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Crystal structure of (1*E*)-*N'*-[(1*E*)-1-(4-chlorophenyl)ethylidene]-2-[1-(4-chlorophenyl)ethylidene]hydrazine-1-carbohydrazonamide, C₁₇H₁₇Cl₂N₅

Figure 1: A perspective view of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. The two molecules (A and B) in the asymmetric unit are linked by N—H...N hydrogen bonds shown as dashed lines. Only the major component of the disordered atoms is shown for clarity.

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Abstract

C₁₇H₁₇Cl₂N₅, monoclinic, *P*₂/c (no. 14), *a* = 14.603(2) Å, *b* = 24.059(4) Å, *c* = 10.1380(16) Å, β = 93.141(3)°, *V* = 3556.4(10) Å³, *Z* = 8, *R*_{gt}(*F*) = 0.0512, *wR*_{ref}(*F*²) = 0.1416, *T* = 296(2) K.

CCDC no.: 2108841

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:	Yellow irregular
Size:	0.32 × 0.22 × 0.12 mm
Wavelength:	Mo <i>K</i> α radiation (0.71073 Å)
μ:	0.37 mm ^{−1}
Diffraction, scan mode:	Bruker APEX-II, φ and ω
θ _{max} , completeness:	27.6°, >99 %
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	30263, 8240, 0.049
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4576
<i>N</i> (<i>param</i>) _{refined} :	474
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4], PLATON [5]

Source of material

Weigh 2 g (0.0159 mol) 1,3-diaminoguanidine hydrochloride salt and put into a 100 mL flask. It is dissolved in a mixture of purified water (15 mL) and methanol (15 mL), and 4.13 mL (2.2 eq) of 4-methylbenzaldehyde is added. After mixing at room for 24 h in a magnetic stirrer, it is

