

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 \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

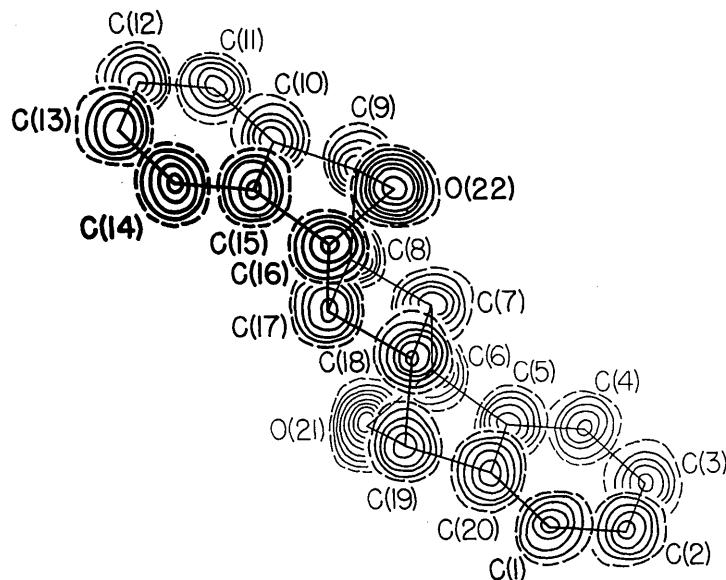


Fig. 1. A composite of sections of a three-dimensional electron density map through each of the heavy atoms, viewed down the c axis. The dashed contour is at $2 \text{ e.}\text{\AA}^{-3}$. The successive contours are at $3, 4, 5, \dots \text{ e.}\text{\AA}^{-3}$.

absence of $h0l$ reflections with h odd indicate that the space group is either $Pca2_1$ 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 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 mm and had a trape-

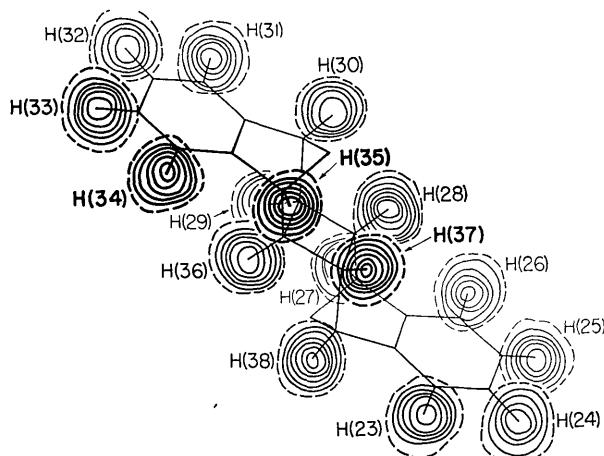


Fig. 2. A composite of sections of a three-dimensional difference electron density map through each of the hydrogen atoms, viewed down the c axis. The dashed contour is at $0.1 \text{ e.}\AA^{-3}$. The successive contours are at $0.2, 0.3, 0.4, \dots \text{e.}\AA^{-3}$.

Table 1. Distribution of normalized structure factors

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

zoidal face with an altitude of 0.3 mm and bases of 0.5 and 0.2 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 \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

