

Effects of H/D Substitution on Thermal Vibrations in Piperazinium Hexanoate-h₁₁,d₁₁

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Abstract

The crystal structures of piperazinium hexanoate-h₁₁, $\frac{1}{2}\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_6\text{H}_{11}\text{O}_2^-$, and piperazinium hexanoate-d₁₁, $\frac{1}{2}\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_6\text{D}_{11}\text{O}_2^-$, have been determined from neutron diffraction data collected at 15 K. Nuclear anisotropic displacement parameters have been analyzed to obtain the internal molecular displacements of the H and D nuclei, given by $\langle u_{\text{obs}}^2 \rangle - \langle u_{\text{ext}}^2 \rangle$ where $\langle u_{\text{ext}}^2 \rangle$ is the contribution assuming all H/D to be carried rigidly on the vibrating molecular framework consisting of the heavier nuclei. In both crystal structures the cation ring is well fitted by the rigid-body model and the anion chain by a model with two rigid segments. In the piperazinium cations the corresponding protons in the two structures have about the same internal vibrational directions and magnitudes except for the two N—H protons, perhaps owing to differences in N—H...O hydrogen bonding. The internal vibrations of corresponding H/D in the h₁₁ and d₁₁ anions have approximately the same vibrational directions. The internal mean-square displacements of the H nuclei are systematically greater than the values of the corresponding D nuclei by an average factor 1.7 (3). For both anions, normal-mode analyses have been carried out using the force fields derived from *ab initio* quantum-mechanical calculations with HF/3-21G and HF/6-31G** basis sets. The values of the resultant H/D internal displacements for C—H(D) bond stretching and methylene out-of-plane vibrations are in good agreement with experiment. However, with either basis set, theory predicts methylene in-plane mean-square displacements significantly greater than the experimental values.

1. Introduction

The primary aim of the present work is to study the effects on nuclear mean-square displacements of H/D isotopic substitution in a simple organic crystal structure. Accurate nuclear positional and thermal parameters have been determined from low-temperature neutron diffraction for the piperazinium salt of a short-chain fatty acid (hexanoic acid) in two isotopically different forms, $[\text{C}_6\text{H}_{11}\text{O}_2]^-$ and $[\text{C}_6\text{D}_{11}\text{O}_2]^-$. The piperazinium cation $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}$ is not isotopically replaced so that it acts as

a reference marker common to the two crystal structures (Fig. 1). We assume that for the H and D nuclei, the observed anisotropic mean-square displacements are the sum of uncorrelated contributions from the external or lattice vibrations and the internal or intramolecular vibrations. For a nuclear vibration in a given direction, the assumption that $\langle u_{\text{obs}}^2 \rangle = \langle u_{\text{ext}}^2 \rangle + \langle u_{\text{int}}^2 \rangle$ is justified by the large differences in the frequency of the external and internal vibrational modes (Willis & Pryor, 1975). Because the molecular weights of the two isotopic forms of the hexanoate anion differ by approximately 10% (115 versus 126) we expect a significant mass effect on $\langle u_{\text{ext}}^2 \rangle$ for all atoms in the structure. Similarly, there should be significant differences in $\langle u_{\text{int}}^2 \rangle$ for corresponding H/D pairs in the two anions, but for corresponding H nuclei in the two piperazinium cations $\langle u_{\text{int}}^2 \rangle$ should be about the same.

If we assume a simple harmonic oscillator model, the mean-square displacements due to C—H (or C—D) bond stretching are (following Cyvin, 1968)

$$\langle u^2 \rangle = (h/8\pi^2\mu\nu)\coth(h\nu/2kT), \quad (1)$$

where ν is the frequency of vibration and μ is the reduced mass. As T approaches 0 K, the hyperbolic cotangent term approaches unity so that

$$\langle u^2 \rangle = h/8\pi^2\mu\nu. \quad (2)$$

Given a force constant $f = \mu\nu^2$, assumed to have the same value for both C—H and C—D bonds, we have

$$\langle u_{\text{H}}^2 \rangle = h/8\pi^2\mu_{\text{H}}\nu_{\text{H}} = h/8\pi^2(f\mu_{\text{H}})^{1/2}$$

and

$$\langle u_{\text{D}}^2 \rangle = h/8\pi^2\mu_{\text{D}}\nu_{\text{D}} = h/8\pi^2(f\mu_{\text{D}})^{1/2}.$$

For the H and D in a C—H or C—D group, the reduced masses are $\mu_{\text{H}} = 0.923$ and $\mu_{\text{D}} = 1.715$. Therefore, with this simplified model, the predicted ratio of mean-square stretching displacements at low temperature (15 K) is

$$\langle u_{\text{H}}^2 \rangle / \langle u_{\text{D}}^2 \rangle = (\mu_{\text{D}}/\mu_{\text{H}})^{1/2} \simeq 1.36.$$

We also compare the differences in $\langle u_{\text{int}}^2 \rangle$ for corresponding H/D pairs obtained from neutron diffraction data with theoretical values obtained from normal-mode calculations on $[\text{C}_6\text{H}_{11}\text{O}_2]^-$ and $[\text{C}_6\text{D}_{11}\text{O}_2]^-$. The force field is derived from *ab initio* molecular-orbital theory assuming HF/3-21G and HF/6-31G** levels of approximation using the *GAUSSIAN* computer program (Frisch *et al.*, 1992). Theory systematically gives much greater internal mean-square displacements for both H and D in the plane of the methylene groups than are found experimentally.

2. Experimental

2.1. Crystal structure determination

Piperazine (Eastman Kodak, Rochester, NY) and hexanoic acid- h_{11} (Sigma Chemical Company, St Louis, MO) or hexanoic acid- d_{11} (Cambridge Isotope Laboratory, Woburn, MA) were dissolved separately in ethanol/water (9:1 by volume). The solutions were then mixed in a piperazinium/hexanoate molar ratio of 1:2. Slow evaporation at room temperature produced large prismatic crystals of the salts. The crystal densities were measured by flotation in chloroform/benzene at room temperature. Melting points were measured using a Thomas Hoover Unimelt capillary melting point measurement apparatus.

The crystal structure of the piperazinium hexanoate- h_{11} salt was first determined from a set of Mo $K\alpha$ X-ray data collected at 298 K using an Enraf-Nonius CAD-4 diffractometer at the Brookhaven National Lab [$\sin\theta/\lambda \leq 0.48 \text{ \AA}^{-1}$, maximum scan speed $6.67^\circ \text{ min}^{-1}$, $R(F) = 0.065$ for 580 independent reflections]. The program *MITHRIL* (Gilmore, 1983) was used in solving the phase problem. All the H atoms were located from a difference electron-density map.

The neutron diffraction data were collected on automatic four-circle diffractometers at ports H6S and H6M of the Brookhaven High Flux Beam Reactor. The experimental conditions are given in Table 1. The neutron beam wavelengths (1.1584 and 1.0462 \AA) were calibrated using a standard KBr crystal at 298 K ($a_0 = 6.600 \text{ \AA}$). The crystals were mounted on a hollow aluminium pin and placed inside a closed-cycle helium refrigerator (Air Products and Chemicals, Inc., Displex Model CS-202). The intensity data were collected at 15 K. The integrated intensity for each reflection was calculated by subtracting the background at the two end 10% parts of the scan. Neutron absorption corrections were applied using *ABSOR*, a program adapted from Templeton & Templeton (1973), with $\mu = 0.284$ and 0.116 mm^{-1} for the h_{11} and d_{11} salts, respectively (Koetzle & McMullan, 1980).

