

# The Crystal Structure of a Photodimer of 1,4-Epoxy-1,4-dihydronaphthalene

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The crystal structure of a photodimer of 1,4-epoxy-1,4-dihydronaphthalene, with empirical formula  $C_{20}H_{16}O_2$ , has been determined by the application of direct methods. Three-dimensional data were collected on a Datex-automated General Electric diffractometer to a minimum spacing of  $1.0 \text{ \AA}$ . The coordinates of all atoms in the molecule, the isotropic temperature factors for the hydrogen atoms, and the anisotropic temperature factors for the other atoms were refined by the method of least squares. The final  $R$  index was 0.027. The crystals are orthorhombic, space group  $Pca2_1$  with  $a=16.52$ ,  $b=7.975$  and  $c=10.58 \text{ \AA}$ . Of four possible configurations, the molecule of the photodimer has the *exo-trans-exo* configuration. Despite the lack of a center of symmetry in the space group, the molecule is centrosymmetric almost within experimental error.

## Introduction

The photodimer,  $C_{20}H_{16}O_2$ , was obtained during a study in these laboratories of the photorearrangement of 1,4-epoxy-1,4-dihydronaphthalene (Ziegler, 1969). Study of the nuclear magnetic resonance spectrum showed that the molecule must have either the *endo-endo* or the *exo-exo* configuration. This structure determination was undertaken to find the true configuration.

## Experimental

Crystals, in the form of large, thin plates, were obtained by slow evaporation of an ethanol solution of the photodimer. Unit-cell parameters were determined from measurements of precession photographs which were calibrated by lines diffracted from a powdered sample of sodium chloride ( $a_0=5.6402 \text{ \AA}$ ). The resulting values for the unit-cell dimensions are:

$$\begin{aligned} a &= 16.520(2) \text{ \AA} \\ b &= 7.975(7) \\ c &= 10.58(1) \end{aligned}$$

The absence of  $0kl$  reflections with  $l$  odd and the

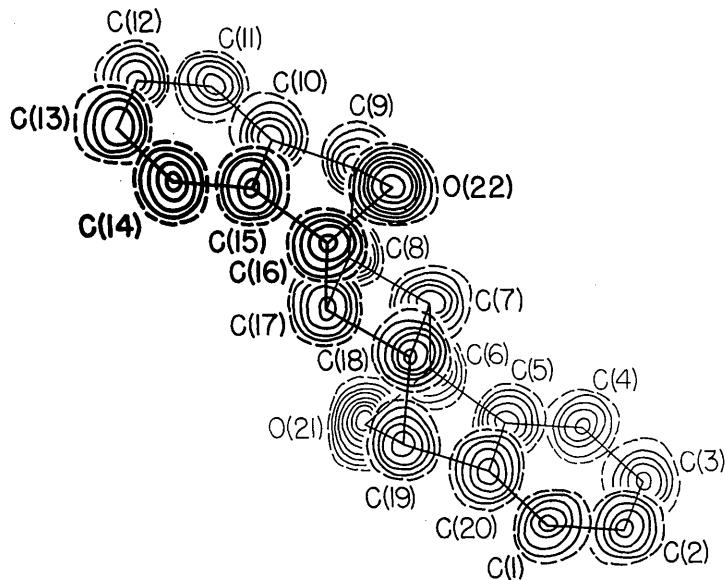


Fig. 1. A composite of sections of a three-dimensional electron density map through each of the heavy atoms, viewed down the  $c$  axis. The dashed contour is at  $2 \text{ e.}\text{\AA}^{-3}$ . The successive contours are at  $3, 4, 5, \dots \text{ e.}\text{\AA}^{-3}$ .

absence of  $h0l$  reflections with  $h$  odd indicate that the space group is either  $Pca_2_1$  or  $Pcam$ .

The density of the crystals measured by the flotation method and the density calculated for the photodimer, assuming four molecules per unit cell, is  $1.374 \text{ g. cm}^{-3}$ .

The intensity data used for final refinement of the structure were collected from a crystal cut from one of the large, thin plates with a razor blade. It had a thickness of approximately  $0.1 \text{ mm}$  and had a trape-

Table 1. Distribution of normalized structure factors

	Observed	Theoretical
	Centric	Acentric
$\langle  E  \rangle$	0.881	0.798 0.886
$\langle  E ^2 - 1 \rangle$	0.720	0.968 0.736
$\langle  E ^2 - 1 \rangle$	0.005	0.000 0.000

zoidal face with an altitude of  $0.3 \text{ mm}$  and bases of  $0.5$  and  $0.2 \text{ mm}$ .

Intensity data were collected by the  $\theta-2\theta$  scan method on a Datex-automated General Electric diffractometer using  $Cu K\alpha$  radiation. An initial set of data was collected from a small crystal with a scan speed of two degrees per minute and a background count was collected for ten seconds at both the beginning and the end of the scan. These data proved to be inadequate for satisfactory refinement of the structure. A second set of data was collected using the new crystal described above. This set was collected with a scan speed of one degree per minute and background count was collected for thirty seconds at both ends of the scan. All reflections were collected to a minimum spacing of  $1 \text{ \AA}$ . These numbered a total of 774, of which 9 were observed to have intensities less than background and were assigned intensities of zero. No correction for absorption was made ( $\mu = 7.0 \text{ cm}^{-1}$ ).

