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# Structure of Ethyl 4-Methyl-2-oxo-3-phenyl-2,3-dihydro-5-benzofurancarboxylate

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**Abstract.** $C_{18}H_{16}O_4$, $M_r = 296{\cdot}322$, monoclinic, $C2/c$, $a = 22{\cdot}92\,(3)$, $b = 8{\cdot}06\,(2)$, $c = 22{\cdot}72\,(2)$ Å, $\beta = 133{\cdot}24\,(3)°$, $V = 3057{\cdot}61\,(3)$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}30$, $D_x = 1{\cdot}29$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7135 Å, $\mu = 0{\cdot}85$ cm$^{-1}$, $F(000) = 1248{\cdot}0$, $T = 298\,(1)$ K, final $R = 0{\cdot}067$ for 1536 observed reflections. The structure has two phenyl rings (I,III), one of which (III) is fused to the furan ring (II). Ring I is perpendicular to III and nearly perpendicular to II, which is in a twist conformation. The C(5)—C(9) single bond is shortened [1·491 (10) Å] owing to the adjacent double bonds.

**Introduction.** The crystal and molecular structure of the title compound was solved as a part of our program of structure analyses of a group of benzofuran derivatives.

**Experimental.** Crystals from ethanol; density measured by flotation in benzene–bromoform, crystal size 0·35 × 0·45 × 0·45 mm; intensity data collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation; cell parameters refined by least-squares fitting of the setting angles of 25 high-angle reflections ($14 \le \theta \le 18°$). 2087 independent reflections collected ($-21 \le h \le 23$, $0 \le k \le 9$, $-22 \le l \le 23$; $2 \le \theta \le 60°$), correction for Lp but not for absorption; space group $C2/c$ or $Cc$ ($hkl$, $h+k$ odd; $h0l$, $h$ and $l$ odd; the space group was shown to be $C2/c$ by the structure analysis); structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); $R$ value was 0·089 after full-matrix least-squares refinement using the program *SHELX76* (Sheldrick, 1976) of all the non-H atoms with anisotropic thermal parameters; all the H atoms located from $\Delta F$ synthesis. Each H atom was assigned the isotropic temperature factor of the attached non-H atom; final two cycles of refinement of the positional and anisotropic thermal parameters of the non-H atoms keeping all the parameters of the H atoms fixed with 1536 observed reflections [$I \ge 2{\cdot}5\sigma(I)$] led to a final $R = 0{\cdot}067$, $S = 1{\cdot}88$, number of parameters refined = 199; $\Delta/\sigma < 0{\cdot}05$ in final refinement; residual $\Delta\rho = 0{\cdot}6$ e Å$^{-3}$. Atomic scattering factors from *Interna-*

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Table 1. *Fractional coordinates and equivalent isotropic temperature factors of non*-H *atoms with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·4238 (2) | −0·2750 (4) | 0·7602 (3) | 0·0658 |
| O(2) | 0·4770 (3) | −0·3009 (5) | 0·8868 (3) | 0·0882 |
| O(3) | 0·3291 (3) | 0·4220 (6) | 0·5812 (3) | 0·0940 |
| O(4) | 0·3700 (3) | 0·2689 (5) | 0·5338 (3) | 0·0833 |
| C(1′) | 0·3860 (3) | 0·0301 (6) | 0·8364 (3) | 0·0477 |
| C(2′) | 0·3065 (3) | −0·0018 (8) | 0·7746 (3) | 0·0712 |
| C(3′) | 0·2504 (4) | 0·0403 (9) | 0·7850 (4) | 0·0820 |
| C(4′) | 0·2830 (4) | 0·1069 (9) | 0·8574 (4) | 0·0777 |
| C(5′) | 0·3645 (4) | 0·1406 (8) | 0·9188 (4) | 0·0776 |
| C(6′) | 0·4155 (3) | 0·1001 (7) | 0·9071 (3) | 0·0636 |
| C(2) | 0·4518 (3) | −0·2110 (8) | 0·8327 (4) | 0·0639 |
| C(3) | 0·4427 (3) | −0·0220 (7) | 0·8260 (3) | 0·0543 |
| C(3a) | 0·4132 (3) | 0·0079 (6) | 0·7439 (3) | 0·0485 |
| C(4) | 0·3985 (3) | 0·1557 (6) | 0·7046 (3) | 0·0507 |
| C(5) | 0·3717 (3) | 0·1406 (7) | 0·6269 (3) | 0·0536 |
| C(6) | 0·3599 (3) | −0·0138 (8) | 0·5933 (3) | 0·0614 |
| C(7) | 0·3753 (3) | −0·1609 (7) | 0·6334 (4) | 0·0617 |
| C(7a) | 0·4026 (3) | −0·1421 (6) | 0·7095 (3) | 0·0546 |
| C(8) | 0·4124 (4) | 0·3167 (7) | 0·7449 (4) | 0·0699 |
| C(9) | 0·3542 (3) | 0·2931 (8) | 0·5800 (4) | 0·0655 |
| C(10) | 0·3512 (5) | 0·4109 (10) | 0·4824 (5) | 0·1225 |
| C(11) | 0·3839 (6) | 0·3738 (11) | 0·4483 (6) | 0·1396 |

