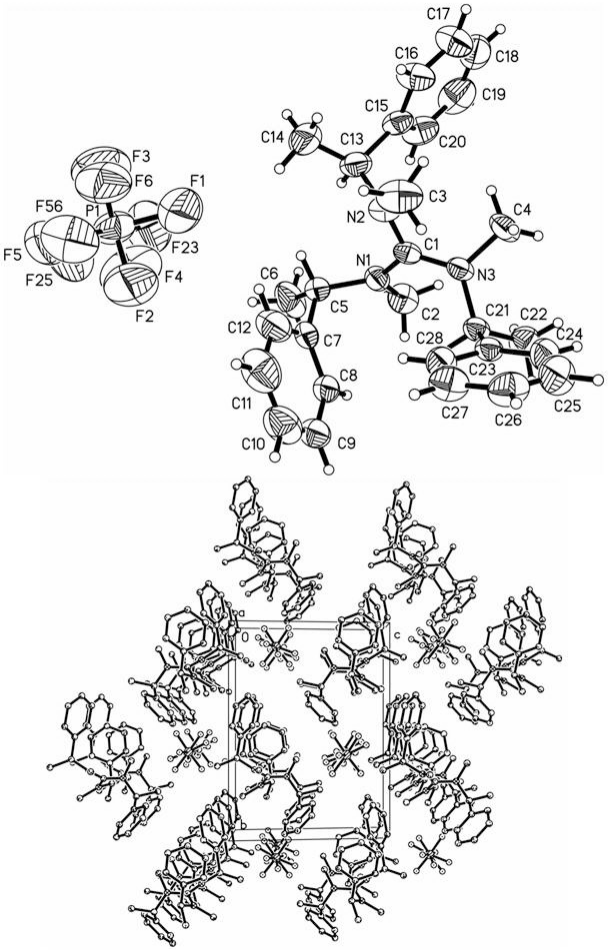
Crystal structure of (*N*,*N*',*N*''-trimethyl-*N*,*N*',*N*''-*tris*-(1-phenylethyl)-guanidinium hexafluorophosphate), $C_{28}H_{36}F_6N_3P$

Wolfgang Frey, Amélie Castiglia and Volker Jäger*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Received December 15, 2011, accepted May 30, 2012, available online July 19, 2012, CCDC no. 1267/3771



Abstract

$C_{28}H_{36}F_6N_3P$, monoclinic, $P2_1$ (No. 4), a = 9.125(1) Å, b = 14.596(3) Å, c = 11.028(2) Å, β = 102.36(1)°, V = 1434.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0783, $wR_{ref}(F^2)$ = 0.1597, T = 293 K.

Source of material

The title compound was prepared by silver salt metathesis [1] of *N*,*N*',*N*''-trimethyl-*N*,*N*',*N*''-*tris*(1-phenylethyl)-guanidinium iodide with silver hexafluorophosphate $AgPF_6$ with exclusion of light at room temperature in a mixture of H_2O/CH_3CN (1:1) [2, 3]. After removal of the by-product silver iodide AgI by filtration, the filtrate was concentrated in vacuo and the residue was recrystallized from acetone/CH_3CN/EtO_2 to give the analytically and spectroscopically pure title product in the form of colourless crystals.

Analysis: m. p. 175-177°C, $[\alpha]_D20$ = 36.2 (c = 1.02, $(CH_3)_2CO$).

* Correspondence author (e-mail: jager.ioc@oc.uni-stuttgart.de)

Experimental details

H atoms were located in the difference fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C–H) ranging from 0.93 to 0.98 Å. In addition, methyl groups were allowed to rotate but not to tip. The Flack parameter is -0.17(19) [4], which is in accordance with the absolute configuration resulting from the synthetic pathway. For better overview displacement parameters are drawn with 40 % probability. The displacement parameters of the fluorine atoms of the anion are enlarged and disordered, which indicates a spherical rotation disorder of the anion.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.3×0.3×0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.56 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff-Scan
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7328, 6916
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3599
$N(param)_{refined}$:	377
Programs:	SHELXS-97 [4]