The determination and initial refinement of the structure were based on the first set of data. They were placed on an absolute scale by Wilson's (1942) statistical method. A Howells, Phillips & Rogers (1950) plot indicated that the crystal was probably

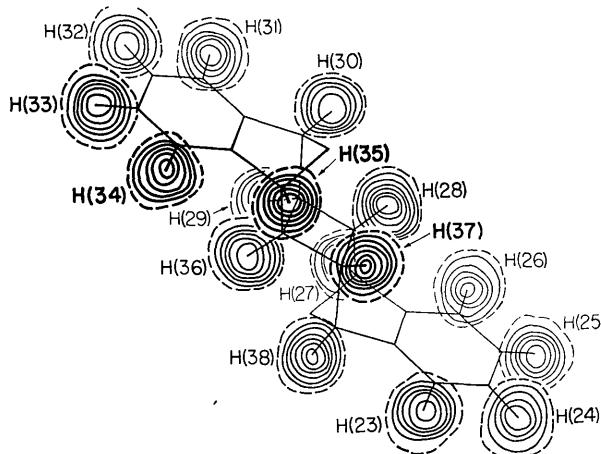


Fig. 2. A composite of sections of a three-dimensional difference electron density map through each of the hydrogen atoms, viewed down the  $c$  axis. The dashed contour is at  $0.1 \text{ e.}\text{\AA}^{-3}$ . The successive contours are at  $0.2, 0.3, 0.4, \dots \text{e.}\text{\AA}^{-3}$ .

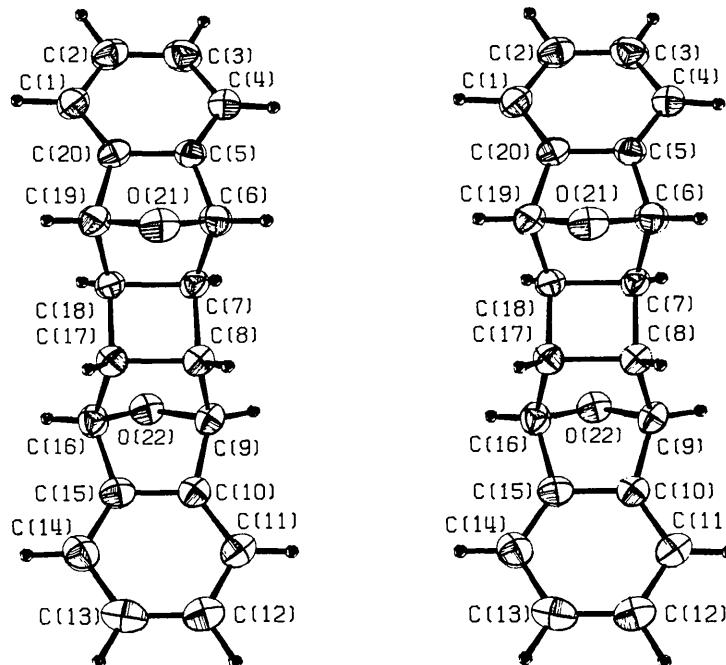


Fig. 3. Stereoscopic view of the photodimer.

noncentrosymmetric; therefore, the space group should be *Pca*<sub>2</sub><sub>1</sub>.

The normalized structure factors |*E*| (Karle & Karle, 1966) were then calculated using an overall temperature parameter of 1.50 Å<sup>2</sup>. The observed and theoretical values for certain statistical averages and distributions of the normalized structure factors are shown in Table 1. A comparison of the observed

values with those calculated for centrosymmetric and noncentrosymmetric structures confirms that the space group is the noncentrosymmetric *Pca*<sub>2</sub><sub>1</sub>.

### Phase determination

A general description of the normal phase determination procedure has been given by Karle & Karle (1966).

Table 2. Observed and calculated structure factors

Within each group the columns contain *k*, 100*F*<sub>o</sub>, 100*F*<sub>c</sub>, and  $\varphi_c$ (°), the phase angle. Reflections marked with an asterisk were assigned zero weight in the final least-squares cycles.

