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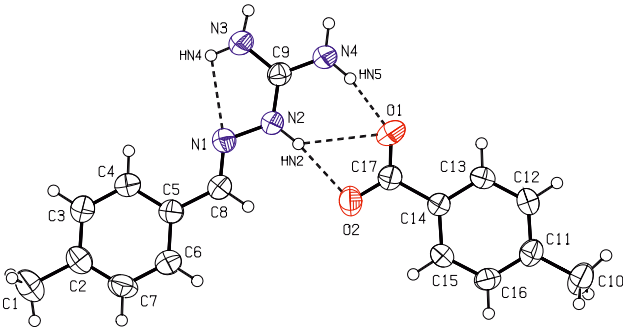
The crystal structure of (*E*)-amino(2-(4-methylbenzylidene)hydrazineyl)methaniminium 4-methylbenzoate, $C_9H_{13}N_4^+$ $C_8H_7O_2^-$



https://doi.org/10.1515/ncrs-2021-0330
Received August 15, 2021; accepted September 9, 2021;
published online September 22, 2021

Abstract

Monoclinic, $P2_1/c$ (no. 14), a = 14.187(15) Å, b = 10.585(11) Å, c = 11.952(13) Å, β = 113.851(16)°, V = 1642(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0479, w$R_{ref}(F^2)$ = 0.1408, T = 296(2) K.

CCDC no.: 2108721

The asymmetric unit of the title crystal structure is shown in the figure (The N–H···N and N–H···O hydrogen bonds are shown as a dashed lines.). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block Size 0.19 × 0.15 × 0.13 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II QUAZAR, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13954, 3738, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2617
$N(param)_{refined}$:	230
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4], PLATON [5]

Source of material

Two gram (0.0181 mol) aminoguanidine hydrochloride salt in a 100 mL round-bottom flask is dissolved in a mixture of purified water (15 mL) and methanol (15 mL), and 2.346 mL (0.0199 mol) of 4-methylbenzaldehyde is added. After mixing in a magnetic stirrer at room conditions for 24 h, it is neutralized with equivalent 0.72 g (1 eq) NaOH. In order for the precipitation to occur well, it is kept in the refrigerator for 30–45 min, the precipitated material is filtered with a crucible, washed with distilled water (3 × 5 mL) and dried under vacuum. After waiting for one day, crystallization is done in ethanol and water (EtOH/H_2O). To purify the substance, it is kept in the refrigerator for 24 h. The crystalline material formed is filtered, washed in cold ethanol, then dried in a vacuum oven (yield: 94%).

Experimental details

The H atoms of the NH and NH_2 groups were located from a difference- Fourier map and refined freely [N2—HN2 = 0.90(2), N3—HN3 = 0.91(2), N3—HN4 = 0.88(2), N4—HN5 = 0.89(2) and N4—HN6 = 0.92(2) Å]. All C-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and 0.96 Å, for aryl and methyl H-atoms, respectively. The U_{iso}(H) were allowed at 1.5U_{eq}(C_{methyl}) or 1.2U_{eq}($C_{non\text{-}methyl}$).

Comment

During the 1960s, Wyeth laboratories, Inc., Philadelphia, produced a series of benzylidene aminoguanidines during the search for new and improved antihyperten-sive medicines.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.86938 (16)	1.0358 (2)	0.4897 (2)	0.0752 (6)
H1A	0.875799	0.989545	0.424033	0.113*
H1B	0.932107	1.028461	0.561874	0.113*
H1C	0.856407	1.123201	0.467148	0.113*
C2	0.78122 (14)	0.98292 (18)	0.51473 (17)	0.0531 (5)
C3	0.76640 (15)	1.0187 (2)	0.6183 (2)	0.0621 (5)
H3	0.811777	1.075861	0.672612	0.075*
C4	0.68618 (15)	0.97140 (19)	0.64232 (18)	0.0577 (5)
H4	0.677829	0.996996	0.712200	0.069*
C5	0.61778 (13)	0.88581 (16)	0.56281 (15)	0.0455 (4)
C6	0.63275 (15)	0.8489 (2)	0.45992 (17)	0.0568 (5)
H6	0.587864	0.791132	0.405823	0.068*
C7	0.71355 (15)	0.8970 (2)	0.43687 (17)	0.0587 (5)
H7	0.722404	0.870887	0.367459	0.070*
C8	0.53151 (13)	0.83450 (17)	0.58509 (16)	0.0482 (4)
H8	0.488801	0.775051	0.530932	0.058*
C9	0.39977 (12)	0.85048 (16)	0.77275 (14)	0.0413 (4)
N1	0.51275 (10)	0.86838 (14)	0.67621 (13)	0.0455 (3)
N2	0.42814 (11)	0.81223 (14)	0.68457 (14)	0.0458 (4)
HN2	0.3917 (15)	0.752 (2)	0.6307 (18)	0.056 (5)*
N3	0.45274 (13)	0.93904 (16)	0.85239 (15)	0.0524 (4)
HN3	0.4290 (16)	0.962 (2)	0.909 (2)	0.069 (6)*
HN4	0.5082 (17)	0.970 (2)	0.8464 (19)	0.070 (7)*
N4	0.31861 (12)	0.79866 (17)	0.78045 (16)	0.0526 (4)
HN5	0.2835 (16)	0.740 (2)	0.726 (2)	0.061 (6)*
HN6	0.3040 (15)	0.8222 (19)	0.846 (2)	0.062 (6)*
C10	−0.01887 (17)	0.1763 (2)	0.2373 (2)	0.0689 (6)
H10A	−0.077803	0.173381	0.257468	0.103*
H10B	0.014108	0.095144	0.252125	0.103*
H10C	−0.040553	0.197979	0.152488	0.103*
C11	0.05592 (13)	0.27439 (16)	0.31529 (16)	0.0482 (4)
C12	0.04366 (14)	0.33101 (17)	0.41305 (17)	0.0514 (4)
H12	−0.011166	0.306817	0.432040	0.062*
C13	0.11115 (13)	0.42268 (16)	0.48294 (16)	0.0463 (4)
H13	0.100970	0.459354	0.547888	0.056*
C14	0.19370 (11)	0.46053 (14)	0.45742 (13)	0.0363 (3)
C15	0.20734 (13)	0.40213 (16)	0.36109 (16)	0.0458 (4)
H17	0.263046	0.424782	0.343162	0.055*
C16	0.13943 (14)	0.31094 (17)	0.29151 (16)	0.0507 (4)
H16	0.150125	0.273318	0.227291	0.061*
C17	0.26092 (13)	0.56737 (16)	0.52905 (14)	0.0422 (4)
O1	0.22962 (11)	0.63005 (13)	0.59552 (12)	0.0644 (4)
O2	0.34371 (10)	0.59063 (13)	0.51714 (12)	0.0581 (4)

