Crystal Structure of 1-(4-Acetylamidophenyl)-3-(4-carboxyphenyl)triazene

Carlos Henrique Oliveira do AMARAL,** Rosmari HÖRNER,* Luiz Gustavo Brenner REETZ,*
Leandro Renato Simon de CAMARGO,** Flávia Cavalieri MACHADO,*** and Manfredo HÖRNER**†

*Departamento de Análises Clínicas e Toxicológicas, Universidade Federal de Santa Maria, 97105-970 Santa Maria, RS, Brazil

**Departamento de Química, Universidade Federal de Santa Maria, Cx. Postal 5031, 97110-900 Santa Maria, RS, Brazil

***Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora, 36036-330 Juiz de Fora, MG, Brazil

The crystal structure of the title compound, $C_{15}H_{14}N_4O_3$, reveals the expected *trans* stereochemistry about the N=N double bond in the diazoamine moiety. The interplanar angle [$36.68(6)^\circ$] between the terminal phenyl rings indicates that the whole molecule deviates significantly from planarity (r.m.s. deviation = $0.3148 \text{ \AA}$). Intermolecular O-H...O classical hydrogen bonds, and hydrogen bonds with a bifurcated geometry generate a three-dimensional molecule arrangement. The distribution of the double-bond character among the N atoms of the diazoamine moiety is unequal, indicating a delocalization of the π electrons over the N=N-N(H) group toward the terminal 4-carboxyphenyl substituent.

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As part of a study of molecular associations through hydrogen bonds in the solid state of asymmetric disubstituted 1,3-diaryltriazenes that present biological activity, we report on the crystal structure of the title molecule, (I), (Fig. 1) based on a single-crystal X-ray structural analysis.

The synthesis of the title complex included reagents and solvents of reagent grade, which were used without further purification. 4-carboxyphenylamine (0.50 g, 3.65 mmol) was dissolved in a 50% aqueous solution of HCl (30 mL) and cooled to -5°C . A sodium nitrite solution (0.30 g, 4.38 mmol) in water (20 mL) was slowly added with continuous stirring. A solution of 4-acetylamidophenylamine (0.55 g, 3.65 mmol) in 50% aqueous glacial acetic acid (30 mL) was added slowly to the reaction mixture. Stirring was continued for 30 min at -5°C . The resulting mixture was neutralized with a 10% aqueous solution of NaHCO_3 . A crude dark-red precipitate was separated by filtration and washed with small portions of cool water. The product was dried over P_2O_5 under vacuum, and recrystallized from a methanol/acetone mixture (1:1). Dark-red bar-shaped crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvent mixture. Yield, 60% (0, 66 g, 2.20 mmol), based on 4-acetylamidophenylamine; m.p., $146 - 148^\circ\text{C}$. IR (KBr pellet, cm^{-1}), 3380 (ν_{as} N-H) s; 1698 [$\nu(\text{C}=\text{O})$, acetylamido-group] vs; 1610 [$\nu(\text{C}=\text{O})$, carboxyl-group] vs; 1405 (ν_{s} N=N) s; 1186 (ν_{s} N=N) s. (IR data: vs, very strong; s, strong). Anal. Calcd for $C_{15}H_{14}N_4O_3$: C, 60.40; H, 4.73; N, 18.78. Found C, 60.32; H, 4.23; N, 19.15.

Fig. 1 Structural chemical diagram of (I).

† To whom correspondence should be addressed.
E-mail: hoerner@mail.ufsm.br

Compound (I) showed activity against the Gram-positive bacteria *Staphylococcus epidermidis* (MIC = $64 \mu\text{g/mL}$) and *Rhodococcus* spp. (MIC = $64 \mu\text{g/mL}$), and against the Gram-negative bacteria *Enterobacter cloacae* (MIC = $32 \mu\text{g/mL}$).

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal and experimental data are listed in Table 1. The structure was solved by direct methods using *SIR2004*.² The non-hydrogen atoms were refined anisotropically by the full-matrix least-square method using *SHELXL97*.³ The

Table 1 Crystal and experimental data

Formula: $C_{15}H_{14}N_4O_3$
Formula weight: 298.30
Crystal system: monoclinic
Space group: $P2_1/n$ $Z = 4$
$a = 7.77230(10) \text{ \AA}$
$b = 9.7365(2) \text{ \AA}$ $\beta = 93.4350(10)^\circ$
$c = 19.3554(3) \text{ \AA}$
$V = 1462.09(4) \text{ \AA}^3$
$D_x = 1.355 \text{ g/cm}^3$
Absorption coefficient = 0.098 mm^{-1}
$F(000) = 624$
Crystal dimensions (mm) = $0.32 \times 0.28 \times 0.19$
$R = 0.0394$
$R_w = 0.1093$
θ range for data collection: 2.89 to 25.50°
Completeness to $\theta = 25.50^\circ$ 99.9%
Goodness-of-fit = 1.038
$(\Delta\rho)_{\text{max}} = 0.227 \text{ e.\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.207 \text{ e.\AA}^{-3}$
No. of reflections used = 3283
No. of parameters = 256
Data collection: COSMO/APEX2; Bruker, 2004 ⁸
Cell refinement and data reduction: SAINT; Bruker, 2004 ⁸
Absorption correction: multi-scan (SADABS; Bruker, 2004) ⁸
Molecular graphics: DIAMOND ⁹
CCDC 669265

