

Diethyl 2-( $\alpha$ -Methoxymethylene)-3-methyl-4,6-dimethoxyhomophthalate

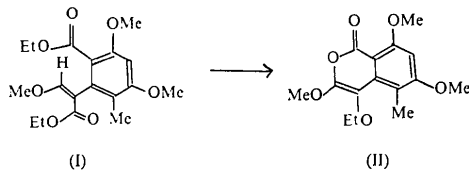
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**Abstract.**  $C_{18}H_{24}O_7$ , M.W. 352.06; monoclinic, space group  $P2_1/a$ ;  $a=19.217$  (3),  $b=8.315$  (1),  $c=13.730$  (2) Å,  $\beta=122.23$  (1) $^\circ$  (from double-radius Weissenberg photographs with Al calibration lines);  $Z=4$ ,  $D_o=1.256$ ,  $D_c=1.260$  g cm $^{-3}$ ;  $\mu=9.35$  cm $^{-1}$ . The final  $R=0.074$ .

**Introduction.** The title compound (I) is an intermediate in the synthesis of the naturally occurring 4-substituted isocoumarin (II) (Aldridge, Grove & Turner, 1966).



The crystal structure determination was undertaken to obtain information about the stereochemistry of (I) in relation to this synthesis.

\* Deceased, 5 August 1973.

The crystal (Uemura & Sakan, 1976) was obtained as a colourless prism by recrystallization from a diethyl ether solution. Intensity data were collected by a multiple-film equi-inclination integrating Weissenberg method, with the intensities obtained *via* comparison with a standard strip. Nickel-filtered Cu  $K\alpha$  radiation was used for data collection. The crystal used for intensity collection had approximate dimensions  $0.3 \times 0.3 \times 0.4$  mm. 3987 reflexions were measured, with 3019 considered observed and the remainder (968) treated as unobserved. Lorentz and polarization corrections were applied to the intensities, but spot size, absorption and extinction corrections were not applied. The intensities were placed on a common scale by using the procedure of Hamilton, Rollett & Sparks (1965).

The structure was determined by the symbolic addition procedure (Karle & Karle, 1966). All hydrogen atoms were found in a difference Fourier map, although there were several ghost peaks. All atoms were refined anisotropically, except hydrogens which were refined isotropically by a block-diagonal least-squares procedure, minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where

