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The crystal and molecular structure of 1,3-diphenyl-1,3-propanedione enol*

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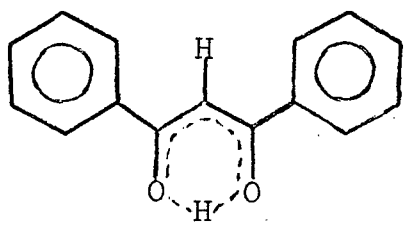
The structure of 1,3-diphenyl-1,3-propanedione enol has been redetermined. The crystals are orthorhombic, space group Pbca, with a = 10.853(1) Å, b = 24.441(1) Å, c = 8.755(1) Å at 23°C; d_c = 1.28 gm/cm^3 for Z = 8, d_o = 1.22 gm/cm^3. The structure was refined to a final R value of 0.027 on 1070 X-ray data. The results of the analysis are very close to those of the previous determination, and parameters are compared.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

The crystal structure of 1,3-diphenyl-1,3-propanedione (HDPP), I, was solved as part of a study of complexes of its anion with alkaline-earth metals (Hollander, 1972) before we learned of another determination of the structure (Williams, 1966). We report our results for comparison with the earlier work as an example of two accurate determinations of the same structure.

(I) 

The HDPP was recrystallized from aqueous ethanol. The crystals are orthorhombic, space group Pbca. The cell dimensions are a = 10.853(1) Å, b = 24.441(1) Å, and c = 8.755(1) Å at 23°C as determined by least-squares on twelve well-centered reflections in good agreement with the previous work (a = 10.857(2), b = 24.446(5), and c = 8.756(2) Å). Intensity data were collected on a crystal of dimensions 0.19 mm x 0.23 mm x 0.12 mm using monochromatized CuKα radiation and a θ-2θ scan technique on a Picker automatic diffractometer. 1724 unique data were collected, of which 1070 had $F > \sigma(F)$ and were included in least-squares.

The structure was solved by direct methods using R. E. Long's (1965) sign determination program. The structure was refined by least-squares to a final $R_1 = \Sigma|\Delta F|/\Sigma|F_o| = 0.027$, with isotropic thermal parameters for hydrogen and anisotropic parameters for the other atoms. Details are given elsewhere (Hollander, 1972).

Our results are similar but not identical to those of Williams (1966). The parameters are compared in Table 1.

We used individual thermal parameters for hydrogen atoms, which Williams did not, and reduced R_1 to 0.027 compared with Williams' $R_1 = 0.059$. Discrepancies in parameters are as great as ten times the standard deviations estimated in the present work, but the significance of these differences is obscured because Williams failed to report standard deviations. However, consideration of the distances and angles (for which Williams does give standard deviations) reveals no differences between the two structures that are much greater than the sum of the standard deviations for each. The differences in thermal parameters may also be of little statistical significance, but they are sufficient to cast some doubt on the details of the analysis of thermal motion presented by Williams.

Distances for this determination are given in Table 2.

The hydrogen atom in the hydrogen bond, H(29), is found more nearly equidistant from the two oxygen atoms than in the earlier determination, and shifts of slightly less than one standard deviation in its coordinates would make it exactly equidistant. The differences in the O(16)—C(13)—C(14)—C(15)—O(17) distances indicate a slight preference for the tautomer with H(29) on O(17) as in the earlier study.

References

Hollander, F. J. (1972). Ph.D. Thesis, University of California, Berkeley, Calif., LBL-670, Lawrence Berkeley Laboratory, Berkeley, Ca. 94720.

Long, R. E. (1965). Ph.D. Thesis, University of California, Los Angeles, Ca. 90024.

Williams, D. E. (1966). Acta Cryst. 21, 340.

