Crystal structure of piperazinium oleate at −150°C[1]

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Abstract The crystal structure of piperazinium oleate ($[C_4H_{12}N_2]^{2+} \cdot 2[C_{18}H_{34}O_2]^-$) has been determined from X-ray diffraction data at −150°C in order to study the oleate chain conformation and molecular packing. Differential scanning calorimetry shows three reversible crystalline state phase transitions (54.5, −34.8, and −54.8°C) in the range from the melting point (84.8°C) to −160°C. The cell constants for a flash-frozen crystal at −150°C are a = 5.630(2), b = 14.900(2), c = 24.825(4) Å, α = 88.77(2), β = 88.12(2), γ = 80.38(2)°; Z = 2, space group $P\bar{1}$; D_c = 1.05 g cm^{-3}, m.p. = 84.8°C. The cell constants are similar at room temperature except for a doubling of b at −150°C. The crystal structure at −150°C has been refined to R(F^2) = 0.116 for 8410 independent reflections. There are two independent oleate anions (A and B), both having an overall extended conformation except for kinks that are different at the *cis* olefin group. The oleate A chain is ordered while the oleate B chain is disordered in two regions. Because of different torsion angles at bonds adjacent to the double bond, the B-chain olefin group adopts two configurations, one of which is predominant. From the olefin group to the terminal methyl group, the B-chain adopts one of two all-*trans* configurations with equal probability. It cannot be determined whether the two kinds of disorder are correlated. Taking into account the centrosymmetrically related oleate chains, the crystal structure contains at least six and possibly eight extended chain conformers with different kinks at the olefin group. Third and fourth order displacement parameters have been determined for the partially resolved atomic sites in the oleate B chain and these have been used to map probability density functions for the disordered atoms. The piperazinium cations are in a chair conformation. Each is hydrogen bonded to four oleate anions, forming an infinite ribbon parallel to (0$\bar{2}$5). These ribbons are stacked upon each other to form a monolayer 24.8 Å thick parallel to (001).—**Luo, J-Q., J. R. Ruble, and B. M. Craven.** Crystal structure of piperazinium oleate at −150°C. *J. Lipid Res.* 1995. **36:** 332-342.

Supplementary key words extended oleate chain conformation • kinking at the olefin • chain disorder • crystalline phase transitions

Long chain fatty acids are of interest because they are an important structural component in biomembranes and surfactant systems. Their dynamical behavior and molecular packing properties are complicated by the flexibility of the hydrocarbon chains. Unsaturated fatty acids display lower melting points than do saturated acids. This property has generally been attributed to the introduction of double bonds into the hydrocarbon chain, which enhances flexibility without lengthening the chain. Oleic acid (9-*cis* octadecenoic acid) contains a single double bond and has been studied in free acid forms by a number of investigators (1, 2). There are three polymorphs of oleic acid crystals: α, β, and γ. The α and γ forms are related in an order-disorder fashion near the terminal methyl groups. The β form is somewhat different (1). In the crystal structure of the γ phase, as determined by Abrahamsson and Ryderstedt-Nahringbauer (2), the oleic acid molecules have a boomerang shape. Petroselinic and erucic acids (3-5) show similar molecular geometry. The crystal structures of these unsaturated fatty acids are dominated by a regular subcell chain packing (2-6) involving the chain segments that form the two arms of the boomerang. The olefin group is accommodated at the apex of the boomerang.

When the oleate chain is incorporated in a crystal structure containing bulky groups that disrupt the regular subcell packing, there is the possibility that the oleate chain will adopt other conformations more complex than the boomerang. This is indeed the case in cholesteryl oleate at room temperature (7) and at −150°C (8). In the crystal structure the bulky steroid ring systems pack efficiently with each other, leaving space to accommodate the loosely packed oleate chains, which are in almost fully extended conformation except for a kink at the olefin group. The kink region is more extensive at room temperature than at −150°C. Such extended conformations for *cis*-unsaturated fatty acid chains are important, as they are likely to occur in condensed lipid systems such as biomembranes and soaps, where both saturated and unsaturated chains must pack with each other.

Abbreviations: esd, estimated standard deviation; m.s., mean square; pdf, probability density function.

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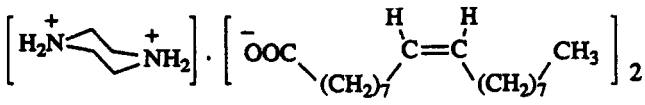

(I)

Piperazinium oleate, (**I**), is a further example of a crystal structure that does not contain regular subcell chain packing because of disruption, in this case by the organic cation. Pollard, Adelson, and Bain (9) found that good crystals could readily be formed of the piperazinium salts of saturated fatty acids with up to 16 carbons. Remarkably large tabular crystals of the myristate and palmitate salts have been grown and the crystal structures have been determined (10). Piperazinium salts of unsaturated acids have higher melting points, form harder crystals, and are much easier to crystallize than the corresponding free acids, e.g., oleic acid melts at 4°C, whereas piperazinium oleate melts at 85°C. A structure determination of the oleate salt at room temperature was attempted by L. Venkatramani and B. M. Craven (unpublished) but little progress was made because of extensive disordering of the oleate chains. Presently we report the structure of a different crystalline form at low temperature.

EXPERIMENTAL

Crystals of piperazinium oleate were grown by slow evaporation from an ethanol solution of piperazine (Eastman Kodak, Rochester, NY) and oleic acid (Sigma, St. Louis, MO) in 1:2 molar proportion. The container was sealed and constantly flushed with nitrogen gas to prevent oxidation of oleic acid. The process usually took 2 to 3 weeks. The soft, easily deformed crystals are generally long thin plates, up to 3.5 × 0.5 × 0.2 mm³ in size, with predominant forms {100}, {010}, and {001}.

In a search for possible phase transitions, differential scanning calorimetry using a Mettler TA 4000 system was carried out on a powder sample in the range 100°C to −160°C. Three reversible crystalline phase transitions (**Fig. 1**) were observed at 54.5°C (ΔH = 22.7 kJ/mol), −34.8°C (ΔH = 2.0 kJ/mol) and at −54.8°C (ΔH = 1.5 kJ/mol). The melting point is 84.8°C (ΔH = 47.9 kJ/mol). On the diffractometer large single crystals became fragmented during slow cooling through the two lower transitions, but this was prevented by flash freezing. Therefore, we did not obtain lattice constants in the temperature range from 3°C (a = 5.727(2), b = 7.453(2), c = 25.93(1)Å, α = 87.29(4), β = 87.02(3), γ = 80.84(2)°), which is above the two low-temperature phase transitions, to −150°C (see Abstract for cell parameters), much below all the phase transitions. It was found that the b unit cell repeat is doubled between room and low temperature. It is possible that the flash frozen single crystal is in a metastable state, corresponding to one of the intermediate phases between the room temperature phase and the stable phase at −150°C.