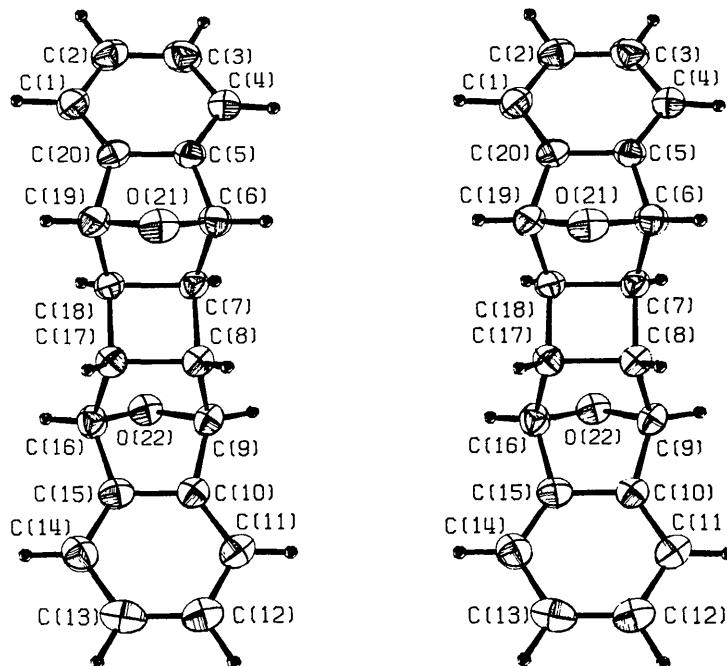


Fig. 3. Stereoscopic view of the photodimer.

noncentrosymmetric; therefore, the space group should be Pca_2 .

The normalized structure factors $|E|$ (Karle & Karle, 1966) were then calculated using an overall temperature parameter of 1.50 \AA^2 . 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_2 .

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 , $100F_0$, $100F_c$, and $\varphi_c(\circ)$, the phase angle. Reflections marked with an asterisk were assigned zero weight in the final least-squares cycles.

