

2.663 (8) Å, close to the most probable range for an O—H...O hydrogen-bond length (Brown, 1976; Mitra & Ramakrishnan, 1977). The N—H and C=O groups of the urethane moiety are not involved in hydrogen-bond formation. This latter result is at variance with the principle that the maximum number of proton donor and acceptor sites will participate in hydrogen bonds, recently put forward in a study of amides and carboxylic acids (Etter, 1982).

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Structure of 1,3-Bis(carboxymethyl)imidazole

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Abstract. $C_7H_8N_2O_4$, $M_r = 184.154$, triclinic, $P\bar{1}$, $a = 7.482$ (4), $b = 7.698$ (5), $c = 8.202$ (3) Å, $\alpha = 107.24$ (4), $\beta = 106.94$ (4), $\gamma = 106.77$ (4)°, $V = 393.6$ (3) Å³, $Z = 2$, $D_m = 1.577$ (4), $D_x = 1.553$ (3) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.121$ mm⁻¹, $F(000) = 192$, $T = 296$ K, $R = 0.052$ for 2818 unique observed reflections. The molecule is a zwitterion, stabilized by charge delocalization. The imidazole moiety shows a planar arrangement with a

maximum deviation of 0.003 (2) Å for C2 and C3. Intermolecular hydrogen bonds of the type O—H...O connect the molecules in an infinite chain along the [111] direction. The chains are joined together by van der Waals forces. The O...O hydrogen-bond length is 2.463 (2) Å.

Introduction. Glyoxal, which occurs in foods as one of numerous degradation products of the main nutrients,

i.e. lipids and saccharides, is one of the most reactive α -dicarbonyl compounds. Owing to its reactivity, it plays a prominent role not only *in vitro* in non-enzymatic browning reactions occurring in foods during processing and storage (Namiki & Hayashi, 1983), but also in living processes such as charge-transfer interactions, participating in the transfer of electronic energy (Gascoyne, Symons & McLaughlin, 1983). It is well known that reactions of glyoxal and other α -dicarbonyl compounds with amino acids proceed *via* the Strecker degradation of the amino acid involved and lead to the formation of numerous N-containing heterocycles such as pyrroles, imidazoles, pyrazines, *etc.* (Velíšek, Davídek, Cuhrová & Kubelka, 1976; Fujimaki, Chuyen & Kurata, 1971). The reaction of glyoxal with amino acids and/or ammonia leads primarily to the formation of imidazole (Debus, 1858); its homologue methylglyoxal forms 4-methylimidazole, *etc.* The latter compound, which occurs as a chemical constituent of caramel-derived food dyes (Buckee & Bailey, 1978), has been shown to have mutagenic properties (Barnes, Spingarn, Garvic-Gould, Vuolo, Wang & Weissburger, 1983). Numerous other imidazoles, mainly polyhydroxyalkyl substituted compounds, have been identified as reaction products of saccharides and structurally similar compounds such as L-ascorbic acid with amino acids and/or ammonia in model systems (Ježo, 1963; Fuji, Tsuchida & Komoto, 1966; Tsuchida & Komoto, 1967). Recently, polyhydroxyalkylimidazoles, *e.g.* 4(5)-acetyl-4(5)-(1,2,3,4-tetrahydroxybutyl)imidazole, were identified as constituents of commercial caramel colour (Kroepflin, Rosdorfer, Greef, van der Long & Goldstein, 1985).

This work was undertaken as part of studies on nonenzymatic browning reactions in simple model systems in order to identify the possible additional imidazoles formed in reactions of α -dicarbonyl compounds with amino acids.