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.98245 (18)	0.17607 (12)	0.4007 (3)	0.0594 (7)
H1	0.936791	0.161750	0.342835	0.071*
C2	1.06576 (19)	0.14891 (13)	0.4150 (3)	0.0655 (8)
H2	1.075867	0.116554	0.367751	0.079*
C3	1.13303 (18)	0.17007 (13)	0.4992 (3)	0.0602 (7)
C4 ^a	1.1233 (6)	0.2205 (4)	0.5598 (10)	0.0640 (19)
H4 ^a	1.172001	0.236487	0.609086	0.077*
C5 ^a	1.0390 (8)	0.2472 (5)	0.5458 (12)	0.062 (2)
H5 ^a	1.031192	0.281168	0.587349	0.074*
C4A ^b	1.1079 (18)	0.2084 (12)	0.587 (3)	0.0640 (19)
H4A ^b	1.147163	0.216109	0.659733	0.077*
C5A ^b	1.026 (2)	0.2365 (14)	0.572 (4)	0.062 (2)
H5A ^b	1.012441	0.264172	0.631923	0.074*
C6	0.96532 (16)	0.22390 (10)	0.4702 (2)	0.0473 (6)
C7	0.87451 (17)	0.25136 (11)	0.4591 (3)	0.0517 (6)
C8	0.8611 (2)	0.30554 (13)	0.5271 (3)	0.0796 (10)
H8A	0.888836	0.334761	0.478693	0.119*
H8B	0.889033	0.303935	0.614943	0.119*
H8C	0.796630	0.312765	0.531419	0.119*
C9	0.65586 (17)	0.21923 (11)	0.3180 (3)	0.0514 (6)
C10	0.45869 (15)	0.24199 (10)	0.1447 (2)	0.0455 (6)
C11	0.4755 (2)	0.30013 (12)	0.1001 (3)	0.0724 (9)
H11A	0.528470	0.300823	0.048014	0.109*
H11B	0.485903	0.323731	0.175833	0.109*
H11C	0.423063	0.313192	0.047919	0.109*
C12	0.37824 (15)	0.21137 (10)	0.0876 (2)	0.0442 (6)
C13	0.33074 (17)	0.17375 (11)	0.1612 (3)	0.0512 (6)
H13	0.349573	0.167554	0.249076	0.061*
C14	0.25601 (19)	0.14530 (11)	0.1066 (3)	0.0594 (7)
H14	0.224226	0.120529	0.157699	0.071*
C15	0.22890 (18)	0.15369 (12)	−0.0229 (3)	0.0592 (7)
C16	0.2755 (2)	0.18980 (13)	−0.0987 (3)	0.0684 (8)
H16	0.257431	0.194755	−0.187287	0.082*
C17	0.34912 (18)	0.21879 (13)	−0.0436 (3)	0.0611 (7)
H17	0.379916	0.243824	−0.095220	0.073*
N1	0.81069 (14)	0.22430 (9)	0.3944 (2)	0.0522 (5)
N2	0.72570 (15)	0.24858 (10)	0.3799 (2)	0.0584 (6)
H2N	0.721 (2)	0.2824 (12)	0.370 (3)	0.070*
N3	0.66766 (18)	0.16488 (10)	0.3000 (3)	0.0710 (8)
H3NA	0.716 (2)	0.1505 (14)	0.324 (3)	0.085*
H3NB	0.624 (2)	0.1462 (14)	0.265 (3)	0.085*
N4	0.58347 (13)	0.24812 (8)	0.2838 (2)	0.0541 (5)
N5	0.51198 (13)	0.21556 (8)	0.2278 (2)	0.0496 (5)
Cl1	1.23700 (5)	0.13522 (4)	0.52022 (10)	0.0941 (3)
Cl2	0.13562 (6)	0.11783 (4)	−0.09404 (10)	0.0943 (3)
C18 ^a	0.4264 (7)	0.4648 (5)	0.7502 (11)	0.0581 (19)
H18 ^a	0.422294	0.434609	0.693014	0.070*
C19 ^a	0.3583 (7)	0.4732 (5)	0.8365 (10)	0.0617 (19)
H19 ^a	0.308137	0.449396	0.836773	0.074*
C18A ^a	0.4481 (19)	0.4565 (15)	0.778 (3)	0.0581 (19)
H18A ^a	0.457363	0.421667	0.740926	0.070*
C19A ^a	0.3810 (18)	0.4639 (14)	0.864 (3)	0.0617 (19)
H19A ^a	0.344311	0.434008	0.885106	0.074*
C20	0.36573 (18)	0.51709 (12)	0.9218 (3)	0.0567 (7)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C21	0.4329 (2)	0.55541 (12)	0.9122 (3)	0.0657 (8)
H21	0.433523	0.587146	0.964623	0.079*
C22	0.50043 (19)	0.54719 (11)	0.8245 (3)	0.0611 (7)
H22	0.546093	0.573863	0.818411	0.073*
C23	0.50231 (17)	0.50082 (10)	0.7460 (2)	0.0476 (6)
C24	0.57422 (16)	0.49163 (10)	0.6518 (2)	0.0468 (6)
C25	0.6417 (2)	0.53660 (12)	0.6260 (3)	0.0659 (8)
H25A	0.698988	0.528675	0.673364	0.099*
H25B	0.618511	0.571593	0.655117	0.099*
H25C	0.651020	0.538387	0.533120	0.099*
C26	0.63407 (16)	0.38669 (10)	0.4322 (2)	0.0466 (6)
C27	0.82185 (17)	0.40787 (11)	0.2563 (2)	0.0504 (6)
C28	0.8205 (2)	0.35922 (13)	0.1632 (3)	0.0767 (9)
H28A	0.760575	0.342657	0.158847	0.115*
H28B	0.864980	0.332252	0.194557	0.115*
H28C	0.834984	0.371678	0.076882	0.115*
C29	0.89736 (17)	0.44853 (10)	0.2558 (2)	0.0485 (6)
C30	0.9702 (2)	0.44238 (13)	0.1747 (3)	0.0699 (8)
H30	0.968988	0.413300	0.114229	0.084*
C31	1.04427 (19)	0.47792 (13)	0.1810 (3)	0.0709 (8)
H31	1.092401	0.472538	0.125936	0.085*
C32	1.04652 (17)	0.52066 (11)	0.2675 (3)	0.0552 (7)
C33 ^a	0.9718 (8)	0.5331 (4)	0.3408 (12)	0.064 (2)
H33 ^a	0.971449	0.564752	0.393490	0.076*
C34 ^a	0.8958 (7)	0.4963 (5)	0.3333 (11)	0.0593 (19)
H34 ^a	0.844527	0.504121	0.380481	0.071*
C33A ^b	0.983 (3)	0.5188 (11)	0.361 (4)	0.064 (2)
H33A ^b	0.989021	0.543121	0.432118	0.076*
C34A ^b	0.9169 (18)	0.4868 (13)	0.356 (3)	0.0593 (19)
H34A ^b	0.877315	0.488219	0.424784	0.071*
N6	0.57311 (14)	0.44386 (9)	0.5944 (2)	0.0499 (5)
N7	0.63867 (15)	0.43353 (9)	0.5060 (2)	0.0549 (6)
H7N	0.6796 (19)	0.4547 (12)	0.494 (3)	0.066*
N8	0.56333 (17)	0.35217 (11)	0.4463 (3)	0.0610 (6)
H8NA	0.530 (2)	0.3569 (12)	0.506 (3)	0.073*
H8NB	0.5619 (19)	0.3212 (13)	0.397 (3)	0.073*
N9	0.69490 (14)	0.37425 (8)	0.3462 (2)	0.0501 (5)
N10	0.76155 (13)	0.41545 (8)	0.3417 (2)	0.0470 (5)
Cl3	0.28131 (5)	0.52635 (4)	1.03409 (8)	0.0800 (3)
Cl4	1.14287 (5)	0.56361 (3)	0.28543 (9)	0.0797 (3)

