

Synthesis and Spectroscopic, Thermal and Crystal Structure Studies of Hydrazinium Hydrogensuccinate

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ABSTRACT

The mono-hydrazinium salt of succinic acid (hydrazinium hydrogensuccinate salt) was prepared by reacting hydrazine hydrate and succinic acid. Its spectral, thermal and structural properties have been determined. The salt, $N_2H_5^+ \cdot C_4H_5O_4^-$, is a molecular salt containing discrete hydrazinium cations and hydrogen succinate anions. The crystal packing consists of infinite chains of anions and cations that are alternatively linked through $O-H \cdots N$ and bifurcated $N-H \cdots O$ bonds and this chain is connected to adjacent antiparallel chains by $N-H \cdots O$ hydrogen bonding. The adjacent chains are cross linked by $N-H \cdots O$ bonds from the donor $N_2H_5^+$ ions, thus forming a three-dimensional network. The salt undergoes melting followed by decomposition to give gaseous products.

KEYWORDS

Hydrazine, succinic acid, hydrazinium hydrogensuccinate, crystal structure, thermal studies.

1. Introduction

Dibasic acids are known to form N_2H_5HA , $(N_2H_5)_2A$ and $N_2H_5HA.H_2A$ type salts (H_2A = dibasic acid) with hydrazine. Though, a number of hydrazinium salts of the former two types with different dibasic acids have been reported,^{1–6} there appear to be very few reports available in the literature on the hydrazinium salts of the third type, *viz.* $N_2H_5HA.H_2A$.⁴ However, such salts of oxalic acid with ammonium⁷ and potassium^{7,8} ions and dipicolinic acid with sodium^{9,10} ions have been studied in detail, including their crystal structures. The preparation of hydrazinium salts has become a subject of recent interest due to their wide use as additives in propellants, drugs to treat cancer and Hodgkin's disease and explosives.¹ They have also been utilized as ligands for the preparation of metal hydrazinium/hydrazine complexes.^{11–13} Some of these salts are also used as flame-retardants^{14,15} and proton conductors.¹⁶ The preparation and thermal behaviour of some of these salts have recently been reported from our laboratory with a few aliphatic^{2,4} and aromatic⁵ carboxylic acids. However, the crystal structure of hydrazinium salts of aliphatic and aromatic carboxylic acids have not been reported. Although crystal structures of hydrazinium salts of some heteroaromatic carboxylic acids have been reported,^{17–19} there appears to be only one report²⁰ available up to now in the Cambridge Structural Database (CSD)²¹ on the hydrazonium salt of the type N_2H_6A . Recently, for the first time, we reported two polymorphic modifications (forms A and B) of the $N_2H_6(HA)_2$ type salt (Fig. 1b) formed by hydrazine with 3,5-pyrazoledicarboxylic acid (Fig. 1a).²²

Hydrazine forms two types of salts with oxalic acid ($H_2C_2O_4$), *viz.* $N_2H_4 \cdot H_2C_2O_4$ and $2N_2H_4 \cdot H_2C_2O_4$. Pratt and Richards²³ studied these compounds with ¹H NMR and have proposed that these compounds could be formulated as $N_2H_5 \cdot HC_2O_4$ and $(N_2H_5)_2 \cdot C_2O_4$, respectively. The structure of the first compound

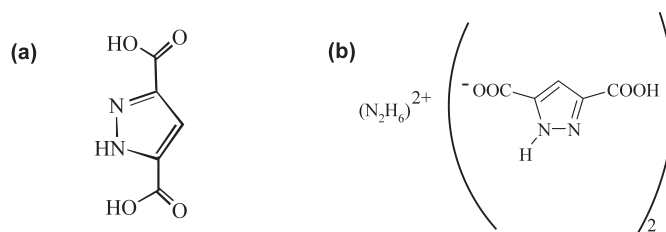


Figure 1 Molecular structure of (a) 3,5-pyrazoledicarboxylic acid, and (b) polymorphic modifications (forms A and B) of $N_2H_6(HA)_2$ type salt formed by hydrazine with 3,5-pyrazoledicarboxylic acid.