<i>O</i>	<i>K</i>	<i>O</i>	5 933 913 153	4 1762 1771 0	5 193 220 20	0 1309 1311 175	5 541 226 230	3 1634 1609 248	8 255 280	3 1599 1594 203	3 679 728 334
1 89	127	0	1 K 8	6 1197 1222 0	1 1531 1517 315	7 171 692 106	5 1276 1267 333	0 574 597 14	4 1303 1286 262	12 K 7	
2 5619	5960	0	1 1137 1145 192	6 676 743 180	3 2515 2452 121	6 1411 1439 252	2 651 627 154	5 1397 1497 143	0 678 666 94		
3 363	341	0	2 163 251 72	4 1948 1960 149	4 2448 2409 96	4 1198 1186 128	7 650 682 330	3 393 398 3	0 670 629 296	1 242 242 211	1 242 242 211
4 3714	3845	0	3 543 560 149	3 K 1	4 2448 2409 96	4 1198 1186 128	0 670 629 296	1 242 242 211	1 242 242 211	1 242 242 211	
5 3706	3606	0	4 388 330 177	1 7275 7235 35	5 742 788 107	1 7275 7235 35	1 397 1413 340	1 1945 1871 286	0 569 493 121	1 242 242 211	1 242 242 211
6 1914	1900	0	5 213 176 250	3 1404 1450 127	6 352 339 323	7 529 532 37	2 116 128 244	2 1316 1317 63	1 2050 2065 3	0 678 666 94	1 242 242 211
7 552	515	0	1 K 9	4 1190 1158 182	3 495 434 284	3 303 303 88	4 417 439 292	6 1321 1328 135	4 1080 1106 42	3 582 612 180	4 1179 1268 180
0 K 2	0	1 2125 2147 272	5 1463 1466 210	0 4 K 5	0 436 418 91	0 269 322 0	5 1959 1966 260	1 2096 2269 180	10 K 7		
0 9254	8966	201	4 424 426 182	3 262 254 52	6 369 396 283	3 270 272 81	6 1321 1328 135	3 979 937 180	1 242 242 211	1 242 242 211	1 242 242 211
1 11919	10926	298	3 424 426 182	4 495 434 284	2 1048 1092 238	1 125 125 180	4 117 439 292	4 1247 1232 249	2 2478 2554 180	1 242 242 211	1 242 242 211
2 7338	7160	13	4 948 938 81	3 K 2	3 225 243 183	2 327 343 180	4 175 185 210	4 1281 1288 180	0 722 786 180	13 K 1	
3 397	5709	282	1 K 9	1 5287 5264 147	2 2211 2239 129	3 3654 3630 180	7 K 4	4 794 746 0	2 862 888 202	2 140 116 103	
5 1849	1809 255	1	3 236 232 51	5 2856 2853 291	5 1002 1029 0	1 532 512 214	5 167 168 180	3 1539 1578 180	3 1539 1578 180		
6 679	678 59	2	5 218 2167 351	5 863 858 324	5 168 174 194	3 324 340 186	6 187 187 210	6 1262 1278 83	4 569 518 219		
7 1616	1603 229	2	4 2760 2626 206	5 168 174 194	5 168 174 194	0 10 K 8	0 893 893 214	13 K 2			
0 K 4	0	5 994 960 0	5 214 154	7 K 9	7 1004 994 0	5 640 805 234	1 1340 1336 337	1 447 494 224	1 2277 2270 111		
0 220	241	28	1 3816 4031 0	7 839 777 275	0 497 535 314	6 553 553 221	2 302 303 200	2 315 315 120	2 315 315 120		
1 6103	6001	315	2 4329 4519 0	7 839 789 306	2 757 756 223	0 1339 1399 178	6 K 1	3 1215 1210 254	11 K 0	1 245 120 120	
2 4118	4083	203	4 537 446 0	3 K 3	3 864 865 268	1 599 605 249	4 1127 1062 180	1 1352 1312 180	4 908 853 99		
3 350	403	103	3 2705 2716 247	5 516 497 107	2 3041 3179 190	2 484 468 148	2 1830 1832 0	2 1830 1832 0			
4 706	706 250	0	5 163 160 129	5 511 563 355	3 3322 3355 283	3 1759 1689 335	6 1664 1686 225	2 294 294 180	13 K 3		
5 1236	1251 27	6	1 639 129 129	3 1904 1929 455	5 308 367 126	5 168 174 194	4 1736 1734 180	5 189 201 180	2 183 183 180		
6 358	363 163	7	7 985 951 0	5 1648 1628 333	5 168 174 194	5 168 174 194	5 2546 2598 151	5 189 201 180	3 988 1016 22		
7 2532	2505 341	0	5 1841 1824 334	6 163 160 129	6 1774 1742 186	6 1774 1742 186	1 622 668 53	1 622 668 53	4 558 533 87		
0 K 6	0	0 7292 7052 126	7 98 340 308	6 936 882 190	0 983 981 0	7 604 505 221	3 501 503 186	1 1204 1204 180	1 493 509 24		
0 4974	4850 243	1	1 7720 7563 11	2 2017 2009 47	6 K 1	1 949 521 516	2 922 911 95	13 K 4			
1 1343	1342 172	2	2 4346 4321 131	3 K 4	3 821 832 315	0 1687 1664 126	5 1696 1701 321	3 1024 1024 357	1 893 909 322		
2 4426	4400 245	3	3 1788 1814 219	1 918 899 30	4 563 582 251	1 653 661 18	3 736 746 190	2 867 930 20	2 637 661 105		
3 390	409 103	4	1 3052 3016 247	5 516 497 107	2 327 343 180	2 4620 4555 111	4 1120 1159 206	5 309 307 261	3 953 965 96		
4 422	372 27	5	5 406 372 317	3 578 569 140	3 2102 2194 180	3 1021 997 319	5 1149 1170 190	5 126 126 180	3 988 1016 22		
5 798	775 185	6	6 805 780 25	4 778 776 57	0 4 K 8	0 2546 2598 151	1 1259 1347 123	11 K 2	1 1154 1005 152		
