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The Crystal and Molecular Structure of Dimedone

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The crystal and molecular structure of dimedone, 5,5-dimethyl-1,3-cyclohexanedione, has been determined from three-dimensional single crystal X-ray diffraction data. The space group is $P2_1/c$, with cell dimensions $a = 10.040(1)$, $b = 6.823(1)$, $c = 12.984(2)$ Å, $\beta = 116.20(1)°$. There are four molecules in the unit cell. The structure has been refined by full matrix least-squares methods to a weighted R-factor of 0.046 for the 1428 independent reflections. The estimated standard deviations in bond lengths involving non-hydrogen atoms are 0.002 Å. The molecules crystallize in the enol form and are hydrogen bonded to each other forming infinite helices parallel to the b axis. The hydrogen bond length is 2.593 Å.

Dimedone (5,5-dimethyl-1,3-cyclohexanedione) is a white crystalline solid of melting point 148 – 149°C. It is commonly used as a reagent for separation and identification of aldehydes.[1] Unlike acyclic β-dicarbonyl compounds, enolization of dimedone gives a *trans*-enol where *intra*-molecular hydrogen bonding is impossible.[2,3] Nevertheless, dimedone is believed to exist largely in the enol form both in solution [5] and in the solid state.[4] In solvents incapable of forming hydrogen bonds the comparatively high enol content has been explained by assuming a hydrogen bonded dimeric enol form.[2,3] Several X-ray investigations of acyclic β-diketones have been carried out,[6–8] but there is a paucity of structural data for the cyclic analogs. An X-ray investigation of dimedone has therefore been undertaken.

EXPERIMENTAL

A commercial sample of dimedone was purified and crystallized from methanol. The observed extinctions, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely determined the space group as $P2_1/c$. The cell dimensions were determined at room temperature on a manual four circle diffractometer using CuK radiation. The crystal used for the collection of intensity data was of nearly spherical form with diameter 0.35 mm. Data were collected on a SYNTEX P$\bar{1}$ diffractometer by the $\omega/2\theta$ scan technique using a graphite monochromator and Mo$K\alpha$ radiation ($= 0.71069$ Å) at 18°C. Each reflection was scanned from $2\theta_{\alpha 1} - 0.85°$ to $2\theta_{\alpha 2} + 0.85°$, at a variable scan rate ranging from 1°/min to 12°/min depending on intensity. Stationary-counter-stationary-crystal background counts were made at the upper and lower extremities of the 2θ scan range for each reflection. A rejection level was also specified to avoid measurement of reflections with intensities less than the threshold value. The intensities of three standard reflections, measured every 50′ reflections, showed no change during the data collection. A total of 1548 independent intensities were recorded, out to $2\theta < 70°$. Of these, 1428 reflections had intensities greater than twice their standard deviations. The intensities and their standard deviations were corrected for Lorentz and polarization effects and a 2 % uncertainty in diffractometer stability was included in the standard deviations. No corrections were made for absorption since intensity errors from this source are less than 1.5 % ($\mu = 0.09$ mm^{-1}). All programs applied are written or revised for CDC 3300 by Dahl *et al.*[11]

CRYSTAL DATA

Dimedone, $C_8H_{12}O_2$, F.W. 140.2, monoclinic; $a = 10.040$ (1), $b = 6.823$ (1), $c = 12.984$ (2) Å, $\beta = 116.20$ (1)°, $V = 798.3$ Å^3, F (000) = 444, $Z = 4$, $\varrho_{obs} = 1.15$ g cm^{-3}, $\varrho_{calc} = 1.15$ g cm^{-3}. Space group $P2_1/c$.

SOLUTION AND REFINEMENT

The phase problem was solved three-dimensionally by a computer program based on

symbolic addition methods. By permuting the signs of two structure invariant reflections with large unitary structure amplitudes, four sets of 350 signs were determined. From one of the resulting Fourier maps, peaks corresponding to all the heavy atoms were located. The trial structure was refined by full-matrix least-squares technique. A difference Fourier synthesis led to the location of the hydrogen atoms with the exception of those of the methyl groups. The coordinates for these atoms were calculated assuming staggered positions of the methyl groups relative to C5. Refinement of all positional and thermal parameters including a common isotropic thermal parameter for the methyl hydrogen atoms terminated at $R_w = 0.046$ and $R = 0.040$. Unobserved reflections were excluded throughout the refinement. Weight analysis showed that weighting based on standard deviations from counter statistics was satisfactory. No correction for secondary extinction was necessary. Atomic form factors were those of Hanson *et al.*[9] except for hydrogen.[10] A final difference Fourier map contained no larger density fluctuations than ± 0.3 e/Å^3. The parameters obtained in the last cycle of refinement are given in Table 1 together with their estimated standard deviations. Table 2 contains the observed and calculated structure factors.

Rigid-body analysis of translational, liberational, and screw motion [11] of the molecule gave a r.m.s. value of 0.0033 Å^2 when all the non-hydrogen atoms were included. When the two methyl carbon atoms were excluded, the r.m.s. value dropped to 0.0022 Å.^{2} The cyclohexene ring and the two oxygen atoms may therefore be regarded as a rigid body. Corrections in bond lengths generally exceed the standard devia-

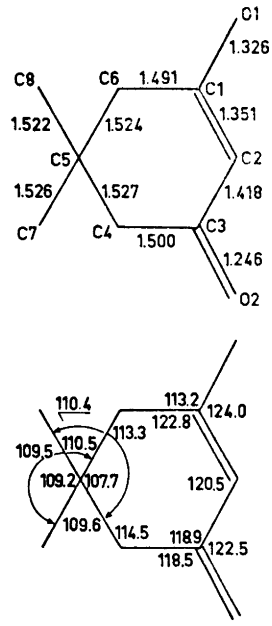

Fig. 1. Schematic drawing of the molecule showing bond distances and angles. (Bond distances uncorrected for librational motion).

