

Fig. 2. Projection of the crystal structure of 8-hydroxy-5-quinoline-sulphonic acid dihydrate on the *ab* plane.

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Structure of 1,4-Dicinnamoylbenzene, C₂₄H₁₈O₂, a Photodimerizable Crystal

BY HACHIRO NAKANISHI

Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

AND MASAKI HASEGAWA AND TORU MORI

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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Abstract. $M_r = 338.4$, triclinic, $P\bar{1}$, $a = 5.798$ (1), $b = 7.923$ (1), $c = 19.307$ (6) Å, $\alpha = 89.12$ (2), $\beta = 82.12$ (2), $\gamma = 88.67$ (1)°, $V = 878.2$ (4) Å³, $Z = 2$, $D_m = 1.28$, $D_x = 1.280$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.55$ mm⁻¹, $F(000) = 356$, $T = 298$ K. Final $R = 0.050$ for 2014 observed diffractometer-measured intensities. Two independent molecules, both of which have a center of symmetry, are stacked along the *b* axis with close contacts between double bonds. Pairs of reacting double bonds have no

symmetry so that the distances between photo-adductive olefin C atoms are 3.973 (4), 4.086 (4), 3.903 (4) and 3.955 (4) Å.

Introduction. 1,4-Dicinnamoylbenzene (1,4-DCB) photodimerizes in the crystalline state to give a dimer containing two cyclobutane rings (Hasegawa, Nohara, Saigo, Mori & Nakanishi, 1983). The fact that the double photoaddition (named 'dupledimerization' by the authors) is such a rare solid-state photocyclization –

occurring for bis(3,4-dichlorostyryl) ketone (Green & Schmidt, 1970), carbonyldiacrylic acid (Midorikawa, 1953), and its methyl ester (Stobbe & Färber, 1925), for which the structures of the dimers in the crystalline states are unknown – led us to analyze the crystal structure of 1,4-DCB.

Experimental. 1,4-DCB prepared by condensation of 1,4-diacetylbenzene with benzaldehyde; yellowish plate-like crystals (from a 1:1 THF/ethyl acetate solution), 0.35 × 0.35 × 0.04 mm. D_m by flotation in a mixture of cyclohexane and carbon tetrachloride. Nicolet automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell dimensions determined by least squares with 2θ values of 25 high-angle reflexions. Intensity data in range $2\theta \leq 130^\circ$ (range of hkl : 0–6, 0–8, –22–22) collected by means of $2\theta/\omega$ scanning, scanning speed 2–16° (2θ) min⁻¹, scan width 1.0° (ω) plus α_1 – α_2 divergence. Three reflexions monitored periodically showed no significant intensity deterioration; no absorption correction. 2652 measured independent reflexions, 552 unobserved with $I < 1.96\sigma(I)$. Structure solved by direct methods and refined using *SHELX76* (Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1.0$; H (from difference map) isotropic; final $R = 0.050$ for 2014 reflexions [$|F_o| \geq 5\sigma(|F_o|)$]. $(\Delta/\sigma)_{\max} = 0.38$. $\Delta\rho$ excursions –0.19 ~ 0.15 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters and bond distances and angles are listed in Tables 1* and 2 respectively. The numbering system used is shown in Fig. 1. The molecule has a center of symmetry, as found in the general photoreactive diolefinic compounds, but is quite different from them in its non-planarity. The terminal benzene ring rotates 18.4° about C(7)–C(8) from the enonic plane, and the central benzene ring rotates 31.9° about C(3)–C(4) in the same direction, *i.e.* the angle between the two benzene rings is 50.3°.

Fig. 2 shows the crystal structure projected onto the (100) plane; the photoadduct olefinic C atoms are expressed as A, A' ; B, B' , etc. The molecules are stacked along the b axis and the two reacting molecules are *skew* to each other. These non-planar and *skew* molecular arrangements result in the fact that there is no symmetry relation between the reacting double

bonds. The projection onto the plane of the central benzene ring (Fig. 1) reveals obvious *skew* orientation in the crystal. Moreover, the angle between these two ethylenic planes is 21.5°.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters of 1,4-DCB

