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Structures of Ethylammonium Hydrogen Succinate and Diethylammonium Hydrogen Succinate at 110 K

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Abstract. $C_2H_5NH_3^+.C_4H_5O_4^-$, $M_r = 163\cdot17$, triclinic, $P\bar{1}$, $a = 8\cdot293$ (1), $b = 9\cdot342$ (6), $c = 10\cdot934$ (2) Å, $\alpha = 88\cdot94$ (3), $\beta = 89\cdot39$ (1), $\gamma = 84\cdot46$ (2)°, $V = 842\cdot9$ (8) Å^3, $Z = 4$, $D_x = 1\cdot286$ g cm^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 1\cdot008$ cm^{-1}, $F(000) = 352$, $T = 110$ K, $R = 0\cdot052$ for 1885 observed reflections. $(C_2H_5)_2NH_2^+.C_4H_5O_4^-$, $M_r = 191\cdot23$, orthorhombic, *Pban*, $a = 12\cdot661$ (2), $b = 10\cdot125$ (1), $c = 8\cdot031$ (1) Å, $V = 1029\cdot5$ (5) Å^3, $Z = 4$, $D_x = 1\cdot234$ g cm^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 0\cdot918$ cm^{-1}, $F(000) = 416$, $T = 110$ K, $R = 0\cdot040$ for 2007 observed reflections. In both compounds the hydrogen succinate ions are linked by very short hydrogen bonds resulting in infinite chains. In ethylammonium hydrogen succinate the chains are formed by two distinct succinate entities which alternate in the structure. They are connected by two short hydrogen bonds, both asymmetric. One hydrogen bond with length 2·483 (4) Å is between a carboxylic acid group and a carboxylate group, while the other short hydrogen bond with length 2·456 (4) Å is between two half ionized, but not identical, COO groups. Diethylammonium hydrogen succinate contains a crystallographically symmetric short hydrogen bond with length 2·4370 (7) Å. The H atom in the short hydrogen bond seems to be best described by two equally populated sites on each side of the center of the
bond. The chains of anions are interconnected by longer hydrogen bonds to the cations in both compounds.

Introduction. The crystal structure determinations of ethylammonium hydrogen succinate (1) and diethylammonium hydrogen succinate (2) have been performed as a continuation of earlier studies of acid salts of malonic acid and succinic acid with special interest in the hydrogen bonding (Kalsbeek & Larsen, 1991). Acid salts of carboxylic acids and dicarboxylic acids have been extensively investigated structurally (Speakman, 1972) and spectroscopically (Hadži, 1965).

One of the main subjects of the research work is to understand the nature of the very short crystallographically symmetric hydrogen bonds linking the anions in infinite chains. Is the H atom effectively centered or is there a dynamical or statistical disorder? The first situation indicates a single minimum potential function for the H atom, the second a double minimum potential function.

Experimental. Suitable crystals for the diffraction studies of (1) and (2) were obtained by slow evaporation from aqueous solutions which contained equivalent molar amounts of succinic acid and the

Table 1. *Crystal data and a summary of results from data reduction and structure refinements*

	Compound (1)	Compound (2)
Crystal size (mm)	0·20 × 0·25 × 0·35	0·25 × 0·25 × 0·35
Intensity data collection		
Maximum $\sin\theta/\lambda$ (Å^{-1})	0·5940	0·9034
Range of h	0–9	0–14
Range of k	$\overline{11}$–11	0–18
Range of l	$\overline{12}$–12	$\overline{17}$–22
Standard reflections	100, 001, 10$\overline{1}$	001, 200, 110
Type of scan	ω–2θ scan	ω–2θ scan
Number of measured reflections	3357	4216
Structure refinement		
Number of unique reflections	2956	3203
Number of reflections used in the refinement	1885	2007
Criterion for significance	$I/\sigma(I) > 4$	$I/\sigma(I) > 2$
Number of variables	277	96
Weights w^{-1}	$\sigma_{cs}^2(F) + 0·0009|F|^2$	$\sigma_{cs}^2(F) + 0·0004|F|^2$
R	0·052	0·040
wR	0·088	0·046
S	2·286	1·276
Maximum shift/e.s.d.	0·01	0·00
Maximum and minimum $\Delta\rho$ (e Å^{-3})	0·318, −0·300	0·292, −0·317