Table 1. The final positional and thermal parameters

The parameters and standard deviations (in parentheses) for the last significant digit of the non-hydrogen atoms are multiplied by  $10^4$ . The expression for the thermal parameter is  $\exp[-(B_{11}h^2 + \dots + B_{12}hk + \dots)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	1934 (1)	1575 (3)	1279 (2)	36 (1)	122 (4)	76 (2)	6 (3)	67 (2)	10 (4)
C(2)	2341 (1)	1430 (3)	2472 (2)	39 (1)	124 (4)	76 (2)	-5 (3)	72 (2)	-5 (4)
C(3)	3101 (2)	634 (3)	3103 (2)	40 (1)	155 (4)	68 (2)	3 (3)	59 (2)	0 (4)
C(4)	3420 (1)	-35 (3)	2487 (2)	34 (1)	158 (4)	70 (2)	15 (3)	51 (2)	3 (4)
C(5)	3018 (1)	90 (3)	1296 (2)	33 (1)	160 (4)	69 (2)	15 (3)	56 (2)	-5 (4)
C(6)	2277 (1)	906 (3)	700 (2)	35 (1)	140 (4)	65 (2)	12 (3)	57 (2)	7 (4)
C(7)	1138 (2)	2468 (3)	613 (2)	40 (1)	140 (1)	86 (2)	12 (3)	81 (2)	6 (4)
C(8)	-300 (2)	2331 (5)	-128 (5)	41 (1)	254 (8)	265 (7)	60 (5)	112 (5)	169 (12)
C(9)	-679 (3)	2140 (6)	550 (5)	67 (2)	325 (11)	249 (7)	57 (8)	159 (7)	-20 (14)
C(10)	1949 (2)	2149 (3)	3063 (2)	49 (1)	143 (4)	82 (2)	-2 (3)	92 (3)	-9 (4)
C(11)	1475 (2)	1031 (4)	3332 (3)	61 (1)	162 (5)	114 (3)	2 (4)	128 (3)	8 (5)
C(12)	518 (3)	727 (5)	3896 (5)	95 (3)	250 (8)	241 (6)	2 (7)	255 (7)	84 (11)
C(13)	-66 (3)	1734 (6)	4010 (5)	87 (3)	328 (11)	234 (7)	-13 (8)	225 (8)	9 (13)
C(14)	1981 (2)	3702 (4)	3296 (2)	57 (1)	157 (5)	96 (2)	-3 (4)	108 (3)	-12 (5)
C(15)	2305 (3)	6405 (4)	3228 (4)	117 (3)	146 (6)	169 (5)	-42 (6)	200 (6)	-52 (8)
C(16)	3562 (2)	503 (4)	4392 (2)	53 (1)	255 (7)	67 (2)	19 (5)	62 (3)	2 (6)
C(17)	4590 (2)	-1289 (4)	2617 (3)	35 (1)	235 (6)	93 (2)	45 (4)	48 (3)	-23 (6)
C(18)	2090 (2)	306 (5)	-1137 (2)	44 (1)	297 (7)	69 (2)	40 (5)	65 (3)	-17 (6)
O(1)	1055 (1)	3758 (3)	181 (2)	51 (1)	189 (4)	188 (3)	56 (3)	128 (3)	170 (6)
O(2)	529 (1)	1665 (3)	555 (3)	38 (1)	178 (4)	216 (3)	27 (3)	101 (3)	147 (6)
O(3)	1479 (2)	-404 (3)	3255 (3)	101 (2)	133 (4)	224 (4)	-4 (4)	243 (5)	12 (5)
O(4)	1019 (2)	1778 (3)	3666 (2)	77 (1)	176 (4)	168 (3)	-12 (3)	191 (3)	-5 (5)
O(5)	2444 (2)	4728 (3)	3092 (2)	82 (1)	138 (3)	144 (2)	-38 (3)	169 (3)	-41 (4)
O(6)	4155 (1)	-825 (3)	3145 (2)	41 (1)	251 (4)	74 (1)	67 (3)	48 (2)	21 (4)
O(7)	1828 (1)	1104 (3)	-470 (1)	43 (1)	209 (4)	63 (1)	52 (3)	60 (2)	21 (3)

Table 1 (cont.)

The positional parameters of the hydrogen atoms are multiplied by  $10^3$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(5)H(1)	325 (2)	-39 (3)	90 (2)	4.6 (6)
C(8)H(2)	-70 (3)	231 (6)	-87 (4)	9.9 (12)
C(8)H(3)	-13 (2)	314 (5)	34 (3)	8.1 (10)
C(9)H(4)	-75 (3)	94 (5)	61 (4)	10.0*
C(9)H(5)	-124 (3)	250 (6)	22 (4)	9.7 (12)
C(9)H(6)	-15 (4)	285 (8)	145 (6)	10.0*
C(12)H(7)	88 (3)	-3 (6)	452 (4)	9.7 (12)
C(12)H(8)	-14 (3)	68 (6)	322 (4)	10.0*
C(13)H(9)	-51 (2)	107 (5)	423 (4)	8.8 (11)
C(13)H(10)	36 (4)	297 (10)	473 (6)	10.0*
C(13)H(11)	-39 (4)	216 (8)	319 (6)	10.0*
C(14)H(12)	163 (2)	419 (3)	359 (2)	4.3 (6)
C(15)H(13)	228 (3)	645 (6)	402 (4)	10.0*
C(15)H(14)	167 (4)	669 (9)	271 (6)	10.0*
C(15)H(15)	260 (3)	706 (6)	297 (4)	10.0*
C(16)H(16)	412 (2)	60 (5)	472 (4)	7.8 (10)
C(16)H(17)	341 (3)	125 (5)	474 (4)	9.6 (12)
C(16)H(18)	348 (3)	-48 (6)	462 (4)	10.0*
C(17)H(19)	420 (2)	-204 (5)	195 (3)	7.1 (9)
C(17)H(20)	475 (2)	-33 (4)	237 (3)	6.3 (8)
C(17)H(21)	512 (2)	-175 (5)	320 (3)	7.2 (9)
C(18)H(22)	168 (2)	55 (4)	-193 (3)	6.1 (8)
C(18)H(23)	266 (2)	69 (4)	-89 (3)	6.4 (8)
C(18)H(24)	207 (2)	-97 (4)	-103 (3)	6.4 (8)

\* Thermal parameter is fixed.