6 1312	1299 269	7	7 423 414 192	5 604 615 252	0 1232 1222 170	5 1115 1070 215	2 943 925 228	2 943 925 228	1 1154 1005 152		
0 K 8	0	0 7292 7052 126	6 1613 1608 149	1 493 516 214	6 1427 1425 141	1 1227 1193 345	3 1002 991 182	2 703 723 162	2 842 819 337		
1 2524	2465 167	1	1 1021 998 29	4 1603 1634 213	7 K 7	3 1004 990 63	3 2202 2291 227	4 2507 2544 180	3 575 527 117		
2 408	408 103	2	2 2017 2009 47	6 680 667 66	0 2052 2003 54	9 K 4	4 517 470 318	5 1126 1078 17	1 1154 1005 152		
3 378	363 245	3	2 5971 586 204	1 796 188 219	1 888 818 215	1 888 818 215	1 933 713 11	1 602 609 295	1 1154 1005 152		
4 1506	1517 87	4	4 1030 996 205	3 286 328 219	0 315 315 219	1 4324 1536 180	2 471 458 321	2 392 402 117	0 504 29 3114 0		
5 751	779 334	5	5 605 265 265	4 766 786 216	1 039 1069 271	3 3473 3389 211	3 927 966 251	3 407 410 104	1 92 189 98 180		
0 K 10	0	6 558 541 197	5 1174 1191 197	2 214 2168 236	4 2123 2094 220	3 614 644 211	4 713 670 200	4 870 895 350	2 189 98 180		
0 2282	2229 99	6	6 805 780 25	4 778 776 57	5 785 784 114	6 129 129 254	5 270 262 237	5 210 284 357	3 520 598 0	4 1545 1634 180	
1 723	746	7	2 K 3	5 945 946 180	3 186 313 118	7 589 602 57	1 212 212 229	1 237 239 224	1 1017 1013 334	1 14 K 2	
2 416	404 299	8	1 051 1584 325	1 855 871 146	0 1122 1100 180	1 0316 1036 208	2 305 305 226	2 305 307 226	0 1441 1411 201	3 442 397 152	
1 024	1 018 248	9	0 6532 6532 228	1 844 844 228	1 299 319 359	1 K 4	1 602 609 295	1 1120 1089 333	14 K 1		
1 363	357 192	10	3 1410 4108 55	3 184 184 337	1 299 319 359	2 202 2006 268	1 992 1015 113	1 981 987 150	0 3464 3412 104		
2 5995	6300 0	11	4 669 561 155	5 1690 1498 96	1 662 657 0	1 4320 4274 41	1 1147 1157 151	1 1226 1228 329	0 312 321 327		
3 288	275	12	5 894 896 80	9 935 977 301	2 289 307 180	3 3473 3389 211	2 1755 1805 200	2 197 207 180	2 272 272 110		
5 153	1533 145	13	6 1103 1134 162	5 1630 1626 184	3 3730 3309 0	4 2984 2926 136	3 606 606 299	3 537 523 303	3 1633 1677 5		
5 1253	1237 180	14	6 1103 1134 162	5 1630 1626 184	4 2668 4268 180	5 2768 2768 200	4 548 548 200	4 1027 1001 104	4 1027 1001 104		
6 1101	1148 190	15	6 1103 1134 219	5 1630 1626 184	5 2768 2768 200	6 2130 2130 211	5 791 793 235	11 K 7	3 824 832 15		
7 223	229 198	16	5 793 805 238	3 302 300 211	5 276 276 211	6 1452 1479 213	9 K 4	1 271 271 211	15 K 0		
1 K 2	0	0 1315 1313 75	3 K 9	5 K 4	0 2260 2262 326	8 K 1	0 1033 1049 274	0 878 889 83	2 141 241 263		
1 3336	3307 292	1	1 3811 3216 219	2 299 319 359	1 274 305 324	2 212 212 180	1 992 1015 113	1 1212 1223 173	3 209 302 180		
2 3470	3429 125	2	2 1329 1323 224	0 6033 6000 0	1 2202 2186 119	2 213 213 180	0 1135 1135 0	0 241 461 461			
3 2645	2637 227	3	3 864 881 107	2 503 539 262	1 270 1736 176	0 246 246 124	0 1135 1135 0	0 241 461 461			
4 713	712 177	4	3 227 322 215	3 468 468 217	4 1698 1698 214	0 247 247 124	0 1135 1135 0	0 241 461 461			
5 1537	1527 227	5	3 694 725 153	3 721 725 153	4 1730 1730 268	0 248 248 124	0 1135 1135 0	0 241 461 461			
5 1537	1527 227	6	3 694 725 153	3 721 725 153	4 1699 1699 276	5 1102 1140 110	4 951 963 105	2 4320 4201 180	1 92 189 98 180		
6 1306	1312 19	7	6 814 888 201	4 1630 1630 160	5 205 205 206	6 610 660 173	5 791 793 235	4 205 205 206	2 191 141 126		
7 1122	1094 45	8	5 232 232 200	5 292 292 200	5 1102 1104 110	6 1238 1238 262	3 2423 2324 278	5 1198 1177 18	2 397 411 233		
1 K 4	0	0 125 152 63	3 3350 3338 211	6 1448 1401 10	6 1251 1251 200	4 2351 2351 200	3 570 531 49	0 344 354 280	16 K 1		
1 295	288 267	1	6 966 947 250	5 K 5	6 404 404 117	6 466 486 0	0 297 309 261	1 1517 1514 351	0 3137 1328 119		
2 582	2198 268	2	1 281 281 177	5 K 4	1 474 502 167	1 104 114 28	1 212 212 180	1 1517 1514 351	0 3137 1328 119		
2 4584	4508 321	3	3 1264 1281 177	5 K 4	1 474 502 167	1 104 114 28	1 212 212 180	1 1517 1514 351	0 3137 1328 119		
3 554	552 35	4	1 908 1878 79								

