Supporting Information

In- or In(I)-Employed Tailoring of the Stereogenic Centers in the Reformatsky-Type Reactions of Simple Ketones, α -Alkoxy Ketones and β -Keto Esters

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General procedure for In- or In(I)-employed Reformatsky-type reactions of simple ketones 5a-k:

Method A: To a solution of an appropriate ketone **5** (1 mmol) and an appropriate α -halo ester **6** (1.6-1.8 mmol, added *via* syringe) in dry THF (2 mL) was added indium metal (1.2 mmol) or indium(I) halide (1.2 mmol) or indium(II) halide (1.1 mmol) at room temperature. The resulting reaction mixture was dipped into a preheated hot bath (66-70 °C) under an inert atmosphere and stirred for an appropriate period (see Table 1 and 2 for specific entries). After this, the reaction mixture was allowed to cool and stand at room temperature. To this mixture cold water (5-7 mL) was added and the contents were subjected to ultrasonication for 1 min. Further, extraction was carried out using diethyl ether (3 X 15 mL). The combined organic layers were concentrated in vacuum and subjected to column to silica gel (5-30% EtOAc-Hexane mixture) chromatographic purification to afford the pure products.

Method B: To a solution of an appropriate ketone (1 mmol) and an appropriate α -halo ester (1.6-1.8 mmol, added *via* syringe) in dry THF (1.5-2 mL) was added indium metal powder (1.2 mmol) or indium(I) halide (1.2 mmol) at room temperature under an inert atmosphere. The reaction flask was dipped into an oil bath at room temperature; the reaction mixture was stirred as well as the temperature was allowed to rise to 66-69 °C over an appropriate period time (see Tables for specific entry). Work up procedure followed as given in method A.

General procedures for indium-employed Reformatsky-type reaction of α -alkoxy ketones or β -keto esters:

In(I)X system: To a solution of an appropriate α -alkoxy ketone or β -keto ester (0.5 or 1 mmol) and an appropriate α - halo ester (mmol as denoted in the tables, added *via* syringe) in dry THF or toluene (1.5 mL) was added indium(I) halide (mmol as denoted in the tables) at room temperature. The resulting reaction mixture was subjected to ultrasonication at rt or dipped into a preheated hot bath (66-70 °C) under an inert atmosphere and stirred for an appropriate period (see Tables for specific entry). Work up was carried out as given in method A.

In-InX₃ system: To a solution of an appropriate ketone (0.5 mmol) and an appropriate α - halo ester (mmol as denoted in the tables, added *via* syringe) in toluene (1.5-2 mL) was added indium metal powder (mmol as denoted in the tables, see the tables for specific entries) and InX₃ (mmol as denoted in the tables) The resulting reaction mixture was subjected to ultrasonication for an appropriate time (see tables for specific entries) and the rest of the procedure followed as given in method A.

Determination of the relative stereochemistry:

a) Determination of stereochemistry of Reformatsky-type reactions of branched α -halo esters with simple ketones:^{1,2}

Determination of stereochemistry major isomer 7ca₁: The repetitive column chromatography purification of the reaction of 4-bromoacetophenone with ethyl-2-bromopropionate in the presence of indium afforded both isomers in pure form **7ca₁** (major isomer) and **7ca₂** (minor isomer) as colorless thick oil. The esterification of

tertiary alcohol **7ca₁** (major isomer) by Vedejs's method was carried out to afford the ester derivative **7caB** as a colorless solid. Repetitive crystallization afforded suitable crystalline for X-ray structure analysis. The X-ray structure analysis thus unambiguously revealed that the major isomer is *anti* isomer. For details of X-ray analysis see the page S43.

References:

- (1) Yasuda, M.; Hirata, K.; Nishino, M.; Yamamoto, A.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 13442.
- (2) Vedejs, E.; Daugulis, O. *J. Org. Chem.* **1996**, *61*, 5702.

Determination of stereochemistry of major isomer 7ga₁: The repetitive column chromatography purification of the reaction of 2-acetylnaphthalene (**5g**) with ethyl-2-bromopropionate in the presence of indium afforded both isomers in pure form **7ga₁** (major isomer) and **7ga₂** (minor isomer) as colorless thick oil. The esterification of tertiary alcohol **7ga₁** (major isomer) by Vedejs's method was carried out to afford the ester derivative **7gaB** as a colorless solid. Repetitive crystallization afforded suitable crystalline for X-ray structure analysis. The X-ray structure analysis thus unambiguously revealed that the major isomer is *anti* isomer. On the basis of similarity in the spectral data and pattern of proton multiplicity and chemical shifts in ¹H NMR spectra and the X-ray structure analyses of the products **7caB** and **7gaB** the stereochemistry of other products were assigned. For details of X-ray analysis see the page S56.

Reduction of compound **13a** (2 mmol) with LiAlH₄ (6 equivalents) in THF (4 mL) at rt was carried out for 1.5 h. Usual work up followed by extraction and purification afforded a thick oil (**13aB**) which solidified on standing for 2 days. Repetitive recrystallization using hexane-ether mixture afforded crystalline forms, suitable for X-ray structure analysis. The X-ray analysis revealed the stereochemistry of product **13a** as shown in the following scheme. The stereochemistry of related products was derived on the basis of this experiment. For details of X-ray analysis see the page S69.

General Procedure, Determination of Active Species: A two neck RB flask containing ethyl iodoacetate in benzene- d_6 was added InCl and subjected to ultrasonication at rt for an appropriate period under an inert atmosphere. About 0.1 mL was transferred into a NMR tube containing benzene- d_6 via a syringe (disposable syringe) under an inert atmosphere, then NMR was recorded immediately.

Later, an excess of benzaldehyde or alkoxy ketone **8a** was added, and ultrasonicated further for an appropriate period and then NMR was recorded.

Note: Similar, In-InCl₃ system was carried out.

Reaction with Benzaldehyde (InCl System)

Reaction with alkoxy ketone 8a (InCl system)

ICH₂COOEt + InCl
3.0 mmol 1.25 mmol

C₆D₆

ultrasonication in an RB flask
45 min

Generation of active species (In-InCl₃ system)

Generation of active species (Indium system)

Generation of active species (indium system)

7ab

7ac1

7ba

7ca1

7ca2

7cb

7da1

7dc1

7dc2

7ga1

7ga2

7gb

7ha

7ia1

7ia2

7ib1

7ib2

11f

X-ray Structure Report for compound **7caB**

Experimental

Data Collection

A colorless prismatic crystal of $C_{20}H_{20}O_4BrCl$ having approximate dimensions of 0.50 x 0.50 x 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $29.30^\circ < 2\theta < 29.96^\circ$ corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned}a &= 11.847(8) \text{ \AA} \\b &= 8.940(7) \text{ \AA} & \beta &= 93.27(4)^\circ \\c &= 19.015(6) \text{ \AA} \\V &= 2010(1) \text{ \AA}^3\end{aligned}$$

For $Z = 4$ and F.W. = 439.73, the calculated density is 1.45 g/cm^3 . The systematic absences of:

$$\begin{aligned}h0l: & h \pm 2n \\0k0: & k \pm 2n\end{aligned}$$

uniquely determine the space group to be:

$$P2_1/a \text{ (\#14)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the ω -2 θ scan technique to a maximum 2θ value of 60.0° . ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 6.0° . Scans of $(1.52 + 0.30 \tan \theta)^\circ$ were made at a speed of $16.0^\circ/\text{min}$ (in ω). The weak reflections ($I < 10.0 (I)$) were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side

of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Data Reduction

Of the 6494 reflections which were collected, 6112 were unique ($R_{int} = 0.034$). The intensities of three representative reflection were measured after every 150 reflections. Over the course of data collection, the standards increased by 19.5%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient, μ , for Mo-K radiation is 22.0 cm^{-1} . An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.80 to 1.00.

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement³ was based on 2406 observed reflections ($I > 2.00(I)$, $2 < 59.98$) and 315 variable parameters and converged (largest parameter shift was 0.75 times its esd) with unweighted and weighted agreement factors of:

$$R = (F_o^2 - F_c^2) / F_o^2 = 0.146$$

$$R_w = [(w(F_o^2 - F_c^2)^2 / w(F_o^2)^2)]^{1/2} = 0.130$$

$$R_1 = ||F_o| - |F_c|| / |F_o| = 0.059 \quad \text{for } I > 2.0(I) \text{ data}$$

The standard deviation of an observation of unit weight⁴ was 1.66. The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to downweight the intense reflections. Plots of $w(F_o^2 - F_c^2)^2$ versus F_o^2 reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no

unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and -0.85 e⁻/ Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in Fcalc⁶; the values for f' and f'' were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbel⁸. All calculations were performed using the teXsan⁹ crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G., (1994). J. Appl. Cryst. 27, 435.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

$$\begin{aligned} \text{Function minimized: } & w(F_o^2 - F_c^2)^2 \text{ where} \\ w &= 1/[2(F_o^2)] = [2_c(F_o^2) + (p \\ &(\text{Max}(F_o^2, 0) + 2F_c^2)/3)^2]^{-1} \\ c(F_o^2) &= \text{e.s.d. based on counting statistics} \\ p &= \text{p-factor} \end{aligned}$$

(4) Standard deviation of an observation of unit weight:

$$\begin{aligned} & [w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} \\ \text{where: } & N_o = \text{number of observations} \\ & N_v = \text{number of variables} \end{aligned}$$

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England,

Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1999).

