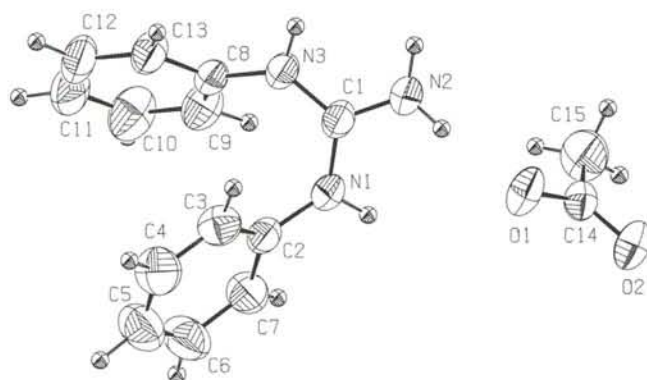


Crystal structure of *N,N'*-diphenylguanidinium acetate, $C_{13}H_{14}N_3^+C_2H_3O_2^-$

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Abstract

$C_{15}H_{17}N_3O_2$, monoclinic, $P12_1/a1$ (No. 14), $a = 11.886(4)$ Å, $b = 10.672(4)$ Å, $c = 12.198(9)$ Å, $\beta = 106.06(4)^\circ$, $V = 1486.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.120$, $T = 293$ K.

Source of material

The compound was synthesized by neutralization of a saturated aqueous solution of diphenylguanidine (98% purity, Aldrich) with acetic acid.

Discussion

This work is part of a project to study the molecular conformations of diphenylguanidine (dpg) compounds and their optical and dielectric properties. Diphenylguanidine (dpg) is a flexible molecule which can assume different molecular conformations due to the low energy-barrier for rotation of the phenyl rings.

In cationic form, stable conformers with the rings positioned *syn-syn*, *anti-anti* and *syn-anti* to the unsubstituted N atom have been observed both in solution and in several salts [1–3]. Two phases of monoclinic and orthorhombic symmetry are known, and in both two symmetry independent molecules are found in the asymmetric unit cell, always adopting *syn-anti* conformations [4, 5].

Ab-initio and Monte Carlo molecular mechanics calculations [6, 7] have shown that the equilibrium concentration of the three dpg⁺ conformers in solution depend to some extent on the counter ion. It was shown that the relative concentration of the *anti-anti* conformer increases from 7% to 30% in a chlorine acetate saline solution mimicking physiological conditions [7].

The present work shows that in dpg⁺ acetate both phenyl rings are in fact *anti* to the unsubstituted N atom. Such a conformation has only been previously observed in dpg⁺ dihydrogen phosphate, bis(dpg⁺) oxalate and bis(dpg⁺) sulfate monohydrate [8–10]. Interestingly, the latter compound has two independent cations in the asymmetric unit, one of which adopts a *syn-syn* and the other an *anti-anti* conformation. The ab initio calculations reported by Nagy and Durant [8] determined that the equilibrium geometry of the *anti-anti* conformer of an isolated dpg⁺ ion has C_2 geometry (binary axis parallel to the C1–N2 bond), with torsion angles $\varphi_1 = C2-N1-C1-N2 = \varphi_2 = C8-N3-C1-N2 = 156.9^\circ$ and $\varphi_3 = C3-C2-N1-C1 = \varphi_4 = C9-C8-N3-C1 = -67.5^\circ$. In the present compound the torsion angles are $\varphi_1 = 152.44(17)^\circ$, $\varphi_2 = 157.25(17)^\circ$, $\varphi_3 = -33.4(3)^\circ$, $\varphi_4 = -37.6(3)^\circ$, which shows that the cation retains an approximate C_2 symmetry in the acetate salt. The dihedral angles between the central planar guanidinium fragment N_3C and the least squares-planes of the phenyl rings are $53.59(10)^\circ$ (C2–C7) and $52.59(10)^\circ$ (C8–C13). The dihedral angle between the planes of the two phenyl rings of each cation is $42.98(9)^\circ$, to be compared with $49.47(7)^\circ$, $53.37(8)^\circ$ and $52.15(19)^\circ$ in the dihydrogenphosphate, oxalate and sulfate salts, respectively.

The C–N bond-lengths of the guanidinium group have values within the range (1.305 Å – 1.353 Å). The average value is close to the standard value of a delocalized C=N bond (sesquibond). The shorter bond within the guanidinium group of the cation is that between the atom C1 and the unsubstituted N2 atom, in agreement with previous structural data on other dpg salts. Also the N1–C2 [1.403(2) Å] and N3–C8 [1.416(2) Å] bond lengths compare well with the values observed in the free base and in other dpg⁺ salts. The geometry of the anion is unexceptional, the carboxy C=O distances [1.247(2) Å] clearly show that the acid molecule is ionized.

The structure is stabilized by a two dimensional hydrogen bond network in the (001) plane with donor-acceptor distances within the range 2.723(2) Å – 2.849(2) Å. The guanidinium NH and NH₂ groups are donors towards the bare oxygen atoms of the acetate ion. Each carboxy O atom is an acceptor of two H-bonds, one towards the NH₂ group and another towards the NH group. Thus, full capability for H-bonding is achieved in this compound as often found in other dpg salts.

Examination of the crystal structure with PLATON [11] shows that there are no solvent-accessible voids in the crystal lattice.

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Table 1. Data collection and handling.

