Crystal structure of diphenylguanidinium dihydrogenphosphite—phosphoric acid—water (2/1/1), $2[(C_{13}N_3H_{14})(H_2PO_3)] \cdot H_3PO_3 \cdot H_2O$

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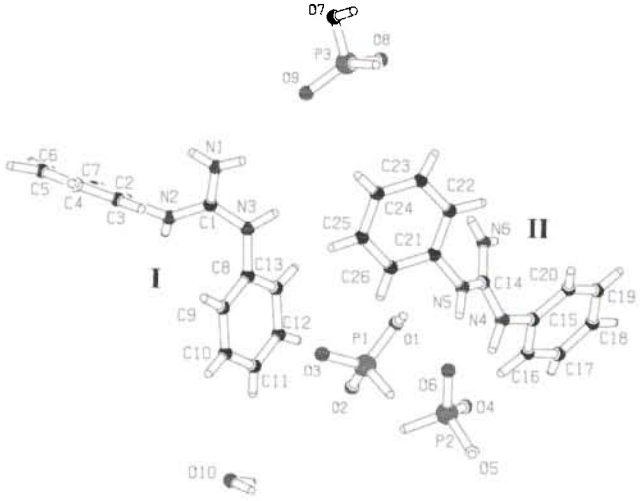

Abstract

$C_{26}H_{37}N_6O_{10}P_3$, triclinic, $P\bar{1}$ (No. 2), a = 10.961(3) Å, b = 12.204(4) Å, c = 14.128(4) Å, α = 76.40(3)°, β = 73.33(3)°, γ = 64.50(4)°, V = 1620.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.158, T = 293 K.

Source of material

The compound was synthesized by neutralizing a 1:1 water/ethanol solution of *N,N'*-diphenylguanidine (Aldrich, 97% purity) with phosphorous acid (Aldrich, 99% purity). After slow evaporation over a period of a few weeks, good quality, transparent single-crystals grew from the solution.

Discussion

Di-aryl-guanidine compounds have pharmacological applications [1]. In addition to their potential terapeutical value, diphenylguanidine (dpg) salts are interesting because the dpg^+ cation can addopt different molecular conformations depending on the counter ion [2]. This work is part of a research project on the structure, optical and dielectric properties of dpg salts. In the compound there are two symmetry independent cations, labelled **I** and **II**, with distinct conformations. In cation **I**, one of the phenyl rings lies *syn* and the other *anti* to the unsubstituted N atom, whereas in cation **II** both rings are in a *syn* position. The *syn-anti* conformation of cation **I** is similar to that of the free base [3, 4] which was also found in dpg^+ perchlorate [5]. A *syn-syn* conformation similar to that of cation **II** was observed in the nitrate, trifluoroacetate, *m*-chlorobenzeneseleninate, hydrogenselenite monohydrate, and formate salts of dpg [6-10]. In a few cases, a conformation in which both phenyl rings are *anti* has been observed [11, 12]. The present compound is the second example of co-crystalization of two different conformations of the dpg^+ cation, the first reported occurence was in bis(dpg^+) sulfate monohydrate [13]. Theoretical calculations have shown that in solution there is an easy interchange between the different conformations due the low potential barrier of rotation of the phenyl rings [2]. The dihedral angles between the central planar guanidinium fragment N_3C and the least squares-planes of the phenyl rings are for **I** 57.49(17)° (C2–C7), 80.86(16)° (C8–C13) and 51.87(22)° (C15–C20), 30.26(23)° (C21–C26) for **II**. The dihedral angle between the planes of the two phenyl rings are for **I** 80.86(16)° and 30.26(23)° for **II**. The C—N bond lengths of the guanidinium group are within the range 1.315 Å – 1.342(5) Å. The guanidinium group is planar, the sum of the valence angles around C1 and C14 is exactly 360°. However, it should be noted that the angle opposite to N6 is much smaller (117.8(4)°) than the other two valence angles, a feature that was also observed in other dpg^+ cations with a *syn-syn* conformation. In cation **I** the smallest internal guanidinium angle is N3–C1–N1 (118.3(4)°). The geometry of the anions is unexceptional. One of the dihydrogenphosphite ions is disordered with a partial interchange of the positions of the non-acidic H atom and atom O8. The structure contains an additional molecule of unionized phosphorous acid and a solvent water molecule. The anions and cations are linked by an complex network of hydrogen bonds between the amino groups and the O atoms with N···O distances within the range 2.757(5) Å – 3.115(6) Å. All H atoms of the guanidinium NH and NH_2 groups are involved in hydrogen bonding. The hydrogenphosphite tetrahedra are also interconnected by hydrogen bonds, the strongest with an O···O distance of 2.548(4) Å.