The atomic parameters obtained from the preliminary X-ray diffraction data were then used as the initial values

for the structure refinement with the neutron diffraction data. For both structures, full-matrix least-squares refinement was carried out with the *UPALS* computer program (Lundgren, 1982) with minimization of $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [\sigma_{\text{ct}}^2(F_o^2) + (C_2 F_o^2)^2 + C_3]^{1/2}$, with $C_2 = 0.02$ for both structures and $C_3 = 0.0$ and 0.1023 for the h_{11} and d_{11} structures, respectively. The value of C_3 (absolute scale) was estimated from the background scattering between neutron reflections. The neutron coherent scattering lengths for C, D, H, N and O were 6.648, 6.674, -3.741 , 9.360 and 5.803 fm (Koester, 1977). In the h_{11} crystal structure extinction effects were found to be negligible, but for the d_{11} structure extinction was appreciable. Various refinements were carried out using extinction models proposed by Nelmes & Thornley (1974) and Becker & Coppens (1974). The best least-squares fit was obtained assuming the crystal to be of type I with a Lorentzian distribution of mosaicity and with anisotropic extinction parameters $g_{11} = 4.5(13)$, $g_{22} = 6.1(3)$, $g_{33} = 2.1(1)$, $g_{12} = -2.2(2)$, $g_{13} = 0.7(1)$ and $g_{23} = -2.1(1) \times 10^4 \text{ rad}^{-1}$. In the d_{11} structure refinement, when the coherent scattering lengths for the 11 D sites were included as variables, small but significant differences were observed, indicating that the D/H replacement ratio along the alkyl chain decreases from the carboxylate (99%) to the methyl group (97%). This variation would appear to be inherent in the hexanoic acid (d_{11}) sample which we purchased. For both structures, refinements were also carried out including third-order nuclear displacement parameters according to the Gram-Charlier formalism (Johnson & Levy, 1974). However, these parameters were subsequently excluded because none of the values were significantly different from zero.

The final agreement factors are in Table 1 and the final nuclear parameters are in Table 2.* Internuclear distances and angles are in Table 3. Comparison of the two structure determinations (Tables 1 and 2) shows that the partially deuterated structure has been determined with considerably greater precision. This is attributed to the greater diffracting power of the partially deuterated crystal. Although the crystal was smaller in volume, the diffracted beams were generally stronger because of the larger coherent scattered intensity from D *versus* H. Also, the partially deuterated crystal being more nearly perfect in texture, the diffracted beams were sharper. The partially deuterated crystal gave rise to less incoherent background scattering from hydrogen and consequently neutron absorption effects were smaller. Furthermore, the use of a shorter wavelength neutron beam made it possible to measure more reflections from the partially deuterated crystal.

* Lists of reflection data for both crystal structures have been deposited with the IUCr (Reference: BK0025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal refinement data for piperazinium hexanoate-h₁₁,d₁₁*

	$\frac{1}{2}\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{C}_6\text{H}_{11}\text{O}_2$	$\frac{1}{2}\text{C}_4\text{H}_{12}\text{N}_2\cdot\text{C}_6\text{D}_{11}\text{O}_2$
<i>(a) Unit-cell data</i>		
Cell setting	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	5.753 (2)	5.750 (1)
<i>b</i> (Å)	7.498 (3)	7.486 (2)
<i>c</i> (Å)	10.649 (4)	10.622 (4)
α (°)	105.71 (3)	105.81 (2)
β (°)	93.64 (3)	93.66 (2)
γ (°)	97.63 (3)	97.66 (2)
<i>V</i> (Å ³)	435.89	433.59
<i>F</i> (000) (fm) ^a	21.12	250.24
<i>Z</i>	2	2
<i>D_x</i> (Mg m ⁻³) (15 K)	1.213	1.305
<i>D_m</i> (Mg m ⁻³) (298 K)	1.145	1.226
M.p. (K)	383.3	384.0
<i>(b) Description of the crystals</i>		
Crystal faces	{100}, {010}, {001}	{100}, {010}, {001}
Crystal size (mm)	4.4 × 2.4 × 1.0	3.4 × 1.6 × 1.6
Crystal volume (mm ³)	10.4	11.4
Crystal weight (mg)	12.62	14.88
μ (mm ⁻¹) ^b	0.345	0.116
<i>(c) Intensity data measurements</i>		
Radiation type	Neutron	Neutron
Wavelength (Å)	1.1584 (1)	1.0462 (1)
Monochromator	Ge(022)	Be(002)
Temperature (K)	15 (1)	15 (1)
(<i>sin</i> θ/ <i>λ</i>) _{max} (Å ⁻¹)	0.707	0.768 (1)
Hemisphere	<i>h</i> ± <i>k</i> ± <i>l</i>	- <i>h</i> ± <i>k</i> ± <i>l</i>
Range of <i>h, k, l</i>	0 → <i>h</i> → 8 -10 → <i>k</i> → 10 -15 → <i>l</i> → 15	-8 → <i>h</i> → 0 -11 → <i>k</i> → 11 -16 → <i>l</i> → 16
Scan range 2θ = <i>a</i> + <i>b</i> sinθ		
<i>a, b</i> (°) (0 < 2θ < 55)	3.0, 0.0	3.0, 0.0
<i>a, b</i> (°) (55 ≤ 2θ < 110)	1.46, 3.01	1.43, 3.44
No. of measured reflections	2980	3657
No. of independent reflections	2535	3235
No. of reflections [<i>F</i> _o ² < -2σ(<i>F</i> ²)]	1	0
<i>R</i> _{int} (<i>F</i> ²) ^c	0.015	0.010
<i>T</i> _{min}	0.449	0.748
<i>T</i> _{max}	0.765	0.854
<i>(d) Least-squares refinement</i>		
No. of observed reflections	2232	3509
No. of variables	253	270
<i>R</i> (<i>F</i> ²)	0.076	0.035
<i>wR</i> (<i>F</i> ²)	0.090	0.049
<i>S</i>	2.703	1.373

(a) Coherent neutron scattering lengths (fm) [6.648 (C), 5.803 (O), 9.36 (N), 6.673 (D), -3.7409 (H)] are from Koester (1977). (b) Mass absorption coefficient (μ/ρ) of hydrogen is from Koetzle & McMullan (1980); values for C, O, N, D are from *International Tables for X-ray Crystallography* (Vol. III, p. 197). (c) *R*_m(*F*²) based on zonal (*0kl*) reflections; 324 for the protonated and 280 for the deuterated salts.

3. The structural results

At 15 K, the crystal structures of piperazinium hexanoate-h₁₁ and piperazinium hexanoate-d₁₁ are very similar. The piperazinium cations in both structures have a crystallographic center of symmetry. These rings are in a chair conformation, similar to that found in other piperazinium fatty-acid salts (Luo, Ruble & Craven, 1995; Venkatramani & Craven, 1991; Sangin & Brisse, 1984*a,b*; Brisse & Sangin, 1982*a,b*). The puckering coordinates for the six-membered rings (*Q*, θ , φ ; Cremer & Pople, 1975) have values (0.574 Å, 0°, 0°) and (0.566 Å, 0°, 0°) for the protonated and

deuterated salts, respectively. The cation bond distances and angles in the two crystal structures are the same within experimental error (Table 3).