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$), isotropic temperature factor and positional parameters ($\times 10^4$) for the hydrogen atoms. The anisotropic temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{22}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

ATOM	X	Y	Z	B	β11	β22	β33	β12	β13	β23
O 1	26132(12)	65879(16)	35714(11)		1361(15)	2793(29)	833(10)	-818(33)	764(21)	549(26)
O 2	-8883(11)	19773(15)	35972(8)		1272(14)	2557(27)	831(9)	-971(31)	821(19)	-386(23)
C 1	21184(15)	51711(19)	48534(12)		1151(17)	2024(32)	732(12)	-11(39)	879(24)	-9(29)
C 2	8335(15)	41651(21)	34848(12)		1125(17)	2247(33)	628(11)	-77(40)	632(22)	-15(38)
C 3	3224(15)	28588(19)	48777(11)		1149(17)	1848(29)	734(11)	-45(40)	899(23)	-366(29)
C 4	12484(16)	25616(23)	63431(12)		1448(21)	2869(34)	699(11)	-337(45)	1081(25)	-107(38)
C 5	28991(15)	29271(21)	57624(12)		1294(19)	2246(32)	597(10)	-74(41)	584(22)	-68(28)
C 6	30788(17)	49165(23)	53854(12)		1268(28)	2492(39)	691(12)	-688(46)	651(25)	-232(33)
C 7	36671(24)	29562(34)	78718(14)		1971(38)	3517(53)	664(13)	-797(69)	505(32)	83(41)
C 8	35809(23)	13281(29)	53343(17)		1632(26)	3869(47)	1849(17)	1259(63)	944(35)	189(47)
H 1	229(15)	4352(28)	2677(12)	3,8(,3)						
H 2	835(17)	3444(22)	5751(13)	4,8(,3)						
H 3	1861(16)	1272(24)	5543(12)	4,4(,3)						
H 4	2833(16)	5968(22)	5733(12)	4,8(,3)						
H 5	4899(19)	5129(23)	5438(12)	5,1(,4)						
H 6	2818(21)	6664(25)	2865(16)	5,9(,4)						
H 7	4728(24)	3197(27)	7379(17)	7,8(,2)						
H 8	3484(21)	1789(29)	7382(15)	7,8(,8)						
H 9	3222(19)	4857(28)	7347(15)	7,8(,8)						
H10	4623(24)	1511(27)	5578(16)	7,8(,8)						
H11	3095(21)	1211(25)	4486(17)	7,8(,8)						
H12	3413(28)	27(28)	5684(15)	7,8(,8)						

Table 2. Observed and calculated structure factors. The columns are l, $10F_o$, $10F_c$ respectively.

