

Lithium Hydrogen Adipate, $\text{Li}^+\cdot\text{C}_6\text{H}_9\text{O}_4^-$

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Abstract. $M_r = 152.1$, monoclinic, $P2_1/c$, $a = 8.222(1)$, $b = 7.448(1)$, $c = 11.569(1)$ Å, $\beta = 92.19(1)^\circ$, $V = 707.9(1)$ Å³, $Z = 4$, $D_m = 1.424(2)$, $D_x = 1.427$ g cm⁻³, $\text{Cu K}\alpha_1$, $\lambda = 1.54051$ Å, $\mu = 2.52$ cm⁻¹, $F(000) = 320$, $T = 293$ K, $R = 0.048$ for 1329 unique reflections. The molecules are arranged in layers parallel to (100) with hydrocarbon chains sandwiched between polar regions consisting of carboxylic acid, carboxylate and Li ions. The Li ion is tetrahedrally coordinated by O atoms, one of the Li...O distances being short [1.896(3) Å]. The carboxylic acid and carboxylate groups cannot be distinguished from their C—O bond lengths. Each has one long [1.289, 1.290(2) Å] and one short [1.231, 1.233(2) Å] C—O bond. The O atoms of the long C—O bonds are bridged by a short asymmetric H-bond [O...O 2.486(2), H...O 1.47(3) Å, O—H...O 166(3)°].

Introduction. It is characteristic of polar lipids with long aliphatic chains that the molecules assemble in layers with the hydrocarbon inside and the polar groups at the outer surfaces. Because of the importance of polar lipids as surfactants and constituents of biomembranes, these structures are of considerable interest. Unfortunately, there are two major obstacles in studying lipids by crystallographic methods. Large good-quality crystals are difficult to grow and the structure determinations are often complicated by the subcell symmetry of the chain packing. For the determination of the charge density and electrostatic potential by X-ray and neutron diffraction, the first obstacle is formidable. Thus we turn to polar lipids with shorter chains for which accurate high-resolution diffraction data might be obtained more readily.

The aliphatic dicarboxylic acids $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, $n = 4$ through 8, their salts and acid salts might be suitable for systematic study. Adipic, suberic and sebacic acids ($n = 4, 6, 8$) have clearly recognizable lipid layers in their crystal structures (Housty & Hospital, 1965*a,b*; 1967). However, none of the crystal structures of their salts have been determined, except for hexamethyldiammonium adipate (Brown, 1966). We present the first results of a crystallographic survey of these salts, and conclude that a charge-density study of lithium hydrogen adipate (Fig. 1) would be feasible, although there might be difficulties due to extinction.

Experimental. Hard (100) plates, decomposing at ~ 580 K, grown from aqueous solution after reaction of LiOH and adipic acid. Crystal density measured by flotation in butyl bromide/ CH_3Br . Data collection by Enraf-Nonius CAD-4 automatic diffractometer (Ni-filtered $\text{Cu K}\alpha$ radiation), crystal $0.06 \times 0.46 \times 0.52$ mm. Cell parameters obtained by least-squares fit of $\sin^2\theta$ for 38 reflections, $29 < |\pm\theta| < 46^\circ$. Intensities measured by $\omega/2\theta$ scans for 1728 reflections in a quadrant with $\sin\theta/\lambda < 0.61$ Å⁻¹. $h = -9$ – 10 , $k = 0$ – 9 , $l = 0$ – 14 . 3 check reflections gave max. variation of 2% of mean intensity. Absorption corrections by Gaussian approximation (Busing & Levy, 1957) gave transmission factors 0.909 to 0.985. Averaging between symmetry-related reflections and multiple observations gave the agreement $R_{\text{int}} = 0.008$, leaving 1329 reflections. Variances of measured intensities assumed as $\sigma^2(I) = \sigma^2_{\text{count}}(I) + (0.02I)^2$, where $\sigma^2_{\text{count}}(I)$ is the variance based on counting statistics. Phase problem solved by *MULTAN* (Germain, Main & Woolfson, 1971). Refinement minimized $\sum w(|F_o| - |F_c|)^2$ by full-matrix least squares (Craven & Weber, 1977). Atomic scattering factors from Cromer & Waber (1965) for O and C, from Stewart (1970) for Li⁺, and from Stewart, Davidson & Simpson (1965) for H. Final agreement for all 1329 reflections gave $R = 0.048$, $R_w = 0.055$, $S = 3.32$, $w = \sigma^{-2}(F_o)$. Extinction was severe with $g = 1.12(7) \times 10^{-4}$ rad⁻¹ (Becker & Coppens, 1974). The reflection most affected was 112, with correction $0.42 |F_c|$. Parameter Δ/σ 0.67 (max.) and 0.03 (mean). Residual electron density in the range