0 0 K 0	5 933 913 153	6 1762 1771 0	0 4 9 K 4	1 541 520 230	3 1634 1609 248	8 K 8	3 1599 1596 203	3 679 728 334
1 89 127	0 1 K 8	6 1197 1222 0	0 1 531 1517 215	2 717 692 106	5 1276 1267 333	0 857 860 320	4 1303 1286 242	0 628 626 94
2 5619 5960	0 1 1137 1145 192	7 664 743 180	2 658 662 122	3 935 1015 275	6 1411 1439 252	1 561 652 154	5 1397 1497 143	1 616 617 261
3 36 343	2 162 163	2 246 247 72	2 248 249 91	4 1198 1180 125	7 650 662 330	3 393 398 3	10 K 6	0 628 626 94
4 374 386	5 156 156	3 1 K 1	4 2448 2469 207	5 169 169 177	4 417 389 292	0 857 860 320	1 616 617 261	1 616 617 261
5 704	0 388 339 177	1 7275 7235 35	5 729 523 37	5 K 9	5 1959 1966 260	1 2696 2629 180	10 K 7	0 628 626 94
6 1916 1990	0 5 213 179 250	2 2467 2527 20	6 352 339 323	1 1397 1413 340	1 1965 1871 286	0 569 493 121	2 142 242 323	1 585 554 180
7 552 515	0	2 1404 1392 288	7 529 523 37	2 116 129 244	2 1316 1317 180	1 2050 2065 3	3 1247 1232 249	2 2678 2657 180
1 K 9	5 1466 210	4 K 5	4 2448 2469 207	3 303 303 88	4 417 389 292	4 1081 1106 42	3 582 612 180	4 1179 1268 180
0 K 2	1 2125 2147 272	5 1463 1466 210	6 K 0	6 1321 1328 135	5 1959 1966 260	1 2696 2629 180	10 K 7	0 628 626 94
0 9254 8966	201	2 571 581 53	6 369 369 283	1 1810 1756 188	2 1218 1224 0	0 722 786 180	13 K 1	0 628 626 94
1 11191 10826 288	3 424 442 175	7 495 495 283	1 2555 2655 136	0 269 322 0	2 1316 1317 180	1 2050 2065 3	1 2442 2351 5	1 2442 2351 5
2 1111 1111	4 946 939 81	2 112 112 182	2 112 112 182	1 112 112 182	2 1316 1317 180	1 2050 2065 3	2 1316 1317 180	1 2442 2351 5
3 5881 5709 155	2 112 112 182	3 K 3	3 225 235 189	2 327 343 180	7 K 4	1 847 861 211	1 847 861 211	1 847 861 211
4 1379 1365 155	1 K 10	1 5287 5264 147	4 2211 2239 129	1 532 512 214	5 507 565 203	2 142 1419 164	3 1247 1232 249	3 1247 1232 249
5 1849 1809 255	1 326 352 51	2 3034 3071 205	5 2856 2845 291	4 1002 1029 0	4 1304 1328 135	3 1247 1232 249	4 1081 1106 42	4 1081 1106 42
6 679 679 59	2 493 493 173	3 3286 3286 206	6 883 859 324	5 169 194 0	5 1397 1413 340	3 1247 1232 249	4 1179 1268 180	4 1179 1268 180
7 1616 1603 229	2 K 0	5 158 158 182	6 2630 2705 0	6 1042 1052 107	9 K 0	0 840 855 205	0 840 855 205	0 840 855 205
8 K 0	5 158 158 182	7 1004 1004 107	5 840 855 205	6 1321 1328 135	0 893 893 214	13 K 2	0 893 893 214	0 893 893 214
0 K 4	0 5947 6260 0	6 826 777 275	4 K 6	6 1321 1328 135	0 893 893 214	1 2277 2270 111	1 2277 2270 111	1 2277 2270 111
0 220 241 28	1 3816 4031 0	7 839 789 303	1 1810 1756 188	2 302 383 200	2 317 248 127	2 317 248 127	2 317 248 127	2 317 248 127
1 610 610 438	3 424 442 175	2 424 442 175	1 1810 1756 188	3 1215 1210 254	3 111 0	3 111 0	3 111 0	3 111 0
2 4111 4088 203	3 457 466 180	3 K 3	3 284 285 189	4 1127 1082 264	4 1024 1024 357	1 893 909 322	1 893 909 322	1 893 909 322
3 450 450 84	4 983 1019 0	1 3205 3216 241	4 516 499 107	4 1304 1328 135	1 893 909 322	2 637 661 105	2 637 661 105	2 637 661 105
4 706 706 250	5 1630 1663 0	2 2794 2750 36	5 511 566 353	3 1204 1204 357	3 110 0	3 110 0	3 110 0	3 110 0
5 1262 1251 27	6 1235 1235 19	1 1904 1928 65	6 580 587 126	4 1304 1328 135	3 110 0	3 110 0	3 110 0	3 110 0
6 359 359 18	7 985 951 0	1 1924 1928 65	7 580 587 126	5 2546 2558 115	3 1204 1204 357	3 988 1016 22	3 988 1016 22	3 988 1016 22
7 2532 2500 341	7 985 951 0	1 1941 1941 334	8 K 7	3 1021 1021 357	3 1204 1204 357	4 550 550 337	4 550 550 337	4 550 550 337
8 K 0	6 936 882 190	9 K 7	7 1004 1004 107	6 1774 1782 186	3 1021 1021 357	1 111 0	1 111 0	1 111 0
0 K 4	0 7929 7052 126	7 1004 1004 107	7 606 505 221	3 1021 1021 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
0 4494 4490 248	0 6286 6157 228	7 1004 1004 107	8 K 0	3 1021 1021 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
1 1343 1345 172	1 6212 6211 131	3 K 3	3 284 285 189	3 1021 1021 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
2 4127 4060 252	3 1789 1814 219	1 918 899 30	4 516 499 107	4 1304 1328 135	3 1021 1021 357	1 111 0	1 111 0	1 111 0
3 390 409 103	4 1765 1711 124	2 2342 2346 15	5 511 566 353	5 1204 1204 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
