g mol^{-1}
crystal system, space group	$P2_1/n$, (No. 14)
a [Å]	15.7308(12)
b [Å]	15.5515(13), β = 109.463(4)°
c [Å]	20.1328(14),
V [Å^3]	4643.8(6)
Z	8
ρ_{calcd} [g cm^{-3}]	1.883
R1[a] ($I > 2\sigma$)	0.053
wR2[b] (all data)	0.094

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Crystal Structure. A crystal of $[Me_4N][N\{P(O)(C_2F_5)_2\}_2]$ suitable for single crystal X-ray diffraction was obtained by recrystallization from an isopropanol/water solution. The crystal structure was determined in space group $P2_1/n$ (Table 3) with two independent formula units per unit cell, one of which is depicted in Figure 3.

The OPNPO skeletons of both $[(C_2F_5)_2P(O)]_2N^-$ anions show approximate C_2 symmetry (rms 0.0624 Å) with the two P═O groups orientated *gauche* to each other (dihedral angles of 59° and −51°). The C_2F_5 groups do not follow the local C_2 symmetry. Average values of selected bond lengths and the PNP angle for the anion are collected in Table 4 and are compared to the structural parameters of the free anion obtained from density-functional theory (DFT) calculations. The predicted and observed structural parameters are almost identical because there are no significant interionic contacts in the salt and the chosen basis set in the calculation

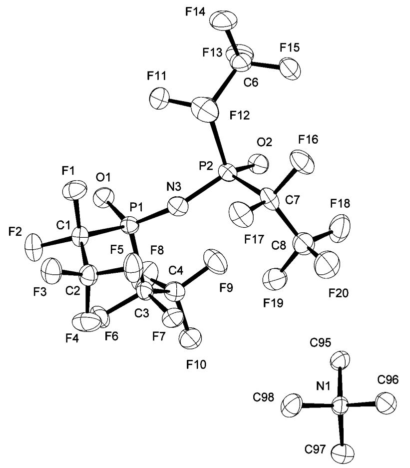


Figure 3. Perspective drawing of one of the two formula units present in the unit cell of $[Me_4N][N\{P(O)(C_2F_5)_2\}_2]$. Thermal ellipsoids are given with 50% probability.

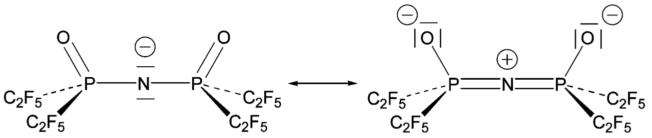
Table 4. Observed and Calculated Average Bond Lengths (Å) and PNP Angle for the $[(C_2F_5)_2P(O)]_2N^-$ Anion

bond	obs./calc.[a]	bond	obs./calc.[a]
$CF_2{-}F$	1.33/1.35	P=O	1.47/1.49
CF−F	1.36/1.37	P−N	1.56/1.59
C−C	1.53/1.55	P−C	1.88/1.92
		PNP angle	144°/143°

[a] B3LYP/6−31+G(d).

is sufficient for this anion. The global minimum for the calculated gas-phase structure also exhibits C_1 symmetry. The shortest distances between the cation and anion are 2.349, 2.382, and 2.392 Å for P=O···H contacts which are about 0.3 Å shorter than the sum of the van der Waals radii.

The P−N bond distances and the P−N−P angle of the anion differ substantially from the related neutral species. The P−N bonds are significantly shortened (1.562(6) Å compared to 1.670(1) Å in $^iPr_2P(O)NHP(O)^iPr_2$ [31]) and the P−N−P angle is more open (143.9(15)° compared to130.1°[31]). For the neutral species, equally long P−N distances and reduced P−N−X angles are observed from the crystal structures of other molecules containing the $R_2P(O)NR'_2$ fragment [an analysis of the CSD Ver. 5.29 [Cambridge Crystallographic Data Centre (CCDC), Cambridge, U.K.] yields 1.65(2) Å for a sample consisting of 11 observations and 126(3)° derived from 7 observations]. On the other hand there is no significant difference between the P=O distances of the anion, 1.471(3) Å, and the neutral species, where this distances averages to 1.48(1) Å. The following mesomeric structures rationalize this effect for the central bonds.



