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Crystal structure of *N,N'*-diphenylguanidinium formate, $C_{14}H_{15}N_3O_2$

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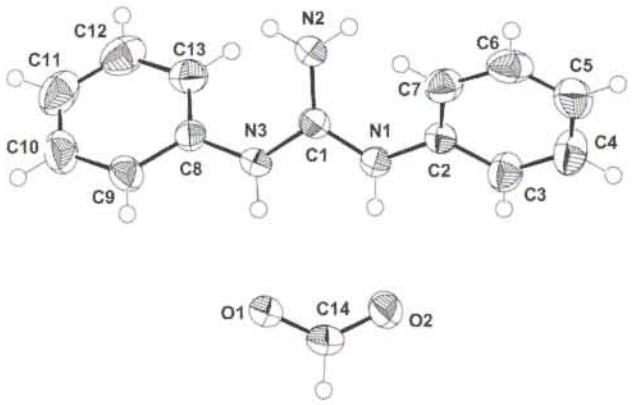

Abstract

$C_{14}H_{15}N_3O_2$, orthorhombic, $P2_1cn$ (No. 33), a = 6.363(4) Å, b = 12.535(4) Å, c = 16.641(3) Å, V = 1327.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR(F^2)$ = 0.077, 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 HCOOH. The precipitate was solubilized by heating the solution to the boiling point for a few minutes. After slow evaporation over a period of a few weeks, good quality, transparent single-crystals of prismatic form grew from the solution.

The structure was solved by direct methods. The hydrogen atoms were placed at calculated positions and refined as riding using the SHELXL-97 defaults: d(N–H) = 0.86 Å, d(C–H) = 0.93 Å [1]. The final structure was examined with PLATON92 [2] showing that there are no solvent-accessible voids.

Discussion

Di-aryl-guanidine compounds are of current interest due to their pharmacological applications [3]. Within this family, diphenylguanidine(dpg) salts, are particularly interesting because the cation dpg$^+$ can adopt different molecular conformations [4]. This work is part of a research project on a series of dpg salts, aiming to correlate the structure with the optical and dielectric properties. In the present compound, both phenyl rings lie *syn* to the unsubstituted N2 atom. This conformation is similar to that found in the hydrogenselenite monohydrate, nitrate, trifluoroacetate and *m*-chlorobenzeneseleninate salts of *N,N'*-dpg$^+$ [5-8] but different from the conformation of the free base were one of the rings is syn and the other *anti* to N2 [9]. In a few cases, an *anti-anti* conformation has also been observed [10]. These different conformations are due the low potential barrier of rotation of the phenyl rings [4]. The dihedral angle between the central planar guanidinium fragment N_3C and the least squares planes of the phenyl rings are 38.28(10)° (C2–C7) and 45.15(11)° (C8–C13). The dihedral angle between the planes of the two phenyl rings is 82.80(9)°. This value is comparable with the corresponding values observed in dpg$^+$ hydrogenselenite monohydrate (82.21(11)°), dpg$^+$ trifluoroacetate (70.53(10)°), dpg$^+$ nitrate (81.49(10)°) and dpg$^+$ *m*-chlorobenzeneseleninate (94.7(2)°). The C–N bond lengths of the guanidinium group are within the range 1.323 Å – 1.337(3) Å, which are typical values for a delocalized C=N bond. The guanidinium group is planar, the sum of the valence angles around C1 is 360.0(2)°. However, the angle opposite to N2 is much smaller (116.1(2)°) than the other two valence angles, a feature that was also observed in other dpg$^+$ cations with a *syn-syn* conformation. The geometry of the anion is unexceptional. The anions and cations are linked by moderately strong hydrogen bonds between the amino and carboxylate groups with N···O distances within the range 2.730(2) Å – 2.876(3) A. All H atoms of the guanidinium NH and NH_2 are involved in hydrogen bonding these groups acting as donors towards the bare oxygen atoms of the cation. The carboxylate O1 and O2 atoms accept two protons each from neighbouring cations. The resulting H-bonding pattern forms uncoupled two-dimensional networks which extend in planes perpendicular to the *c* axis.

Table 1. Data collection and handling.

