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

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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  $Cu K\alpha$  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; Vandenneuvel, 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  $a=9.36(2)$ ,  $b=5.58(1)$ ,  $c=54.53(5)$  Å,  $\beta=90.40(8)^\circ$  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 1.366 g.cm<sup>-3</sup> (by flotation in aqueous potassium iodide solution); the calculated density is 1.368 g.cm<sup>-3</sup>.

Intensity data were collected using a manually operated General Electric XRD-6 single crystal orienter system. Nickel filtered Cu *K*α radiation ( $\lambda=1.5418$ ) scattered by the crystal with the *b* axis mounted coincident with the  $\varphi$  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  $-1.67^\circ$  in  $2\theta$ .

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:

$$I(j) = I'(j)\{K(n)/[1.0 + S(n)(j - J_0(n))]\}$$

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 1;

$S(n)$  = the fractional intensity decline per observation;

$J_0(n)$  = the value of *j* for the first observation on crystal *n*.

The following values were used:

<i>n</i>	<i>K</i> ( <i>n</i> )	<i>S</i> ( <i>n</i> )	<i>J</i> <sub>0</sub> ( <i>n</i> )
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  $2\theta$  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  $5 \times 10^{-6}$ . 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 semi-empirical 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-

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

The anisotropic coefficients have the form:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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 (8)	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)
O-	0.1037 (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)	0.0000 (0)	2.0230 (13)	0.23506 (10)	0.0115 (7)	0.0434 (28)	0.00031 (2)	-0.0006 (24)	0.00003 (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 ( $\mu_{Cu K\alpha}$ ) is  $39.7 \text{ cm}^{-1}$  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  $\beta_{ij}$  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  $R(\sum |F_{\text{obs}}| - |F_{\text{calc}}| / \sum |F_{\text{obs}}|)$  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  $k \ln 2^N = R \ln 2 = 1.38 \text{ cal/mole degree}$ ; (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-

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 Σw(|Fo|² - |kFc|²)². The final value for the quantity S =

Table 2. Comparison of observed and calculated structure factors

Each column contains the value of I, |Fo| and Fc. \* denotes an unobserved reflection; R denotes a reflection omitted from least-squares; Z denotes F(0,0,0).

Table with multiple columns containing numerical data for reflections, including indices (h, k, l), observed intensity (I), observed structure factor (|Fo|), and calculated structure factor (Fc). The table is organized into several sections based on reflection types (e.g., 0,0,L; 1,0,0; 1,1,1).

Table 2 (cont.)