was extensively studied by X-ray^{24,25} and neutron²⁶ diffraction methods and found to consist of chains of $N_2H_5^+$ and $HC_2O_4^-$ ions. The chains are cross-linked by $N-H \cdots O$ bonds from the $N_2H_5^+$ ions, thus forming a three-dimensional network. Although much has been reported on the $N_2H_5HC_2O_4$ salt, the crystal structure of the corresponding hydrazinium salt of succinic acid [$HOOC(CH_2)_2COOH$], $N_2H_5(HOOC(CH_2)_2COO)$, has not been determined. In this paper we present the single crystal X-ray diffraction structure of the salt, $N_2H_5(HOOC(CH_2)_2COO)$ (Fig. 2) along with its spectral and thermal properties.

2. Experimental

2.1. Preparation of Hydrazinium Hydrogensuccinate, $N_2H_5(HOOC-(CH_2)_2-COO)$

Hydrazinium hydrogensuccinate was prepared by mixing an aqueous solution of 10 % hydrazine hydrate (2 mL, 4 mmol) in 20 mL of distilled water and a 20 mL aqueous solution containing 0.476 g (4 mmol) succinic acid. The resulting clear solution was concentrated on a water-bath to about 20 mL and kept at room temperature for crystallization. The colourless crystals obtained

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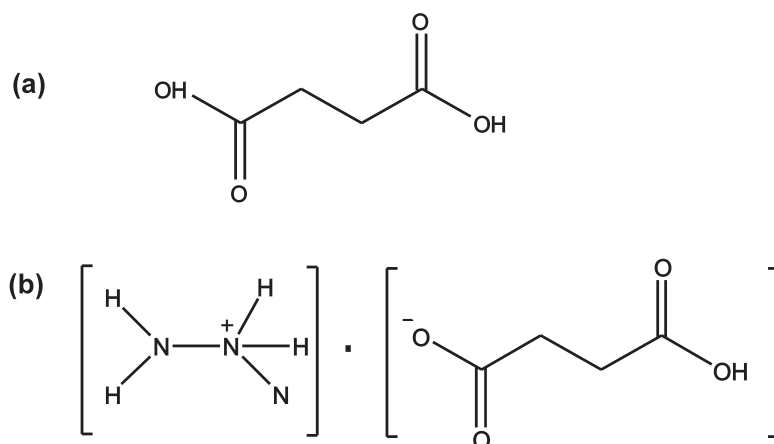


Figure 2 Chemical structure diagram of (a) succinic acid, and (b) hydrazinium hydrogensuccinate.

after two days were separated and washed with dry ethanol, and air dried (yield: 85 %). Elemental analysis: C (%): 31.28 (Cald. 31.97); H (%): 5.90 (6.66); N (%): 17.93 (18.65); and % hydrazine: 21.08 (Cald. 21.31).

2.2. Physico-chemical Characterization

The hydrazine content of the salt was determined volumetrically by using a standard (0.025 M) KIO_3 solution under Andrews' condition.²⁷ IR spectra were recorded as KBr pellets with a Shimadzu FTIR 8000 spectrophotometer in the 4000–400 cm^{-1} range. Elemental analyses were performed on a Perkin-Elmer 240 B CHN analyser. Simultaneous TG-DTA measurements were carried out by using a Diamond TG/DTA thermal analyzer. The experiments were carried out in air with platinum cups as sample holders containing 5–10 mg of the samples at a heating rate of 10 $^\circ\text{C min}^{-1}$, up to 830 $^\circ\text{C}$.

2.3. Single Crystal X-ray Diffraction Analysis

Preliminary examination and data collection were performed with a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer at 218 K using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) equipped with a sealed tube X-ray source. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages²⁸ were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids. Collected data were corrected for systematic errors using SADABS²⁹ based on the Laue symmetry using equivalent reflections. Structure solution and refinements were carried out by using the SHELXTL software package.³⁰ The structure was solved by direct methods and refined successfully in the triclinic space group $P\bar{1}$. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were located and refined freely.

3. Results and Discussion

The analytical data for the hydrazinium hydrogensuccinate crystals (Fig. 2) agree with the proposed formula for the salt. The title compound is soluble in water and stable in air. The melting point of the salt was found to be 137–138 $^\circ\text{C}$.

