Asymmetric Reaction. XV. Structure and Relative Configuration of a Reductive Dimerization Product of Ethyl Phenylglyoxylate, Diethyl Diphenyltartrate [1]

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The hydrogenation of ethyl phenylglyoxylate catalyzed by bis(dimethylglyoximato)cobalt(II)-quinine gave a novel reductive dimerization product, diethyl diphenyltartrate, with a slight optical activity. The crystals obtained from its benzene-hexane solution were investigated by X-ray diffraction method. The crystal is triclinic, space group p$\bar{1}$, a = 10.078(3), b = 10.283(2), c = 9.781(3) Å, α = 109.80(2), β = 102.35(3), γ = 78.50(2)°, Z = 2, V = 922.7 Å^3, Dc = 1.29 g cm^{-3}, μ = 7.46 cm^{-1} for Cu Kα. The structure was solved by the direct method, and refined by a block-diagonal least-squares procedure: R = 0.059 for 2568 reflections with $|Fo| > 3\sigma(|Fo|)$. The relative configuration around the two chiral carbons indicated that the molecule is in the *threo*-form, and the Newman projection showed that the molecule has the staggered conformation. There were two relatively strong intramolecular hydrogen bonds between the two hydroxyl groups and the two carbonyl oxygen atoms of ethoxycarbonyl groups.

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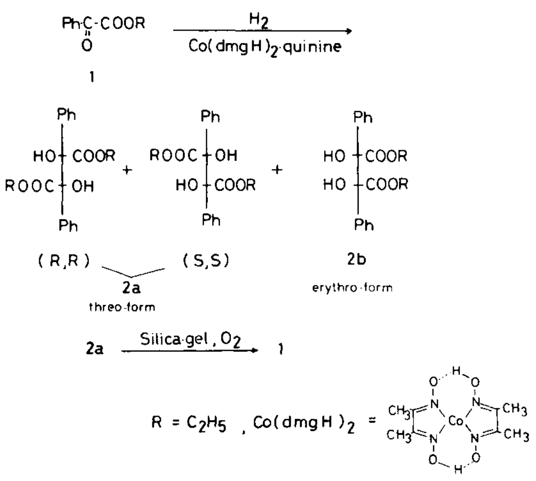
The hydrogenation of ethyl phenylglyoxylate (**1**) catalyzed by bis(dimethylglyoximato)cobalt(II)-base gave a reductive dimerization product, diethyl diphenyltartrate (**2**), with a slight optical activity. The optical rotation diminished to zero (mp 123-124°) [2] by repeated recrystallization of the product from benzene-hexane solution. More recently, we have noticed that the product was easily converted to ethyl phenylglyoxylate during the isolation and purification procedure by silica gel column chromatography [3]. In addition, the relatively sharp and strong ir absorption (about 3480 cm^{-1}) of the compound indicated that the existence of intramolecular hydrogen bonds in the solid state.

SCHEME



The reductive dimerization product with mp 123-124° can exist in two possible configurations, the *threo*-form, **2a**, and *erythro*-form, **2b**, as shown in the Scheme. The molecular structure of **2** has been determined by the X-ray diffraction method in order to establish the conformation and configuration of **2** and to correlate the structural information with the ir and chromatographic data.

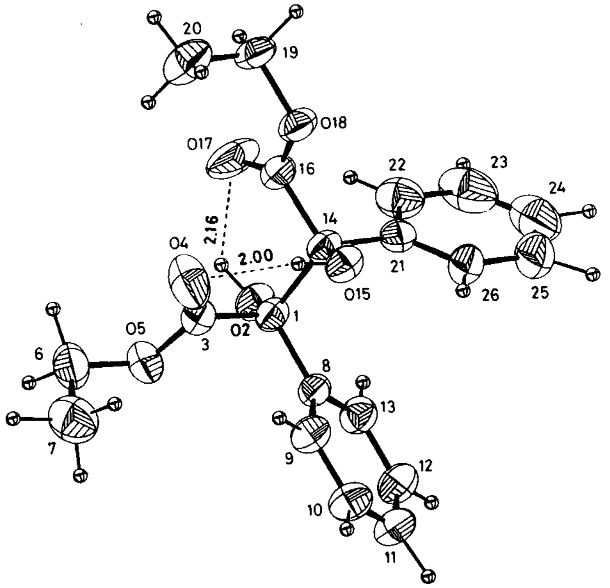


Figure 1. Molecular structure (ORTEP drawing) [11] of the title compound **2a**. Non-hydrogen atoms are drawn as thermal ellipsoids with 50% probability level and hydrogen atoms as spheres of arbitrary radius.

