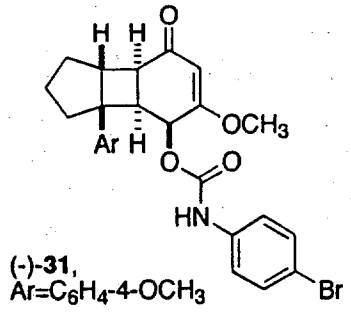
Ref. No.: Crystal-203

X-RAY STRUCTURE REPORT

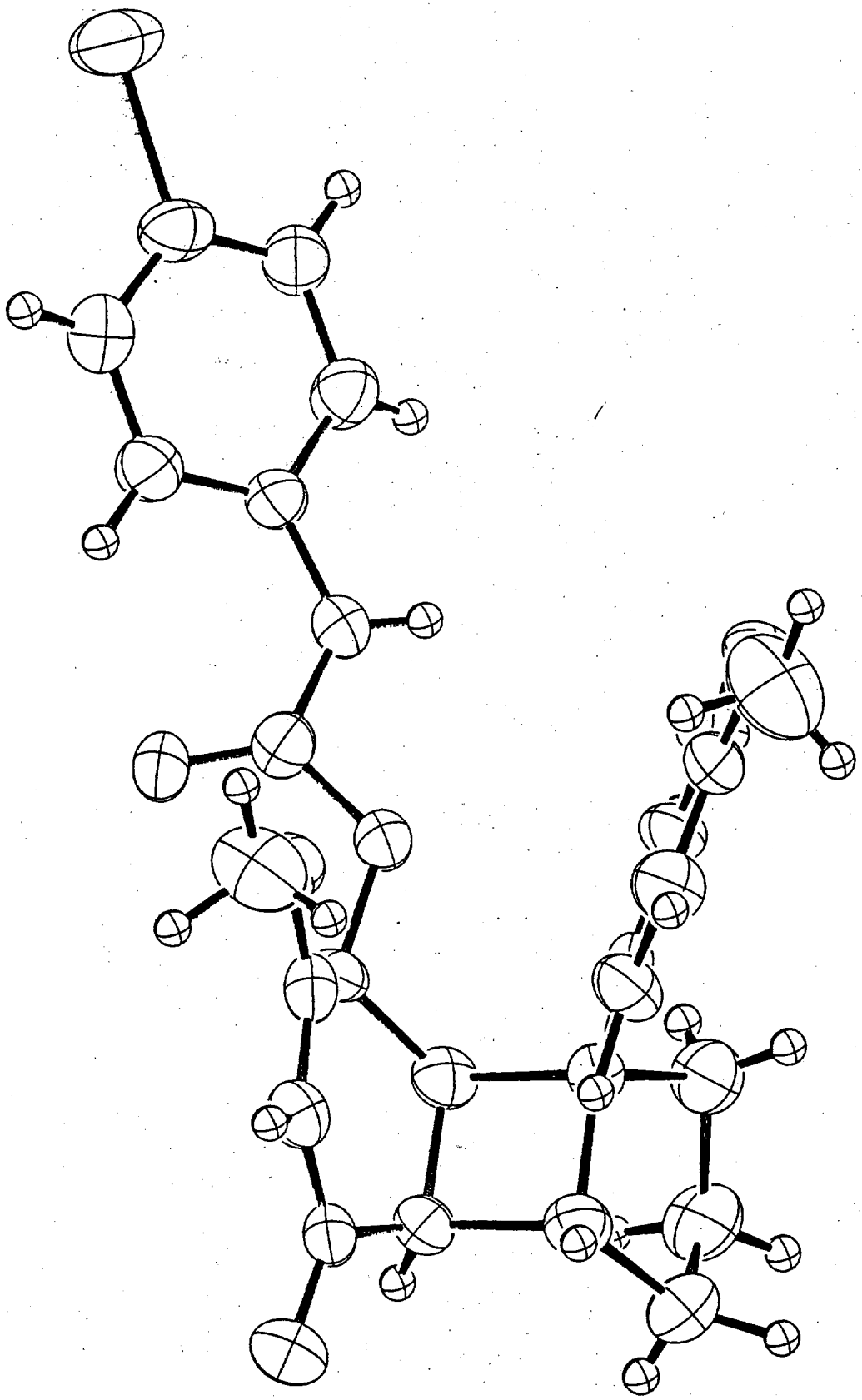
for

Prof. Tom Engler

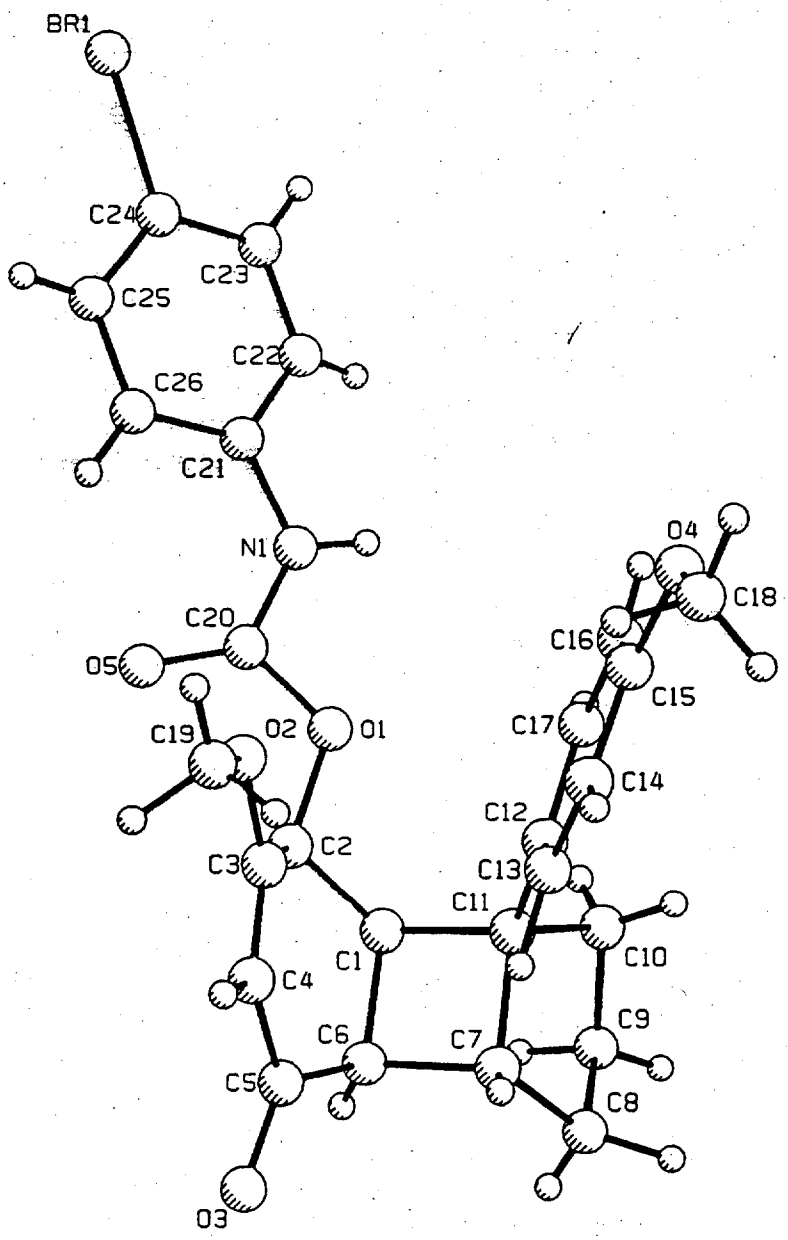


(-)-**31**,
Ar=C_6H_4-4-OCH_3

23-JUN-96



Crustal-203


BR1
C24
C23
C25
C22
C26
C21
N1
C20
O5
O2
O1
C19
C3
C2
C4
C1
C6
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INTRODUCTION

The absolute configuration of the molecule has been determined by using the anomalous dispersion effect of the Br-atom. The refinement results are:

	Assigned structure	Enantiomorph structure
R-factor	0.045	0.052
Weighted R-factor	0.047	0.057
Goodness fit (S)	1.12	1.48

According to Hamilton's R-factor test [W.C. Hamilton, Acta Cryst., 18, 502-510 (1965)], the assigned structure gives significantly better fit to the data than its enantiomorph structure at the 99.5% significant level.

