Refinement of the Crystal Structure of the *anti* Head-to-head Photodimer of 1,1-Dimethylnaphthalen-2(1*H*)-one [1]

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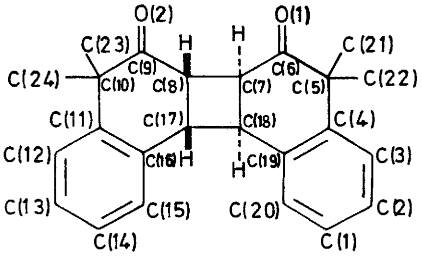
The structure of the title compound was determined by the symbolic-addition direct method and refined by least-squares to R 0·055. Crystals are monoclinic with $a = 11{\cdot}556(8)$, $b = 12{\cdot}004(8)$, $c = 13{\cdot}486(9)$ Å, $\beta = 101{\cdot}03(5)$, $Z = 4$, space group $P2_1/n$.

THE preparation of 6aα,6bβ,12bβ,12cα-tetrahydro-5,5,8,8-tetramethyldinaphtho[1,2-*a*;1′,2′-*c*]cyclobutene-6(5*H*),-7(8*H*)-dione (I) by the effect of sunlight on 1,1-dimethylnaphthalen-2(1*H*)-one and the preliminary results of the crystal-structure determination have already been given.[1]



(I)

Atom numbering system used in analysis

The refinement of the structure has now been completed and this confirms all the features of the dimer molecule discussed in the earlier communication.

EXPERIMENTAL

The crystals were obtained from an ethanol solution and the unit-cell dimensions were obtained from high sin θ reflections on Weissenberg photographs and from measurements of θ on a Wooster four-circle diffractometer with Cu-K_α radiation. Most of the intensities were recorded on a Hilger linear diffractometer with Mo-K_α radiation, but some measurements were carried out on the Wooster four-circle diffractometer with Cu-K_α radiation. Owing to computer store difficulties the least-squares refinement was restricted to 2900 reflections out of the total of 3940 recorded. No corrections were made for absorption.

Crystal Data.—$C_{24}H_{24}O_2$, $M = 344{\cdot}21$. Monoclinic, $a = 11{\cdot}556(8)$, $b = 12{\cdot}004(8)$, $c = 13{\cdot}486(9)$ Å, $\beta = 101{\cdot}03°(5)$, $U = 1836{\cdot}2$ Å^3, $D_m = 1{\cdot}241(2)$, $Z = 4$, $D_c = 1{\cdot}245$, $F(000) = 736$. Space group $P2_1/n$, from systematic absences: $0k0$ when k odd, $h0l$ when $h + l$ odd. Mo-K_α radiation, $\lambda = 0{\cdot}71069$, μ(Mo-K_α) = 0·751 cm^{-1}; Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 5·325 cm^{-1}.

Structure Determination.—The intensities were placed on an approximately absolute scale by a Wilson plot and normalized structure factors (E) calculated. Triple products were listed by computer and then the symbolic-addition procedure was carried out by hand. The following

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[1] J. Carnduff, J. Iball, D. G. Leppard, and J. N. Low, *Chem. Comm.*, 1969, 1218.

reflections with their assigned phases were used to define the origin, 528 (0°), $\bar{8}52$ (0°), $\bar{2}33$ (180°). Four additional reflections, 786, $\bar{7}71$, $\bar{6}14$, and $\bar{8}51$ were initially given symbols. From these, 236 phases were obtained and a subsequent E Fourier synthesis revealed 21 peaks identified as atoms. This was followed by a structure-factor calculation which produced a further 110 phases and a second E Fourier synthesis gave all 26 well resolved peaks which form the molecule (apart from hydrogen atoms).

Refinement.—Block-diagonal least-squares refinement with isotropic temperature parameters was followed by difference Fourier syntheses to determine the hydrogen atom positions. Those of the methyl groups, however, could not be treated satisfactorily so each group was given six ' half-hydrogen ' atoms on a circle. The hydrogen atoms were not refined but were included in the structure-factor calculations. Anisotropic temperature parameters were introduced for the carbon and oxygen atoms and the final R was 0·055. Final co-ordinates are given in Table 1. Temperature parameters and structure-factors are listed in Supplementary Publication No. SUP 21040 (17 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviation in brackets