The hexanoate chains are in an almost fully extended conformation (Fig. 1 and Table 3*e*), except for a twist at the junction with the carboxylate group where the O2—C1—C2—C3 torsion angle is -21.6 (2)°. After thermal vibration corrections, the carboxylate C—O bond lengths are essentially the same in both structures, with the distances 1.270 and 1.266 (2) Å for C1—O1 (which extends the zigzag chain) being possibly longer than for C1—O2, 1.262 and 1.264 (2) Å. In both hydrocarbon chains, the C_{tetra}—C_{tetra} bond distances

Table 2. Nuclear positional and mean-square displacement parameters and site factors

(a) Values for piperazinium hexanoate-h₁₁ (above) and hexanoate-d₁₁ (below) with e.s.d.'s in parentheses. The anisotropic displacement factors have the form $T = \exp(-2\pi^2 \sum_i \Sigma_j h_i h_j a_i^* a_j^* U^{ij})$, U^{ij} in Å² × 10⁴.

	x (× 10 ⁴)	y (× 10 ⁴)	z (× 10 ⁵)	U ¹¹ (× 10 ⁴)	U ²² (× 10 ⁴)	U ³³ (× 10 ⁴)	U ¹² (× 10 ⁴)	U ¹³ (× 10 ⁴)	U ²³ (× 10 ⁴)		
O1	4744 (2)	2160 (2)	92000 (13)	63 (6)	84 (5)	112 (6)	7 (4)	14 (4)	77 (4)		
	4750 (1)	2165 (1)	92033 (6)	62 (2)	87 (2)	88 (2)	9 (2)	20 (2)	63 (2)		
O2	7687 (2)	3901 (2)	86069 (13)	66 (6)	80 (5)	118 (6)	19 (4)	-2 (4)	67 (4)		
	7691 (1)	3907 (1)	86053 (6)	45 (2)	79 (2)	100 (2)	2 (2)	4 (2)	53 (2)		
C1	5533 (2)	3273 (2)	85620 (10)	64 (5)	51 (4)	71 (5)	8 (4)	5 (4)	40 (4)		
	5535 (1)	3272 (1)	85631 (4)	42 (2)	54 (2)	55 (2)	8 (1)	8 (1)	28 (1)		
C2	3774 (2)	3802 (2)	76446 (11)	86 (5)	71 (5)	100 (5)	2 (4)	-5 (4)	53 (4)		
	3773 (1)	3799 (1)	76397 (5)	53 (2)	70 (2)	78 (2)	1 (1)	0 (1)	42 (1)		
C3	4641 (2)	5571 (2)	72595 (11)	84 (5)	68 (5)	78 (5)	14 (4)	-5 (4)	39 (4)		
	4640 (1)	5572 (1)	72571 (5)	60 (2)	59 (2)	60 (2)	7 (1)	6 (1)	29 (1)		
C4	2925 (2)	5976 (2)	62561 (11)	88 (5)	65 (4)	77 (5)	15 (4)	-7 (4)	35 (4)		
	2919 (1)	5972 (1)	62498 (5)	61 (2)	57 (2)	57 (2)	7 (1)	4 (1)	24 (1)		
C5	3727 (2)	7840 (2)	59723 (11)	99 (5)	64 (5)	102 (5)	13 (4)	-7 (4)	44 (4)		
	3726 (1)	7840 (1)	59687 (5)	73 (2)	59 (2)	78 (2)	8 (1)	4 (2)	33 (1)		
C6	2048 (2)	8249 (2)	49565 (12)	124 (6)	89 (5)	111 (5)	24 (4)	-8 (4)	53 (4)		
	2043 (1)	8246 (1)	49488 (5)	92 (2)	77 (2)	86 (2)	16 (2)	2 (2)	42 (2)		
N	10128 (2)	1644 (1)	95353 (8)	73 (4)	49 (3)	80 (3)	7 (3)	1 (3)	39 (3)		
	10130 (1)	1647 (1)	95383 (3)	56 (1)	51 (1)	65 (1)	7 (1)	12 (1)	28 (1)		
C7	9715 (2)	1747 (2)	109157 (11)	80 (5)	56 (5)	68 (5)	13 (4)	3 (4)	23 (4)		
	9712 (1)	1746 (1)	109183 (5)	67 (2)	48 (2)	57 (2)	11 (1)	13 (1)	11 (1)		
C8	9186 (2)	-253 (2)	86446 (11)	92 (5)	63 (5)	62 (5)	11 (4)	-9 (4)	21 (4)		
	9191 (1)	-250 (1)	86430 (5)	74 (2)	60 (2)	50 (2)	12 (1)	2 (1)	20 (1)		
H21	2114 (5)	3944 (4)	80974 (31)	174 (12)	362 (15)	361 (15)	91 (12)	89 (11)	223 (12)		
D21	2117 (1)	3932 (1)	80856 (7)	104 (3)	279 (4)	276 (4)	54 (2)	69 (2)	181 (3)		
H22	3369 (6)	2594 (4)	67726 (28)	393 (17)	148 (11)	220 (12)	-16 (11)	-97 (11)	34 (9)		
D22	3372 (1)	2583 (1)	67583 (7)	278 (4)	124 (3)	159 (3)	-15 (2)	-69 (2)	22 (2)		
H31	4962 (5)	6756 (4)	81505 (26)	307 (14)	140 (11)	190 (12)	21 (10)	-40 (10)	16 (9)		
D31	4953 (1)	6759 (1)	81542 (6)	210 (3)	120 (3)	126 (3)	13 (2)	-21 (2)	6 (2)		
H32	6364 (5)	5454 (4)	68666 (28)	171 (12)	264 (13)	275 (13)	52 (10)	61 (10)	132 (10)		
D32	6351 (1)	5454 (1)	68654 (7)	98 (3)	203 (3)	200 (3)	38 (2)	50 (2)	101 (2)		
H41	1155 (5)	5975 (4)	66049 (28)	168 (12)	277 (13)	276 (13)	40 (10)	53 (10)	136 (11)		
D41	1155 (1)	5970 (1)	65937 (7)	107 (3)	212 (3)	206 (3)	32 (2)	42 (2)	99 (2)		
H42	2712 (5)	4834 (4)	53351 (26)	314 (14)	162 (11)	164 (11)	38 (10)	-30 (10)	18 (9)		
D42	2709 (1)	4828 (1)	53284 (6)	230 (3)	125 (3)	116 (3)	24 (2)	-6 (2)	7 (2)		
H51	5499 (5)	7826 (4)	56296 (31)	169 (12)	303 (14)	362 (15)	39 (11)	69 (11)	184 (12)		
D51	5491 (1)	7821 (1)	56289 (7)	114 (3)	224 (3)	260 (4)	28 (2)	50 (2)	137 (3)		
H52	3936 (6)	8985 (4)	68913 (27)	347 (16)	147 (11)	209 (12)	23 (10)	-48 (10)	12 (9)		
D52	3934 (1)	8985 (1)	68908 (7)	252 (4)	118 (3)	141 (3)	12 (2)	-30 (2)	9 (2)		
H61	2638 (6)	9600 (4)	47863 (34)	350 (17)	228 (14)	426 (18)	-4 (12)	-36 (13)	229 (12)		
D61	2639 (1)	9598 (1)	47815 (8)	265 (4)	170 (3)	292 (4)	3 (2)	-20 (3)	153 (3)		
H62	280 (5)	8286 (5)	52790 (33)	215 (14)	431 (17)	354 (16)	110 (13)	60 (12)	186 (14)		
D62	280 (1)	8286 (1)	52727 (8)	135 (3)	311 (4)	257 (4)	79 (3)	43 (2)	125 (3)		
H63	1874 (6)	7175 (4)	40013 (30)	429 (18)	263 (14)	199 (13)	107 (13)	-47 (12)	6 (10)		
D63	1867 (2)	7173 (1)	40027 (7)	308 (4)	214 (3)	129 (3)	73 (3)	-21 (2)	10 (2)		
HN1	9218 (4)	2646 (4)	92323 (24)	166 (11)	167 (11)	189 (10)	26 (9)	-17 (9)	79 (8)		
	9214 (2)	2659 (2)	92338 (11)	185 (5)	150 (4)	182 (4)	47 (4)	22 (4)	70 (3)		
HN2	11984 (4)	1965 (4)	94421 (25)	158 (12)	174 (11)	213 (12)	24 (9)	34 (9)	81 (9)		
	11976 (2)	1960 (2)	94439 (11)	146 (4)	178 (4)	190 (4)	2 (4)	28 (4)	75 (4)		
H71	7790 (5)	1547 (4)	109471 (26)	134 (11)	260 (12)	239 (12)	47 (10)	41 (9)	97 (10)		
	7796 (2)	1550 (2)	109555 (12)	140 (4)	247 (5)	219 (5)	47 (4)	60 (4)	86 (4)		
H72	10490 (5)	3155 (3)	115138 (25)	280 (14)	118 (10)	189 (11)	16 (9)	0 (10)	14 (8)		
	10490 (2)	3158 (2)	115233 (12)	265 (6)	124 (4)	179 (5)	13 (4)	-3 (4)	5 (3)		
H81	7262 (5)	-452 (4)	86596 (28)	151 (12)	197 (12)	284 (13)	16 (9)	-20 (9)	56 (10)		
	7268 (2)	-452 (2)	86549 (13)	121 (4)	203 (5)	263 (5)	7 (4)	-9 (4)	60 (4)		
H82	9602 (6)	-280 (4)	76480 (25)	356 (15)	245 (12)	126 (10)	50 (12)	56 (10)	85 (9)		
	9602 (3)	-271 (2)	76455 (11)	315 (6)	228 (5)	128 (4)	58 (5)	46 (4)	67 (4)		
Site	b _{obs}	D%	Site	b _{obs}	D%	Site	b _{obs}	D%	Site	b _{obs}	D%
D21	6.55 (3)	98.8	D22	6.62 (3)	99.4	D31	6.53 (3)	98.6	D32	6.43 (3)	97.6
D41	6.48 (3)	98.1	D42	6.48 (3)	98.1	D51	6.35 (3)	96.9	D52	6.32 (3)	96.6
D61	6.32 (3)	96.6	D62	6.28 (3)	96.2	D63	6.37 (3)	97.1			

