- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS: A FORTRAN Crystallographic Least-Squares Program. Publication ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104.
- DEWAR, M. J. S. (1958). Steric Effects in Conjugated Systems, pp. 46-51. Edited by G. W. GRAY. London: Butterworths.
- EFFINGER, J., GERMAIN, G., MEUNIER, J., VANDERAUWERA, J. & VAN MEERSSCHE, M. (1960). Bull. Soc. Chim. Belges, 69, 387.
- FURNAS, T. C. (1957). Single Crystal Orienter Instruction Manual. Milwaukee, Wisconsin: General Electric Co.
- GERMAIN, G., PATTERNOTTE, C., PIRET, P. & VAN MEERS-SCHE, M. (1964). J. Chim. Phys. 61, 1059.
- GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DEKERF, J. (1961), Bull. Soc. chim. Fr. p. 1407.
- GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DEKERF, J. (1962). Acta Cryst. 15, 373.
- IBERS, J. A. & HAMILTON, W. C. (1966). Private communication.
- International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP: A FORTRAN Thermal Ellipsoid Program for Crystal Structure Illustrations. Publication ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

- Karle, J. & Karle, I. L. (1967). J. Amer. Chem. Soc. 89, 804.
- KAWADA, I. & ALLMANN, R. (1968). Angew. Chem. Internat. Edit. 7, 69.
- LIDE, D. R. (1962). Tetrahedron, 17, 125.
- PAULING, L. (1960). The Nature of the Chemical Bond. 3rd Ed. Ithaca: Cornell Univ. Press.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). Acta Cryst. 12, 600.
- SHEPPARD, S. E., LAMBERT, R. H. & WALKER, R. D. (1941). J. Chem. Phys. 9, 96.
- SINGH, C. (1965). Acta Cryst. 19, 861.
- SMITH, D. L. (1966). Unpublished program.
- SMITH, D. L. (1969). Acta Cryst. B25, 625.
- SMITH, D. L. & LUSS, H. R. (1969). Unpublished results.
- SRIVASTAVA, R. C. & LINGAFELTER, E. C. (1966). Acta Cryst. 20, 918.
- SUTTON, L. E. (1965). Interatomic Distances, Supplement. Special Publication No. 18, London: The Chemical Society.
- TOMAN, K. & OCENASKOVA, D. (1966). Acta Cryst. 20, 514.
- TROTTER, J. (1965). Private communication.
- VORONTSOVA, L. G., ZVONKOVA, Z. V. & ZHDANOV, G. S. (1963). Kristallografiya 8, 374.
- WHEATLEY, P. J. (1959a). J. Chem. Soc. p. 3245.
- WHEATLEY, P. J. (1959b). J. Chem. Soc. p. 4096.

Acta Cryst. (1971). B27, 977

The Crystal Structure of the 1,3-Diglyceride of 11-Bromoundecanoic Acid

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(Received 8 April 1970 and in revised form 13 August 1970)

The symmetric diglyceride of 11-bromoundecanoic acid, $C_{25}H_{46}Br_2O_5$ (DBU), was crystallized from chloroform showing a tabular monoclinic aspect and having space group C2/c, with unit-cell dimensions a=9.36, b=5.58, c=54.53 Å, $\beta=90.40^{\circ}$ and with Z=4. The structure was determined by a three-dimensional X-ray diffraction analysis. Data were collected with a General Electric XRD-6 manual diffractometer and nickel-filtered Cu Ka radiation. The structure was solved by the heavy atom method. Block-diagonal least-squares refinement led to an R of 0.09. A pseudo twofold axis of molecular symmetry is utilized as a statistical axis of symmetry by the space group. The two hydrocarbon chain tails in the molecule point in opposite directions and are packed in layers with the chain axis parallel. The direction of the chain tilt, however, alternates in successive layers.

Introduction

Several rather detailed models (O'Brien, 1965; Vandenheuvel, 1963) for the unit membrane (Robertson, 1959; Korn, 1966) have been postulated. Most of these models incorporate the Finean (1967) conformations for the phospholipids in which the two fatty acid chains are folded in a parallel orientation. Because very few relevant single-crystal structure results have been reported for diacyl compounds, we have undertaken a series of crystallographic studies with the purpose of establishing experimentally the stable crystal conformation of these molecules.

We chose to begin our studies using the simple synthetic diacyl derivatives of 11-bromoundecanoic acid in order to have a heavy atom present in the structure. From the similarities in long spacing and polymorphism (Finean, 1967) between the diglycerides and the phospholipids it is clear that the hydrocarbon chain packing has a dominating influence. We may expect conformational similarities in the chain structure between the diglycerides and the diacyl phospholipids. It is very difficult to grow single crystals of diacyl phospholipids suitable for X-ray work; we have therefore performed a structure determination of the hydrophobic moiety. The purpose of these studies is, first, to elucidate the molecular conformations and, second, to provide accurate dimensional information for the glycerol region of the molecule.

Experimental

We had intended to prepare the 1,2-diglyceride following the procedures of Howe & Malkin (1951). The X-ray analysis, however, showed that the diglyceride obtained from our synthesis was the symmetric one. Tabular crystals for X-ray work were grown from chloroform by very slow evaporation over a period of about two weeks. The $\{001\}$ form is well developed. The crystals are elongated along **b**. The melting point of single crystals observed on a hot stage ranges between 47.5 and 49 °C.

Crystals of the 1,3-diglyceride of 11-bromoundecanoic acid (DBU) are monoclinic with $a=9\cdot36(2)$, $b=5\cdot58(1)$, $c=54\cdot53(5)$ Å, $\beta=90\cdot40(8)^{\circ}$ and $t=27(4)^{\circ}$. The confidence limits cited are subjective estimates. The space group is C2/c with four molecules per unit cell. A pseudo twofold axis of molecular symmetry is utilized as a statistical axis of symmetry by the space group. The observed density is $1\cdot366 \text{ g.cm}^{-3}$ (by flotation in aqueous potassium iodide solution); the calculated density is $1\cdot368 \text{ g.cm}^{-3}$.

Intensity data were collected using a manually operated General Electric XRD-6 single crystal orienter system. Nickel filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$) scattered by the crystal with the *b* axis mounted coincident with the φ axis was detected by a scintillation counter with a pulse height analyzer system. The stationary-crystal stationary-counter technique was used with a take-off angle of 5°. Peak counts were observed for forty seconds; background counts were observed for twenty seconds at a point -1.67° in 2θ .

The diffractometer angles for the 0,6,0, 10,0,0 and 0,0,56 reflections, obtained at a 1° take-off angle, were input to a modified version of the *SCO*-6 program (D. E. Williams, private communication) to compute the transformation matrix, the unit-cell parameters and the setting angles for the other reflections. Periodic checks showed that the reflections were well centered in the diffracted beam collimator.

Owing to a deterioration of the crystal in the X-ray beam, four crystals were needed to collect a full set of three-dimensional intensity data. Intensity data were gathered in zones of constant k. A set of 69 standard reflections was collected before beginning each zone. This set of standard reflections contained a representative sampling from the three-dimensional data set. The set was used for providing correlation factors between the different crystals and also for the intensity decline correction. A set of four standard reflections was used to further monitor the intensity decay of each crystal. The 222 reflection was measured after each group of 25 data reflections, the 040 and the 600 were observed after groups of 50 data reflections and the 0,0,56 was observed after groups of 75 data reflections.

3675 serially recorded observations including redundancies due to the standard and scaling reflections were corrected for approximately linear intensity decline using the expression:

$$I(j) = I'(j) \{ K(n) / [1 \cdot 0 + S(n)(j - J_0(n))] \}$$

where

- I(j) = the intensity value corrected for 'linear' decay;
- I'(j) = the uncorrected intensity for observation j;
- K(n) = the scaling ratio between crystal *n* and crystal *l*;
- S(n) = the fractional intensity decline per observation;
- $J_o(n)$ = the value of j for the first observation on crystal n.