The method used in this case, however, is somewhat unconventional. The phases of three reflections were assigned to specify the origin in space group *Pca2<sub>1</sub>* (Hauptman & Karle, 1956). These reflections were chosen on the basis of their large *E* values and the large number of relationships which they formed with other reflections with large *E* values. The reflections chosen were 14,1,3, 7,5,5 and 10,2,1 and their assigned phases were  $\pi/4$ ,  $\pi/2$ , and  $-\pi/4$ , respectively. The application of the phase determining formula

$$\varphi_h \approx \langle \varphi_k + \varphi_{h-k} \rangle_{k_r}$$

to the reflection 14,0,0 gives a strong indication of its sign. The right-hand side contains nine terms of the type  $\varphi(7kl) + \varphi(7\bar{k}\bar{l})$ ; eight of these terms indicate a phase of 0 and one a phase of  $\pi$ . The phase of the 14,0,0 reflection was therefore assumed to be 0.

At this time a program for the iterative application of the tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_h = \frac{\sum_k |E_k E_{h-k}| \sin(\varphi_k + \varphi_{h-k})}{\sum_k |E_k E_{h-k}| \cos(\varphi_k + \varphi_{h-k})},$$

was being written and tested. While testing the program with the three origin-determining reflections and the 14,0,0 reflection, it was evident that just these

four reflections generated very many relationships with other reflections. By introducing the phases determined in this way into the list of known phases, it was possible by cyclic application of the tangent formula to determine eventually the phases for 274 reflections with *E* values greater than 1·0.

The reflections whose phases had been determined in the method described above were used to calculate an *E* map, the normalized structure factors, *E<sub>h</sub>*, being used as Fourier coefficients. Twelve of the carbon atoms and both of the oxygen atoms were easily located in this map. The alternate calculation of structure factors and electron density maps led quickly to the complete elucidation of the structure.

Two phenomena observed during this structure determination bear special notice. First, the application of direct methods led to the correct structure in spite of the rather poor quality of the data; second, the distribution of the *E* values (Table 1) gave no indication of the pseudo-centrosymmetric nature of the molecule.

### Refinement of the structure

All calculations below were carried out on an IBM 7094 computer with subprograms operating under the

Table 3. Heavy-atom parameters and their standard deviations

The values have been multiplied by 10<sup>4</sup>. The temperature factor is in the form

$$T = \exp \{ -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \}.$$

	$\alpha$	$\beta$	$\gamma$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
C(1)	-1969(2)	7107(4)	7847(4)	36(2)	104(7)	65(4)	12(6)	8(-)	0(9)
C(2)	-2738(2)	7219(4)	7269(5)	32(2)	126(7)	84(4)	28(5)	18(5)	10(10)
C(3)	-2902(2)	6245(5)	6231(4)	28(2)	166(8)	92(5)	28(6)	-14(5)	14(11)
C(4)	-2338(2)	5188(4)	5178(4)	33(2)	130(6)	71(4)	28(6)	-15(5)	-16(9)
C(5)	-1589(2)	5063(4)	6278(4)	27(2)	100(6)	53(4)	17(5)	-14(4)	17(9)
C(6)	-851(2)	3989(5)	6079(4)	30(2)	135(7)	55(4)	24(6)	5(4)	1(9)
C(7)	-856(2)	2648(4)	7109(4)	22(1)	81(6)	64(4)	-1(5)	-4(4)	-11(9)
C(8)	-62(2)	1671(4)	7271(4)	23(1)	93(6)	58(4)	-6(5)	10(4)	5(9)
C(9)	-160(2)	-81(4)	7855(4)	27(2)	97(6)	60(4)	-2(-)	13(4)	-13(9)
C(10)	676(2)	-662(4)	8234(4)	25(1)	84(6)	57(4)	-11(5)	8(4)	25(9)
C(11)	1229(2)	-1752(4)	7722(4)	32(2)	105(7)	80(4)	14(-)	12(-)	-5(10)
C(12)	1979(2)	-1883(5)	8287(5)	29(2)	134(7)	95(5)	22(6)	11(5)	10(10)
C(13)	2176(2)	-918(5)	9326(5)	25(2)	138(8)	107(5)	1(5)	-8(5)	75(11)
C(14)	1623(2)	211(4)	9832(4)	35(2)	112(7)	72(4)	-15(6)	-13(5)	36(10)
C(15)	868(2)	314(4)	9288(4)	28(2)	96(6)	64(4)	-1(5)	7(-)	40(9)
C(16)	142(2)	1410(5)	9491(4)	30(2)	121(7)	52(4)	-1(5)	3(4)	1(8)
C(17)	146(2)	2730(4)	8456(4)	24(1)	96(6)	60(4)	-15(5)	-4(4)	10(9)
C(18)	-652(2)	3714(4)	8292(4)	24(1)	90(7)	58(5)	11(5)	3(4)	5(8)
C(19)	-373(2)	5472(4)	7730(4)	30(2)	96(7)	73(4)	-4(5)	-15(4)	-2(9)
C(20)	-1410(2)	6026(4)	7356(4)	27(1)	81(6)	67(4)	-1(5)	4(4)	17(9)
C(21)	-212(1)	5104(3)	6513	27(1)	125(4)	80(3)	2(4)	15(3)	38(6)
C(22)	-579(1)	336(3)	9082(3)	28(1)	114(4)	70(3)	-1(4)	10(3)	24(6)

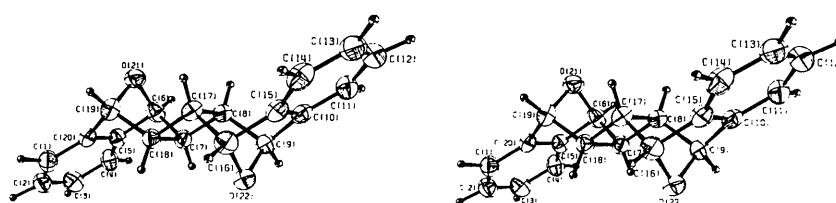


Fig. 4. Stereoscopic view of the photodimer.