A crystal measuring 0.52 × 0.46 × 0.2 mm³ was kept at −150 ± 2°C over the period of data collection. Lattice parameters were refined using 25 reflections in the range $11.5° < \theta < 40°$. Reflections with $\theta < 75°$ ($-7 \le h \le 0$, $-18 \le k \le 18$, $-31 \le l \le 31$) were measured ($\sin\theta/\lambda_{max}$ = 0.82 Å^{-1}) in $\omega/2\theta$ scanning mode with variable scanning speed. The radiation used was CuKα (λ = 1.5418 Å). A total of 10,001 reflections with full profile of 96 steps was collected. The data were processed with programs from

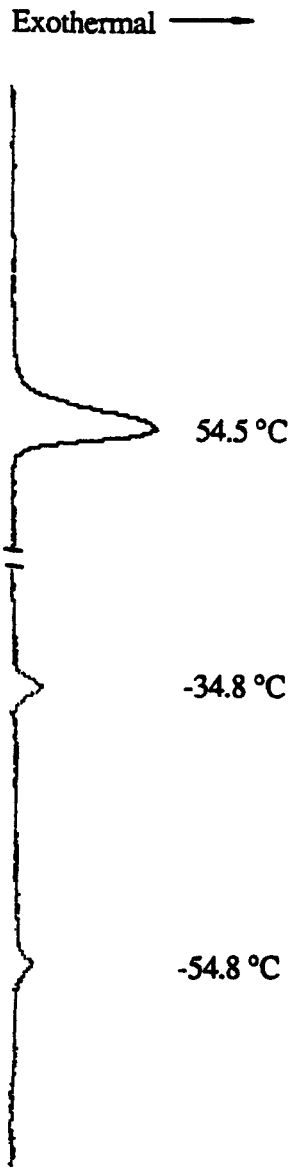

Fig. 1. The differential scanning calorimetry of peperazinium oleate. The analysis was carried out for the temperature range 75°C to −160°C at a rate of 2°C/min. The curve has been slightly edited to save space.

TABLE 1. The higher order m.s. displacement parameters for some atoms of the oleate B chain. These are defined by the expression $T = \exp[-2\pi^2\Sigma_i\Sigma_j h_i h_j a_i^* a_j^* U_{ij}]\ [1-4/3\pi^3 i\Sigma_i\Sigma_j\Sigma_k h_i h_j h_k a_i^* a_j^* a_k^* C_{ijk} - 2/3\pi^4 h_i h_j h_k h_l a_i^* a_j^* a_k^* a_l^* D_{ijkl}]$

(a) The 3rd orders ($Å^3 \times 10^3$)

Atom	C111	C222	C333	C112	C122	C113	C133	C223	C233	C123
C8B	- 15(7)	91(13)	- 22(13)	- 10(5)	1(6)	9(5)	- 11(6)	- 80(7)	68(7)	- 8(4)
C11B	268(22)	- 25(23)	75(18)	- 102(16)	- 54(16)	- 93(14)	- 71(13)	81(17)	- 63(15)	- 70(12)
C12B	- 34(11)	62(16)	6(9)	51(10)	- 88(11)	24(7)	36(7)	- 33(9)	26(8)	- 7(7)
C14B	17(10)	- 50(11)	- 18(9)	- 31(7)	27(8)	10(6)	- 6(6)	24(7)	35(6)	- 27(5)
C16B	41(11)	- 3(8)	4(8)	- 30(7)	- 7(7)	- 23(7)	9(6)	- 1(6)	15(6)	4(5)
C18B	115(28)	2(17)	41(14)	- 119(19)	32(16)	- 45(15)	- 10(12)	- 15(11)	34(10)	8(11)

(b) The 4th orders ($Å^4 \times 10^3$)

Atom	D1111	D2222	D3333	D1112	D1222	D1113	D1333	D2223	D2333	D1122
C8B	- 30(6)	32(13)	27(13)	15(4)	23(6)	1(3)	3(5)	2(7)	- 1(6)	- 6(3)
C11B	- 279(21)	- 4(30)	6(23)	- 79(14)	261(24)	74(45)	- 139(15)	- 24(18)	- 15(15)	114(16)
C18B	- 237(30)	- 11(20)	64(24)	151(19)	30(15)	- 20(15)	- 30(14)	25(11)	23(12)	- 73(15)

Atom	D1133	D2233	D1123	D1223	D1233
C8B	- 9(3)	23(5)	5(2)	- 9(3)	1(3)
C11B	55(12)	28(15)	- 110(11)	- 172(15)	179(14)
C18B	5(12)	28(9)	34(10)	- 22(9)	- 13(9)

Blessing (11). There were 8414 unique reflections (R_{int} = 0.024), of which 7047 have $F^2 > \sigma(F^2)$. Absorption corrections were applied with μ = 4.43 cm^{-1}. The maximum and minimum correction factors were 1.22 and 1.09.

The crystal structure was determined using the software package MITHRIL (12). There are two oleate molecules and one piperazinium ring in a linear arrangement. In the electron density, atoms of the ring and one oleate chain (oleate A) appeared in well-resolved single peaks, but the other oleate chain (oleate B) showed a split tail with two peaks each for C13, C15, and C17. The difference electron density map also revealed three small residual peaks near C8B and C11B. It was suspected that these residual densities were due to the occurrence of a second minor conformation for the olefin group of oleate molecule B. Refinement results showed that the occupancy of minor sites for C8B through C11B was about 20%. The minor conformation corresponds to an alternative configuration centered upon the *cis* double bond. No splitting was observed for the even numbered carbon atoms of oleate B (C12B, C14B, C16B, and C18B).

