Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	0.1622 (1)	0.6654 (1)	0.28298 (6)	0.0602 (4)
O2	−0.0172 (1)	0.3265 (2)	0.37692 (6)	0.0679 (4)
O3	−0.0063 (2)	0.8017 (2)	0.28586 (7)	0.0776 (5)
O4	0.1941 (1)	0.3611 (1)	0.42438 (7)	0.0663 (4)
N1	0.1446 (2)	0.4269 (2)	0.32599 (8)	0.0582 (5)
C1	0.0870 (2)	0.7498 (2)	0.3126 (1)	0.0567 (5)
C2	0.1358 (2)	0.7639 (2)	0.38002 (9)	0.0528 (5)
C3	0.2199 (3)	0.6526 (2)	0.39157 (9)	0.0570 (5)
C4	0.2685 (2)	0.6164 (2)	0.32587 (9)	0.0520 (5)
C5	0.2792 (2)	0.4851 (2)	0.31510 (9)	0.0506 (5)
C6	0.3345 (2)	0.4537 (2)	0.2489 (1)	0.0566 (5)
C7	0.4851 (2)	0.4926 (2)	0.23799 (8)	0.0480 (5)
C8	0.5175 (3)	0.5838 (2)	0.1980 (1)	0.0652 (6)
C9	0.6569 (3)	0.6181 (2)	0.1890 (1)	0.0821 (7)
C10	0.7630 (3)	0.5622 (3)	0.2211 (2)	0.0883 (9)
C11	0.7327 (3)	0.4711 (3)	0.2604 (1)	0.0811 (8)
C12	0.5946 (2)	0.4367 (2)	0.2686 (1)	0.0630 (6)
C13	0.1147 (2)	0.3696 (2)	0.37974 (9)	0.0492 (5)
C14	−0.0800 (2)	0.2615 (2)	0.4294 (1)	0.0566 (5)
C15	0.0040 (4)	0.1517 (3)	0.4437 (2)	0.109 (1)
C16	−0.2263 (3)	0.2356 (4)	0.4046 (2)	0.095 (1)
C17	−0.0886 (4)	0.3398 (3)	0.4869 (1)	0.0837 (8)
C18	0.0131 (3)	0.7856 (3)	0.4246 (1)	0.0646 (6)
C19	0.0555 (2)	0.7855 (2)	0.4936 (1)	0.0561 (5)
C20	0.0329 (3)	0.6909 (3)	0.5318 (1)	0.0798 (7)
C21	0.0732 (4)	0.6935 (3)	0.5948 (1)	0.094 (1)
C22	0.1354 (3)	0.7891 (3)	0.6200 (1)	0.0811 (7)
C23	0.1581 (3)	0.8835 (3)	0.5832 (1)	0.0802 (7)
C24	0.1196 (3)	0.8814 (2)	0.5205 (1)	0.0707 (7)

Table 2. *Selected torsion angles (°)*

C4—C5—C6—C7	65.1 (3)
C5—C6—C7—C8	−108.9 (2)
C5—N1—C13—O4	0.7 (3)
C5—N1—C13—O2	179.0 (2)
C3—C2—C18—C19	55.4 (3)
C2—C18—C19—C20	−101.0 (3)
H1—N1—C13—O4	165 (2)
H1—N1—C13—O2	−17 (2)

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1989*a*). Cell refinement: *CAD-4/PC Software*. Data reduction: *CADRED* (Enraf–Nonius, 1989*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *O* (Jones & Kjeldgaard, 1993). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethylmethylglyoxal Bis(amidinohydrazonium) Dichloride–Water (1/2)

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Abstract

The title compound, $C_7H_{18}N_8^{2+}.2Cl^-.2H_2O$, has been found to exist as the *anti–anti* isomer, with an all-*trans* configuration of the bis(amidinohydrazone) chain, just like glyoxal bis(amidinohydrazone) and all its mono- and dialkylglyoxal analogues studied so far. The bis(amidinohydrazone) backbone of the dication is planar in contrast to the corresponding sulfate salt.

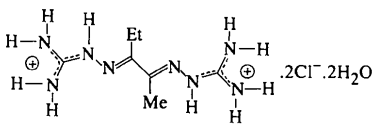
Comment

Ethylmethylglyoxal bis(amidinohydrazone) (EMGBG) is a potent and highly specific inhibitor of *S*-adenosylmethionine decarboxylase (AdoMetDC), one of the two rate-limiting enzymes of polyamine biosynthesis (Elo *et al.*, 1986). The compound is therefore an important tool in the investigation of polyamine metabolism and of the largely unknown physiological functions of the natural polyamines. Potent polyamine antimetabolites, including EMGBG, may also be potential anticancer agents.