Hk	0,Ke	0	6	101	97	- 6	289	281	- 1	32	33	2	58	51	Hk	2,Ke	8	- 8	9	10	9	31	32
2	486	489	7	37	33	- 5	202	198	0	82	85	3	182	174	- 9	23	21	- 4	15	15	11	28	28
4	304	293	8	41	38	- 4	251	250	1	49	52	4	102	103	0	30	30	- 3	83	80	12	20	16
6	16	16	9	52	54	- 3	242	241	2	19	19	5	37	38	Hk	2,Ke	10	- 2	33	31	Hk	4,Ke	2
8	20	14	10	56	54	- 2	798	822	3	67	64	7	125	126	- 3	23	20	- 1	14	15	-16	13	15
10	68	79	11	31	31	- 1	155	153	5	107	110	8	111	118	6	16	11	0	39	39	-15	37	35
12	30	23	13	47	46	0	353	351	6	61	61	9	35	34	Hk	3,Ke	0	1	55	56	-13	33	36
14	21	27	14	28	21	1	357	352	7	113	114	14	39	36	-18	26	22	3	78	79	-12	19	23
16	63	54	15	22	22	2	233	220	8	33	33	Hk	2,Ke	3	-12	23	19	4	27	27	-11	38	40
18	34	30	Hk	0,Ke	5	3	117	114	11	35	34	-15	56	51	-10	142	150	6	21	20	-10	20	18
Hk	0,Ke	1	-12	25	27	4	409	389	Hk	1,Ke	6	-14	55	54	- 8	60	61	7	30	32	- 9	87	89
-17	26	24	-11	42	42	5	246	232	- 9	51	54	-12	13	13	- 6	118	112	11	22	22	- 8	54	53
-14	18	15	- 9	40	39	6	49	46	- 8	28	27	-11	80	83	- 4	26	26	13	22	22	- 7	55	54
-10	37	36	- 8	23	24	7	67	65	- 5	59	60	-10	15	16	- 2	501	498	Hk	3,Ke	8	- 6	139	132
- 8	15	16	- 7	125	126	8	87	90	- 4	28	32	- 9	90	92	0	480	475	-17	22	19	- 5	18	19
- 7	9	5	- 6	48	49	10	30	41	- 2	57	56	- 8	92	97	2	205	197	-10	31	33	- 4	284	282
- 6	344	342	- 5	27	29	12	18	21	- 1	89	92	- 7	29	26	4	140	135	- 7	15	20	- 3	255	249
- 5	70	68	- 4	57	58	13	17	15	0	61	62	- 6	53	54	8	76	79	- 5	16	15	- 2	15	10
- 4	153	146	- 3	116	118	16	31	28	1	66	69	- 5	124	121	10	56	54	- 4	61	62	- 1	40	39
- 3	245	242	- 2	59	62	Hk	1,Ke	2	3	29	30	- 4	316	307	14	30	29	- 3	20	19	0	124	119
- 2	143	147	- 1	139	140	-15	22	22	5	34	33	- 3	259	259	Hk	3,Ke	1	- 2	62	61	1	172	164
- 1	475	484	1	139	140	-12	19	22	6	39	38	- 2	271	269	-16	58	53	- 1	78	78	2	18	15
1	473	484	2	62	62	-10	63	68	11	20	21	- 1	113	108	- 9	84	86	1	79	80	3	17	18
2	143	147	3	118	118	- 9	31	33	Hk	1,Ke	7	0	63	61	- 8	16	16	3	59	59	4	31	31
3	245	242	4	59	57	- 8	49	53	- 9	28	21	1	104	103	- 7	83	85	4	24	21	5	65	65
4	154	145	5	27	29	- 7	101	105	- 4	30	27	2	165	167	- 5	58	55	6	28	25	7	32	30
5	70	68	6	48	49	- 6	11	8	- 3	24	26	3	112	108	- 4	229	220	7	29	27	8	18	19
6	345	342	7	126	126	- 5	29	31	- 1	41	40	4	44	44	- 3	44	41	Hk	3,Ke	6	9	31	31
7	9	6	8	24	23	- 4	33	34	0	48	44	5	92	94	- 1	13	9	-12	51	50	10	16	14
8	14	16	9	41	39	- 3	116	114	2	26	27	6	53	50	0	310	314	-10	35	31	12	68	63
10	38	36	11	42	42	- 2	551	553	3	24	24	7	98	101	1	60	54	- 7	33	35	14	13	14
13	23	24	12	24	27	- 1	22	22	5	27	25	8	48	49	2	58	54	- 6	33	33	Hk	4,Ke	3
17	26	24	13	19	17	0	226	227	6	21	20	10	37	38	3	28	24	- 5	34	42	-18	28	22
Hk	0,Ke	2	15	15	11	1	215	217	Hk	1,Ke	8	13	50	47	4	26	26	- 4	10	9	-12	39	40
-14	38	34	Hk	0,Ke	6	2	17	13	-10	24	21	14	36	35	5	56	55	- 2	117	116	-11	82	83
-13	39	36	-10	13	15	3	24	24	- 9	21	19	Hk	2,Ke	4	6	67	67	- 1	47	44	-10	72	78
-12	19	18	- 9	21	21	4	94	93	- 4	29	29	- 9	34	37	7	55	59	0	30	30	- 9	111	114
- 8	22	22	- 7	27	27	5	24	25	- 1	55	50	- 8	118	121	9	33	35	1	23	25	- 8	36	35
- 7	53	57	- 5	33	34	6	11	9	0	12	14	- 7	28	29	11	27	26	2	44	46	- 7	124	126
- 6	31	31	- 4	23	26	7	44	44	2	15	17	- 6	67	69	12	37	35	3	30	31	- 6	79	73
- 5	149	149	- 3	39	38	8	96	101	3	45	42	- 5	27	29	Hk	3,Ke	2	4	55	53	- 4	10	4
- 4	114	110	- 1	47	47	9	42	42	5	20	19	- 4	64	60	-17	30	28	5	26	24	- 3	203	200
- 3	10	7	0	46	47	11	30	32	6	32	30	- 3	105	101	-13	67	66	6	75	74	- 2	100	106
- 2	81	78	1	46	47	14	31	26	8	37	33	- 2	80	78	-12	23	22	7	34	33	- 1	32	30
- 1	255	249	2	9	11	16	23	19	Hk	1,Ke	9	- 1	74	71	-11	39	40	Hk	3,Ke	7	0	56	61
0	436	428	3	37	38	Hk	1,Ke	3	- 6	16	17	1	32	32	-10	234	240	-11	54	49	1	202	202
1	256	249	4	24	26	- 9	160	167	2	35	34	2	56	56	- 9	13	20	- 8	15	15	2	30	28
2	82	78	5	30	34	- 8	169	174	4	14	17	3	44	46	- 8	183	187	- 6	41	45	3	46	43
3	11	7	6	13	16	- 7	125	132	Hk	2,Ke	0	4	24	25	- 7	189	186	- 5	14	13	4	21	20
4	113	110	7	27	27	- 6	138	142	-14	36	37	5	78	78	- 6	173	162	- 3	66	67	5	64	67