Discussion

The title compound (figure, top) crystallizes with one independent ion pair in the asymmetric unit of the acentric space group $P2_1$. The carbon-nitrogen distances of the guanidinium ion are identical with respect to their standard deviations. The distances are C1–N1 (1.350(5) Å), C1–N2 (1.345(5) Å), and C1–N3 (1.336(5) Å). The substituents attached to the nitrogen atoms are forced out-of-plane in relation to the guanidinium core. The interplanar angle between the guanidinium core C1, N1, N2 and N3 and N1, C2 and C5 is 37.6(3)°. The same angle with N2, C3 and C13 is 42.7(3)° and finally the angle with N3, C4 and C21 is 36.7(3)°. The packing diagram of the cell plot (figure, bottom) shows non-polar layers in the *ac*-plane stacking along the *b*-axis formed by the phenyl moieties of the guanidinium ions. There are also polar channels built up by the PF_6^- anions along the *a*-axis.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	2*a*	0.2809	0.3198	0.9523	0.107
H(2B)	2*a*	0.4184	0.37	0.918	0.107
H(2C)	2*a*	0.4422	0.2779	0.9928	0.107
H(3A)	2*a*	0.0873	0.0863	0.6486	0.144
H(3B)	2*a*	0.1205	0.1133	0.5195	0.144
H(3C)	2*a*	–0.0231	0.1511	0.5591	0.144

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(4A)	2*a*	–0.0592	0.2233	0.7503	0.115
H(4B)	2*a*	–0.0609	0.1959	0.8875	0.115
H(4C)	2*a*	–0.0576	0.1197	0.788	0.115
H(5)	2*a*	0.4384	0.2549	0.6589	0.075
H(6A)	2*a*	0.5511	0.3816	0.7712	0.153
H(6B)	2*a*	0.6711	0.3173	0.7329	0.153
H(6C)	2*a*	0.6469	0.3157	0.8694	0.153
H(8)	2*a*	0.6133	0.1579	0.9542	0.075
H(9)	2*a*	0.7173	0.0134	0.9788	0.098
H(10)	2*a*	0.7127	–0.0774	0.8093	0.123
H(11)	2*a*	0.6150	–0.0232	0.6154	0.135
H(12)	2*a*	0.5088	0.1203	0.5886	0.107
H(13)	2*a*	0.2451	0.3380	0.6098	0.083
H(14A)	2*a*	0.2841	0.2458	0.4477	0.167
H(14B)	2*a*	0.1973	0.3352	0.3963	0.167

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(14C)	2*a*	0.1107	0.2422	0.3935	0.167
H(16)	2*a*	–0.1194	0.2850	0.4272	0.104
H(17)	2*a*	–0.3313	0.3662	0.4335	0.129
H(18)	2*a*	–0.3303	0.4783	0.5791	0.127
H(19)	2*a*	–0.1081	0.5138	0.7136	0.129
H(20)	2*a*	0.1058	0.4326	0.7099	0.102
H(21)	2*a*	0.3249	0.1385	0.9696	0.061
H(22A)	2*a*	0.1931	0.2282	1.0875	0.112
H(22B)	2*a*	0.2282	0.1313	1.1482	0.112
H(22C)	2*a*	0.0667	0.1537	1.0717	0.112
H(24)	2*a*	0.0211	0.0100	1.0269	0.091
H(25)	2*a*	–0.0158	–0.1438	0.9887	0.115
H(26)	2*a*	0.1225	–0.2205	0.8703	0.100
H(27)	2*a*	0.3084	–0.1455	0.7977	0.096
H(28)	2*a*	0.3431	0.0102	0.8338	0.077