Table 4. Hydrogen atom parameters and their standard deviations

The values for the coordinates have been multiplied by  $10^3$ . The values for the isotropic temperature factors have been multiplied by 10.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(23)	-181 (1)	790 (4)	859 (3)	37 (8)
H(24)	-314 (2)	813 (4)	759 (4)	50 (8)
H(25)	-340 (2)	640 (4)	585 (3)	39 (8)
H(26)	-246 (2)	444 (3)	505 (4)	45 (8)
H(27)	-74 (1)	359 (3)	525 (3)	16 (6)
H(28)	-133 (1)	198 (3)	709 (2)	16 (6)
H(29)	31 (2)	175 (4)	658 (3)	30 (7)
H(30)	-57 (2)	-89 (4)	740 (3)	42 (8)
H(31)	113 (2)	-242 (4)	699 (3)	38 (8)
H(32)	235 (2)	-275 (4)	798 (3)	52 (9)
H(33)	271 (2)	-99 (4)	969 (3)	35 (8)
H(34)	178 (2)	88 (4)	1054 (3)	45 (9)
H(35)	6 (2)	182 (4)	1031 (3)	34 (8)
H(36)	64 (2)	339 (4)	846 (3)	26 (7)
H(37)	-102 (2)	367 (4)	903 (3)	29 (7)
H(38)	-24 (1)	627 (4)	818 (3)	24 (7)

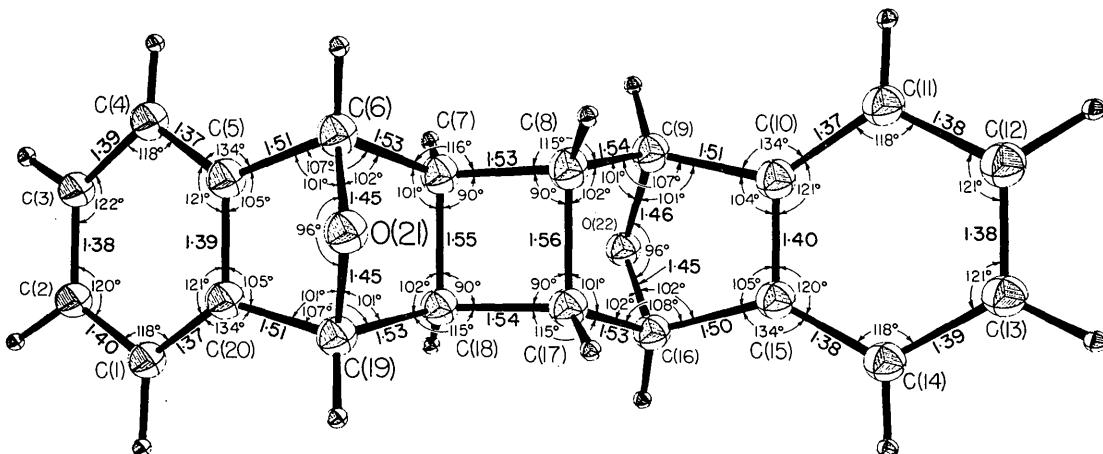
CRYRM system (Duchamp, 1964). The atomic scattering factors for C and O were taken from International Tables for X-ray Crystallography (1962). The atomic

scattering factor for H is that given by Stewart, Davidson & Simpson (1965). The least-squares routine minimizes the quantity  $\sum w(F_o^2 - F_c^2)^2$ . The weights,  $w$ , used throughout the refinement of the structure, were set equal to  $1/\sigma^2(F_o^2)$  which were derived from counting statistics. The variance of the intensity was calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2,$$

where  $S$  is the total counts collected during the scan;  $B_1$  and  $B_2$  are the numbers of counts collected for each background;  $\alpha$  is the scan time to total background time ratio;  $d$  is an empirical constant of 0.02.

Approximate coordinates for all twenty-two heavier atoms were obtained by the Fourier technique described above. In space group  $Pca2_1$  the location of the origin in the  $z$  direction is arbitrary. Accordingly, the  $z$  coordinate of atom O(21) was held constant throughout the refinement of the structure. The proposed structure was put through several cycles of least-squares refinement, but the  $R$  index could not be reduced below 18%. A careful survey of the data indicated that this was probably the best fit that could be obtained with the first set of data that had



been collected. The second set of more carefully collected data was then obtained and was used in final and complete refinement of the structure.