The crystal and molecular structures of several mono- and dialkylglyoxal bis(amidinohydrazones) have been determined previously, including methylglyoxal bis(amidinohydrazone) dichloride monohy-

drate (Hamilton & La Placa, 1968), dimethylglyoxal bis(amidinohydrazone) dihydrochloride dihydrate (Edmonds & Hamilton, 1972), glyoxal bis(amidinohydrazone) dihydrochloride (Mutikainen, Elo & Lumme, 1986), propylglyoxal bis(amidinohydrazone) sulfate dihydrate (Lumme, Mutikainen & Elo, 1986), EMGBG sulfate (Elo *et al.*, 1986) and glyoxal bis(amidinohydrazone) free base and monohydrochloride (Mutikainen, Elo & Tilus, 1993). Structural studies, including X-ray diffraction and NMR spectrometry (Elo, 1989*a*,*b*) have proved to be essential in investigations concerning the action mechanism of bis(amidinohydrazone)-type antineoplastic agents and the reasons for the unusually strict structure–activity relationships of these drugs (Elo, 1989*c*).

In the case of EMGBG sulfate (Elo *et al.*, 1986), the bis(amidinohydrazone) chain was found to be markedly non-planar, in contrast to most other bis(amidinohydrazone) dications. Since it was not known whether the non-planarity is an intrinsic property of the EMGBG dication or the result of the crystal packing and related factors, further studies on other salts of EMGBG were proposed. Later, studies on different salts of EMGBG and other bis(amidinohydrazones) have become even more important, since planarity appears to be of crucial importance for the biochemical properties of bis(amidinohydrazones) and related agents (Stanek, Caravatti, Capraro *et al.*, 1993; Stanek, Caravatti, Frei *et al.*, 1993).



(I)

In the present study, the EMGBG dication in the crystalline chloride salt, (I), was found to exist exclusively in the form of the same geometrical isomer as glyoxal bis(amidinohydrazone) and all of its mono- and dialkylglyoxal analogues studied so far by crystallography, *i.e.* in the *anti–anti* isomer and, just like the others, was also found to have an all-*trans* configuration of the bis(amidinohydrazone) chain. However, atom C6 of the ethyl substituent is clearly above the plane of the backbone of the dication and the terminal amidino groups are slightly out of the plane. Most importantly, the bis(amidinohydrazone) backbone of the dication was found to be planar in contrast to EMGBG sulfate (Elo *et al.*, 1986). Thus, the EMGBG dication apparently does not have any intrinsic tendency to be markedly non-planar. Other structural features of the EMGBG dichloride generally agree with earlier results obtained for glyoxal bis(amidinohydrazone) and its mono- and dialkylglyoxal analogues and their various salts.

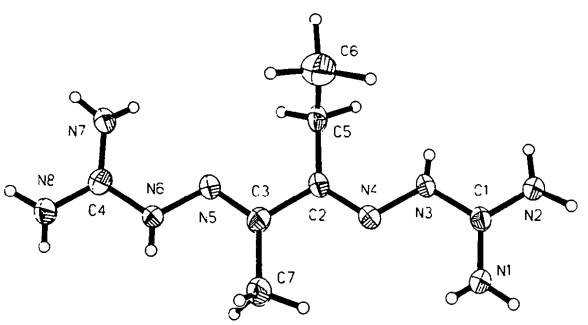


Fig. 1. View of the EMGBG dication as present in the dichloride dihydrate salt. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Ethylmethylglyoxal bis(amidinohydrazone) free base was prepared by previously published procedures (Elo *et al.*, 1986). 0.63 g of the free base was dissolved in 50 ml of 0.3 *M* aqueous hydrochloric acid at 338 K. Crystals were obtained by allowing the solution to evaporate to dryness at room temperature.