3,3,L	4,6	0*	10	35	270	-280	38	127	-132	32	416	-341	24	446	432	31	398	-262	39	12*	-14	-12	91	154	-3	157	140	15	0*	1	-24	0*	-49					
-53	113	130	137	-115	37	135	-128	40	112	-133	36	76	-74	26	276	275	25	458	-448	31	169	-172	-13	0* <td>-1</td> <td>72*</td> <td>70</td> <td>21</td> <td>78</td> <td>-79</td> <td>-22</td> <td>4*</td> <td>-13</td>	-1	72*	70	21	78	-79	-22	4*	-13					
-52	144	50	131	-109	37	188	-139	39	111	-131	33	356	-341	27	356	341	27	356	-341	27	356	-341	27	356	-341	27	356	-341	27	356	-341	27	356	-341	27			
-51	114	130	50	-117	39	80	-79	42	140	-145	36	377	-378	28	373	276	25	458	-448	31	169	-172	-13	0* <td>-1</td> <td>72*</td> <td>70</td> <td>21</td> <td>78</td> <td>-79</td> <td>-22</td> <td>4*</td> <td>-13</td> <td>36</td>	-1	72*	70	21	78	-79	-22	4*	-13	36				
-50	166	-193	51	-208	-37	40	47*	-12	43	106	-128	37	101	-93	29	449	425	26	262	-262	34	195	-169	-10	63* <td>-144</td> <td>2</td> <td>187</td> <td>-162</td> <td>24</td> <td>121</td> <td>-146</td> <td>-19</td> <td>0* </td>	-144	2	187	-162	24	121	-146	-19	0*				
-49	91	113	52	-181	41	47* <td>-19</td> <td>-26</td> <td>41* <td>-3</td> <td>43</td> <td>163</td> <td>-163</td> <td>33</td> <td>278</td> <td>286</td> <td>27</td> <td>389</td> <td>-386</td> <td>35</td> <td>218</td> <td>-199</td> <td>-9</td> <td>120* <td>-778</td> <td>3</td> <td>180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> </td></td></td></td>	-19	-26	41* <td>-3</td> <td>43</td> <td>163</td> <td>-163</td> <td>33</td> <td>278</td> <td>286</td> <td>27</td> <td>389</td> <td>-386</td> <td>35</td> <td>218</td> <td>-199</td> <td>-9</td> <td>120* <td>-778</td> <td>3</td> <td>180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> </td></td></td>	-3	43	163	-163	33	278	286	27	389	-386	35	218	-199	-9	120* <td>-778</td> <td>3</td> <td>180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> </td></td>	-778	3	180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> </td>	-83	151	-119	-20	44* <td>-36</td>	-36					
-48	197	-213	53	-181	-42	95	94	61* <td>-110</td> <td>44</td> <td>182</td> <td>164</td> <td>-28</td> <td>0* <td>-30</td> <td>318</td> <td>-290</td> <td>31</td> <td>249</td> <td>249</td> <td>28</td> <td>112</td> <td>-122</td> <td>-16</td> <td>0* <td>3</td> <td>4</td> <td>201</td> <td>-196</td> <td>26</td> <td>134</td> <td>-176</td> <td>-17</td> <td>37* </td></td></td>	-110	44	182	164	-28	0* <td>-30</td> <td>318</td> <td>-290</td> <td>31</td> <td>249</td> <td>249</td> <td>28</td> <td>112</td> <td>-122</td> <td>-16</td> <td>0* <td>3</td> <td>4</td> <td>201</td> <td>-196</td> <td>26</td> <td>134</td> <td>-176</td> <td>-17</td> <td>37* </td></td>	-30	318	-290	31	249	249	28	112	-122	-16	0* <td>3</td> <td>4</td> <td>201</td> <td>-196</td> <td>26</td> <td>134</td> <td>-176</td> <td>-17</td> <td>37* </td>	3	4	201	-196	26	134	-176	-17	37*				
-47	7*	65	54	-110	44	182	164	-28	0* <td>-30</td> <td>318</td> <td>-290</td> <td>31</td> <td>249</td> <td>249</td> <td>28</td> <td>112</td> <td>-122</td> <td>-16</td> <td>0* <td>3</td> <td>4</td> <td>201</td> <td>-196</td> <td>26</td> <td>134</td> <td>-176</td> <td>-17</td> <td>37* <td>119</td> <td>9</td> <td>46* <td>-7</td> </td></td></td>	-30	318	-290	31	249	249	28	112	-122	-16	0* <td>3</td> <td>4</td> <td>201</td> <td>-196</td> <td>26</td> <td>134</td> <td>-176</td> <td>-17</td> <td>37* <td>119</td> <td>9</td> <td>46* <td>-7</td> </td></td>	3	4	201	-196	26	134	-176	-17	37* <td>119</td> <td>9</td> <td>46* <td>-7</td> </td>	119	9	46* <td>-7</td>	-7					
-46	178	-191	55	30	-45	61* <td>76</td> <td>-27</td> <td>45* <td>-64</td> <td>42</td> <td>23</td> <td>-130</td> <td>34</td> <td>308</td> <td>289</td> <td>31</td> <td>99</td> <td>-103</td> <td>38</td> <td>156</td> <td>-140</td> <td>-5</td> <td>220* <td>-344</td> <td>7</td> <td>308</td> <td>-296</td> <td>29</td> <td>205</td> <td>-218</td> <td>50* <td>-46</td> <td>74* </td></td></td></td>	76	-27	45* <td>-64</td> <td>42</td> <td>23</td> <td>-130</td> <td>34</td> <td>308</td> <td>289</td> <td>31</td> <td>99</td> <td>-103</td> <td>38</td> <td>156</td> <td>-140</td> <td>-5</td> <td>220* <td>-344</td> <td>7</td> <td>308</td> <td>-296</td> <td>29</td> <td>205</td> <td>-218</td> <td>50* <td>-46</td> <td>74* </td></td></td>	-64	42	23	-130	34	308	289	31	99	-103	38	156	-140	-5	220* <td>-344</td> <td>7</td> <td>308</td> <td>-296</td> <td>29</td> <td>205</td> <td>-218</td> <td>50* <td>-46</td> <td>74* </td></td>	-344	7	308	-296	29	205	-218	50* <td>-46</td> <td>74* </td>	-46	74*				