After several cycles of refinement with anisotropic temperature factors, hydrogen atoms were introduced at their expected positions. Both the coordinates and isotropic temperature factors for the hydrogen atoms were included in the refinement. In the later stages of refinement a secondary extinction factor was also included; the expression used is  $F_{\text{corrected}}^2 = (F_{\text{cal}})^2 / (1 + g\beta(F_{\text{cal}})^2)$  (Larson, 1967). During the final cycles of refinement the atomic coordinates for all atoms were contained in one matrix and the temperature factors, scale factor, and secondary extinction factor were included in a second matrix. The final value obtained for the secondary extinction factor  $g$  is  $17.6 (\pm 0.7) \times 10^{-6}$ . The final  $R$  index is 0.027. The observed and calculated structure factors,  $F_o$  and  $F_c$ , and the phase angles,  $\phi$ , are listed in Table 2.

The final coordinates and anisotropic temperature factors for the heavy atoms and their standard deviations, calculated from the least-squares residuals, are given in Table 3. The positional parameters and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table 4. The shifts calculated for the parameters in the final cycle of least squares were all less than one-tenth of the standard deviations.

### Description of the structure

A composite of the final electron density map viewed along the  $c$  axis is shown in Fig. 1. An analogous composite of a difference synthesis for which the contributions of the hydrogen atoms were omitted from  $F_c$  is shown in Fig. 2. No other significant features appeared in the difference map. Two stereoscopic views of the molecule are shown in Figs. 3 and 4. [Figs. 3, 4, 5 and 6 were drawn on a CALCOMP plotter controlled by an IBM 360/75 computer using the ORTEP program (Johnson, 1965).]

The bond distances and angles involving the heavy atoms are shown in Fig. 5. The standard deviations in the atomic coordinates (Tables 3 and 4) correspond to positional uncertainties of approximately 0.004 Å for the carbon atoms, 0.002 Å for the oxygen atoms and 0.03 Å for the hydrogen atoms. The standard deviations are expected to be about 0.006 Å for C-C distances, 0.005 Å for C-O distances and 0.03 Å for C-H distances. The standard deviations in the bond angles between heavy atoms are about 15' and about 2° in angles involving hydrogen atoms; the agreement among chemically equivalent bonds suggests that these standard deviations are reasonable. Distances and angles involving hydrogen atoms are listed in Table 5.

The molecule, within a close approximation, possesses the symmetry  $2/m$ . The position of the center of symmetry, obtained by averaging the positions of

Table 5. Bond distances and angles involving hydrogen atoms

$\text{H}(1)-\text{C}(1)$	1.11 Å	$\text{H}(2')-\text{C}(1)-\text{C}(2)$	1.35*	$\text{H}(1)-\text{C}(12)$	1.36 Å	$\text{H}(32)-\text{C}(14)-\text{C}(15)$	1.37*
$\text{H}(2)-\text{C}(1)$	1.11	$\text{H}(2)-\text{C}(1)-\text{C}(12)$	1.39	$\text{H}(2)-\text{C}(12)$	1.36	$\text{H}(32)-\text{C}(12)-\text{C}(13)$	1.37
$\text{H}(1)-\text{C}(2)$	1.11	$\text{H}(2)-\text{C}(5)-\text{C}(3)$	1.18	$\text{H}(32)-\text{C}(13)$	1.36	$\text{H}(33)-\text{C}(12)-\text{C}(12)$	1.37
$\text{H}(2)-\text{C}(2)$	1.11	$\text{H}(2)-\text{C}(2)-\text{C}(3)$	1.19	$\text{H}(32)-\text{C}(12)-\text{C}(12)$	1.36	$\text{H}(34)-\text{C}(12)-\text{C}(13)$	1.37
$\text{H}(1)-\text{C}(6)$	0.99	$\text{H}(2)-\text{C}(6)-\text{C}(5)$	1.11	$\text{H}(32)-\text{C}(20)$	1.36	$\text{H}(35)-\text{C}(16)-\text{C}(15)$	1.37
$\text{H}(2)-\text{C}(6)$	0.99	$\text{H}(2)-\text{C}(6)-\text{C}(7)$	1.11	$\text{H}(32)-\text{C}(16)$	1.36	$\text{H}(35)-\text{C}(16)-\text{C}(17)$	1.37
$\text{H}(1)-\text{C}(7)$	1.11	$\text{H}(2)-\text{C}(7)-\text{C}(6)$	1.19	$\text{H}(36)-\text{C}(1)$	1.36	$\text{H}(35)-\text{C}(16)-\text{C}(20)$	1.37
$\text{H}(2)-\text{C}(7)$	1.11	$\text{H}(2)-\text{C}(7)-\text{C}(18)$	1.19	$\text{H}(36)-\text{C}(1)$	1.36	$\text{H}(36)-\text{C}(17)-\text{C}(16)$	1.37
$\text{H}(1)-\text{C}(12)$	1.11	$\text{H}(2)-\text{C}(12)-\text{C}(11)$	1.16	$\text{H}(37)-\text{C}(12)$	1.36	$\text{H}(37)-\text{C}(12)-\text{C}(13)$	1.37
$\text{H}(2)-\text{C}(12)$	1.11	$\text{H}(2)-\text{C}(12)-\text{C}(13)$	1.16	$\text{H}(37)-\text{C}(12)-\text{C}(13)$	1.36	$\text{H}(37)-\text{C}(12)-\text{C}(14)$	1.37
$\text{H}(1)-\text{C}(13)$	1.11	$\text{H}(2)-\text{C}(9)-\text{C}(8)$	1.16	$\text{H}(37)-\text{C}(12)$	1.36	$\text{H}(38)-\text{C}(20)-\text{C}(19)$	1.37
$\text{H}(2)-\text{C}(13)$	1.11	$\text{H}(2)-\text{C}(9)-\text{C}(12)$	1.17	$\text{H}(37)-\text{C}(12)$	1.36	$\text{H}(38)-\text{C}(20)-\text{C}(18)$	1.37
$\text{H}(1)-\text{C}(14)$	1.11	$\text{H}(2)-\text{C}(9)-\text{C}(13)$	1.17	$\text{H}(37)-\text{C}(12)$	1.36	$\text{H}(38)-\text{C}(20)-\text{C}(17)$	1.37