4 422 422 27	5 404 372 317	3 5758 5693 140	6 K 0	6 1204 1204 357	6 1204 1204 357	1 111 0	1 111 0	1 111 0
5 422 422 27	5 604 615 252	4 2211 2239 129	7 1004 1004 107	7 1677 1677 230	7 1677 1677 230	1 111 0	1 111 0	1 111 0
6 1312 1299 269	7 423 414 192	5 604 615 252	8 K 0	8 K 0	8 K 0	1 111 0	1 111 0	1 111 0
7 2532 2500 341	7 423 414 192	6 1235 1235 19	9 K 7	9 K 7	9 K 7	1 111 0	1 111 0	1 111 0
0 K 8	2 K 2	6 936 882 190	10 K 7	10 K 7	10 K 7	1 111 0	1 111 0	1 111 0
1 2592 2465 167	1 6212 6211 131	7 1004 1004 107	11 K 3	11 K 3	11 K 3	1 111 0	1 111 0	1 111 0
2 2604 2634 88	2 5971 5886 204	1 796 783 17	12 K 6	12 K 6	12 K 6	1 111 0	1 111 0	1 111 0
3 378 362 214	3 4785 4734 286	2 1089 1110 335	13 K 9	13 K 9	13 K 9	1 111 0	1 111 0	1 111 0
4 1506 1517 87	4 1030 996 205	3 3286 3286 205	14 K 9	14 K 9	14 K 9	1 111 0	1 111 0	1 111 0
5 751 777 334	5 605 624 249	4 2211 2239 129	15 K 9	15 K 9	15 K 9	1 111 0	1 111 0	1 111 0
6 1122 1109 180	6 1134 1133 162	5 1204 1204 357	16 K 0	16 K 0	16 K 0	1 111 0	1 111 0	1 111 0
7 1253 1237 180	7 1083 1080 160	6 1235 1235 19	17 K 6	17 K 6	17 K 6	1 111 0	1 111 0	1 111 0
8 K 6	8 K 6	7 1004 1004 107	18 K 6	18 K 6	18 K 6	1 111 0	1 111 0	1 111 0
0 2282 2269 99	1 K 23	8 K 6	19 K 6	19 K 6	19 K 6	1 111 0	1 111 0	1 111 0
1 723 743 4	2 K 3	10 K 6	20 K 6	20 K 6	20 K 6	1 111 0	1 111 0	1 111 0
2 418 404 299	1 K 23	21 K 6	22 K 6	22 K 6	22 K 6	1 111 0	1 111 0	1 111 0
1 K 23	22 K 6	23 K 6	24 K 6	24 K 6	24 K 6	1 111 0	1 111 0	1 111 0
2 418 404 299	1 K 23	23 K 6	24 K 6	24 K 6	24 K 6	1 111 0	1 111 0	1 111 0
3 2751 2776 159	2 2337 2232 211	3 K 3	2 1797 1835 171	3 1204 1204 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
4 2172 2103 44	4 1165 1178 19	1 721 697 300	3 415 406 300	4 1304 1328 135	3 1021 1021 357	1 111 0	1 111 0	1 111 0
5 1563 1533 145	6 2065 2060 294	2 1177 1145 60	4 1309 1306 226	5 1204 1204 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
6 685 664 45	7 2308 2272 197	3 365 400 270	5 1197 1210 170	6 1204 1204 357	3 1021 1021 357	1 111 0	1 111 0	1 111 0
7 1491 1419 133	7 2532 2500 341	6 1235 1235 19	7 302 262 311	6 K 6	6 1204 1204 357	1 111 0	1 111 0	1 111 0
8 K 6	8 K 6	9 K 6	10 K 6	10 K 6	10 K 6	1 111 0	1 111 0	1 111 0
1 K 2	1 3315 3397 292	10 K 6	11 K 6	11 K 6	11 K 6	1 111 0	1 111 0	1 111 0
2 4494 4490 248	2 2331 2337 234	11 K 6	12 K 6	12 K 6	12 K 6	1 111 0	1 111 0	1 111 0
3 4657 4578 102	3 2337 2337 234	12 K 6	13 K 6	13 K 6	13 K 6	1 111 0	1 111 0	1 111 0
4 768 753 225	4 444 422 312	13 K 6	14 K 6	14 K 6	14 K 6	1 111 0	1 111 0	1 111 0
5 1317 1277 14	5 2463 2475 183	14 K 6	15 K 6	15 K 6	15 K 6	1 111 0	1 111 0	1 111 0
6 1306 1277 14	6 2117 2117 145	15 K 6	16 K 6	16 K 6	16 K 6	1 111 0	1 111 0	1 111 0
7 1122 1109 186	7 1086 1081 311	16 K 6	17 K 6	17 K 6	17 K 6	1 111 0	1 111 0	1 111 0
8 K 6	8 K 6	17 K 6	18 K 6	18 K 6	18 K 6	1 111 0	1 111 0	1 111 0
1 K 4	1 3295 3223 306	18 K 6	19 K 6	19 K 6	19 K 6	1 111 0	1 111 0	1 111 0
2 4200 4190 256	2 2916 2895 91	19 K 6	20 K 6	20 K 6	20 K 6	1 111 0	1 111 0	1 111 0
3 4565 4559 102	3 2337 2337 234	20 K 6	21 K 6	21 K 6	21 K 6	1 111 0	1 111 0	1 111 0
4 554 552 335	4 1074 1067 189	21 K 6	22 K 6	22 K 6	22 K 6	1 111 0	1 111 0	1 111 0
5 978 972 292	5 766 719 124	22 K 6	23 K 6	23 K 6	23 K 6	1 111 0	1 111 0	1 111 0
5 1475 1508 277	1 2882 2880 237	23 K 6	24 K 6	24 K 6	24 K 6	1 111 0	1 111 0	1 111 0
6 1255 1240 298	6 1269 263 167	24 K 6	25 K 6	25 K 6	25 K 6	1 111 0	1 111 0	1 111 0
7 1927 1891 305	7 488 405 117	25 K 6	26 K 6	26 K 6	26 K 6	1 111 0	1 111 0	1 111 0
8 K 6	8 K 6	26 K 6	27 K 6	27 K 6	27 K 6	1 111 0	1 111 0	1 111 0
1 K 5	1 2000 1950 256	27 K 6	28 K 6	28 K 6	28 K 6	1 111 0	1 111 0	1 111 0
2 4200 4190 256	2 2916 2895 91	28 K 6	29 K 6	29 K 6	29 K 6	1 111 0	1 111 0	1 111 0
3 4565 4559 102	3 2337 2337 234	29 K 6	30 K 6	30 K 6	30 K 6	1 111 0	1 111 0	1 111 0
4 554 552 335	4 1074 1067 189	30 K 6	31 K 6	31 K 6	31 K 6	1 111 0	1 111 0	1 111 0
5 337 297 58	5 765 809 126	31 K 6	32 K 6	32 K 6	32 K 6	1 111 0	1 111 0	1 111 0
6 102 134 2								