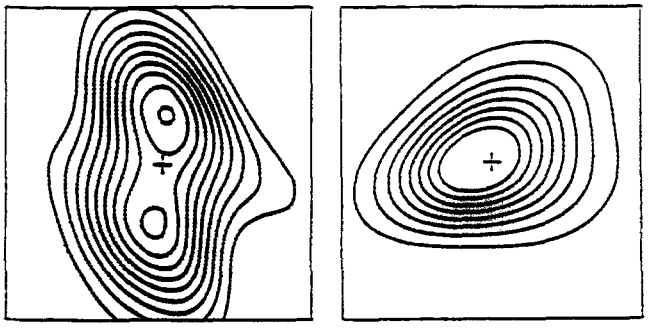

Fig. 2. The total probability density functions of C11B (bimodal, left) and C12B (right). The map for C11B is in the plane bisecting C10B-C11B-C12B, and for C12B in the plane bisecting C11B-C12B-C13B. The maps are for areas of 1.5 × 1.5 $Å^2$. Contours are at equal but arbitrary levels.

Considering the possibility that the apparent disorder might be the result of imposing a center of symmetry upon a noncentrosymmetric ordered crystal structure with true space group P1, we refined two ordered chain configurations for oleate B assuming the lower symmetry space group. Although the number of variables was almost doubled, the resulting fit to the electron density was not improved, and the agreement factors were not significantly different from refinement assuming the disordered structure in space group $P\bar{1}$. Following the advice of Marsh (13), the higher symmetry space group $P\bar{1}$ was chosen for piperazinium oleate, even though the alternative could not be completely ruled out. It is also interesting to note that the center of symmetry lies between the oleate-piperazinium-oleate complexes and not in the center of the piperazinium ring, as might be expected by analogy with related structures (10).

Some bond distances and angles (C-C = 1.39 to 1.64 Å, C-C-C = 108° to 130°) of oleate molecule B were significantly different from normal values. These departures

TABLE 2. (a) Positional (× 10^4) and m.s. displacement parameters ($Å^2$ × 10^4) for piperazinium oleate. Esd's are in parentheses. The anisotropic m.s. displacement factors have the form $T = \exp[-2\pi^2\Sigma_i\Sigma_j h_i h_j a_i^* a_j^* U_{ij}]$. For disordered and H atoms $T = \exp[-8\pi^2 U_{iso}\sin^2\theta/\lambda^2]$. In the atom labels, the second letter means: A = oleate A; B = oleate B and first half of the split tail, C = oleate B and second half of the split tail, D = minor conformer of oleate B, P = piperazinium. No entry in "Site" column represents an occupancy factor of 1.0.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Site
Piperazinium										
N1P	10203(3)	1694(1)	4768(1)	141(8)	161(8)	483(12)	− 39(6)	9(7)	− 49(8)	
N2P	9736(3)	3317(1)	5392(1)	133(8)	157(8)	467(12)	− 45(6)	6(7)	− 36(8)	
C1P	10301(4)	3339(1)	4807(1)	172(10)	186(10)	459(14)	− 71(8)	− 2(9)	21(9)	
C2P	10698(4)	2412(1)	5631(1)	186(10)	201(10)	431(14)	− 56(8)	− 9(9)	9(9)	
C3P	9665(4)	1672(1)	5357(1)	185(10)	191(10)	461(14)	− 59(8)	− 1(9)	33(9)	
C4P	9264(4)	2601(1)	4530(1)	172(10)	206(10)	451(14)	− 48(8)	− 6(9)	24(9)	
Oleate molecule A										
O1A	4968(2)	1392(2)	4569(1)	164(7)	265(8)	617(12)	− 52(6)	32(7)	− 118(8)	
O2A	8218(2)	498(1)	4237(1)	142(7)	244(8)	614(11)	− 27(6)	− 9(7)	− 112(7)	
C1A	5975(4)	787(1)	4249(1)	171(10)	185(10)	488(14)	− 49(8)	21(9)	− 16(9)	
C2A	4472(4)	396(2)	3848(1)	183(10)	238(11)	497(15)	− 22(8)	− 8(9)	− 39(10)	
C3A	5103(4)	− 629(2)	3787(1)	169(10)	222(10)	495(15)	− 45(8)	− 5(9)	− 11(10)	
C4A	3443(4)	− 980(2)	3395(1)	232(11)	274(12)	429(14)	− 59(9)	− 3(9)	− 24(10)	
C5A	3950(4)	− 2009(2)	3314(1)	242(11)	267(12)	448(15)	− 67(9)	10(10)	− 36(10)	
C6A	2143(5)	− 2320(2)	2943(1)	342(13)	285(12)	377(14)	− 104(10)	− 25(10)	− 14(10)	
C7A	2246(5)	− 3348(2)	2921(1)	385(14)	281(12)	469(16)	− 89(10)	− 22(11)	− 62(11)	
C8A	249(5)	− 3606(2)	2585(1)	491(17)	342(14)	672(20)	− 135(12)	− 96(14)	− 83(13)	
C9A	5(6)	− 4584(2)	2628(1)	572(18)	429(16)	578(19)	− 199(14)	− 134(14)	35(14)	
C10A	− 701(6)	− 5084(2)	2242(1)	676(21)	384(16)	672(21)	− 207(14)	− 240(16)	65(14)	
C11A	− 1396(6)	− 4776(2)	1696(1)	780(23)	445(17)	650(21)	− 302(16)	− 297(19)	81(15)	
C12A	− 3554(7)	− 5172(2)	1501(2)	733(23)	398(16)	768(23)	− 215(15)	− 390(19)	99(15)	
C13A	− 3065(6)	− 6183(2)	1409(1)	529(17)	434(16)	484(17)	− 213(13)	− 132(13)	7(13)	
C14A	− 5148(6)	− 6552(2)	1167(1)	569(19)	519(17)	513(18)	− 264(14)	− 223(14)	65(14)	
C15A	− 4615(5)	− 7567(2)	1067(1)	473(16)	552(17)	418(16)	− 248(13)	− 43(13)	− 69(13)	
C16A	− 6632(7)	− 7931(3)	796(2)	627(21)	700(22)	600(21)	− 348(17)	− 159(16)	− 82(17)	
C17A	− 6084(8)	− 8950(3)	703(2)	653(25)	801(27)	1094(35)	− 337(20)	− 53(22)	− 453(25)	
C18A	− 8083(9)	− 9315(4)	426(3)	878(33)	1076(37)	1289(43)	− 542(27)	− 117(30)	− 488(33)	
Oleate molecule B										
O1B	4938(2)	3708(1)	5536(1)	144(7)	183(7)	545(10)	− 40(5)	28(6)	− 78(7)	
O2B	1664(2)	4626(1)	5836(1)	135(7)	232(8)	591(11)	− 56(6)	32(7)	− 89(7)	
C1B	3911(4)	4450(1)	5739(1)	150(10)	206(10)	401(13)	− 43(8)	14(8)	4(9)	
C2B	5390(4)	5185(2)	5851(1)	165(10)	218(11)	499(15)	− 76(8)	32(9)	− 41(7)	
C3B	4700(4)	5725(2)	6360(1)	193(11)	235(11)	464(14)	− 77(8)	37(9)	− 37(10)	
C4B	6367(4)	6424(2)	6433(1)	214(11)	239(11)	468(14)	− 80(8)	38(9)	− 49(10)	
C5B	6050(4)	6916(2)	6967(1)	299(12)	326(13)	468(15)	− 150(10)	53(10)	− 55(11)	
C6B	8064(4)	7465(1)	7053(1)	267(12)	280(11)	407(14)	− 86(9)	17(9)	− 44(10)	
C7B	7806(5)	7986(2)	7576(1)	428(15)	400(14)	453(16)	− 197(12)	61(12)	− 80(12)	
C8B	9995(5)	8413(2)	7707(1)	414(15)	527(17)	502(17)	− 147(13)	− 18(12)	− 130(13)	
C9B	10599(6)	9093(2)	7340(1)	351(17)	384(18)	385(18)	− 117(14)	− 80(13)	16(14)	0.78
C10B	11254(6)	9868(2)	7461(1)	357(17)	344(17)	470(20)	− 108(13)	− 16(14)	5(14)	0.78