respective amine (ethylamine and diethylamine). Both compounds form colorless needle-shaped crystals. The data collection was performed at 110 K using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\overline{\alpha}$ radiation. Unit-cell dimensions were determined from a least-squares refinement of 22 reflections with θ in the range 15·3–16·6° (1) and 15·4–23·4° (2). The different experimental conditions and results from refinements are summarized in Table 1. Data reduction included Lp corrections. The remeasurement of three standard reflections every 10 000 s showed no significant change in intensity during exposure time. No corrections for decay and absorption were performed. The symmetry equivalent reflections were averaged giving $R_{int} = 0·017$ for (1) and 0·016 for (2).

Both structures were solved by direct methods with the program *SHELXS*86 (Sheldrick, 1990) and refined using the full-matrix least-squares method minimizing $\Sigma w(|F_o| - |F_c|)^2$. Using $I/\sigma(I) > 2$ and weights $w^{-1} = \sigma_{cs}^2(F) + 0·0004|F|^2$ in the refinement of the structure for (1) led to a final $R = 0·057$. The diffraction from the crystal of (1) resulted in broad reflections and probably a scan width which was too small had been chosen. This affected weak reflections relatively more than strong reflections. Using $I/\sigma(I) > 4$ and weights $w^{-1} = \sigma_{cs}^2(F) + 0·0009|F|^2$ reduced this problem and led to a final $R = 0·052$. The positions of the H atoms were shown clearly in the difference Fourier electron density maps. Their positional parameters were included in the refinement for (1), while both positional and displacement parameters for the H atoms were refined for (2).

As performed earlier by Kalsbeek & Larsen (1991), two refinement models were examined for the position of the H atom in the short hydrogen bond

in (2). In agreement with their observations the displacement parameter was much larger [$B = 6·2$ (7) Å^2] when the H atom was placed in the special position, than when it was in a general position corresponding to two half populated sites on each side of the center of the hydrogen bond, $B = 3·6$ (6) Å^2. The separation between the two half populated H-atom sites is 0·58 (4) Å.

All calculations except the structure determinations were performed with the Enraf–Nonius *SDP* program system (Enraf–Nonius, 1985). Scattering factor values for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and used as contained in the program system.

Discussion. The final positional parameters and equivalent isotropic displacement parameters are given in Table 2.* Ethylammonium hydrogen succinate (1) forms triclinic crystals with two formula units in the asymmetric unit and none of the ions bound by crystallographic symmetry. This is rare since most other investigated hydrogen succinate salts contain both anion and cation on crystallographic symmetry elements (McAdam, Currie & Speakman, 1971; McAdam & Speakman, 1971; Küppers, 1982; Kalsbeek & Larsen, 1991). In the structure of diethylammonium hydrogen succinate (2) both anion and cation are found on crystallographic symmetry elements as would be expected (the second choice of origin, on $\overline{1}$, has been used for space group *Pban*).

The chains of anions in the structure of (1) are formed by two different succinate entities that are connected by two short asymmetric hydrogen bonds illustrated in Fig. 1. From Tables 3 and 4 it can be seen that one hydrogen bond with length 2·483 (4) Å is between a carboxylic acid group C(14)—O(13)— O(14) and a carboxylate group C(21)—O(21)— O(22). The other hydrogen bond of length 2·456 (4) Å is significantly shorter and between two very similar, but not identical, COO groups. Table 3 illustrates that the geometry of these two COO groups is intermediate between that of a real carboxylic acid group and a carboxylate group. This resembles Speakman's (1972) type A_2 salts, where the two COO groups are equivalent by crystallographic symmetry. From the final difference Fourier map H(11) in the shortest hydrogen bond O(11)—O(23) was found closest to O(11) making C(11)—O(11)—O(12) a carboxylic acid group. This is surprising if one considers the similarity of the two COO groups.