EXPERIMENTAL

DATA COLLECTION

A colorless prism crystal of $C_{26}H_{25}O_5NBr$ having approximate dimensions of 0.300 x 0.100 x 0.300 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Cu Kα radiation and a 12KW 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 $21.50 < 2\theta < 45.21°$ corresponded to an orthorhombic cell with dimensions:

a = 13.697 (2)Å
b = 19.150 (3)Å
c = 8.820 (1)Å
V = 2314 (1)Å^3

For $Z = 4$ and F.W. = 511.39, the calculated density is 1.468 g/cm^3. Based on the systematic absences of:

h00: h ≠ 2n
0k0: k ≠ 2n
00l: l ≠ 2n

and the successful solution and refinement of the structure, the space group was determined to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 110.1°. Omega 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 (1.05 + 0.30 tan θ)° were made at a speed of 32.0°/min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure 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 0.5 mm and the crystal to detector distance was 400.0 mm.

DATA REDUCTION

A total of 1722 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Cu Kα is 27.3 cm^{-1}. An empirical absorption correction, using the program DIFABS[3], was applied which resulted in transmission factors ranging from 0.94 to 1.04. The data were corrected for Lorentz and polarization effects.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods[4]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[5] was based on 1614 observed reflections ($I > 0.01\sigma(I)$) and 380 variable parameters and converged (largest parameter shift was 0.45 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.045$$

$$R_w = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.047$$

The standard deviation of an observation of unit weight[6] was 1.12. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, 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 0.37 and -0.26 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[7]. Anomalous dispersion effects were included in Fcalc[8]; the values for Δf′ and Δf″ were those of Cromer[9]. All calculations were performed using the TEXSAN[10] crystallographic software package of Molecular Structure Corporation.

References

(1) PLUTO:
Motherwell,S. & Clegg,W.; PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England (1978).

(2) ORTEP:
Johnson,C.K.; ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

(3) DIFABS:
Walker & Stuart, Acta Cryst. A39, 158-166, (1983).

(4) Structure Solution Methods:
MITHRIL
Gilmore,C.J.; MITHRIL - an integrated direct methods computer program. J. Appl. Cryst. 17, 42-46, Univ. of Glasgow, Scotland, (1984).
DIRDIF
Beurskens,P.T.; DIRDIF: Direct Methods for Difference Structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(5) Least-Squares:

Function minimized: $\Sigma\, w\,(|Fo| - |Fc|)^2$

where: $w = 4Fo^2/\sigma^2(Fo^2)$

$\sigma^2(Fo^2) = [S^2(C+R^2B) + (pFo^2)^2]/Lp^2$

S = Scan rate
C = Total Integrated Peak Count
R = Ratio of Scan Time to background counting time.
B = Total Background Count
Lp = Lorentz-polarization factor
p = p-factor

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

$$[\Sigma\, w(|Fo| - |Fc|)^2/(No - Nv)]^{1/2}$$

where: No = number of observations
Nv = number of variables

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

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

(9) D.T. Cromer, "International Tables for X-ray

Crystallography", Vol/ IV, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).

(10) TEXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{26}H_{25}O_5NBr$
Formula Weight	511.39
Crystal Color, Habit	colorless, prism
Crystal Dimensions (mm)	0.300 X 0.100 X 0.300
Crystal System	orthorhombic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (21.5 - 45.2°)
Omega Scan Peak Width at Half-height	0.32
Lattice Parameters:	a = 13.697 (2)Å b = 19.150 (3)Å c = 8.820 (1)Å V = 2314 (1)Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.468 g/cm^3
F_{000}	1052
μ(CuKα)	27.34 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5S
Radiation	CuKα (λ = 1.54178 Å)
Temperature	23°C
Attenuators	Zr foil (factors: 4.1, 14.5, 54.4)
Take-off Angle	6.0°

Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	40 cm
Scan Type	ω–2θ
Scan Rate	32.0°/min (in omega) (2 rescans)
Scan Width	(1.05 + 0.30 tanθ)°
$2\theta_{max}$	110.1°
No. of Reflections Measured	Total: 1722
Corrections	Lorentz-polarization Absorption (trans. factors: 0.94 - 1.04)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least-squares Weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.05
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.01σ(I))	1614
No. Variables	380
Reflection/Parameter Ratio	4.25
Residuals: R; R_w	0.045; 0.047
Goodness of Fit Indicator	1.12
Max Shift/Error in Final Cycle	0.45
Maximum Peak in Final Diff. Map	0.37 $e^-/Å^3$
Minimum Peak in Final Diff. Map	-0.26 $e^-/Å^3$

Positional parameters for crystal-203

atom	x	y	z
Br(1)	0.58177(7)	0.98868(5)	0.4428(1)
O(1)	0.5206(3)	0.7967(2)	-0.3766(5)
O(2)	0.4059(4)	0.6981(2)	-0.2640(5)
O(3)	0.2839(4)	0.6499(3)	-0.7540(7)
O(4)	0.7237(4)	0.5538(3)	-0.1183(6)
O(5)	0.4036(3)	0.8532(3)	-0.2441(6)
N(1)	0.5654(5)	0.8669(3)	-0.1887(7)
C(1)	0.4964(5)	0.7530(4)	-0.6250(8)
C(2)	0.4479(4)	0.7685(3)	-0.4764(7)
C(3)	0.3989(5)	0.7040(3)	-0.4153(8)
C(4)	0.3465(5)	0.6633(4)	-0.5079(8)
C(5)	0.3480(5)	0.6744(4)	-0.6689(9)
C(6)	0.4329(5)	0.7117(4)	-0.7392(8)
C(7)	0.5192(5)	0.6588(4)	-0.762(1)
C(8)	0.5786(8)	0.6659(6)	-0.909(1)
C(9)	0.6386(7)	0.7328(6)	-0.889(1)
C(10)	0.6698(6)	0.7266(5)	-0.722(1)
C(11)	0.5802(5)	0.6969(3)	-0.6376(7)
C(12)	0.6105(4)	0.6584(3)	-0.4946(7)
C(13)	0.5761(5)	0.5929(3)	-0.4568(8)
C(14)	0.6104(5)	0.5567(4)	-0.3290(9)
C(15)	0.6813(5)	0.5864(4)	-0.2427(8)
C(16)	0.7145(5)	0.6529(4)	-0.2745(8)
C(17)	0.6802(5)	0.6870(4)	-0.3980(8)

Positional parameters for crystal-203

atom	x	y	z
C(18)	0.6963(7)	0.4835(6)	-0.088(1)
C(19)	0.3602(6)	0.6391(5)	-0.195(1)
C(20)	0.4884(5)	0.8403(3)	-0.2653(8)
C(21)	0.5615(5)	0.9016(3)	-0.0491(8)
C(22)	0.6455(6)	0.9342(4)	0.001(1)
C(23)	0.6512(6)	0.9632(4)	0.143(1)
C(24)	0.5715(6)	0.9586(3)	0.2376(8)
C(25)	0.4847(6)	0.9301(4)	0.187(1)
C(26)	0.4791(5)	0.9026(4)	0.0424(9)
H(1)	0.622(4)	0.857(2)	-0.213(6)
H(2)	0.510(5)	0.792(3)	-0.662(8)
H(3)	0.309(4)	0.628(3)	-0.469(7)
H(4)	0.415(5)	0.744(3)	-0.822(7)
H(5)	0.499(4)	0.620(3)	-0.743(7)
H(6)	0.538(5)	0.674(4)	-0.970(8)
H(7)	0.628(7)	0.631(5)	-0.95(1)
H(8)	0.592(6)	0.778(4)	-0.903(9)
H(9)	0.691(6)	0.738(4)	-0.97(1)
H(10)	0.681(4)	0.767(3)	-0.691(7)
H(11)	0.721(5)	0.697(4)	-0.699(8)
H(12)	0.523(5)	0.571(3)	-0.535(9)
H(13)	0.587(4)	0.512(3)	-0.312(6)
H(14)	0.754(4)	0.667(3)	-0.208(7)
H(15)	0.709(6)	0.731(4)	-0.423(9)
H(16)	0.6275	0.4821	-0.0729