the heavy atoms, is  $x = -0.0362$ ,  $y = 0.2687$ , and  $z = 0.7784$ . The root-mean-square deviation from this center of the midpoints of lines joining centrosymmetrically related atoms is 0.016 Å; the average deviation is 0.015 Å. The equation for the mirror plane, obtained by a least-squares fit to the midpoints of lines joining atoms symmetrically related by the mirror plane, is

$$0.2211X + 0.5469Y + 0.8075Z - 7.6916 = 0,$$

where  $X$ ,  $Y$ , and  $Z$  are the coordinates in Ångstrom units. The root-mean-square deviation of the midpoints from this plane is 0.013 Å and the average deviation is 0.011 Å.

Table 6. Least-squares planes of the benzene and cyclobutane rings and atomic deviations from the plane

Coefficients are directions cosines relative to the crystallographic axes.

$$\begin{aligned} \text{Plane through atoms C(7), C(8), C(17) and C(18)} \\ -0.4679X - 0.6655Y - 0.5815Z = 3.632 \end{aligned}$$

	Deviation
C(7)	-0.002 Å
C(8)	0.002
C(17)	-0.002
C(18)	0.002

$$\begin{aligned} \text{Plane through atoms C(1), C(2), C(3), C(4), C(5), and C(20)} \\ -0.3347X - 0.7296Y + 0.5964Z = 1.901 \end{aligned}$$

	Deviation
C(1)	0.004
C(2)	-0.006
C(3)	0.002
C(4)	0.005
C(5)	-0.007
C(20)	0.002

$$\begin{aligned} \text{Plane through atoms C(10), C(11), C(12), C(13), C(14), and} \\ \text{C(15)} \end{aligned}$$

$$-0.3404X - 0.7207Y + 0.6040Z = 5.259$$

	Deviation
C(10)	0.003
C(11)	-0.009
C(12)	0.006
C(13)	0.004
C(14)	-0.011
C(15)	0.007

This structure is an example of the unusual situation of a nearly centrosymmetric molecule which crystallizes in a non-centrosymmetric space group. Another molecule which has a center of symmetry, but crystallizes in a non-centrosymmetric space group, is  $\beta$ -1:2-5:6-dibenzanthracene (Robertson & White, 1956). Biphenylene (Waser & Lu, 1944; Fawcett & Trotter, 1966) crystallizes in space group  $P2_1/a$  with six molecules per unit cell. Two of the molecular centers fall on centers of symmetry, but the other four molecules are in general positions despite their apparent center of symmetry.

The equations of the least-squares planes through the benzene and cyclobutane rings and the deviations of the individual atoms from their respective planes are given in Table 6. The second benzene ring shows a slight degree of non-planarity.

A stereoscopic view down the  $b$  axis showing the packing of the molecules is given in Fig. 6. There are no short contacts between molecules. The shortest heavy-atom-to-hydrogen intermolecular distance is 2.73 Å between H(24) of the base molecule and C(15) of the molecule in equivalent position  $x-\frac{1}{2}, -y+1, z$ . The shortest hydrogen-to-hydrogen intermolecular

distance is 2.45 Å between H(32) of the base molecule and H(28) of the molecule in the equivalent position  $x+\frac{1}{2}, -y, z$ .

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## The Crystal Structure of Bis(L-serinato)zinc\*

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The crystal structure of bis(L-serinato)zinc,  $ZnC_6H_{12}O_6N_2$ , has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group  $P2_1$ , with  $a=9.542$ ,  $b=8.818$ ,  $c=5.666$  Å and  $\beta=96.7^\circ$ . The final  $R$  value for 950 reflections is 0.036; the standard deviations are about 0.006 Å for the C, N and O atom positions. The compound is not isostructural with either the Ni or Cu complex of L-serine. The zinc coordination is intermediate between a square pyramid and a trigonal bipyramidal with the first one being slightly favored. The two serine molecules have different conformations for the hydroxyl group; one serine molecule having the unusual *anti-gauche* conformation.

### Introduction

The structure of the Zn chelate of L-serine was determined as one of a series of L-serine chelates (van der Helm & Franks, 1969; Van der Helm & Hossain, 1969) to obtain information about the relative influence of transition metal ions on the configuration of an amino acid. No two of the three complexes of serine thus far

determined are isomorphous. Zinc was chosen as one of the transition metal ions because its role in biological reactions has long been known.

### Experimental

The compound bis(L-serinato)zinc was prepared by reacting two moles of L-serine with one mole each of zinc sulfate and barium hydroxide in a minimal amount of water. The barium sulfate produced was removed by centrifugation. The solution produced, which tended to become supersaturated, was then diluted about fifty times with absolute ethanol in order to ob-

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