Further analysis of the crystal structures suggests a small but significant shortening of the C−F bonds of the terminal CF_3-groups (1.327(5) Å) compared to the CF_2-groups (1.359(6) Å) by 0.032(6) Å. At least in part, this will be due to the larger anisotropic displacement parameters of the terminal CF_3-groups, which causes an apparent reduction of the bond length.[32] However, the effect is also present, albeit less pronounced, in the geometry-optimized molecular structure obtained from DFT calculations.

The different natures of the CF_2 and CF_3 group are also reflected by their different ^{19}F NMR-chemical shifts and CF stretching frequencies. On the NMR time scale in solution, the CF_3 groups freely rotate while the rotation of the CF_2 group along the P−C bond is strongly hindered. As a consequence, the two CF bonds are not equivalent and they result in an AA′ spin system in the ^{19}F NMR spectrum (see above).

Experimental Section

Synthetic Reactions. Synthesis of Bis[bis(pentafluoroethyl)-phosphinyl] Imide $HN[P(O)(C_2F_5)_2]_2$. A solution of 45 g (140 mmol) of bis(pentafluoroethyl)phophinic acid chloride[33] in 40 mL of dry diethylether was placed in a 250 mL bulb equipped with a PTFE valve (Young, London) and cooled to −78 °C (dry ice/ethanol bath). A container charged with 4.7 g (276 mmol) of ammonia was connected to the reactor and then the ammonia slowly added. The mixture was stirred and allowed to warm up to room temperature within 4 h. A white deposit was formed, and the solution examined by ^{31}P NMR spectroscopy: $(C_2F_5)_2P(O)Cl$ (9%), $(C_2F_5)_2P(O)NH_2$ (24%), $C_2F_5P(O)(NH_2)_2$ (3%) NH_4^+ $[(C_2F_5)_2PO_2]^-$ (15%) and $NH_4^+[N\{P(O)(C_2F_5)_2\}_2]^-$ (49%). Subsequently, 12 g (37 mmol) of $(C_2F_5)_2P(O)Cl$ and 10 g (99 mmol) of triethylamine were added to the reaction mixture within 30 min at 0 °C. After an additional 30 min stirring, the deposit of NH_4Cl was filtered off and washed three times with 20 mL of dry diethyl ether. After removing the solvent under vacuum, the white solid was dissolved in 2-propanol and then, by addition of water, pure $[Et_3NH][N\{P(O)(C_2F_5)_2\}_2]$ precipitated. After drying under vacuum, 50 g of the product (yield: 79%) was obtained. mp: 106−107 °C.

Concentrated sulfuric acid (35 mL) was added to the salt and heated under vacuum ($<10^{-2}$ mbar) to 120−135 °C. The product sublimed through an ascending glass tube and 41.7 g was collected in a bulb at 0 °C. The white solid $HN[P(O)(C_2F_5)_2]_2$, is very hygroscopic and must be handled under dry nitrogen.

Yield: 97.3%, mp 47 °C.

Elemental analysis, found, %: C 16.07, H 0.11, N 2.45; calculated, %: C 16.42, H 0.17, N 2.39.

^{19}F NMR spectrum, (solvent CD_3CN, 376.4 MHz), δ, ppm: −81.2 s (CF_3); −123.8 m, ($2CF_A$); −126.4 m, ($2CF_B$); $^2J_{P,FA} = 82.4$ Hz; $^2J_{P,FB} = 88.5$ Hz; $^2J_{FA,FB} = 329$ Hz.

^1H NMR spectrum, (solvent CD_3CN, 400 MHz), δ, ppm: 9−12 br. m (NH).

^{31}P NMR spectrum, (solvent CD_3CN, 161.9 MHz), δ, ppm: −7.8 q (2P);$^2J_{P,F} = 86$ Hz.