Crystal:	colourless, transparent plate, size 0.10 × 0.44 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.89 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3119, 1281
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1140
$N(param)_{refined}$:	173
Programs:	PLATON [1], SHELXL-97 [2], SDP [11], ORTEP [12]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*a*	0.8452	0.3005	0.3032	0.048
H(2A)	4*a*	0.8056	0.5469	0.2300	0.054
H(2B)	4*a*	0.6201	0.5231	0.1784	0.054
H(3)	4*a*	0.5520	0.2767	0.2443	0.049
H(3A)	4*a*	1.1997	0.3042	0.3459	0.058
H(4)	4*a*	1.4522	0.3906	0.4198	0.074
H(5)	4*a*	1.4040	0.5655	0.4589	0.077
H(6)	4*a*	1.0941	0.6504	0.4279	0.072
H(7)	4*a*	0.8375	0.5652	0.3551	0.057
H(9)	4*a*	0.1911	0.2638	0.2028	0.053
H(10)	4*a*	–0.0366	0.2671	0.0954	0.070
H(11)	4*a*	0.0630	0.3458	–0.0239	0.079
H(12)	4*a*	0.3917	0.4204	–0.0352	0.073
H(13)	4*a*	0.6227	0.4175	0.0711	0.057
H(14)	4*a*	0.6880	0.0362	0.3385	0.063

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}
N(1)	4*a*	0.8466(3)	0.3682(1)	0.2950(1)	0.039(1)	0.0282(8)	0.054(1)	–0.0030(8)	–0.0106(9)	0.0028(7)
N(2)	4*a*	0.7117(4)	0.5029(1)	0.2132(1)	0.041(1)	0.0340(8)	0.059(1)	–0.0092(9)	–0.013(1)	0.0086(8)
N(3)	4*a*	0.5641(3)	0.3337(1)	0.2161(1)	0.041(1)	0.0332(8)	0.050(1)	–0.0096(9)	–0.0077(9)	0.0103(8)
C(1)	4*a*	0.7083(4)	0.4040(2)	0.2409(1)	0.031(1)	0.0312(9)	0.045(1)	–0.002(1)	0.001(1)	0.0027(8)
C(2)	4*a*	0.9945(4)	0.4265(2)	0.3403(1)	0.038(1)	0.036(1)	0.038(1)	–0.004(1)	–0.002(1)	0.0043(8)
C(3)	4*a*	1.1784(4)	0.3746(2)	0.3617(1)	0.047(2)	0.048(1)	0.049(1)	0.004(1)	–0.008(1)	–0.006(1)
C(4)	4*a*	1.3292(5)	0.4262(2)	0.4059(2)	0.050(2)	0.075(2)	0.061(2)	0.002(1)	–0.018(1)	–0.002(1)
C(5)	4*a*	1.3001(5)	0.5300(2)	0.4300(2)	0.074(2)	0.062(2)	0.058(2)	–0.022(2)	–0.024(2)	0.005(1)
C(6)	4*a*	1.1158(6)	0.5806(2)	0.4109(1)	0.093(2)	0.039(1)	0.048(1)	–0.014(1)	–0.012(2)	0.001(1)
C(7)	4*a*	0.9624(5)	0.5301(2)	0.3669(1)	0.057(2)	0.038(1)	0.048(1)	0.002(1)	–0.004(1)	0.001(1)
C(8)	4*a*	0.4295(4)	0.3420(2)	0.1490(1)	0.037(1)	0.0268(9)	0.047(1)	0.0028(9)	–0.005(1)	–0.0020(8)
C(9)	4*a*	0.2321(4)	0.2960(2)	0.1550(1)	0.043(1)	0.037(1)	0.052(1)	–0.004(1)	–0.003(1)	–0.0050(9)
C(10)	4*a*	0.0960(5)	0.2977(2)	0.0906(2)	0.048(1)	0.051(1)	0.076(2)	–0.003(1)	–0.018(2)	–0.013(1)
C(11)	4*a*	0.1551(6)	0.3444(2)	0.0195(2)	0.079(2)	0.057(2)	0.061(2)	0.010(2)	–0.032(2)	–0.010(1)
C(12)	4*a*	0.3514(5)	0.3889(2)	0.0130(2)	0.083(2)	0.055(2)	0.045(1)	0.008(2)	–0.009(2)	0.003(1)
C(13)	4*a*	0.4896(4)	0.3877(2)	0.0766(1)	0.052(1)	0.041(1)	0.051(1)	0.001(1)	0.003(1)	0.004(1)
C(14)	4*a*	0.6975(5)	0.1077(2)	0.3239(2)	0.051(1)	0.032(1)	0.073(2)	–0.004(1)	–0.005(1)	0.010(1)
O(1)	4*a*	0.5307(3)	0.1516(1)	0.3050(1)	0.042(1)	0.0363(8)	0.063(1)	–0.0056(8)	–0.0056(9)	0.0096(7)
O(2)	4*a*	0.8755(3)	0.1471(1)	0.3259(1)	0.041(1)	0.0390(9)	0.087(1)	–0.0014(8)	–0.009(1)	0.0014(8)

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