-45	21	-234	56	236	-229	45	119	-26	41* <td>-3</td> <td>43</td> <td>163</td> <td>-163</td> <td>33</td> <td>278</td> <td>286</td> <td>27</td> <td>389</td> <td>-386</td> <td>35</td> <td>218</td> <td>-199</td> <td>-9</td> <td>120* <td>-778</td> <td>3</td> <td>180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> <td>38</td> </td></td></td>	-3	43	163	-163	33	278	286	27	389	-386	35	218	-199	-9	120* <td>-778</td> <td>3</td> <td>180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> <td>38</td> </td></td>	-778	3	180* <td>-83</td> <td>151</td> <td>-119</td> <td>-20</td> <td>44* <td>-36</td> <td>38</td> </td>	-83	151	-119	-20	44* <td>-36</td> <td>38</td>	-36	38				
-44	3	-53	5,3,L	47	169	150	-25	19*	-41	44	118	93	36	119	90	33	119	90	33	119	90	33	119	90	33	119	90	33	119	90	33	119	90	33	119	90		
-43	15*	-157	5*	72	46	272	247	-24	29*	-25	45	0* <td>8</td> <td>37</td> <td>147</td> <td>310</td> <td>34</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td> <td>3</td> <td>195</td> <td>173</td>	8	37	147	310	34	195	173	3	195	173	3	195	173	3	195	173	3	195	173	3	195	173	3	195	173	
-42	106	-165	-51	0* <td>42</td> <td>50</td> <td>104</td> <td>105</td> <td>-22</td> <td>44* <td>-46</td> <td>47</td> <td>75</td> <td>-36</td> <td>39</td> <td>50* <td>35</td> <td>36</td> <td>220</td> <td>187</td> <td>-27</td> <td>32* <td>6</td> <td>0</td> <td>72</td> <td>9</td> <td>1</td> <td>268</td> <td>-236</td> <td>13</td> <td>341</td> <td>-338</td> <td>0* <td>2</td> <td>8</td> </td></td></td></td>	42	50	104	105	-22	44* <td>-46</td> <td>47</td> <td>75</td> <td>-36</td> <td>39</td> <td>50* <td>35</td> <td>36</td> <td>220</td> <td>187</td> <td>-27</td> <td>32* <td>6</td> <td>0</td> <td>72</td> <td>9</td> <td>1</td> <td>268</td> <td>-236</td> <td>13</td> <td>341</td> <td>-338</td> <td>0* <td>2</td> <td>8</td> </td></td></td>	-46	47	75	-36	39	50* <td>35</td> <td>36</td> <td>220</td> <td>187</td> <td>-27</td> <td>32* <td>6</td> <td>0</td> <td>72</td> <td>9</td> <td>1</td> <td>268</td> <td>-236</td> <td>13</td> <td>341</td> <td>-338</td> <td>0* <td>2</td> <td>8</td> </td></td>	35	36	220	187	-27	32* <td>6</td> <td>0</td> <td>72</td> <td>9</td> <td>1</td> <td>268</td> <td>-236</td> <td>13</td> <td>341</td> <td>-338</td> <td>0* <td>2</td> <td>8</td> </td>	6	0	72	9	1	268	-236	13	341	-338	0* <td>2</td> <td>8</td>	2	8			
-41	220	-299	50	42* <td>99</td> <td>51</td> <td>175</td> <td>173</td> <td>-21</td> <td>45* <td>-57</td> <td>50</td> <td>60</td> <td>194</td> <td>158</td> <td>41</td> <td>0* <td>-131</td> <td>37</td> <td>177</td> <td>165</td> <td>47</td> <td>52</td> <td>2</td> <td>142</td> <td>117</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td> </td></td>	99	51	175	173	-21	45* <td>-57</td> <td>50</td> <td>60</td> <td>194</td> <td>158</td> <td>41</td> <td>0* <td>-131</td> <td>37</td> <td>177</td> <td>165</td> <td>47</td> <td>52</td> <td>2</td> <td>142</td> <td>117</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td> </td>	-57	50	60	194	158	41	0* <td>-131</td> <td>37</td> <td>177</td> <td>165</td> <td>47</td> <td>52</td> <td>2</td> <td>142</td> <td>117</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td> <td>14</td> <td>429</td> <td>-330</td>	-131	37	177	165	47	52	2	142	117	14	429	-330	14	429	-330	14	429	-330			
-40	97	-106	49	0* <td>-22</td> <td>51</td> <td>39</td> <td>39* <td>-20</td> <td>39* <td>52</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td></td></td></td></td></td>	-22	51	39	39* <td>-20</td> <td>39* <td>52</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td></td></td></td></td>	-20	39* <td>52</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td></td></td></td>	52	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* <td>-1</td> <td>18</td> <td>0* </td></td>	-1	18	0* <td>-1</td> <td>18</td> <td>0* </td>	-1	18	0*	
-39	101	-70	48	45* <td>92</td> <td>7,3,L</td> <td>19</td> <td>180</td> <td>113</td> <td>11</td> <td>51</td> <td>60</td> <td>213</td> <td>165</td> <td>42</td> <td>167</td> <td>40</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td> <td>23</td>	92	7,3,L	19	180	113	11	51	60	213	165	42	167	40	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	
-38	9*	-79	-47	95	86	7,3,L	19	180	113	11	51	60	213	165	42	167	40	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	
