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

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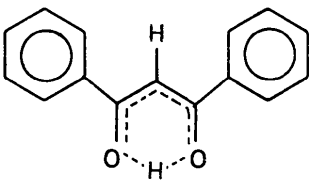
The structure of 1,3-diphenyl-1,3-propanedione enol has been redetermined. The crystals are orthorhombic, space group *Pbca*, with $a=10{\cdot}853$ (1), $b=24{\cdot}441$ (1), $c=8{\cdot}755$ (1) Å at 23°C; $d_c=1{\cdot}28$ g cm^{-3} for $Z=8$, $d_o=1{\cdot}22$ g cm^{-3}. The structure was refined to a final R value of 0·027 for 1070 X-ray data. The results of the analysis are close to those of the previous determination by Williams [*Acta Cryst.* (1966). **21**, 340–349], but probability plots indicate that standard deviations should be increased by 20% for hydrogen coordinates and 40% for coordinates and thermal parameters of other atoms.

Introduction

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)

Experimental

The HDPP was recrystallized from aqueous ethanol. The crystals are orthorhombic, space group *Pbca*. The cell

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Table 1. *Comparison of coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^2$) *for carbon and oxygen atoms*

The results of this study are given first, followed in the next line by those of Williams. The standard deviations of the least significant digits are given in parentheses. The form of the temperature factor (B's in units of Å^2) is: $T=\exp[-0{\cdot}25(B_{11}h^2a^{*2}+2B_{12}hka^*b^*+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	−568 (2)	−189·2 (7)	1881 (2)	378 (8)	424 (8)	378 (10)	−99 (7)	41 (7)	26 (8)
	−578 (4)	−187·6 (19)	1900 (6)	346 (23)	447 (24)	420 (28)	−122 (20)	25 (24)	−7 (25)
C(2)	−1214 (2)	−518·3 (9)	862 (2)	442 (9)	580 (10)	460 (11)	−116 (8)	−22 (9)	−7 (9)
	−1213 (5)	−513·9 (25)	853 (6)	468 (26)	612 (33)	472 (31)	−58 (26)	−6 (26)	21 (27)
C(3)	−756 (2)	−1022·1 (9)	438 (3)	596 (12)	574 (12)	532 (13)	−172 (10)	1 (10)	−122 (10)
	−754 (6)	−1019·9 (25)	437 (7)	533 (32)	547 (32)	562 (36)	−120 (25)	−27 (29)	−87 (28)
C(4)	348 (2)	−1203·6 (9)	997 (3)	616 (12)	475 (10)	562 (13)	−76 (9)	28 (10)	−78 (10)
	340 (6)	−1198·8 (23)	1003 (7)	585 (32)	447 (28)	637 (40)	−19 (26)	64 (30)	−59 (28)
C(5)	1001 (2)	−881·9 (8)	1993 (3)	579 (11)	431 (9)	611 (12)	−24 (9)	−86 (11)	−72 (9)
	1000 (6)	−881·2 (21)	2008 (7)	611 (30)	397 (25)	624 (35)	−33 (24)	−90 (31)	−24 (26)
C(6)	549 (2)	−377·8 (7)	2435 (3)	497 (10)	421 (9)	487 (11)	−86 (8)	−54 (9)	−19 (8)
	551 (5)	−371·2 (20)	2435 (7)	480 (27)	457 (26)	489 (31)	−110 (23)	−46 (25)	−23 (25)
C(7)	−332 (2)	1616·2 (6)	4698 (2)	456 (9)	356 (8)	442 (10)	7 (7)	97 (8)	42 (7)
	−334 (5)	1617·3 (20)	4713 (6)	433 (25)	394 (24)	438 (29)	46 (22)	87 (24)	71 (24)
C(8)	−1032 (2)	2055·1 (8)	5250 (3)	580 (11)	424 (9)	526 (11)	103 (8)	68 (10)	50 (9)
	−1028 (5)	2050·5 (23)	5241 (7)	553 (29)	442 (26)	559 (33)	66 (29)	48 (30)	44 (27)
C(9)	−515 (3)	2427·9 (9)	6239 (3)	790 (15)	431 (10)	585 (13)	119 (10)	123 (12)	−22 (10)
	−526 (6)	2422·0 (24)	6253 (8)	687 (38)	394 (29)	755 (42)	131 (27)	60 (36)	−52 (30)
C(10)	694 (3)	2379·1 (8)	6673 (3)	784 (16)	448 (11)	635 (15)	−30 (11)	38 (12)	−67 (10)
	700 (7)	2378·0 (22)	6667 (7)	856 (43)	371 (27)	592 (38)	−54 (28)	16 (37)	−27 (26)
C(11)	1394 (2)	1950·7 (8)	6143 (3)	553 (12)	488 (10)	693 (14)	−26 (9)	23 (11)	−92 (10)
	1397 (5)	1947·6 (23)	6136 (7)	506 (29)	442 (27)	765 (41)	−71 (25)	7 (30)	−99 (30)
C(12)	885 (2)	1569·8 (8)	5167 (2)	470 (10)	406 (8)	573 (12)	11 (7)	87 (9)	−55 (9)
	872 (5)	1568·2 (21)	5179 (7)	430 (26)	423 (26)	608 (34)	39 (23)	76 (25)	−80 (28)
C(13)	−1056 (2)	354·4 (7)	2309 (2)	391 (8)	477 (9)	430 (10)	−73 (7)	48 (8)	79 (8)
	−1066 (4)	359·7 (19)	2306 (6)	354 (22)	447 (22)	465 (27)	−126 (20)	66 (23)	47 (23)
C(14)	−456 (2)	709·1 (7)	3336 (2)	406 (9)	439 (9)	454 (11)	−4 (7)	−31 (8)	−10 (8)
	−455 (4)	708·5 (19)	3330 (6)	329 (20)	416 (23)	500 (30)	−38 (20)	−38 (24)	−9 (24)
C(15)	−918 (2)	1224·4 (7)	3641 (2)	379 (8)	440 (8)	458 (10)	13 (7)	72 (8)	89 (9)
	−921 (4)	1220·0 (20)	3647 (6)	366 (23)	430 (25)	516 (32)	36 (21)	62 (25)	60 (23)
O(16)	−2081 (1)	500·0 (6)	1691 (2)	427 (6)	574 (7)	685 (9)	−35 (6)	−95 (6)	45 (6)
	−2085 (3)	503·4 (14)	1698 (4)	358 (15)	564 (19)	791 (25)	−22 (14)	−99 (17)	51 (19)
O(17)	−1937 (1)	1389·0 (5)	2998 (2)	446 (6)	538 (6)	724 (9)	67 (5)	−50 (6)	39 (7)
	−1933 (3)	1391·1 (14)	3009 (5)	447 (17)	545 (18)	761 (25)	70 (15)	−48 (19)	14 (18)