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*a*		0.3524(4)	0.2600(2)	0.8126(3)	0.044(2)	0.055(2)	0.058(2)	0.001(2)	0.011(2)	0.003(2)
C(1)	2*a*		0.2203(5)	0.2176(3)	0.7688(4)	0.047(2)	0.039(2)	0.058(3)	0.012(2)	0.005(2)	0.005(2)
C(2)	2*a*		0.3755(5)	0.3113(3)	0.9289(5)	0.068(3)	0.060(3)	0.082(4)	–0.012(2)	0.009(3)	–0.006(3)
N(2)	2*a*		0.1661(4)	0.2149(3)	0.6454(3)	0.065(2)	0.055(2)	0.058(2)	0.003(2)	–0.001(2)	–0.000(2)
N(3)	2*a*		0.1423(3)	0.1812(2)	0.8465(3)	0.039(2)	0.045(2)	0.065(2)	0.005(2)	0.004(2)	0.008(2)
C(3)	2*a*		0.0802(7)	0.1343(4)	0.5881(6)	0.113(5)	0.071(4)	0.086(4)	–0.001(3)	–0.017(3)	–0.018(3)
C(4)	2*a*		–0.0234(5)	0.1799(4)	0.8154(5)	0.036(2)	0.077(3)	0.114(4)	0.004(2)	0.010(2)	0.027(3)
C(5)	2*a*		0.4801(5)	0.2482(3)	0.7480(4)	0.050(2)	0.078(3)	0.061(3)	0.008(2)	0.013(2)	0.023(2)
C(6)	2*a*		0.5982(6)	0.3225(4)	0.7837(7)	0.065(3)	0.073(4)	0.178(6)	–0.004(3)	0.047(4)	0.029(4)
C(7)	2*a*		0.5470(5)	0.1540(3)	0.7672(5)	0.041(2)	0.070(3)	0.065(3)	0.000(2)	0.016(2)	0.010(2)
C(8)	2*a*		0.6120(5)	0.1213(3)	0.8850(5)	0.054(3)	0.065(3)	0.071(3)	0.003(2)	0.019(2)	0.014(2)
C(9)	2*a*		0.6743(6)	0.0349(4)	0.8998(6)	0.064(3)	0.082(4)	0.101(5)	0.012(3)	0.022(3)	0.028(4)
C(10)	2*a*		0.6727(7)	–0.0186(5)	0.7992(8)	0.090(5)	0.074(4)	0.145(7)	0.015(3)	0.032(5)	0.003(5)
C(11)	2*a*		0.6133(8)	0.0132(5)	0.6842(8)	0.106(5)	0.112(6)	0.121(6)	0.009(5)	0.027(5)	–0.040(5)
C(12)	2*a*		0.5500(6)	0.0994(5)	0.6683(6)	0.074(4)	0.105(5)	0.085(4)	0.022(4)	0.007(3)	–0.010(4)
C(13)	2*a*		0.1625(6)	0.2989(3)	0.5676(4)	0.071(3)	0.071(3)	0.061(3)	0.008(2)	0.003(2)	0.016(3)
C(14)	2*a*		0.1913(8)	0.2786(5)	0.4395(5)	0.116(5)	0.156(6)	0.069(4)	0.051(5)	0.035(4)	0.023(4)
C(15)	2*a*		0.0182(6)	0.3513(3)	0.5672(4)	0.078(3)	0.055(3)	0.057(3)	0.012(2)	0.008(2)	0.016(2)
C(16)	2*a*		–0.1159(6)	0.3314(4)	0.4855(5)	0.081(4)	0.087(4)	0.081(4)	0.020(3)	–0.006(3)	–0.001(3)
C(17)	2*a*		–0.2428(7)	0.3796(5)	0.4901(7)	0.075(4)	0.125(6)	0.119(6)	0.026(4)	0.009(4)	0.020(5)
C(18)	2*a*		–0.2427(9)	0.4468(5)	0.5755(8)	0.112(6)	0.102(6)	0.117(6)	0.042(5)	0.053(5)	0.040(5)
C(19)	2*a*		–0.111(1)	0.4670(4)	0.6560(7)	0.161(7)	0.070(4)	0.101(5)	0.033(5)	0.046(5)	0.011(4)
C(20)	2*a*		0.0177(8)	0.4189(4)	0.6528(5)	0.111(5)	0.066(3)	0.072(4)	0.004(3)	0.004(3)	0.006(3)
C(21)	2*a*		0.2166(4)	0.1292(3)	0.9590(4)	0.043(2)	0.044(2)	0.065(3)	0.001(2)	0.007(2)	0.008(2)