The following values were used:

n	K(n)	S(n)	$J_o(n)$
1	1.000	0.000445	1
2	0.746	0.000542	610
3	0.680	0.000244	1086
4	0.649	0.000277	2442

The deterioration did not show a detectable 2θ dependence. The multiple values for the 69 scaling and 4 standard reflections were averaged to remove redundancies.

The total counts were corrected for counting losses assuming a time constant of 5×10^{-6} . They were then corrected for background and linear decline. A conversion from peak intensity to integrated intensity was made according to the procedures of Alexander & Smith (1962). Lorentz and polarization corrections were made. No corrections were made for absorption or extinction. The standard deviation of the intensity was computed according to the formula:

$$\sigma(I) = \{C_t + C_b + [0.05(C_t - C_b)]^2 + (0.05C_b)^2\}^{1/2},\$$

where C_t = total counts and C_b = background counts. A reflection was designated as unobserved if its intensity was less than or equal to two times $\sigma(I)$. 2100 reflections of the 2722 unique reflections measured were designated as observed, and 622 were designated as unobserved. 56 of the observed reflections were omitted in the final least-squares cycle owing to either absorption, extinction or probable SCO angle setting errors.

The lipid nature of the crystals precludes grinding spherical shapes. When intensity deterioration requires the use of multiple crystals, the usefulness of semiempirical methods for absorption correction is limited since precious time is needed to make accurate measurement of the transmission surface for a series of axial reflections. Although the crystals are plate-like, they are usually irregular; nevertheless, the best method for making absorption corrections appears to be the com-

		The anisotr	opic coefficients ha	ve the form: exp	$[-(\beta_{11}h^2 + \beta_{22}k^2)]$	$(+\beta_{33})^2 + \beta_{12}hk +$	$+\beta_{13}hl+\beta_{23}kl)].$		
	x/a	y/b	z/c	β_{11}	β22	β_{33}	β_{12}	<i>β</i> 13	β_{23}
Br	-0.1886(1)	-0.0312 (2)	0.01973 (1)	0-0216(1)	0-0564 (4)	0.00047 (0)	-0.0229 (4)	0.00029 (3)	-0.00399 (6)
C(11)	-0.0645(7)	0.2107 (17)	0.03441 (13)	0.0128 (8)	0.0597 (40)	0-00050 (3)	-0.0114(31)	0.00024 (23)	-0.00517 (59)
C(10)	-0.1355(7)	0-3415 (14)	0.05485 (11)	0.0140(8)	0-0411 (26)	0.00033 (2)	-0.0066 (27)	0.00021 (20)	-0.00176 (43)
C(9)	-0.0314 (7)	0-5093 (13)	0.06743 (11)	0.0134 (8)	0.0433 (31)	0.00039 (2)	-0.0042 (26)	0.00068 (20)	-0.00251 (47)
C(8)	-0.1037(7)	0-6595 (14)	0-08755 (11)	0-0125 (7)	0-0396 (27)	0-00037 (2)	-0.0038 (25)	0-00053 (20)	-0.00237 (43)
C(7)	-0.0005 (6)	0-8207 (13)	0.10146 (11)	0-0119 (7)	0-0391 (28)	0-00037 (2)	-0.0047 (24)	0.00024 (19)	-0.00160 (42)
C(6)	-0.0714 (6)	0.9738 (13)	0.12082 (11)	0.0114 (7)	0-0394 (27)	0.00035 (2)	-0.0021 (24)	0.00023 (18)	-0.00213 (42)
C(5)	0-0316 (6)	1.1284 (15)	0.13545 (10)	0-0111 (7)	0.0483 (29)	0-00032 (2)	-0.0050(26)	0-00032 (18)	-0.00188 (44)
C(4)	-0.0412 (6)	1.2943 (13)	0.15360 (10)	0.0113 (7)	0.0418(27)	0-00031 (2)	-0.0038 (23)	-0.00005 (18)	-0.00165 (40)
C(3)	0.0621 (6)	1-4363 (13)	0.16925 (10)	0.0115 (7)	0.0396(26)	0.00031 (2)	-0.0026 (24)	-0.00000 (18)	-0.00181 (40)
C(2)	-0.0133(6)	1-6092 (14)	0.18641 (10)	0-0101 (7)	0.0462 (29)	0.00033 (2)	-0.0031 (24)	-0.00001 (17)	-0.00126 (43)
C(1)	0.0867 (6)	1.7322 (12)	0-20365 (9)	0-0111 (7)	0.0372 (24)	0-00026 (2)	0-0005 (23)	0.00022 (16)	-0.00089 (37)
O=	0.2124 (4)	1-6965 (12)	0.20574 (8)	0-0087 (5)	0-0726 (31)	0.00052 (2)	0-0032 (21)	0-00001 (14)	-0.00591 (43)
ģ	0.0187 (4)	1.8932 (10)	0.21755 (7)	0.0109 (5)	0-0471 (21)	0.00039 (1)	0-0059 (18)	-0.00042 (13)	-0.00307 (31)
GC(1)	0.1037 (6)	2-0230 (13)	0-23506 (10)	0-0115 (7)	0-0434 (28)	0.00031 (2)	-0.0006 (24)	0-00031 (18)	-0.00166 (41)
GC(2)	(0) 0000.0	2.1743 (18)	0.25000 (0)	0-0139 (11)	0-0361 (35)	0.00024 (2)	0.0000 (0)	0-00069 (25)	0.00000 (0)
GO(2)	0.0586 (8)	2-3467 (18)	0.26259 (13)	0-0126 (10)	0-0385 (33)	0-00028 (2)	-0.0035 (34)	-0.00044 (24)	-0.00080 (54)

putation of the absorption correction factors, A*, utilizing the crystal shapes. Unfortunately we did not make sufficiently accurate measurements in the case of DBU. Furthermore it would seem to be necessary to establish that the transmission surfaces of the crystal do not change appreciably as a function of time owing to the crystal deterioration.

The calculated value of the mass absorption coefficient (μ Cu $K\alpha$) is 39.7 cm⁻¹ leading to A^* values of the order from 1.3 to 1.8. The neglect of absorption corrections may have introduced some systematic error into the refinement especially into the β_{ij} values.

Structure determination

Structure analysis was started in the space group Cc because the unit cell contained only four molecules and we believed the molecule to be the asymmetric diglyceride. The heavy atom technique was used to solve the structure in the (010) projection and refined to an $R(\sum ||F_{obs}| - |F_{calc}||/\sum |F_{obs}|)$ of 0.14. The peak positions were incorrectly rationalized as reasonable for the asymmetric diglyceride. At this point we proceeded to the three-dimensional analysis.

The bromine coordinates and the chain tilt were found from the Patterson synthesis. Two iterations of the structure factor Fourier calculations were required to reveal the arrangement of atoms in the vicinity of the glycerol group. The electron density map showed that the molecule was the symmetric rather than the asymmetric diglyceride and that the hydroxyl oxygen atom attached to the middle carbon atom of the glycerol group appeared ambiguously as two peaks related by a pseudo-symmetry axis. All attempts to remove the ambiguity failed. We finally concluded that the molecules were disordered and two half oxygen atoms were needed.

Block-diagonal least-squares refinement in the space group Cc slowly converged to an R=0.20, where improvement seemed to cease. The indicated shifts in positional and thermal parameters remained as large as their estimated standard deviations. The anisotropic thermal parameters for the bromine atoms persistently went nonpositive definite. On comparison with the previous cycles of least-squares, there seemed to be a correlation between the symmetrically related atoms of the diglyceride.

