Acta Cryst. (1986). C**42**, 1209–1211

Structure of Propylglyoxal Bis(amidinohydrazone) Sulfate Dihydrate

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(*Received* 2 *December* 1985; *accepted* 1 *April* 1986)

Abstract. $C_7H_{18}N_8^{2+}.SO_4^{2-}.2H_2O$, $M_r = 346{\cdot}36$, orthorombic, $P2_12_12_1$, $a = 7{\cdot}066$ (2), $b = 13{\cdot}528$ (4), $c = 16{\cdot}179$ (4) Å, $V = 1546{\cdot}5$ (8) Å^3, $Z = 4$, $D_m = 1{\cdot}49$ g cm^{-3}, $D_x = 1{\cdot}49$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}6$ cm^{-1}, $F(000) = 736$, $T = 291$ K, final $R = 0{\cdot}059$ for 1245 unique observed reflections. The acid H atoms bind to the imino groups so that the crystal structure consists of columns of nonplanar $C_7H_{18}N_8^{2+}$ ions along the a axis at a mean distance of 3·55 Å. The structure is stabilized through an extensive hydrogen-bond network.

Introduction. Propylglyoxal bis(amidinohydrazone) (PGBA), like methylglyoxal bis(amidinohydrazone) (MGBA) and glyoxal bis(amidinohydrazone) (GBA), has an inhibitor effect on eukaryotic *S*-adenosylmethionine decarboxylase (EC 4.1.1.50) (Seppänen, Fagerström, Alhonen-Hongisto, Elo, Lumme & Jänne, 1984). Its synthesis as the sulfate dihydrate and biochemical characterization have been described recently (Elo, Laine, Alhonen-Hongisto, Jänne, Mutikainen & Lumme, 1985).

To throw more light on the substituent size effect and to allow comparison with the structures of MGBA (Hamilton & La Placa, 1968) and GBA (Mutikainen, Elo & Lumme, 1986), we have solved the crystal structure of the sulfate salt and the results are described in this paper.

Experimental. Samples for X-ray study were obtained by recrystallization from water at 303 K. The crystal selected for the intensity data collection had the dimensions 0·7 × 0·55 × 0·40 mm and was sealed in a Lindemann-glass capillary because of rapid fracture in the atmosphere. Density of the crystals by the flotation method. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 18 reflections measured on a Nicolet P3F diffractometer. The intensity measurements were carried out at room temperature (291 K) with graphite-monochromatized Mo $K\alpha$ radiation and the ω–2θ scan technique. The scan rate varied from 2·5 to 29·3° min^{-1}, depending on the number of counts measured in a fast preliminary scan through the peak.

A set of 1245 unique reflections was obtained from 1588 reflections measured from $2\theta = 3$–$45°$ (h 0→8, k 0→16, l 0→19). 1085 reflections with $I_o > 2\sigma(I_o)$ were considered as observed and used in refinement. One strong reflection (201) monitored periodically during data collection exhibited no significant intensity variation. The intensities were corrected for Lorentz and polarization effects. Corrections for absorption and extinction effects were considered unnecessary.

Systematic absences: $h00$, $h = 2n+1$; $0k0$, $k = 2n+1$; and $00l$, $l = 2n+1$ established the space group as orthorhombic $P2_12_12_1$ (No. 19). The structure was solved by direct methods (Gilmore, 1984). Successive Fourier calculations and full-matrix least-squares refinement on F (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) with all non-H atoms anisotropic, and H atoms with $U = 0{\cdot}05$ Å^2 and fixed led to $R =$ $= 0{\cdot}059$ and $wR = 0{\cdot}043$, where $w = 1/\sigma(F_o)^2$. After the last cycle the average shift/e.s.d. was 0·099 and maximum shift/e.s.d. 0·511.

The maximum and minimum peaks in the final difference map were 0·33 and −0·31 e Å^{-3}, respectively. Scattering factors were from Cromer & Mann (1968) and the anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a UNIVAC 1100/61 E1 computer.