It is interesting to note that oxalic and succinic acids both form mono-hydrazinium and dihydrazinium salts, whereas malonic acid only forms the mono-hydrazinium salt, *viz.* $\text{N}_2\text{H}_5(\text{HOOC-CH}_2\text{-COO})$. Sulfoacetic acid did not yield any

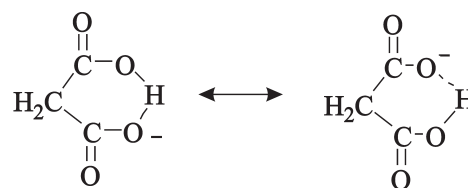


Figure 3 The schematic illustration of the formation of a six-membered ring structure of hydrogenmalonate anion.

expected hydrazinium salt. The reasons are very difficult to generalize.

As reported,⁶ oxalic acid forms both salts. The hydrogenoxalate anion which is represented as HOOC-COO^- has a strong electron withdrawing inductive effect ($-I$ effect) due to the $-\text{OC-COO}^-$ group that makes the O-H bond more labile. This leads to the formation of a dihydrazinium salt. In the case of the hydrogenmalonate anion, the O-H bond is stabilized by the formation of a six-membered ring anion due to strong intramolecular hydrogen bonding as shown in Fig. 3 and as a result a proton cannot be abstracted by a weak base like N_2H_4 which prevents the formation of the dihydrazinium salt. In the case of the hydrogensuccinate anion, the intramolecular hydrogen bonding is not preferred due to an increase in size of the ring. Also the $-I$ effect of the carboxylate group makes the O-H bond more labile. This helps to form the dihydrazinium salt.

3.1. Infrared Spectra

The IR spectra of succinic acid and its hydrazinium salt are given in Figs 4 and 5, respectively for comparison. The IR spectra of succinic acid and its monohydrazinium salt show absorption frequencies in the region 3465–3385 cm^{-1} due to O-H stretching of the free COOH group. The N-N stretching frequency of the free N_2H_5^+ ion is known to occur in the 990–960 cm^{-1} region.¹ The observed N-N stretching frequency at 965 cm^{-1} (Fig. 5) clearly reveals the presence of the N_2H_5^+ ion in the salt. The bands at 1630 and 1410 cm^{-1} , for the hydrazinium salt, are assigned to asymmetric and symmetric stretching frequencies of the carboxylate ions, respectively. The free carboxyl groups of the acid and salt show the free carbonyl asymmetric stretching frequencies in the region 1715–1705 cm^{-1} .

3.2. Thermal Analysis

The simultaneous TG and DTA data of the hydrazinium hydrogensuccinate salt are shown in Fig. 6. The DTA of the hydrazinium hydrogensuccinate salt shows two endotherms (~ 135 and ~ 168 $^\circ\text{C}$); the first sharp endotherm at 135 $^\circ\text{C}$ is attributed to melting (no mass loss observed in TG), whereas the