5	150	149	8	23	21	- 5	129	123	-12	16	16	7	61	61	- 4	435	421	- 1	22	22	6	75	79
6	32	31	Hk	0,Ke	7	- 4	12	12	-10	42	42	8	56	55	- 3	373	366	0	27	26	7	45	48
7	55	57	- 8	26	25	- 3	171	166	- 8	163	162	9	37	40	- 2	35	35	1	80	81	8	22	25
8	23	22	- 7	39	41	- 2	111	111	- 6	217	215	10	32	34	- 1	188	190	3	29	29	9	16	19
13	41	36	- 2	16	17	- 1	36	35	- 4	74	72	Hk	2,Ke	5	0	55	59	5	64	63	10	18	20
14	36	34	- 1	19	18	0	107	108	- 2	498	506	-10	52	52	1	203	195	7	44	43	13	21	20
Hk	0,Ke	3	1	19	18	1	111	114	0	400	403	- 9	21	23	2	193	197	Hk	3,Ke	8	Hk	4,Ke	4
-15	29	25	7	4,	41	3	204	203	4	54	54	- 8	43	44	3	313	310	- 6	23	24	-17	13	12
-13	30	31	8	26	25	5	92	89	6	161	170	- 6	57	55	5	64	64	- 4	26	25	-15	22	24
-12	22	18	Hk	0,Ke	8	6	32	31	8	51	54	- 4	104	103	6	117	123	- 2	16	16	-12	36	35
-11	20	19	- 5	17	18	7	96	96	12	22	19	- 3	58	59	7	106	105	Hk	3,Ke	9	-11	27	29
- 8	22	21	- 4	34	31	8	59	59	Hk	2,Ke	1	- 2	50	51	8	141	149	- 2	20	18	-10	55	57
- 7	66	69	- 3	28	27	9	133	137	-17	18	18	- 1	177	180	11	36	38	1	16	16	- 8	16	18
- 6	107	110	- 2	40	40	10	56	61	-15	17	17	0	71	70	12	47	45	Hk	4,Ke	0	- 7	34	39
- 5	25	23	- 1	20	21	11	24	27	-14	17	17	1	13	12	14	34	29	-16	28	26	- 6	103	101
- 4	31	32	1	21	21	13	20	22	-10	30	33	2	50	50	Hk	3,Ke	3	-12	130	133	- 5	79	84
- 3	186	186	2	40	40	15	22	21	- 9	36	34	3	66	66	-16	15	9	-10	111	111	- 4	23	19
- 2	25	25	3	27	27	Hk	1,Ke	4	- 7	11	9	4	19	21	-14	27	30	- 8	22	23	- 2	138	139
- 1	113	115	4	35	31	-13	23	25	- 6	164	157	5	32	31	-13	12	12	- 6	88	86	- 1	111	110
1	113	115	5	20	18	-12	25	23	- 5	163	163	8	33	33	-11	69	71	- 4	81	84	0	20	20
2	23	25	Hk	0,Ke	9	-11	54	58	- 4	52	46	11	31	28	-10	110	109	- 2	152	149	2	31	33
3	185	186	- 8	23	18	-10	136	137	- 3	85	85	Hk	2,Ke	6	- 9	91	92	0	92	93	3	14	11
4	30	32	- 2	37	37	- 9	73	77	- 2	814	837	-12	31	32	- 8	36	39	2	146	147	4	13	15
5	25	23	- 1	25	26	- 8	103	106	- 1	586	592	-10	15	16	- 7	13	13	4	264	275	6	42	42
6	107	110	1	28	26	- 7	130	134	0	284	278	- 9	52	51	- 6	34	37	6	150	159	7	13	18
7	67	69	2	38	37	- 5	55	55	1	20	22	- 8	67	67	- 5	202	197	8	18	17	8	31	29
8	24	21	Hk	1,Ke	0	- 4	45	44	2	312	308	- 6	33	38	- 4	276	279	12	34	28	9	15	13
12	19	16	-12	53	63	- 2	180	185	3	129	121	- 4	25	28	- 3	328	328	Hk	4,Ke	1	Hk	4,Ke	5
13	32	31	- 8	159	163	- 1	21	19	4	17	14	- 3	40	38	- 2	78	71	-18	25	21	-13	40	35
15	33	25	- 6	548	518	0	92	93	5	15	14	0	89	87	0	154	147	-16	37	38	-10	19	18
Hk	0,Ke	4	- 4	148	144	1	119	119	6	97	94	1	37	34	1	55	53	-15	15	13	- 8	34	36
-14	23	21	- 2	78	77	2	20	18	7	14	8	2	24	22	2	28	24	-13	37	43	- 7	60	63
-13	47	46	0	374	368	3	11	16	12	40	40	3	84	83	4	68	68	-12	143	147	- 6	12	12
-11	30	31	2	29	25	4	37	33	14	47	41	4	75	76	5	64	66	-11	51	52	- 5	47	44
-10	57	54	4	698	686	5	129	125	16	23	24	5	69	68	6	63	63	-10	99	102	- 4	59	60
- 9	50	54	6	343	335	6	51	52	Hk	2,Ke	2	6	49	49	7	95	98	- 9	65	66	- 3	10	7
- 8	39	38	8	29	27	7	37	39	-16	41	34	7	56	55	8	60	61	- 8	180	178	- 2	50	50
- 7	35	33	10	84	89	8	83	84	-14	28	23	9	36	36	11	18	15	- 6	160	162	- 1	87	86
- 6	99	97	12	17	9	9	98	96	-11	80	83	10	20	18	12	36	34	- 5	136	130	0	71	72
- 5	128	125	14	14	16	10	19	23	-10	128	131	Hk	2,Ke	7	13	30	26	- 4	254	247	1	37	36
- 4	36	38	16	30	25	12	19	20	- 9	36	40	-15	24	21	14	24	24	- 3	74	76	2	17	18
- 3	27	23	Hk	1,Ke	1	Hk	1,Ke	5	- 8	233	236	- 6	21	21	Hk	3,Ke	4	- 1	151	155	3	66	70
- 2	142	139	-15	23	23	-12	23	24	- 7	141	146	- 5	13	10	-14	15	13	0	147	146	4	33	35
- 1	227	225	-13	15	18	-11	43	42	- 6	101	104	- 4	22	22	-12	22	26	1	214	209	5	95	97
0	135	133	-12	30	30	-10	64	64	- 5	131	127	- 3	36	36	-11	32	30	2	173	161	Hk	4,Ke	6
1	225	225	-11	42	47	- 9	38	35	- 4	97	90	- 2	17	17	-10	31	31	3	56	54	-17	17	15
2	142	139	-10	47	48	- 8	16	16	- 3	98	102	0	63	62	- 9	68	70	4	53	54	-11	25	20
3	26	23	- 9	35	34	- 6	18	14	- 2	402	392	1	88	86	- 8	32	33	5	157	163	- 9	28	29
4	38	37	- 8	195	201	- 4	64	67	- 1	525	516	2	44	44	- 7	58	58	6	224	230	- 8	25	26
5	130	125	- 7	100	97	- 3	60	61	0	196	202	3	34	34	- 6	23	23	8	13	14	- 6	19	18