Discussion. The atomic coordinates and equivalent isotropic values of the anisotropic temperature factor coefficients (Hamilton, 1959) for the non-H atoms are listed in Table 1.† The bond lengths and angles are given in Table 2, and the hydrogen-bond distances and angles are listed in Table 3.

The molecular structure of PGBA (Fig. 1) resembles closely those of MGBA (Hamilton & La Placa, 1968) and unsubstituted GBA (Mutikainen *et al.*, 1986),

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† Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, H-atom positions, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42967 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/86/091209-03$01.50

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10⁴) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
N(1)	8922 (11)	4659 (5)	3548 (4)	397
N(2)	9120 (12)	4833 (5)	4946 (4)	430
C(1)	8935 (13)	5209 (6)	4220 (5)	283
N(3)	8787 (10)	6209 (4)	4112 (4)	284
N(4)	9001 (10)	6787 (4)	4793 (4)	267
C(2)	8781 (12)	7732 (6)	4711 (5)	268
C(3)	9126 (14)	8263 (6)	5469 (5)	283
N(5)	8889 (11)	9198 (4)	5504 (4)	257
N(6)	9197 (11)	9636 (5)	6263 (4)	348
C(4)	9130 (13)	10625 (6)	6308 (5)	308
N(7)	8811 (12)	11161 (5)	5648 (4)	433
N(8)	9343 (10)	11029 (4)	7040 (4)	334
C(5)	8246 (13)	8282 (5)	3945 (4)	248
C(6)	9987 (13)	8697 (7)	3491 (5)	428
C(7)	11162 (14)	7940 (7)	3080 (6)	599
S(1)	8325 (3)	3759 (1)	6923 (1)	264
O(1)	8178 (9)	3137 (4)	6188 (3)	402
O(2)	6462 (9)	4063 (4)	7194 (3)	501
O(3)	9242 (10)	3203 (4)	7599 (3)	516
O(4)	9496 (8)	4640 (4)	6744 (3)	420
O(5)	8113 (9)	967 (4)	3851 (4)	492
O(6)	9642 (11)	2770 (4)	4216 (4)	645

Table 2. *Bond distances* (Å) *and angles* (°)

(*a*) PGBA molecule			
N(1)—C(1)	1·318 (10)	C(3)—N(5)	1·277 (10)
N(2)—C(1)	1·287 (10)	N(5)—N(6)	1·381 (9)
C(1)—N(3)	1·368 (10)	N(6)—C(4)	1·341 (11)
N(3)—N(4)	1·360 (9)	C(4)—N(7)	1·310 (11)
N(4)—C(2)	1·295 (10)	C(4)—N(8)	1·313 (10)
C(2)—C(3)	1·442 (12)	C(5)—C(6)	1·539 (12)
C(2)—C(5)	1·494 (11)	C(6)—C(7)	1·477 (13)
N(1)—C(1)—N(2)	122·1 (8)	C(2)—C(3)—N(5)	120·6 (8)
N(1)—C(1)—N(3)	116·9 (7)	C(3)—N(5)—N(6)	116·3 (7)
N(2)—C(1)—N(3)	121·0 (7)	N(5)—N(6)—C(4)	118·1 (6)
C(1)—N(3)—N(4)	117·2 (6)	N(6)—C(4)—N(7)	120·9 (7)
N(3)—N(4)—C(2)	118·1 (6)	N(6)—C(4)—N(8)	117·4 (7)
N(4)—C(2)—C(3)	112·6 (7)	N(7)—C(4)—N(8)	121·6 (7)
N(4)—C(2)—C(5)	127·4 (7)	C(2)—C(5)—C(6)	112·0 (7)
C(3)—C(2)—C(5)	120·0 (7)	C(5)—C(6)—C(7)	114·3 (8)
(*b*) Sulfate anion			
S(1)—O(1)	1·460 (5)	S(1)—O(3)	1·477 (6)
S(1)—O(2)	1·447 (7)	S(1)—O(4)	1·480 (6)
O(1)—S(1)—O(2)	110·2 (3)	O(2)—S(1)—O(3)	108·6 (3)
O(1)—S(1)—O(3)	109·9 (3)	O(2)—S(1)—O(4)	109·8 (3)
O(1)—S(1)—O(4)	110·2 (3)	O(3)—S(1)—O(4)	108·0 (3)