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| O(1)—C(2) | 1·394 (11) | C(6)—C(7) | 1·385 (9) |
| O(1)—C(7a) | 1·394 (7) | C(7)—C(7a) | 1·386 (11) |
| O(2)—C(2) | 1·182 (9) | C(9)—O(4) | 1·339 (14) |
| C(2)—C(3) | 1·531 (9) | C(9)—O(3) | 1·197 (9) |
| C(3)—C(3a) | 1·505 (10) | C(10)—O(4) | 1·473 (11) |
| C(3)—C(1′) | 1·530 (12) | C(10)—C(11) | 1·531 (23) |
| C(3a)—C(4) | 1·385 (8) | C(1′)—C(2′) | 1·361 (6) |
| C(3a)—C(7a) | 1·368 (8) | C(1′)—C(6′) | 1·367 (9) |
| C(4)—C(5) | 1·422 (10) | C(2′)—C(3′) | 1·427 (14) |
| C(4)—C(8) | 1·491 (9) | C(3′)—C(4′) | 1·367 (12) |
| C(5)—C(6) | 1·386 (9) | C(4′)—C(5′) | 1·392 (9) |
| C(5)—C(9) | 1·490 (10) | C(5′)—C(6′) | 1·403 (14) |

| | | | |
|---|---|---|---|
| C(2)—O(1)—C(7a) | 108·0 (4) | C(3a)—C(4)—C(5) | 115·7 (5) |
| C(9)—O(4)—C(10) | 114·8 (6) | C(3a)—C(4)—C(8) | 119·8 (5) |
| O(1)—C(2)—O(2) | 120·2 (6) | C(5)—C(4)—C(8) | 124·4 (5) |
| O(2)—C(2)—C(3) | 130·5 (6) | C(4)—C(5)—C(6) | 121·0 (5) |
| O(1)—C(2)—C(3) | 109·2 (5) | C(4)—C(5)—C(9) | 119·5 (5) |
| C(1′)—C(3)—C(2) | 109·3 (5) | C(6)—C(5)—C(9) | 119·4 (5) |
| C(2)—C(3)—C(3a) | 101·4 (5) | C(5)—C(6)—C(7) | 122·7 (5) |
| C(1′)—C(3)—C(3a) | 116·1 (5) | C(6)—C(7)—C(7a) | 114·9 (5) |
| C(3)—C(3a)—C(4) | 129·9 (5) | O(1)—C(7a)—C(3a) | 112·5 (5) |
| C(3)—C(3a)—C(7a) | 108·6 (4) | O(1)—C(7a)—C(7) | 123·4 (5) |
| C(4)—C(3a)—C(7a) | 121·5 (5) | C(3a)—C(7a)—C(7) | 124·1 (5) |
| O(3)—C(9)—O(4) | 122·5 (6) | C(1′)—C(2′)—C(3′) | 118·8 (5) |
| O(3)—C(9)—C(5) | 126·7 (7) | C(2′)—C(3′)—C(4′) | 117·3 (7) |
| O(4)—C(9)—C(5) | 110·8 (6) | C(3′)—C(4′)—C(5′) | 122·3 (9) |
| O(4)—C(10)—C(11) | 106·8 (7) | C(4′)—C(5′)—C(6′) | 119·0 (7) |
| C(2′)—C(1′)—C(3) | 117·9 (5) | C(1′)—C(6′)—C(5′) | 120·9 (6) |
| C(2′)—C(1′)—C(6′) | 121·7 (7) | | |
| C(3)—C(1′)—C(6′) | 120·4 (6) | | |

*tional Tables for X-ray Crystallography* (1974). Final atomic parameters are listed in Table 1.*

**Discussion.** The bond lengths and bond angles are listed in Table 2. The conformation of the benzofuran derivative is represented in Fig. 1. The maximum deviations of individual atoms from the mean plane of the ring are −0·013 (7) and −0·010 (8) Å for the C(4′) and C(5) atoms in rings I and III. The maximum deviations from the mean value for the endocyclic angles are 5·1 (5) and 2·7 (5)° for the angles C(7)—C(7a)—C(3a) and C(4′)—C(3′)—C(2′). The algebraic sums of the torsion angles are approximately zero in each ring.

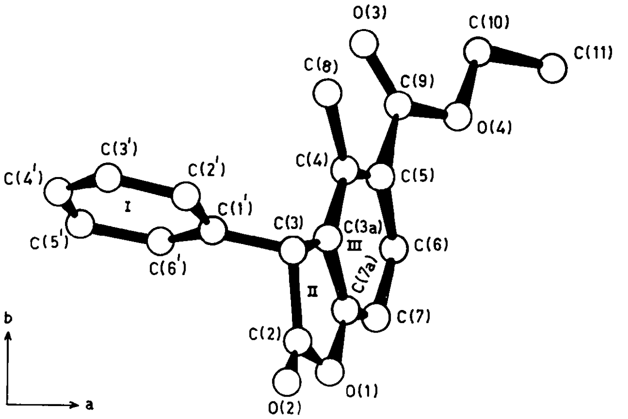

Fig. 1. A view of the title molecule with the atom numbering.