dimensions are $a=10{\cdot}853$ (1), $b=24{\cdot}441$ (1), and $c=8{\cdot}755$ (1) Å at 23 °C as determined by least-squares calculations on twelve well centered reflections, in good agreement with the previous work [$a=10{\cdot}857$ (2), $b=24{\cdot}446$ (5), and $c=8{\cdot}756$ (2) Å]. Intensity data were collected on a crystal of dimensions $0{\cdot}19\times0{\cdot}23\times0{\cdot}12$ mm using monochromated Cu $K\alpha$ 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 refinement.

The structure was solved by direct methods using Long's (1965) sign-determination program. The structure was refined by least-squares to a final $R_1=\sum|\Delta F|/\sum|F_o|=0{\cdot}027$, with isotropic thermal parameters for hydrogen and anisotropic parameters for the other atoms. We used the scattering factors of Cromer & Waber (1965) for carbon and oxygen atoms and the spherical values of Stewart, Davidson & Simpson (1965) for hydrogen. Other details are given elsewhere (Hollander, 1972).*

Discussion

Our results are similar but not identical to those of Williams (1966). The parameters are compared in Tables 1 and 2.

We used individual thermal parameters for hydrogen atoms, which Williams did not, and reduced R_1 to 0·027 compared with Williams's $R_1=0{\cdot}059$. The standard deviations estimated by Williams (1972) are two or three times larger than ours. Differences in corresponding parameters are as large as 4σ, where $\sigma=(\sigma_1^2+\sigma_2^2)^{1/2}$. Analysis of these differences by the methods of normal and half-normal probability plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) indicated that the distributions correspond to standard deviations about 1·2 times larger than estimated by least squares for hydrogen coordinates and about 1·4 times larger for coordinates and thermal parameters of the other atoms. The B_{11} and B_{33} thermal parameters exhibit a systematic bias, our values for B_{11} being larger by an average of 0·26 Å^2 and our B_{33} values being smaller by 0·42 Å^2. Otherwise the distributions give reasonably straight probability plots.

This consistency of coordinates is gratifying. There is no novelty in the idea that the method of least-squares gives optimistic standard deviations, nor surprise that thermal parameters are prone to systematic error.

Bond distances for this determination are given in Table 3. 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. The peak for H(29) in a difference map has a single maximum and a rather irregular shape. The noise level of this map, and of a later one after hydrogen atoms were subtracted, makes us doubt that a more detailed analysis of this hydrogen atom is justified with this data set.

* A table of observed and calculated structure-factor amplitudes has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30089 (8 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Comparison of parameters for hydrogen atoms, arranged as in Table* 1

The form of the temperature factor is $T=\exp(-B\lambda^{-2}\sin^2\theta)$. Williams did not refine the thermal parameters of the hydrogen atoms.

	10^3x	10^4y	10^3z	B
H(18)	−196 (2)	−362 (7)	45 (2)	5·0 (4)
	−203 (5)	−385 (21)	48 (6)	4·0
H(19)	−125 (2)	−1236 (8)	−24 (3)	6·8 (6)
	−129 (5)	−1244 (20)	−26 (6)	4·0
H(20)	64 (2)	−1589 (9)	66 (3)	7·9 (6)
	75 (5)	−1540 (21)	70 (6)	4·0
H(21)	183 (2)	−996 (8)	238 (2)	6·6 (6)
	182 (5)	−1037 (19)	240 (6)	4·0
H(22)	105 (2)	−154 (7)	308 (2)	4·6 (4)
	101 (5)	−211 (21)	320 (6)	4·0
H(23)	−191 (2)	2070 (7)	491 (2)	5·8 (5)
	−183 (5)	2069 (22)	490 (6)	4·0
H(24)	−103 (2)	2725 (8)	662 (2)	7·3 (6)
	−105 (5)	2717 (21)	663 (6)	4·0
H(25)	108 (2)	2622 (9)	732 (3)	7·3 (6)
	108 (5)	2647 (20)	732 (7)	4·0
H(26)	228 (2)	1912 (8)	644 (2)	6·9 (6)
	231 (5)	1914 (19)	649 (6)	4·0
H(27)	136 (2)	1257 (8)	482 (2)	5·3 (5)
	144 (5)	1302 (21)	485 (6)	4·0
H(28)	28 (2)	591 (6)	383 (2)	4·3 (4)
	32 (5)	645 (20)	387 (6)	4·0
H(29)	−220 (2)	981 (11)	226 (3)	11·1 (8)
	−220 (5)	1017 (23)	222 (6)	4·0

Table 3. *Bond distances* (Å)

Distances are not corrected for thermal motion. The standard deviation of the least significant digit is given in parentheses.

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)

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