Experimental. Crystals of 1,3-bis(carboxymethyl)imidazole were obtained by reaction of glyoxal with glycine and recrystallized from water. Detailed information concerning the isolation and the identification of the compound studied can be found in Velíšek, Davídek, Velcová & Kvasnička (1988). The density was determined by flotation in tetrachloromethane/hexane. Colourless crystal (0.75 × 0.65 × 0.50 mm), Syntex P2₁ diffractometer, lattice parameters refined from setting angles ($14 \leq 2\theta \leq 25^\circ$) of 25 centred reflections, data collection ($\theta-2\theta$ scan, $2\theta \leq 70^\circ$, *hkl* range 0 to 16, -16 to 16, -16 to 16), three standard reflections (200, 030, 006), no significant intensity fluctuation observed, 3482 reflections measured, 2818 unique observed reflections [$I > 1.96\sigma(I)$], absorption ignored, phase problem solved by direct methods, H-atom positions obtained from ΔF synthesis, the quantity $\sum w(|F_o| - |F_c|)^2$ minimized by full-matrix

Table 1. *Final atomic parameters (for non-H atoms $\times 10^4$, for H atoms $\times 10^3$)*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}/U_{iso}(\text{Å}^2)$
O1	-8280 (2)	-2311 (2)	306 (2)	372 (3)
O2	-7926 (2)	53 (1)	-761 (1)	378 (3)
O3	-193 (1)	7502 (1)	6033 (1)	268 (2)
O4	2017 (1)	9152 (2)	5124 (2)	362 (3)
N1	-5496 (1)	3028 (1)	2579 (1)	216 (2)
N2	-3222 (1)	5518 (1)	2585 (1)	213 (2)
C1	-3607 (2)	3776 (2)	2696 (2)	219 (3)
C2	-4939 (2)	5914 (2)	2391 (2)	285 (3)
C3	-6364 (2)	4352 (2)	2377 (2)	297 (3)
C4	-6467 (2)	1061 (2)	2526 (2)	256 (3)
C5	-7654 (2)	-569 (2)	552 (2)	238 (3)
C6	-1242 (2)	6813 (2)	2778 (2)	249 (3)
C7	348 (2)	7941 (2)	4815 (2)	224 (3)
HO2	-873 (5)	-122 (5)	-199 (5)	108 (10)
HC1	-246 (4)	341 (4)	307 (4)	89 (8)
HC2	-498 (3)	705 (3)	237 (3)	36 (4)
HC3	-787 (4)	417 (5)	258 (5)	104 (10)
H1C4	-547 (3)	79 (3)	328 (3)	46 (5)
H2C4	-742 (3)	106 (3)	313 (3)	44 (5)
H1C6	-47 (3)	625 (3)	214 (3)	57 (6)
H2C6	-135 (3)	782 (3)	225 (3)	51 (5)

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

Symmetry code: (i) x-1, y-1, z-1.

C7-O4	1.223 (2)	N1-C1	1.326 (2)
C7-O3	1.278 (2)	C1-N1	1.325 (2)
C7-C6	1.532 (2)	N1-C4	1.460 (2)
C6-N2	1.460 (2)	C4-C5	1.516 (1)
N2-C2	1.380 (2)	C5-O2	1.290 (2)
C2-C3	1.352 (2)	C5-O1	1.217 (2)
C3-N1	1.381 (2)		
Hydrogen bond			
O2...O3 ⁱ	2.463 (2)		
O4-C7-O3	126.1 (2)	C3-N1-C1	108.1 (2)
O4-C7-C6	117.4 (2)	N1-C1-N2	109.4 (2)
O3-C7-C6	116.5 (2)	C3-N1-C4	127.9 (2)
C7-C6-N2	112.9 (2)	C1-N1-C4	123.8 (2)
C6-N2-C2	127.4 (2)	N1-C4-C5	113.1 (2)
C6-N2-C1	124.1 (2)	C4-C5-O1	119.9 (2)
C2-N2-C1	108.4 (2)	C4-C5-O2	115.0 (2)
N2-C2-C3	106.9 (2)	O2-C5-O1	125.1 (2)
C2-C3-N1	107.2 (2)		
C1-N1-C4-C5	-91.2 (2)	C1-N2-C6-C7	-76.2 (3)
C3-N1-C4-C5	83.4 (3)	C2-N2-C6-C7	99.0 (3)
N1-C4-C5-O1	169.0 (2)	N2-C6-C7-O3	5.2 (3)
N1-C4-C5-O2	-11.4 (3)	N2-C6-C7-O4	-175.8 (2)