Positional parameters for crystal-203

atom	x	y	z
H(17)	0.7290	0.4695	0.0002
H(18)	0.7141	0.4568	-0.1720
H(19)	0.2884	0.6428	-0.2235
H(20)	0.3648	0.6387	-0.0940
H(21)	0.3813	0.5975	-0.2433
H(22)	0.690(6)	0.940(4)	-0.06(1)
H(23)	0.707(5)	0.981(4)	0.183(9)
H(24)	0.435(6)	0.928(4)	0.250(9)
H(25)	0.419(6)	0.879(4)	0.008(8)

U values for crystal-203

ATOM	U11	U22	U33	U12	U13	U23
Br(1)	0.0864(6)	0.0846(6)	0.0471(5)	-0.0037(6)	-0.0061(5)	-0.0168(5)
O(1)	0.033(2)	0.049(3)	0.050(3)	0.004(2)	-0.004(2)	-0.015(3)
O(2)	0.048(3)	0.060(3)	0.042(3)	-0.003(3)	-0.001(3)	0.006(2)
O(3)	0.049(3)	0.099(4)	0.068(4)	-0.001(3)	-0.017(3)	-0.027(4)
O(4)	0.061(3)	0.076(4)	0.050(3)	0.012(3)	-0.017(3)	0.011(3)
O(5)	0.037(3)	0.081(4)	0.069(3)	0.014(3)	-0.003(3)	-0.036(3)
N(1)	0.031(4)	0.058(4)	0.050(4)	0.002(3)	-0.003(3)	-0.012(3)
C(1)	0.045(4)	0.037(4)	0.035(4)	0.003(4)	-0.005(4)	0.008(3)
C(2)	0.035(3)	0.042(4)	0.035(4)	0.001(3)	-0.011(3)	-0.003(3)
C(3)	0.031(4)	0.047(4)	0.047(4)	0.006(3)	0.004(4)	-0.003(3)
C(4)	0.035(4)	0.043(4)	0.048(4)	-0.002(4)	0.001(4)	0.004(4)
C(5)	0.031(4)	0.055(5)	0.054(5)	0.009(4)	-0.005(4)	-0.020(4)
C(6)	0.042(4)	0.054(4)	0.037(4)	0.015(4)	-0.009(4)	-0.002(4)
C(7)	0.046(4)	0.042(5)	0.047(5)	0.003(4)	-0.008(4)	-0.007(4)
C(8)	0.058(5)	0.121(8)	0.044(5)	0.012(7)	0.005(5)	-0.024(5)
C(9)	0.059(5)	0.108(8)	0.040(4)	-0.009(6)	0.019(5)	0.002(5)
C(10)	0.049(5)	0.062(6)	0.048(5)	-0.003(5)	0.005(4)	0.003(5)

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U values for crystal-203

ATOM	U11	U22	U33	U12	U13	U23
C(11)	0.033(4)	0.048(4)	0.036(3)	0.005(4)	-0.001(3)	-0.003(3)
C(12)	0.028(4)	0.046(4)	0.037(4)	0.011(3)	0.002(3)	-0.008(3)
C(13)	0.038(4)	0.045(4)	0.056(4)	-0.002(4)	-0.011(4)	-0.002(4)
C(14)	0.055(5)	0.036(4)	0.056(5)	0.004(4)	-0.006(4)	0.001(4)
C(15)	0.039(4)	0.055(5)	0.038(4)	0.013(4)	-0.007(4)	-0.000(4)
C(16)	0.047(4)	0.061(5)	0.038(4)	-0.001(4)	-0.012(4)	-0.016(4)
C(17)	0.034(4)	0.051(4)	0.041(4)	-0.009(4)	-0.005(3)	-0.004(4)
C(18)	0.082(7)	0.085(7)	0.097(8)	0.004(6)	-0.011(6)	0.042(7)
C(19)	0.068(6)	0.083(7)	0.064(6)	-0.018(5)	-0.004(5)	0.026(5)
C(20)	0.046(5)	0.047(4)	0.041(4)	0.006(4)	0.000(4)	-0.003(4)
C(21)	0.040(4)	0.039(4)	0.042(4)	0.004(3)	-0.006(4)	-0.008(4)
C(22)	0.046(5)	0.052(4)	0.048(5)	-0.005(4)	0.007(4)	-0.006(4)
C(23)	0.043(5)	0.051(5)	0.063(6)	-0.002(4)	-0.002(4)	-0.017(4)
C(24)	0.062(5)	0.037(4)	0.046(4)	0.004(4)	-0.009(5)	-0.007(3)
C(25)	0.046(5)	0.050(4)	0.057(5)	0.002(4)	0.006(4)	0.001(4)
C(26)	0.039(4)	0.052(4)	0.046(5)	-0.007(4)	0.001(4)	-0.005(4)
H(1)	0.01(1)					
H(2)	0.04(2)					