EXPERIMENTAL DETAILS

A. Crystal Data for **7caB**

Empirical Formula	C ₂₀ H ₂₀ O ₄ BrCl
Formula Weight	439.73
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.50 X 0.50 X 0.50 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 range)	25 (29.3 - 30.0°)
Omega Scan Peak Width	
at Half-height	0.32°
Lattice Parameters	a = 11.847(8) Å b = 8.940(7) Å c = 19.015(6) Å = 93.27(4)° V = 2010(1) Å ³
Space Group	P2 ₁ /a (#14)
Z value	4
D _{calc}	1.452 g/cm ³
F ₀₀₀	896.00
(MoK)	22.04 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC5R (rotating anode)
Radiation	MoK (= 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.22,
10.70, 35.51)	
Temperature	23.0 °C
Collimator Size	1.0 mm
Take-off Angle	6.0°

Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	258 mm
Scan Type	-2
Scan Rate	16.0°/min (in) (up to 5 scans)
Scan Width	(1.52 + 0.30 tan)°
2 max	60.0°
No. of Reflections Measured	Total: 6494 Unique: 6112 ($R_{int} = 0.034$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8000 -
0.9994)	Decay (19.53% increase)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sum (F_o^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 2.00 \sigma(I)$, $2 < 59.98^\circ$)	2406
No. Variables	315
Reflection/Parameter Ratio	7.64
Residuals: R ; R_w	0.146 ; 0.130
Residuals: R_1	0.059
No. of Reflections to calc R_1	2406
Goodness of Fit Indicator	1.66
Max Shift/Error in Final Cycle	0.755
Maximum peak in Final Diff. Map	0.50 e ⁻ / Å ³
Minimum peak in Final Diff. Map	-0.85 e ⁻ / Å ³

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Br(1)	0.74494(6)	-0.35344(8)	0.52927(4)	5.18(2)
Cl(1)	0.9993(2)	0.2524(3)	1.0525(1)	7.59(6)
O(1)	0.6934(3)	0.5216(4)	0.7296(2)	3.87(9)
O(2)	0.5048(4)	0.5235(5)	0.7137(3)	5.5(1)
O(3)	0.6553(3)	0.2054(4)	0.7675(2)	3.29(9)
O(4)	0.6017(4)	-0.0104(5)	0.8192(2)	5.1(1)
C(1)	0.8057(8)	0.6995(10)	0.7954(6)	7.1(2)
C(2)	0.6867(6)	0.6580(8)	0.7716(4)	4.7(2)
C(3)	0.5946(5)	0.4659(7)	0.7037(3)	3.6(1)
C(4)	0.6107(5)	0.3248(6)	0.6603(3)	3.1(1)
C(5)	0.5390(7)	0.3368(9)	0.5903(4)	4.6(2)
C(6)	0.5818(4)	0.1826(6)	0.7036(3)	3.2(1)
C(7)	0.4580(5)	0.1793(8)	0.7225(4)	4.3(2)
C(8)	0.6191(4)	0.0447(6)	0.6641(3)	2.9(1)
C(9)	0.7339(5)	0.0105(6)	0.6629(3)	3.2(1)
C(10)	0.7719(5)	-0.1071(6)	0.6237(3)	3.3(1)
C(11)	0.6939(5)	-0.1932(6)	0.5851(3)	3.4(1)
C(12)	0.5794(5)	-0.1637(7)	0.5860(3)	4.0(2)
C(13)	0.5432(5)	-0.0465(7)	0.6255(3)	3.8(1)
C(14)	0.6578(5)	0.1009(7)	0.8201(3)	3.7(1)
C(15)	0.7395(5)	0.1477(7)	0.8782(3)	3.7(1)
C(16)	0.8033(6)	0.2772(7)	0.8766(3)	4.1(2)
C(17)	0.8832(6)	0.3098(8)	0.9293(4)	5.0(2)
C(18)	0.8980(6)	0.2111(8)	0.9862(3)	4.7(2)
C(19)	0.8356(7)	0.0842(9)	0.9886(4)	5.8(2)
C(20)	0.7577(7)	0.0492(8)	0.9350(4)	5.3(2)
H(1)	0.807(10)	0.78(1)	0.819(6)	11(2)
H(2)	0.850(6)	0.626(7)	0.824(3)	6(1)
H(3)	0.85(1)	0.72(2)	0.749(7)	22(3)
H(4)	0.634(5)	0.643(6)	0.811(3)	3(1)
H(5)	0.644(6)	0.759(8)	0.743(3)	7(1)
H(6)	0.695(6)	0.316(7)	0.643(3)	6(1)
H(7)	0.465(6)	0.356(7)	0.594(3)	5(1)
H(8)	0.560(5)	0.428(7)	0.563(3)	4(1)
H(9)	0.543(5)	0.234(7)	0.567(3)	4(1)
H(10)	0.407(6)	0.179(8)	0.681(4)	6(1)
H(11)	0.443(5)	0.271(7)	0.763(3)	5(1)
H(12)	0.438(6)	0.099(7)	0.748(3)	6(1)
H(13)	0.788(4)	0.075(6)	0.691(3)	3(1)
H(14)	0.850(5)	-0.133(6)	0.618(3)	4(1)
H(15)	0.530(5)	-0.224(7)	0.564(3)	4(1)
H(16)	0.466(5)	-0.028(6)	0.623(3)	4(1)

H(17)	0.792(4)	0.344(6)	0.840(3)	3(1)
H(18)	0.923(5)	0.408(7)	0.927(3)	5(1)
H(19)	0.849(5)	0.015(7)	1.024(3)	4(1)
H(20)	0.722(6)	-0.046(8)	0.928(3)	5(1)

$$B_{eq} = 8/3 \left(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb*)\cos + 2U_{13}(aa*cc*)\cos + 2U_{23}(bb*cc*)\cos \right)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	0.0566(4)	0.0672(5)	0.0733(5)	-0.0020(4)	0.0069(3)	-0.0303(4)
Cl(1)	0.104(2)	0.107(2)	0.072(1)	0.019(1)	-0.042(1)	-0.021(1)
O(1)	0.043(2)	0.044(2)	0.058(3)	-0.002(2)	-0.012(2)	-0.007(2)
O(2)	0.044(3)	0.063(3)	0.102(4)	0.017(2)	-0.010(2)	-0.024(3)
O(3)	0.047(2)	0.037(2)	0.040(2)	-0.004(2)	-0.006(2)	-0.001(2)
O(4)	0.079(3)	0.054(3)	0.057(3)	-0.024(3)	-0.006(2)	0.008(2)
C(1)	0.095(7)	0.054(5)	0.112(7)	0.000(5)	-0.063(6)	-0.019(5)
C(2)	0.068(5)	0.045(4)	0.065(5)	0.000(4)	-0.009(4)	-0.011(3)
C(3)	0.044(4)	0.042(3)	0.050(4)	0.001(3)	-0.006(3)	0.001(3)
C(4)	0.035(3)	0.035(3)	0.047(3)	0.004(2)	-0.006(3)	0.001(2)
C(5)	0.059(4)	0.062(5)	0.050(4)	-0.001(4)	-0.021(3)	0.003(4)
C(6)	0.033(3)	0.049(4)	0.039(3)	0.000(3)	-0.006(2)	-0.001(3)
C(7)	0.032(3)	0.065(5)	0.068(5)	-0.006(3)	0.012(3)	-0.004(4)
C(8)	0.029(3)	0.037(3)	0.043(3)	-0.005(2)	0.000(2)	-0.003(3)
C(9)	0.030(3)	0.041(3)	0.051(4)	-0.007(3)	-0.003(3)	-0.004(3)
C(10)	0.029(3)	0.043(3)	0.055(4)	-0.001(3)	-0.002(3)	-0.004(3)
C(11)	0.042(3)	0.047(3)	0.039(3)	-0.001(3)	0.005(3)	-0.008(3)
C(12)	0.039(3)	0.057(4)	0.056(4)	-0.006(3)	-0.009(3)	-0.021(3)
C(13)	0.029(3)	0.061(4)	0.054(4)	0.000(3)	-0.006(3)	-0.012(3)
C(14)	0.051(4)	0.048(4)	0.043(4)	0.003(3)	0.005(3)	0.000(3)
C(15)	0.059(4)	0.045(3)	0.035(3)	0.001(3)	-0.004(3)	-0.002(3)
C(16)	0.065(4)	0.050(4)	0.041(4)	-0.002(3)	-0.001(3)	0.000(3)
C(17)	0.076(5)	0.058(4)	0.056(4)	-0.005(4)	-0.008(4)	-0.009(3)
C(18)	0.069(4)	0.068(5)	0.040(4)	0.013(4)	-0.015(3)	-0.013(3)
C(19)	0.107(6)	0.065(5)	0.044(4)	0.009(5)	-0.017(4)	0.011(4)
C(20)	0.099(6)	0.053(4)	0.049(4)	-0.005(4)	-0.009(4)	0.007(3)