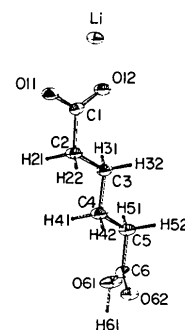


Fig. 1. The molecular structure of lithium hydrogen adipate. Thermal ellipsoids have 50% probability for including the atom centers (Johnson, 1976).

-0.32 to $+0.31 \text{ e } \text{Å}^{-3}$. Atomic positional and thermal parameters with their e.s.d.'s are given in Table 1, and bond distances, bond angles, and torsion angles are in Table 2. The crystal structure is shown in Fig. 2.*

Discussion. The C—C bond lengths at the ends of the adipate chain [1.503, 1.515 (2) Å] appear to be significantly shorter than those near the middle [1.528, 1.524 (2) Å]. However, as in the crystal structure of γ -aminobutyric acid (Weber, Craven & McMullan, 1983), the effect may be due to anisotropic thermal motion. It would be difficult to find the correction in this case, since the simple rigid-body model would be inappropriate. The C—H bond lengths, ranging from 0.96 to 1.03 (2) Å, and the methylene bond angles involving H atoms, which range from 106 (2) to 111 (1)°, are not exceptional.

Unexpectedly, the carboxylate group at C(1) and the carboxylic acid group at C(6) have pairs of C—O bond lengths which are the same within experimental error. In each group there is one long C—O bond [1.289, 1.290 (2) Å] and one short [1.231, 1.233 (2) Å]. This is in contrast to the C—O bond lengths in the crystal structure of lithium hydrogen oxalate (Thomas, 1972) which are 1.309, 1.210 (1) Å in the carboxylic acid group and more nearly equal [1.240, 1.259 (1) Å] in the carboxylate group. Since the two long C—O bonds involve the two O atoms, O(61) and O(11), which are bridged by the H bond (Fig. 2, Table 2), we considered the possibility that the H atom might be disordered, thereby making the carboxylic acid and carboxylate group indistinguishable. After the structure refinement, the hydroxyl H atom was omitted from the calculated

* An additional chain-packing figure, tables of anisotropic thermal parameters, bond distances and angles involving H atoms, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39334 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

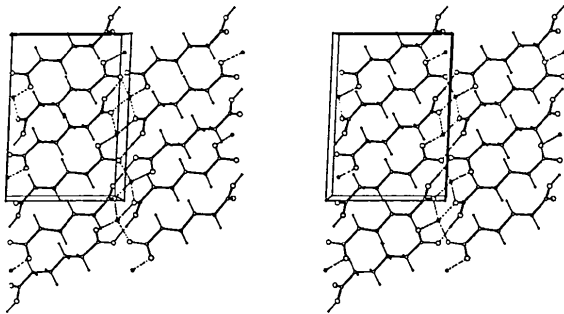


Fig. 2. Stereoview of the crystal structure seen along *b* (Johnson, 1976). The *a* axis is directed from left to right and the *c* axis from top to bottom of the page. Atoms are represented as spheres of decreasing size for O, C, H, with Li ions solid.