Examination of the structure at this time showed: (1) a very evident twofold axis of molecular symmetry; (2) the disorder does not perturb the packing lattice energy; (3) the free energy of the crystal is probably lower in the disordered form by a residual entropy contribution of k ln $2^N = R$ ln 2 = 1.38 cal/mole degree; (4) by placing the twofold axis of pseudo molecular symmetry coincident to a twofold axis in the space group C2/c, only half as many independent parameters are needed to describe the structure. The further use of space group Cc seemed indefensible. Upon subsequent refinement using space group C2/c all of the diffi-

Table 1. Fractional atomic coordinates and thermal parameters with standard deviations in parentheses

culties mentioned in the preceding paragraph disappeared.

The final cycle of least squares, including the hydrogen atoms at precalculated positions, gave an R value of 0.09. The C-H bond distance of 1.0 Å and the C-C-H bond angle of 109° were assumed. The calculations were performed on a Univac 1108 computer. The data work up and least-squares programs were written by A. H. The Fourier program is an adaptation from the Stewart X-ray 67 System. The quantity being refined by the least-squares program is $\sum w(|F_o|^2 - |kF_c|^2)^2$. The final value for the quantity S =

Table 2. Comparison of observed and calculated structure factors

Each column contains the value of l, 10 $|F_o|$ and F_c . * denotes an unobserved reflection; R denotes a reflection omitted from least-squares; Z denotes F(0,0,0).

Ø,Ø,L -6 1187 Ø N2 12151 -2 339 2 587 855 6 643 4 15147 2946 2 576 6 627,8 848 4 455 6 627,8 848 4 455 561 656 6 6693	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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24 0304 798 36 442 26 0808 716 36 144 28 1153 1344 38 277 39 239 -239 42 118 32 191 185 42 108 34 298 -292 44 9* 36 417 -442 46 16* 38 361 -356 48 121	-300 -31 130R -31 -27 128 -304 -20 372 388 -26 391 -119 -28 77 72 -25 222 -121 -27 89 104 -24 1461 11 -26 491 -487 -23 1186 -10 -25 290 294 -22 136 -15 -24 358 -466 -21 171	00/7 -13 259 -245 3 56* -4 136 -18 174 -17 1 179 180 412 -17 261 -264 5 150 -159 181 286 -16 128 -138 6 95 85 1476 -15 335 -331 7 171 141 2117 -14 36# 312 8 285 264 1979 -13 57* 46 9 188 191 134 -12 266 264 9 188 361	-14 50* -18 -26 629 579 -16 885 739 -13 0** -2 -25 101 140 -15 777 -666 -12 51* -38 -24 796 711 -14 1771 1576 -11 49* -33 -23 906 814 -13 321 -280 -10 54* -40 -22 328 278 -12 848 790 -9 19* 25 -21 90 2 -11 285 249 -8 36* 5 -20 678 -563 -10 1093 1402 -7 58* -56 -19 117 -51 -9 278 336	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
40 788 -765 50 96 42 369 -354 52 246 44 778 -754 54 68 46 392 -381 56 125 48 511 -487 50 385 -358 8,0,1 50 385 -358 8,0,1 51 282 -263 -46 01	94 -23 340 -281 -220 1673 245 -22 300 -349 -19 210 30 -21 69 82 -18 1365 101 -20 1888 -2066 -17 651 -19 865 852 -16 849 L -18 1405 -1471 -15 227 -17 26* -4 141 -15 227 -17 26* -4 14 1446 -110 -16 2173 -2398 -13 414	1869 -11 633 -578 11 98 -83 -197 -18 792 741 12 641 588 1381 -9 417 376 13 577 551 567 -8 742 781 14 716 658 822 -7 438 -376 15 164 -122 239 -6 1888 931 16 158 64 -127 168 93 16 168 57 1341 -5 254 931 66 152 448 -1 4874 66 152 448 -1 4874 66 152 448 -1 4874 66 152 -1 52 54 1874 66 152 -1 54 1874 66 154 -1 54 1874 66 154 1874 66 154 -1 54 1874 66 1874 66 1874 66	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
56 218 -219 -44 128 58 228 242 -42 16* 68 355 307 -40 166 62 44* -36 -38 301. 64 183 198 -36 199 4,8,L -32 2251	-135 -15 01 55 -12 870 -18 -14 1448 -1486 -11 536 -198 -13 344 -345 -10 572 321 -13 344 -345 -10 572 321 -12 3057 -3318 -9 830 -43 -11 2015 -3318 -9 830 -43 -11 2015 -3318 -9 830 -43 -12 2015 -3318 -7 337 -594 -9 1441 -2014 -7 337 -594 -6 1441 -7 -7 347 -7 347 -7 347	-743 -3 150 155 19 258 247 -458 -2 1218 10 169 26 25 25 755 -1 118 10 46 21 140 -149 775 0 1956 957 22 323 295 262 -497 1 664 555 23 225 262 233 2 948 863 24 296 265 -59 -2 25 668 -59	2 76 -53 -18 1265 -1130 - 01 356 47* 90 - 3 888 313 1 554 555 58 52 -7 312 263 3 329 5 59 52 -7 312 263 3 329 325 6 0* 25 -6142 -1336 417 -166 7 0* 11 -5 423 -372 5 555 588 8 112 96 -41323 -1218 6 885 -94.0 8 112 -96 -41323 -1218 6 885 -94.0 8 112 -96 -41323 -1218 6 885 -94.0 8 12 -96 -41323 -1218 6 885 -94.0 9 - 413 - 54 -555 - 558	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
-62 115 121 -28 343 -68 219 231 -26 69 -58 143 132 -24 339 -56 166 154 -22 283 -54 188 71 -28 238 -54 188 92 -16 242 -58 92 -6 -16 133	367 -7 516 -782 -1 188 88 -6 1868 -922 -3 287 384 -6 1868 -922 -3 287 384 -6 1868 -922 -3 287 210 -4 3255 291 -1 398 273 -3 511 -337 6 1473 269 +2 117 -1197 1 1453 179 -1 199 -1 129 -1	-1068 4 /44 999 26 158 148 256 704 652 27 158 148 -1179 7 255 255 29 0* -10 1533 8 478 402 30 91 72 -1326 9 299 283 31 35* 7 R -70 10 42* 28 32 226 -235 R -70 10 42* 35 33 45 358	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
48 55* 43 -14 156 46 264 -279 -18 95 42 27 -338 -8 189 42 27 -338 -8 189 42 27 -338 -8 189 46 451 -467 -4 142 -36 889 -908 -2 434 -34 1474 -1661 8 488	176 8 925 703 3 498 82 1 87 153 4 1958 183 2 9628 689 5 468 7201 3 1528 622 6 257 -772 4 15908 1371 7 412 -126 5 852 715 8 461 -462 6 1206 1002 9 1055 -398 7 1248 -108 10 108	409 12 115 79 34 308 -298 -1739 13 182 156 35 98 -91 R 373 14 424 -352 36 70 -22 -2286 15 278 -247 37 64* -67 R -270 16 1332 -1211 38 239 -27 -481 17 728 -701 39 67 -19 -978 18 715 -668 40 144 -142 -988 19 242 184 41 124 -122	5 686 -619 15 173 116 0 1336 1196 6 436 -416 16 586 -577 1 179 167 7 974 -968 17 997 -988 2 1366 166 8 748 -653 18 455 -452 3 217 237 9 775 -884 19 11* -69 4 1864 1220 18 879 849 26 537 -571 5 527 582 11 786 522 21 716 -731 6 934 1051 21 985 1828 23 161 -388	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
-32 43* -16 2 324 -30 346 -376 4 489 -28 163 141 6 249 -26 336 -349 8 387 -24 593 588 10 181 -22 159 173 12 0* -28 864 838 14 27* -18 928 946 16 16	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 386 446 13 26 256 23 52 42 416 416 416 416 416 416 416 416 416 416	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
-16 919 914 18 150 -14 1560 1513 20 428 -12 1002 952 22 646 -10 1608 1480 24 223 -8 1111 1068 26 190	171 16 805R 1020 19 666 443 17 0+ −157 20 1205 678 18 626R 796 21 0 −229 19 861R 1093 22 381 205 20 615R 773 23 168	594 28 216 214 50 99 -98 1188 29 145 -91 51 29* 9 -76 30 474 -44 419 31 137 -150 9,1,L 166 32 237 -235	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	516* 45 16 8597 -57 €.) 181 52 50* 46 17 53* -57 -56 7499 18 32* -79 -55 122 146 8,2,⊾ 19 46* -68 -54 135 -158 28 133 -152

Table 2 (cont.)