Atom	x/a	y/b	z/c	U_{iso}	Site
C11B	11446(9)	10257(3)	7993(2)	792(14)	0.78
C12B	13042(9)	10939(4)	8056(2)	652(9)	1.00
C13B	13076(10)	11397(3)	8560(2)	503(14)	0.50
C14B	14984(8)	11971(3)	8647(2)	573(8)	1.00
C15B	14919(12)	12458(4)	9146(2)	588(16)	0.50
C16B	17007(9)	12978(3)	9238(2)	556(8)	1.00
C17B	16618(14)	13564(5)	9721(2)	740(20)	0.50
C18B	18922(11)	14017(4)	9818(2)	920(13)	1.00
C13C	14221(10)	11117(3)	8553(3)	569(16)	0.50
C15C	16454(9)	12072(3)	9134(2)	492(14)	0.50
C17C	18723(12)	13027(4)	9707(2)	637(17)	0.50
C9D	9826(17)	9088(7)	8141(4)	410(27)	0.22
C10D	10740(15)	9826(5)	8241(3)	286(21)	0.22
C11D	12079(15)	10225(8)	7791(5)	839(53)	0.22

(b) Positional and isotropic m.s. displacement parameters for H atoms. No entry in the "Site" column represents an occupancy of 1.0. The meanings of the second letter in the atom label are as in Table 2(a).

TABLE 2. Continued

Atom	x/a	y/b	z/c	U_{iso}	Site
Piperazinium					
HN11	11874(49)	1534(16)	4683(10)	424(74)	
HN12	9461(45)	1235(17)	4571(9)	354(68)	
HN21	8067(49)	3460(18)	5470(10)	410(73)	
HN22	10512(48)	3775(18)	5568(10)	431(75)	
H1P1	12048(38)	3236(14)	4753(8)	187(54)	
H1P2	9624(39)	3945(15)	4648(9)	225(57)	
H2P1	10258(42)	2383(16)	6025(10)	323(66)	
H2P2	12450(38)	2313(14)	5591(8)	168(53)	
H3P1	10334(44)	1024(17)	5483(10)	372(69)	
H3P2	7826(42)	1761(16)	5397(9)	292(63)	
H4P1	7551(40)	2664(15)	4553(9)	248(59)	
H4P2	9736(40)	2571(15)	4121(9)	247(59)	
Oleate molecule A					
H2A1	4725(48)	663(18)	3498(11)	463(79)	
H2A2	2729(62)	565(22)	3961(13)	783(106)	
H3A1	5054(42)	−930(16)	4149(9)	304(64)	
H3A2	6850(47)	−802(17)	3671(10)	394(71)	
H4A1	1873(54)	−833(19)	3556(11)	547(86)	
H4A2	3619(41)	−715(16)	3033(10)	301(64)	
H5A1	3890(43)	−2297(17)	3676(10)	346(68)	
H5A2	5563(50)	−2204(18)	3146(11)	480(80)	
H6A1	529(52)	−2044(19)	3068(11)	514(83)	
H6A2	2358(42)	−2097(16)	2563(10)	310(64)	
H7A1	2089(51)	−3569(19)	3301(12)	537(85)	
H7A2	3720(49)	−3628(18)	2750(11)	434(76)	
H8A1	−1311(48)	−3216(18)	2681(11)	876(119)	
H8A2	−274(40)	−3409(15)	2201(9)	232(59)	
H9A	410(66)	−4786(25)	3035(15)	980(128)	
H10A	−1085(60)	−5728(22)	2358(13)	791(108)	
H11A1	−91(56)	−4898(20)	1426(12)	1056(144)	
H11A2	−1650(43)	−3962(17)	1775(10)	340(66)	
H12A1	−4991(57)	−5048(21)	1777(12)	640(99)	
H12A2	−4075(57)	−4864(22)	1141(13)	707(101)	
H13A1	−2740(43)	−6495(16)	1766(10)	327(66)	
H13A2	−1721(54)	−6304(20)	1166(12)	593(93)	
H14A1	−6768(54)	−6390(20)	1420(12)	607(93)	
H14A2	−5529(49)	−6258(19)	828(12)	485(80)	
H15A1	−4393(42)	−7874(16)	1412(10)	321(67)	
H15A2	−3349(60)	−7658(22)	815(13)	729(105)	
H16A1	−8177(61)	−7753(22)	1029(13)	739(106)	
H16A2	−6735(53)	−7668(20)	452(12)	578(93)	
H17A1	−5942(85)	−9199(32)	1036(19)	1370(185)	
H17A2	−4672(73)	−9054(26)	482(16)	1018(138)	
H18A1	−7741(86)	−9968(34)	340(19)	1414(183)	
H18A2	−8358(71)	−8957(27)	27(16)	1031(144)	
H18A3	−9382(77)	−9194(29)	616(17)	1104(156)	
Oleate molecule B					
H2B1	5233(44)	5563(17)	5538(10)	363(70)	
H2B2	7156(49)	4930(18)	5888(10)	452(76)	
H3B1	4849(46)	5319(18)	6686(10)	414(74)	
H3B2	3038(49)	6059(18)	6344(10)	441(75)	
H4B1	8057(48)	6133(17)	6386(10)	397(71)	
H4B2	6120(44)	6899(17)	6120(10)	374(70)	
H5B1	6027(48)	6495(19)	7264(11)	472(79)	
H5B2	4507(52)	7353(19)	6983(11)	499(81)	
H6B1	9616(44)	7031(16)	7052(9)	313(64)	
H6B2	8203(41)	7907(16)	6737(9)	299(63)	
H7B1	6350(54)	8384(20)	7584(12)	579(89)	
H7B2	7469(56)	7589(21)	7871(13)	666(98)	
H8B1	9708	8680	8069	558	0.78
H8B2	11402	7914	7730	558	0.78
H9B	10542	8970	6967	441	0.78
H10B	11661	10231	7163	469	0.78
H11B1	11980	9745	8246	1083	0.78