The general temperature factor expression:

$$\exp(-2 \left(a^2 U_{11} h^2 + b^2 U_{22} k^2 + c^2 U_{33} l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl \right))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Br(1)	C(11)	1.902(5)	Cl(1)	C(18)	1.730(6)
O(1)	C(2)	1.462(7)	O(1)	C(3)	1.339(6)
O(2)	C(3)	1.207(7)	O(3)	C(6)	1.468(6)
O(3)	C(14)	1.369(7)	O(4)	C(14)	1.196(7)
C(1)	C(2)	1.50(1)	C(1)	H(1)	0.8(1)
C(1)	H(2)	0.99(7)	C(1)	H(3)	1.1(1)
C(2)	H(4)	1.01(6)	C(2)	H(5)	1.16(7)
C(3)	C(4)	1.526(8)	C(4)	C(5)	1.541(8)
C(4)	C(6)	1.563(8)	C(4)	H(6)	1.08(7)
C(5)	H(7)	0.90(7)	C(5)	H(8)	1.01(6)
C(5)	H(9)	1.02(6)	C(6)	C(7)	1.531(8)
C(6)	C(8)	1.521(7)	C(7)	H(10)	0.97(7)
C(7)	H(11)	1.15(6)	C(7)	H(12)	0.91(7)
C(8)	C(9)	1.396(7)	C(8)	C(13)	1.392(7)
C(9)	C(10)	1.379(7)	C(9)	H(13)	1.00(5)
C(10)	C(11)	1.382(8)	C(10)	H(14)	0.96(6)
C(11)	C(12)	1.382(8)	C(12)	C(13)	1.372(8)
C(12)	H(15)	0.88(6)	C(13)	H(16)	0.92(5)
C(14)	C(15)	1.486(8)	C(15)	C(16)	1.384(8)
C(15)	C(20)	1.402(8)	C(16)	C(17)	1.370(9)
C(16)	H(17)	0.92(5)	C(17)	C(18)	1.399(9)
C(17)	H(18)	1.00(6)	C(18)	C(19)	1.36(1)
C(19)	C(20)	1.371(10)	C(19)	H(19)	0.92(6)
C(20)	H(20)	0.95(7)			

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	O(1)	C(3)	116.0(5)	C(6)	O(3)	C(14)	119.8(4)
C(2)	C(1)	H(1)	110(8)	C(2)	C(1)	H(2)	117(3)
C(2)	C(1)	H(3)	106(7)	H(1)	C(1)	H(2)	106(7)
H(1)	C(1)	H(3)	107(10)	H(2)	C(1)	H(3)	107(9)
O(1)	C(2)	C(1)	106.9(6)	O(1)	C(2)	H(4)	110(3)
O(1)	C(2)	H(5)	115(3)	C(1)	C(2)	H(4)	114(3)
C(1)	C(2)	H(5)	109(3)	H(4)	C(2)	H(5)	99(4)
O(1)	C(3)	O(2)	122.9(5)	O(1)	C(3)	C(4)	111.9(5)
O(2)	C(3)	C(4)	125.2(5)	C(3)	C(4)	C(5)	109.3(5)
C(3)	C(4)	C(6)	110.5(5)	C(3)	C(4)	H(6)	112(3)
C(5)	C(4)	C(6)	112.7(5)	C(5)	C(4)	H(6)	102(3)

C(6)	C(4)	H(6)	109(3)	C(4)	C(5)	H(7)	115(4)
C(4)	C(5)	H(8)	111(3)	C(4)	C(5)	H(9)	106(3)
H(7)	C(5)	H(8)	98(5)	H(7)	C(5)	H(9)	105(5)
H(8)	C(5)	H(9)	119(4)	O(3)	C(6)	C(4)	100.7(4)
O(3)	C(6)	C(7)	109.8(5)	O(3)	C(6)	C(8)	110.2(4)
C(4)	C(6)	C(7)	112.4(5)	C(4)	C(6)	C(8)	108.7(4)
C(7)	C(6)	C(8)	114.2(5)	C(6)	C(7)	H(10)	111(4)
C(6)	C(7)	H(11)	109(3)	C(6)	C(7)	H(12)	115(4)
H(10)	C(7)	H(11)	116(5)	H(10)	C(7)	H(12)	105(5)
H(11)	C(7)	H(12)	98(5)	C(6)	C(8)	C(9)	119.8(4)
C(6)	C(8)	C(13)	122.5(5)	C(9)	C(8)	C(13)	117.6(5)
C(8)	C(9)	C(10)	121.7(5)	C(8)	C(9)	H(13)	117(2)
C(10)	C(9)	H(13)	120(2)	C(9)	C(10)	C(11)	118.8(5)
C(9)	C(10)	H(14)	125(3)	C(11)	C(10)	H(14)	115(3)
Br(1)	C(11)	C(10)	119.4(4)	Br(1)	C(11)	C(12)	119.6(4)
C(10)	C(11)	C(12)	120.9(5)	C(11)	C(12)	C(13)	119.3(5)
C(11)	C(12)	H(15)	120(3)	C(13)	C(12)	H(15)	120(3)
C(8)	C(13)	C(12)	121.6(5)	C(8)	C(13)	H(16)	122(3)
C(12)	C(13)	H(16)	116(3)	O(3)	C(14)	O(4)	124.6(5)
O(3)	C(14)	C(15)	109.7(5)	O(4)	C(14)	C(15)	125.7(6)
C(14)	C(15)	C(16)	123.6(5)	C(14)	C(15)	C(20)	117.4(6)
C(16)	C(15)	C(20)	118.8(6)	C(15)	C(16)	C(17)	121.2(6)
C(15)	C(16)	H(17)	120(3)	C(17)	C(16)	H(17)	118(3)
C(16)	C(17)	C(18)	118.8(7)	C(16)	C(17)	H(18)	117(3)
C(18)	C(17)	H(18)	123(3)	Cl(1)	C(18)	C(17)	118.7(6)
Cl(1)	C(18)	C(19)	120.7(6)	C(17)	C(18)	C(19)	120.6(6)
C(18)	C(19)	C(20)	120.7(7)	C(18)	C(19)	H(19)	121(3)
C(20)	C(19)	H(19)	117(3)	C(15)	C(20)	C(19)	119.8(7)
C(15)	C(20)	H(20)	113(4)	C(19)	C(20)	H(20)	125(4)

Table 5. Torsion Angles($^{\circ}$)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Br(1)	C(11)	C(10)	C(9)	178.8(4)	Br(1)	C(11)	C(12)	C(13)	-179.0(5)
Cl(1)	C(18)	C(17)	C(16)	179.7(5)	Cl(1)	C(18)	C(19)	C(20)	-178.0(6)
O(1)	C(3)	C(4)	C(5)	-132.9(6)	O(1)	C(3)	C(4)	C(6)	102.7(5)
O(2)	C(3)	O(1)	C(2)	0.2(9)	O(2)	C(3)	C(4)	C(5)	46.4(8)
O(2)	C(3)	C(4)	C(6)	-78.0(7)	O(3)	C(6)	C(4)	C(3)	-54.0(5)
O(3)	C(6)	C(4)	C(5)	-176.5(5)	O(3)	C(6)	C(8)	C(9)	-35.9(7)
O(3)	C(6)	C(8)	C(13)	147.5(5)	O(3)	C(14)	C(15)	C(16)	-1.0(8)
O(3)	C(14)	C(15)	C(20)	-176.5(5)	O(4)	C(14)	O(3)	C(6)	-1.4(8)
O(4)	C(14)	C(15)	C(16)	179.5(6)	O(4)	C(14)	C(15)	C(20)	4.0(10)
C(1)	C(2)	O(1)	C(3)	179.7(6)	C(2)	O(1)	C(3)	C(4)	179.5(5)
C(3)	C(4)	C(6)	C(7)	62.8(6)	C(3)	C(4)	C(6)	C(8)	-169.8(4)

C(4)	C(6)	O(3)	C(14)	-178.5(4)	C(4)	C(6)	C(8)	C(9)	73.5(6)
C(4)	C(6)	C(8)	C(13)	-103.0(6)	C(5)	C(4)	C(6)	C(7)	-59.7(7)
C(5)	C(4)	C(6)	C(8)	67.7(6)	C(6)	O(3)	C(14)	C(15)	179.0(4)
C(6)	C(8)	C(9)	C(10)	-175.3(5)	C(6)	C(8)	C(13)	C(12)	175.0(6)
C(7)	C(6)	O(3)	C(14)	62.8(6)	C(7)	C(6)	C(8)	C(9)	-160.1(6)
C(7)	C(6)	C(8)	C(13)	23.4(8)	C(8)	C(6)	O(3)	C(14)	-63.9(6)
C(8)	C(9)	C(10)	C(11)	-0.2(9)	C(8)	C(13)	C(12)	C(11)	0.7(10)
C(9)	C(8)	C(13)	C(12)	-1.6(9)	C(9)	C(10)	C(11)	C(12)	-0.8(9)
C(10)	C(9)	C(8)	C(13)	1.4(8)	C(10)	C(11)	C(12)	C(13)	0.6(10)
C(14)	C(15)	C(16)	C(17)	-175.4(6)	C(14)	C(15)	C(20)	C(19)	177.4(7)
C(15)	C(16)	C(17)	C(18)	-1(1)	C(15)	C(20)	C(19)	C(18)	-2(1)
C(16)	C(15)	C(20)	C(19)	1(1)	C(16)	C(17)	C(18)	C(19)	0(1)
C(17)	C(16)	C(15)	C(20)	0.0(10)	C(17)	C(18)	C(19)	C(20)	0(1)