3,	1,L	46 47	6+ 8+	10 28	35 270 36 188	-280	38 39	127 -	32 32 93 33	416 356	-411 -341	24 446 25 502	432	21 3	88 -2	87 38	142*	-146	-15 -14	91 172R	154 -491	-3	157 54*	194 1 -68 2	23	-46	-24	6* _4 6* 10	9
-53 11 -52 14 -51 11	-150 130	48 49 50	137 Ø* 131	-115 -29 -117	37 136 38 52 39 80	-128	40 41 42	112 -	26 34 88 35 45 36	76* 345 377	-74 -29Ø -368	26 276 27 247 28 373	276 231 345	23 4 24 1 25 2	58 -4 92 -1 71 -7	43 31 98 32 45 33	169 216 128	-172 -196 -121	-13 -12 -11	86 36*	95 -16Ø -86	-1 Ø 1	72*	70 2 -115 2 17 2	1 78 2 116 2 91	-79 -139 -120	-22 4	3* -1 4* 9	367
-54 160	-193	51	6Ø* 223	-32 -186	41 47	-12 -30	43	186 -	28 37	101 252	-93	29 549	495 285	26 2	62 -2 89 -3	62 34 Ø6 35	195	-169	-10	63* 128R	-144	2	182	-162 2	121	-146	-19	¢• 13 6• -3	6
-47 -46 17	• 62 -191	54	134 98	-118	43 24	75 164	-28	9,3,L	30 41	233	-198	32 232 33 335	221 279	29 T 30	34 -1	28 37 78 38	232	-214	-7	135R 74+	-231 -193	56	131	-124 2	148	-162	-16	6 12	2
-43 21	-234	56	236 5.3.L	-229	45 61 46 142 47 169	119	-27 -26 -25	41* 19*	64 42 -3 43 41 44	191 118	-149 93	34 300 35 125 36 119	289 117 94	31 1 32 1 33 1	99 -1 26 10 -	Ø3 39 81 4Ø 89	180	-140	-5 -4 -3	220R 41+ 216	-344	8	368 242 145	-796 7 -733 3 -117 3	9 205 9 150 1 137	-218 -187 -172	-14 5 -13 -12 4	p+ _4 p+ 7 2= 1	2
-42 150	-157	-52	8*	72	48 272	247 152 185	-24 -23	29* 59	25 45 47 46 46 47	28*	47 - 28	37 347 38 96	310	34 1	95 1 43•	73	8,4,0		-2 -1	8J 318 72	-328	10	53* 177 -	-21 3 -178 3	2 141	-164 -190	-11 1	4* 8 8* -4	8
-39 220	-209	-50	42	-22	51 175	173	-21	45• 39•	36 48 57 49	298 194	144	40 144	-131	37 1	77 1	65 -76 20 -25	47	52 18	1	26# 142	-236	13	341 . 429 .	-330	7,5,L	-175	-8 -7	8• 4 8•	2
-36 0	* -79 -374	47	95	85 29	-43 42	• -28	-18 -17	108	13 51	94 98	76	42 16/ 43 115 44 232	-124 -99 -175	40 2 41 2	29 1 79 2 97 2	81 -24 30 -23 44 -22	30+ 61	80 57 91	4	79 120	-232 67 	16	84 332	-70 -1 -354 -1	46•	45 -63	-5 -5 -4 1	Ø* 7 4* -11	3
-33 316	-348	-44	56* 73*	58 94	-42 46	• -10 • -15	-16 -15 -14	96 69 171	81 53 68 80	94 2.4.L	60	45 204 46 280 47 224	-168 -215 -195	42 2	97 2 44 2 55 2	32 -21 05 -20 14 -19	91 95	91 102	6 7 8	203 94 223	181 -63 233	18 19 20	181 · 195 · 63*	-190 -1 -205 -1 -6 -1	72 5 9* 5 57	104 19 53	-3 5	1* -8 0* -11 1 -14	8 7 4
-30 26	-148 274 -465	-42 -41 -40	2Ø8 53*	-25 215 -15	-39 31 -38 176 -37 96	* -15 149 -58	-13 -12 -11	168 89	9 56 -52 05 -51	116 37*	-1#8 6	48 215 49 250 50 317	-178 -194 -255	45 3	36 2 25 2 87 2	67 -18 65 -17 37 -16	67 87 42*	102 65 -12	10	172 312 252	156 297 227	21 22 23	60• 53*	-172 -1 -73 -1 -86 -1	32 32 37	- <u>37</u> -26	0 5 1 8 2	5 -3 0 -8	1 8 1
-28 161 -27 246 -26 548	198 -220 542	-39 -38 -37	120 Ø* 191	63 - -39 - 215 -	-36 313 -35 48 -34 164	* 41 145	-10 -9 -8	83 205 62*	91 -50 06 -49 20 -48	69 108 33*	-56 -98	51 289 52 149	-240	48 1	36 1 4 1	36 -15 -14 -13	0* 0* 184	-1 51 178	12	320	314 -31 -164	24 25 26	41+ 13+ 53+	82 -1 -10 -1	41*	-68 -65	3 5	8* -3 Ø -6	9
-25 193	-198 363	-36	87 39* 205	-121 - 65 - 214	-33 111	93 138	-7 -6	0+ 37+	24 -47	166 177	-119	4,4, 18 70	۱. ۱.	-41	44+	-12 8 -11	199	194	15	151	149	27	81 136	73 - 153 -	0+ 55	-56 -80	6 12	1 -13 7 -11	1
-22 649	632 - 30	-33	89 220	-255	-30 t17 -29 129	98 99	-4	107R 69	88 -44 88 -43	106	107 -226 -	47 177	-117	-39 -38	57 0*	41 -9	35.	24 98	18	121 241	110	30	166	171 -	66 49•	-84	9 12	8 -19	999
-19 20	185 533	-30	250	-292	-27 112	102	-1	37.	76 -41	183 322	-149 -	44 89	-62 79	-36	14 + 77 1	43 -6 Ø1 -5	107	-76 -36	21 22	424	383	33	177	203 -	99 96	-149	13 4	0- 1 27	9
-16 49	457	-27	290 300	-328	-24 49	• 50 189	23		19 -38 16 -37	107	-331 -	41 156	-216 131 -55	-33 1 -32	26 1 19*	27 -3	51*	28 -173	24	182 387	269 269	36	201	213 226	1012	-95 -169 -137	14 3 15 3 16 3	1* -5 7* -8 1* 6	8
-13 660	641 379	-25 -24 -23	208 231 176	-221 -158	-22 52 -21 28 -20 33	- 70 50 10	56	84	04 -36 30 -35 -7 -34	184 107 300	-92 - 392 -	39 51 38 236 37 51	-231 38	-31 1 -30 -29	25 1 44* 79	94 -1 72 9 94 1	100 230 85	-220 -85	26 27 28	131 159 23+	104 165 -17	38 39 40	218 204 107	233 227 135	109 70 74	-112 -94	17 18 3 19	0* 2 0* 1 0* 1	3
-10 109	341 46 749	-22 -21 -20	355 250 124	-370 -	-19 177 -18 95 -17 96	173 -93 56	7 8 9	97 - 212 - 88 -	12 -33 94 -32 30 -31	171 162 Ø*	-155 - 161 - -57 -	-36 157 -35 67* -34 106	-142 -34 -103	-28 -27 -26	40* 57 9* -	-9 2 67 3 46 4	212 173	-67 -198 -154	29 3Ø 31	85 Ø* 71	95 13 46	41	Ø* 5.5.1	19	37* 62 77	-25 -89	20 9	6 12 3 9	1
-8 99 -7 180 -6 290	70 189 277	-19 -18 -17	33Ø 289 229	-322 -286 -213 -	-16 37 -15 37 -14 280	• -16 • 20 -272	10 11 12	71* 145 - 210 -	76 -30 70 -29 97 -28	349 66* 94	347 -	33 79 32 188 31 118	-64	-25 1 -24 1	19 -1 54 -1	49 5 54 6 14 7	178 148 221	-16Ø -135 -193	32 33	105	-90 -83	-34	Ø* 74	-81 1	41*	-27 94	23 9	5 14 3 9	23