Table 2. Continued.

= 5	59	60	6	39	39	=11	11	5	= 9	10	0	= 4	13	15	Hx	8,Kx	6	3	19	20	= 6	35	35
= 4	12	11	10	25	25	=10	79	82	= 8	46	42	= 3	29	31	=14	27	25	Hx	9,Kx	8	= 4	29	32
= 2	76	81	Hx	5,Kx	4	= 9	69	71	= 6	56	59	= 1	32	31	=13	23	10	=12	28	25	= 3	30	31
= 1	134	138	=14	16	13	= 8	68	65	= 4	20	14	2	21	19	=12	36	30	= 8	51	51	= 2	17	18
0	62	61	=10	44	43	= 6	46	43	= 2	54	55	Hx	7,Kx	7	=11	22	22	= 2	32	29	0	37	35
1	39	39	= 9	25	26	= 5	60	60	0	73	71	= 7	31	28	= 8	21	19	Hx	9,Kx	7	1	21	16
2	43	42	= 8	60	66	= 4	43	46	2	69	73	= 5	56	50	= 7	44	39	= 9	35	33	Hx	11,Kx	2
3	23	24	= 7	64	63	= 2	59	59	4	60	59	= 3	15	14	= 6	21	20	= 8	13	14	= 7	14	14
4	23	25	= 6	81	78	= 1	33	35	6	16	18	= 2	12	12	= 5	45	47	= 7	43	41	= 6	12	12
5	22	19	= 5	114	116	0	57	63	8	46	46	3	13	11	= 2	25	27	1	18	15	= 2	17	16
7	23	21	= 4	155	157	1	62	62	Hx	7,Kx	1	Hx	7,Kx	8	2	13	12	Hx	10,Kx	0	0	19	18
9	16	16	= 3	183	186	2	9	4	=19	18	19	=11	31	27	4	31	28	=18	12	11	1	12	14
Hx	4,Kx	7	= 2	64	64	3	92	93	=16	16	18	= 9	18	17	5	23	18	=10	33	32	Hx	11,Kx	3
= 8	22	22	= 1	120	123	4	49	49	=15	25	24	= 5	22	18	Hx	8,Kx	7	= 8	105	103	=10	27	25
= 6	28	29	1	58	63	5	18	17	=14	20	21	3	18	14	=13	41	35	= 6	56	54	= 8	17	16
= 5	18	17	2	58	57	6	32	30	=13	32	34	Hx	8,Kx	0	=11	23	20	0	37	37	= 7	23	25
= 4	21	22	3	56	58	7	21	16	=12	83	84	=12	39	39	= 9	29	27	2	32	30	= 5	12	10
= 3	25	23	4	31	30	Hx	6,Kx	3	=11	57	60	=10	81	82	= 6	19	20	8	31	26	= 3	19	19
= 1	42	38	10	14	13	=14	28	25	= 9	57	56	= 8	35	34	0	23	21	Hx	10,Kx	1	0	37	33
2	29	28	11	28	27	=12	24	25	= 8	25	23	= 6	68	67	3	20	19	=18	18	16	2	19	18
3	21	21	12	23	20	=11	45	45	= 7	83	83	= 4	61	62	4	25	20	=14	27	28	Hx	11,Kx	4
4	27	28	Hx	5,Kx	5	=10	51	55	= 6	62	59	= 2	58	58	Hx	8,Kx	8	=13	27	25	=16	25	17
5	32	31	=14	18	19	= 9	46	46	= 4	165	164	Hx	8,Kx	1	= 7	23	20	=12	37	36	=13	20	17
Hx	4,Kx	8	=12	27	25	= 8	26	31	= 3	98	101	=15	42	41	Hx	9,Kx	0	=10	31	31	=11	15	18
=12	22	19	=11	36	35	= 7	16	18	= 2	114	116	=14	17	16	=16	39	38	= 9	61	62	=10	32	31
= 2	23	20	= 9	20	27	= 5	70	71	= 1	72	76	=13	29	26	=14	42	40	= 8	87	86	= 8	29	27
= 1	34	34	= 8	34	36	= 4	29	30	0	91	90	=12	40	41	=10	12	7	= 7	28	27	= 6	26	24
2	21	19	= 7	51	59	= 3	49	48	1	17	14	=10	27	28	= 8	24	20	= 6	26	22	= 3	33	32
3	29	27	= 6	72	72	= 2	42	42	2	61	60	= 9	14	16	= 6	68	71	= 5	37	36	= 2	26	28
4	21	22	= 5	61	63	0	9	13	3	23	23	= 8	82	83	= 2	23	27	= 4	68	68	0	39	31
Hx	4,Kx	10	= 3	159	161	1	47	50	4	56	57	= 7	21	24	2	49	47	= 3	27	27	1	44	40
= 2	20	19	= 2	34	37	2	87	84	5	33	36	= 6	95	93	4	29	29	= 2	39	41	Hx	11,Kx	5
Hx	5,Kx	0	0	55	53	4	43	43	6	41	42	= 4	60	62	6	15	13	= 1	54	53	=17	23	20
=20	21	19	1	49	51	6	21	19	8	38	35	= 3	21	23	Hx	9,Kx	1	0	27	25	=13	23	22
=18	62	55	3	61	62	10	21	18	9	33	30	= 2	63	51	=14	29	30	1	18	20	=10	25	21
=14	66	67	4	68	70	Hx	6,Kx	4	Hx	7,Kx	2	0	48	48	=13	13	16	3	12	14	= 8	17	13
=10	131	132	6	18	18	=16	16	14	=16	22	23	1	75	75	=12	64	60	Hx	10,Kx	2	= 5	18	18
= 8	111	110	Hx	5,Kx	6	=14	29	25	=15	16	17	2	66	67	= 7	62	61	=13	29	27	= 4	26	23
= 6	278	271	= 5	39	35	=13	26	30	=14	33	30	3	69	71	= 6	53	54	=12	16	16	= 2	20	21
= 4	63	59	= 1	24	24	=12	23	22	=12	24	22	4	49	48	= 5	83	83	= 9	21	21	Hx	11,Kx	6
= 2	427	423	0	23	24	=11	13	6	=11	35	36	6	24	23	= 4	10	10	= 6	19	20	= 5	20	14
0	310	302	3	53	53	=10	45	45	=10	17	17	8	13	15	= 2	44	46	= 5	36	36	Hx	12,Kx	0
2	125	127	5	33	33	= 9	102	109	= 9	36	36	10	24	20	= 1	17	18	= 4	43	45	=16	19	17
4	54	59	Hx	5,Kx	7	= 8	28	26	= 8	74	76	Hx	8,Kx	2	0	46	47	0	22	23	=14	25	22
6	51	51	=13	24	17	= 7	12	12	= 7	55	56	=16	38	36	3	14	12	3	30	26	=10	60	54
8	12	10	=11	25	22	= 5	108	110	= 6	126	125	=15	28	29	4	19	19	5	20	15	= 8	31	32
10	99	95	= 9	14	15	= 4	152	157	= 5	28	27	=14	55	55	8	20	23	Hx	10,Kx	3	= 6	65	65
Hx	5,Kx	1	1	19	12	= 3	42	43	= 4	104	107	=12	57	57	Hx	9,Kx	2	=16	25	25	= 4	28	28
=19	17	15	2	25	26	= 2	133	135	= 3	54	50	=11	67	66	=17	19	18	=14	27	24	= 2	47	42
=18	15	15	4	26	25	= 1	83	87	= 2	33	29	=10	44	37	=14	34	32	= 9	20	18	Hx	12,Kx	1
=15	18	21	5	24	20	0	38	40	0	37	44	= 8	14	13	=13	34	35	= 7	29	27	=11	28	27
=14	16	18	Hx	5,Kx	8	1	66	72	1	37	33	= 7	91	92	=11	35	38	= 6	34	34	=10	33	30