The method used in this case, however, is somewhat unconventional. The phases of three reflections were assigned to specify the origin in space group *Pca*2₁ (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

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

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 π . 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_h , 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 10⁴. The temperature factor is in the form

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

	\mathbf{z}	\mathbf{z}	\mathbf{z}	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(4)	0(9)
C(2)	-2738(2)	7019(4)	7669(5)	32(2)	126(7)	8(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)	5148(4)	5118(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)	-866(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)	-16(2)	-81(4)	7855(4)	27(2)	97(6)	60(4)	-2(5)	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(5)	12(4)	-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)	28(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(4)	40(9)
C(16)	142(2)	1410(5)	9491(4)	30(2)	121(7)	52(4)	-1(5)	3(4)	4(8)
C(17)	146(2)	2750(4)	8456(4)	24(1)	96(6)	60(4)	-15(5)	-4(4)	10(9)
C(18)	-652(2)	374(4)	8292(4)	24(1)	90(7)	54(3)	11(5)	3(4)	5(8)
C(19)	-673(2)	5472(4)	7730(4)	30(2)	96(7)	73(4)	-4(5)	-23(4)	-2(9)
C(20)	-1410(2)	6025(4)	7336(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(5)	38(6)
C(22)	-509(1)	326(3)	9082(3)	28(1)	114(4)	70(3)	-1(4)	10(3)	24(6)