after thermal vibrational corrections range from 1.525 to 1.529 Å and the C—C—C angles at C3, C4 and C5 range from 112.4 to 113.5° ($\sigma = 0.01^\circ$). These are in good agreement with the values 1.526 (2) Å

and 112.4 (2)° for propane from microwave data (Lide, 1960). The C_{trig}—C_{tetra} bond lengths C1—C2 [1.526 (2), 1.529 (1) Å for hexanoate-h₁₁ and -d₁₁] are similar to the C_{tetra}—C_{tetra} distances along the chain.

Table 3. Internuclear distances (\AA) and angles ($^\circ$) in piperazinium hexanoate- h_{11} and hexanoate- d_{11} (a) Bond distances between non-hydrogen nuclei. Values on the right are corrected for the vibrations of the molecular frame (Table 4a). C8' is at $2-x, -y, 2-z$.

	Uncorrected		Corrected	
	h_{11}	d_{11}	h_{11}	d_{11}
O1—C1	1.2686 (18)	1.2647 (7)	1.270	1.266
O2—C1	1.2592 (18)	1.2606 (8)	1.262	1.264
C1—C2	1.5253 (16)	1.5280 (7)	1.526	1.529
C2—C3	1.5234 (17)	1.5227 (7)	1.525	1.525
C3—C4	1.5265 (17)	1.5271 (7)	1.527	1.529
C4—C5	1.5271 (17)	1.5271 (7)	1.529	1.529
C5—C6	1.5243 (17)	1.5253 (8)	1.525	1.527
N—C7	1.4869 (14)	1.4841 (6)	1.489	1.486
N—C8	1.4883 (15)	1.4855 (7)	1.490	1.487
C7—C8'	1.5194 (17)	1.5180 (7)	1.521	1.519

(b) Uncorrected bond distances involving H or D nuclei.

	h_{11}		d_{11}	
	h_{11}	d_{11}	h_{11}	d_{11}
C2—H/D21	1.102 (3)	1.0949 (9)	N—HN1	1.076 (3)
C2—H/D22	1.095 (3)	1.1004 (9)	N—HN2	1.080 (3)
C3—H/D31	1.096 (3)	1.0970 (8)	C7—H71	1.102 (3)
C3—H/D32	1.105 (3)	1.0976 (8)	C7—H72	1.093 (3)
C4—H/D41	1.106 (3)	1.1000 (8)	C8—H81	1.098 (3)
C4—H/D42	1.101 (3)	1.0984 (9)	C8—H82	1.098 (3)
C5—H/D51	1.105 (3)	1.0993 (9)		
C5—H/D52	1.101 (3)	1.0991 (9)		
C6—H/D61	1.091 (4)	1.0893 (9)		
C6—H/D62	1.094 (4)	1.0931 (9)		
C6—H/D63	1.102 (4)	1.0913 (9)		

(c) Bond angles involving heavy nuclei. C7' and C8' are at $2-x, -y, 2-z$.

	h_{11}		d_{11}	
	h_{11}	d_{11}	h_{11}	d_{11}
O1—C1—O2	123.64 (13)	123.85 (5)	C3—C4—C5	112.66 (10)
O1—C1—C2	117.78 (11)	117.88 (5)	C4—C5—C6	113.24 (10)
O2—C1—C2	118.52 (11)	118.22 (4)	C7—N—C8	110.98 (8)
C1—C2—C3	114.76 (10)	114.73 (4)	N—C7—C8'	110.56 (9)
C2—C3—C4	113.52 (10)	113.37 (4)	N—C8—C7'	110.47 (9)

(d) Selected bond angles involving H or D.

	h_{11}		d_{11}	
	h_{11}	d_{11}	h_{11}	d_{11}
H/D21—C2—H/D22	106.3 (3)	106.11 (7)	H/D62—C6—H/D63	107.2 (3)
H/D31—C3—H/D32	106.2 (3)	106.58 (7)	H/D63—C6—H/D61	107.2 (3)
H/D41—C4—H/D42	105.7 (2)	105.62 (7)	HN1—N—HN2	108.9 (2)
H/D51—C5—H/D52	105.9 (3)	105.98 (7)	H71—C7—H72	109.7 (2)
H/D61—C6—H/D62	107.3 (3)	107.32 (8)	H81—C8—H82	109.1 (2)

(e) Torsion angles for the hexanoate backbones.

	h_{11}		d_{11}	
	h_{11}	d_{11}	h_{11}	d_{11}
O1—C1—C2—C3	161.13 (12)	160.86 (6)	C2—C3—C4—C5	175.05 (10)
O2—C1—C2—C3	-21.60 (16)	-21.77 (8)	C3—C4—C5—C6	179.15 (10)
C1—C2—C3—C4	175.34 (10)	175.41 (5)		

(f) Hydrogen bonds (h_{11} above, d_{11} below).

N—H \cdots O	H \cdots O(\AA)	N \cdots O(\AA)	N—H \cdots O($^\circ$)
N—HN1 \cdots O2'	1.609 (3)	2.678 (3)	171.9 (2)
	1.603 (1)	2.680 (2)	171.8 (1)
N—HN2 \cdots O1''	1.619 (3)	2.693 (2)	172.5 (2)
	1.625 (1)	2.694 (1)	173.0 (1)

Symmetry codes: (i) x, y, z ; (ii) $1+x, y, z$.

Such a similarity was also observed in γ -aminobutyric acid at 122 K (Weber, Craven & McMullan, 1983) and in a series of other amino-acid zwitterions (Koetzle & Lehmann, 1976). However, in suberic acid at 123 K (Gao, Weber, Craven & McMullan, 1994), which has uncharged carboxylic acid groups, the $C_{\text{trig}}-C_{\text{tetra}}$

distance [1.502 (1) \AA] is appreciably shorter ($>0.02 \text{\AA}$) than the chain $C_{\text{tetra}}-C_{\text{tetra}}$ distances.