Table 1. Atomic coordinates ($\times 10^4$ for non-H atoms, $\times 10^3$ for H atoms) and isotropic temperature factors ($\text{Å}^2 \times 10^3$; $\text{Å}^2 \times 10^2$ for H atoms)

For non-H atoms, $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos\beta)$, where U_{ij} are given by the temperature factor expression

$$T = \exp\{-2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij}\}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
C(1)	1811 (2)	2257 (2)	2461 (1)	236 (8)
C(2)	3039 (2)	1836 (3)	1556 (2)	295 (10)
C(3)	4603 (2)	2909 (3)	1652 (2)	296 (10)
C(4)	5746 (2)	2414 (3)	696 (2)	309 (10)
C(5)	7282 (2)	3569 (3)	727 (2)	278 (9)
C(6)	8422 (2)	3004 (3)	-190 (1)	240 (8)
O(11)	471 (1)	1361 (2)	2369 (1)	306 (7)
O(12)	2104 (2)	3378 (2)	3223 (1)	312 (7)
O(61)	8655 (2)	4164 (2)	-995 (1)	414 (8)
O(62)	9053 (1)	1502 (2)	-170 (1)	278 (7)
Li	489 (3)	4869 (4)	3850 (2)	285 (15)
H(21)	246 (3)	201 (3)	77 (2)	46 (6)
H(22)	334 (3)	49 (3)	161 (2)	47 (6)
H(31)	433 (3)	421 (3)	159 (2)	41 (6)
H(32)	515 (3)	272 (3)	240 (2)	43 (6)
H(41)	517 (3)	253 (3)	-7 (2)	51 (7)
H(42)	607 (3)	111 (3)	77 (2)	41 (6)
H(51)	700 (3)	481 (3)	63 (2)	45 (6)
H(52)	788 (3)	341 (3)	148 (2)	41 (6)
H(61)	942 (4)	376 (4)	-164 (3)	86 (10)

Table 2. Interatomic distances (Å) and valence and torsion angles (°)

C(1)—O(11)	1.289 (2)	C(2)—C(1)—O(11)	115.2 (1)
C(1)—O(12)	1.231 (2)	C(2)—C(1)—O(12)	121.2 (2)
C(1)—C(2)	1.515 (2)	O(11)—C(1)—O(12)	123.6 (2)
C(2)—C(3)	1.515 (3)	C(1)—C(2)—C(3)	115.3 (2)
C(3)—C(4)	1.524 (3)	C(2)—C(3)—C(4)	111.4 (2)
C(4)—C(5)	1.528 (2)	C(3)—C(4)—C(5)	112.3 (2)
C(5)—C(6)	1.503 (2)	C(4)—C(5)—C(6)	113.3 (2)
C(6)—O(61)	1.290 (2)	C(5)—C(6)—O(61)	115.8 (2)
C(6)—O(62)	1.233 (2)	C(5)—C(6)—O(62)	120.9 (2)
O(61)—H(61)	1.04 (3)	O(61)—C(6)—O(62)	123.2 (2)
Li—O(11 ⁱⁱ)	1.940 (3)		
Li—O(12)	1.896 (3)	O(12)—Li—O(11 ⁱⁱ)	109.2 (2)
Li—O(62 ^{iv})	1.955 (3)	O(11 ⁱⁱ)—Li—O(62 ^{iv})	105.7 (1)
Li—O(62 ⁱⁱⁱ)	1.977 (3)	O(11 ⁱⁱ)—Li—O(62 ⁱⁱⁱ)	118.9 (2)
		O(12)—Li—O(62 ^{iv})	122.7 (2)
O(61)···O(11 ⁱ)	2.486 (2)	O(12)—Li—O(62 ⁱⁱⁱ)	111.3 (2)
H(61)···O(11 ⁱ)	1.47 (3)	O(62 ^{iv})—Li—O(62 ⁱⁱⁱ)	88.6 (1)
H(22)···H(32 ^v)	2.65 (3)		
C(1)···C(5 ^v)	3.518 (2)	O(61)—H(61)—O(11 ⁱ)	166 (3)
O(11)—C(1)—C(2)—C(3)	179.1 (2)		
O(12)—C(1)—C(2)—C(3)	-1.1 (2)		
C(1)—C(2)—C(3)—C(4)	-179.1 (2)		
C(2)—C(3)—C(4)—C(5)	176.2 (2)		
C(3)—C(4)—C(5)—C(6)	177.5 (2)		
C(4)—C(5)—C(6)—O(61)	114.5 (2)		
C(4)—C(5)—C(6)—O(62)	-64.0 (2)		
C(5)—C(6)—O(61)—H(61)	-178 (2)		