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	0.7217 (6)	0.4314 (4)	0.4915 (2)	0.051
C(2)	0.3680 (5)	0.4991 (4)	0.4454 (2)	0.051
C(3)	0.5923 (5)	0.4305 (4)	0.4356 (2)	0.047
C(4)	0.7032 (6)	0.3609 (4)	0.3678 (2)	0.054
O(5)	0.9162 (4)	0.3489 (4)	0.3546 (1)	0.078
C(6)	0.5537 (6)	0.3049 (4)	0.3163 (2)	0.053
C(7)	0.6408 (6)	0.2734 (4)	0.2513 (2)	0.050
C(8)	0.5168 (5)	0.2126 (4)	0.1954 (2)	0.047
C(9)	0.6177 (6)	0.2288 (5)	0.1258 (2)	0.057
C(10)	0.5051 (7)	0.1728 (5)	0.0718 (2)	0.069
C(11)	0.2910 (7)	0.0969 (5)	0.0870 (2)	0.069
C(12)	0.1899 (7)	0.0789 (5)	0.1554 (2)	0.064
C(13)	0.2995 (6)	0.1381 (4)	0.2098 (2)	0.053
C(1')	0.2992 (5)	0.0337 (4)	0.4713 (2)	0.052
C(2')	0.3180 (6)	0.0919 (5)	0.5373 (2)	0.051
C(3')	0.5218 (5)	0.0579 (4)	0.5667 (2)	0.046
C(4')	0.5581 (6)	0.1247 (4)	0.6365 (2)	0.051
O(5')	0.7568 (4)	0.1258 (3)	0.6519 (1)	0.065
C(6')	0.3572 (6)	0.1849 (4)	0.6856 (2)	0.052
C(7')	0.3815 (6)	0.2250 (4)	0.7503 (2)	0.050
C(8')	0.2012 (5)	0.2862 (4)	0.8047 (2)	0.047
C(9')	0.2356 (6)	0.2716 (5)	0.8749 (2)	0.057
C(10')	0.0665 (7)	0.3294 (5)	0.9280 (2)	0.068
C(11')	–0.1365 (7)	0.4055 (5)	0.9116 (2)	0.065
C(12')	–0.1705 (6)	0.4220 (5)	0.8422 (2)	0.062
C(13')	–0.0057 (6)	0.3627 (4)	0.7893 (2)	0.054

Table 2. Bond distances (Å) and angles (°)

C(1)–C(2)	1.375 (4)	C(1')–C(2')	1.380 (5)
C(1)–C(3)	1.397 (4)	C(1')–C(3')	1.384 (4)
C(2)–C(3)	1.388 (4)	C(2')–C(3')	1.399 (4)
C(3)–C(4)	1.485 (4)	C(3')–C(4')	1.498 (4)
C(4)–O(5)	1.228 (4)	C(4')–O(5')	1.229 (4)
C(4)–C(6)	1.485 (4)	C(4')–C(6')	1.473 (4)
C(6)–C(7)	1.313 (4)	C(6')–C(7')	1.319 (4)
C(7)–C(8)	1.469 (4)	C(7')–C(8')	1.457 (4)
C(8)–C(9)	1.395 (4)	C(8')–C(9')	1.400 (4)
C(9)–C(10)	1.387 (5)	C(9')–C(10')	1.393 (5)
C(10)–C(11)	1.385 (5)	C(10')–C(11')	1.383 (5)
C(11)–C(12)	1.375 (5)	C(11')–C(12')	1.385 (5)
C(12)–C(13)	1.392 (5)	C(12')–C(13')	1.380 (5)
C(13)–C(8)	1.395 (4)	C(13')–C(8')	1.397 (4)
C(1)–C(2)–C(3)	120.3 (3)	C(1')–C(2')–C(3')	119.6 (3)
C(2)–C(1)–C(3)	121.2 (3)	C(2')–C(1')–C(3')	121.4 (3)
C(1)–C(3)–C(2)	118.4 (3)	C(1')–C(3')–C(2')	119.0 (3)
C(1)–C(3)–C(4)	118.6 (3)	C(1')–C(3')–C(4')	118.7 (3)
C(2)–C(3)–C(4)	123.0 (3)	C(2')–C(3')–C(4')	122.3 (3)
C(3)–C(4)–O(5)	120.4 (3)	C(3')–C(4')–O(5')	118.7 (3)
C(3)–C(4)–C(6)	119.3 (3)	C(3')–C(4')–C(6')	120.0 (3)
C(6)–C(4)–O(5)	120.3 (3)	C(6')–C(4')–O(5')	121.2 (3)
C(4)–C(6)–C(7)	121.3 (3)	C(4')–C(6')–C(7')	120.9 (3)
C(6)–C(7)–C(8)	127.4 (3)	C(6')–C(7')–C(8')	127.4 (3)
C(7)–C(8)–C(13)	121.8 (3)	C(7')–C(8')–C(13')	122.2 (3)
C(7)–C(8)–C(9)	119.6 (3)	C(7')–C(8')–C(9')	119.6 (3)
C(8)–C(9)–C(10)	121.1 (4)	C(8')–C(9')–C(10')	120.8 (3)
C(9)–C(10)–C(11)	119.6 (4)	C(9')–C(10')–C(11')	120.0 (4)
C(10)–C(11)–C(12)	120.0 (4)	C(10')–C(11')–C(12')	119.4 (4)
C(11)–C(12)–C(13)	120.6 (4)	C(11')–C(12')–C(13')	121.0 (4)
C(12)–C(13)–C(8)	120.0 (3)	C(12')–C(13')–C(8')	120.5 (3)