Table 2. Final positional and equivalent isotropic displacement parameters (Å²)

H atoms were not included in the refinement in (1) and refined isotropically in (2). U_{eq} is defined as $(1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Compound (1)				
O(11)	0·1278 (4)	0·3905 (3)	−0·2968 (3)	0·0171 (8)
O(12)	−0·1144 (4)	0·4752 (3)	−0·3662 (3)	0·0182 (8)
O(13)	0·0407 (4)	0·0995 (3)	−0·6636 (3)	0·0176 (8)
O(14)	−0·2279 (4)	0·0894 (3)	−0·6710 (3)	0·0185 (8)
C(11)	0·0060 (5)	0·3861 (5)	−0·3675 (4)	0·0139 (10)
C(12)	0·0211 (6)	0·2634 (5)	−0·4558 (4)	0·0171 (11)
C(13)	−0·1257 (5)	0·2559 (5)	−0·5362 (4)	0·0147 (10)
C(14)	−0·1085 (5)	0·1394 (5)	−0·6300 (4)	0·0161 (10)
O(21)	0·0725 (4)	0·9047 (3)	0·1840 (3)	0·0180 (8)
O(22)	0·2032 (4)	1·0566 (3)	0·0693 (3)	0·0168 (8)
O(23)	0·1087 (4)	0·5928 (3)	−0·1553 (3)	0·0155 (8)
O(24)	0·2471 (4)	0·4334 (3)	−0·0322 (3)	0·0185 (8)
C(21)	0·1530 (5)	0·9359 (5)	0·0902 (4)	0·0115 (10)
C(22)	0·1882 (5)	0·8188 (5)	−0·0050 (4)	0·0139 (10)
C(23)	0·1701 (6)	0·6678 (5)	0·0452 (4)	0·0196 (11)
C(24)	0·1784 (5)	0·5547 (5)	−0·0525 (4)	0·0127 (10)
N(1)	0·2719 (4)	0·1402 (4)	0·8270 (3)	0·0158 (9)
C(31)	0·4489 (5)	0·1538 (5)	0·8216 (4)	0·0210 (11)
C(32)	0·5092 (6)	0·1703 (6)	0·6947 (5)	0·0317 (13)
N(2)	0·2389 (4)	0·3134 (4)	0·2015 (3)	0·0163 (9)
C(41)	0·4028 (5)	0·2743 (5)	0·2557 (4)	0·0214 (11)
C(42)	0·4893 (6)	0·4076 (6)	0·2710 (5)	0·0329 (13)
H(11)	0·132 (6)	0·462 (5)	−0·281 (4)	0·025
H(21)	0·051 (6)	0·042 (5)	−0·722 (4)	0·025
H(12)	0·126 (6)	0·262 (5)	−0·512 (4)	0·025
H(13)	0·043 (6)	0·184 (5)	−0·406 (4)	0·025
H(14)	−0·137 (6)	0·334 (5)	−0·571 (4)	0·025
H(15)	−0·223 (6)	0·246 (5)	−0·492 (4)	0·025
H(22)	0·308 (6)	0·823 (5)	−0·030 (4)	0·025
H(23)	0·121 (6)	0·842 (5)	−0·072 (4)	0·025
H(24)	0·068 (6)	0·667 (5)	0·082 (4)	0·025
H(25)	0·267 (6)	0·628 (5)	0·108 (4)	0·025
H(31)	0·212 (6)	0·228 (5)	0·794 (4)	0·025
H(32)	0·249 (6)	0·071 (5)	0·798 (4)	0·025
H(33)	0·246 (6)	0·108 (5)	0·906 (4)	0·025
H(34)	0·451 (6)	0·253 (5)	0·872 (4)	0·025
H(35)	0·516 (6)	0·065 (5)	0·875 (4)	0·025
H(36)	0·487 (6)	0·080 (5)	0·643 (4)	0·025
H(37)	0·625 (6)	0·189 (5)	0·697 (4)	0·025
H(38)	0·449 (6)	0·259 (5)	0·643 (4)	0·025
H(41)	0·167 (6)	0·225 (5)	0·176 (4)	0·025
H(42)	0·240 (6)	0·367 (5)	0·118 (4)	0·025
H(43)	0·190 (6)	0·372 (5)	0·239 (4)	0·025
H(44)	0·460 (6)	0·211 (5)	0·194 (4)	0·025
H(45)	0·403 (6)	0·219 (5)	0·337 (4)	0·025
H(46)	0·433 (6)	0·469 (5)	0·353 (4)	0·025
H(47)	0·507 (6)	0·458 (5)	0·200 (4)	0·025
H(48)	0·582 (6)	0·386 (5)	0·312 (4)	0·025
Compound (2)				
O(1)	0·70554 (4)	0·04905 (6)	0·36544 (6)	0·0154 (1)
O(2)	0·85597 (5)	0·12262 (6)	0·25320 (6)	0·0154 (1)
C(1)	0·76439 (6)	0·08194 (7)	0·24093 (8)	0·0101 (1)
C(2)	0·71168 (6)	0·06820 (8)	0·07277 (8)	0·0124 (1)
N	0·52667 (7)	0·25000	0·50000	0·0120 (1)
C(3)	0·46348 (6)	0·15863 (8)	0·39198 (10)	0·0144 (1)
C(4)	0·40675 (7)	0·23236 (9)	0·25425 (11)	0·0208 (1)
H(1)	0·7398 (32)	0·0428 (22)	0·4675 (37)	0·046 (8)
H(2)	0·6659 (9)	−0·0136 (13)	0·0722 (14)	0·022 (3)
H(3)	0·6593 (10)	0·1418 (12)	0·0645 (14)	0·025 (4)
H(4)	0·5680 (11)	0·1976 (12)	0·5676 (15)	0·028 (3)
H(5)	0·4133 (9)	0·1096 (11)	0·4655 (15)	0·018 (3)
H(6)	0·5120 (10)	0·0966 (12)	0·3486 (15)	0·022 (3)
H(7)	0·3701 (11)	0·1644 (14)	0·1814 (18)	0·035 (4)
H(8)	0·4564 (10)	0·2834 (13)	0·1856 (17)	0·032 (4)
H(9)	0·3538 (11)	0·2980 (15)	0·2985 (18)	0·039 (4)