-5 221	179 -386 651	-16 -15 -14	91 359 92	-31 -360 -69	-13 72 -12 130 -11 136	41 -114 -102	14	115 - 76 - 155 -	06 -27 43 -26 54 -25	485 111	20 544 -	30 44* 29 192 28 144	-27 -169 -168	-22	86 - 4ø≁ - 45 -1	70 8 26 9 92 10	195 163 171	-173 -136 -144	35 36 17	86 142	-49 -124 -178	-32 -31 -30	0* 0*	-26 1 31 1 -97 1	20 20	44 21 41	26 7 27 4 28 4	6R 18 9* 16	57
-2 959 -1 47 Ø 129	-984 -481 -1162	-13 -12 -11	155 88 233	-137 35 -213	-10 536 -9 247 -8 541	-533 206 -510	16 17 18	118 - 146 - 284 -	28 -24 50 -23 17 -22	158 351 90	169 - 351 -	27 188	-182 93 -368	-19 1	44 - 33 -1 22 -2	14 11 92 12 18 13	253 15Ø 71	-225	38 39	215	-188	-29 -28	49*	16 1 -74 1	67 44*	51 74	29 6	4R 16	4
1 98 2 489 3 177	-1 -470 -179	-1ø -9 -8	158 155 165	150 142 123	-7 429 -6 87 -5 84	-421 -116 -89	19 20 21	52* - 137 - 227 -	10 -21 43 -20 20 -19	423	439 -	24 44	-239	-16 2	53 -2 76 -1 78 -1	43 14 78 15 72 16	49* 51* 85	-38 -65 48	41	180	-172	-26	57* ·	105 1	3 45. 70	82 1Ø5	-21	Ø* -7	ş
4 974 5 273 6 583	-898 -217 -540	-7 -6	336 1110 141	-267	-4 @ -3 @	• -7 • 13 -91	22	0* 66 78	12 -18 14 -17 65 -16	77 355 182	-53 -	21 265	-266 105	-13 -12 1	Ø* 19 1	1 17 29 18 74 19	40+ 58	26 -36 -87	44	157	-183	-23	41* 36*	-88	Ø,6,L	174	-19 2	6• -5 Ø• 1	5
7 362	-378 -698 -529	-4	815 597 502	806 544 434	-1 517 Ø 382	466	25	53* 0*	42 -15	498	484 -	18 214	192	-10 2	31 -2 37 -2	62 20 85 21	49* 56	31	-41	37.	-69	-20	37	41 -68	31*	26 128	-16 4 -15 5	4 2 1 -1	4
10 591	-593 -364	-1	194 103	-161	2 37	• 49 -350	28	25*	-11	323	-395 -	15 88	-52	-7 2	12 -2 15 -1	13 23	49*	42	-39	58 69	-89	-17 1 -16	155R	-257	Ø* 55*	46	-13 -12	0	8
13 69	-647 -430	ż	584 318	561 306	5 118 6 128	-121	ø	0,4,C 477 4	-9 20 -8	123	-31 -574	12 549	46ø 183	1 1	Ø -1	51 26	132	135	-37 -36 -35	53* 43* 139	-89 57 -172	-15 -14 -13 1	46* • 31* 155R •	-109 -39 -247	76 47• 8	-102 129 125	-11 -10 4 -9 2	0 41 3 71 2 1	3 9 8
16 109	-108 -478	56	411 498	392 493	8 51 9 55	* -53 * -70	23	465	51 -6 14 -5	329 78	-295	-9 29* -8 92	200	-1 1	-1 -1	-9 11 50 -44	49*	22	-34 -33 -32	30 98 36	-114 -12	-12 -11 -10	37* 14* Ø*	-58 1	101 70 86	165 -10 133	-8 2 -7 3	3• 13 5• 7	3
19 229	-122 -231 119	8 9	367 86 408	335 92 399	10 138 11 0 12 112	* -11 144	456	354 278 400 L	97 -4 99 -3 56 -2	616 392 254	-548 -311 -212	-7 31Ø -6 386 -5 298	267 329 264	2 4	9 - 9 3 •8 -3	84 -43 84 -42 88 -41	121 186	-54 157 -112	-31 -30 -29	123 6#* 87	-164 97 -139	-9 -8 -7	78 - 58• Ø•	-144 11 68 1	51* 141R 62	106 203	-5 5	8+ 14 8+ 7 5+ 13	1 6
21 124 22 257 23 56	-97 220 * -35	10 11 12	335 293 148	325 749 -127	13 24 14 206 15 124	* 52 242 138	7 8 9	432 L 252 2	79 –1 76 Ø 52 1	317 584 489	-268 -582 -485	-4 108 -3 456 -2 374	79 394 333	4 2 5 2	58 1 23 1	75 -40 29 -39 93 -38	26 44* 48*	-22 72	-28 -27 -26	31* 67 75	-85 123	-6 -5 -4	8* 24* 78*	44 19 -8 11 92 1	90 86 82	118 65 131	-2 -1 0 4	0*	3
24 485 25 147 26 995	443 -113 954	13 14 15	239 98 173	259 79 151	16 223 17 126 18 308	244 161 334	10 11 12	249 1 622 0 129 1	43 2 55 3 18 4	201 659 299	-154 -571 -250	-1 360 Ø 87 1 428	322	7 8 2 9 3	51• 57 2	50 -37 29 -36 16 -35	56* 41* 23*	36 21 63	-25	67 31 •	-124	-3	31*	76 11	47	13 93	1 9 2 8	6 15 6 12	2
27 362 28 429 29 238	348 436 268	16 17 18	317 53* 213	-297 -10 -205	19 231 20 160 21 214	258 174 233	13 14 15	376 3 88 478 4	91 5 30 6 77 7	343 323 504	-298 -281 -464	2 439	388 -47	10 2	2 2	60 -34 85 -33	121	142	-22	131R 70	208	0 1	31	118 2 150 2	49+ 36+	32 -12	4 36	5* 1	5
30 248	232 -16 248	19 20	74+ 454 166	-450	22 400	419 241	16 17	91 363	-7 8 68 9	111	-393	5 472 6 276	-217	13 3	10 3 31 2	45 -31 68 -30	89R 54+	185	-19	87 46+	127	1	16	226 21	47*	-77 -19	7 7	8 8	8
33 449	430	22	493	-498 -156	25 283 26 182	292 209	19	205 1	86 11	346	- 325	8 207	-162	16 2	6 2	24 -28	80 218	-92 240	-16 -15	102	166	6 1	90	191 2 161 2	37*	-38	10 6	2 -16	55
36 287 37 382	254	25	389	-394	28 52 29 151	78	22	801 -7 492 -4	49 14 77 15	252	214	11 73* 12 284	-250	19 2	4 2	41 -25	166	197	-13 -12	143	193	9 7	33	236 30 280 31	26* 155	-144	13 2	2 -30	2
39 298 40 134	299 175	28 29	25Ø 283	-249	31 91 32 0	98 25	25	202 - 1 276 1 132 -	67 16 63 17 99 18	163 552	3// 148 514	14 475 15 383	-1/1 -434 -373	22 23 1	1* 17 1	27 -22 12 -21	54• 91	-57 88	-11 -10 -9	218R 42* 151	375	12 1	64 66	98 189 169	2,6,L		16 6 17 6	/ -109 3 -82 0 -96	2
41 312 42 146 43 189	277 177 156	3Ø 31 32	347 372 261	-373 -404 -287	33 47 34 Ø 35 Ø	20 -54 -4	27 28 29	337 -4 450 -4 136 -1	82 19 37 20 57 21	476 515 51*	47Ø 511 37	16 356 17 266 18 318	-321 -239 -296	24 25 26	3* 38 79 -	52 -20 67 -19 65 -18	101R 89 46•	-210 154 -136	-8 -7 -6	31* 209 37*	276	14 15 1	66* 49 41*	-99 -29 183 -78 60 -21	0+ 11+ 39+	62 31 79	18 7 19 9 20	2 -126 4R -176 8* -70	3
44 32	137	32	209 135	-216 -149	36 24 37 66	• _43 • _53	3Ø 31	137 -1 349 -2	Ø6 22 85 23	9Ø	-51	19 252 20 208	-213	27 28 1	2* -1	47 -17 10 -16	95R 66*	-203 -128	-2	128 37*	17Ø -55	17 18	49* 85	24 -26 -95 -29	47× Ø*	-18 27			

