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 φ of 19 (9)° calculated for this ring indicates that it assumes one of the ten 'twist' conformations. However, the Z_j coordinates ($Z_1 = -0\cdot0005 \simeq Z_2 + Z_5 = -0\cdot0162 + 0\cdot0170 \simeq Z_3 + Z_4 = 0\cdot0267 - 0\cdot0270 \simeq 0$) (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.

The authors thank Mr D. Chattopadhyay of Saha Institute of Nuclear Physics, Calcutta, for his help during the course of this work.

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Acta Cryst. (1989). C**45**, 1738–1740

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

By Simon G. Bott, Kwang-Hyun Ahn and Stephen J. Lippard

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, *USA*

(*Received* 22 *November* 1988; *accepted* 22 *March* 1989)

Abstract. $C_{23}H_{24}N_2$, $M_r = 328\cdot46$, orthorhombic, $P2_12_12_1$, $a = 5\cdot888\ (2)$, $b = 14\cdot325\ (3)$, $c = 22\cdot651\ (5)$ Å, $V = 1911$ Å^3, $Z = 4$, $D_m = 1\cdot13\ (1)$, $D_x = 1\cdot142$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot62$ cm^{-1}, $F(000) = 704$, $T = 295\ (1)$ K, $R = 0\cdot038$ 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).

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
N(1)	1·0587 (5)	0·5330 (2)	0·8759 (1)	4·2 (1)
N(2)	0·7906 (5)	0·6560 (2)	0·8380 (1)	4·0 (1)
C(11)	0·9156 (6)	0·5659 (2)	0·9179 (1)	3·8 (1)
C(12)	0·9271 (7)	0·5326 (2)	0·9747 (1)	4·6 (2)
C(13)	0·7972 (8)	0·5529 (2)	1·0249 (1)	5·4 (2)
C(14)	0·6177 (8)	0·6117 (3)	1·0312 (2)	5·7 (2)
C(15)	0·5250 (7)	0·6688 (3)	0·9872 (2)	5·5 (2)
C(16)	0·5857 (6)	0·6804 (2)	0·9298 (1)	4·7 (2)
C(17)	0·7575 (6)	0·6379 (2)	0·8938 (1)	3·6 (1)
C(21)	1·2463 (6)	0·4687 (2)	0·8848 (1)	3·9 (1)
C(22)	1·1725 (6)	0·3703 (2)	0·8993 (1)	3·6 (1)
C(23)	0·9718 (6)	0·3326 (2)	0·8794 (2)	4·5 (2)
C(24)	0·9154 (7)	0·2405 (2)	0·8908 (2)	5·2 (2)
C(25)	1·0592 (8)	0·1852 (2)	0·9227 (2)	5·4 (2)
C(26)	1·2587 (8)	0·2218 (3)	0·9435 (2)	5·7 (2)
C(27)	1·3146 (6)	0·3135 (2)	0·9319 (1)	4·8 (2)
C(28)	1·3894 (6)	0·4687 (2)	0·8288 (1)	4·7 (2)
C(31)	0·6521 (6)	0·7251 (2)	0·8065 (1)	4·0 (1)
C(32)	0·7602 (6)	0·8208 (2)	0·8115 (1)	3·7 (1)
C(33)	0·6475 (7)	0·8941 (2)	0·8368 (1)	4·7 (2)
C(34)	0·741 (1)	0·9827 (2)	0·8391 (2)	6·1 (2)
C(35)	0·950 (1)	0·9986 (3)	0·8152 (2)	6·4 (2)
C(36)	1·0659 (7)	0·9269 (3)	0·7900 (2)	6·2 (2)
C(37)	0·9754 (6)	0·8376 (3)	0·7883 (1)	4·7 (2)
C(38)	0·6289 (8)	0·6954 (2)	0·7426 (2)	5·8 (2)
H(1N)	1·043 (7)	0·565 (2)	0·842 (2)	6 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