Table 3. *Distances* (Å) *and angles* (°) *in interactions of the type D*—H···*A*

D	H	*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
N(7)	H(9)	O(1$^{\rm i}$)	1·09	2·848 (9)	1·851	150
N(7)	H(8)	O(5$^{\rm i}$)	0·81	2·961 (9)	2·235	150
N(8)	H(11)	O(3$^{\rm i}$)	0·93	3·078 (8)	2·251	147
N(2)	H(3)	O(1$^{\rm ii}$)	0·83	3·122 (9)	2·580	124
N(2)	H(4)	O(4$^{\rm ii}$)	0·70	2·933 (8)	2·450	128
N(2)	H(3)	O(6$^{\rm ii}$)	0·83	3·053 (9)	2·361	142
N(1)	H(1)	O(6$^{\rm ii}$)	0·63	2·821 (9)	2·309	140
O(6)	H(22)	O(5$^{\rm ii}$)	1·02	2·732 (8)	1·780	155
O(6)	H(21)	N(1$^{\rm ii}$)	1·03	2·821 (9)	2·016	133
N(1)	H(2)	O(2$^{\rm iii}$)	0·87	2·804 (8)	2·006	153
N(3)	H(5)	O(2$^{\rm iii}$)	0·93	3·130 (8)	2·340	143
O(5)	H(20)	O(2$^{\rm iv}$)	1·00	2·909 (9)	1·975	155
O(5)	H(19)	O(4$^{\rm v}$)	0·76	2·852 (8)	2·143	156
N(6)	H(7)	O(3$^{\rm vi}$)	0·83	2·892 (9)	2·091	162
N(8)	H(10)	O(4$^{\rm vi}$)	0·87	2·842 (8)	1·993	165

Symmetry code: (i) $x, y+1, z$; (ii) x, y, z; (iii) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vi) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

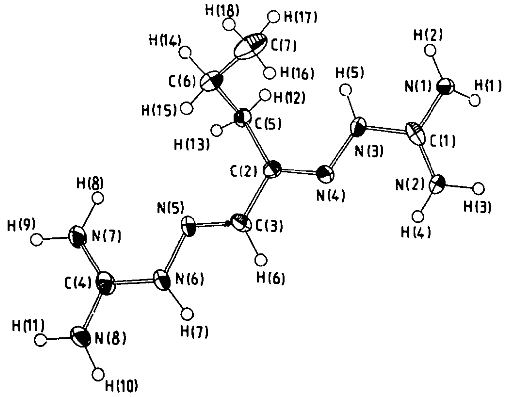
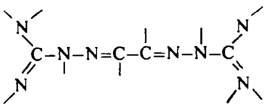


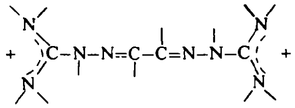
Fig. 1. *ORTEP* (Johnson, 1965) drawing with the numbering scheme of the PGBA molecular ion viewed along **a** (50% probability ellipsoids are shown for the non-H atoms).

which are protonated in their mineral-acid salts. The H atoms of the acid bind to the imino groups of the molecular base to form positively charged $C_7H_{18}N_8^{2+}$ ions (Fig. 1).

Consideration of the bond distances of the molecule (Table 2) confirms the formal bond-order representation shown in (I) for PGBA, the protonated form adopting structure (II). This means that C(1)—N(1), C(1)—N(2), C(4)—N(7) and C(4)—N(8) would have 50% double-bond character and C(2)—N(4) and C(3)—N(5) would be near to double bonds, with all other bonds single.