TABLE 2. Continued

H11B2	9802	10538	8115	1083	0.78
H12B1	14710	10633	7972	827	0.50
H12B2	12627	11414	7774	827	0.50
H13B1	13203	10928	8851	625	0.50
H13B2	11490	11793	8612	625	0.50
H14B1	16570	11570	8614	700	0.50
H14B2	14112	12424	8347	700	0.50
H15B1	14864	12016	9447	751	0.50
H15B2	13396	12899	9165	751	0.50
H16B1	18510	12533	9279	682	0.50
H16B2	17225	13363	8916	682	0.50
H17B1	16286	13192	10042	967	0.50
H17B2	15200	14045	9670	967	0.50
H18B1	18639	14397	10139	1526	0.50
H18B2	19229	14395	9504	1526	0.50
H18B3	20322	13540	9872	1526	0.50
H12C1	11651	11443	8052	827	0.50
H12C2	14179	11112	7775	827	0.50
H13C1	13110	11012	8856	756	0.50
H13C2	15565	10640	8584	756	0.50
H14C1	13519	12442	8668	700	0.50
H14C1	15932	12120	8324	700	0.50
H15C1	15582	11873	9456	612	0.50
H15C2	17998	11646	9097	612	0.50
H16C1	15476	13393	9316	682	0.50
H16C2	17737	13206	8905	682	0.50
H17C1	18105	12744	10035	773	0.50
H17C2	20339	12683	9613	773	0.50
H18C1	20010	14037	10116	1526	0.50
H18C2	17324	14355	9915	1526	0.50
H18C3	19560	14294	9495	1526	0.50
H8D1	11305	7904	7799	558	0.22
H8D2	10515	8700	7372	558	0.22
H9D	9826	9088	8141	554	0.22
H10D	10553	10094	8587	366	0.22
H11D1	10984	10477	7501	872	0.22
H11D2	13386	9766	7638	872	0.22

from accepted hydrocarbon geometry are attributed to disorder effects and the near superposition of atomic sites from the different chain conformations. In order to model the distribution of partially resolved atoms, selected atoms were assigned third and fourth order atomic displacement parameters according to the Gram-Charlier formalism (14). This was done for C8B, C11B, C12B, C14B, C16B, and C18B, using the computer program POP (15). Refinement showed that the fourth order displacement parameters for C12B, C14B, and C16B were not significantly different from zero, and they were omitted in further refinements in order to reduce the number of variables. The atomic displacement parameters obtained (**Table 1**) were used to calculate the total probability density functions (pdf's) for C11B and C12B using a program by Craven, He, and Weber (16). These pdf's refer to the displacement of point atoms and thus have higher resolution than the corresponding electron density distribution. In their interpretation, it must be recognized that each pdf represents the combination of atomic displacements caused by thermal vibration and disorder. The pdf maps for C11B, C12B are given in **Fig. 2.** The pdf for C11B shows a pronounced bimodal character with maxima separated by 0.5 Å, while the pdf for C12B is highly skewed. Maps for C14B, C16B, and C18B (not shown) also show skewed features similar to C12B. It seems reasonable to attribute these results to disorder of the oleate B chain. C11B is considered to be disordered over two positions for the major chain, similar to C13, C15, and C17. The other atoms appear to show the effects of near superposition of the atomic sites for the two different chain conformers.

In further structure refinement using the program SHELXL93 (17), the disordered part of the oleate B chain was first subjected to the restraint that the corresponding C-C bonds of the two conformers be equal in length within an esd of 0.03 Å. In the final POP refinement, for the disordered region of the oleate B chain, the atoms were fixed at their restrained positions with only their isotropic m.s. displacement parameters as variables.

Many of the hydrogen atom positions were obtained from difference Fourier maps. The positional and isotropic thermal parameters for the H atoms belonging to the piperazine cation and oleate A and the methylene groups of the carboxylate segment of oleate B were refined. For the disordered part of oleate B, H atom positions were calculated at standard geometry and were fixed at 0.99 Å (0.95 Å for methine) from the C atoms to which they are bonded. Their isotropic thermal parameters were then fixed to $B_{eq}(C) \times 1.2$ Å^2 for methine and methylene H atoms, and $B_{eq}(C) \times 1.5$ Å^2 for the methyl H atoms according to Sheldrick (17). In the above formula B_{eq} (C) is the (equivalent) isotropic m.s. displacement parameter of the carbon atom to which the hydrogens are attached. The H atom parameters are given in Table 2(b). There were a total of 579 variables including the scale factor, positional and anisotropic m.s. displacement parameters for non-H atoms and positional and isotropic displacement parameters for some H atoms and all carbon atoms of the disordered part of oleate B. Four reflections (001, $0\bar{2}5$, $\bar{1}04$, $\bar{1}2\bar{1}$) were excluded from the final least squares refinement because of possible extinction or unbalanced background effects. At convergence $R(F^2) = 0.116$, $wR(F^2) = 0.20$, and $S = 3.62$ for all 8410 reflections.[3] Atomic positional and m.s. displacement parameters are given in **Table 2,** and bond distances, angles and torsion angles are in **Table 3.**