C(1)	−1049(5)	3948(4)	5982(4)
C(2)	−2196(5)	4155(5)	5493(4)
C(3)	−2506(4)	4013(4)	4458(4)
C(4)	−1685(4)	3631(4)	3895(3)
C(5)	−2017(4)	3469(4)	2748(3)
C(6)	−1497(4)	2343(4)	2551(3)
C(7)	−183(4)	2253(4)	2883(3)
C(8)	297(4)	1173(4)	3427(3)
C(9)	1010(4)	402(4)	2908(3)
C(10)	2078(4)	−113(4)	3600(3)
C(11)	2845(4)	885(4)	4013(3)
C(12)	4070(4)	885(5)	4065(4)
C(13)	4746(5)	1800(6)	4463(5)
C(14)	4232(5)	2715(6)	4818(5)
C(15)	3017(4)	2729(5)	4766(4)
C(16)	2326(4)	1825(4)	4357(3)
C(17)	1011(4)	1865(4)	4309(3)
C(18)	369(4)	2945(3)	3836(3)
C(19)	−536(4)	3399(3)	4401(3)
C(20)	−221(4)	3582(4)	5441(3)
C(21)	−3345(5)	3475(5)	2355(4)
C(22)	−1425(5)	4370(4)	2194(4)
C(23)	2685(5)	−940(5)	3011(4)
C(24)	1662(5)	−727(4)	4480(4)
O(1)	−2084(3)	1563(3)	2177(3)
O(2)	772(3)	233(3)	2004(3)
H1(C1)	−803	4071	6792
H2(C2)	−2848	4426	5920
H3(C3)	−3398	4205	4084
H20(C20)	677	3439	5830
H12(C12)	4500	177	3796
H13(C13)	5691	1805	4498
H14(C14)	4777	3413	5131
H15(C15)	2608	3444	5046
H7(C7)	229	2396	2292
H8(C8)	−313	729	3630
H17(C17)	770	1771	5000
H18(C18)	1000	3500	3700
H41(C21)	−3660	4210	2480
H42(C21)	−3690	2890	2700
H43(C21)	−3490	3320	1620
H51(C22)	−1700	5090	2340
H52(C22)	−1700	4200	1410
H53(C22)	−550	4480	2480
H61(C23)	2100	−1540	2700
H62(C23)	2900	−620	2390
H63(C23)	3380	−1160	3480
H71(C24)	1110	−1300	4200
H72(C24)	1230	−250	4880
H73(C24)	2280	−1070	4880

RESULTS AND DISCUSSION

Bond lengths and angles are given in Table 2 and a perspective drawing of the molecule, as viewed down the

TABLE 2

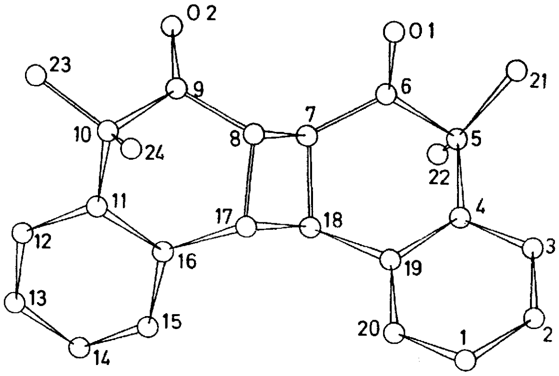
Molecular geometry, with standard deviations in parentheses

(*a*) Bond lengths (Å)

C(1)–C(2)	1·386(7)	C(13)–C(14)	1·377(10)
C(1)–C(20)	1·381(8)	C(14)–C(15)	1·392(8)
C(2)–C(3)	1·383(7)	C(12)–C(13)	1·394(9)
C(3)–C(4)	1·400(7)	C(11)–C(12)	1·404(7)
C(4)–C(5)	1·533(6)	C(10)–C(11)	1·530(6)
C(4)–C(19)	1·400(6)	C(11)–C(16)	1·399(7)
C(5)–C(6)	1·523(7)	C(9)–C(10)	1·528(6)
C(5)–C(21)	1·525(7)	C(10)–C(23)	1·524(8)
C(5)–C(22)	1·547(7)	C(10)–C(24)	1·550(7)
C(6)–C(7)	1·503(6)	C(8)–C(9)	1·499(6)
C(6)–O(1)	1·209(6)	C(9)–O(2)	1·215(5)
C(7)–C(18)	1·560(5)	C(8)–C(17)	1·552(5)
C(18)–C(19)	1·509(6)	C(16)–C(17)	1·510(6)
C(19)–C(20)	1·397(6)	C(15)–C(16)	1·396(7)
C(7)–C(8)	1·540(6)	C(17)–C(18)	1·568(6)

(*b*) Bond angles (deg.)