Table 1. Data collection and handling.

Crystal:	colourless plate, size 0.13 × 0.31 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.5 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6331, 5470
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2829
$N(param)_{refined}$:	517
Programs:	HELENA [14], SHELXS-97 [15], SHELXL-97 [16], PLATON [17]

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

Atom	Site	x	y	z	U_{iso}
H(29)	2*i*	0.253(4)	0.774(4)	0.505(3)	0.062
H(30)	2*i*	–0.306(3)	1.570(3)	0.868(2)	0.029(9)
H(31)	2*i*	0.625(1)	0.871(1)	0.5403(9)	0.108
H(1)	2*i*	0.230(5)	0.935(5)	0.587(4)	0.082
H(5)	2*i*	–0.427(5)	1.519(4)	1.054(3)	0.07(2)
H(7)	2*i*	0.3341	0.9466	0.6477	0.133
H(8)	2*i*	0.6679	0.9040	0.6324	0.107
H(1A)	2*i*	0.239(4)	1.506(4)	0.866(3)	0.049
H(1B)	2*i*	0.236(4)	1.585(4)	0.770(3)	0.049
H(2)	2*i*	0.029(4)	1.388(3)	0.877(3)	0.044
H(3)	2*i*	0.074(4)	1.610(4)	0.694(3)	0.053
H(4)	2*i*	–0.112(4)	1.220(4)	0.868(3)	0.053
H(5)	2*i*	–0.315(4)	1.286(4)	0.827(3)	0.054
H(6A)	2*i*	–0.151(4)	1.063(4)	0.682(3)	0.057
H(6B)	2*i*	–0.023(5)	1.016(4)	0.712(3)	0.057
H(3)	2*i*	0.366(4)	1.282(4)	0.851(3)	0.055
H(4)	2*i*	0.488(5)	1.159(4)	0.969(3)	0.072
H(5)	2*i*	0.379(5)	1.109(4)	1.128(3)	0.078
H(6)	2*i*	0.126(5)	1.228(4)	1.172(4)	0.076

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(7)	2*i*	0.014(4)	1.348(4)	1.049(3)	0.054
H(9)	2*i*	0.177(4)	1.311(4)	0.684(3)	0.060
H(10)	2*i*	0.089(5)	1.224(5)	0.608(4)	0.077
H(11)	2*i*	–0.108(5)	1.334(5)	0.563(4)	0.088
H(12)	2*i*	–0.241(5)	1.541(4)	0.588(4)	0.080
H(13)	2*i*	–0.154(4)	1.625(4)	0.657(3)	0.062
H(16)	2*i*	0.132(5)	1.168(4)	0.842(3)	0.075
H(17)	2*i*	0.333(6)	1.014(6)	0.870(5)	0.101
H(18)	2*i*	0.379(5)	0.804(5)	0.908(4)	0.085
H(19)	2*i*	0.193(5)	0.769(5)	0.908(4)	0.080
H(20)	2*i*	–0.009(5)	0.918(4)	0.880(3)	0.068
H(22)	2*i*	–0.376(4)	1.081(4)	0.746(3)	0.051
H(23)	2*i*	–0.515(4)	1.133(4)	0.641(3)	0.066
H(24)	2*i*	–0.611(5)	1.335(4)	0.563(3)	0.067
H(25)	2*i*	–0.563(4)	1.485(4)	0.592(3)	0.064
H(26)	2*i*	–0.423(4)	1.434(4)	0.696(3)	0.058
H(27)	2*i*	–0.204(7)	0.918(6)	0.645(4)	0.103
H(28)	2*i*	–0.059(6)	0.860(5)	0.598(4)	0.103