RESULTS AND DISCUSSION

Molecular structure

The asymmetric unit in the crystal consists of a piperazinium dication and two oleate anions (**Fig. 3**). The piperazinium cation is in a chair conformation, similar to that observed in the crystal structures of piperazinium myristate and palmitate (10), except that in the oleate salt the cation does not sit on a crystallographic center of symmetry. The ring puckering parameters (19) are ($Q = 0.58$ Å, $\theta = 0°$, $\phi = 0°$), slightly deformed in comparison with an ideal cyclohexane molecule ($Q = 0.63$ Å, $\theta = 0°$, $\phi = 0°$). Cation bond distances and angles (Table 3) agree with those in piperazinium myristate and palmitate. The two oleate anions are almost fully extended. The overall chain length, the distance from C1 to C18, is 21.2 Å and 20.8 Å, respectively, for oleate A and oleate B. Each chain is composed of two all-*trans* segments separated by a kink at the double bond. As noted earlier, oleate A is well ordered and the C–C bond distances and angles (Table 3) agree with values given by Lide (20). The oleate A chain has a pattern of rotations about the C–C bonds given by ···tt$\bar{s}$C$\bar{s}\bar{g}$tt···,[4] starting from the carboxylate group. This sequence is similar to that in cholesteryl oleate at −150°C (8). The bonds C8–C9 and C10–C11 adjacent to the double bond have torsion angles (−148° and −140°) outside the range for the preferred ± *skew* conformations ± (90° to 130°) observed for other *cis*-olefins (21). The (−)-*gauche* torsion angle (−65°) at C11–C12 ensures that the overall chain conformation is almost straight, rather than a boomerang. The crystallographic symmetry requires a kink of the opposite handedness ···tt$\bar{s}$C$\bar{s}\bar{g}$tt··· on the centrosymmetrically related oleate A anion.

The carboxylate end of the oleate B chain is ordered and is similar to the oleate A chain in both bond distances and angles. However, from C8 through C18, this chain is highly disordered. Three of the chain carbon atoms (C13, C15, and C17) are split evenly over two sites, indicating the presence of two equally weighted conformers. Also, the four atom olefin group (C8–C9=C10–C11) takes on a minor conformation with 20% occupancy. Three atoms of this group (C9D, C10D, and C11D) take alternative positions while C8 almost superposes on the corresponding site of the major conformers. The *cis*-olefin group deviates slightly from planarity ($\tau = 2.7(7)°$) for the major conformers. The sequence for the two major conformations C8 to C18 can be described as ···tt$\bar{g}\bar{s}$Ctttt···. A more detailed consideration of the torsion angles (Table 3) shows that a single simplified notation can only be used for both major conformers by neglecting differences of 33 and 34° in torsion about the bonds C11–C12 and C12–C13. The minor conformers are more twisted at the double bond ($\tau = 11°$) with torsion angle sequence ···tt$\bar{s}$C$\bar{t}\bar{g}$t···. The centrosymmetrically related B-chains have kinks with opposite chirality.

Thus the crystal structure contains oleate chains in a variety of extended conformations exhibiting at least six different kinks and possibly eight if there is no correlation between the two kinds of disorder in the B-chains.

Molecular packing

Each piperazinium cation makes four N–H···O hydrogen bonds to four oleate anions. Each oleate anion makes two hydrogen bonds to two cations through its carboxyl oxygen atoms (Fig. 3(a)). In this manner an infinite ribbon approximately parallel to plane ($0\bar{2}5$) is formed

[3] $R(F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$; $wR(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma(wF_o^2)^2]^{1/2}$; $S = [w|F_o^2 - F_c^2|^2/(n - v)]^{1/2}$; $w = 1/\sigma^2(F_o^2)$.

[4] t = *trans*; $\bar{g}$ = (+)-*gauche*; $\bar{g}$ = (−)-*gauche*; $\bar{s}$ = (+)-*skew*; $\bar{s}$ = (−)-*skew*; *C* = *cis*-double bond. Each sequence begins at the carboxylate end of the chain.

TABLE 3. Bond distances, angles, and torsion angles involving non-H atoms. (Esd's for those that involve all atoms from C8B to the terminal methyl group of oleate molecule B are estimated from non-constrained refinements and are only included for reference.)

Bond distances (Å)

Piperazinium	
N1P-C3P	1.482(3)
N1P-C4P	1.484(3)
N2P-C1P	1.477(3)
N2P-C2P	1.485(3)
C2P-C3P	1.514(3)
C1P-C4P	1.516(3)

Oleate molecule A		Oleate molecule B	
O1A-C1A	1.263(3)	O1B-C1B	1.266(3)
O2A-C1A	1.264(3)	O2B-C1B	1.264(3)
C1A-C2A	1.514(3)	C1B-C2B	1.518(3)
C2A-C3A	1.519(3)	C2B-C3B	1.518(3)
C3A-C4A	1.530(3)	C3B-C4B	1.531(3)
C4A-C5A	1.527(4)	C4B-C5B	1.520(4)
C5A-C6A	1.529(4)	C5B-C6B	1.528(4)
C6A-C7A	1.525(4)	C6B-C7B	1.517(4)
C7A-C8A	1.527(4)	C7B-C8B	1.526(4)
C8A-C9A	1.489(4)	C8B-C9B	1.423(4)
		C8B-C9D	1.479(9)
C9A=C10A	1.334(5)	C9B=C10B	1.313(5)
		C9D=C10D	1.322(9)
C10A-C11A	1.466(5)	C10B-C11B	1.469(6)
		C10D-C11D	1.496(9)
C11A-C12A	1.535(5)	C11B-C12B	1.478(7)
		C11D-C12B	1.449(8)
C12A-C13A	1.506(5)	C12B-C13B	1.441(7)
		C12B-C13C	1.470(8)
C13A-C14A	1.522(5)	C13B-C14B	1.504(7)
		C13C-C14B	1.436(7)
C14A-C15A	1.517(5)	C14B-C15B	1.456(7)
		C14B-C15C	1.512(7)
C15A-C16A	1.519(5)	C15B-C16B	1.537(7)
		C15C-C16B	1.465(7)
C16A-C17A	1.519(6)	C16B-C17B	1.488(8)
		C16B-C17C	1.547(8)
C17A-C18A	1.520(7)	C17B-C18B	1.587(9)
		C17C-C18B	1.530(8)

Bond angles (°)

Piperazinium	
C3P-N1P-C4P	111.1(2)
C1P-N2P-C2P	110.8(2)
N2P-C1P-C4P	110.1(2)
N2P-C2P-C3P	110.4(2)
C2P-C3P-N1P	110.2(2)
N1P-C4P-C1P	110.5(2)