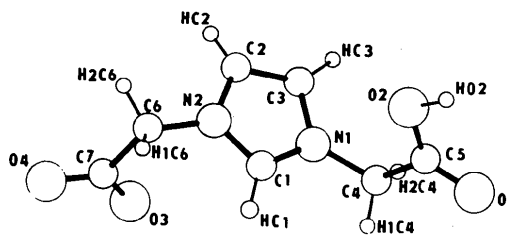


Fig. 1. Perspective view of the molecule with atom numbering.

least squares, positional and anisotropic thermal parameters of non-H atoms and positional and isotropic thermal parameters of H atoms refined in two blocks, $R = 0.052$, $wR = 0.064$, $w = 2.7453/[\sigma^2(F_o) + 0.0009F_o^2]$, $(\Delta/\sigma)_{\max} = 0.09$, max. height in the final ΔF map $0.38 \text{ e } \text{Å}^{-3}$, min. height $-0.33 \text{ e } \text{Å}^{-3}$, *MULTAN80* (Main *et al.*, 1980), *SHELX76* (Sheldrick, 1976), *PARST* (Nardelli, 1984), *PLUTO* (Motherwell, 1976) programs used, atomic scattering factors those incorporated in *SHELX76*. EC 1033, IBM 370/135 computers.*

Discussion. The title compound is the next representative of 1,3 (or *N,N'*) symmetrically substituted imidazole structures. Until now crystal-structure information has been available for 1,3-diphosphorylimidazole (Beard & Lenhart, 1968) and 1,3-dimethylimidazole-2(3*H*)-thione (Ansell, 1972).

The final atomic parameters of 1,3-bis(carboxymethyl)imidazole are listed in Table 1. Bond lengths and angles are given in Table 2. A perspective drawing

* Lists of structure factors, anisotropic thermal parameters, least-squares-plane details, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44962 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

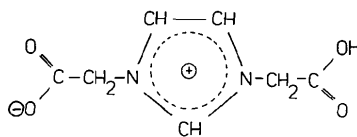


Fig. 2. The zwitterion stabilized by charge delocalization.

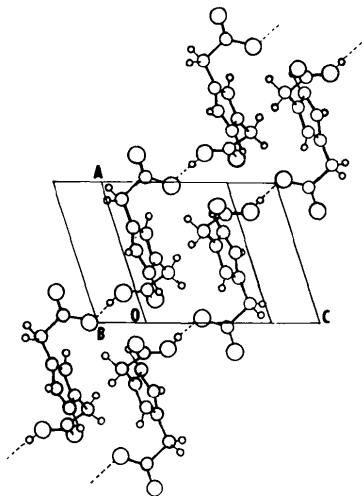


Fig. 3. Projection of the unit-cell packing. Dashed lines indicate the hydrogen bonding.

of the molecule with atom numbering is given in Fig. 1. The imidazole ring is almost planar with a maximum displacement of $0.003 (2) \text{ Å}$, for the C2 and C3 atoms. The carboxymethyl group involving atoms C6, C7, O3 and O4 is located below the imidazole plane, while the group involving C4, C5, O1 and O2 protrudes above this plane. Both C—CO₂ groups are planar and inclined $82.60 (9)$ and $76.61 (8)^\circ$, respectively, to the imidazole ring plane. The N1 and N2 atoms are $0.259 (2)$ and $-0.107 (2) \text{ Å}$ away from their carboxymethyl group plane. The mutual angle of these planes is $46.6 (1)^\circ$. The conformation is further described by the dihedral angles given in Table 2.

In consequence of the stoichiometry the compound under study is a zwitterion, stabilized by charge delocalization (Fig. 2). The molecular packing and hydrogen-bonding scheme are illustrated in Fig. 3. Intermolecular hydrogen-bridge contacts of the type O—H...O give rise to infinite chains of molecules parallel to the [111] direction. The chains are joined together by van der Waals forces. The C5—O2 (H donor) and C7—O3 (H acceptor) bonds take part in intermolecular hydrogen-bonding contacts [O2—HO2...O3ⁱ $1.57 (4)^\circ$; O2—HO2 $1.03 (3)$; HO2...O3ⁱ $1.48 (3)$; O2...O3ⁱ $2.463 (2) \text{ Å}$]. On the other hand C5—O1 and C7—O4 are typical terminal bonds.