Table 1. Comparison of coordinates and thermal parameters. The standard deviation of the least significant digits of the parameters of the present study are given in parentheses. Standard deviations were not reported by Williams. The form of the temperature factor ($\underline{B}$'s in units of $\AA^2$) is : $\underline{T}$ = $\exp(-0.25(\underline{B}_{11}\underline{h}^2\underline{a}^{*2} + \underline{B}_{22}\underline{k}^2\underline{b}^{*2} + \underline{B}_{33}\underline{l}^2\underline{c}^{*2} + 2\underline{B}_{12}\underline{hk}\underline{a}^*\underline{b}^* + 2\underline{B}_{13}\underline{hl}\underline{a}^*\underline{c}^* + 2\underline{B}_{23}\underline{kl}\underline{b}^*\underline{c}^*))$ for anisotropic, and $\underline{T} = \exp(-\underline{B}\ \sin^2\theta/\lambda^2)$ for isotropic thermal parameters.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	-.0568(2)	-.01892(7)	.1881(2)	3.78(8)	4.24(8)	3.78(10)	- .99(7)	.41(7)	.26(8)
	-.0578	-.01876	.1900	3.46	4.47	4.20	-1.22	.25	- .07
C(2)	-.1214(2)	-.05183(9)	.0862(2)	4.42(9)	5.80(10)	4.60(11)	-1.16(8)	- .22(9)	- .07(9)
	-.1213	-.05139	.0853	4.68	6.12	4.72	- .58	- .06	.21
C(3)	-.0756(2)	-.10221(9)	.0438(3)	5.96(12)	5.74(12)	5.32(13)	-1.72(10)	.01(10)	-1.22(10)
	-.0754	-.10199	.0437	5.33	5.47	5.62	-1.20	- .27	- .87
C(4)	.0348(2)	-.12036(9)	.0997(3)	6.16(12)	4.75(10)	5.62(13)	- .76(9)	.28(10)	- .78(10)
	.0340	-.11988	.1003	5.85	4.47	6.37	- .19	.64	- .59
C(5)	.1001(2)	-.08819(8)	.1993(3)	5.79(11)	4.31(9)	6.11(12)	- .24(9)	- .86(11)	- .72(9)
	.1000	-.08812	.2008	6.11	3.97	6.24	- .33	- .90	- .24
C(6)	.0549(2)	-.03778(7)	.2435(3)	4.97(10)	4.21(9)	4.87(11)	- .86(8)	- .54(9)	- .19(8)
	.0551	-.03712	.2435	4.80	4.57	4.89	-1.10	- .46	- .23
C(7)	-.0332(2)	.16162(6)	.4698(2)	4.56(9)	3.56(8)	4.42(10)	.07(7)	.97(8)	.42(7)
	-.0334	.16173	.4713	4.33	3.94	4.38	.46	.87	.71
C(8)	-.1032(2)	.20551(8)	.5250(3)	5.80(11)	4.24(9)	5.26(11)	1.03(8)	.68(10)	.50(9)
	-.1028	.20505	.5241	5.53	4.42	5.59	.66	.48	.44
C(9)	-.0515(3)	.24279(9)	.6239(3)	7.90(15)	4.31(10)	5.85(13)	1.19(10)	1.23(12)	- .22(10)
	-.0526	.24220	.6253	6.87	3.94	7.55	1.31	.60	- .52
C(10)	.0694(3)	.23791(8)	.6673(3)	7.84(16)	4.48(11)	6.35(15)	- .30(11)	.38(12)	- .67(10)
	.0700	.23780	.6667	8.56	3.71	5.92	- .54	.16	- .27
C(11)	.1394(2)	.19507(8)	.6143(3)	5.53(12)	4.88(10)	6.93(14)	- .26(9)	.23(11)	- .92(10)
	.1397	.19476	.6136	5.06	4.42	7.65	- .71	.07	- .99
C(12)	.0885(2)	.15698(8)	.5167(2)	4.70(10)	4.06(8)	5.73(12)	.11(7)	.87(9)	- .55(9)
	.0872	.15682	.5179	4.30	4.23	6.08	.39	.76	- .80
C(13)	-.1056(2)	.03544(7)	.2309(2)	3.91(8)	4.77(9)	4.30(10)	- .73(7)	.48(8)	.79(8)
	-.1066	.03597	.2306	3.54	4.47	4.65	-1.26	.66	.47
C(14)	-.0456(2)	.07091(7)	.3336(2)	4.06(9)	4.39(9)	4.54(11)	- .04(7)	- .31(8)	- .10(8)
	-.0455	.07085	.3330	3.29	4.16	5.00	.38	- .38	- .09
C(15)	-.0918(2)	.12244(7)	.3641(2)	3.79(8)	4.40(8)	4.58(10)	.13(7)	.72(8)	.89(9)
	-.0921	.12200	.3647	3.66	4.30	5.16	.36	.62	.60
O(16)	-.2081(1)	.05000(6)	.1691(2)	4.27(6)	5.74(7)	6.85(9)	- .35(6)	- .95(6)	.45(6)
	-.2085	.05034	.1698	3.58	5.64	7.91	- .22	- .99	.51
O(17)	-.1937(1)	.13890(5)	.2998(2)	4.46(6)	5.38(6)	7.24(9)	.67(5)	- .50(6)	.39(7)
	-.1933	.13911	.3009	4.47	5.45	7.61	.70	- .48	.14
H(18)	-.196(2)	-.0362(7)	.045(2)	5.0(4)					
	-.203	-.0385	.048	4.0					
H(19)	-.125(2)	-.1236(8)	-.024(3)	6.8(6)					
	-.129	-.1244	-.026	4.0					
H(20)	.064(2)	-.1589(9)	.066(3)	7.9(6)					
	.075	-.1540	.070	4.0					
H(21)	.183(2)	-.0996(8)	.238(2)	6.6(6)					
	.182	-.1037	.240	4.0					
H(22)	.105(2)	-.0154(7)	.308(2)	4.6(4)					
	.101	-.0211	.320	4.0					
H(23)	-.191(2)	.2070(7)	.491(2)	5.8(5)					
	-.183	.2069	.490	4.0					
H(24)	-.103(2)	.2725(8)	.662(2)	7.3(6)					
	-.105	.2717	.663	4.0					
H(25)	.108(2)	.2622(9)	.732(3)	7.3(6)					
	.108	.2647	.732	4.0					
H(26)	.228(2)	.1912(8)	.644(2)	6.9(6)					
	.231	.1914	.649	4.0					
H(27)	.136(2)	.1257(8)	.482(2)	5.3(5)					
	.144	.1302	.485	4.0					
H(28)	.028(2)	.0591(6)	.383(2)	4.3(4)					
	.032	.0645	.387	4.0					
H(29)	-.220(2)	.0981(11)	.226(3)	11.1(8)					
	-.220	.1017	.222	4.0					