Syntheses of Salts Containing the $[(C_2F_5)_2P(O)]_2N^-$ Anion. The salts were prepared by reacting aqueous solutions of $HN[P(O)(C_2F_5)_2]_2$ at 0 °C by slowly adding equal molar amounts of carbonate or hydroxide solutions to the acid in a round bottomed flask while stirring. It is important to prevent local high basic conditions because otherwise the anion decomposes forming C_2F_5H. The neutral

---

(31) Cupertino, D.; Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chim. Acta* **1999**, *290*, 1.

(32) Cruickshank, D. W. J. *Acta Crystallogr., Section A: Foundations* **1956**, *9*, 757–758.

(33) Ignatiev, N.; Schulte, M. ; Aust, E.; Bejan, D.; Willner, H. Patent Application Merck GmbH, Germany, 2008.

aqueous solutions were evaporated and then heated under vacuum ($<10^{-2}$ mbar) at 60−80 °C for 12 h. The NMR spectra of all salts are almost identical to those of the acid mentioned above.

$Na^+[N\{P(O)(C_2F_5)_2\}_2]^-$. A solution 0.086 g (2.1 mmol) of NaOH in H_2O (3 mL) was slowly added to a solution of $HN[P(O)(C_2F_5)_2]_2$ (1.26 g, 2.1 mmol) in H_2O (3 mL) by stirring at 0 °C. The resulting neutral solution was then dried in vacuum, yielding $Na^+[N\{P(O)(C_2F_5)_2\}_2]^-$ as a hygroscopic microcrystalline solid. Yield: 96%, (1.25 g).

Elemental analysis, %: C 15.83, N 2.31; calculated, %: C 15.76, N 2.4.

$K^+[N\{P(O)(C_2F_5)_2\}_2]^-$. To 0.33 g (2.3 mmol) of K_2CO_3 in H_2O (3 mL) was added a solution of 2.80 g (2.3 mmol) of $HN[P(O)(C_2F_5)_2]_2$ in H_2O (5 mL) and stirred as described above. The resulting solution was concentrated by rotary evaporation and dried in vacuum ($<10^{-2}$ mbar) at 60 °C overnight. This yielded 2.95 g (98%) of the white, hygroscopic $K^+[N\{P(O)(C_2F_5)_2\}_2]^-$.

Elemental analysis, found %: C 15.29, N 2.34; calculated, %: C 15.42, N 2.25.

$Cs^+[N\{P(O)(C_2F_5)_2\}_2]^-$. A solution of 0.72 g (4.2 mmol) of $CsOH\cdot xH_2O$ in H_2O (5 mL) was added to 2.5 g (4.2 mmol) of $HN[P(O)(C_2F_5)_2]_2$ in H_2O (5 mL) as described above. The resulting neutral solution was dried in vacuum, and 2.90 g $Cs^+[N\{P(O)(C_2F_5)_2\}_2]^-$ as a microcrystalline solid was obtained (yield 94%).

Elemental analysis, %: C 13.51, N 2.10; calculated, %: C 13.40, N 1.95.

$Ag^+[P(O)(C_2F_5)_2]_2N^-$. A 0.55 g (1.9 mmol, excess) quantity of Ag_2CO_3 was added to 2.04 g (3.4 mmol) of $HN[P(O)(C_2F_5)_2]_2$ dissolved in H_2O. The suspension was stirred at room temperature for 1 h. Filtration and drying in vacuum ($<10^{-2}$ mbar) gave 2.17 g of $Ag^+[N\{P(O)(C_2F_5)_2\}_2]^-$ (yield 90%).

Elemental analysis, %: C 13.96, N 2.24; calculated, %: C 13.89, N 2.02.

$[(CH_3)_4N]^+ [N\{P(O)(C_2F_5)_2\}_2]^-$. A solution of 1.6 g (2.7 mmol) of $HN[P(O)(C_2F_5)_2]_2$ in 5 mL of water was added by stirring at room temperature to a solution of 0.3 g (2.7 mmol) of $[(CH_3)_4N]^+Cl^-$ in water (5 mL). After the mixture had stood for 20 min, the white precipitate was filtered off and washed four times with 10 mL of water until the test for chloride was negative. The product was dried in vacuum at 50 °C for 3 h, and 1.68 g of tetramethylammonium bis[bis(pentafluoroethylphosphinyl]imide was obtained (yield 93%). Single crystals were obtained by recrystallization in *i*-propanol/H_2O solution.