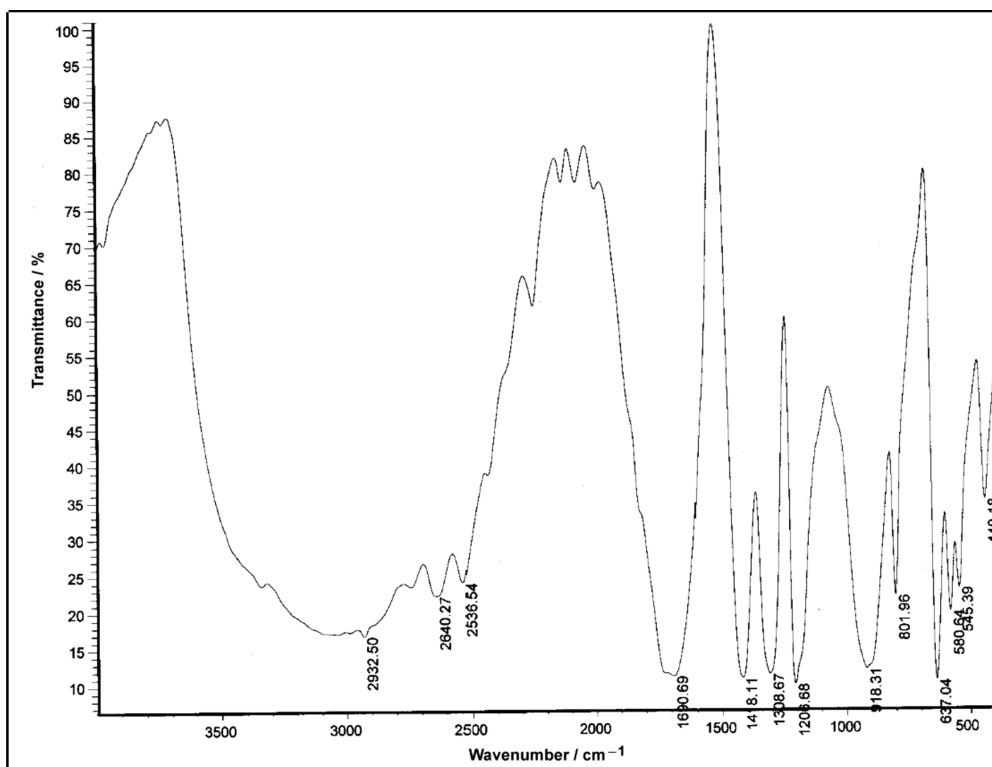


Figure 4 Infrared spectrum of succinic acid.

second endotherm at 168 °C may be assigned to dehydration of the melt to form succinic acid as an intermediate which further undergoes exothermic (multiplets) decomposition to give gaseous products similar to that of other simple salts.⁵ The decomposition of the melt is initiated at 168 °C and 99.9 % loss was observed by 600 °C. This is observed as a continuous decomposition in TG.

3.3. Single Crystal X-ray Diffraction Studies

Results of the single crystal X-ray diffraction studies for $N_2H_5(HOOC(CH_2)_2COO)$ are presented in Tables 1–3.

The crystal structure is built up of $N_2H_5^+$ cations and hydrogen succinate anions, $HOOC(CH_2)_2COO^-$, which are joined by hydrogen bonds. The structure of $N_2H_5^+(HOOC(CH_2)_2COO)^-$ is shown in Fig. 7. The N–N distance of the $N_2H_5^+$ ion is 1.4535