Thermal vibration corrections for the C—H, C—D and N—H bond lengths have not been made. For temperatures in the range 20–123 K, corrections for harmonic and anharmonic motion are roughly equal

(0.02 Å) and opposite in sign (Ibers, 1959; Craven & Swaminathan, 1984; Jeffrey & Ruble, 1984), with an uncertainty comparable to the net correction. Average uncorrected distances from Table 3(b) are 1.101 (4) Å for C—H, 1.097 (3) Å for C—D in the hexanoate anions and 1.078 (4) Å for N—H. Here the e.s.d.'s are obtained from the observed distributions. The averages are taken excluding C6—H61 (1.091 Å) and C6—D61 (1.089 Å), which are the shortest bond lengths in each set. These distances are for the methyl C—H (C—D) bond, which is in the plane of the carbon zigzag. Average methylene bond angles in the hydrocarbon chain are 106.0 (2)° for H—C—H and 106.1 (4)° for D—C—D. These average values from Tables 3(b) and 3(d) agree with values obtained for cholesteryl acetate at 20 K by neutron diffraction, namely 1.102 (8) Å for 44 methylene C—H distances and 106.2 (9)° for 22 methylene H—C—H angles. In the piperazinium cation, the average H—C—H angle is 109.3 (3)°, which is significantly greater. In the two crystal structures there is no indication of differences in covalent bond lengths and angles arising from isotopic replacement of H by D.

Each piperazinium cation is hydrogen bonded to four different hexanoate anions to form ribbons (Fig. 2) which are parallel to the plane (012) and extend along the *a* axis (Fig. 3). Two of these anions together with a central piperazinium cation form a collinear centrosymmetric cluster. The long axis of this cluster is approximately parallel to the direction [22̄1]. There are two distinct N—H...O hydrogen bonds with almost the same H...O distances (1.61 Å for the hydrogen bonds within the same collinear hexanoate...piperazinium...hexanoate cluster and 1.62 Å for the hydrogen bonds which link these clusters). In the view down the long axis of the collinear clusters (Fig. 3) it can be seen that they are hexagonally packed. Laterally, because of

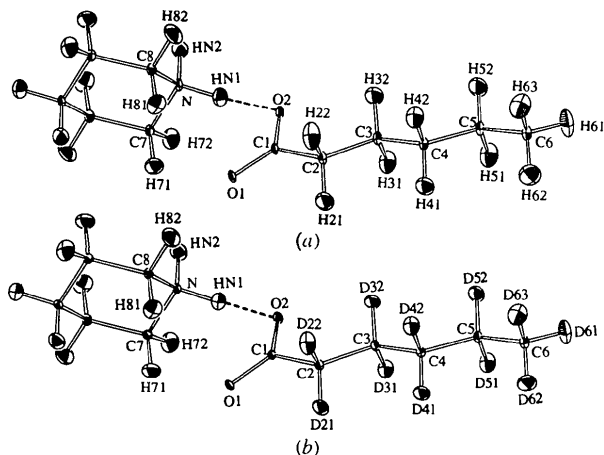


Fig. 1. The crystal structures of (a) piperazinium hexanoate- h_{11} and (b) hexanoate- d_{11} . The thermal ellipsoids are drawn at the 50% probability level (Johnson, 1976). Broken lines represent hydrogen bonds.

the cluster tilting, there is no subcell packing of the hydrocarbon chains as is commonly observed in longer-chain fatty-acid crystal structures (Abrahamsson & Ryderstedt-Nahringbauer, 1962; Abrahamsson, Dahlen, Lofgren & Pascher, 1978).

4. Thermal vibration analysis

4.1. Observed nuclear mean-square displacements

The anisotropic displacement parameters for each nucleus, as obtained from Bragg diffraction data, are the time and space average of mean-square displacements over a large number of normal-mode vibrations taking place in the crystal.* In a molecular crystal such as piperazinium hexanoate, the great majority of these can be regarded as external or lattice modes in which the molecules vibrate as rigid bodies about their mean positions and orientations. For an isolated hexanoate anion, there are 51 internal modes in which the molecular vibrations are nonrigid. Assuming a partitioning into external and internal modes, we write the mean-square displacement of a nucleus in a certain direction as $\langle u_{\text{obs}}^2 \rangle = \langle u_{\text{ext}}^2 \rangle + \langle u_{\text{int}}^2 \rangle$. The distinction between external and internal modes is a convenient approximation which is justified because the intramolecular forces required for covalent bond stretching and bond-angle bending are generally stronger than the intermolecular forces and therefore the internal modes which involve such molecular deformations will have higher frequencies (Willis & Pryor, 1975). The distinction between external and internal vibrations is less clear for modes which involve torsional motion about covalent bonds because such molecular deformations require forces similar in magnitude to the intermolecular forces. As pointed out by Dunitz, Schomaker & Trueblood (1988), when a molecule is treated as a segmented-body having internal torsional librations, it is necessary to consider possible

* This averaging will also include any static displacements or disordering of the nuclei from their average positions. In the case of piperazinium hexanoate at 15 K, there is no reason to suppose the presence of such effects.

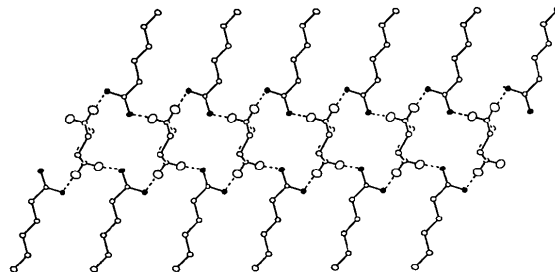


Fig. 2. The hydrogen-bonding scheme in piperazinium hexanoate. The carboxylate O atoms are drawn as filled ellipses. H atoms are omitted for clarity except those involved in hydrogen bonding. Broken lines represent O...H—N hydrogen bonds.

correlations in the motions of the internal and the external modes.

From the 50% probability ellipsoids in Fig. 1, it can be seen that at 15 K, the observed mean-square displacements for the molecular framework C, O and N nuclei are considerably smaller than those of the H and D nuclei. Because the H and D nuclei are at the periphery of the molecule, their mean-square displacements owing to external or rigid-body motion will be somewhat larger than those of the framework nuclei. However, from the considerably greater size of the H and D ellipsoids (Fig. 1) it seems unlikely that H and D nuclei are being carried rigidly on the heavier nuclei framework. An appreciable contribution from the internal modes is to be expected.

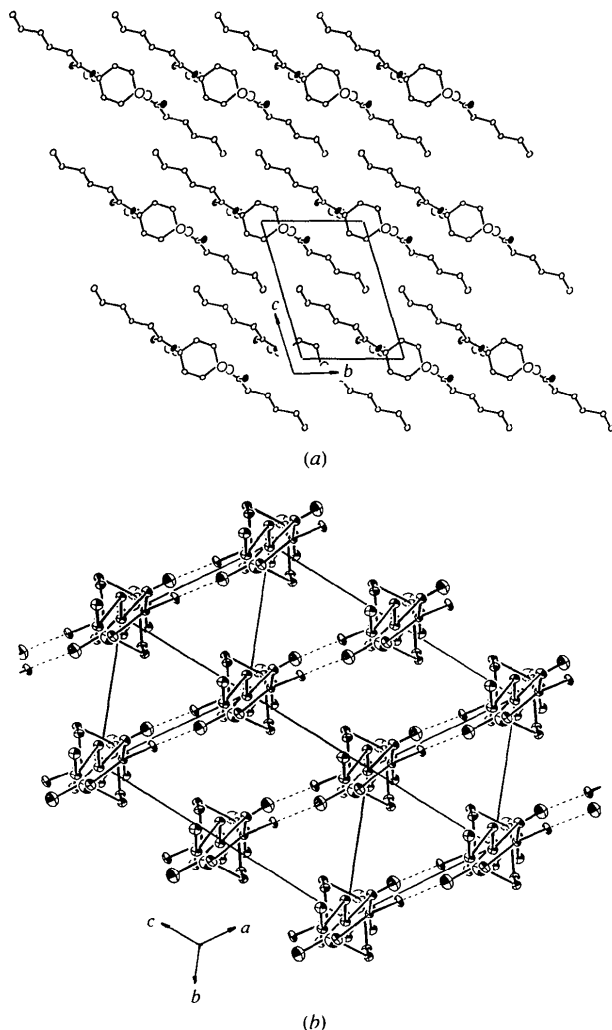


Fig. 3. Molecular packing of piperazinium hexanoate. H atoms are omitted except those involved in hydrogen bonding. Filled ellipses are O atoms. (a) View down the *a* axis. (b) View along the long axis of hexanoate ··· piperazinium ··· hexanoate hydrogen-bonded complex (approximately [221]). The broken lines are hydrogen bonds between adjacent complexes.