-37	103	-374	-46	0* <td>29</td> <td>-43</td> <td>42* <td>-28</td> <td>17</td> <td>0* <td>-2</td> <td>52</td> <td>98</td> <td>75</td> <td>44</td> <td>32</td> <td>-175</td> <td>41</td> <td>297</td> <td>244</td> <td>-22</td> <td>61</td> <td>91</td> <td>5</td> <td>120* <td>-85</td> <td>17</td> <td>332</td> <td>-158</td> <td>-19</td> <td>46*</td> <td>-65</td> <td>-4</td> <td>-10</td> <td>-113</td> </td></td></td>	29	-43	42* <td>-28</td> <td>17</td> <td>0* <td>-2</td> <td>52</td> <td>98</td> <td>75</td> <td>44</td> <td>32</td> <td>-175</td> <td>41</td> <td>297</td> <td>244</td> <td>-22</td> <td>61</td> <td>91</td> <td>5</td> <td>120* <td>-85</td> <td>17</td> <td>332</td> <td>-158</td> <td>-19</td> <td>46*</td> <td>-65</td> <td>-4</td> <td>-10</td> <td>-113</td> </td></td>	-28	17	0* <td>-2</td> <td>52</td> <td>98</td> <td>75</td> <td>44</td> <td>32</td> <td>-175</td> <td>41</td> <td>297</td> <td>244</td> <td>-22</td> <td>61</td> <td>91</td> <td>5</td> <td>120* <td>-85</td> <td>17</td> <td>332</td> <td>-158</td> <td>-19</td> <td>46*</td> <td>-65</td> <td>-4</td> <td>-10</td> <td>-113</td> </td>	-2	52	98	75	44	32	-175	41	297	244	-22	61	91	5	120* <td>-85</td> <td>17</td> <td>332</td> <td>-158</td> <td>-19</td> <td>46*</td> <td>-65</td> <td>-4</td> <td>-10</td> <td>-113</td>	-85	17	332	-158	-19	46*	-65	-4	-10	-113			
-36	145	194	-45	119	187	-42	166	40	116	96	81	53	94	60	46	208	144	40	144	40	144	40	144	40	144	40	144	40	144	40	144	40	144	40	144	40	144	40
-35	133	191	-149	-44	58	-41	11* <td>-10</td> <td>1</td> <td>18</td> <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	-10	1	18	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td></td>	0* <td>0* <td>0* <td>0* <td>0* </td></td></td></td>	0* <td>0* <td>0* <td>0* </td></td></td>	0* <td>0* <td>0* </td></td>	0* <td>0* </td>	0*		
-34	394	407	-43	73* <td>94</td> <td>20</td> <td>-15</td> <td>-14</td> <td>171</td> <td>188</td> <td>9</td> <td>2,4,L</td> <td>47</td> <td>224</td> <td>-168</td> <td>44</td> <td>255</td> <td>214</td> <td>-19</td> <td>95</td> <td>102</td> <td>8</td> <td>223</td> <td>233</td> <td>20</td> <td>93</td> <td>63</td> <td>-6</td> <td>-15</td> <td>57</td> <td>-1</td> <td>51</td> <td>-144</td> <td>0* </td>	94	20	-15	-14	171	188	9	2,4,L	47	224	-168	44	255	214	-19	95	102	8	223	233	20	93	63	-6	-15	57	-1	51	-144	0*				
-33	265	274	-41	208	215	-38	176	149	-12	168	156	-52	116	-108	40	290	46	255	265	107	87	65	10	312	297	17	87	65	10	312	297	17	87	65	10	312	297	
-32	265	274	-41	208	215	-38	176	149	-12	168	156	-52	116	-108	40	290	46	255	265	107	87	65	10	312	297	17	87	65	10	312	297	17	87	65	10	312	297	
-31	161	198	-39	128	63	313	294	-10	83	91	-50	65	-56	51	60	50	317	-255	47	380	-12	111	252	22	53	86	-12	53	86	-12	53	86	-12	53	86	-12		
-30	265	274	-41	208	215	-38	176	149	-12	168	156	-52	116	-108	40	290	46	255	265	107	87	65	10	312	297	17	87	65	10	312	297	17	87	65	10	312	297	
-29	465	-465	-40	53	-15	37	96	-51	89	105	-51	37	96	-51	89	105	-51	37	96	-51	89	105	-51	37	96	-51	89	105	-51	37	96	-51	37	96	-51	89	105	
-28	548	542	-39	128	63	313	294	-10	83	91	-50	65	-56	51	60	50	317	-255	47	380	-12	111	252	22	53	86	-12	53	86	-12	53	86	-12	53	86	-12		
-27	248	-220	-38	0* <td>-39</td> <td>35</td> <td>46* <td>41</td> <td>-9</td> <td>205</td> <td>206</td> <td>-49</td> <td>108</td> <td>-99</td> <td>52</td> <td>149</td> <td>-143</td> <td>6</td> <td>1,4,L</td> <td>6,1,L</td> <td>13</td> <td>104</td> <td>178</td> <td>14</td> <td>176</td> <td>-164</td> <td>26</td> <td>57*</td> <td>44</td> <td>-9</td> <td>57</td> <td>44</td> <td>-9</td> <td>57</td> <td>44</td> </td>	-39	35	46* <td>41</td> <td>-9</td> <td>205</td> <td>206</td> <td>-49</td> <td>108</td> <td>-99</td> <td>52</td> <td>149</td> <td>-143</td> <td>6</td> <td>1,4,L</td> <td>6,1,L</td> <td>13</td> <td>104</td> <td>178</td> <td>14</td> <td>176</td> <td>-164</td> <td>26</td> <td>57*</td> <td>44</td> <td>-9</td> <td>57</td> <td>44</td> <td>-9</td> <td>57</td> <td>44</td>	41	-9	205	206	-49	108	-99	52	149	-143	6	1,4,L	6,1,L	13	104	178	14	176	-164	26	57*	44	-9	57	44	-9	57	44			
-26	192	-198	-37	87	21	34	164	145	-8	62* <td>-20</td> <td>-48</td> <td>33* <td>-119</td> <td>5</td> <td>4,4,L</td> <td>-4</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> </td>	-20	-48	33* <td>-119</td> <td>5</td> <td>4,4,L</td> <td>-4</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td> <td>1</td>	-119	5	4,4,L	-4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
-25	264	363	-35	39	65	-32	132	138	-6	37* <td>38</td> <td>-46</td> <td>0* <td>-14</td> <td>-6</td> <td>7</td> <td>8</td> <td>-1</td> <td>159</td> <td>141</td> <td>16</td> <td>340</td> <td>353</td> <td>28</td> <td>136</td> <td>153</td> <td>-7</td> <td>55</td> <td>-80</td> <td>7</td> <td>97</td> <td>-117</td> <td>0* <td>-194</td> </td></td>	38	-46	0* <td>-14</td> <td>-6</td> <td>7</td> <td>8</td> <td>-1</td> <td>159</td> <td>141</td> <td>16</td> <td>340</td> <td>353</td> <td>28</td> <td>136</td> <td>153</td> <td>-7</td> <td>55</td> <td>-80</td> <td>7</td> <td>97</td> <td>-117</td> <td>0* <td>-194</td> </td>	-14	-6	7	8	-1	159	141	16	340	353	28	136	153	-7	55	-80	7	97	-117	0* <td>-194</td>	-194				