Table 2. Bond distances (Å)[a]. Distances are not corrected for thermal motion

Atoms		Distance	Atoms		Distance
C(1)	C(2)	1.391(2)	C(13)	O(16)	1.287(2)
C(2)	C(3)	1.379(3)	C(15)	O(17)	1.304(2)
C(3)	C(4)	1.368(3)	O(16)	O(17)	2.460(2)
C(4)	C(5)	1.372(3)	C(2)	H(18)	0.97(2)
C(5)	C(6)	1.381(3)	C(3)	H(19)	0.96(2)
C(6)	C(1)	1.384(2)	C(4)	H(20)	1.04(2)
C(7)	C(8)	1.400(3)	C(5)	H(21)	1.00(2)
C(8)	C(9)	1.376(3)	C(6)	H(22)	0.95(2)
C(9)	C(10)	1.371(3)	C(8)	H(23)	0.99(2)
C(10)	C(11)	1.374(3)	C(9)	H(24)	0.98(2)
C(11)	C(12)	1.379(3)	C(10)	H(25)	0.92(2)
C(12)	C(7)	1.387(3)	C(11)	H(26)	1.00(2)
C(1)	C(13)	1.479(2)	C(12)	H(27)	0.97(2)
C(13)	C(14)	1.408(3)	C(14)	H(28)	0.96(2)
C(14)	C(15)	1.382(2)	O(16)	H(29)	1.28(3)
C(15)	C(7)	1.476(3)	O(17)	H(29)	1.22(3)

(a) Standard deviation of least significant digit(s) is given in parentheses.

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