Elemental analysis, found %: C 21.89, H 1.8, N 4.09; calculated, %: C 21.90, H 1.84, N 4.26.

Thermal Analysis. Thermo-analytical measurements were performed with a differential scanning calorimeter (DSC) and a TG Netzsch STA 409 instrument. Temperature and sensitivity calibrations in the temperature range of 30−600 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 25−40 mg of solid samples were weighed and sealed in an aluminum crucible for DSC placed in ceramic pans for thermogravimetry measurements in the temperature range 30−600 °C with a heating rate of 10 °C min^{-1} under an atmosphere of dry nitrogen. The data were processed with the Netzsch Protens 4.0 software.

Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on an FTIR spectrometer TENSOR 27 (Bruker, Karsruhe, Germany) equipped with a DTGS detector and a KBr/Ge beam splitter operating in the region 4000−400 cm^{-1}. For each spectrum, 64 scans were added with a resolution of 2 cm^{-1}. The solid samples were measured as KBr pellets.

Raman spectra were recorded at room temperature on a Bruker EQUINOX 55 FT Raman spectrometer using the 9394.8 cm^{-1} exciting line (500 mW) of a Nd:YAG laser. Solid samples were placed in melting point capillaries and used for recording spectra in the region 3000−50 cm^{-1} with a resolution of 2 cm^{-1}. For each spectrum, 500 scans were added.

NMR Spectroscopy. NMR spectra for all compounds were measured in CD_3CN at room temperature on a Bruker Avance DRX-400 (^1H, 400.13 MHz; ^{19}F, 376.49 MHz; ^{31}P, 161.97 MHz) spectrometer. The chemical shifts are referenced to external TMS (^1H), $CFCl_3$ (^{19}F), and H_3PO_4 (^{31}P).

Theoretical Calculations. Starting from the experimental geometry of the anion (Figure 3) the structure was fully optimized at the B3LYP/6−31+G(d) level using the Gaussian 03W program package (version 6.0, revision B.04).[34] The vibrational frequencies and the IR intensities for the anion have been calculated at the energy-minimized structure of C_1 symmetry for which no imaginary vibrational frequency was found.

Single Crystal X-ray Diffraction. Single-crystal diffraction data were collected at 100 K on a Kappa CCD diffractometer (Bruker AXS) using Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure of $[N(CH_3)_4][N\{P(O)(C_2F_5)_2\}_2]$ was solved by direct methods using SHELXS-97,[35] and full-matrix least-squares refinement on F^2 was performed with SHELXL-97.[36] Diffracted intensities of this very small crystal (0.1 × 0.02 × 0.014 mm) were corrected initially for absorption based on indexed crystal faces, T_{min}, and T_{max}: 0.977 and 0.995; however, the final refinement was based on a multiscan absorption correction using SADABS. Experimental details and crystal data are collected in Table 3.

CCDC reference number: 686746. Crystallographic data in cif format can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, U.K. (fax: (+44)-1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. Financial support by the Merck KGaA Company in Darmstadt and the Fonds der Chemischen Industrie is acknowledged. We thank Dr. E. Bernhardt for his support for quantum-chemical calculations and valuable discussions.

Supporting Information Available: Further results of the quantum-chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801088Q

---

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. ; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N. ; Burant, J. C.; Millam, J. M.; Iyengar, S. S. T., J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C. ; Pople, J. A. *Gaussian 03W*, Version 6.0, Rev. B04; Gaussian, Inc.: Wallingford, CT, 2003.

(35) Sheldrik, G. M. *SHELX-97 Program Package, SHELXS-97 - Program for Crystal Structure Solution, and SHELXL-97 - Program for Crystal Structure Refinement (Release 97−2)*; University of Göttingen: Göttingen, Germany, 1997.

(36) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.