From the location of H(11) (1) could be formulated as containing one succinic acid molecule and one succinate ion. It is still preferable to describe the investigated compound as ethylammonium hydrogen succinate, as the dimensions of the COO groups are found to be more decisive than the location of one H atom. Asymmetric hydrogen bonds are generally

Table 3. Bond lengths (Å) and bond angles (°)

Anions
Compound (1)

	j = 1	j = 2		j = 1	j = 2
C(j1)—O(j1)	1·283 (5)	1·263 (5)	O(j3)—C(j4)—C(j3)	114·8 (4)	116·2 (4)
C(j1)—O(j2)	1·236 (5)	1·255 (5)	O(j4)—C(j4)—C(j3)	121·0 (4)	120·4 (4)
C(j4)—O(j3)	1·308 (5)	1·298 (5)	C(j1)—C(j2)	1·507 (6)	1·529 (6)
C(j4)—O(j4)	1·227 (6)	1·236 (5)	C(j2)—C(j3)	1·517 (6)	1·524 (6)
O(j1)—C(j1)—O(j2)	123·8 (4)	124·5 (4)	C(j3)—C(j4)	1·505 (6)	1·513 (6)
O(j1)—C(j1)—C(j2)	114·6 (4)	117·3 (4)	C(j1)—C(j2)—C(j3)	114·4 (4)	113·3 (3)
O(j2)—C(j1)—C(j2)	121·6 (4)	118·2 (4)	C(j2)—C(j3)—C(j4)	115·0 (4)	113·5 (4)
O(j3)—C(j4)—O(j4)	124·2 (4)	123·4 (4)			

Compound (2)