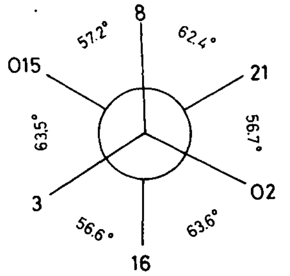


Figure 2. Newman-projection drawings to illustrate conformation about the C1-C14 bond.

Table 1

Physical and Crystallographic Data

Formula unit	$C_{20}H_{22}O_6$
M	358.39
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	10.078(3)
b/Å	10.283(2)
c/Å	9.781(3)
α/Å	109.80(2)
β/Å	102.35(3)
γ/Å	78.50(2)
V/Å³	922.7
Z	2
Dx/g cm⁻³	1.29
Radiation	Cu Kα
λ/Å	1.54178
No. of Reflections	
Measured	3082
Observed [| Fo | >3σ(| Fo |)]	2568
R	0.059

EXPERIMENTAL

Preparation of Diethyl Diphenyltartrate.

Catalytic reductive dimerization of ethyl phenylglyoxylate was carried out according to the procedure described in a previous paper [2]. A syrupy product (7 g) was obtained from 7.12 g of ethyl phenylglyoxylate. The raw products were treated with hexane to give 3.1 g of crystals with $[\alpha]_D = +3.2°$ (c 2.55, benzene) which were again suspended into hexane and pressed well with a spatula. The undissolved crystals (2.3 g) were filtered, which had $[\alpha]_D = +1.01°$ (c 2.24, benzene). The compound (2 g) was recrystallized from benzene/hexane (1/1) solution to give 1.57 g of crystals with mp 122.5-124°, $[\alpha]_D = 0°$. Further recrystallization did not change the melting point (mp 122.5-123°). The sample obtained was used for the X-ray analysis.

Collection and Reduction of Data.

The crystal used for the X-ray study had approximate dimensions of 0.30 x 0.30 x 0.25 mm. The unit cell parameters at room temperature were refined by least-squares using the Bragg angles (Cu Kα, $\lambda = 1.54178$ Å) of 24 reflections ($30° < 2\theta < 45°$). The crystal data are given in Table 1. Intensity data were collected at room temperature on a Rigaku AFC diffractometer utilizing nickel-filtered Cu Kα radiation. The θ-2θ scan mode was employed. The scan rate was 5° min⁻¹ in θ, and the scan range in θ was varied by 1.2° + 0.15° tan θ. Backgrounds were counted for 4 s at both ends of the scan with an offset of 50% of the scan range from the calculated position of the Kα peak. A total of 3082 unique reflections of the type ±h, ±k,l were measured with $2\theta < 125°$. The intensities of three standard reflections measured after every 57 reflections dropped by an average of a few percent over the period of data collection, but no correction was applied for this fluctuation. Lorentz and polarization corrections were applied by the usual manner, but no absorption correction was applied ($\mu = 7.46$ cm⁻¹ for Cu Kα). Standard deviations in the intensities, σ(| Fo |), were derived directly from counting statistics.

Table 2

Final Atomic Parameters of Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

Atoms	x	y	z	Beq/Å²
C 1	0.1296(4)	0.6744(4)	0.3010(4)	3.57
C 2	0.1931(3)	0.5407(3)	0.2249(3)	4.13
C 3	−0.0206(4)	0.6692(4)	0.3006(4)	4.62
O 4	−0.1138(3)	0.7522(4)	0.2695(4)	9.25
O 5	−0.0370(3)	0.5637(3)	0.3406(3)	5.30
C 6	−0.1782(5)	0.5456(5)	0.3380(5)	6.43
C 7	−0.2308(5)	0.6394(5)	0.4729(6)	7.95
C 8	0.2073(4)	0.7170(4)	0.4577(4)	3.60
C 9	0.3454(4)	0.6661(4)	0.4852(4)	4.47
C10	0.4176(4)	0.7048(5)	0.6274(5)	5.43
C11	0.3528(4)	0.7960(5)	0.7425(4)	5.63
C12	0.2149(4)	0.8456(4)	0.7145(4)	5.18
C13	0.1423(4)	0.8066(4)	0.5736(4)	4.34
C14	0.1330(4)	0.7866(4)	0.2226(4)	3.51
O15	0.0765(3)	0.9197(3)	0.3074(3)	3.94
C16	0.0474(4)	0.7436(4)	0.0673(4)	4.49
O17	0.0398(4)	0.6248(3)	−0.0061(3)	7.60
O18	−0.0096(3)	0.8524(3)	0.0231(3)	4.72
C19	−0.0984(4)	0.8242(4)	−0.1221(4)	5.37
C20	−0.2421(5)	0.8304(5)	−0.1053(5)	6.89
C21	0.2772(4)	0.7957(4)	0.2090(4)	4.35
C22	0.3467(5)	0.6970(5)	0.1007(5)	6.43
C23	0.4789(5)	0.7088(6)	0.0927(6)	9.03
C24	0.5425(5)	0.8184(7)	0.1901(6)	10.73
C25	0.4750(5)	0.9177(6)	0.2973(6)	8.76
C26	0.3435(4)	0.9057(5)	0.3071(5)	5.86