In the analysis of the nuclear anisotropic displacement parameters U_{obs}^{ij} (Table 4), we first carried out a rigid-bond test (Harel & Hirshfeld, 1975; Hirshfeld, 1976). For all covalently bonded pairs of atoms $A-B$, we calculated the difference $\Delta_{AB} = \langle u_B^2 \rangle - \langle u_A^2 \rangle$ for the observed mean-square displacements along the $A-B$ bond direction. A zero value for Δ_{AB} is inconclusive but a nonzero value indicates a nonrigid bond.

For all covalent bonds of the molecular framework in both the anion and cation, values of Δ_{AB} are insignificantly different from zero except possibly for C1—C2 in the d_{11} structure for which $\Delta_{AB} = 0.0008(3) \text{ \AA}^2$ or 2.8σ . As pointed out by Rosenfeld, Trueblood & Dunitz (1978), the rigidity test can be applied to any pair of atoms, whether covalently bonded or not. When atom A belongs to the carboxylate group and atom B is C4, C5 or C6 at the other end of the same molecule, nonzero Δ_{AB} values are obtained, the most significant being for C1···C6 (0.0025 \AA^2 or 3.2σ in h_{11} and 0.0015 \AA^2 or 5.1σ in d_{11}). Even larger Δ_{AB} values are obtained when atom A is in an anion and B is in one of the two cations which are hydrogen bonded to it. The most significant are for C1···C8($1+x, y, z$) which is 0.0034 \AA^2 or 4.9σ in h_{11} and 0.0029 \AA^2 or 10.5σ in d_{11} . These are strong indications that the anion chains are vibrating nonrigidly and that the anions are vibrating nonrigidly with respect to the cations.

Values of Δ_{AB} for the covalent bonds involving H or D are given on the left in Table 4(b). For the piperazinium cation, Δ_{CH} has average values $0.0052(11)$ and $0.0063(6) \text{ \AA}^2$ in the h_{11} and d_{11} structures, respectively. Average values for Δ_{NH} are $0.0081(5)$ and $0.0080(4) \text{ \AA}^2$. Thus for the cation, corresponding values in the two structures are the same within experimental error. For hexanoate- h_{11} , the average Δ_{CH} is $0.0057(6) \text{ \AA}^2$ and for hexanoate- d_{11} , the average Δ_{CD} is $0.0034(3) \text{ \AA}^2$. The average of the ratios ($\Delta_{\text{CH}}/\Delta_{\text{CD}}$) is $1.7(3)$, which does not differ significantly from the value 1.36 predicted for the isotope effect on the basis of a simple model for the isolated C—H group (see Introduction, above).

The molecular frameworks (H and D omitted) of the piperazinium cation and hexanoate anion in each structure were then analyzed in terms of the rigid-body model (Schomaker & Trueblood, 1968) using the computer program *EKRT* (He & Craven, 1993). The residual $\sum w(U_{\text{obs}}^{ij} - U_{\text{cal}}^{ij})^2$ with $w = 1/\sigma^2(U_{\text{cal}})$ was minimized. A good fit was obtained with $wR = 0.049, 0.019$ for both piperazinium cations, and $0.092, 0.082$ for the hexanoate- h_{11} and - d_{11} anions, respectively. The goodness-of-fit was 1.24, 1.02 for the piperazinium cations (18 observations and 12 variables) and 1.69, 2.91 for hexanoate- h_{11} and - d_{11} , respectively (48 observations, 21 variables). By trial and error, various segmented-body models (He & Craven, 1993) for the anion chain backbone were then tested. For hexanoate- d_{11} an improved fit (Table 4a) was obtained using a

Table 4. Analysis of nuclear mean-square displacement parameters

(a) Molecular framework (H and D nuclei neglected)

Rigid-body **T**, **L** and **S** tensor components (Schomaker & Trueblood, 1968) are with respect to the principal axes of the moments of inertia for each cation or anion and with the origin at the center of mass. The axes I_1 , I_2 and I_3 are in order of increasing moment of inertia so that I_3 is along the molecular long axis and I_1 is normal to the best molecular plane. The hexanoate anion is treated as having two rigid segments (He & Craven, 1993), one consisting of the carboxylate group with C2 and C3 and the other of C4—C5—C6. Columns headed h_{11} or d_{11} refer to results from the two crystal structures.

	Piperazinium cation		Hexanoate anion	
	h_{11}	d_{11}	h_{11}	d_{11}
wR (U)	0.049	0.019	0.079	0.055
Goodness of fit	1.24	1.02	1.44	2.02
Translational tensor T ($\text{\AA}^2 \times 10^4$)				
T_{11}	53 (8)	40 (3)	74 (5)	52 (3)
T_{22}	61 (2)	49 (1)	72 (4)	45 (2)
T_{33}	33 (2)	41 (1)	41 (3)	45 (1)
T_{12}	-9 (2)	3 (1)	-5 (4)	4 (2)
T_{13}	3 (2)	5 (1)	-7 (3)	1 (1)
T_{23}	-2 (1)	0 (1)	-6 (3)	-6 (1)
Principal values	49	35	78	56
	68	50	71	50
	32	45	39	39
Librational tensor L (deg^2)				
L_{11}	3.6 (4)	2.8 (1)	0.3 (1)	0.5 (1)
L_{22}	3.3 (8)	2.2 (4)	0.6 (2)	0.5 (1)
L_{33}	6.7 (9)	5.8 (4)	17.0 (25)	15.9 (13)
L_{12}	0.0 (4)	0.1 (1)	-0.1 (2)	0.0 (1)
L_{13}	0.8 (4)	0.6 (1)	0.4 (6)	0.5 (3)
L_{23}	-1.4 (3)	-0.9 (1)	-0.8 (4)	-0.7 (2)
Principal values	3.6	2.8	0.3	0.4
	2.8	1.8	0.6	0.6
	7.3	6.1	17.0	16.0

Cross tensor **S** ($\text{\AA} \text{ deg} \times 10^3$)

For the anion, the constraint $S_{11} = -(S_{22} + S_{33})$ was imposed. This avoided a very strong least-squares correlation (0.96) between S_{11} and S_{33} obtained when using the standard constraint $S_{33} = -(S_{11} + S_{22})$.

S_{11}	0	0	-4	-3
S_{12}	0	0	-17 (3)	-8 (2)
S_{13}	0	0	-7 (5)	1 (3)
S_{21}	0	0	4 (4)	0 (2)
S_{22}	0	0	-16 (7)	-9 (4)
S_{23}	0	0	0 (5)	-3 (3)
S_{31}	0	0	29 (14)	24 (8)
S_{32}	0	0	-14 (22)	9 (12)
S_{33}	0	0	19 (23)	12 (12)

Hexanoate framework internal vibrations (deg^2)

The internal vibrational modes are uncorrelated with each other and with the overall rigid-body variations. For each internal mode, all nuclei are in motion because of the constraint that the angular momentum of the anion is zero throughout the vibration (He & Craven, 1993).

		h_{11}	d_{11}
Torsional libration about C2—C3	$\langle \tau^2 \rangle$	11 (4)	10 (2)
Angle bending, C2—C3—C4	$\langle \theta^2 \rangle$	2.1 (18)	2.6 (9)

(b) Mean-square amplitudes of internal vibrations for H and D ($\text{\AA}^2 \times 10^4$)