^aOccupancy: 0.73(2), ^bOccupancy: 0.27(2).

refluxed for 2 h, then the reaction is stopped, cooled to room temperature and neutralized with 0.64 g (1 eq) NaOH. For precipitation the mixture 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 performed in ethanol (EtOH), kept in the refrigerator for 24 h, the crystalline substance formed is filtered, washed in cold ethanol, the impurity of the substance is checked with TLC (Thin Layer

Chromatogram) paper, then dried in a vacuum oven. 5.05 g and the yield was 94%.

Experimental details

The hydrogen atoms of the NH and NH_2 groups of molecules A and B were located from a difference–Fourier map and refined freely with $U_{iso}(H) = 1.5U_{eq}(N)$. All C-bound H atoms were refined using a riding model with $d(C-H) = 0.93 \text{ \AA}$, $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and $0.96 \text{ \AA}$, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. Atoms C4, C5, C18, C19, C33 and C34 of the chlorobenzene rings of molecules A and B were refined as disordered over two sets of sites with site occupancies of 0.73 (2) and 0.27 (2). Ellipsoid displacement (EADP) constraints were applied to disordered atom groups C4/C4A, C5/C5A, C18/C18A, C19/C19A, C33/C33A and C34/C34A.

Comment

Aminoguanidine is a guanidine derivative known for centuries. It is a compound that is structurally similar to the amino acid L-arginine, which contains a guanidine structure. In addition, aminoguanidine is an important molecule in the formation of nitric oxide by the catalytic effect of nitric oxide synthase [6]. In addition, aminoguanidine was administered to rats with cataracts and it was stated that aminoguanidine had cataract-preventing activity in this application. In recent years, aminoguanidine has been found to be a new promising compound that delays aging. At the same time, it has been observed that atherosclerosis, which increases with age, decreases with the application of aminoguanidine [7].

Moreover, compounds containing an imidazole core are structural isosteres of naturally occurring nucleotides, allowing them to readily interact with biopolymers responsible for numerous biological activities and functions of the living system [8].