Oleate molecule A		Oleate molecule B	
O1A-C1A-O2A	123.1(2)	O1B-C1B-O2B	122.8(2)
O1A-C1A-C2A	119.5(2)	O1B-C1B-C2B	119.4(2)
O2A-C1A-C2A	117.4(2)	O2B-C1B-C2B	117.7(2)
C1A-C2A-C3A	114.3(2)	C1B-C2B-C3B	116.1(2)
C2A-C3A-C4A	111.4(2)	C2B-C3B-C4B	110.9(2)
C3A-C4A-C5A	114.7(2)	C3B-C4B-C5B	115.2(2)
C4A-C5A-C6A	112.0(2)	C4B-C5B-C6B	112.0(2)
C5A-C6A-C7A	115.0(2)	C5B-C6B-C7B	114.2(2)
C6A-C7A-C8A	112.2(2)	C6B-C7B-C8B	114.4(2)

TABLE 3. Continued

C7A-C8A-C9A	114.3(3)	C7B-C8B-C9B	116.7(3)
		C7B-C8B-C9D	120.1(6)
C8A-C9A-C10A	126.5(3)	C8B-C9B-C10B	127.1(3)
		C8B-C9D-C10D	137.5(8)
C9A-C10A-C11A	126.8(3)	C9B-C10B-C11B	129.0(3)
		C9D-C10D-C11D	117.6(7)
C10A-C11A-C12A	113.0(3)	C10B-C11B-C12B	119.4(6)
		C10D-C11D-C12B	102.6(5)
C11A-C12A-C13A	114.8(3)	C11B-C12B-C13B	120.4(5)
		C11B-C12B-C13C	126.0(5)
C12A-C13A-C14A	114.1(3)	C12B-C13B-C14B	119.6(4)
		C12B-C13C-C14B	122.3(5)
C13A-C14A-C15A	113.6(3)	C13B-C14B-C15B	118.7(4)
		C13C-C14B-C15C	119.6(4)
C14A-C15A-C16A	113.9(3)	C14B-C15B-C16B	117.1(4)
		C14B-C15C-C16B	117.5(4)
C15A-C16A-C17A	113.3(3)	C15B-C16B-C17B	113.3(4)
		C15C-C16B-C17C	115.5(4)
C16A-C17A-C18A	113.5(4)	C16B-C17B-C18B	110.6(5)
		C16B-C17C-C18B	110.5(5)

Torsion angles (°)

Oleate molecule A		Oleate molecule B	
O1A-C1A-C2A-C3A	- 137.8(2)	O1B-C1B-C2B-C3B	- 142.7(2)
O2A-C1A-C2A-C3A	43.6(3)	O2B-C1B-C2B-C3B	40.0(3)
C1A-C2A-C3A-C4A	177.5(2)	C1B-C2B-C3B-C4B	178.5(2)
C2A-C3A-C4A-C5A	- 179.6(2)	C2B-C3B-C4B-C5B	- 172.3(2)
C3A-C4A-C5A-C6A	176.9(2)	C3B-C4B-C5B-C6B	169.3(2)
C4A-C5A-C6A-C7A	- 169.6(2)	C4B-C5B-C6B-C7B	178.8(2)
C5A-C6A-C7A-C8A	174.8(2)	C5B-C6B-C7B-C8B	170.9(2)
C6A-C7A-C8A-C9A	- 170.0(2)	C6B-C7B-C8B-C9B	63.1(3)
		C6B-C7B-C8B-C9D	167.8(5)
C7A-C8A-C9A=C10A	- 148.2(3)	C7B-C8B-C9B=C10B	137.4(4)
		C7B-C8B-C9D=C10D	- 146.1(9)
C8A-C9A=C10A-C11A	- 0.3(6)	C8B-C9B=C10B-C11B	- 2.7(6)
		C8B-C9D=C10D-C11D	10.8(8)
C9A=C10A-C11A-C12A	- 140.3(3)	C9B=C10B-C11B-C12B	156.9(5)
		C9D=C10D-C11D-C12B	- 173.6(9)
C10A-C11A-C12A-C13A	- 67.7(4)	C10B-C11B-C12B-C13B	173.7(4)
		C10B-C11B-C12B-C13C	- 153.1(5)
		C10D-C11D-C12B-C13C	43.1(1)
C11A-C12A-C13A-C14A	- 174.6(3)	C11B-C12B-C13B-C14B	170.1(5)
		C11B-C12B-C13C-C14B	- 156.5(5)
		C11D-C12B-C13C-C14B	- 177.9(5)
C12A-C13A-C14A-C15A	179.0(3)	C12B-C13B-C14B-C15B	177.3(3)
		C12B-C13C-C14B-C15C	- 172.6(3)
C13A-C14A-C15A-C16A	- 176.7(3)	C13B-C14B-C15B-C16B	175.4(2)
		C13C-C14B-C15C-C16B	- 174.8(2)
C14A-C15A-C16A-C17A	- 179.5(3)	C14B-C15B-C16B-C17B	171.7(3)
		C14B-C15C-C16B-C17C	- 174.2(3)
C15A-C16A-C17A-C18A	- 179.3(4)	C15B-C16B-C17B-C18B	175.5(4)
		C15C-C16B-C17C-C18B	- 173.3(4)