C(1)—O(1)	1·2908 (9)	O(2)—C(1)—C(2)	121·09 (6)
C(1)—O(2)	1·2344 (9)	C(1)—C(2)	1·5129 (10)
O(1)—C(1)—O(2)	124·50 (6)	C(2)—C(2')	1·5191 (10)
O(1)—C(1)—C(2)	114·41 (6)	C(1)—C(2)—C(2')	113·89 (6)

Cations
Compound (1)

N(1)—C(31)	1·486 (6)	N(2)—C(41)	1·498 (6)
C(31)—C(32)	1·481 (7)	C(41)—C(42)	1·508 (7)
N(1)—C(31)—C(32)	112·4 (4)	N(2)—C(41)—C(42)	110·1 (4)

Compound (2)

N—C(3)	1·4996 (9)	C(3)—N—C(3ⁱⁱ)	115·50 (7)
C(3)—C(4)	1·5155 (12)	N—C(3)—C(4)	111·79 (6)

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

Table 4. Hydrogen-bond geometry (Å,°) where A = donor atom and B = acceptor atom

A—H⋯B	A⋯B	A—H	H⋯B	A—H⋯B
Compound (1)				
O(11)—H(11)⋯O(23)	2·456 (4)	0·69 (5)	1·85 (5)	145 (5)
O(13)—H(21)⋯O(21ⁱ)	2·483 (4)	0·84 (5)	1·65 (5)	169 (5)
N(1)—H(31)⋯O(11ⁱⁱ)	2·848 (4)	0·98 (5)	1·88 (5)	168 (4)
N(1)—H(32)⋯O(14ⁱⁱⁱ)	2·818 (5)	0·77 (5)	2·08 (5)	161 (5)
N(1)—H(33)⋯O(22ⁱⱽ)	2·816 (5)	0·94 (5)	1·88 (5)	175 (4)
N(2)—H(41)⋯O(22ⱽ)	2·864 (5)	1·10 (5)	1·97 (5)	135 (4)
N(2)—H(42)⋯O(24)	2·773 (5)	1·03 (5)	1·75 (5)	172 (4)
N(2)—H(43)⋯O(12ⱽⁱ)	2·813 (5)	0·77 (5)	2·06 (5)	165 (5)
Compound (2)				
O(1)—H(1)⋯O(1ⱽⁱⁱ)	2·4370 (7)	0·93 (3)	1·51 (3)	174 (2)
N—H(4)⋯O(2ⱽⁱⁱ)	2·7928 (7)	0·92 (1)	1·89 (1)	166 (1)

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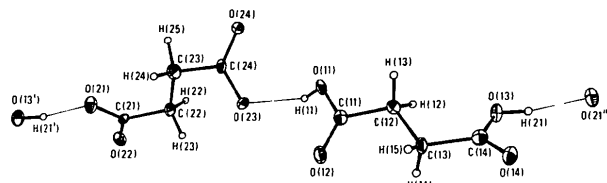

Fig. 1. ORTEP drawing of the two succinate entities found in (1), illustrating the atom-numbering scheme and the two short hydrogen bonds. The thermal ellipsoids inclose 50% probability, the H atoms are drawn as spheres. (i) $x, y + 1, z + 1$; (ii) $x, y - 1, z - 1$.

longer than symmetric hydrogen bonds. This fits well with the observation that the hydrogen bond O(13)—O(21) between the carboxylic acid group and the carboxylate group is longer [2·483 (4) Å] than that, O(11)—O(23) with length 2·456 (4) Å, between the more equivalent COO groups. This value is longer than the truly symmetric short hydrogen bond found in the crystal structure of (2), which is 2·4370 (7) Å.