$$\mathrm{Beq} = (U_{11} + U_{22} + U_{33})$$

$$(\text{where } U_{11}) = \frac{B_{11}}{8\pi^2 a^{*2}}, \textit{etc}).$$

Solution and Refinement of the Structure.

The structure was solved by direct methods using MULTAN 78 [4] to calculate phases of the 200 | E | values with | E | >1.82. The E map computed from the phase set with the largest combined figure of merit (2.81) revealed all non-hydrogen atoms except for one carbon atom of a benzene ring. The subsequent difference Fourier map readily gave the remaining atom. Atomic parameters were refined by the block-diagonal least-squares procedure. The function minimized was $\Sigma w(| Fo | - | Fc |)^2$, where w was taken as $1/\sigma(| Fo |)$. All of the hydrogen atoms were readily located on the difference Fourier map. In the further refinement, anisotropic and isotropic thermal parameters were applied to the non-hydrogen and hydrogen atoms, respectively. The refinement converged to a conventional $R = \Sigma | | Fo | - | Fc | | / \Sigma | Fo |$ of 0.059 and a weighted $Rw = \Sigma w ((| Fo | - | Fc |)^2 / \Sigma w | Fo |^2)^{1/2}$ of 0.060 with a QOF of 0.75 (Quality of fit = [Σw(| Fo |

Table 3

Bond Lengths (Å) and Angles (°)

(a) Bond Lengths for Non-hydrogen Atoms

C 1 - O 2	1.419(4)	C 1 - C 3	1.525(5)	C 1 - C 8	1.525(5)
C 1 - C14	1.596(4)	C 3 - O 4	1.199(5)	C 3 - O 5	1.322(4)
O 5 - C 6	1.465(5)	C 6 - C 7	1.479(7)	C 8 - C 9	1.389(5)
C 8 - C13	1.391(5)	C 9 - C10	1.390(5)	C10 - C11	1.390(6)
C11 - C12	1.385(6)	C12 - C13	1.381(5)	C14 - O15	1.417(4)
C14 - C16	1.545(5)	C14 - C21	1.511(5)	C16 - O17	1.198(4)
C16 - O18	1.317(4)	O18 - C19	1.478(4)	C19 - C20	1.479(6)
C21 - C22	1.397(6)	C21 - C26	1.393(5)	C22 - C23	1.383(6)
C23 - C24	1.375(8)	C24 - C25	1.382(7)	C25 - C26	1.381(6)

(b) Bond Angles

C14 - C 1 - C 8	109.9 (3)	C14 - C 1 - C 3	107.2(3)
C14 - C 1 - O 2	111.0(2)	C 8 - C 1 - C 3	111.0(3)
C 8 - C 1 - O 2	107.8(2)	C 3 - C 1 - O 2	110.0(3)
O 5 - C 3 - O 4	123.4(3)	O 5 - C 3 - C 1	112.4(3)
O 4 - C 3 - C 1	124.1(3)	C 6 - O 5 - C 3	116.8(3)
C 7 - C 6 - O 5	111.0(3)	C13 - C 8 - C 9	119.4(3)
C13 - C 8 - C 1	121.0(3)	C 9 - C 8 - C 1	119.5(3)
C10 - C 9 - C 8	120.1(3)	C11 - C10 - C 9	120.3(3)
C12 - C11 - C10	119.3(4)	C13 - C12 - C11	120.7(3)
C12 - C13 - C 8	120.2(3)	C21 - C14 - C16	109.1(3)
C21 - C14 - O15	108.0(3)	C21 - C14 - C 1	112.2(3)
C16 - C14 - O15	110.4(3)	C16 - C14 - C 1	108.2(3)
O15 - C14 - C 1	108.9(2)	O18 - C16 - O17	124.5(3)
O18 - C16 - C14	111.9(3)	O17 - C16 - C14	123.5(3)
C19 - O18 - C16	116.7(3)	C20 - C19 - O18	110.2(3)
C26 - C21 - C22	118.6(3)	C26 - C21 - C14	119.4(3)
C22 - C21 - C14	122.1(3)	C23 - C22 - C21	120.2(4)
C24 - C23 - C22	120.4(5)	C25 - C24 - C23	120.2(4)
C26 - C25 - C24	119.7(5)	C25 - C26 - C21	120.9(4)