C(22)	2*a*		0.1720(6)	0.1639(3)	1.0778(5)	0.085(4)	0.067(3)	0.075(4)	0.010(3)	0.022(3)	0.003(3)
C(23)	2*a*		0.1864(5)	0.0270(3)	0.9362(4)	0.046(2)	0.046(2)	0.062(3)	0.006(2)	0.007(2)	0.013(2)
C(24)	2*a*		0.0795(6)	–0.0205(4)	0.9803(5)	0.065(3)	0.061(3)	0.104(4)	0.000(3)	0.028(3)	0.013(3)
C(25)	2*a*		0.0567(7)	–0.1126(4)	0.9570(7)	0.084(4)	0.065(4)	0.140(6)	–0.018(3)	0.028(4)	0.024(4)
C(26)	2*a*		0.1401(7)	–0.1586(4)	0.8874(5)	0.092(4)	0.054(3)	0.097(4)	–0.015(3)	0.001(4)	0.011(3)
C(27)	2*a*		0.2494(7)	–0.1140(3)	0.8428(6)	0.089(4)	0.053(3)	0.095(4)	0.003(3)	0.011(3)	–0.004(3)
C(28)	2*a*		0.2708(5)	–0.0209(3)	0.8659(5)	0.063(3)	0.055(3)	0.078(3)	–0.005(2)	0.018(3)	0.002(2)
P(1)	2*a*		0.6150(2)	0.1054(1)	0.2820(2)	0.097(1)	0.079(1)	0.090(1)	–0.0150(9)	0.001(1)	0.0224(9)
F(1)	2*a*		0.4672(5)	0.1047(5)	0.3291(5)	0.141(4)	0.245(6)	0.167(5)	0.004(4)	0.047(3)	0.080(5)
F(2)	2*a*	0.6	0.703(1)	0.139(1)	0.4034(8)	0.19(1)	0.27(1)	0.130(7)	–0.109(9)	–0.049(7)	–0.003(8)
F(3)	2*a*		0.5642(6)	0.1874(4)	0.1964(6)	0.214(5)	0.160(5)	0.229(6)	0.005(4)	0.031(5)	0.113(5)
F(4)	2*a*	0.9	0.6488(7)	0.0183(4)	0.3616(7)	0.203(6)	0.161(5)	0.230(7)	0.052(5)	0.066(5)	0.123(5)
F(5)	2*a*	0.6	0.755(1)	0.0976(9)	0.2248(9)	0.121(7)	0.23(1)	0.20(1)	0.034(8)	0.061(7)	0.091(9)
F(6)	2*a*	0.7	0.5098(8)	0.0608(5)	0.1653(5)	0.149(6)	0.158(6)	0.112(5)	0.004(5)	–0.029(4)	–0.026(4)
F(23)	2*a*	0.4	0.608(2)	0.1889(8)	0.367(1)	0.17(1)	0.13(1)	0.18(1)	0.007(9)	0.05(1)	–0.047(9)
F(25)	2*a*	0.4	0.774(1)	0.146(1)	0.297(2)	0.104(8)	0.15(1)	0.22(2)	–0.063(7)	0.034(9)	–0.04(1)
F(56)	2*a*	0.4	0.656(2)	0.0227(7)	0.209(1)	0.16(1)	0.086(7)	0.16(1)	0.006(7)	–0.010(9)	–0.049(7)

References

1. Wilkes, J.S.; Zaworotko, M. J.: Air and water stable 1-ethyl-3-methylimidazolium based liqids. J. Chem. Soc., Chem Commun. **1992**, 965-967.
2. Castiglia, A.: Synthesis of Aryl-Substituted Pyrrolidinediols with Potent Activity as α-L-Fucosidase Inhibitors. Synthesis and Characterization of a new Chiral Guanidine and its Derived Guanidinium Salts, Dissertation Universität Stuttgart (2011).
3. Synthesis and Characterization of Chiral Guanidines and Guanidinium Salts Derived from 1-Phenylethylamine. Z. Naturforsch. **67b** (2012) 337-346.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
5. Flack, H. D.: On enantiomorph-polarity estimation. Acta Crystallogr. **A39** (1983) 876-881.