N(1)—C(11)	1·355 (4)	N(1)—C(21)	1·452 (4)
N(2)—C(17)	1·305 (4)	N(2)—C(31)	1·467 (4)
C(11)—C(12)	1·374 (4)	C(11)—C(17)	1·494 (4)
C(12)—C(13)	1·400 (5)	C(13)—C(14)	1·359 (6)
C(14)—C(15)	1·400 (5)	C(15)—C(16)	1·358 (5)
C(16)—C(17)	1·435 (5)	C(21)—C(22)	1·511 (4)
C(21)—C(28)	1·521 (5)	C(31)—C(32)	1·517 (4)
C(31)—C(38)	1·515 (5)	N(1)—H(1*N*)	0·91 (4)
C(22)—C(23)	1·375 (4)	C(32)—C(33)	1·368 (4)
C(23)—C(24)	1·385 (5)	C(33)—C(34)	1·383 (5)
C(24)—C(25)	1·365 (5)	C(34)—C(35)	1·362 (7)
C(25)—C(26)	1·371 (6)	C(35)—C(36)	1·361 (6)
C(26)—C(27)	1·379 (5)	C(36)—C(37)	1·386 (6)
C(27)—C(22)	1·381 (4)	C(37)—C(32)	1·393 (5)

C(11)—N(1)—C(21)	126·6 (3)	C(11)—N(1)—H(1*N*)	111 (2)
C(21)—N(1)—H(1*N*)	121 (3)	C(17)—N(2)—C(31)	121·4 (3)
N(1)—C(11)—C(12)	120·4 (3)	N(1)—C(11)—C(17)	111·7 (2)
C(11)—C(12)—C(13)	131·4 (4)	C(12)—C(13)—C(14)	129·7 (3)
C(13)—C(14)—C(15)	126·2 (3)	C(14)—C(15)—C(16)	130·5 (4)
C(15)—C(16)—C(17)	132·7 ([illegible])	C(12)—C(11)—C(17)	127·8 (3)
C(16)—C(17)—C(11)	121·6 (3)	N(2)—C(17)—C(11)	113·5 (3)
N(2)—C(17)—C(16)	124·9 (3)	N(1)—C(21)—C(22)	113·7 (3)
N(1)—C(21)—C(28)	107·9 (2)	C(22)—C(21)—C(28)	110·0 (3)
N(2)—C(31)—C(32)	110·0 (3)	N(2)—C(31)—C(38)	108·9 (3)
C(32)—C(31)—C(38)	111·2 (3)	C(27)—C(22)—C(21)	119·5 (3)
C(22)—C(23)—C(24)	121·3 (3)	C(25)—C(24)—C(23)	120·1 (3)
C(24)—C(25)—C(26)	119·5 (3)	C(25)—C(26)—C(27)	120·2 (4)
C(26)—C(27)—C(22)	121·2 (4)	C(33)—C(32)—C(37)	117·8 (3)
C(33)—C(32)—C(31)	121·5 (3)	C(37)—C(32)—C(31)	120·7 (3)
C(32)—C(33)—C(34)	121·8 (4)	C(35)—C(34)—C(33)	119·8 (4)
C(36)—C(35)—C(34)	119·6 (4)	C(35)—C(36)—C(37)	121·0 (4)
C(23)—C(22)—C(27)	117·6 (3)	C(36)—C(37)—C(32)	119·9 (4)
C(23)—C(22)—C(21)	122·8 (3)		

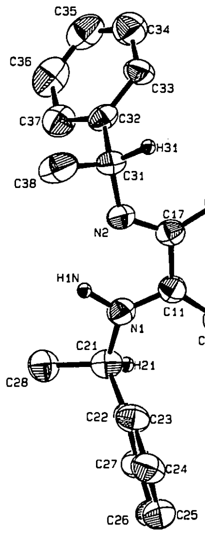

Fig. 1. View of the molecule showing the atom numbering scheme.

Density measured by flotation. Transparent yellow blocks, 0·35 × 0·40 × 0·55 mm, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, cell parameters from least-squares fit of 24 high-angle reflections ($2\theta > 35°$). Intensity data collection in $\omega/2\theta$ scan mode, scan width $(0·8 + 0·35\tan\theta)°$ and, in addition, 25% before and after each reflection for background determination, scan time = 10–120 s, $2\theta = 50$, h 0→7, k 0→17, l −26→26, no significant variation of three standard reflections, data not corrected for absorption or extinction. 3696 reflections collected, after averaging ($R = 0·034$) 1907 unique of which 1196 with $F > 6\sigma(F)$. Structure solution by automatic direct methods and difference Fourier syntheses, full-matrix refinement on F with $w = \sigma(F)^{-2}$, anisotropic thermal parameters. Hydrogens located and allowed to ride on the appropriate carbon $[B(\mathrm{H}) = 1·2\,B_{eq}(\mathrm{C})]$ except for the hydrogen-bonded amino proton, the coordinates and isotropic thermal parameter of which were refined. 230 parameters, $R = 0·038$, $wR = 0·046$, max. $\Delta/\sigma < 0·01$, max. $\Delta\rho = 0·12$, min. $= -0·20$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974), *TEXSAN* programs (Molecular Structure Corporation, 1988).