Columns are as follows. $\Delta_{A-B} = \langle u_A^2 \rangle - \langle u_B^2 \rangle$ is the difference in mean-square displacements for nuclei *A* and *B* along the direction of the covalent bond *A*—*B* as determined from U_{obs}^A for nuclei *A* and *B* (Hirshfeld, 1976). U^A are the components of the difference tensor $U_{\text{int}}^A = U_{\text{obs}}^A - U_{\text{ext}}^A$ referred to a local Cartesian axial system for each H(D) nucleus. Here, U_{ext}^A is determined assuming the H(D) nuclei are carried rigidly on the frame vibrating as in (a) above. Local axes are defined in terms of the internuclear vectors **u** and **v**. For H21 in the methylene group at C2, **u** is along C2 → H21 and **v** is along C2 → H22. The local *x* axis is then along **u** and *z* is along **u** × **v** which is normal to the methylene plane. The local *y* axis, which completes a right-handed axial system, is then normal to C2 → H21 and in the methylene plane. Thus, U^{11} is the internal mean-square displacement of H21 along the C2—H21 bond, U^{22} is the internal mean-square displacement in the methylene plane and U^{33} is the internal mean-square displacement normal to this plane. All H(D) nuclei in methylene or NH₂ groups have local axes defined in a similar way. For H61 in a methyl group, **u** is along C6 → H61 and **v** is along C6 → C5. The local *x* axis is along **u** and *z* along **u** × **v**. Thus, U^{11} is an internal mean-square displacement along the C6—H61 bond, U^{22} is an umbrella-type vibration in the C5—C6—H61 plane and U^{33} is an internal torsional libration about the C5—C6 bond. Local axes for other methyl H(D) are defined in a similar way. U_1 , U_2 and U_3 are the principal values of U_{int}^A and U_{int}^B . U_2^{int} and U_3^{int} are the principal values obtained from the normal-mode analysis using GAUSSIAN with an HF/3-21G basis set. Values obtained with an HF/6-31G** basis set are given by Luo (1994).

(i) Piperazinium cation in the h_{11} crystal structure.

	Δ_{A-H}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_1	U_2	U_3
HN1	86 (16)	83	79	78	20	-21	14	43	104	93
HN2	76 (13)	78	102	91	13	7	3	70	110	91

Table 4 (cont.)

	Δ_{A-H}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_1	U_2	U_3
H71	48 (13)	47	189	123	-3	-6	11	47	191	122
H72	59 (9)	66	149	99	-17	8	-14	62	157	96
H81	66 (13)	66	193	122	-3	-1	-12	66	195	121
H82	36 (14)	38	189	132	8	-12	14	36	192	131

(ii) Piperazinium cation in the d_{11} crystal structure.

	Δ_{A-H}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_1	U_2	U_3
HN1	76 (7)	77	111	91	-1	5	-8	75	114	89
HN2	84 (4)	83	114	97	-9	-10	15	78	126	90
H71	64 (5)	64	179	125	-8	6	11	63	182	124
H72	67 (4)	65	165	116	-11	0	-2	63	167	116
H81	53 (5)	52	184	139	-7	-7	-4	51	184	139
H82	68 (6)	68	172	126	-7	-3	-2	67	172	127

(iii) Hexanoate anion in the h_{11} crystal structure.

	Δ_{C-H}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_1	U_2	U_3	U_1^{nm}	U_2^{nm}	U_3^{nm}
H21	55 (16)	60	233	138	0	1	-2	60	233	138	69	466	184
H22	56 (10)	61	249	138	-29	5	5	56	253	138	72	434	146
H31	55 (10)	54	177	143	-28	-1	-4	48	183	143	78	551	141
H32	64 (15)	63	158	158	-15	-3	-1	60	161	158	73	483	149
H41	62 (15)	58	125	151	9	-16	4	54	126	154	65	427	150
H42	60 (10)	58	112	135	1	-2	-11	58	108	139	62	422	141
H51	51 (16)	52	167	175	-20	11	9	48	166	181	46	526	182
H52	57 (10)	56	157	161	-18	-9	-3	52	159	163	43	500	179
H61	45 (19)	51	198	365	15	-12	-19	49	197	368	56	248	431
H62	68 (17)	70	226	244	-10	22	-48	67	187	286	69	284	595
H63	57 (12)	60	166	273	-6	2	36	59	155	284	61	231	600

(iv) Hexanoate anion in the d_{11} crystal structure.

	Δ_{C-D}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	U_1	U_2	U_3	U_1^{nm}	U_2^{nm}	U_3^{nm}
D21	33 (4)	38	145	85	-14	-4	-1	36	146	85	42	228	113
D22	33 (3)	37	164	101	-13	0	2	36	166	101	42	221	97
D31	32 (3)	30	94	103	-17	10	-4	25	95	108	47	315	84
D32	26 (4)	24	106	98	-13	-11	-4	21	108	95	44	283	81
D41	38 (4)	36	65	105	7	0	5	36	66	105	41	229	82
D42	37 (3)	33	66	103	11	-1	-1	30	70	103	41	229	83
D51	34 (4)	36	94	105	-10	-2	2	34	95	105	30	293	103
D52	33 (3)	34	87	106	-10	3	-3	32	88	107	30	278	101
D61	39 (5)	42	127	241	12	1	-5	40	128	241	34	123	211
D62	32 (4)	30	159	133	-17	14	-33	27	185	111	37	144	306
D63	34 (4)	36	115	164	3	18	35	33	97	184	36	150	336

model with two rigid segments, O1—O2—C1—C2—C3 and C4—C5—C6 and with two independent internal vibrations, namely an internal torsional libration about the C3—C4 bond and a bending vibration of the bond angle C3—C4—C5. When the same model was applied to the hexanoate- h_{11} chain, the values obtained for the internal mean-square displacements were similar, but with reduced significance because of the larger e.s.d.'s. Results of the analysis of molecular framework vibrations are given in Table 4(a).

The anisotropic displacement parameters U_{ext}^{ij} for all H and D nuclei were calculated from the molecular parameters in Table 4(a), assuming that the H and D nuclei are carried rigidly on the appropriate molecular framework. The internal mean-square displacements for the H and D nuclei were then obtained as the difference tensor, $U_{\text{int}}^{ij} = U_{\text{obs}}^{ij} - U_{\text{ext}}^{ij}$. Fig. 4 represents U_{int}^{ij} for the H nuclei of hexanoate- h_{11} and the D nuclei of the hexanoate- d_{11} anions as 50% probability ellipsoids.

Table 4(b) lists the components of the difference tensors U_{int}^{ij} with respect to local Cartesian axes defined for each H or D nucleus. Axes are chosen so that for a methylene H, U_{int}^{11} is the mean-square displacement of H along the C—H bond, U_{int}^{22} is the mean-square displacement of H in the plane of the CH_2 group and normal to the C—H bond and U_{int}^{33} is the mean-square displacement of H normal to the plane of the CH_2 group. Local axes for H nuclei in the NH_2 and D in CD_2 groups are defined in a similar way. For H (or D) in the hexanoate methyl group, U_{int}^{11} is the mean-square displacement of H along the C—H bond, U_{int}^{22} is the mean-square displacement of H within the C5—C6—H plane and normal to the C6—H bond and is thus an umbrella-type motion with C5—C6 as the umbrella shaft. U_{int}^{33} is the mean-square displacement of H normal to the C5—C6—H plane and normal to the C—H bond and thus corresponds to a librational motion about the C5—C6 bond. Table 4(b) also lists the principal values

(U_1 , U_2 and U_3) of the difference tensors U_{int}^{ij} . For most H and D it can be seen that the principal values are similar to the diagonal components of the U_{int}^{ij} tensor and the off-diagonal components are relatively small. Thus, the principal values are for vibrations in directions close to those of the local axes.

In comparing U_{int}^{ij} values obtained for corresponding nuclei in the two crystal structures, those of the piperazinium H nuclei should be the same and indeed, it can be seen from Tables 4(b)(i) and 4(b)(ii) that the agreement is generally good. The largest differences are in U_1 for HN1 and H82, which are marginally significant (2.7σ and 2.1σ , respectively).