-24	60* <td>36</td> <td>39</td> <td>65</td> <td>-32</td> <td>132</td> <td>138</td> <td>-6</td> <td>37* <td>38</td> <td>-46</td> <td>0* <td>-14</td> <td>-6</td> <td>7</td> <td>8</td> <td>-1</td> <td>159</td> <td>141</td> <td>16</td> <td>340</td> <td>353</td> <td>28</td> <td>136</td> <td>153</td> <td>-7</td> <td>55</td> <td>-80</td> <td>7</td> <td>97</td> <td>-117</td> <td>0* <td>-194</td> <td>0* </td></td></td></td>	36	39	65	-32	132	138	-6	37* <td>38</td> <td>-46</td> <td>0* <td>-14</td> <td>-6</td> <td>7</td> <td>8</td> <td>-1</td> <td>159</td> <td>141</td> <td>16</td> <td>340</td> <td>353</td> <td>28</td> <td>136</td> <td>153</td> <td>-7</td> <td>55</td> <td>-80</td> <td>7</td> <td>97</td> <td>-117</td> <td>0* <td>-194</td> <td>0* </td></td></td>	38	-46	0* <td>-14</td> <td>-6</td> <td>7</td> <td>8</td> <td>-1</td> <td>159</td> <td>141</td> <td>16</td> <td>340</td> <td>353</td> <td>28</td> <td>136</td> <td>153</td> <td>-7</td> <td>55</td> <td>-80</td> <td>7</td> <td>97</td> <td>-117</td> <td>0* <td>-194</td> <td>0* </td></td>	-14	-6	7	8	-1	159	141	16	340	353	28	136	153	-7	55	-80	7	97	-117	0* <td>-194</td> <td>0* </td>	-194	0*				
-23	649	632	-33	99	128	30	117	38	-4	107	200	-44	106	107	117	162	-65	39	47	41	-10	59	24	18	11	20	139	-6	86	-119	9	8	-10	-113				
-22	40	30	-32	228	-255	29	129	99	-3	69	108	43	274	-226	-46	31	-117	-38	0* <td>7</td> <td>8</td> <td>-1</td> <td>113</td> <td>98</td> <td>19</td> <td>241</td> <td>229</td> <td>31</td> <td>166</td> <td>171</td> <td>-4</td> <td>99</td> <td>-84</td> <td>10</td> <td>98</td>	7	8	-1	113	98	19	241	229	31	166	171	-4	99	-84	10	98			
-21	44	48	-30	182	-219	46	142	131	-1	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111		
-20	207	185	-30	250	-252	27	112	102	-2	37* <td>76</td> <td>-141</td> <td>183</td> <td>-146</td> <td>44</td> <td>86</td> <td>-62</td> <td>-36</td> <td>44* <td>43</td> <td>-6</td> <td>107</td> <td>-76</td> <td>21</td> <td>484</td> <td>383</td> <td>33</td> <td>177</td> <td>201</td> <td>-4</td> <td>99</td> <td>-84</td> <td>10</td> <td>98</td> </td>	76	-141	183	-146	44	86	-62	-36	44* <td>43</td> <td>-6</td> <td>107</td> <td>-76</td> <td>21</td> <td>484</td> <td>383</td> <td>33</td> <td>177</td> <td>201</td> <td>-4</td> <td>99</td> <td>-84</td> <td>10</td> <td>98</td>	43	-6	107	-76	21	484	383	33	177	201	-4	99	-84	10	98				
-19	44	48	-30	182	-219	46	142	131	-1	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111	111		
-18	355	423	-28	296	319	-26	105	134	1	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82		
-17	959	527	-27	0* <td>4</td> <td>2</td> <td>60* <td>2</td> <td>0* <td>19</td> <td>-38</td> <td>107</td> <td>130</td> <td>-14</td> <td>3</td> <td>156</td> <td>131</td> <td>-33</td> <td>126</td> <td>127</td> <td>-3</td> <td>51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> </td></td></td>	4	2	60* <td>2</td> <td>0* <td>19</td> <td>-38</td> <td>107</td> <td>130</td> <td>-14</td> <td>3</td> <td>156</td> <td>131</td> <td>-33</td> <td>126</td> <td>127</td> <td>-3</td> <td>51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> </td></td>	2	0* <td>19</td> <td>-38</td> <td>107</td> <td>130</td> <td>-14</td> <td>3</td> <td>156</td> <td>131</td> <td>-33</td> <td>126</td> <td>127</td> <td>-3</td> <td>51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> </td>	19	-38	107	130	-14	3	156	131	-33	126	127	-3	51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td>	-36	22	156	157	34	194	218	-1	96	-210	1	96				
-16	20	20	-26	308	-329	59	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145	-2	158	145
-15	10	10	-24	288	-187	-22	52* <td>70</td> <td>4</td> <td>0* <td>30</td> <td>-15</td> <td>107</td> <td>-166</td> <td>39</td> <td>51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td> </td></td>	70	4	0* <td>30</td> <td>-15</td> <td>107</td> <td>-166</td> <td>39</td> <td>51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td> </td>	30	-15	107	-166	39	51* <td>-36</td> <td>22</td> <td>156</td> <td>157</td> <td>34</td> <td>194</td> <td>218</td> <td>-1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td> <td>1</td> <td>96</td> <td>-210</td>	-36	22	156	157	34	194	218	-1	96	-210	1	96	-210	1	96	-210						