 $(\sum w(|F_o|^2 - |F_c|^2)^2/(n-p))^{1/2}$ is 2.55. Reflections having a value greater than 3S were omitted from the least squares and are identified by an R after the F_{obs} value in the structure factor list in Table 2. Stereo drawings were made using the Johnson (1965) ORTEP computer program. The X-ray scattering curves used were for neutral atoms (International Tables for X-ray Crystallography, 1962, pp. 202-207), with the bromine curve corrected for the anomalous dispersion term $\Delta f' =$ -0.9e (International Tables for X-ray Crystallography, 1962, p. 215). The term $\Delta f'' = 1.4e$ was neglected. This neglect appeared to be justified in that a trial calculation including it led to no improvement in R and no significant changes in all parameters. The Aikens method with 4 differences was used for making interpolation between the tabulated values.

Results and discussion

The atom numbering is in accordance with the usual convention used by lipid chemists. The fatty acid is

numbered from C(1) at the carboxyl group through C(11) and Br at the terminal end. The glycerol group atoms are prefixed by the letter G, GC(2) being the central glycerol carbon atom. The final positional coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1. The list of final structure factors is given in Table 2. The bond distances and angles in the molecule are given in Table 3. The standard deviations estimated from least-squares treatment are 0.001 Å for the bromine atom, 0.007 Å for the carbon atom, 0.005 Å for the oxygen atoms, and 0.008 Å for the disordered oxygen atom.

(i) Bond distances and angles

Fig. 1 shows a view of the molecule along the pseudo twofold axis. The bond distance and angle values are normal. The average values uncorrected for thermal motion are: C-C 1·51 (1) Å; C=O 1·20 Å; C-O 1·36 Å; C-Br 1·95 Å; C-C-C 112·9 (1)°. The spread amongst the 8 C-C bond distances between the equivalent fatty acid CH₂ units (C(1) and C(11) being excluded on the

	Distar	nce				Ang	le
	Uncorrected	Corrected				Uncorrected	Corrected
BrC(11)	1·95 Å	1·99 Å	Br	C(11)	C(10)	112·2°	108.5
C(11) - C(10)	1.49	1.53	C(11)	C(10)	C(9)	110.6	106.6
C(10) - C(9)	1.51	1.55	C(10)	C(9)	C(8)	112-0	107.9
C(9) - C(8)	1.54	1.58	C(9)	C(8)	C(7)	113.3	109-2
C(8) - C(7)	1.51	1.56	C(8)	C(7)	C(6)	113.7	109.5
C(7) - C(6)	1.51	1.55	C(7)	C(6)	C(5)	114.0	109-9
C(6) - C(5)	1.52	1.55	C(6)	C(5)	C(4)	113.8	109.6
C(5) - C(4)	1.52	1.56	C(5)	C(4)	C(3)	113.5	109.5
C(4) - C(3)	1.51	1.55	C(4)	C(3)	C(2)	112.5	108.5
C(3) - C(2)	1.52	1.56	C(3)	C(2)	C(1)	112.8	108.9
C(2) - C(1)	1.49	1.52	C(2)	C(1)	=O	126.6	128.5
C(1) = 0	1.20	1.20	C(2)	C(1)	-0-	111.5	107.6
C(1)O-	1.34	1.38	-0-	C(1)	=O	121.9	123.9
-OGC(1)	1.43	1.38	C(1)	-0-	GC(1)	116.8	113-2
GC(1)-GC(2)	1.53		-0-	GC(1)	GC(2)	106.4	
GC(2)-GO(2)	1.30		GC(1)	GC(2)	GC(1) (5553)	112.8	
			GO(2)	GC(2)	GC(1) (5553)	113.3	

Table 3. Intramolecular bond distances and angles

basis of nuclear magnetic resonance chemical shifts) has a mean of 1.52 Å and a standard deviation of 0.008 Å. After correction for rotational oscillations (Cruickshank, 1961), the average becomes 1.56 (1) while the average for the 7 equivalent C-C-C angles becomes 109.2 (1)°.

(ii) Hydrogen bonding and crystal packing

Fig. 2 is a stereographic drawing illustrating the hydrogen bonding present in the crystal. The hydrogen bonds link the molecules together along the diagonal directions in the *ab* plane. Table 4 is a list of symmetry operations.

Table 4. Symmetry operations

The four-digit code used in Table 5 and 7, and in the text denotes how the atomic parameters can be derived from the corresponding atom in the crystal asymmetric unit. The first three digits code a lattice translation, *e.g.* 564 means a translation of (5-5)a+(6-5)b+(4-5)c or (b-c). The fourth digit refers to one of the following symmetry operations:

Code digit	Sym	metry opera	tion
1	х,	у,	Z
2	-x,	-y,	-z
3	-x,	у,	$\frac{1}{2}-z$
4	х,	-y,	$\frac{1}{2} + z$
5	$\frac{1}{2} + x$,	$\frac{1}{2} + y$,	z
6	$\frac{1}{2} - x$,	$\frac{1}{2} - y$,	-z
7	$\frac{1}{2} - x$,	$\frac{1}{2} + y$,	$\frac{1}{2} - z$
8	$\frac{1}{3} + x$	$\frac{1}{2} - \gamma$	$\frac{1}{3} + z$

Table 5 lists the intermolecular distances less than 3.8 Å that involve the disordered oxygen atom. The hydrogen bond distance is 2.87 Å and the angle $COH \cdots O$ is 114.34°. Owing to the crystal symmetry it can be seen that the disordered oxygen can occupy either of the two positions [GO(2) (5551) or GO(2) (5553)] without affecting any of the short range packing distances. Without the disorder, the hydrogen bonds would link molecules together in lathlike strings. The disorder cross links these strings into sheets to produce a layer network of hydrogen bonded molecules.