Table 6. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
Br(1)	H(8) ¹⁾	3.03(6)	Br(1)	H(16) ²⁾	3.26(6)
Br(1)	H(9) ³⁾	3.29(6)	Br(1)	H(7) ⁴⁾	3.32(7)
Br(1)	H(15) ²⁾	3.47(6)	Cl(1)	H(2) ⁵⁾	3.07(7)
Cl(1)	H(18) ⁵⁾	3.19(6)	Cl(1)	H(20) ⁶⁾	3.22(7)
Cl(1)	H(4) ⁷⁾	3.27(6)	Cl(1)	H(1) ⁵⁾	3.3(1)
Cl(1)	H(19) ⁸⁾	3.37(6)	Cl(1)	O(4) ⁶⁾	3.496(5)
O(1)	H(12) ⁹⁾	3.09(7)	O(1)	H(10) ⁹⁾	3.28(7)
O(2)	H(14) ¹⁰⁾	2.69(6)	O(2)	H(13) ¹⁰⁾	2.72(5)
O(2)	H(3) ¹¹⁾	3.0(2)	O(2)	C(10) ¹⁰⁾	3.250(7)
O(2)	C(9) ¹⁰⁾	3.313(7)	O(3)	H(11) ⁹⁾	3.42(6)
O(4)	H(5) ¹⁾	2.58(7)	O(4)	H(1) ¹⁾	3.1(1)
O(4)	H(4) ¹⁾	3.13(5)	O(4)	H(18) ¹⁰⁾	3.16(6)
O(4)	H(2) ¹⁰⁾	3.16(7)	O(4)	C(2) ¹⁾	3.275(8)
O(4)	C(1) ¹⁾	3.59(1)	C(1)	H(12) ⁹⁾	3.25(7)
C(1)	H(20) ¹²⁾	3.58(7)	C(3)	H(14) ¹⁰⁾	3.57(6)
C(4)	H(10) ⁹⁾	3.51(7)	C(5)	H(15) ⁴⁾	3.17(6)
C(5)	H(14) ¹⁰⁾	3.52(6)	C(7)	H(13) ¹⁰⁾	3.02(5)
C(7)	H(17) ¹⁰⁾	3.08(5)	C(7)	H(6) ¹⁰⁾	3.39(7)
C(7)	C(16) ¹⁰⁾	3.564(9)	C(8)	H(5) ¹⁾	2.97(7)
C(9)	H(5) ¹⁾	2.95(7)	C(9)	H(7) ⁹⁾	3.33(7)
C(9)	H(3) ¹⁾	3.3(2)	C(9)	H(10) ⁹⁾	3.46(7)
C(10)	H(3) ¹⁾	3.0(1)	C(10)	H(5) ¹⁾	3.05(7)
C(10)	H(7) ⁹⁾	3.28(7)	C(11)	H(5) ¹⁾	3.13(6)

C(12)	H(5) ¹⁾	3.12(7)	C(12)	H(9) ⁴⁾	3.23(6)
C(12)	H(14) ¹³⁾	3.36(6)	C(13)	H(5) ¹⁾	3.03(7)
C(14)	H(1) ¹⁾	3.4(1)	C(14)	H(5) ¹⁾	3.38(7)
C(14)	H(18) ¹⁰⁾	3.53(6)	C(15)	H(11) ⁹⁾	3.42(6)
C(15)	H(1) ¹⁾	3.6(1)	C(16)	H(11) ⁹⁾	2.82(6)
C(16)	H(12) ⁹⁾	3.19(7)	C(16)	H(19) ⁶⁾	3.42(6)
C(17)	H(20) ⁶⁾	3.31(7)	C(17)	H(11) ⁹⁾	3.35(6)
C(17)	H(19) ⁶⁾	3.46(6)	C(18)	H(20) ⁶⁾	3.11(7)
C(20)	H(1) ¹⁾	3.3(1)	H(1)	H(20) ¹²⁾	2.8(1)
H(1)	H(13) ¹²⁾	3.6(1)	H(2)	H(12) ⁹⁾	2.72(9)
H(3)	H(14) ¹²⁾	2.8(2)	H(3)	H(12) ⁹⁾	3.0(2)
H(3)	H(16) ⁹⁾	3.3(2)	H(3)	H(13) ¹²⁾	3.4(2)
H(3)	H(5) ¹⁴⁾	3.5(2)	H(4)	H(19) ⁶⁾	3.34(8)
H(5)	H(13) ¹²⁾	3.47(9)	H(5)	H(16) ¹²⁾	3.57(9)
H(5)	H(15) ¹²⁾	3.59(9)	H(6)	H(10) ⁹⁾	2.6(1)
H(6)	H(12) ⁹⁾	3.49(10)	H(7)	H(14) ¹⁰⁾	2.88(9)
H(7)	H(13) ¹⁰⁾	2.94(8)	H(7)	H(15) ⁴⁾	3.23(8)
H(7)	H(8) ¹⁵⁾	3.55(8)	H(8)	H(8) ¹⁵⁾	3.0(1)
H(8)	H(15) ¹²⁾	3.13(9)	H(8)	H(15) ⁴⁾	3.16(8)
H(8)	H(14) ¹⁰⁾	3.30(8)	H(9)	H(15) ⁴⁾	2.59(7)
H(10)	H(13) ¹⁰⁾	2.63(8)	H(10)	H(17) ¹⁰⁾	3.41(9)
H(11)	H(17) ¹⁰⁾	2.59(8)	H(11)	H(13) ¹⁰⁾	2.62(8)
H(11)	H(18) ¹⁰⁾	3.51(8)	H(12)	H(17) ¹⁰⁾	2.59(9)
H(12)	H(18) ¹⁰⁾	3.41(9)	H(12)	H(13) ¹⁰⁾	3.55(8)
H(14)	H(15) ²⁾	2.73(8)	H(14)	H(16) ²⁾	3.33(8)
H(17)	H(19) ⁶⁾	3.50(8)	H(18)	H(20) ⁶⁾	3.36(8)
H(18)	H(19) ⁶⁾	3.54(9)			

Symmetry operations

(1)	X, Y-1, Z	(2)	X+1/2, -Y-1/2, Z
(3)	-X+3/2, Y-1/2, -Z+1	(4)	-X+1, -Y, -Z+1
(5)	-X+2, -Y+1, -Z+2	(6)	-X+3/2, Y+1/2, -Z+2
(7)	-X+3/2, Y-1/2, -Z+2	(8)	-X+2, -Y, -Z+2
(9)	X+1/2, -Y+1/2, Z	(10)	X-1/2, -Y+1/2, Z
(11)	X-1/2, -Y+3/2, Z	(12)	X, Y+1, Z
(13)	X-1/2, -Y-1/2, Z	(14)	X+1/2, -Y+3/2, Z
(15)	-X+1, -Y+1, -Z+1		

X-ray Structure Report for **7gaB**

Experimental

Data Collection

A colorless prism crystal of $C_{24}ClH_{23}O_4$ having approximate dimensions of 0.65 x 0.40 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K radiation.

Indexing was performed from 3 oscillations which were exposed for 3.0 minutes. The camera radius was 127.40 mm. Readout was performed in the 0.125 mm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned} a &= 9.4195(3) \text{ \AA} \\ b &= 21.7175(6) \text{ \AA} & \beta &= 90.8136(7)^\circ \\ c &= 10.4372(3) \text{ \AA} \\ V &= 2134.9(1) \text{ \AA}^3 \end{aligned}$$

For $Z = 4$ and F.W. = 410.90, the calculated density is 1.28 g/cm³. The systematic absences of:

$$\begin{aligned} h0l: & l \neq 2n \\ 0k0: & k \neq 2n \end{aligned}$$

uniquely determine the space group to be:

$$P2_1/c \text{ (\#14)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ to a maximum 2θ value of 60.6° . A total of 74 images, corresponding to 222.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 1.00 minutes per degree. The camera radius was 127.40 mm. Readout was performed in the 0.125 mm pixel mode. Data were processed by the PROCESS-AUTO program package.

Data Reduction

Of the 23431 reflections which were collected, 6379 were unique ($R_{\text{int}} = 0.059$).

The linear absorption coefficient, μ , for Mo-K radiation is 2.1 cm^{-1} . A symmetry-related absorption correction using the program ABSCOR¹ was applied which resulted in transmission factors ranging from 0.30 to 0.94. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques³. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement⁴ was based on 3806 observed reflections ($I > 2.00 (I)$, $2\theta < 60.59$) and 354 variable parameters and converged (largest parameter shift was 3.42 times its esd) with unweighted and weighted agreement factors of:

$$R = (\sum (F_o^2 - F_c^2) / \sum F_o^2) = 0.093$$

$$R_w = [(\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2)]^{1/2} = 0.169$$

$$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|) = 0.080 \quad \text{for } I > 2.0 (I) \text{ data}$$

The standard deviation of an observation of unit weight⁵ was 2.23. The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to downweight the intense reflections. Plots of $w (F_o^2 - F_c^2)^2$ versus F_o^2 reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and $-0.28 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁶. Anomalous dispersion effects were included in F_{calc} ⁷; the values for f' and f'' were those of Creagh and McAuley⁸. The

values for the mass attenuation coefficients are those of Creagh and Hubbel⁹. All calculations were performed using the teXsan¹⁰ crystallographic software package of Molecular Structure Corporation.

References

(1) ABSCOR: Higashi T. (1995). Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan.

(2) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G., (1994). J. Appl. Cryst. 27, 435.

(3) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least-Squares:

Function minimized: $w(F_o^2 - F_c^2)^2$ where
 $w = 1/[^2(F_o^2)] = [^2_c(F_o^2) + (p$
 $(\text{Max}(F_o^2, 0) + 2F_c^2)/3)^2]^{-1}$
 $_c(F_o^2) = \text{e.s.d. based on counting statistics}$
 $p = p\text{-factor}$

(5) Standard deviation of an observation of unit weight:

$[w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$
 where: N_o = number of observations
 N_v = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

- (8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (9) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
- (10) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1999).