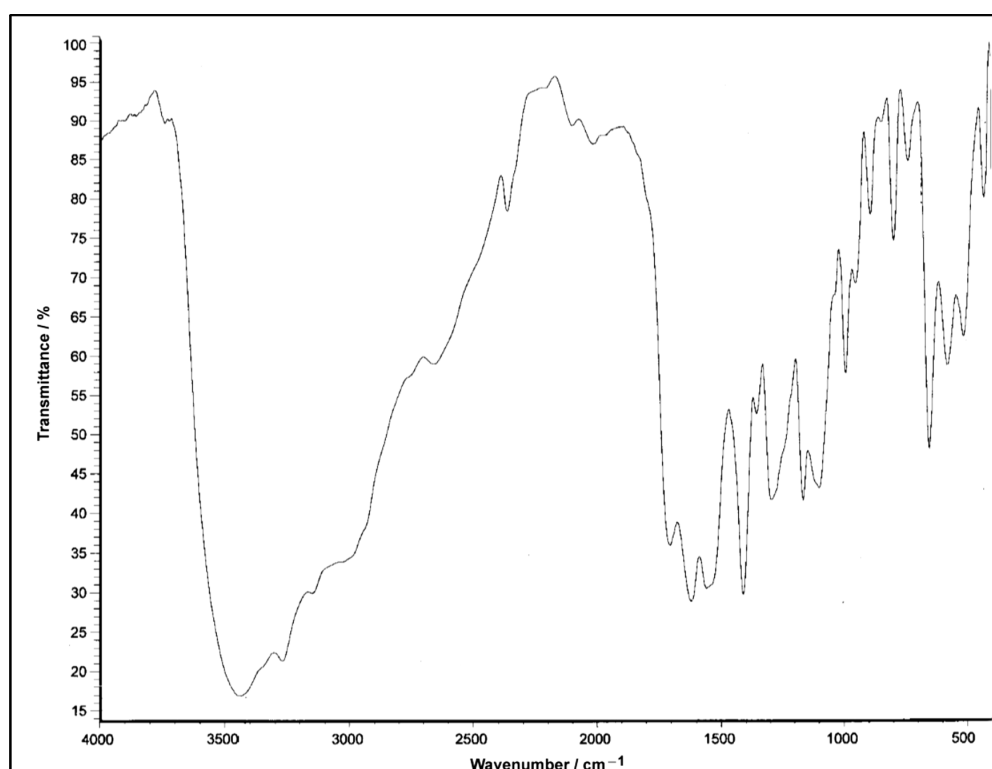


Figure 5 Infrared spectrum of the hydrazinium hydrogensuccinate salt.

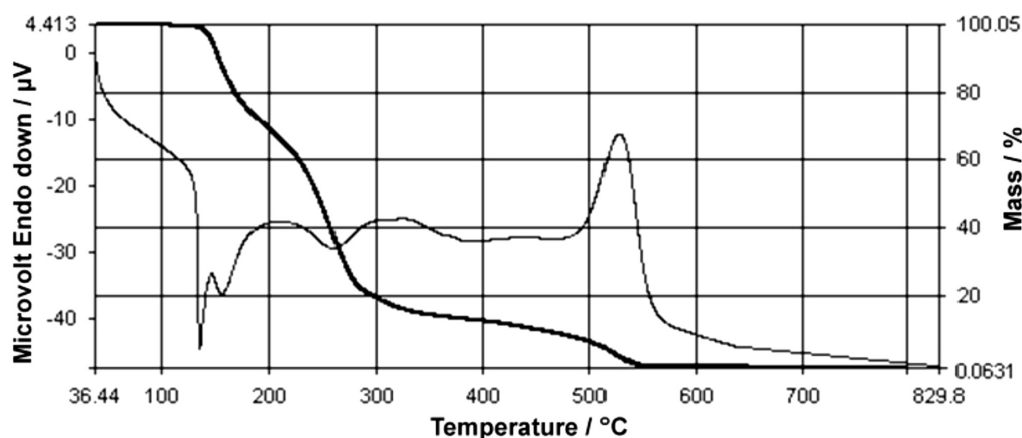


Figure 6 Simultaneous TG-DTA of hydrazinium hydrogensuccinate salt.

Table 1 Crystal data for $N_2H_5OOC(CH_2)_2COOH$.

Empirical formula	$C_4H_{10}N_2O_4$
Formula weight	150.14
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 5.74380(10)$ Å $b = 7.31300(10)$ Å $c = 8.5613(2)$ Å $\alpha = 66.9880(10)^\circ$ $\beta = 74.5840(10)^\circ$ $\gamma = 74.8060(10)^\circ$
Volume	$313.976(10)$ Å ³
Z	2
Density (calculated)	1.588 mg/m ³
Absorption coefficient	0.141 mm ⁻¹
F(000)	160
Crystal size	$0.29 \times 0.17 \times 0.11$ mm ³
Theta range for data collection	2.63 to 27.99°
Index ranges	$-7 \leq h \leq 7, -9 \leq k \leq 9, -11 \leq l \leq 11$
Reflections collected	4926
Independent reflections	1495 [R(int) = 0.0186]
Completeness to theta	27.99° 98.3 %
Absorption correction	None
Max. and min. transmission	0.9847 and 0.9602
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1495 / 0 / 131
Goodness-of-fit on F ²	1.04
Final R indices [I > 2σ(I)]	R1 = 0.0338, wR2 = 0.0830
R indices (all data)	R1 = 0.0431, wR2 = 0.0892
Largest diff. peak and hole	0.342 and -0.288 e. Å ⁻³

(14) Å which is in agreement with the value reported for $N_2H_5HC_2O_4$ ^{24,25} in which the N–N bond length is 1.443 (5) Å. The C–O and C–C bond lengths (Table 2) of the carboxylate groups are in agreement with the corresponding bond distances reported for hydrazinium hydrogenoxalate.^{24,25}