Table 3. *Intramolecular bond distances and angles*

	Distance					Angle	
	Uncorrected	Corrected				Uncorrected	Corrected
Br—C(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)=O	1.20	1.20	C(2)	C(1)	—O—	111.5	107.6
C(1)—O—	1.34	1.38	—O—	C(1)	=O	121.9	123.9
—O—GC(1)	1.43	1.38	C(1)	—O—	GC(1)	116.8	113.2
GC(1)—GC(2)	1.53		—O—	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	

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	Symmetry operation		
1	<i>x</i> ,	<i>y</i> ,	<i>z</i>
2	- <i>x</i> ,	- <i>y</i> ,	- <i>z</i>
3	- <i>x</i> ,	<i>y</i> ,	$\frac{1}{2}$ - <i>z</i>
4	<i>x</i> ,	- <i>y</i> ,	$\frac{1}{2}$ + <i>z</i>
5	$\frac{1}{2}$ + <i>x</i> ,	$\frac{1}{2}$ + <i>y</i> ,	<i>z</i>
6	$\frac{1}{2}$ - <i>x</i> ,	$\frac{1}{2}$ - <i>y</i> ,	- <i>z</i>
7	$\frac{1}{2}$ - <i>x</i> ,	$\frac{1}{2}$ + <i>y</i> ,	$\frac{1}{2}$ - <i>z</i>
8	$\frac{1}{2}$ + <i>x</i> ,	$\frac{1}{2}$ - <i>y</i> ,	$\frac{1}{2}$ + <i>z</i>

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...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) to	Distance	from GO(2) (5553) 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:

$$a_s = 4.14 (5), b_s = 5.39 (5), c_s = 2.54 (5) \text{ \AA},$$

$$\alpha_s = 78 (1), \beta_s = 107 (1), \text{ and } \gamma_s = 120 (1)^\circ.$$

The volume per CH<sub>2</sub> 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 *A*<sub>1</sub> and *A*<sub>2</sub> 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°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:

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

$\Delta_1$  are the out-of-plane distances;  $\Delta_2$  and  $\Delta_3$  are the in-plane coordinates.