EXPERIMENTAL DETAILS

A. Crystal Data for **7gaB**

Empirical Formula	C ₂₄ ClH ₂₃ O ₄
Formula Weight	410.90
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.65 X 0.40 X 0.30 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 range)	22912 (4.3 - 60.6°)
Indexing Images	3 oscillations at 3.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 9.4195(3) Å b = 21.7175(6) Å c = 10.4372(3) Å = 90.8136(7)° V = 2134.9(1) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.278 g/cm ³
F ₀₀₀	864.00
(MoK)	2.06 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoK (= 0.71069 Å) graphite monochromated
Temperature	23.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.8 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	74 exposures at 1.0 minutes per degree
Oscillation Range (=0.0°, =45.0°)	130.0 - 190.0° with 3.0° step

Oscillation Range (ϕ =180.0 $^\circ$, ω =45.0 $^\circ$)	0.0 - 162.0 $^\circ$ with 3.0 $^\circ$ step
Camera Radius	127.40 mm
Pixel Size	0.125 mm
$2\theta_{\text{max}}$	60.6 $^\circ$
No. of Reflections Measured	Total: 23431 Unique: 6379 ($R_{\text{int}} = 0.059$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.3030 - 0.9402)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1 / \sigma^2(F_o^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Observations ($I > 2.00 \langle I \rangle$, $2\theta < 60.59^\circ$)	3806
No. Variables	354
Reflection/Parameter Ratio	10.75
Residuals: R ; R_w	0.093 ; 0.169
Residuals: R_1	0.080
No. of Reflections to calc R_1	3806
Goodness of Fit Indicator	2.23
Max Shift/Error in Final Cycle	3.418
Maximum peak in Final Diff. Map	0.47 e $^-$ / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.28 e $^-$ / $\text{\AA}^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
C1	1.1946(1)	0.00551(4)	-0.73158(8)	5.74(2)
O(1)	1.4143(3)	0.1183(1)	-0.0970(2)	5.87(6)
O(2)	1.3985(3)	0.2176(1)	-0.0509(4)	8.56(10)
O(3)	1.1025(2)	0.13769(9)	-0.1704(2)	3.56(4)
O(4)	0.8968(2)	0.1703(1)	-0.2619(2)	4.80(5)
C(1)	1.5277(6)	0.1451(5)	-0.2955(5)	9.6(2)
C(2)	1.5497(5)	0.1313(4)	-0.1609(5)	8.0(1)
C(3)	1.3535(4)	0.1666(2)	-0.0456(3)	4.86(8)
C(4)	1.2183(3)	0.1495(1)	0.0267(3)	3.52(6)
C(5)	1.2291(5)	0.1759(2)	0.1615(3)	4.81(9)
C(6)	1.0825(3)	0.1693(1)	-0.0474(2)	3.27(6)
C(7)	1.0744(5)	0.2384(1)	-0.0694(4)	4.76(8)
C(8)	0.9529(3)	0.1432(1)	0.0189(2)	3.12(5)
C(9)	0.9175(3)	0.0800(1)	0.0039(3)	3.68(6)
C(10)	0.8084(4)	0.0545(1)	0.0678(3)	4.20(7)
C(11)	0.7285(3)	0.0885(1)	0.1546(3)	3.80(6)
C(12)	0.6156(4)	0.0633(2)	0.2280(4)	5.20(9)
C(13)	0.5480(4)	0.0982(2)	0.3152(4)	6.1(1)
C(14)	0.5842(4)	0.1605(2)	0.3350(4)	5.82(10)
C(15)	0.6874(4)	0.1864(2)	0.2640(3)	4.78(8)
C(16)	0.7627(3)	0.1517(1)	0.1726(3)	3.53(6)
C(17)	0.8741(3)	0.1774(1)	0.1016(3)	3.58(6)
C(18)	1.0061(3)	0.1419(1)	-0.2667(3)	3.40(6)
C(19)	1.0538(3)	0.1066(1)	-0.3805(2)	3.09(5)
C(20)	1.1764(3)	0.0712(1)	-0.3770(3)	3.67(6)
C(21)	1.2194(4)	0.0396(1)	-0.4846(3)	4.16(7)
C(22)	1.1401(3)	0.0442(1)	-0.5953(3)	3.71(6)
C(23)	1.0175(4)	0.0782(1)	-0.6011(3)	4.17(7)
C(24)	0.9742(4)	0.1098(1)	-0.4930(3)	3.86(7)
H(1)	1.632(7)	0.156(2)	-0.338(6)	11(1)
H(2)	1.493(7)	0.110(3)	-0.338(6)	11(1)
H(3)	1.492(8)	0.180(3)	-0.313(8)	22(2)
H(4)	1.614(7)	0.102(2)	-0.142(6)	11(1)
H(5)	1.592(5)	0.174(2)	-0.123(5)	9(1)
H(6)	1.240(4)	0.221(2)	0.156(4)	6.5(9)
H(7)	1.319(5)	0.167(2)	0.203(4)	6.9(10)
H(8)	1.142(5)	0.169(2)	0.209(4)	7(1)
H(9)	1.215(3)	0.111(1)	0.032(2)	1.9(5)
H(10)	1.082(4)	0.260(2)	0.003(4)	5.6(9)
H(11)	1.147(4)	0.249(2)	-0.127(4)	6.2(9)
H(12)	0.971(5)	0.249(2)	-0.120(4)	7(1)
H(13)	0.972(4)	0.055(1)	-0.059(3)	5.5(8)

H(14)	0.776(4)	0.017(2)	0.055(3)	5.5(8)
H(15)	0.595(3)	0.020(2)	0.199(3)	4.8(7)
H(16)	0.475(4)	0.077(2)	0.365(4)	6.9(9)
H(17)	0.535(4)	0.186(2)	0.407(4)	6.9(9)
H(18)	0.706(4)	0.231(2)	0.276(3)	5.4(8)
H(19)	0.891(2)	0.221(1)	0.112(2)	1.9(4)
H(20)	1.226(3)	0.070(1)	-0.299(3)	3.9(7)
H(21)	1.294(4)	0.013(2)	-0.487(4)	6.0(9)
H(22)	0.965(3)	0.082(1)	-0.683(3)	4.1(7)
H(23)	0.897(4)	0.134(1)	-0.488(3)	5.1(7)

$$B_{eq} = 8/3 \quad 2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb*)\cos \quad + \\ 2U_{13}(aa*cc*)\cos \quad + 2U_{23}(bb*cc*)\cos \quad)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cl	0.1004(8)	0.0753(6)	0.0430(4)	-0.0180(5)	0.0181(4)	-0.0181(4)
O(1)	0.056(1)	0.104(2)	0.064(2)	0.006(1)	0.012(1)	-0.015(1)
O(2)	0.095(2)	0.088(2)	0.144(3)	-0.035(2)	0.050(2)	-0.005(2)
O(3)	0.051(1)	0.056(1)	0.0292(9)	0.0068(9)	0.0042(8)	-0.0044(8)
O(4)	0.057(1)	0.068(1)	0.058(1)	0.018(1)	-0.001(1)	-0.003(1)
C(1)	0.068(3)	0.228(8)	0.069(3)	-0.041(4)	0.019(2)	-0.006(4)
C(2)	0.047(2)	0.181(6)	0.075(3)	0.005(3)	0.019(2)	-0.007(3)
C(3)	0.066(2)	0.070(2)	0.049(2)	-0.002(2)	0.007(2)	-0.003(2)
C(4)	0.050(2)	0.046(2)	0.038(1)	-0.007(1)	0.008(1)	-0.004(1)
C(5)	0.065(2)	0.076(2)	0.042(2)	-0.009(2)	-0.001(2)	-0.013(2)
C(6)	0.053(2)	0.040(1)	0.032(1)	0.001(1)	0.008(1)	-0.004(1)
C(7)	0.087(3)	0.042(2)	0.052(2)	-0.006(2)	0.017(2)	0.003(1)
C(8)	0.047(2)	0.040(1)	0.032(1)	0.003(1)	0.002(1)	-0.002(1)
C(9)	0.054(2)	0.043(2)	0.043(2)	0.002(1)	0.005(1)	-0.003(1)
C(10)	0.062(2)	0.042(2)	0.055(2)	-0.003(1)	0.000(2)	0.001(1)
C(11)	0.041(2)	0.055(2)	0.049(2)	0.001(1)	-0.002(1)	0.008(1)
C(12)	0.056(2)	0.069(2)	0.072(2)	-0.004(2)	0.006(2)	0.019(2)
C(13)	0.048(2)	0.102(3)	0.080(3)	0.005(2)	0.023(2)	0.024(2)
C(14)	0.055(2)	0.097(3)	0.069(2)	0.019(2)	0.017(2)	0.004(2)
C(15)	0.056(2)	0.068(2)	0.058(2)	0.014(2)	0.013(2)	-0.008(2)
C(16)	0.042(2)	0.051(2)	0.042(1)	0.009(1)	0.003(1)	0.000(1)
C(17)	0.053(2)	0.037(1)	0.046(2)	0.003(1)	0.006(1)	-0.004(1)
C(18)	0.051(2)	0.041(1)	0.037(1)	0.000(1)	0.005(1)	0.003(1)
C(19)	0.046(2)	0.039(1)	0.033(1)	-0.004(1)	0.004(1)	0.003(1)
C(20)	0.049(2)	0.058(2)	0.032(1)	-0.001(1)	0.000(1)	-0.002(1)
C(21)	0.057(2)	0.058(2)	0.043(2)	0.002(2)	0.008(1)	-0.004(1)
C(22)	0.062(2)	0.045(2)	0.034(1)	-0.016(1)	0.011(1)	-0.003(1)
C(23)	0.070(2)	0.056(2)	0.033(1)	-0.016(2)	-0.008(1)	0.003(1)
C(24)	0.057(2)	0.047(2)	0.042(2)	-0.001(1)	-0.002(1)	0.006(1)