In diethylammonium hydrogen succinate (2) two-fold rotation axes pass through the hydrogen succinate ion and the diethylammonium ion. This arrangement in the crystal implies that the very short hydrogen bond linking the anions into infinite chains is across a crystallographic twofold axis. The short hydrogen bond is symmetric due to crystallographic symmetry and a type A_2 salt according to Speakman (1972). Like the earlier investigated hydrogen succinate salts of methylammonium and dimethylammonium (Kalsbeek & Larsen, 1991) and of lithium (Küppers, 1982) the H atom in the short hydrogen bond in (2) is best described by two half populated H atoms placed on each side of the twofold axis. Kalsbeek & Larsen (1991) discussed the crystallographic site symmetry of the hydrogen succinate ion in different salts, which is either $\bar{1}$ or $2/m$. In the investigated diethylammonium salt the site symmetry of the anion is 2. The hydrogen succinate ion is illustrated in Fig. 2. In this salt the deviation from 180° for the torsion angle O(1)—C(1)—C(2)—C(2') of the anion is larger than in the earlier discussed salts, 163° compared to 177–180°. This larger deviation from 180° is permitted by the change in site symmetry of the anion. The conformation of the hydrogen succinate entities in the structure of (1) differ significantly from these observations as illustrated by the torsion angles O(11)—C(11)—C(12)—C(13), O(13)—C(14)—C(13)—C(12), O(21)—C(21)—C(22)—C(23) and O(23)—C(24)—C(23)—C(22) being 178, 26, 19 and 38° respectively.

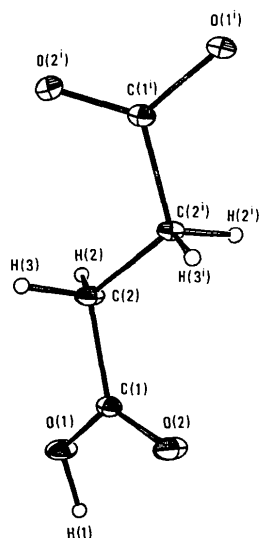The packing in the two structures is illustrated by the stereo pairs drawn in Fig. 3. In both compounds longer hydrogen bonds interconnect the chains of anions to the cations. The geometry of the hydrogen bonds is given in Table 4. In (1) all six H atoms attached to the two N atoms are involved in hydrogen bonding. Three of the N—O distances are equivalent [2·813 (5)–2·818 (5) Å], these all connect an N atom to an O atom not involved in the short hydrogen bonds. The equivalent hydrogen bond in (2) has the magnitude 2·7928 (7) Å. The remaining three hydrogen bonds in (1) consist of two longer and one shorter hydrogen bond. The two longer hydrogen bonds of 2·848 (4) and 2·864 (5) Å are to O atoms, which are involved in two hydrogen bonds, namely O(11) and O(22). This can explain why the N—O distances are longer and why the linearities of the hydrogen bonds O(11)—O(23) and N(2)—O(22) show great variation from the usual linear hydrogen bonds, the angles being 145 (5) and 135 (4)° respectively.

In the structure of (1) one of the O atoms, O(11), involved in the shortest hydrogen bond linking the anions in chains is also an acceptor atom in a hydrogen bond to one of the cations. This is not observed in other acid salts of malonic acid and succinic acid, but a similar observation was made by Currie, Speakman, Kanters & Kroon (1975) in the structure of potassium hydrogen *meso*-tartrate. In this compound the O atoms in one of the two crystallographically symmetric hydrogen bonds accept a second H atom. This weakens the bond which has a length of 2·483 (2) compared to
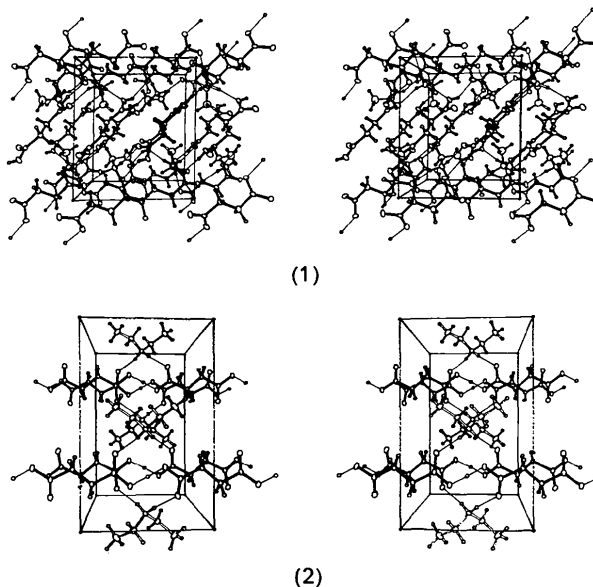

Fig. 2. *ORTEP* drawing of the hydrogen succinate ion found in (2), made as described in Fig. 1 and illustrating the atom-numbering scheme. (i) $-x + \frac{3}{2}, y, -z$.