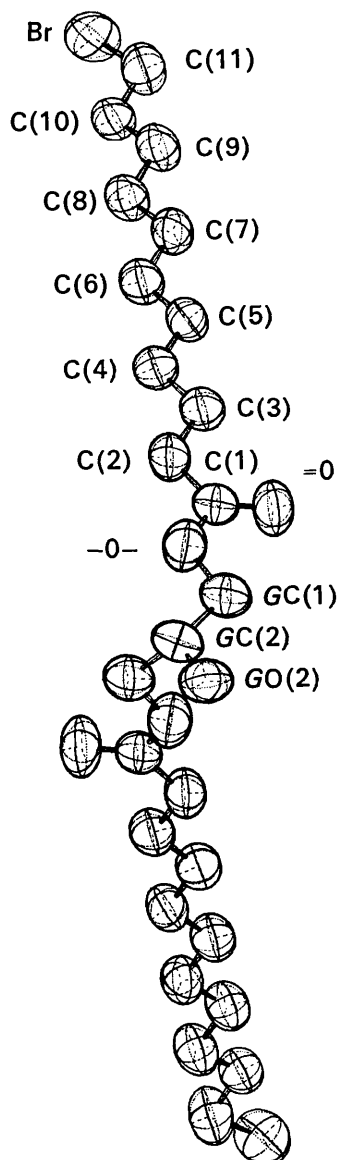


Fig. 1. The molecular structure of the symmetric 1,3-diglyceride of 11-bromoundecanoic acid.

Table 6 (cont.)

	Least-squares weighting	$\Delta_1$	$\Delta_2$	$\Delta_3$
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	-0.02	-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	-0.02	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
=O	0.0	-0.55	1.36	7.07
-O-	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
GO(2)	0.0	0.20	-0.61	11.59

Table 7. *Closest intermolecular distances*

A. Across end group planes (DMAX=4.5 Å)

Br	Br(4456)	3.45 Å
	C(11) (5552)	3.93
	Br(4556)	3.97
	C(11) (4556)	4.14
	Br(5552)	4.16
C(11)	Br(5552)	3.93
	Br(4556)	4.14

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

Br	C(11) (4455)	3.89 Å
	C(9) (5451)	3.93
	C(10) (5451)	4.02
	C(9) (4455)	4.15
	C(8) (5451)	4.15
C(11)	Br(5555)	3.89
C(10)	Br(5651)	4.02
	C(7) (5451)	4.06
	C(6) (5451)	4.18
C(9)	Br(5651)	3.93
	Br(5555)	4.15
	C(6) (5451)	4.19
C(8)	C(5) (5451)	4.14
	Br(5651)	4.15
	C(4) (5451)	4.17
C(7)	C(2) (5651)	4.06
	C(4) (5451)	4.11
C(6)	C(2) (5451)	4.15
	C(10) (5651)	4.18
	C(3) (5451)	4.18
	C(9) (5651)	4.19
C(5)	C(2) (5451)	4.04
	C(8) (5651)	4.14
C(4)	=O(4455)	3.71
	C(7) (5651)	4.11
	C(8) (5651)	4.17
	-O-(5451)	4.18
C(3)	GO(2) (5453)	3.92
	-O-(5451)	4.04
	=O(4455)	4.07
	C(6) (5651)	4.18

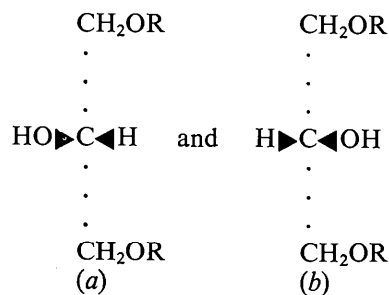
Table 7 (cont.)

C(2)	GO(2) (5453)	3.17
	=O(4455)	3.61
	C(5) (5651)	4.04
	C(6) (5651)	4.15
C(1)	GO(2) (5453)	3.15
	GO(2) (5457)	3.84
	GO(2) (5451)	3.88
	GC(2) (5451)	4.09
=O	GO(2) (5457)	2.87
	-O-(5455)	3.39
	GC(2) (5455)	3.60
	C(2) (5555)	3.61
	GO(2) (5453)	3.65
	C(4) (5555)	3.71
	GC(1) (5457)	3.77
	GO(2) (5451)	3.94
	C(3) (5555)	4.07
	GC(1) (5455)	4.10
-O-	GO(2) (5453)	3.32
	=O(4555)	3.39
	GO(2) (5451)	3.93
	C(3) (5651)	4.04
	GO(2) (5457)	4.10
GC(1)	GO(2) (5457)	3.31
	=O(5557)	3.77
	GO(2) (5453)	4.07
	GO(2) (5451)	4.08
GC(2)	=O(4555)	3.60
	=O(5557)	3.60
	C(1) (5651)	4.09
	C(1) (5653)	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:



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  $\beta_{ij}$  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.