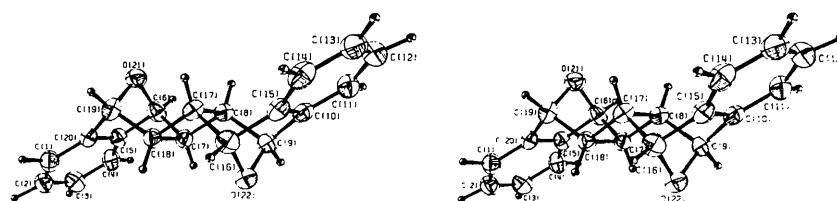


Fig. 4. Stereoscopic view of the photodimer.

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)

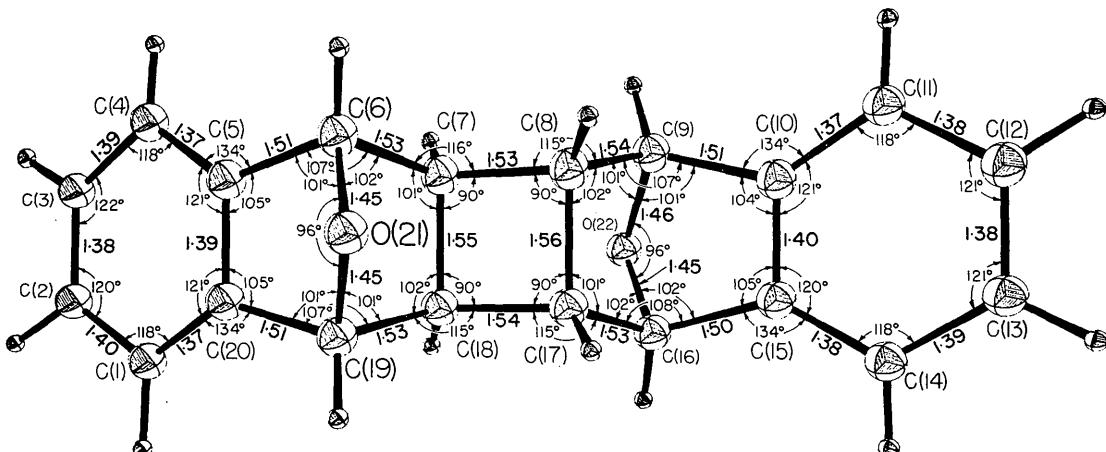
CRYRM system (Duchamp, 1964). The atomic scattering factors for C and O were taken from International Tables for X-ray Crystallography (1962). The atomic

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; α 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, ϕ , 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

H(1)-C(1),	1.1 ± 0.2	H(C _{1'})-C(1)-C(2),	1.27	H(1)-C(1),	1.16 Å	H(31)-C(11)-C(12),	117°
H(2)-C(1),	1.1	H(2)-C(1)-C(2),	119	H(2)-C(1),	0.98	H(32)-C(12)-C(11),	117°
H(1)-C(2),	1.1	H(2)-C(1)-C(2),	121	H(32)-C(12)-C(13),	121°		
H(2)-C(2),	1.1	H(2)-C(2)-C(3),	118	H(33)-C(13),	0.96	H(33)-C(13)-C(12),	122°
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(33)-C(13)-C(14),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(34)-C(14)-C(13),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(34)-C(14)-C(15),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(15)-C(14),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(15)-C(16),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(16)-C(15),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(16)-C(17),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(17)-C(16),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(35)-C(17)-C(18),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(17),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(16),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(15),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(14),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(13),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(12),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(11),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(10),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(9),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(8),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(7),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(6),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(5),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(4),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(3),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(2),	111°		
H(2)-C(2)-C(3),	1.1	H(2)-C(2)-C(3),	121	H(36)-C(18)-C(1),	111°		

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 β -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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