Crystal data

$C_7H_{18}N_8^{2+}.2Cl^-.2H_2O$
M_r = 321.23
Monoclinic, No. 14
$P2_1/c$
a = 14.945 (3) Å
b = 11.416 (2) Å
c = 9.674 (2) Å
β = 105.03 (3)°
V = 1594.0 (5) Å^3
Z = 4
D_x = 1.339 Mg m^{-3}
D_m = 1.32 (1) Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3.0–8.0°
μ = 0.420 mm^{-1}
T = 193 (2) K
Prismatic
0.30 × 0.20 × 0.15 mm
Colorless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2312 measured reflections
2312 independent reflections
1712 observed reflections [$F^2 > 2\sigma(F^2)$]
θ_{max} = 25.01°
$h = -17 \rightarrow 17$
$k = -13 \rightarrow 0$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0696
$wR(F^2)$ = 0.2017
S = 0.944
2286 reflections
213 parameters
H atoms: riding model for methyl and ethyl H
$w = 1/[\sigma^2(F_o^2) + (0.1165P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.024
$\Delta\rho_{max}$ = 0.528 e Å^{-3}
$\Delta\rho_{min}$ = −0.355 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.52440 (11)	0.48225 (13)	0.2543 (2)	0.0467 (5)
Cl2	0.97357 (11)	0.20781 (12)	0.2345 (2)	0.0424 (5)
O1	1.3582 (3)	−0.4973 (4)	−0.0268 (5)	0.0462 (12)
O2	1.1601 (3)	0.7250 (4)	0.0620 (5)	0.0441 (11)
N1	1.1859 (4)	0.4765 (4)	0.0597 (6)	0.0349 (12)
N2	1.0638 (3)	0.4453 (4)	0.1592 (5)	0.0333 (11)
C1	1.1289 (3)	0.4065 (4)	0.1020 (5)	0.0247 (11)
N3	1.1368 (3)	0.2898 (4)	0.0893 (5)	0.0332 (12)
N4	1.2015 (3)	0.2478 (4)	0.0239 (5)	0.0313 (11)
C2	1.2024 (4)	0.1359 (5)	0.0043 (6)	0.0339 (14)
C3	1.2770 (4)	0.0934 (5)	−0.0588 (6)	0.0338 (13)
N5	1.2820 (3)	−0.0175 (4)	−0.0688 (5)	0.0311 (10)
N6	1.3508 (3)	−0.0613 (4)	−0.1241 (6)	0.0350 (12)
C4	1.3636 (4)	−0.1784 (5)	−0.1232 (6)	0.0337 (13)
N7	1.3128 (4)	−0.2482 (5)	−0.0684 (7)	0.0441 (14)
N8	1.4292 (4)	−0.2187 (4)	−0.1780 (7)	0.052 (2)
C5	1.1366 (3)	0.0501 (4)	0.0407 (5)	0.0378 (14)
C6	1.1669 (3)	0.0113 (4)	0.1905 (5)	0.070 (2)
C7	1.3399 (4)	0.1806 (6)	−0.1054 (8)	0.056 (2)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.308 (7)	C3—N5	1.274 (6)
N2—C1	1.314 (6)	C3—C7	1.515 (8)
C1—N3	1.346 (7)	N5—N6	1.370 (6)
N3—N4	1.372 (6)	N6—C4	1.350 (7)
N4—C2	1.292 (7)	C4—N7	1.305 (7)
C2—C3	1.485 (7)	C4—N8	1.313 (7)
C2—C5	1.493 (7)	C5—C6	1.47
N2—C1—N1	122.6 (5)	N5—C3—C7	125.3 (5)
N2—C1—N3	117.6 (5)	C2—C3—C7	119.8 (5)
N1—C1—N3	119.8 (5)	C3—N5—N6	117.2 (5)
C1—N3—N4	118.5 (4)	C4—N6—N5	118.6 (4)
C2—N4—N3	116.6 (4)	N7—C4—N8	121.6 (5)
N4—C2—C3	114.9 (5)	N7—C4—N6	120.7 (5)
N4—C2—C5	125.6 (5)	N8—C4—N6	117.7 (5)
C3—C2—C5	119.6 (4)	C6—C5—C2	112.1 (3)
N5—C3—C2	114.9 (5)		

The crystal for the X-ray measurements was mounted on a glass fibre using the oil-drop method (Kottke & Stalke, 1993). The distance C5—C6 was constrained to 1.47 Å in the refinement.

Data collection: *AFC-7S Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *AFC-7S Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1391). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(*tert*-Butoxycarbonyl)-2-phenylglycine

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Abstract

In solution at room temperature *N*-(*tert*-butoxycarbonyl)-2-phenylglycine, $C_{13}H_{17}NO_4$, shows the presence of two confomers, *Z* and *E* in the ratio 1:3, as a result of restricted rotation about the N—CO bond. In the solid state, however, only the *Z* isomer was observed [HN—N—C2—O4 173.1 (4)°] with the N—CO bond showing considerable double-bond character [N—C2 1.357 (3) Å].

Comment

As a part of our research directed towards the synthesis of 3-aryl-4(3*H*)-isoquinolinone derivatives, we have