$w=0.6$  for  $|F_o| < 1.5$ ;  $w=1.0$  for  $1.5 \leq |F_o| \leq 2.0$ ; and  $w=2.0/|F_o|$  for  $|F_o| > 2.0$ . The final agreement indices are  $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.074$  for all atoms and  $0.092$  for non-hydrogen atoms; and  $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2} = 0.105$  for all atoms and  $0.123$  for non-hydrogen atoms. Some of the hydrogens had large thermal parameters ( $11 \sim 16 \text{ \AA}^2$ ) and were fixed at  $10 \text{ \AA}^2$  during refinement. The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962), except for hydrogen, for which the scattering factor of Stewart, Davidson & Simpson (1965) was used. The positional and thermal parameters are given in Table 1.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31772 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

C(1)-C(2)	1.394 (4)	C(8)-C(9)	1.465 (11)
C(1)-C(6)	1.391 (5)	C(8)-O(2)	1.460 (4)
C(1)-C(7)	1.495 (3)	C(10)-C(11)	1.480 (5)
C(2)-C(3)	1.404 (3)	C(10)-C(14)	1.324 (4)
C(2)-C(10)	1.495 (5)	C(11)-O(3)	1.198 (4)
C(3)-C(4)	1.398 (5)	C(11)-O(4)	1.339 (6)
C(3)-C(16)	1.502 (4)	C(12)-C(13)	1.474 (9)
C(4)-C(5)	1.391 (4)	C(12)-O(4)	1.454 (7)
C(4)-O(6)	1.372 (3)	C(14)-O(5)	1.336 (5)
C(5)-C(6)	1.384 (3)	C(15)-O(5)	1.441 (5)
C(6)-O(7)	1.369 (3)	C(17)-O(6)	1.421 (5)
C(7)-O(1)	1.195 (4)	C(18)-O(7)	1.423 (5)
C(7)-O(2)	1.312 (4)		
C(2)-C(1)-C(6)	119.8 (2)	C(1)-C(7)-O(2)	111.9 (2)
C(2)-C(1)-C(7)	120.8 (3)	O(1)-C(7)-O(2)	123.2 (3)
C(6)-C(1)-C(7)	119.4 (2)	C(9)-C(8)-O(2)	107.0 (4)
C(1)-C(2)-C(3)	120.9 (3)	C(2)-C(10)-C(11)	116.1 (3)
C(1)-C(2)-C(10)	118.3 (2)	C(2)-C(10)-C(14)	123.3 (3)
C(3)-C(2)-C(10)	120.9 (2)	C(11)-C(10)-C(14)	120.5 (4)
C(2)-C(3)-C(4)	117.5 (2)	C(10)-C(11)-O(3)	124.7 (4)
C(2)-C(3)-C(16)	121.8 (3)	C(10)-C(11)-O(4)	113.4 (3)
C(4)-C(3)-C(16)	120.7 (3)	O(3)-C(11)-O(4)	121.9 (4)
C(3)-C(4)-C(5)	122.3 (2)	C(13)-C(12)-O(4)	108.2 (4)
C(3)-C(4)-O(6)	115.0 (2)	C(10)-C(14)-O(5)	121.7 (4)
C(5)-C(4)-O(6)	122.8 (3)	C(7)-O(2)-C(8)	118.6 (3)
C(4)-C(5)-C(6)	118.9 (3)	C(11)-O(4)-C(12)	115.2 (3)
C(5)-C(6)-C(1)	120.7 (2)	C(14)-O(5)-C(15)	115.3 (4)
C(5)-C(6)-O(7)	124.0 (3)	C(4)-O(6)-C(17)	118.2 (2)
C(1)-C(6)-O(7)	115.4 (2)	C(16)-O(7)-C(18)	118.8 (2)
C(1)-C(7)-O(1)	124.9 (3)		