(1)

(2)

Fig. 3. Stereo drawings of (1) and (2). (1) is seen along the *a* axis, the *b* axis is horizontal and the *c* axis vertical. (2) is seen along the *b* axis, the *a* axis is vertical and the *c* axis horizontal. In both drawings the anions are shown with filled bonds and the cations with open bonds.

2·452 (2) Å for the second hydrogen bond. In the structure of (1) the opposite is observed, O(11)—O(23) [2·456 (4) Å] being shorter than O(13)—O(21) [2·483 (4) Å].

The C—C distances in each succinate residue in (1) are internally equivalent within the standard deviations, but there is a difference between the two residues. The mean C—C distance in the first residue is 1·510 compared to 1·522 Å in the second. The same mean C—C distance in (2) is 1·5150 Å. The longer mean C—C distance in the second residue in (1) can be explained by the observation that O(24) in this residue is involved in the shortest N—O hydrogen bond [2·773 (5) Å] in (1), thereby stretching the succinate entity.

The dimensions of the cations are listed in Table 3. The three N—C distances are equivalent within the standard deviations. The C—C distances for the second residue in (1) and (2) are equivalent, while the C—C distance for the first residue is slightly smaller.

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The Structure of a Benzoquinone Diimine N,N'-Dioxide Derivative

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Abstract. N,N'-Di-tert-butyl-1,4-benzoquinone diimine N,N'-dioxide, $C_{14}H_{22}N_2O_2$, $M_r = 250 \cdot 34$, monoclinic, $P2_1/c$, $a = 10 \cdot 5832$ (8), $b = 11 \cdot 8392$ (10), $c = 11 \cdot 6698$ (7) Å, $\beta = 96 \cdot 714$ (6)°, $V = 1452 \cdot 2$ (2) Å^3, $Z = 4$, $D_x = 1 \cdot 145$ g cm^{-3}, λ(Mo $K\overline{\alpha}$, graphite monochromated) $= 0 \cdot 71069$ Å, $\mu = 0 \cdot 718$ cm^{-1}, $F(000) = 544$, room temperature, $R = 0 \cdot 046$ for 1440 observed reflections. The molecules lie on an inversion centre, with the independent unit formed by two different half molecules. The N atoms show an sp^2 hybridization so that, apart from the tert-butyl group, the molecule is planar. The pattern of bond lengths, in particular the ring deformation, suggests an important contribution of the quinone diimine limiting form to the possible resonating structures.

Introduction. The reaction of 1,4-dinitrobenzene (DNB) with alkyl Grignard reagents leads predomi-

nantly to ring alkylated products from conjugate addition to the nitro group (Bartoli, Dalpozzo & Grossi, 1989). However, when DNB was reacted with tert-butylmagnesium chloride only traces of the alkylated product were found (Dalpozzo, Grossi & Ganazzoli, 1991). Upon quenching with saturated ammonium chloride solution the only characterizable product was the title compound N,N'-di-tert-butyl-1,4-benzoquinone diimine N,N'-dioxide, recovered in low yields. On the other hand, ESR analysis revealed at least three radical species (Lemaire, Marechal, Ramasseul & Rassat, 1965; Barbarella & Rassat, 1969; Dalpozzo et al., 1991). Upon reduction with lithium aluminium hydride and palladium on charcoal, N-(4-tert-butylphenyl)-N-tert-butyl-hydroxylamine and the title compound could be isolated in comparable good yields. While the former compound was recognized as the parent of one of the radical species observed, the latter cannot account for any of them, although it might exist in a diamagnetic quinonic form or in a dinitroxide form. To

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