The crystal structure is stabilized through N–H⋯O and O–H⋯O hydrogen bonds. The crystal packing is shown in Fig. 8. The packing consists of infinite chains of anions and cations that are alternatively linked through O–H⋯N and bifurcated N–H⋯O (O1–H1⋯N1, N2–H2C⋯O3 and N2–H2C⋯O4) hydrogen bonding with bond lengths of 2.6638 (14)–3.2191 (14) Å and this chain is connected to adjacent antiparallel chains by N1–H1B⋯O4 hydrogen bonding. These antiparallel chains run across the *bc* plane. Further, the adjacent antiparallel chain pairs are linked through N2–H2E⋯O3 bonding to form a two-

Table 2 Bond lengths/Å and angles/° for $N_2H_5OOC(CH_2)_2COOH$.

O(1)–C(1)	1.3181(15)	O(2)–C(1)–O(1)	122.15(11)
O(2)–C(1)	1.2195(15)	O(2)–C(1)–C(2)	121.93(11)
O(3)–C(4)	1.2626(14)	O(1)–C(1)–C(2)	115.91(10)
O(4)–C(4)	1.2610(15)	C(1)–C(2)–C(3)	116.28(10)
C(1)–C(2)	1.5071(17)	C(4)–C(3)–C(2)	111.78(10)
C(2)–C(3)	1.5247(16)	O(4)–C(4)–O(3)	123.35(11)
C(3)–C(4)	1.5225(17)	O(4)–C(4)–C(3)	117.95(10)
N(1)–N(2)	1.4535(14)	O(3)–C(4)–C(3)	118.67(11)

Table 3 Hydrogen bond lengths/Å and angles/° for $N_2H_5(HOOC(CH_2)_2COO)$.

	D–H	H⋯A	D–H⋯A	D–H⋯A
O–H1⋯N1i	0.99 (2)	1.67 (2)	2.6638 (14)	176 (2)
O1–H1⋯N2i	0.99 (2)	2.61 (2)	3.5059 (14)	149.7 (17)
N1–H1A⋯O2ii	0.915 (19)	2.121 (19)	3.0230 (14)	168.2 (16)
N1–H1B⋯O4	0.902 (18)	2.047 (18)	2.9185 (14)	161.9 (16)
N2–H2C⋯O4iii	0.99 (2)	1.74 (2)	2.7270 (14)	72.8 (16)
N2–H2D⋯O3iv	0.894 (19)	1.963 (19)	2.8310 (14)	163.5 (16)
N2–H2E⋯	0.895 (18)	1.936 (18)	2.7910 (14)	159.2 (16)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y, -z+2$; (iv) $-x, -y, -z+2$; (v) $x, y+1, z$.

dimensional sheet-like structure. These sheets are stacked along the *a* axis through N1–H1A⋯O2 and N2–H2D⋯O3 interactions furnishing a three-dimensional network structure. In simple salts, generally the hydrogen of the carboxylate adopts head to tail O–H⋯O hydrogen bonding leading to one-dimensional chains. Surprisingly, this is absent in this case, whereas the same is effectively present in hydrazinium hydrogen oxalate.²⁴ The OH and NH hydrogen atoms form H-bonds with bond distances D–H = 0.894 (19) to 0.99 (2) Å and H⋯A = 1.67 (2) to 2.61 (2) Å. The hydrazinium nitrogen N2 is bonded to the hydrogens H2C, H2D and H2E with NH distances of 0.99(2), 0.894 (19) and 0.895 (18) Å (Table 3), respectively. Elongation of one of the three NH bonds (N2–H2C bond) is most likely due to the fact that it is *trans* to a strong O–H⋯N hydrogen bond (torsion angle (O1)H1⋯N1–N2–H2C = 179.6°).

4. Conclusions

The reaction of succinic acid with hydrazine hydrate gives the hydrazinium hydrogensuccinate salt. The salt undergoes melting followed by decomposition to give gaseous products.