The general temperature factor expression:

$$\exp(-2^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Cl(1)	C(7)	1.736(3)	O(1)	C(8)	1.348(3)
O(1)	C(11)	1.471(3)	O(2)	C(8)	1.202(3)
O(3)	C(18)	1.313(4)	O(3)	C(23)	1.474(5)
O(4)	C(18)	1.189(4)	C(1)	C(4)	1.365(4)
C(1)	C(6)	1.422(4)	C(1)	C(11)	1.521(4)
C(2)	C(10)	1.387(4)	C(2)	C(16)	1.382(4)
C(3)	C(11)	1.547(4)	C(3)	C(14)	1.521(4)
C(3)	C(18)	1.535(4)	C(4)	C(25)	1.409(4)
C(5)	C(10)	1.386(4)	C(5)	C(15)	1.386(4)
C(6)	C(12)	1.352(4)	C(7)	C(15)	1.372(4)
C(7)	C(16)	1.370(4)	C(8)	C(10)	1.487(4)
C(9)	C(12)	1.398(4)	C(9)	C(19)	1.429(4)
C(9)	C(25)	1.421(4)	C(11)	C(13)	1.518(4)
C(19)	C(20)	1.350(5)	C(20)	C(22)	1.411(6)
C(21)	C(22)	1.353(5)	C(21)	C(25)	1.414(4)
C(23)	C(24)	1.449(8)			

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
C(2)	H(20)	0.94(3)	C(3)	H(1)	0.83(2)
C(4)	H(9)	0.97(2)	C(5)	H(19)	0.89(3)
C(6)	H(15)	1.00(3)	C(12)	H(10)	0.89(3)
C(13)	H(13)	0.89(4)	C(13)	H(14)	0.95(4)
C(13)	H(22)	1.13(5)	C(14)	H(2)	0.98(4)
C(14)	H(3)	0.98(4)	C(14)	H(4)	0.97(4)
C(15)	H(18)	0.99(3)	C(16)	H(21)	0.92(4)
C(19)	H(5)	1.02(3)	C(20)	H(8)	0.98(4)
C(21)	H(7)	0.98(3)	C(22)	H(6)	1.04(4)
C(23)	H(11)	0.89(6)	C(23)	H(12)	1.09(5)
C(24)	H(16)	1.10(6)	C(24)	H(17)	0.94(6)
C(24)	H(23)	0.84(7)			

Table 5. Bond Angles($^{\circ}$)

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	O(1)	C(11)	121.7(2)	C(18)	O(3)	C(23)	114.7(4)
C(4)	C(1)	C(6)	117.8(3)	C(4)	C(1)	C(11)	122.1(2)
C(6)	C(1)	C(11)	119.9(2)	C(10)	C(2)	C(16)	120.5(3)
C(11)	C(3)	C(14)	113.7(3)	C(11)	C(3)	C(18)	111.9(2)
C(14)	C(3)	C(18)	108.6(3)	C(1)	C(4)	C(25)	122.2(3)
C(10)	C(5)	C(15)	120.2(3)	C(1)	C(6)	C(12)	121.4(3)
Cl(1)	C(7)	C(15)	118.9(2)	Cl(1)	C(7)	C(16)	119.5(2)
C(15)	C(7)	C(16)	121.6(3)	O(1)	C(8)	O(2)	124.9(2)
O(1)	C(8)	C(10)	110.7(2)	O(2)	C(8)	C(10)	124.5(3)
C(12)	C(9)	C(19)	123.8(3)	C(12)	C(9)	C(25)	118.3(3)
C(19)	C(9)	C(25)	117.9(3)	C(2)	C(10)	C(5)	119.3(3)
C(2)	C(10)	C(8)	121.7(2)	C(5)	C(10)	C(8)	119.0(3)
O(1)	C(11)	C(1)	109.7(2)	O(1)	C(11)	C(3)	101.0(2)
O(1)	C(11)	C(13)	109.6(2)	C(1)	C(11)	C(3)	109.4(2)
C(1)	C(11)	C(13)	113.5(2)	C(3)	C(11)	C(13)	113.0(3)
C(6)	C(12)	C(9)	121.5(3)	C(5)	C(15)	C(7)	119.2(3)
C(2)	C(16)	C(7)	119.1(3)	O(3)	C(18)	O(4)	124.6(3)
O(3)	C(18)	C(3)	112.2(3)	O(4)	C(18)	C(3)	123.2(3)
C(9)	C(19)	C(20)	120.6(3)	C(19)	C(20)	C(22)	121.4(3)
C(22)	C(21)	C(25)	121.2(3)	C(20)	C(22)	C(21)	119.5(3)
O(3)	C(23)	C(24)	111.4(4)	C(4)	C(25)	C(9)	118.8(2)
C(4)	C(25)	C(21)	121.9(3)	C(9)	C(25)	C(21)	119.3(3)

Table 6. Bond Angles($^{\circ}$)

atom	atom	atom	angle	atom	atom	atom	angle
C(10)	C(2)	H(20)	116(1)	C(16)	C(2)	H(20)	123(1)
C(11)	C(3)	H(1)	106(1)	C(14)	C(3)	H(1)	108(1)
C(18)	C(3)	H(1)	107(1)	C(1)	C(4)	H(9)	120(1)
C(25)	C(4)	H(9)	116(1)	C(10)	C(5)	H(19)	113(2)
C(15)	C(5)	H(19)	125(2)	C(1)	C(6)	H(15)	118(1)
C(12)	C(6)	H(15)	120(1)	C(6)	C(12)	H(10)	124(2)
C(9)	C(12)	H(10)	113(2)	C(11)	C(13)	H(13)	112(2)
C(11)	C(13)	H(14)	108(2)	C(11)	C(13)	H(22)	108(2)
H(13)	C(13)	H(14)	111(3)	H(13)	C(13)	H(22)	110(3)
H(14)	C(13)	H(22)	105(3)	C(3)	C(14)	H(2)	109(2)
C(3)	C(14)	H(3)	111(2)	C(3)	C(14)	H(4)	112(2)
H(2)	C(14)	H(3)	106(3)	H(2)	C(14)	H(4)	97(3)
H(3)	C(14)	H(4)	118(3)	C(5)	C(15)	H(18)	120(1)

C(7)	C(15)	H(18)	119(1)	C(2)	C(16)	H(21)	125(2)
C(7)	C(16)	H(21)	115(2)	C(9)	C(19)	H(5)	109(1)
C(20)	C(19)	H(5)	129(1)	C(19)	C(20)	H(8)	116(2)
C(22)	C(20)	H(8)	122(2)	C(22)	C(21)	H(7)	117(1)
C(25)	C(21)	H(7)	120(1)	C(20)	C(22)	H(6)	119(2)
C(21)	C(22)	H(6)	120(2)	O(3)	C(23)	H(11)	110(3)
O(3)	C(23)	H(12)	108(2)	C(24)	C(23)	H(11)	116(3)
C(24)	C(23)	H(12)	102(2)	H(11)	C(23)	H(12)	106(4)
C(23)	C(24)	H(16)	108(3)	C(23)	C(24)	H(17)	109(4)
C(23)	C(24)	H(23)	116(5)	H(16)	C(24)	H(17)	106(4)
H(16)	C(24)	H(23)	94(5)	H(17)	C(24)	H(23)	119(6)