* Lists of structure factors, anisotropic thermal parameters of C and O atoms, least-squares planes of the expected planar moieties, atomic coordinates of H atoms and bond distances between H and non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39010 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

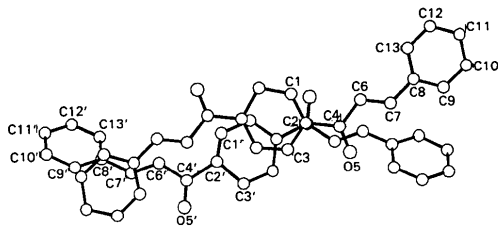


Fig. 1. The intermolecular overlapping of reactive molecules, viewed along the normal to the central benzene ring.

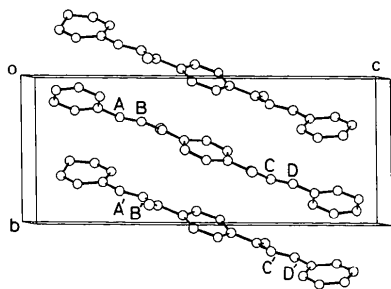


Fig. 2. The crystal structure projected onto the (100) plane. Intermolecular distances $A-A'$, $B-B'$, $C-C'$, and $D-D'$ are 3.973, 4.086, 3.903, and 3.955 Å, respectively.

Consequently, it is noteworthy that 1,4-DCB anomalously dimerizes in spite of a non-parallel arrangement of both photoreactive C—C double-bond pairs. Although the solid-state photodimerization of 7-methoxycoumarin, packed non-parallel in crystals, has been reported (Ramasubbu, Row, Venkatesan, Ramamurthy & Rao, 1982), this reaction is the first example of a non-parallel diolefinic compound to dimerize on irradiation.

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5-Benzylidene-1,2,3,4,4a,5,6,7,8,9a-decahydro-4a-morpholino-9-phenylxanthene, $C_{30}H_{35}NO_2$ (DBM), and 5-Benzylidene-1,2,3,4,4a,5,6,7,8,9a-decahydro-9-phenyl-4a-piperidinoxanthene, $C_{31}H_{37}NO$ (DBP)

BY M. N. PONNUSWAMY AND JAMES TROTTER

Department of Chemistry, The University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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Abstract. DBM, DBP, $M_r = 441.62$, 439.65, triclinic, $P\bar{1}$, $a = 10.945$ (2), 10.879 (2), $b = 13.545$ (3), 13.502 (5), $c = 9.478$ (1), 9.587 (2) Å, $\alpha = 99.62$ (2), 99.12 (2), $\beta = 114.36$ (1), 114.55 (2), $\gamma = 73.02$ (2), 73.66 (2)°, $V = 1222.4$ (4), 1227.8 (7) Å³, $Z = 2$, D_m (flotation) = 1.160, 1.185, $D_x = 1.199$, 1.189 g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.748$, 0.690 cm⁻¹, $F(000) = 476$, 476, room temperature, final $R = 0.059$, 0.051 for 2579, 3022 reflections. The crystals are isostructural, both molecules having *cis*-fused *B/C* rings, with the morpholino and piperidino substituents axially oriented with respect to the *C* ring.

Introduction. In a study of the synthesis of dihydropyrans (Balaji Rao & Bhide, 1969; Reddy, 1982; Reddy & Balaji Rao, 1982), spectroscopic data, namely IR and NMR, suggested two different configurations

for (1) and (2), with *trans*- and *cis*-fused *B/C* ring junctions, respectively. Since it is unusual that a remote oxygen atom should play such a decisive role in the course of the reaction, crystal structure studies have been undertaken to establish the molecular configurations conclusively.