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	2*i*	0.1986(1)	0.7919(1)	0.59941(9)	0.0412(6)	0.0374(6)	0.0481(7)	–0.0188(5)	–0.0054(5)	–0.0078(5)
P(2)	2*i*	–0.2960(1)	1.4622(1)	0.92096(8)	0.0321(6)	0.0390(6)	0.0443(6)	–0.0130(5)	–0.0101(5)	–0.0119(5)
P(3)	2*i*	0.5311(2)	0.8489(1)	0.6207(1)	0.0785(9)	0.079(1)	0.087(1)	–0.0497(8)	–0.0395(8)	0.0042(8)
O(1)	2*i*	0.1780(3)	0.9221(3)	0.6041(3)	0.045(2)	0.034(2)	0.087(2)	–0.017(1)	–0.013(2)	–0.008(2)
O(2)	2*i*	0.3068(3)	0.6989(2)	0.6578(2)	0.047(2)	0.039(2)	0.079(2)	–0.020(1)	–0.020(2)	0.003(2)
O(3)	2*i*	0.0669(3)	0.7722(3)	0.6334(2)	0.039(2)	0.049(2)	0.078(2)	–0.024(1)	–0.017(2)	0.006(2)
O(4)	2*i*	–0.1499(2)	1.3736(2)	0.9026(2)	0.033(1)	0.047(2)	0.055(2)	–0.017(1)	–0.006(1)	–0.016(1)
O(5)	2*i*	–0.3449(3)	1.4932(3)	1.0290(2)	0.030(2)	0.072(2)	0.053(2)	–0.015(2)	–0.009(1)	–0.034(2)
O(6)	2*i*	–0.3958(3)	1.4203(3)	0.8989(2)	0.033(2)	0.085(2)	0.070(2)	–0.020(2)	–0.010(1)	–0.049(2)
O(7)	2*i*	0.3990(4)	0.9546(3)	0.6042(3)	0.089(2)	0.082(3)	0.119(3)	–0.055(2)	–0.039(2)	0.009(2)
O(8)	2*i*	0.6169(5)	0.8740(5)	0.6734(4)	0.084(4)	0.108(4)	0.060(3)	–0.069(3)	–0.026(3)	–0.004(3)
O(9)	2*i*	0.5172(3)	0.7302(3)	0.6577(3)	0.061(2)	0.066(2)	0.135(3)	–0.033(2)	–0.030(2)	–0.001(2)
N(1)	2*i*	0.2132(4)	1.5335(3)	0.8152(3)	0.050(2)	0.047(2)	0.041(2)	–0.032(2)	–0.016(2)	0.002(2)
N(2)	2*i*	0.1020(3)	1.3986(3)	0.8676(2)	0.032(2)	0.041(2)	0.044(2)	–0.021(2)	–0.014(2)	0.002(2)
N(3)	2*i*	0.0699(3)	1.5362(3)	0.7238(3)	0.053(2)	0.040(2)	0.051(2)	–0.026(2)	–0.027(2)	0.007(2)
N(4)	2*i*	–0.0809(3)	1.1451(3)	0.8400(3)	0.043(2)	0.043(2)	0.054(2)	–0.011(2)	–0.019(2)	–0.019(2)
N(5)	2*i*	–0.2846(3)	1.2272(3)	0.7891(3)	0.036(2)	0.051(2)	0.053(2)	–0.012(2)	–0.010(2)	–0.027(2)
N(6)	2*i*	–0.1060(4)	1.0624(3)	0.7195(3)	0.036(2)	0.050(2)	0.060(2)	–0.004(2)	–0.019(2)	–0.027(2)
C(1)	2*i*	0.1302(4)	1.4876(3)	0.8025(3)	0.030(2)	0.038(2)	0.040(2)	–0.011(2)	–0.009(2)	–0.011(2)
C(2)	2*i*	0.1782(4)	1.3238(3)	0.9415(3)	0.035(2)	0.032(2)	0.037(2)	–0.017(2)	–0.012(2)	–0.007(2)
C(3)	2*i*	0.3194(4)	1.2686(4)	0.9167(3)	0.037(2)	0.056(3)	0.044(3)	–0.019(2)	–0.010(2)	–0.004(2)
C(4)	2*i*	0.3915(5)	1.1931(4)	0.9887(4)	0.045(3)	0.058(3)	0.079(4)	–0.018(2)	–0.025(3)	–0.002(3)
C(5)	2*i*	0.3252(6)	1.1730(5)	1.0842(4)	0.082(4)	0.060(3)	0.064(3)	–0.030(3)	–0.042(3)	0.010(3)