In 1969, one of the chemicals in this class, E-2,6-dichlorobenzylidene aminoguanidine acetate, was found as a new, strong hypotensive agent [6].

The title salt is composed of one cation and one anion in the asymmetric unit. The cations and the anions of the title salt are nearly co-planar: the maximum deviations from the mean plane of the non−H atoms are −0.592(1) Å for O2, 0.328(2) Å for N3 and 0.250(2) Å for N4, respectively.

The cation group is stabilized by the N—H ⋯ N hydrogen bond [N3—HN4/N1: HN4/N1 = 2.33(2) Å, N3 ⋯ N1 = 2.677(4) Å with angle at HN4 = 103.9(16)°], forming a S(5) ring [7].

In the cation, the C—N bond distances are N3—C9 = 1.331(2) Å and N4—C9 = 1.312(2) Å. The C=N bond distance is N1—C8 = 1.273(2) and N2—C9 = 1.334(2) Å. The N—N bond distance of 1.3852(19) Å is shorter than a single bond and indicating significant delocalization along the NNC(NH_2)N moiety. All bond length and bond angles in the title salt can be compared with those of the related compounds which are 2-((2,6-dichlorophenyl)methylene) hydrazinecarboxamide acetate (CSD refcode HIVYOB: orthorhombic space group: *Pbca* (61), *a* = 13.389(5), *b* = 11.007(6), *c* = 17.342(5) Å, *Z* = 4) [8] and N"-[(2,6-dichlorophenyl)methylidene] carbonohydrazonic diamide (Form I (CSD refcode SOMZOM): monoclinic space group: $P2_1/c$ (14), *a* = 16.3082(4) Å, *b* = 8.2933(3) Å, *c* = 7.4489(3) Å, β = 98.201(3)°, *Z* = 4; Form II (SOMRUK): triclinic space group: $P\bar{1}$ (2), *a* = 7.9018(3) Å, *b* = 10.8460(7) Å, *c* = 12.9559(8) Å, α = 78.313(5)°, β = 72.515(4)°, γ = 83.119(4)°, *Z* = 4) [9].

In the crystal, the cations and anions of the title salt which are co-planar are linked by N—H ⋯ O hydrogen bonds N2—HN2/O1: HN2/O1 = 2.52(2) Å, N2/O1 = 3.219(4) Å with angle at HN2 = 134.4(18) Å, N2—HN2/O2: HN2/O2 = 2.12(2) Å, N2/O2 = 3.001(4) Å with angle at HN2 = 166(2)° and N4—HN5/O1: HN5/O1 = 1.85(2) Å, N4/O1 = 2.722(4) Å with angle at HN5 = 167(2)°], forming the $R_1^2(6)$ and $R_1^2(4)$ ring motifs. Furthermore the cations and anions are connected by the N—H ⋯ O [N3—HN3/O2: HN3/O2 = 2.17(2) Å, N3/O2 = 2.972(4) Å with angle at HN3 = 147.6(19)°, N3—HN4/O2: HN4/O2 = 2.44(2) Å, N3/O2 = 3.115(4) Å with angle at HN4 = 134.2(18)° and N4—HN6/O2: HN6/O2 = 2.10(2) Å, N4/O2 = 2.948(4) Å with angle at HN6 = 152(2)°], C—H ⋯ O [C4—H4/O1: H4/O1 = 2.56 Å, C4/O1 = 3.322(4) Å with angle at H4 = 140°] and very weak π-π stacking interactions [Cg1(C2—C7)⋯Cg2(C11—C16)^i = 3.916(4) Å, angle = 7.45(9)° and slippage = 1.320 Å; Cg2(C11—C16) ⋯ Cg1(C2—C7)^i = 3.916(4) Å, angle = 7.45(9)° and slippage = 1.78 Å for symmetry operation (i): 1 − *x*, 1 − *y*, 1 − *z*], generating the molecular layers paralel to the (100) plane.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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