Table 7. Torsion Angles($^{\circ}$)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Cl(1)	C(7)	C(15)	C(5)	-179.3(2)	Cl(1)	C(7)	C(16)	C(2)	179.1(2)
O(1)	C(8)	C(10)	C(2)	4.9(4)	O(1)	C(8)	C(10)	C(5)	-174.6(2)
O(1)	C(11)	C(1)	C(4)	-152.0(2)	O(1)	C(11)	C(1)	C(6)	33.2(3)
O(1)	C(11)	C(3)	C(14)	179.8(2)	O(1)	C(11)	C(3)	C(18)	56.3(3)
O(2)	C(8)	O(1)	C(11)	-0.9(4)	O(2)	C(8)	C(10)	C(2)	-175.4(3)
O(2)	C(8)	C(10)	C(5)	5.1(4)	O(3)	C(18)	C(3)	C(11)	-106.2(3)
O(3)	C(18)	C(3)	C(14)	127.5(3)	O(4)	C(18)	O(3)	C(23)	1.9(6)
O(4)	C(18)	C(3)	C(11)	75.5(4)	O(4)	C(18)	C(3)	C(14)	-50.8(5)
C(1)	C(4)	C(25)	C(9)	-2.0(4)	C(1)	C(4)	C(25)	C(21)	175.9(3)
C(1)	C(6)	C(12)	C(9)	-2.1(5)	C(1)	C(11)	O(1)	C(8)	64.2(3)
C(1)	C(11)	C(3)	C(14)	-64.6(3)	C(1)	C(11)	C(3)	C(18)	171.9(2)
C(2)	C(10)	C(5)	C(15)	-0.6(4)	C(2)	C(16)	C(7)	C(15)	-1.4(4)
C(3)	C(11)	O(1)	C(8)	179.6(2)	C(3)	C(11)	C(1)	C(4)	98.1(3)
C(3)	C(11)	C(1)	C(6)	-76.7(3)	C(3)	C(18)	O(3)	C(23)	-176.4(3)
C(4)	C(1)	C(6)	C(12)	0.8(4)	C(4)	C(1)	C(11)	C(13)	-29.0(4)
C(4)	C(25)	C(9)	C(12)	0.7(4)	C(4)	C(25)	C(9)	C(19)	179.7(3)
C(4)	C(25)	C(21)	C(22)	-177.4(3)	C(5)	C(10)	C(2)	C(16)	0.4(4)
C(5)	C(15)	C(7)	C(16)	1.2(4)	C(6)	C(1)	C(4)	C(25)	1.2(4)
C(6)	C(1)	C(11)	C(13)	156.2(3)	C(6)	C(12)	C(9)	C(19)	-177.7(3)
C(6)	C(12)	C(9)	C(25)	1.3(5)	C(7)	C(15)	C(5)	C(10)	-0.2(4)
C(7)	C(16)	C(2)	C(10)	0.5(4)	C(8)	O(1)	C(11)	C(13)	-61.0(3)
C(8)	C(10)	C(2)	C(16)	-179.0(3)	C(8)	C(10)	C(5)	C(15)	178.9(2)
C(9)	C(19)	C(20)	C(22)	1.2(6)	C(9)	C(25)	C(21)	C(22)	0.4(5)
C(10)	C(8)	O(1)	C(11)	178.9(2)	C(11)	C(1)	C(4)	C(25)	-173.6(3)
C(11)	C(1)	C(6)	C(12)	175.8(3)	C(12)	C(9)	C(19)	C(20)	176.4(3)
C(12)	C(9)	C(25)	C(21)	-177.3(3)	C(13)	C(11)	C(3)	C(14)	62.8(3)
C(13)	C(11)	C(3)	C(18)	-60.7(3)	C(18)	O(3)	C(23)	C(24)	-91.4(7)
C(19)	C(9)	C(25)	C(21)	1.8(4)	C(19)	C(20)	C(22)	C(21)	1.1(6)
C(20)	C(19)	C(9)	C(25)	-2.6(5)	C(20)	C(22)	C(21)	C(25)	-1.9(6)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
Cl(1)	C(6) ¹⁾	3.544(3)	Cl(1)	C(10) ¹⁾	3.585(3)
O(2)	C(24) ²⁾	3.532(6)	O(2)	C(23) ²⁾	3.552(5)
O(4)	C(22) ³⁾	3.397(5)	C(5)	C(13) ⁴⁾	3.525(4)
C(15)	C(16) ¹⁾	3.520(4)			

Symmetry operations

(1)	-X+2,-Y,-Z-1	(2)	X-1,Y,Z
(3)	X+1,-Y+1/2,Z-1/2	(4)	X,-Y+1/2,Z-1/2

X-ray Structure Report of **13aB**

13aB

Experimental

Data Collection

A colorless prism crystal of $C_{13}H_{20}O_3$ having approximate dimensions of 0.00 x 0.15 x 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation.

Indexing was performed from 2 oscillations which were exposed for 3.0 minutes. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned}a &= 5.9017(1) \text{ \AA} \\b &= 8.0644(6) \text{ \AA} \quad \beta = 94.785(2)^\circ \\c &= 13.7216(5) \text{ \AA} \\V &= 650.79(6) \text{ \AA}^3\end{aligned}$$

For $Z = 2$ and F.W. = 224.30, the calculated density is 1.14 g/cm³. Based on the systematic absences of:

$$0k0: k \pm 2n$$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$P2_1 \text{ (#4)}$$

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ to a maximum 2θ value of 60.4° . A total of 55 images, corresponding to 220.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 2.50 minutes per degree. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. Data were processed by the PROCESS-AUTO program package.

Data Reduction

Of the 5854 reflections which were collected, 3477 were unique ($R_{\text{int}} = 0.221$).

The linear absorption coefficient, μ , for Mo-K α radiation is 0.8 cm⁻¹. A symmetry-related absorption correction using the program ABSCOR¹ was applied which resulted in transmission factors ranging from 0.00 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques³. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement⁴ was based on 3471 all reflections ($2\theta < 60.43$) and 226 variable parameters and converged (largest parameter shift was 6.66 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma (F_o^2 - F_c^2) / \Sigma F_o^2 = 0.335$$

$$R_w = [(\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2)]^{1/2} = 0.389$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.186 \quad \text{for } l > 2.0\sigma(l) \text{ data}$$

The standard deviation of an observation of unit weight⁵ was 3.03. The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to downweight the intense reflections. Plots of $\sum w (F_o^2 - F_c^2)^2$ versus F_o^2 reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.22 and -0.73 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁶. Anomalous dispersion effects were included in Fcalc⁷; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁸. The values for the mass attenuation coefficients are those of Creagh and Hubbel⁹. All calculations were performed using the teXsan¹⁰ crystallographic software package of Molecular Structure Corporation.

References

- (1) ABSCOR: Higashi T. (1995). Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan.
- (2) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G., (1994). J. Appl. Cryst. 27, 435.
- (3) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- (4) Least-Squares:

Function minimized: $\sum w(F_o^2 - F_c^2)^2$ where

$$w = 1/[\sigma^2(F_o^2)] = [\sigma_c^2(F_o^2) + (p (\text{Max}(F_o^2, 0) + 2F_c^2)/3)^2]^{-1}$$

$\sigma_c(F_o^2)$ = e.s.d. based on counting statistics

p = p-factor

- (5) Standard deviation of an observation of unit weight:

$$[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

- (6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- (7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
- (8) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (9) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer

Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1999).

EXPERIMENTAL DETAILS

A. Crystal Data for **13aB**

Empirical Formula	C ₁₃ H ₂₀ O ₃
Formula Weight	224.30
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.00 X 0.15 X 0.40 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2 θ range)	3112 (3.0 - 60.2 ^o)
Indexing Images	2 oscillations at 3.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 5.9017(1) Å b = 8.0644(6) Å c = 13.7216(5) Å β = 94.785(2) ^o V = 650.79(6) Å ³
Space Group	P2 ₁ (#4)
Z value	2
D _{calc}	1.145 g/cm ³
F ₀₀₀	244.00
μ (MoK α)	0.80 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoK α (λ = 0.71069 Å) graphite monochromated
Temperature	23.0 °C
Voltage, Current	50 kV, 40 mA

Collimator Size	0.8 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	55 exposures at 2.5 minutes per degree
Oscillation Range ($\phi=0.0^\circ, \chi=45.0^\circ$)	ω 130.0 - 190.0 $^\circ$ with 4.0 $^\circ$ step
Oscillation Range ($\phi=180.0^\circ, \chi=45.0^\circ$)	ω 0.0 - 160.0 $^\circ$ with 4.0 $^\circ$ step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\text{max}}$	60.4 $^\circ$
No. of Reflections Measured	Total: 5854 Unique: 3477 ($R_{\text{int}} = 0.221$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.0003 - 1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Reflections (All, $2\sigma < 60.43^\circ$)	3471
No. Variables	226
Reflection/Parameter Ratio	15.36
Residuals: R; Rw	0.335 ; 0.389
Residuals: R1	0.186
No. of Reflections to calc R1	1436
Goodness of Fit Indicator	3.03
Max Shift/Error in Final Cycle	6.656
Maximum peak in Final Diff. Map	1.22 e $^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.73 e $^-/\text{\AA}^3$

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
O(1)	1.0272(6)	0.2295(6)	0.7161(3)	4.85(8)
O(2)	0.9209(7)	-0.2458(6)	0.5839(3)	6.22(10)
O(3)	0.8661(9)	0.4280(7)	0.5616(3)	7.2(1)
C(1)	0.461(1)	0.580(1)	0.7472(7)	7.5(2)
C(2)	0.645(1)	0.4489(9)	0.7621(4)	4.7(1)
C(3)	0.627(1)	0.3082(8)	0.6849(4)	5.1(1)
C(4)	0.8013(9)	0.1594(7)	0.7153(4)	4.10(9)
C(5)	0.780(1)	0.0163(8)	0.6413(4)	4.5(1)
C(6)	0.9292(10)	-0.1308(8)	0.6609(4)	4.4(1)
C(7)	0.640(1)	0.3704(9)	0.5811(4)	5.8(1)
C(8)	0.7702(8)	0.0991(8)	0.8189(4)	4.03(9)
C(9)	0.554(1)	0.0226(9)	0.8333(5)	5.7(1)
C(10)	0.532(2)	-0.037(1)	0.9303(5)	8.0(2)
C(11)	0.686(1)	-0.039(1)	0.9968(5)	8.6(2)
C(12)	0.911(2)	0.043(1)	0.9857(5)	8.9(2)
C(13)	0.939(1)	0.106(1)	0.8939(4)	5.8(1)
H(1)	0.47(1)	0.664(8)	0.810(4)	7(1)
H(2)	0.34(1)	0.534(9)	0.740(5)	9(1)
H(3)	0.47(1)	0.63(1)	0.698(6)	12(1)
H(4)	0.68(1)	0.407(8)	0.833(4)	7(1)
H(5)	0.76(1)	0.495(8)	0.758(4)	8(1)
H(6)	0.481(9)	0.270(8)	0.690(4)	6(1)
H(7)	1.137(9)	0.184(7)	0.737(4)	5(1)
H(8)	0.62(1)	-0.022(7)	0.629(4)	6(1)