=12	122	125	= 9	24	19	2	87	93	2	104	106	= 6	102	101	=10	10	9	= 3	37	36	= 9	44	43
=11	71	68	= 7	20	16	3	69	72	3	25	28	= 5	48	49	= 9	52	53	= 1	13	18	= 8	16	14
=10	27	25	= 6	12	10	4	48	47	12	24	19	= 4	27	29	= 8	65	65	0	26	24	= 4	16	12
= 9	47	47	= 4	43	42	5	40	45	Hx	7,Kx	3	= 3	101	104	= 7	72	74	1	32	33	= 3	20	21
= 8	117	112	= 1	30	29	6	28	24	=14	22	22	= 2	63	61	= 6	164	166	Hx	10,Kx	4	= 2	28	26
= 7	52	52	1	15	14	8	21	19	=13	12	12	= 1	25	27	= 5	15	14	=15	23	23	Hx	12,Kx	2
= 6	66	62	3	26	26	Hx	6,Kx	5	=11	24	27	0	85	90	= 4	26	25	=14	19	19	=10	23	20
= 5	29	27	5	22	19	=15	23	20	= 9	39	43	1	22	20	= 3	48	47	=11	26	26	= 8	17	16
= 4	190	183	Hx	5,Kx	9	=14	18	14	= 8	20	22	2	99	98	= 2	80	85	= 8	43	40	= 7	17	18
= 3	83	80	=10	15	15	=13	26	25	= 7	71	72	3	41	42	= 1	42	38	= 6	43	43	= 4	20	16
= 1	182	180	= 8	28	24	=12	37	39	= 5	181	183	4	20	17	0	27	26	= 5	13	11	Hx	12,Kx	3
0	177	178	Hx	6,Kx	0	=10	16	14	= 4	189	195	5	41	37	1	53	53	= 4	16	10	=10	23	20
1	71	68	=18	18	17	= 9	14	14	= 3	35	37	7	31	30	2	43	44	= 3	17	18	Hx	12,Kx	4
2	23	25	=14	128	131	= 8	39	39	= 2	27	26	Hx	8,Kx	3	3	16	17	0	36	37	=16	25	21
4	145	150	=12	66	62	= 7	72	73	= 1	116	118	=16	14	10	4	13	12	2	36	34	=15	16	13
5	113	115	=10	162	162	= 6	13	14	0	18	23	=14	29	30	7	24	24	Hx	10,Kx	5	=12	23	21
6	103	105	= 8	23	25	= 5	32	35	1	41	41	=13	33	37	10	23	19	=15	21	21	= 9	20	17
7	45	47	= 6	179	180	= 3	135	138	3	25	27	=11	44	50	Hx	9,Kx	3	=14	26	23	0	30	27
8	15	14	= 4	31	35	= 2	83	80	Hx	7,Kx	4	=10	67	68	=13	36	35	=11	31	27	Hx	12,Kx	5
9	40	39	= 2	94	91	= 1	28	28	=16	16	15	= 9	40	44	=10	36	36	= 9	29	29	1	19	17
10	43	39	= 1	8	0	0	48	46	=14	26	26	= 7	73	76	= 9	28	31	= 1	12	14	Hx	13,Kx	1
Hx	5,Kx	2	0	146	140	1	76	76	=11	22	22	= 6	32	32	= 7	42	46	1	20	18	=14	16	14
=12	42	43	2	185	190	2	17	11	=10	37	37	= 4	90	85	= 6	29	27	2	33	25	=10	37	35
=10	13	16	4	280	290	3	42	41	= 9	42	46	= 3	58	57	= 5	33	33	3	29	26	= 8	36	32
= 9	18	21	6	54	53	4	24	23	= 8	24	26	= 2	25	28	= 4	31	30	4	23	21	= 5	21	23
= 7	46	43	8	47	49	5	29	29	= 7	17	17	= 1	27	32	= 3	21	20	Hx	10,Kx	6	Hx	13,Kx	2
= 6	27	25	10	22	21	6	13	13	= 6	60	60	0	93	97	= 1	48	45	=15	21	18	=16	18	15
= 4	127	123	Hx	6,Kx	1	Hx	6,Kx	6	= 5	106	109	1	44	47	0	52	51	=14	19	15	=12	19	16
= 3	180	174	=14	19	19	= 7	31	33	= 4	78	76	4	20	23	1	25	25	=11	21	18	=11	13	11
= 2	76	79	=13	85	85	= 6	23	24	= 3	45	45	6	27	25	3	37	35	= 9	17	12	= 8	24	22
= 1	100	99	=12	15	15	= 4	20	19	= 2	10	12	Hx	8,Kx	4	4	18	21	= 8	21	22	= 2	27	26
0	102	95	=11	20	18	= 3	20	19	= 1	56	57	=13	24	20	5	20	17	2	24	23	0	19	15
1	72	74	=10	12	10	1	21	23	0	31	32	= 9	17	15	Hx	9,Kx	4	3	23	20	Hx	13,Kx	3
3	24	23	= 9	65	64	2	26	29	2	89	90	= 7	31	29	=14	24	19	Hx	11,Kx	0	=17	15	9
5	62	64	= 8	13	9	Hx	6,Kx	7	4	22	22	= 6	23	23	= 9	15	12	=16	23	22	= 1	32	28
Hx	5,Kx	3	= 7	45	44	=11	20	17	Hx	7,Kx	5	= 5	19	22	= 7	32	32	=14	37	35	0	16	16
=14	30	29	= 6	26	26	= 9	30	24	= 8	45	46	= 4	40	41	= 5	20	24	=12	36	35	Hx	14,Kx	1
=12	47	47	= 5	111	110	= 7	23	21	= 7	48	53	= 3	25	24	= 4	43	44	=10	33	30	=10	20	16
=11	40	44	= 4	18	18	= 5	13	12	= 6	71	76	0	18	20	= 3	18	18	= 8	89	86	= 8	16	14
= 9	18	18	= 3	64	66	= 4	21	21	= 2	19	17	1	12	16	0	30	28	= 6	73	69	= 4	19	18
= 8	15	17	= 2	137	129	= 3	29	28	= 1	22	20	2	29	28	2	19	18	= 4	46	49	Hx	14,Kx	2
= 7	104	104	= 1	102	97	5	14	8	0	17	15	4	14	16	Hx	9,Kx	5	= 2	21	24	=16	16	17
= 6	36	40	0	42	45	Hx	6,Kx	8	1	27	26	Hx	8,Kx	5	=15	25	20	0	26	26	= 9	12	12
= 5	212	216	2	32	36	=12	19	14	4	18	15	=11	25	26	=13	24	22	2	32	28	= 7	27	24
= 4	77	79	3	123	128	=11	24	22	9	29	24	= 6	47	49	=11	12	8	4	14	15	Hx	14,Kx	3
= 3	38	34	4	55	55	Hx	6,Kx	9	Hx	7,Kx	6	= 4	22	20	= 8	13	12	Hx	11,Kx	1	=10	24	22
= 2	111	116	5	61	63	= 3	26	25	=11	41	37	= 3	13	12	= 6	21	18	=18	14	14	Hx	15,Kx	0
= 1	99	99	7	23	22	Hx	7,Kx	0	= 9	29	30	= 2	30	33	= 4	34	29	=10	20	19	=12	14	14
0	20	22	8	34	34	=16	25	22	= 7	28	27	0	29	29	= 3	19	16	= 9	22	28	Hx	15,Kx	2
1	83	79	10	25	22	=14	13	19	= 6	40	40	1	19	18	= 2	17	13	= 8	31	33	= 4	16	12
4	82	80	Hx	6,Kx	2	=12	31	34	= 5	35	37	3	35	34	2	14	11	= 7	54	53	= 3	16	13
5	23	20	=12	56	56																		