**Discussion.** The bond lengths and angles are given in Table 2. There are no abnormal values. Fig. 1 shows a stereoscopic view of the molecule. One can roughly consider the molecule as being constructed of three planar sections: (1) a 3-methyl-4,6-dimethoxybenzene group; (2) an ethoxycarbonyl group; and (3) the remainder of the molecule. Methyl groups in each section deviate significantly from the least-squares planes given in Table 3 and were not included in the least-squares plane calculations. The benzene ring is essentially planar; the vicinal C(7), C(10), C(16), O(6) and O(7) atoms deviate slightly from the ring plane so as to avoid abnormal short contacts with each other. Sections (2) and (3) also exhibit good planarity as shown in Table 3. The dihedral angles between the planes of sections (1) and (2) and sections (1) and (3) are  $72.7$  and  $80.9^\circ$  respectively. The torsional angles C(2)-C(1)-C(7)-O(2) and C(1)-C(2)-C(10)-C(14) are

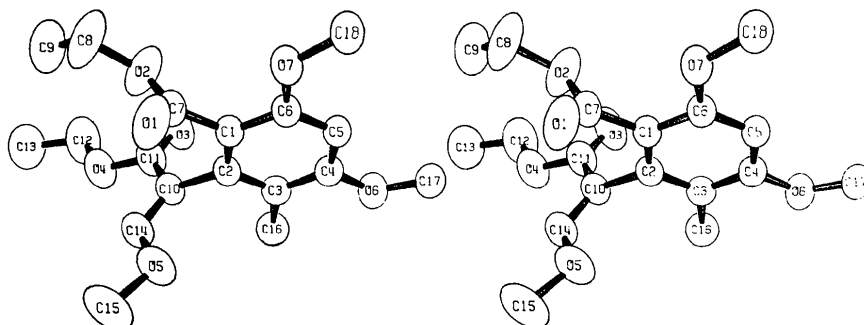


Fig. 1. A stereoscopic illustration of the molecule.

72.5 and 86.4° respectively. From this molecular conformation, a 72.5° rotation about the C(1)–C(7) bond and an 86.4° rotation about the C(2)–C(10) bond are necessary for the formation of an isocoumarin ring linking the C(14) and O(2) atoms. The C(16) methyl group, however, sterically hinders the latter rotation. This cyclization has been shown to occur readily when the methyl group does not reside in the 3-position of the benzene ring (Haworth, Pindred & Jefferies, 1954).

The present X-ray investigation suggests that the synthesis of a methyl-substituted isocoumarin com-

pound should be approached by synthesizing a compound similar to the title compound but with a smaller substituent than the methyl group in the 3-position of the benzene ring. The cyclization of such a compound should then occur, after which one could exchange a methyl group for the small substituent.

All calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University, using programs *UNICS* (Sakurai, 1967) and *SHILCS* (Hirotsu, Yoshioka, Takusagawa & Nakatsu, 1974).

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Table 3. *Least-squares planes and deviations* (Å)

The coordinate system used for the least-squares planes is:  
 $X = ax + cz\cos\beta$ ;  $Y = by$ ;  $Z = cz\sin\beta$ .

(1) Equation of least-squares plane for C(1), C(2), C(3), C(4), C(5) and C(6):

$$0.5070X + 0.8558Y + 0.1023Z = 2.6815$$

C(1)	0.000	C(10)	-0.026
C(2)	-0.007	C(16)	0.038
C(3)	0.007	C(17)	0.212
C(4)	-0.002	C(18)	-0.140
C(5)	-0.004	O(6)	-0.014
C(6)	0.005	O(7)	0.003
C(7)	0.028		

(2) Equation of least-squares plane for C(7), C(8), O(1) and O(2):

$$-0.3453X + 0.4563Y + 0.8200Z = 0.9357$$

C(7)	-0.015	O(2)	0.013
C(8)	-0.006	C(1)	-0.080
O(1)	0.008	C(9)	0.989

(3) Equation of least-squares plane for C(10), C(11), C(12), C(14), O(3), O(4) and O(5):

$$0.2830X - 0.0960Y + 0.9542Z = 3.7329$$

C(10)	-0.084	O(4)	-0.017
C(11)	-0.010	O(5)	0.004
C(12)	0.001	C(2)	-0.346
C(14)	0.069	C(13)	-0.298
O(3)	0.036	C(15)	-0.082

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