C(2)–C(1)–C(20)	120·0(4)	C(13)–C(14)–C(15)	119·3(6)
C(1)–C(2)–C(3)	119·9(5)	C(12)–C(13)–C(14)	121·0(5)
C(2)–C(3)–C(4)	121·1(4)	C(11)–C(12)–C(13)	120·3(6)
C(3)–C(4)–C(5)	121·6(4)	C(10)–C(11)–C(12)	121·8(4)
C(3)–C(4)–C(19)	118·6(4)	C(12)–C(11)–C(16)	118·4(4)
C(5)–C(4)–C(19)	119·9(4)	C(10)–C(11)–C(16)	119·9(4)
C(4)–C(5)–C(6)	104·9(3)	C(9)–C(10)–C(11)	104·5(4)
C(4)–C(5)–C(21)	113·0(4)	C(11)–C(10)–C(23)	114·1(4)
C(4)–C(5)–C(22)	110·5(4)	C(11)–C(10)–C(24)	109·7(4)
C(6)–C(5)–C(21)	110·4(4)	C(9)–C(10)–C(23)	110·1(4)
C(6)–C(5)–C(22)	108·1(4)	C(9)–C(10)–C(24)	109·1(4)
C(21)–C(5)–C(22)	109·7(4)	C(23)–C(10)–C(24)	109·3(4)
C(5)–C(6)–C(7)	115·0(4)	C(8)–C(9)–C(10)	114·6(4)
C(5)–C(6)–O(1)	123·5(4)	C(10)–C(9)–O(2)	123·2(4)
C(7)–C(6)–O(1)	121·6(4)	C(8)–C(9)–O(2)	122·2(4)
C(6)–C(7)–C(8)	117·0(4)	C(7)–C(8)–C(9)	118·5(4)
C(6)–C(7)–C(18)	116·0(4)	C(9)–C(8)–C(17)	115·4(3)
C(8)–C(7)–C(18)	90·1(3)	C(7)–C(8)–C(17)	90·3(3)
C(1)–C(20)–C(19)	120·5(4)	C(14)–C(15)–C(16)	120·4(5)
C(4)–C(19)–C(20)	119·9(4)	C(11)–C(16)–C(15)	120·6(4)
C(4)–C(19)–C(18)	120·7(4)	C(11)–C(16)–C(17)	120·2(4)
C(18)–C(19)–C(20)	119·4(4)	C(15)–C(16)–C(17)	119·2(4)
C(7)–C(18)–C(19)	113·3(3)	C(8)–C(17)–C(16)	113·6(4)
C(7)–C(18)–C(17)	89·0(3)	C(8)–C(17)–C(18)	89·4(3)
C(17)–C(18)–C(19)	114·4(3)	C(16)–C(17)–C(18)	116·0(4)



Perspective drawing of the molecule viewed along the normal to its mean plane

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

TABLE 3

Equations of mean planes in the form $lX + mY + nZ = d$ where X, Y, and Z are co-ordinates referred to orthogonal axes scaled in Å. [X is parallel to a, Y is parallel to b, and Z is perpendicular to a and b.] Deviations (Å) from the mean planes are given in square brackets

	l	*m*	*n*	*d*
Plane (1): the cyclobutane ring, C(7), C(8), C(17), C(18) [C(7) −0·056, C(8) 0·057, C(17) −0·056, C(18) 0·055]	−0·887	−0·123	0·446	2·269
Plane (2): C(1)—(4), C(19), C(20) [C(1) 0·001, C(2) −0·012, C(3) 0·009, C(4) 0·004, C(19) −0·01 C(20) 0·012]	0·289	0·945	−0·152	2·485
Plane (3): C(11)—(16) [C(11) 0·007, C(12) 0·000, C(13) −0·006, C(14) 0·004, C(15) 0·003, C(16) −0·009]	−0·049	−0·411	0·910	4·280
Plane (4): C(8)—(11), C(16), C(17) [C(8) 0·002, C(9) −0·319, C(10) 0·381, C(11) −0·122, C(16) −0·179, C(17) 0·236]	−0·326	−0·557	0·764	2·855
Plane (5): C(4)—(7), C(18), C(19) [C(4) −0·130, C(5) 0·376, C(6) −0·305, C(7) −0·006, C(18) 0·231, C(19) −0·168]	0·409	0·789	−0·459	0·000

normal to its mean plane, is shown in the Figure. The mean planes were calculated of the cyclobutane ring, the two benzene rings, and the other two six-membered rings (Table 3).

In Table 2 the bond lengths and bond angles of one half of the molecule are on the left and those of the other half on the right. It will be seen that the values agree, within experimental error. On the other hand, C(7)–C(8) and C(17)–C(18) differ by a small but significant amount. The molecule therefore has, in effect, a two-fold symmetry axis passing through the mid-points of these bonds. The difference in lengths would appear to be due to the repulsion of the hydrogens attached to atoms C(15) and C(20). The Figure is a perspective drawing of the molecule viewed along the normal to its mean plane.

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