Table 3. Bond distances, bond angles and hydrogen bond lengths and angles. Estimated standard deviations in bond lengths between heavy atoms are 0.002 Å, in angles 0.1°, for bonds and angles involving hydrogen atoms 0.02 Å and 1.0°, respectively. Distances in parenthesis are corrected for librational motion.

Bond distances (Å)			Bond angles (°)	
C1 – C2	1.351	(1.357)	C6 – C1 – C2	122.8
C2 – C3	1.418	(1.425)	C1 – C2 – C3	120.5
C3 – C4	1.500	(1.510)	C2 – C3 – C4	118.9
C4 – C5	1.527	(1.534)	C3 – C4 – C5	114.5
C5 – C6	1.524	(1.530)	C4 – C5 – C6	107.7
C5 – C7	1.526	(1.534)	C4 – C5 – C7	109.5
C5 – C8	1.522	(1.531)	C4 – C5 – C8	110.3
C6 – C1	1.491	(1.495)	C5 – C6 – C1	113.3
C1 – O1	1.326	(1.329)	C6 – C5 – C7	109.5
C3 – O2	1.246	(1.249)	C6 – C5 – C8	110.5
C2 – H1	0.96		C7 – C5 – C8	109.2
C4 – H2	1.00		C2 – C1 – O1	123.9
C4 – H3	0.96		C6 – C1 – O1	113.2
C6 – H4	1.00		C2 – C3 – O2	122.5
C6 – H5	0.97		C4 – C3 – O2	118.5
C7 – H7	0.97			
C7 – H8	0.99			
C7 – H9	1.01			
C8 – H10	0.96			
C8 – H11	0.99			
C8 – H12	0.99			