Atomic parameters are given in Table 1, selected bond distances and angles in Table 2. Atomic numbering scheme is shown in Fig. 1.*

Discussion. The molecular structure of H(CHIRAMT) consists of a nearly planar amino-

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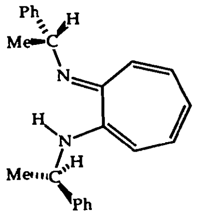
* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52071 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

troponeimine ring with bond alterations consistent with the following tautomer:



The amino proton on N(1) is intramolecularly hydrogen bonded to the imino nitrogen atom N(2), the (N1)H···N(2) distance and N(1)—H(1N)···N(2) angle being 1·98 (4) Å and 116 (3)°, respectively (Fig. 1). These results may be contrasted with those reported previously for the structure determination of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene, in which C_2 symmetry was observed (Goldstein & Trueblood, 1967). Another important feature of H(CHIRAMT) is the positioning of hydrogen atoms H(21) and H(31) toward the tropone ring hydrogens on C(12) and C(16). This steric locking of the conformation may be of significance in orienting the phenyl and methyl groups in the transition state responsible for the chiral induction observed in the catalytic enantioselective conjugate addition reaction.

This research was supported by a grant from the National Science Foundation.

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Acta Cryst. (1989). C**45**, 1740–1743

Structures of (±)-*trans*-4-(2,3-Dimethoxyphenyl)- (I) and (+)-*trans*-4-(4-Methylphenyl)-2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]-[1]benzopyran-5-one (II)

By Gerard Ruggiero, Oliver Platt Jr and Edward J. Valente

Department of Chemistry, Mississippi College, Clinton, MS 39058, USA

and Drake S. Eggleston

Department of Physical & Structural Chemistry, Smith, Kline & French Laboratories, King of Prussia, PA 19406, USA

(*Received* 21 *July* 1988; *accepted* 21 *March* 1989)

Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (I) Racemic *trans*-2-hydroxy-4-(2,3-dimethoxyphenyl), $C_{21}H_{20}O_6$, $M_r = 368·40$, monoclinic, $C2/c$, $a = 19·403$ (7), $b = 10·636$ (8), $c = 21·456$ (13) Å, $\beta = 123·94$ (5)°, $V = 3673·8$ (85) Å^3, $Z = 8$; $D_x = 1·33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71078 Å, $\mu = 0·913$ cm^{-1}, $F(000) = 1552$, $T = 295$ K, final $R = 0·056$ for 2463 observations [$I \geq 2\sigma(I)$]. Molecules are hydrogen bonded between hydroxyls and coumarin carbonyls, O···O 2·812 (3) Å. The dihydropyran ring is in the *d,e*-diplanar conformation. (II) Resolved (2*R*,4*R*)-(+)-*trans*-2-hydroxy-4-(4-methylphenyl), $C_{20}H_{18}O_4$, $M_r = 322·36$, orthorhombic, $P2_12_12_1$, $a = 10·578$ (4), $b = 10·450$ (5), $c = 14·803$ (7) Å, $V = 1636·4$ (22) Å^3, $Z = 4$, $D_x = 1·31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71078 Å, $\mu = 0·540$ cm^{-1}, $F(000) = 680$, $T = 294$ K, final $R = 0·044$ for 1580 observations [$I \geq 3\sigma(I)$]. Molecules are hydrogen bonded along a screw axis between hydroxyls and coumarin carbonyls, O···O 2·746 (3) Å. The dihydropyran ring is a nearly undistorted half-chair.

Introduction. Warfarin is a widely used anticoagulant agent. It and its derivatives crystallize as cyclic hemiketals containing a dihydropyran ring, which has been found to display a range of conformations. As part of a series of crystallographic studies on

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