Table 2 Selected bond lengths (Å) and angles (°)

C1–O1	1.200(2)	O1–C1–O2	122.42(14)
C1–C14	1.479(2)	C14–C1–O2	114.44(13)
C1–O2	1.3110(19)	N12–N11–C11	119.83(12)
N11–C11	1.3922(18)	N11–N12–N13	112.46(12)
N11–N12	1.3357(17)	N12–N13–C21	112.60(11)
N12–N13	1.2660(17)	C24–N4–C2	126.11(13)
N13–C21	1.4290(18)	N4–C2–O3	122.17(13)
N4–C24	1.41955(18)	N4–C2–C3	116.05(13)
N4–C2	1.3408(19)		
C2–O3	1.2328(18)		
C2–C3	1.495(2)		

positional parameters of the H atoms bonded to C atoms were obtained geometrically, with the C–H distances fixed (0.96 Å for Csp^3 and 0.93 Å for Csp^2), and refined as riding on their respective C atoms, with $U_{iso}(H) = 1.5U_{eq}(Csp^3)$ and $U_{iso}(H) = 1.2U_{eq}(Csp^2)$. The positional parameters of atoms H1, H2 and H3 were obtained from a difference map and refinement with an isotropic displacement parameter. Selected bond distances and angles are given in Table 2. The molecular structure is shown in Fig. 2.

The molecular structure of (I) shows the characteristic *trans* stereochemistry about the N=N double bond of the diazoamino group of free triazenes. Deviation observed from normal N–N and C_{aryl} –N bond length indicate a delocalization of the π electrons on the triazene group towards the terminal 4-carboxyphenyl substituent of the N=N–N(H) moiety. The N12=N13 bond [1.2660(17) Å] is longer than the typical value for a double bond (1.236 Å), whereas the N11–N12 bond [1.3357(17) Å] is shorter than the typical value for a single bond (1.404 Å).⁴ In addition, the C11–N11 [1.3922(18) Å] bond is shorter than the characteristic N– C_{aryl} single bonds (secondary amines, R_2NH , $R = Csp^2$; 1.452 Å).⁵ These values are in good agreement with those observed in a similar compound, 1,3-bis(2,4-dibromophenyl)triazene, hereafter (II) [N=N = 1.267(7) Å, N–N = 1.332(7) Å, C–N = 1.388(8) Å].⁶ As a consequence, the interplanar angles between the phenyl ring C11/C16 and the N11–N12=N13 group [6.5(2)°], and the phenyl ring C11/C16 and the O2–C1(=O1) group of the carboxyl substituent [3.5(3)°], demonstrate that this part of the molecule is almost planar (r.m.s. = 0.0713 Å). On the other hand, the interplanar angles between the phenyl ring C21/C26 and the N11–N12=N13 group [33.60(11)°], and the phenyl ring C21/C26 and the N4–C2(=O3)–C3 group [35.71(7)°] indicates that the delocalization of the π electrons on the triazene group towards to the terminal 4-acetylamidophenyl substituent is hindered, and contributes to the lack of planarity of the whole molecule (r.m.s. deviation = 0.3148 Å). The bond angle of the N=N–N triad [N11–N12–N13 = 112.46(12)°] is close to that angle found in (II) [111.6(5)°].⁶

Molecules of (I) related by an inversion center are associated by intermolecular hydrogen bonds with a bifurcated geometry, (D_1 –H₁, D_2 –H₂)...(*A*) (*D*, donor atom; *A*, acceptor atom), (N4–H3, C3–H3A)...O1''', symmetry code (') 2–*x*, –*y*, –*z*. Each molecule of this centrosymmetric pair generates another centrosymmetric dimer *via* a classical N11–H1...N13' intermolecular hydrogen bond, symmetry code (') 1–*x*, 1–*y*, –*z*. This resulting centrosymmetric assemblage is related by an axial 2₁ screw axis along the [010] direction, generating an infinite two-dimensional array of molecules that expand to a three-dimensional framework *via* a classical O2–H2...O3'' intermolecular hydrogen bond along the [100] direction, symmetry code (") 3/2+*x*, 1/2–*y*, –1/2+*z* (Table 3).⁷

Beside the geometrical parameters mentioned in Table 3, the

Fig. 2 Molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii.

Table 3 Hydrogen-bonding geometric parameters (Å, °)

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N11–H1...N13'	0.94(2)	2.29(2)	3.2205(18)	169.2(16)
O2–H2...O3''	1.02(2)	1.57(2)	2.5895(16)	172(2)
N4–H3...O1'''	0.882(18)	1.976(18)	2.851(2)	170.9(17)
C3–H3A...O1'''	0.96	2.58	3.420(2)	147

(*D* = donor atom, *A* = acceptor atom)

Symmetry codes: (') 1–*x*, 1–*y*, –*z*, (") 3/2+*x*, 1/2–*y*, –1/2+*z*, (""') 2–*x*, –*y*, –*z*

angle H3...O1'''...H3A is 53.4°, and the six-member ring, H3A...O1'''...H3–N4–C2–C3 observed in the centrosymmetric assemblage is almost planar (r.m.s. = 0.00485 Å).

The phenyl rings C11/C16 (r.m.s. deviation 0.0010 Å) and C21/C26 (r.m.s. deviation 0.0084 Å) are planar within the experimental error, and make an interplanar angle of 36.68(6)° which demonstrates that the whole molecule deviates significantly from planarity.

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