Crystal:	translucent plate, size 0.03 × 0.25 × 0.37 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	0.83 cm ⁻¹
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\max}$:	50.96°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2908, 2765
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1865
$N(\text{param})_{\text{refined}}$:	250
Programs:	PLATON [11], SHELXL-97 [12], ORTEPII [13]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2A)	4e	0.818(2)	0.743(2)	0.514(2)	0.069(6)
H(2B)	4e	0.695(2)	0.678(2)	0.476(2)	0.066(6)
H(1)	4e	0.670(2)	0.506(2)	0.358(2)	0.074(6)
H(3)	4e	0.930(2)	0.721(2)	0.403(2)	0.068(6)
H(3A)	4e	0.727(2)	0.689(2)	0.152(2)	0.061(5)
H(4)	4e	0.693(2)	0.645(2)	0.039(2)	0.102(8)
H(7)	4e	0.660(2)	0.337(2)	0.223(2)	0.077(6)
H(5)	4e	0.636(2)	0.432(2)	0.102(2)	0.090(7)
H(6)	4e	0.620(2)	0.289(3)	0.032(2)	0.095(8)
H(9)	4e	0.922(2)	0.420(2)	0.359(2)	0.080(6)
H(10)	4e	1.017(2)	0.307(2)	0.244(2)	0.094(7)
H(11)	4e	1.105(2)	0.416(2)	0.116(2)	0.092(7)
H(12)	4e	1.099(2)	0.634(2)	0.111(2)	0.096(7)
H(13)	4e	0.996(2)	0.747(2)	0.219(2)	0.075(6)
H(15A)	4e	0.578(3)	0.504(3)	0.706(3)	0.13(1)
H(15B)	4e	0.668(3)	0.522(3)	0.632(3)	0.13(1)
H(15C)	4e	0.650(4)	0.610(4)	0.727(3)	0.16(1)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4e	0.7154(1)	0.5465(1)	0.3197(1)	0.0461(7)	0.0573(9)	0.0515(8)	0.0130(6)	0.0239(6)	0.0033(7)
N(2)	4e	0.7666(1)	0.6827(2)	0.4702(1)	0.0466(8)	0.075(1)	0.0586(9)	0.0090(8)	0.0270(7)	0.0160(8)
N(3)	4e	0.8899(1)	0.6636(1)	0.3586(1)	0.0449(7)	0.0558(9)	0.0629(9)	0.0116(6)	0.0277(7)	0.0162(7)
C(1)	4e	0.7910(1)	0.6312(2)	0.3825(1)	0.0417(8)	0.0501(9)	0.0506(9)	0.0021(7)	0.0213(7)	0.0004(7)
C(2)	4e	0.6976(1)	0.5186(2)	0.2037(1)	0.0380(8)	0.0529(9)	0.0482(9)	0.0037(7)	0.0164(6)	0.0021(7)
C(3)	4e	0.7073(2)	0.6075(2)	0.1251(2)	0.056(1)	0.051(1)	0.060(1)	0.0034(8)	0.0135(8)	0.0075(9)
C(4)	4e	0.6854(2)	0.5752(2)	0.0121(2)	0.085(1)	0.080(2)	0.056(1)	0.008(1)	0.018(1)	0.019(1)
C(5)	4e	0.6527(2)	0.4560(2)	0.0240(2)	0.101(2)	0.090(2)	0.051(1)	0.017(1)	0.018(1)	0.004(1)
C(6)	4e	0.6412(2)	0.3686(2)	0.0531(2)	0.098(2)	0.066(1)	0.061(1)	0.020(1)	0.021(1)	0.011(1)
C(7)	4e	0.6638(2)	0.3982(2)	0.1665(2)	0.074(1)	0.055(1)	0.056(1)	0.0156(9)	0.0219(9)	0.0004(9)
C(8)	4e	0.9506(1)	0.5921(2)	0.2953(1)	0.0368(7)	0.050(1)	0.0506(9)	0.0024(7)	0.0171(7)	0.0049(7)
C(9)	4e	0.9590(2)	0.4634(2)	0.3039(2)	0.055(1)	0.055(1)	0.075(1)	0.0086(8)	0.0268(9)	0.0115(9)
C(10)	4e	1.0161(2)	0.3989(2)	0.2386(2)	0.073(1)	0.055(1)	0.117(2)	0.017(1)	0.044(1)	0.003(1)
C(11)	4e	1.0674(2)	0.4605(2)	0.1666(2)	0.068(1)	0.076(2)	0.098(2)	0.005(1)	0.046(1)	0.022(1)
C(12)	4e	1.0621(2)	0.5883(2)	0.1605(2)	0.068(1)	0.082(2)	0.079(1)	0.009(1)	0.047(1)	0.007(1)
C(13)	4e	1.0041(2)	0.6548(2)	0.2248(2)	0.058(1)	0.052(1)	0.074(1)	0.0056(8)	0.0356(9)	0.0032(9)
O(1)	4e	0.5439(1)	0.6799(1)	0.5016(1)	0.0490(7)	0.0744(8)	0.0671(8)	0.0118(6)	0.0297(6)	0.0254(6)
O(2)	4e	0.4146(1)	0.6227(1)	0.5898(1)	0.0602(8)	0.0636(8)	0.0727(8)	0.0025(6)	0.0383(6)	0.0130(6)
C(14)	4e	0.5164(1)	0.6236(2)	0.5800(1)	0.0510(9)	0.0507(9)	0.0446(9)	0.0003(7)	0.0204(7)	0.0014(7)
C(15)	4e	0.6108(2)	0.5556(3)	0.6660(2)	0.075(1)	0.106(2)	0.058(1)	0.008(1)	0.012(1)	0.025(1)

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