In contrast, the diagonal tensor components and principal values of U_{int}^{ij} for the hexanoate- h_{11} H nuclei [Table 4(b)(iii)] are systematically greater than corresponding values for the hexanoate- d_{11} D nuclei

[Table 4(b)(iv)]. Average mean-square amplitudes for the methylene H nuclei in hexanoate- h_{11} are $0.0058(4) \text{ \AA}^2$ for U_{int}^{11} , $0.0172(48) \text{ \AA}^2$ for U_{int}^{22} and $0.0150(14) \text{ \AA}^2$ for U_{int}^{33} . Corresponding values for the D nuclei in hexanoate- d_{11} are $0.0034(5)$, $0.0103(47)$ and $0.0101(7) \text{ \AA}^2$. In their Table 6, Weber *et al.* (1991) report internal mean-square displacements for H and D obtained by neutron diffraction from the crystal structures of the steroids cholesteryl acetate (20 and 123 K) and 20-methylpregnenediol methanolate (123 K). Their values are somewhat smaller than those reported here. However, for γ -aminobutyric acid (123 K), which is chemically more closely related to the hexanoate anion, the values given in their Table 6 are closer to those reported here.

Ab initio quantum-mechanical calculations were carried out for the hexanoate- h_{11} and - d_{11} anions using the GAUSSIAN computer program (Frisch *et al.*, 1992) assuming two different basis sets (HF/3-21G and HF/6-31G**). In each calculation, the molecular geometry was optimized except for the C3—C2—C1—O1 torsion angle, which was fixed at the value 160.9° in order to preserve the tilt of the carboxylate group with respect to the hydrocarbon chain framework as observed in the crystal structure. When this torsion angle was optimized, the molecule indeed became planar as would be expected for an isolated hexanoate anion. Based on the calculated potential energy surfaces for displacement of nuclei from their optimized positions, a normal-mode analysis was also carried out. The mean-square displacements from each of the 51 normal modes were summed to obtain estimates of U_{int}^{ij} at 15 K for all nuclei. The resulting principal values obtained using the HF/3-21G basis set, which are given as U_1^{mm} , U_2^{mm} and U_3^{mm} in Table 4(b), have vibrational directions which correspond approximately to U_1 , U_2 and U_3 , respectively. Results obtained for the optimized planar anions were not significantly different from those given here. The results using the other basis set are listed by Luo (1994).

The normal-mode analyses for hexanoate gave mean-square displacements smaller than 0.001 \AA^2 for all the heavier nuclei. This is roughly consistent with the neutron diffraction results assuming the segmented-body model, which gave a maximum value 0.0016 \AA^2 for the internal displacements of the framework nuclei. For the methylene H/D nuclei, values of U_1^{mm} and U_3^{mm} obtained using both basis sets match the experimental values quite well. However, values for U_2^{mm} are consistently greater than the corresponding values of U_2 . It was expected that the more extensive HF/6-31G** basis set might provide better agreement between U_2^{mm} and U_2 , but in fact the disagreement is even greater. We conclude that at the H/D nuclei and within the methylene plane, the calculations give a potential energy well that is too broad. Also, for the methyl H/D nuclei, except for H61 and D61, an overly broadened well for the librational motion about the C5—C6 bond is obtained.

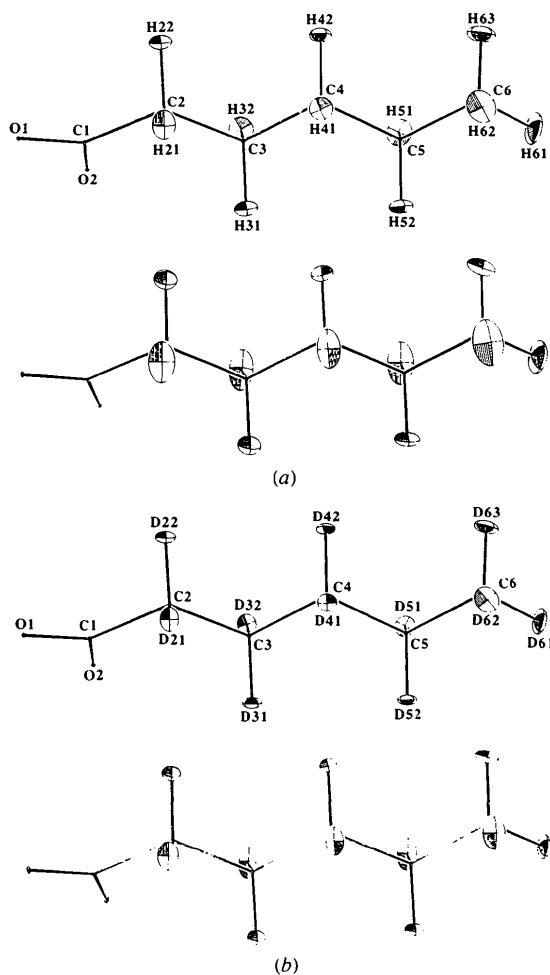


Fig. 4. Ellipsoids of internal vibrations of H/D atoms at the 50% probability level (Johnson, 1976). In both (a) and (b) the top figure is drawn with experimental values and heavy atoms at an arbitrary size. The bottom figure is drawn with values from normal-mode analyses. (a) Hexanoate- h_{11} ; (b) hexanoate- d_{11} .

Nevertheless, the effects of isotopic substitution on the internal mean-square displacements of the H/D nuclei are evident both from neutron diffraction and from the normal-mode analysis. From Table 4(b) it can be seen that the D nuclei generally have smaller mean-square displacements than the corresponding H nuclei. For C—H/D bond stretching, as might be expected, the ratio between $U_{\text{int}}^{\text{H}}$ values for corresponding methylene C—H and C—D bonds has an average value of 1.71, in agreement with the ratio obtained from $\Delta_{\text{C—H}}$ and $\Delta_{\text{D—H}}$. The ratios using U_1^{mm} values from the normal-mode analysis are in the ranges 1.43–1.86 and 1.52–1.85 with averages 1.63 (12) and 1.66 (12) from the HF/3-21G and HF/6-31G** calculations, respectively. These values are in agreement, although somewhat different from 1.36 as obtained from the simple model for a mass-weighted diatomic species (see *Introduction*).

With a simple harmonic model (1) for the internal vibrations and the average values for the mean-square displacements obtained from neutron diffraction (Table 4b), the frequencies for the methylene C—H/D bond stretching, in-plane and out-of-plane vibrations are 3382, 949 and 1194 cm^{-1} for the CH_2 groups and 3072, 806 and 958 cm^{-1} for the CD_2 groups. We find that the term $(h\nu/2kT) > 3.0$ and $\coth(h\nu/2kT) \simeq 1.0$ for all three modes and for temperatures up to 200 K. Therefore, (2) holds and the mean-square internal displacements of the H(D) nuclei in these groups are almost independent of temperature up to 200 K. Similar conclusions by Weber, Craven, Sawzik & McMullan (1991) were based on their study of cholesteryl acetate at 20 and 120 K using neutron diffraction and more recently by Kampermann, Sabine, Craven & McMullan (1995) from neutron diffraction studies of hexamethylenetetramine at six temperatures in the range 15–200 K. Values of the internal C—H/D mean-square displacements such as those presently reported seem to be roughly transferable to other chemically similar molecules. If $U_{\text{ext}}^{\text{H}}$ can be estimated by analysis of vibrations for the heavy-atom frame, it then becomes possible to derive anisotropic displacement parameters for H/D atoms in a crystal structure for which neutron diffraction data are not available. This approach can be useful in carrying out a charge-density study (Klooster & Craven, 1992; Chen & Craven, 1995). If only X-ray data are available, having a reliable independent estimate of the H/D vibrations is valuable in efforts to obtain an unbiased estimate of the charge distribution.

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