There is no symmetry relationship between two molecules A (with Cl1) and B (with Cl3) of the title compound in the asymmetric unit Figure 1. The dihedral angles between the aromatic rings (C1–C6, C12–C17 and C18–C22, C29–C34) of the major components of the disordered molecules A and B are $86.6(2)$ and $6.0(3)^\circ$ for molecule A and B, respectively. The dihedral angles between the aromatic rings [(C1–C3, C4A, C5A, C6), (C12–C17) and (C18A, C19A, C20–C22), (C29–C32, C33A, C34A)] of the minor components of the disordered molecules A and B are $88.3(7)$ and $19.2(9)^\circ$ for molecule A and B, respectively. The conformations of the molecules A and B are different. This may be attributed

to the different steric interactions that occur due to having the different environments in the crystal.

The bond length values in the title compound can be compared with those of the related compounds which are 1,2-bis((pentafluorobenzylidene)amino)guanidine methanol solvate (CSD refcode EMOCIT [9]), 1,3-bis((pentafluorobenzylidene)amino)guanidinium benzoate benzoic acid solvate (EMOCUF [9]) and 1,3-bis((1-naphthylmethylene) amino)guanidinium benzoate benzoic acid solvate (EMOCOZ [9]).

In the crystal, molecules A and B are connected by N–H...N hydrogen bonds [N2–H2N/N9: H2N/N9 = $2.25(3) \text{ \AA}$, N2/N9 = $3.073(3) \text{ \AA}$ with angle at H2N = $175(3)^\circ$ and N8–H8NB/N4: H8NB/N4 = $2.13(3) \text{ \AA}$, N8/N4 = $3.020(3) \text{ \AA}$ with angle at H8NB = $170(3)^\circ$], forming a $R_2^2(8)$ ring motif parallel to the (001) plane. Furthermore, molecules are linked by C–H...Cl contacts C11–H11C/Cl1ⁱ: H11C/Cl1ⁱ = $2.99 \text{ \AA}$, C11/Cl1ⁱ = $3.860(3) \text{ \AA}$ with angle at H11C = 151.9° for symmetry operation (i): $-1 + x, 1/2 - y, -1/2 + z$; C19–H19/Cl1ⁱⁱ: H19/Cl1ⁱⁱ = $2.98 \text{ \AA}$, C19/Cl1ⁱⁱ = $3.711(10) \text{ \AA}$ with angle at H19 = 136.3° for (ii): $-1 + x, 1/2 - y, 1/2 + z$; C19A–H19A/Cl1ⁱⁱ: H19A/Cl1ⁱⁱ = $2.71 \text{ \AA}$, C19A/Cl1ⁱⁱ = $3.60(3) \text{ \AA}$ with angle at H19A = 161.8° for (ii): $-1 + x, 1/2 - y, 1/2 + z$ and C33–H33/Cl2ⁱⁱⁱ: H33/Cl2ⁱⁱⁱ = $2.93 \text{ \AA}$, C33/Cl2ⁱⁱⁱ = $3.694(11) \text{ \AA}$ with angle at H33 = 140.9° for (iii): $1 - x, 1/2 + y, 1/2 - z$, C–Cl... π interactions [C15–Cl2/Cg(C29–C34)]^{iv}: Cl2/Cg(C29–C34)^{iv} = $3.729(3) \text{ \AA}$ with angle at Cl2 = $167.09(11)^\circ$; C15–Cl2/Cg(C29–C32/C33A, C34A)]^{iv}: Cl2/Cg(C29–C32/C33A, C34A)]^{iv} = $3.590(8) \text{ \AA}$ with angle at Cl2 = $167.21(16)^\circ$ for (iv) $-1 + x, 1/2 - y, -1/2 + z$ and $\pi - \pi$ stacking interactions [Cg1(C18–C23)...Cg1(C18–C23)]^v = $3.892(4) \text{ \AA}$, angle = $0.0(3)^\circ$ and slippage = $1.68 \text{ \AA}$; Cg2(C20–C23/C18A, C19A)...Cg2(C20–C23/C18A, C19A)]^v = $3.618(10) \text{ \AA}$, angle = $0.0(9)^\circ$ and slippage = $1.15 \text{ \AA}$ for (v) $1 - x, 1 - y, 2 - z$, forming a three-dimensional network.

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