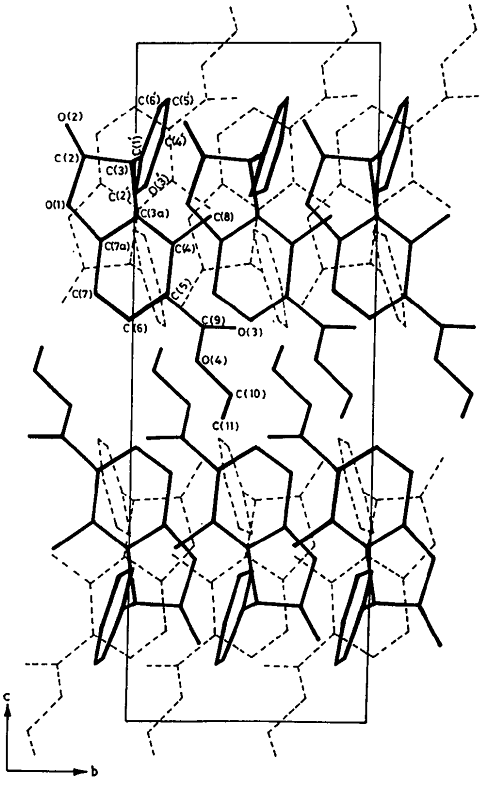

Fig. 2. A view of the crystal-packing arrangement.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, least-squares planes, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52036 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The O(3) atom attached to C(9) by a double bond is nearly *cis* to C(10) [O(3)—C(9)—O(4)—C(10) −2·22 (11)°], and is in an *endo* conformation with the methyl group. Phenyl ring I is perpendicular to phenyl ring III and is nearly perpendicular to the five-membered ring II. The dihedral angles between rings I and III and rings I and II are 90·66 (25) and 93·19 (27)°. Ring III is almost in the same plane as ring II. The dihedral angle between the mean planes of the five-membered ring II and the six-membered ring III is 2·56 (30)°.

The torsion angles of the five-membered ring II are small but they are not zero, showing the non-planarity of the ring. The puckering parameter $\varphi$ of 19 (9)° calculated for this ring indicates that it assumes one of the ten 'twist' conformations. However, the $Z_j$ coordinates $(Z_1 = -0{\cdot}0005 \simeq Z_2 + Z_5 = -0{\cdot}0162 + 0{\cdot}0170 \simeq Z_3 + Z_4 = 0{\cdot}0267 - 0{\cdot}0270 \simeq 0)$ (Cremer & Pople, 1975) suggest that the conformation is 'twist' with the axis through C(7a).

Some shortening is observed for the C(5)—C(9) single bond [1·491 (10) Å] owing to its position between two double bonds (Pauling, 1960).

The molecular packing in the crystal structure is shown in Fig. 2. There are no forces other than van der Waals forces stabilizing the structure. The packing clearly shows that the molecules are arranged in zones with notably less-dense regions in between, which may perhaps explain the tendency for cleavage of the molecule along the (001) plane. There appears to be some overlap of the phenyl rings which possibly stabilizes the structure.

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# Structure of 1-[(*R*)-α-Methylbenzylamino]-7-[(*R*)-α-methylbenzylimino]-1,3,5-cycloheptatriene, H(CHIRAMT), a Ligand used for Enantioselective Conjugate Addition Cuprate Catalysis

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**Abstract.** $C_{23}H_{24}N_2$, $M_r = 328{\cdot}46$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}888\,(2)$, $b = 14{\cdot}325\,(3)$, $c = 22{\cdot}651\,(5)$ Å, $V = 1911$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}13\,(1)$, $D_x = 1{\cdot}142$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}62$ cm$^{-1}$, $F(000) = 704$, $T = 295\,(1)$ K, $R = 0{\cdot}038$ for 1196 observed reflections with $F > 6\sigma(F)$. The amino proton is intramolecularly hydrogen bonded to the imino nitrogen, thus fixing the compound in the probable conformation adopted in the catalytically active copper complex.

**Introduction.** The title compound, first prepared by Brunner, Knott, Benn & Rufinska (1985), has been successfully used as a ligand to synthesize cuprate complexes that catalyze the 1,4-conjugate addition of Grignard reagents to enones (Villacorta, Rao & Lippard, 1988). Recent improvements in this reaction chemistry have resulted in enantioselectivities (*ee* values) of ~80% (Ahn & Lippard, in preparation). In order to examine the nature of the stereochemical pocket that might form when (CHIRAMT)$^-$ coordinates to copper(I), we have determined the crystal and molecular structure of H(CHIRAMT) by X-ray diffraction, the results of which are presented here.

**Experimental.** Crystals were obtained by the reaction of (*R*)-α-methylbenzylamine with 1-methoxy-7-[(*R*)-α-methylbenzylimino]-1,3,5-cycloheptatriene in anhydrous ethanol followed by recrystallization from methanol/water (Villacorta, Rao & Lippard, 1988).