C(6)	2*i*	0.1829(6)	1.2259(5)	1.1087(4)	0.085(4)	0.077(4)	0.040(3)	–0.044(3)	–0.014(3)	–0.005(3)
C(7)	2*i*	0.1082(4)	1.3023(4)	1.0374(3)	0.043(2)	0.047(3)	0.045(3)	–0.019(2)	–0.007(2)	–0.009(2)
C(8)	2*i*	0.0158(4)	1.4763(4)	0.6804(3)	0.045(2)	0.049(3)	0.035(2)	–0.028(2)	–0.012(2)	–0.000(2)
C(9)	2*i*	0.0875(5)	1.3573(4)	0.6646(3)	0.053(3)	0.060(3)	0.051(3)	–0.034(2)	–0.007(2)	–0.014(2)
C(10)	2*i*	0.0355(6)	1.3041(5)	0.6186(4)	0.074(4)	0.074(3)	0.059(3)	–0.046(3)	0.000(3)	–0.020(3)
C(11)	2*i*	–0.0872(6)	1.3735(6)	0.5872(4)	0.106(4)	0.110(5)	0.048(3)	–0.082(4)	–0.019(3)	–0.009(3)
C(12)	2*i*	–0.1571(6)	1.4907(6)	0.6033(4)	0.070(3)	0.095(4)	0.060(3)	–0.050(3)	–0.036(3)	0.007(3)
C(13)	2*i*	–0.1072(5)	1.5453(4)	0.6511(3)	0.050(3)	0.059(3)	0.052(3)	–0.027(2)	–0.025(2)	0.009(2)
C(14)	2*i*	–0.1579(4)	1.1435(4)	0.7825(3)	0.037(2)	0.042(2)	0.044(2)	–0.017(2)	–0.006(2)	–0.012(2)
C(15)	2*i*	0.0468(4)	1.0501(4)	0.8559(3)	0.048(2)	0.036(2)	0.039(2)	–0.017(2)	–0.013(2)	–0.008(2)
C(16)	2*i*	0.1526(5)	1.0817(4)	0.8576(4)	0.054(3)	0.041(3)	0.104(4)	–0.017(2)	–0.034(3)	–0.009(3)
C(17)	2*i*	0.2757(6)	0.9897(6)	0.8782(6)	0.056(3)	0.068(4)	0.145(6)	–0.023(3)	–0.046(4)	–0.012(4)
C(18)	2*i*	0.2945(6)	0.8712(5)	0.8949(4)	0.065(3)	0.053(3)	0.098(4)	–0.010(3)	–0.045(3)	–0.008(3)
C(19)	2*i*	0.1909(6)	0.8403(4)	0.8928(4)	0.097(4)	0.040(3)	0.074(4)	–0.025(3)	–0.047(3)	0.006(3)
C(20)	2*i*	0.0657(5)	0.9292(4)	0.8763(4)	0.072(3)	0.061(3)	0.056(3)	–0.041(3)	–0.028(3)	0.005(2)
C(21)	2*i*	–0.3757(4)	1.2541(4)	0.7236(3)	0.031(2)	0.041(2)	0.039(2)	–0.011(2)	–0.006(2)	–0.014(2)
C(22)	2*i*	–0.4091(4)	1.1641(4)	0.7068(3)	0.036(2)	0.043(2)	0.050(3)	–0.016(2)	–0.007(2)	–0.014(2)
C(23)	2*i*	–0.5000(5)	1.1961(5)	0.6445(4)	0.042(3)	0.066(3)	0.066(3)	–0.021(2)	–0.012(2)	–0.028(3)
C(24)	2*i*	–0.5548(5)	1.3129(5)	0.6006(4)	0.040(3)	0.067(3)	0.054(3)	–0.006(2)	–0.015(2)	–0.018(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(25)	2*i*	–0.5257(5)	1.4035(5)	0.6205(4)	0.048(3)	0.049(3)	0.054(3)	–0.010(2)	–0.007(2)	–0.011(2)
C(26)	2*i*	–0.4337(4)	1.3724(4)	0.6810(3)	0.045(2)	0.046(3)	0.057(3)	–0.019(2)	–0.005(2)	–0.016(2)
O(10)	2*i*	0.1747(3)	1.0677(3)	0.4112(3)	0.048(2)	0.068(2)	0.091(3)	–0.020(2)	–0.019(2)	–0.014(2)

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