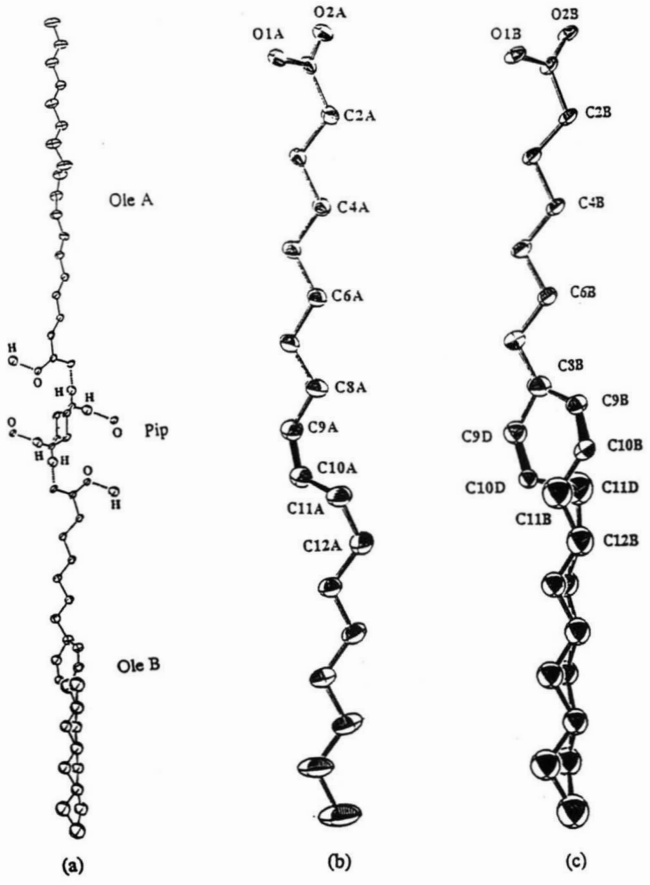

Fig. 3. (a) The molecules of the oleate···piperazinium···oleate asymmetric unit, drawn with the ORTEP program (18). The H bonding scheme is shown as broken lines. Atoms are represented by ellipsoids with 50% probability of enclosing the atom. (b) Oleate A chain. (c) Oleate B chain. The minor conformer is shown by the second letter D in the atomic labels. Solid bonds represent the *cis* double bonds.

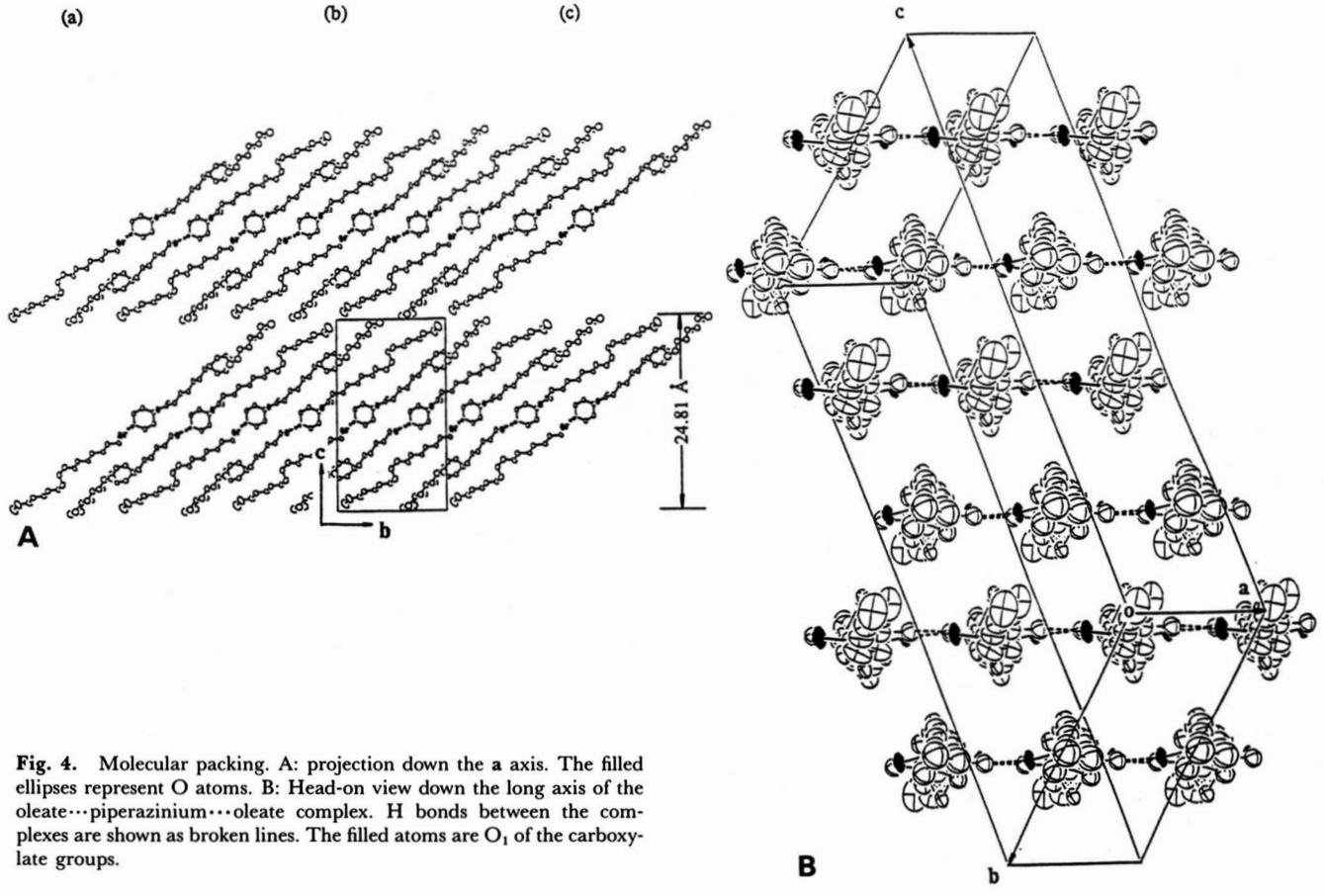

Fig. 4. Molecular packing. A: projection down the **a** axis. The filled ellipses represent O atoms. B: Head-on view down the long axis of the oleate···piperazinium···oleate complex. H bonds between the complexes are shown as broken lines. The filled atoms are O_1 of the carboxylate groups.

which has an overall 1:2 composition ratio between piperazinium and oleate. These ribbons extend along the *a* direction and pack upon each other with all oleate chains parallel to form a monolayer of thickness d_{001} = 24.81 Å, as shown in **Fig. 4A.** A regular subcell packing of the hydrocarbon chain is absent. All complete oleate···piperazinium···oleate H bonded complexes are aligned approximately along the crystallographic direction [852], which makes an angle of 31° with respect to the monolayer. The length of a complex plus the van der Waals radii, is roughly 53.6 Å at −150°C. The molecular packing is also shown in a view along the anion-cation chains (Fig. 4B). There is no intermolecular C···C distance shorter than 3.5 Å between adjacent oleate molecules.

Owing to the crystal being obtained by flash freezing and therefore possibly being in a metastable form, we cannot identify which low temperature phase corresponds to the structure that we have determined. We are also limited in any speculation about the structural relationships that might occur among these phases. However, we point out that in Table 2, the difference between pairs of disordered sites for the oleate B chains is primarily in their *x*-coordinates. Consequently, we suggest that one of the other phases has an ordered structure related to the structure reported here by a doubling of the *a* unit cell repeat. Thus both *a* and *b* would be doubled by comparison with the room temperature structure.

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