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

structure factors and the resulting residual electron density was obtained. The largest peak [0.49 (2) $\text{e } \text{Å}^{-3}$] corresponded to the H atom forming a hydroxyl group O(61)—H(61). There was no indication of disordering or elongation of the peak along the H bond towards the

other O atom, O(11). The relative mean square displacements of atoms along the covalent bonds of the molecule were calculated from the atomic anisotropic thermal parameters. A significantly non-zero value for a bond would indicate either a non-rigid stretching vibration or possible disorder with respect to structures with small differences in bond length. The only significant value, $0.0356(12) \text{ \AA}^2$, was obtained for the C(6)—O(61) bond, the value for C(1)—O(11) being $0.0020(11) \text{ \AA}^2$. Since these two m.s. displacements are not comparable in magnitude and the H atom is bonded to O(61), it is concluded that the crystal structure is ordered and has the carboxylic acid group at the C(6) end of the adipate chain. The relative m.s. displacement along the C(6)—O(61) bond is attributed to non-rigid thermal vibration and the difference in C—O(11) and C—O(12) bond lengths in the carboxylate group to the differences in the crystal environment of the O atoms. Thus atom O(11), which forms the longer C—O bond, is involved in coordination with an Li ion as well as the H bond, whereas atom O(12) is involved only in coordination with an Li ion (Table 2).

As seen from the torsion angles (Table 2), the adipate chains are almost fully extended except for a twist of the carboxylate group about the bond C(5)—C(6). This twist enables pairs of molecules to come together end to end for cross-linking by the H-bond O(61)—H(61)···O(11') and by an Li ion bridge O(62)···Li···O(12'') (Fig. 2). Other Li ion bridges, O(11)···Li···O(62''), link the molecules laterally to form chains.† Each Li ion is tetrahedrally coordinated by O atoms (Table 2), as in some other carboxylate salts (Klapper & Küppers, 1973; Town & Small, 1973; Soriano-Garcia & Parthasarathy, 1978).‡ The presently reported Li···O(12) distance, $1.896(3) \text{ \AA}$, is the shortest occurring in any of these crystal structures.

The crystal structure consists of layers extending parallel to (100) with regions of hydrocarbon chains sandwiched between sheets made up of the Li ions, carboxylate and carboxylic acid groups (Fig. 2). The layer repeat distance is $d_{100} = 8.22 \text{ \AA}$. Within each layer, there is an angle of 16.2° between the axes of adjacent chains which are related by the *c*-glide. All chains are tilted 29.4° with respect to the layer normal, *a**. The chains are packed side by side, so that each has six near neighbors. For two of these, the best

least-squares plane through the C atoms of the chain is parallel to that of the central molecule, with the plane of the others turned through a dihedral angle 84.8° .* Thus the chain packing is of a complex orthorhombic type (Segerman, 1965). The shortest of the intermolecular methylene H···H distances [$2.65(3) \text{ \AA}$, Table 2] is somewhat greater than the sum of the van der Waals radii (2.4 \AA). This indicates that the chains are not in closest packing, presumably because the arrangement is dominated by the polar interactions involving the adipate O atoms.

There is resemblance between the crystal structures of lithium hydrogen adipate and adipic acid (Housty & Hospital, 1965a). The latter is also a layer structure with similar chain packing but with a smaller layer spacing (6.86 vs 8.22 \AA) and a greater tilt of the chains (44.2 vs 29.4°). These effects may be due to the greater Coulombic repulsions between sheets of polar groups in the acid salt.

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* See deposition footnote.

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† See deposition footnote.

‡ Li ion pentacoordinated by O atoms is also observed (Thomas, 1972; Herbertsson, 1976).