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Structure of Bis(quinuclidine)iodine(I) Tetrafluoroborate

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Abstract. $[(C_7H_{13}N)_2I]BF_4$, $M_r = 436.08$, cubic, $P2_13$, $a = 12.1355$ (6) Å, $V = 1787.2$ (4) Å³, $Z = 4$, $D_x = 1.621$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 18.0$ cm⁻¹, $F(000) = 872$, $T = 295$ (1) K, $R = 0.029$ for 62 variables and the 371 reflections having $I > 3\sigma(I)$ and $4 < 2\theta < 60^\circ$ [$(\sin\theta)/\lambda < 0.704$ Å⁻¹]. The structure is isostructural with that of bis(quinuclidine)bromine(I) tetrafluoroborate [Blair, Parris, Hii & Brock (1983). *J. Am. Chem. Soc.* **105**, 3649–3653]. Linear [(quinuclidine)₂I]⁺ cations and discrete BF₄⁻ anions are located on C₃ axes; the anions are disordered. The lengths of the two I–N bonds, 2.320 (3) and 2.267 (4) Å, differ by 0.053 (5) Å. The average I–N distance, 2.294 (5) Å, is typical of the average I–N distances found for similar complexes. The two quinuclidine cages are rotated by *ca* 30 (3)° with respect to each other. The cages themselves are twisted; the two N–C–C–C torsion angles are –6.0 (9) and 10.7 (10)°.

Introduction. This structure was determined as part of a study of bis(amine) complexes of Br^I and I^I. Bis(quinuclidine)iodine(I) tetrafluoroborate was studied earlier by Pritzkow (1977; quoted by Hagedorn, Pritzkow & Jander, 1977), but nothing other than the average I–N distance, given as 2.29 (1) Å, seems to have been published.

Experimental. The title compound was synthesized by the same route as the analogous Br compound (Blair, Parris, Hii & Brock, 1983). Chunk-shaped, colorless crystal, 0.2–0.3 mm on a side, grown from acetonitrile used for data collection; data measured with an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator and operating in the ω – 2θ mode; 20 reflections (θ range 12–14°) used to

determine lattice parameters. Octant of data with $h, k, l \leq 17$; correction for average intensity loss for three control reflections of –0.54% overall. Although the linear absorption coefficient (18.0 cm⁻¹) is not small, 360° ψ scans for eight reflections showed a maximum deviation of 1.5% from the average; no absorption correction was attempted.

The compound $[(C_7H_{13}N)_2X]BF_4$, $X = I$ (this work) appeared to be isostructural with the compound having $X = Br$ (Blair, Parris, Hii & Brock, 1983). The latter crystallizes in the cubic group $P2_13$ with the Br atoms on *xxx* positions very near the origin. Crystals of the I-containing compound are dark at all orientations when viewed between crossed polarizers, and have a cubic cell dimension 0.107 Å longer than found for the Br-containing crystals. The systematic absences ($h00$ for $h = 2n + 1$, and similarly for $0k0$ and $00l$) are consistent with the space groups $P2_13$ and $P4_232$; the two groups can be distinguished on the basis of the Laue symmetry. Averaging in $m\bar{3}$ of the 2921 observed intensities, which do not include any Friedel pairs, yielded 981 unique data; the R factor based on I for averaging is 0.029. Averaging in $m\bar{3}m$ yielded 449 reflections and an R factor of 0.071. We concluded that the space group is $P2_13$. Comparisons of the intensities of the 2196 reflections of mixed parity is even more convincing. These reflections are systematically weaker than the reflections with h, k, l all even or all odd because of the much smaller contribution of the I atom. Averaging of these weaker data in $m\bar{3}$ gave 732 unique reflections and an R factor of 0.096, while averaging in $m\bar{3}m$ gave 405 reflections and an R factor of 0.695. In $P2_13$, both ions are required to conform to crystallographic threefold rotation symmetry. If the space group had been $P4_232$, the required symmetry would have been 32.