(I)



(II)

Unlike the MGBA and GBA structures, the C—N=N—C groupings of the PGBA molecule are not totally planar and their planes are tilted 4·7 (9)° against each other. The largest deviation of the plane-defining atoms from the mean molecular plane is 0·097 (1) Å for the N(1) atom. The CN_3 groupings at the ends of the molecule are planar within e.s.d.'s and their interplanar angle is 5·4 (8)°. The propyl group forms an angle of 65·3 (3)° with the GBA plane.

The crystal structure consists of columns along the a axis formed by parallel-stacked $C_7H_{18}N_8^{2+}$ ions (Fig. 2). The mean distance between the GBA units in the columns is 3·55 Å and the stacking is rather extensive indicating considerable π–π interaction between the molecules in the columns. The sulfate ions and water molecules also form columns in the **a** direction. The columnar network is held together by an extensive hydrogen-bond network through the SO_4^{2-} ions and the water molecules such that all PGBA N atoms carrying H atoms take part in from one to three hydrogen bonds (Table 3).

Comparison of the structural results with earlier work (Mutikainen *et al.*, 1986; Elo *et al.*, 1985) confirms the opinion that the observed differences between the biological efficiencies of GBA and its alkyl derivatives are not dependent on their crystal structures in the solid state but only on the composition and size of the alkyl substituents, which also affect the hydrophobicity of the compounds.

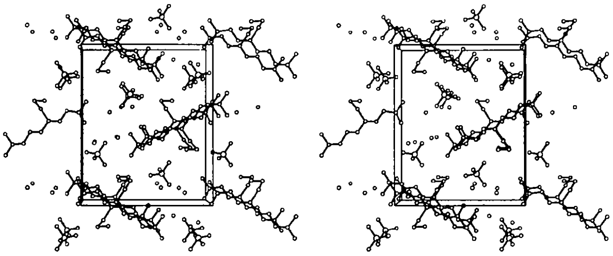


Fig. 2. Stereoview of the packing of the molecules as viewed down **a**.

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Acta Cryst. (1986). C**42**, 1211–1217

Transitions de Phase Structurales dans les Polyphényles. IX. Affinements des Structures du *p*-Terphényle Hydrogéné à 200 K (Diffraction des Rayons X) et du Biphényle Deutéré à 40 K (Diffraction des Neutrons)

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(*Reçu le* 25 *juin* 1985, *accepté le* 16 *mai* 1986)

Abstract. (I): $C_{18}H_{14}$, $M_r = 230·3$, monoclinic, $P2_1/a$, $a = 8·019$ (2), $b = 5·576$ (2), $c = 13·578$ (2) Å, $\beta = 92·10$ (2)°, $V = 606·7$ Å^3, $Z = 2$, $D_x = 1·261$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·66$ cm^{-1}, $F(000) = 244$, $T = 200$ K, $R = 0·083$ for 1034 independent reflections. (II): $C_{12}D_{10}$, $M_r = 164·3$, monoclinic, $P2_1/a$, $a = 7·78$ (2), $b = 5·565$ (8), $c = 9·44$ (2) Å, $\beta = 93·9$ (2)°, $V = 407·8$ Å^3, $Z = 2$, $D_x = 1·338$ g cm^{-3}, $\lambda = 1·177$ Å, $\mu = 0·0002$ cm^{-1}, $F(000) = 293$, $T = 40$ K, $R = 0·064$ for 414 independent reflections. A double-well potential model for librations around the long molecular axis confirms that the central phenyl ring of *p*-terphenyl jumps between two sites separated by a rotation angle of 26·6°. This angle is independent of temperature above the transition temperature $T_c = 191$ K, in agreement with an order–disorder process. On the other hand, biphenyl exhibits a normal decrease of librational amplitude when the temperature is lowered from room temperature to the transition temperature $T_c \simeq 40$ K, without any obvious indication of disorder, as expected for a displacive process.

Introduction. La différence de nature entre les mécanismes de transition du *p*-terphényle (transition ordre–désordre) et du biphényle (transition displacive) est mise en évidence par l'analyse des mouvements thermiques de libration autour de l'axe long des molécules. Un affinement du *p*-terphényle hydrogéné à

0108-2701/86/091211-07$01.50