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ (continued)

atom	x	y	z	B_{eq}
H(9)	0.823(7)	0.061(5)	0.588(3)	2.3(9)
H(10)	0.862(7)	-0.181(6)	0.715(3)	3.0(10)
H(11)	1.060(10)	-0.105(7)	0.674(3)	5(1)
H(12)	0.99(1)	-0.204(9)	0.536(5)	9(1)
H(13)	0.90(1)	0.38(1)	0.510(7)	11(1)
H(14)	0.626(9)	0.277(8)	0.538(4)	5(1)
H(15)	0.541(9)	0.461(8)	0.568(3)	4(1)
H(16)	0.43(1)	-0.012(9)	0.793(4)	9(1)
H(17)	0.37(1)	-0.085(9)	0.934(4)	8(1)
H(18)	0.67(1)	-0.10(1)	1.048(5)	11(1)
H(19)	1.05(2)	0.07(1)	1.044(5)	13(1)
H(20)	1.083(8)	0.168(6)	0.884(3)	3(1)

$$B_{\text{eq}} = 8/3 \text{PI}^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	0.039(2)	0.050(2)	0.094(2)	0.003(2)	-0.007(2)	0.002(2)
O(2)	0.121(3)	0.028(2)	0.096(2)	-0.011(2)	0.064(2)	-0.012(2)
O(3)	0.161(4)	0.040(2)	0.085(3)	-0.007(2)	0.074(3)	-0.001(2)
C(1)	0.077(4)	0.048(4)	0.159(7)	0.008(3)	0.008(5)	-0.018(4)
C(2)	0.071(4)	0.040(3)	0.069(3)	0.000(3)	0.014(3)	-0.008(2)
C(3)	0.094(4)	0.029(3)	0.072(3)	0.018(3)	0.005(3)	0.007(2)
C(4)	0.055(2)	0.034(2)	0.063(2)	-0.016(2)	-0.013(2)	0.024(2)
C(5)	0.079(4)	0.036(2)	0.058(3)	-0.004(2)	0.017(3)	0.017(2)
C(6)	0.068(3)	0.034(2)	0.072(3)	-0.009(2)	0.040(3)	0.003(2)
C(7)	0.125(4)	0.032(3)	0.059(3)	0.014(3)	-0.024(3)	-0.002(3)
C(8)	0.066(3)	0.031(2)	0.060(2)	0.012(2)	0.024(2)	0.000(2)
C(9)	0.078(4)	0.054(3)	0.090(3)	-0.009(3)	0.036(4)	0.011(3)
C(10)	0.128(6)	0.084(5)	0.102(4)	0.023(5)	0.070(3)	0.044(4)
C(11)	0.142(5)	0.108(6)	0.087(4)	0.061(4)	0.073(3)	0.057(4)
C(12)	0.133(6)	0.142(8)	0.064(3)	0.031(5)	0.013(5)	0.030(4)
C(13)	0.077(4)	0.086(5)	0.057(2)	-0.011(4)	0.009(2)	-0.010(3)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(6)	1.40(1)	O(2)	C(1)	1.447(10)
O(3)	C(4)	1.46(2)	C(1)	C(2)	1.53(1)
C(1)	C(5)	1.61(1)	C(1)	C(10)	1.54(1)
C(2)	C(3)	1.45(1)	C(2)	C(7)	1.37(1)
C(3)	C(13)	1.43(2)	C(4)	C(5)	1.52(1)
C(5)	C(8)	1.55(1)	C(6)	C(10)	1.49(1)
C(7)	C(12)	1.38(2)	C(8)	C(9)	1.52(2)
C(11)	C(12)	1.50(2)	C(11)	C(13)	1.23(2)

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	H(73)	0.9(1)	O(2)	H(74)	0.78(10)
O(3)	H(77)	0.8(2)	C(3)	H(96)	0.9(1)
C(4)	H(1)	1.0(1)	C(4)	H(2)	0.9(1)
C(5)	H(54)	0.93(9)	C(6)	H(45)	0.96(8)
C(6)	H(79)	0.80(10)	C(7)	H(27)	1.01(8)
C(8)	H(80)	1.0(1)	C(8)	H(81)	0.8(1)
C(9)	H(90)	1.1(1)	C(9)	H(91)	0.8(1)
C(9)	H(92)	0.8(1)	C(10)	H(9)	0.87(7)
C(10)	H(85)	1.0(1)	C(11)	H(68)	0.9(1)
C(12)	H(97)	1.1(1)	C(13)	H(61)	1.1(1)

Table 5. Bond Angles(^o)

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	C(1)	C(2)	107.4(7)	O(2)	C(1)	C(5)	106.2(7)
O(2)	C(1)	C(10)	108.8(8)	C(2)	C(1)	C(5)	110.7(7)
C(2)	C(1)	C(10)	111.5(7)	C(5)	C(1)	C(10)	111.9(7)
C(1)	C(2)	C(3)	116.0(9)	C(1)	C(2)	C(7)	123.3(8)
C(3)	C(2)	C(7)	120.5(9)	C(2)	C(3)	C(13)	114(1)
O(3)	C(4)	C(5)	113.4(10)	C(1)	C(5)	C(4)	114.0(9)
C(1)	C(5)	C(8)	111.1(8)	C(4)	C(5)	C(8)	113.2(9)
O(1)	C(6)	C(10)	114.1(9)	C(2)	C(7)	C(12)	122(1)
C(5)	C(8)	C(9)	114(1)	C(1)	C(10)	C(6)	117.8(9)
C(12)	C(11)	C(13)	121(1)	C(7)	C(12)	C(11)	115(1)
C(3)	C(13)	C(11)	125(1)				

Table 6. Bond Angles(^o)

atom	atom	atom	angle	atom	atom	atom	angle
C(6)	O(1)	H(73)	108(7)	C(1)	O(2)	H(74)	123(7)
C(4)	O(3)	H(77)	108(9)	C(2)	C(3)	H(96)	135(6)
C(13)	C(3)	H(96)	108(6)	O(3)	C(4)	H(1)	99(5)
O(3)	C(4)	H(2)	106(5)	C(5)	C(4)	H(1)	108(5)
C(5)	C(4)	H(2)	110(4)	H(1)	C(4)	H(2)	117(7)
C(1)	C(5)	H(54)	108(6)	C(4)	C(5)	H(54)	108(6)
C(8)	C(5)	H(54)	101(6)	O(1)	C(6)	H(45)	107(5)
O(1)	C(6)	H(79)	107(6)	C(10)	C(6)	H(45)	101(4)
C(10)	C(6)	H(79)	112(7)	H(45)	C(6)	H(79)	112(7)
C(2)	C(7)	H(27)	118(4)	C(12)	C(7)	H(27)	118(4)
C(5)	C(8)	H(80)	113(6)	C(5)	C(8)	H(81)	108(8)
C(9)	C(8)	H(80)	114(6)	C(9)	C(8)	H(81)	106(8)
H(80)	C(8)	H(81)	97(10)	C(8)	C(9)	H(90)	109(5)
C(8)	C(9)	H(91)	109(11)	C(8)	C(9)	H(92)	108(9)
H(90)	C(9)	H(91)	112(12)	H(90)	C(9)	H(92)	111(10)
H(91)	C(9)	H(92)	105(14)	C(1)	C(10)	H(9)	103(5)
C(1)	C(10)	H(85)	112(5)	C(6)	C(10)	H(9)	105(4)
C(6)	C(10)	H(85)	108(6)	H(9)	C(10)	H(85)	108(7)
C(12)	C(11)	H(68)	119(9)	C(13)	C(11)	H(68)	118(9)
C(7)	C(12)	H(97)	118(8)	C(11)	C(12)	H(97)	126(7)
C(3)	C(13)	H(61)	108(6)	C(11)	C(13)	H(61)	125(6)

Table 7. Torsion Angles(⁰)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(6)	C(10)	C(1)	-172.1(8)	O(2)	C(1)	C(2)	C(3)	-179.4(8)
O(2)	C(1)	C(2)	C(7)	-3(1)	O(2)	C(1)	C(5)	C(4)	66(1)
O(2)	C(1)	C(5)	C(8)	-63.2(10)	O(2)	C(1)	C(10)	C(6)	63.8(10)
O(3)	C(4)	C(5)	C(1)	-57(1)	O(3)	C(4)	C(5)	C(8)	70(1)
C(1)	C(2)	C(3)	C(13)	178.4(9)	C(1)	C(2)	C(7)	C(12)	-176(1)
C(1)	C(5)	C(8)	C(9)	-170.8(10)	C(2)	C(1)	C(5)	C(4)	-177.6(9)
C(2)	C(1)	C(5)	C(8)	53(1)	C(2)	C(1)	C(10)	C(6)	-54(1)
C(2)	C(3)	C(13)	C(11)	-6(2)	C(2)	C(7)	C(12)	C(11)	1(1)
C(3)	C(2)	C(1)	C(5)	65(1)	C(3)	C(2)	C(1)	C(10)	-60(1)
C(3)	C(2)	C(7)	C(12)	0(1)	C(3)	C(13)	C(11)	C(12)	8(2)
C(4)	C(5)	C(1)	C(10)	-52(1)	C(4)	C(5)	C(8)	C(9)	59(1)
C(5)	C(1)	C(2)	C(7)	-118(1)	C(5)	C(1)	C(10)	C(6)	-179.1(8)
C(7)	C(2)	C(1)	C(10)	115(1)	C(7)	C(2)	C(3)	C(13)	2(1)
C(7)	C(12)	C(11)	C(13)	-5(2)	C(8)	C(5)	C(1)	C(10)	178.2(9)

Table 8. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O(1)	O(3) ¹⁾	2.665(9)	O(1)	O(3) ²⁾	2.819(9)
O(1)	C(4) ¹⁾	3.51(1)	O(3)	C(6) ³⁾	3.41(1)

Symmetry operations

(1)	X,Y-1,Z	(2)	-X+2,Y-1/2,-Z+1
(3)	-X+2,Y+1/2,-Z+1		
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