 Table 5. Intermolecular distances involving the disordered hydroxyl group

Symmetry operation (5553) is the pseudo twofold molecular axis.

from GO(2) (5551)	Distance	from GO(2) (5553)
to		to
=O(5557)	2∙868 Å	=O(4555)
C(1) (5653)	3.146	C(1) (5651)
C(2) (5653)	3.173	C(2) (5651)
GC(1) (5557)	3.312	GC(1) (4555)
-O-(5653)	3.318	-O-(5651)
=O(5653)	3.645	=O(5651)

Fig. 3 shows the molecular packing within the crystal. The hydrocarbon chain tails are parallel in double layers and tilted at the same angle toward the end group planes, but the direction of chain-tilt alternates in successive double layers of the chain. This arrangement is similar to that found in the 1,3-diglyceride of 3-thiadodecanoic acid (Larsson, 1963). The angle made between the terminal bromine atoms and the glycerol central carbon is 91.6° . It has been pointed out by Abrahamsson & Westerdahl (1963) that bent long-chain molecules are rather common in structures where the hydrocarbon chain packing is disturbed by the presence of groups other than the ethylene groups in the chain.

The chain packing is of the common triclinic type (T||), and the dimensions of the methylene subcell are:

 $a_s = 4.14$ (5), $b_s = 5.39$ (5), $c_s = 2.54$ (5) Å,

 $\alpha_s = 78$ (1), $\beta_s = 107$ (1), and $\gamma_s = 120$ (1)°.

The volume per CH₂ group is 23.4 Å.

(iii) A helical twist in the fatty acid chain

There is a helical pitch in the hydrocarbon chain. Examination of the Δ_1 and Δ_2 coordinates from the best least-squares plane calculation given in Table 6 shows a uniform twist along the chain. This helical twist probably arises from the optimization of both the hydrogen bond packing in the vicinity of the glycerol group and the bromine to bromine end group packing. The helix has a 0.84 Å diameter and approximately a 148 Å pitch. The angle between the projection of the C(1) to C(2) bond and the projection of the C(11) to Br bond as viewed along the chain axis is $34^{\circ}40'$. The planes of the zigzag chains in 2-monolaurin (Larsson, 1964) also appear to be twisted.

Table 6. Least-squares plane

The equation of the least-squares plane is in the form

$$Ax + By + Cz = D$$

where D is expressed in Å and x, y and z are fractional coordinates. The equation of the plane is:

$$-1.355x + 4.042y - 36.68z = 0.4271$$

 Δ_1 are the out-of-plane distances; Δ_2 and Δ_3 are the in-plane coordinates.



Fig. 1. The molecular structure of the symmetric 1,3-diglyceride of 11-bromoundecanoic acid.

		Table 6 (co	ont.)	
	Least-squares weighting	\varDelta_1	⊿₂	⊿3
Br	1.0	−0·17 Å	−0·47 Å	-7·27 Å
C(11)	1.0	0.10	0.54	-5.63
C(10)	1.0	-0.05	-0.32	-4.41
C(9)	1.0	0.06	0.51	- 3.16
C(8)	1.0	0.02	-0.36	- 1.88
C(7)	1.0	0.02	0.45	-0.60
C(6)	1.0	0.03	- 0.39	0.65
C(5)	1.0	-0.05	0.41	1.94
C(4)	1.0	0.08	-0.44	3.20
C(3)	1.0	-0.06	0.35	4.47
C(2)	1.0	0.11	-0.51	5.71
C(1)	1.0	-0.16	0.23	6.98
=0	0.0	-0.55	1.36	7.07
-0-	0.0	0.75	-0.53	8.05
GC(1)	0.0	-0.16	0.07	9.33
GC(2)	0.0	0.05	-1.03	10.37
GOO	0.0	0.20	0.61	11.50

Table 7. Closest intermolecular distances

A. A	Across end grou	ip planes (DMAX=4	4·5 Å)
	Br	Br(4456) C(11) (5552)	3·45 Å 3·93
		Br(4556) C(11) (4556) Br(5552)	3.97 4.14
	C (11)	Br(5552)	3.93
		Br(4556)	4.14

B. Between chains within a layer (DMAX = 4.2 Å)

	•	,
Br	C(11) (4455) C(9) (5451) C(10) (5451) C(9) (4455) C(8) (5451)	3.89 Å 3.93 4.02 4.15 4.15
C(11)	Br(5555)	3.89
C(10)	Br(5651) C(7) (5451) C(6) (5451)	4·02 4·06 4·18
C(9)	Br(5651) Br(5555) C(6) (5451)	3·93 4·15 4·19
C(8)	C(5) (5451) Br(5651) C(4) (5451)	4·14 4·15 4·17
C(7)	C(2) (5651) C(4) (5451)	4∙06 4∙11
C(6)	C(2) (5451) C(10) (5651) C(3) (5451) C(9) (5651)	4·15 4·18 4·18 4·19
C(5)	C(2) (5451) C(8) (5651)	4∙04 4∙14
C(4)	=O(4455) C(7) (5651) C(8) (5651) -O-(5451)	3·71 4·11 4·17 4·18
C(3)	GO(2) (5453) -O-(5451) =O(4455) C(6) (5651)	3·92 4·04 4·07 4·18

Table	7 ((cont.)	
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C(2)	GO(2) (5453) =O(4455) C(5) (5651) C(6) (5651)	3·17 3·61 4·04 4·15
C(1)	GO(2) (5453) GO(2) (5457) GO(2) (5451) GC(2) (5451)	3·15 3·84 3·88 4·09
=0	$\begin{array}{c} GO(2) \ (5457) \\ -O-(5455) \\ GC(2) \ (5455) \\ C(2) \ (5555) \\ GO(2) \ (5453) \\ C(4) \ (5555) \\ GC(1) \ (5457) \\ GO(2) \ (5451) \\ C(3) \ (5555) \\ GC(1) \ (5455) \end{array}$	2.87 3.39 3.60 3.61 3.65 3.71 3.77 3.94 4.07 4.10
-0-	GO(2) (5453) =O(4555) GO(2) (5451) C(3) (5651) GO(2) (5457) C(4) (5651)	3·32 3·39 3·93 4·04 4·10 4·18
GC(1)	GO(2) (5457) =O(5557) GO(2) (5453) GO(2) (5451)	3·31 3·77 4·07 4·08
GC(2)	=O(4555) =O(5557) C(1) (5651) C(1) (5653)	3·60 3·60 4·09 4·09

(iv) Disorder as entropy twinning

Though glycerol possesses reflective symmetry in that it can be superimposed on its mirror image, glycerol does not possess rotation symmetry. This rotational asymmetry does not give rise to optical antipodes, but does allow a distinction to be made between the two primary hydroxyl groups (Ansell & Hawthorne, 1964) as shown below:

CH ₂ OR	CH ₂ OR
•	•
•	•
•	•
HO▶C∢H and	Н▶С◀ОН
•	•
•	•
•	•
CH ₂ OR	CH ₂ OR
(<i>a</i>)	<i>(b)</i>

The disorder results from the competitive occupancy for each site by rotational isomers (a) and (b).

The disorder may be described as a form of entropy twinning. By analogy to twinning by merohedry, the space group of an untwinned crystal would be Cc; any of the additional symmetry elements of the space group C2/c can be used randomly as twin elements to relate a pair of molecules.

(v) Thermal motion

It appears that the motion of all the nonhydrogen atoms is significantly anisotropic in that at least one of their β_{ij} terms (Table 1) differs by more than three e.s.d.'s from the value it would have assuming isotropic motion with *B* equal to the mean principal axis B_i . The ellipsoids (Fig. 1) do not exhibit the excessive distortion which is sometimes characteristic of a meaningless refinement.