$-|F_c|)/(N_{obsd}-N_{para})]^{1/2}$). The refinement was completed when the largest shift in any parameters of the non-hydrogen atoms was 0.20, while the largest shift for the hydrogen atoms was 0.83. Atomic scattering factors were taken from those of "International Tables for X-ray Crystallography" [5]. Mathematical and computational details are noted elsewhere [6]. Calculations were carried out by using UNICS [7] program system on ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and ACOS 900 computer at Computation Center of Niigata University. The final positional parameters [8] of non-hydrogen atoms with equivalent isotropic temperature factors are given in Table 2.

Discussion.

The structure of the title compound obtained from the reductive dimerization catalyzed by bis(dimethylglyoximato)cobalt(II)-quinine has been established to be a novel dimer of ethyl phenylglyoxylate in the *threo*-form, **2a** as in Scheme. The molecular structure and the atom labelling are presented by the ORTEP drawing in Figure 1. The bond lengths and bond angles are given in Table 3 together with their estimated standard deviations. The average C-C lengths of the two benzene rings are 1.388 and 1.385 Å, respectively, which are compared well with the normal value of 1.395 (3) Å [9]. Concerning the bond lengths around atoms C1 and C14, the average value of C-OH bonds is 1.418 Å, and that of C=O bonds is 1.199 Å. These values are normal; furthermore the two halves of the molecules bisected by the center of the C1-C14 bond are equivalent within experimental errors. The C1-C14 bond length (1.596(4) Å) is exceptionally long in comparison with the normal value of 1.541(3) Å [9] and the elongation indicates severe weakness in the bond. Such weakness is consistent with the behaviour of the title compound during its purification using silica gel column chromatography, where ready cleavage of C1-C14 bond yields the corresponding monomer, ethyl phenylglyoxylate (**1**).

One of the goal of this work was to examine the possibility of the presence of strong intramolecular hydrogen bonds. The present X-ray studies reveal that both hydroxyl groups (H-O2 and H-O15) form intramolecular hydrogen bonds with the carbonyl oxygen atoms (O17 and O4, respectively) of ethoxycarbonyl groups to form two fused six-membered rings (ring I: O4-C3-C1-C14-O15-H, and ring II: O17-C16-C14-C1-O2-H as shown in Figure 1). Both six-membered rings I and II share the C1-C14 bond and these two intramolecular hydrogen bonds agree well within experimental errors. The hydrogen bond parameters for O2...O17 bond are 2.746 Å, (O2)H...O17, 2.16(5) Å, and O2-H...O17 angle, 151.7(4) °; whereas the corresponding values for (O15-H...O4) bond are 2.714(4), 2.00(4) Å, and 131.4(4) °, respectively. These values are comparable to the intermolecular hydrogen bonds ranged from 2.633 to 2.909 A in an analogue of (*R,R*)-tartaric acid (**3**) [10], but the hydrogen bonding scheme is different from each other.

The relative configuration around the chiral centers C1 and C14 can be deduced from the Newman projection of Figure 2. The relative configuration of each chiral carbon is specified by the (*R,R*)- or (*S,S*)-system related to the center of symmetry, which is designated as a *threo*-form in the Fisher projection formula, **2a**, of the Scheme. As shown in Figure 2, the two phenyl groups are in synclinal orientation. The title compound possesses the staggered conformation which is presumably the result of the two intramolecular hydrogen bonds described above. The dihedral angle between the least-square planes of the two benzene rings was 43.47°.

The crystal-packing arrangements of the molecules resulted from the intramolecular hydrogen bonds are ordinary, and the intermolecular contacts are characterized by the normal van der Waals interaction (greater than 3.247(4) Å).

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