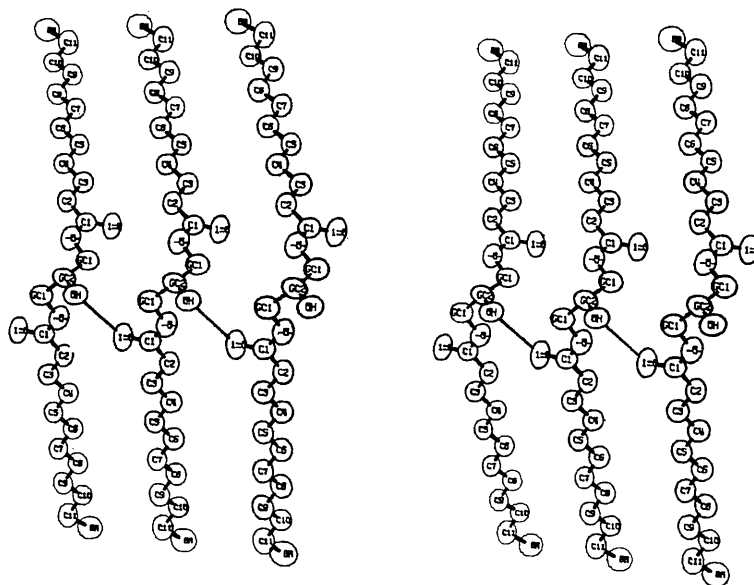


Fig. 2. A stereo view of the hydrogen bonding in the symmetric 1,3-diglyceride of 11-bromoundecanoic acid. The disorder is not illustrated.



Table 8. *The translational and rotational vibration tensors*

The direction cosines of the  $\tau$  and  $\omega$  vibrational tensors are relative to the least-squares plane  $A_1$ ,  $A_2$  and  $A_3$  orthonormal coordinate system. The root mean square values are in Å and degrees.

$\tau(10^{-2} \text{ \AA}^2)$			r.m.s.	$DCA_1$	$DCA_2$	$DCA_3$
(3.80	-0.53	0.61	0.18	-0.848	-0.258	0.463
	4.90	-0.07	0.21	0.271	0.540	0.797
		4.38	0.23	0.456	-0.801	0.387
$\omega(\text{deg}^2)$			r.m.s.	$DCA_1$	$DCA_2$	$DCA_3$
(0.76	-0.11	-7.11	0.76	-0.839	-0.543	-0.013
	0.88	-5.61	0.97	0.543	-0.839	-0.001
		698.57	26.43	0.010	0.008	-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  $\tau$  and  $\omega$  tensors are given in Table 8. The most striking feature is the very large rotational vibration (r.m.s.  $26.4^\circ$ ) 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  $3.7^\circ$ . These represent changes that are  $5\sigma$  for lengths and  $40\sigma$  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  $3\sigma$ . 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).

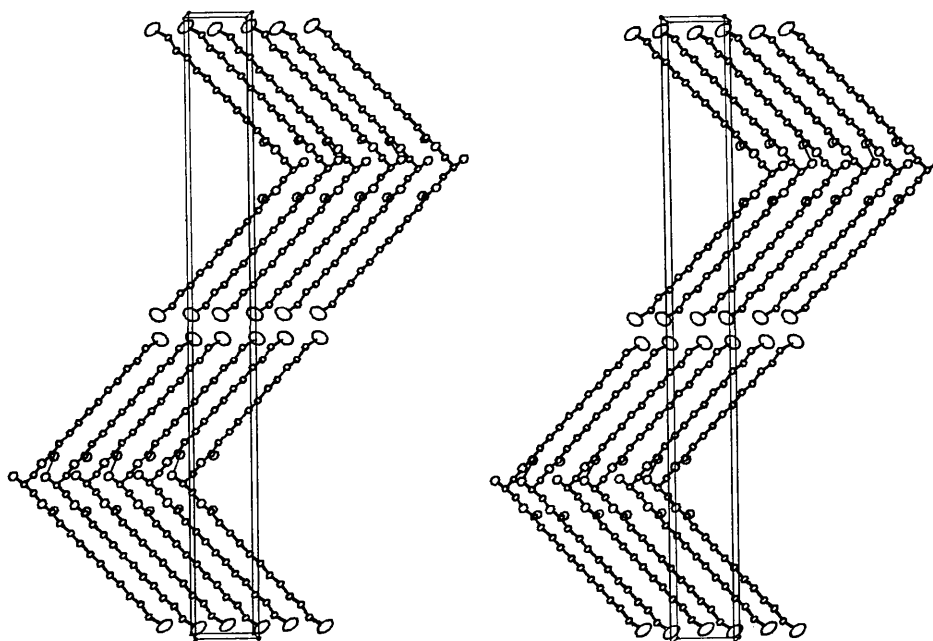


Fig. 3. A stereo view of the molecular packing of the symmetric 1,3-diglyceride of 11-bromoundecanoic acid. The disorder is not illustrated.

Larsson, Lundquist, Stålhberg-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 multilayer 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.

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## 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  $a = 5.636 \pm 0.012$ ,  $b = 9.775 \pm 0.021$ ,  $c = 17.516 \pm 0.031$  Å,  $\beta = 97.4 \pm 0.2^\circ$ . 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...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...O angle is  $176.1^\circ$ .

### Introduction

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

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

\* Contribution No. 306 from the Centre of Advanced Study in Physics, University of Madras, Madras-25, India.