The crystal structure of hydrazinium hydrogensuccinate has been determined by means of X-ray diffraction. The structure

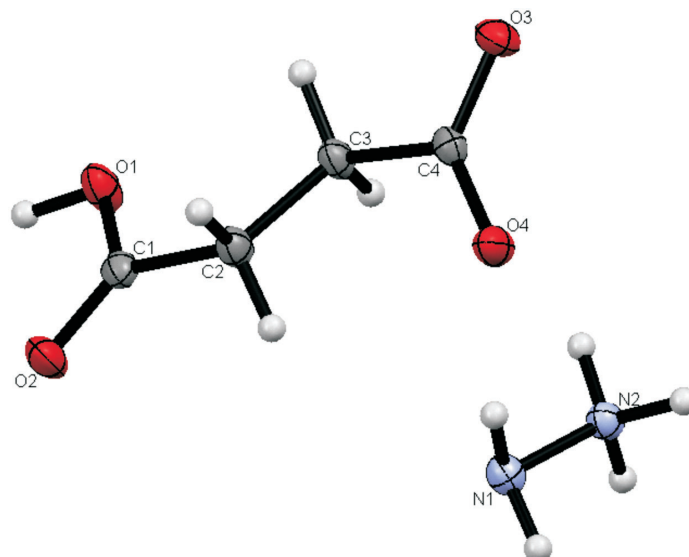


Figure 7 Molecular structure of $\text{N}_2\text{H}_5^+(\text{HOOC}(\text{CH}_2)_2\text{COO})^-$ showing 50 % probability displacement ellipsoids (arbitrary sphere for the H atoms).

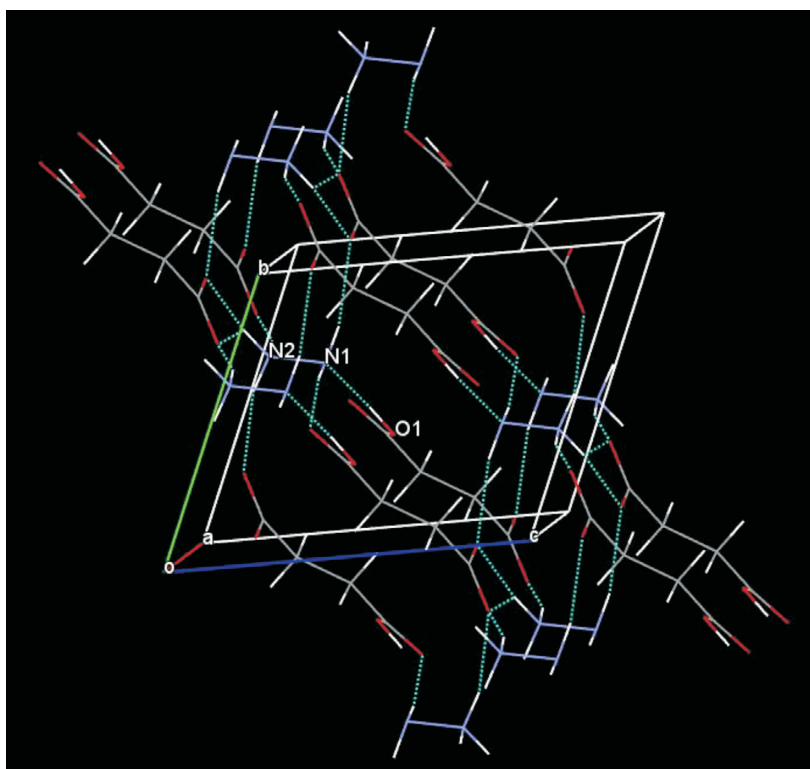


Figure 8 Packing diagram of $\text{N}_2\text{H}_5^+(\text{HOOC}(\text{CH}_2)_2\text{COO})^-$.

contains N_2H_5^+ cations and hydrogen succinate anions, $\text{HOOC}(\text{CH}_2)_2\text{COO}^-$, which are joined by hydrogen bonds. The crystal structure is stabilized through $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. It has been observed that the hydrazinium nitrogen N2 is bonded to the hydrogens H2C, H2D and H2E with NH distances of 0.99 (2), 0.894 (19) and 0.895 (18) Å, respectively. Elongation of one of the three NH bonds (N2-H2C bond) is most likely due to the fact that it is *trans* to a strong $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond (torsion angle $(\text{O1})\text{H1}\cdots\text{N1}-\text{N2}-\text{H2C} = 179.6^\circ$).

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