Hydrogen bond lengths (Å)		Hydrogen bond angles (°)	
O1···O2	2.593	O1 – H6···O2	177
O1 – H6	0.87	C1 – O1···O2	112.7
O2···H6	1.74	C1 – O1 – H6	111
		C3 – O2···O1	129.7
		C3 – O2···H6	129

tions as shown in Table 3. The r.m.s. translational amplitudes corresponding to the discrepancy of 0.0022 Å are 0.22, 0.20, and 0.18 Å and the r.m.s. liberational amplitudes are 5.5, 3.9, and 2.9°.

DISCUSSION

Bond lengths and angles are given in Table 3 and Fig. 1. The molecular arrangement in the unit cell is shown in Fig. 2. The compound crystallizes in the *trans*-enol form as expected from spectroscopic investigations,[2,4] and there is an *inter*-molecular hydrogen bond (2.593 Å) between the hydrogen atom of the enol hydroxyl and the oxygen atom of the carbonyl group. These bonds tie the molecules in helices along the two-fold screw axes. The molecules thus form polymers rather than dimers as has been found in solution. However, formation of a dimer with two hydrogen bridges as suggested,[2,3] seems to be incompatible with normal hydrogen bonds if reasonable van der Waals distances are assumed. The O···O distance is significantly larger than corresponding distances found in analoguous *cis*-enolized β-diketones (2.43 – 2.50 Å).[6-8] In the open *trans* arrangement in dimedone, *inter*-molecular nonbonded repulsions may preferably give an expansion of the O···O distance, whereas in the *cis*-enolized β-diketones investigated,[6-8] there are varying amounts of *intra*-molecular nonbonded repulsions giving the opposite effect. The hydrogen atom (H6) is unambiguously located in an asymmetric position near O1 (O1 – H6 = 0.87 Å), and is situated very close to the least-squares plane through the conjugated enol system. The angle O1 – H6···O2 is 177°.

The distances in the enol system reveal a considerable degree of conjugation, although not as much as in the *cis*-analogues.[6-8] Similar conjugation effects have also been found in ascorbic,[13] dialuric,[14] and α-methyltetronic acids.[15] Changes in bond lengths due to hydrogen bond formation in the conjugated system in barbiturates have been discussed by Craven *et al.*[16] It is also reasonable to assume that formation of hydrogen bonds is partly responsible for the relatively large amount of conjugation in the above mentioned systems.

The conformation of the molecule might be described as an envelope. The carbon atom C5 is displaced by 0.61 Å from a least-squares plane through the other carbon atoms in the ring and the oxygen atoms (Table 4). The deviations from the plane are probably significant. The oxygen atoms and C4, and the other carbon atoms are displaced on opposite sides of the plane. The deviations thus give the cyclohexene ring a slightly curved boat-shaped form. The small deviation of O1 from a plane through C2, C1, and C6 is possibly associated with the formation of the hydrogen bond. The other deviations may be due to non-bonded interactions, expecially between O2 and C1′ across the two-fold screw axis in $x = 0$ and O2 and H1 across the centre of symmetry in $x = 0$. Very

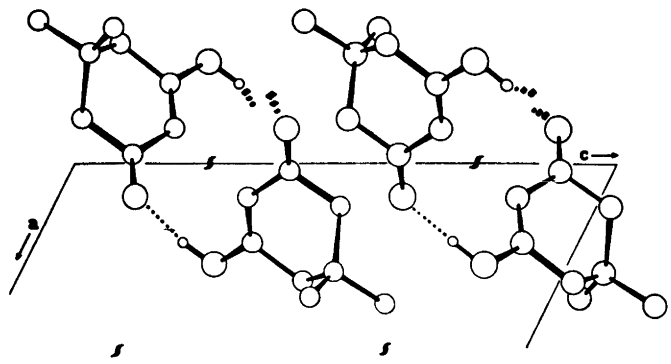

Fig. 2. The structure viewed along the *b* axis.

Table 4. Deviation (Å) of atoms from least-squares plane through parts of the ring system in dimedone. Distances to atoms not defining the plane in parenthesis.

O1	0.035
O2	0.025
C1	−0.024
C2	−0.049
C3	−0.017
C4	0.017
C6	−0.007
C5	(−0.61)
H1	(−0.063)
H6	(0.087)

similar deviations are found in the conformation of related six-membered rings.[17]

The sp^2-sp^3 and sp^3-sp^3 bonds have fairly normal values.[18] The angles inside the ring progressively decrease from values close to 120° near the double bond to a tetrahedral value at C5. The arrangements around C5, C7, and C8 are very regular, none of the angles departing much from tetrahedral values, and the hydrogen atoms at C4 and C6 are in staggered positions relative to the methyl groups at C7 and C8.

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