Fig. 2. A stereo view of the hydrogen bonding in the symmetric 1,3-diglyceride of 11-bromoundecanoic acid. The disorder is not illustrated,

Table 8. The translational and rotational vibration tensors

The direction cosines of the τ and ω vibrational tensors are relative to the least-squares plane Δ_1 , Δ_2 and Δ_3 orthonormal coordinate system. The root mean square values are in Å and degrees.

	τ(10 ⁻² Å ²))	r.m.s.	$DC\Delta_1$	$DC\Delta_2$	DC∆3
$(^{3 \cdot 80})$	-0.53	0.61	0.18	-0.848	-0.258	0.463
	4.90	$\begin{pmatrix} -0.07\\ 4.38 \end{pmatrix}$	0·21 0·23	0·271 0·456	-0.340 -0.801	0.797
·	$\omega(deg^2)$,	r.m.s.	DCd_1	$DC\Delta_2$	DC∆3
/ 0·76	-0.11	-7.11	0.76	-0.839	-0.543	-0.013
	0.88	-5.61 698.57	0·97 26·43	0·543 0·010	-0.839 0.008	-0.001 -1.000

An analysis (Cruickshank, 1956) of the individual atom vibrational tensors in terms of the anisotropic rigid-body translational and rotational vibration tensors for the same portion of the fatty acid group as used in the least-squares plane calculation was made. The τ and ω tensors are given in Table 8. The most striking feature is the very large rotational vibration (r.m.s. 26.4°) about the chain axis. Although there is no reason to believe that the fatty acid chain is rigid, it seems that the overall out-of-plane twisting can be approximated by a rigid rotational vibration. By applying rotational oscillation corrections to the positional coordinates, the average C–C bond distance is lengthened by 0.05 Å and the average C-C-C angle is reduced by 3.7°. These represent changes that are 5σ for lengths and 40σ for angles.

The independent packing behavior at the end group planes and the glycerol region would suggest the possible existence of two symmetric fulcrum points within the molecule at which the three molecular parts interact in a coupled fashion. The C(8)-C(9) bond (1.58 Å corr.,

1.54 Å uncorr.) is longer than the average (1.56 Å corr.) by almost 3σ . If the thermal motion of atoms C(8) and C(9) is coupled in such a way that the bond direction always remains nearly parallel, then the rigid-body rotational correction would cause an incorrect lengthening. The C(8)–C(9) bond may be the location of the fulcrum.

(vi) The extrapolation to membranes

The implication of these results suggests that the stable crystalline forms of long chain diacyl molecules are extended or partially extended structures. The similarities in long spacing and polymorphism between the diglycerides and the phospholipids are an indication that the hydrocarbon chain packing may be similar. We propose that the unit membrane model may incorporate regions of extended chain phospholipids with bimolecular intercalation of cholesterol. This idea is in agreement with the fact that the major type of lipid-protein interaction in membranes appears to be a hydrophobic bonding (Green & Fleischer, 1963).



Fig. 3. A stereo view of the molecular packing of the symmetric 1,3-diglyceride of 11-bromoundecanoic acid. The disorder is not illustrated.

Larsson, Lundquist, Stälhberg-Stenhagen & Stenhagen (1969) have made some recent studies of the structural arrangements of lipids in surface layers and interphases. In their studies it was shown that a monolayer phase can be compressed to a duplex film and successively to a multifilm containing up to 8 layers. Triglycerides in monolayers have the E form while in the solid state they are in the tuning-fork conformation. Compression of triglyceride monolayer beyond the monolayer collapse point produces a duplex layer with molecules of different conformation in the lower and upper parts. They suggest that the upper part is in the tuning-fork arrangement, while the lower part is in the E form.

The interface between the upper and lower parts is hydrophobic. This would suggest that in the case of biological membrane in those regions where the protein interface is hydrophobic the lipid arrangement could be an extended monolayer, while in those regions where the interface is aqueous or ionic the arrangement is the usual bilayer form.

This work was supported by a grant GM-12376 and HE 11914 from the National Institutes of Health to A. H. D. D. was supported by a training grant from NIG MS to the Department of Biophysics of the University of Maryland. The computer time was supported in part by NASA grant NsG 398 to the Computer Science Center of the University of Maryland.

References

- ABRAHAMSSON, S. & WESTERDAHL, A. (1963). Acta Cryst. 16, 404.
- ALEXANDER, L. & SMITH, G. (1962). Acta Cryst. 15, 983.
- ANSELL, G. B. & HAWTHORNE, J. N. (1964). *Phospholipids*, p. 404–407. Amsterdam: Elsevier.
- CRUICKSHANK, D. W. J. (1956). Acta Cryst. 9, 754.
- CRUICKSHANK, D. W. J. (1961). Acta Cryst. 14, 896.
- FINEAN, J. (1967). ENGSTROM-FINEAN Biological Ultrastructure. 2nd ed. p. 260-262. New York: Academic Press.
- GREEN, D. & FLEISCHER, S. (1963). Biochim. Biophys. Acta, 70, 554.
- Howe, R. & MALKIN, T. (1951). J. Chem. Soc. p. 2663.
- International Tables for X-ray Crystallography (1962). Vol. III, Birmingham: Kynoch Press.
- JOHNSON, C. (1965). ORTEP. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration. Oak Ridge National Laboratory ORNL-3794 UC-4-Chemistry TID-4500 (41sted.).
- KORN, E. (1963). Science, 153, 1491.
- LARSSON, K. (1963). Acta Cryst. 16, 741.
- LARSSON, K. (1964). Ark. Kem. 23, 23.
- LARSSON, K., LUNDQUIST, M., STÄLHBERG-STENHAGEN, S. & STENHAGEN, E. (1969). J. Coll. Interface Sci. 29, 268.
- O'BRIEN, J. (1965). Science 147, 1099.
- ROBERTSON, J. (1959). Sym. Biochem. Soc. 16, 3.
- STEWART, J. (1967). Technical Report 67–58 from the Computer Science Center, Univ. of Maryland.
- VANDENHEUVEL, F. (1963). J. Amer. Oil Chemists' Soc. 40, 455.

Acta Cryst. (1971). B27, 986

Crystal and Molecular Structure of 3-p-Bromophenyl-1-nitroso-2-pyrazoline*

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(Received 11 May 1970)

The bromoderivative of the product $C_9H_9N_3O$, obtained when diazomethane is reacted with benzonitrile oxide in ether, has been examined by X-ray single-crystal techniques and shown to have the structure of 3-*p*-bromophenyl-1-nitroso-2-pyrazoline. The crystals are monoclinic with space group $P2_1/c$ and $a=5.636\pm0.012$, $b=9.775\pm0.021$, $c=17.516\pm0.031$ Å, $\beta=97.4\pm0.2^\circ$. The final *R* index with all the non-hydrogen atoms anisotropically refined is 0.094 for 1075 visually estimated intensities. The molecule is slightly but significantly non-planar. The structure is stabilized mainly by van der Waals interactions; however, a short $Br \cdots O$ contact of length 3.298 Å, which is slightly less than the expected van der Waals separation, suggests that weak charge transfer interaction may be present. The C-Br \cdots O angle is 176.1°.

Introduction

The reaction between diazomethane and benzonitrile oxide in ether gives a light-yellow crystalline product

* Contribution No. 306 from the Centre of Advanced Study in Physics, University of Madras, Madras-25, India, with chemical formula $C_9N_3OH_9$. From nuclear magnetic resonance (n.m.r.) and ultraviolet spectra of this compound, three possible structures, shown in Fig. 1, were proposed although structure III was considered to be less likely than the other two (Nagarajan, 1965; Nagarajan & Rajagopalan, 1967). It seemed worthwhile to carry out an X-ray analysis to establish the