U values for crystal-203

ATOM	U11	U22	U33	U12	U13	U23
H(3)	0.03(2)					
H(4)	0.04(2)					
H(5)	0.02(2)					
H(6)	0.04(2)					
H(7)	0.11(3)					
H(8)	0.08(3)					
H(9)	0.08(3)					
H(10)	0.02(2)					
H(11)	0.04(2)					
H(12)	0.07(2)					
H(13)	0.03(2)					
H(14)	0.03(2)					
H(15)	0.07(3)					
H(16)	0.14(4)					
H(17)	0.19(6)					
H(18)	0.16(6)					
H(19)	0.05(2)					
H(20)	0.09(3)					

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U values for crystal-203

ATOM	U11	U22	U33	U12	U13	U23
H(21)	0.16(6)					
H(22)	0.08(3)					
H(23)	0.07(2)					
H(24)	0.07(3)					
H(25)	0.06(2)					

Intramolecular Distances

atom	atom	distance	atom	atom	distance
BR1	C24	1.905(7)	C8	C9	1.53(1)
O1	C2	1.434(7)	C8	H6	0.79(7)
O1	C20	1.362(8)	C8	H7	1.0(1)
O2	C3	1.342(8)	C9	C10	1.53(1)
O2	C19	1.428(9)	C9	H8	1.09(8)
O3	C5	1.246(8)	C9	H9	0.99(8)
O4	C15	1.390(8)	C10	C11	1.55(1)
O4	C18	1.42(1)	C10	H10	0.84(5)
O5	C20	1.203(8)	C10	H11	0.92(7)
N1	C20	1.352(9)	C11	C12	1.519(9)
N1	C21	1.400(9)	C12	C13	1.381(9)
N1	H1	0.83(5)	C12	C17	1.392(9)
C1	C2	1.499(9)	C13	C14	1.40(1)
C1	C6	1.55(1)	C13	H12	1.08(7)
C1	C11	1.576(9)	C14	C15	1.36(1)
C1	H2	0.83(6)	C14	H13	0.93(6)
C2	C3	1.505(9)	C15	C16	1.38(1)
C3	C4	1.338(9)	C16	C17	1.35(1)
C4	C5	1.44(1)	C16	H14	0.84(6)
C4	H3	0.92(6)	C17	H15	0.97(8)
C5	C6	1.50(1)	C18	H16	0.95(1)
C6	C7	1.57(1)	C18	H17	0.94(1)
C6	H4	0.98(6)	C18	H18	0.93(1)
C7	C8	1.54(1)	C19	H19	1.017(9)
C7	C11	1.56(1)	C19	H20	0.897(9)
C7	H5	0.81(6)	C19	H21	0.95(1)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

(cont)

Intramolecular Distances

atom	atom	distance	atom	atom	distance
C21	C22	1.380(9)			
C21	C26	1.39(1)			
C22	C23	1.38(1)			
C22	H22	0.83(8)			
C23	C24	1.38(1)			
C23	H23	0.91(7)			
C24	C25	1.38(1)			
C25	C26	1.38(1)			
C25	H24	0.88(8)			
C26	H25	0.98(8)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
C2	O1	C20	116.6(5)	C1	C6	H4	108(3)
C3	O2	C19	117.1(6)	C5	C6	C7	109.2(6)
C15	O4	C18	117.5(7)	C5	C6	H4	114(4)
C20	N1	C21	126.1(6)	C7	C6	H4	120(4)
C20	N1	H1	121(4)	C6	C7	C8	116.6(8)
C21	N1	H1	111(4)	C6	C7	C11	90.8(5)
C2	C1	C6	114.9(6)	C6	C7	H5	109(4)
C2	C1	C11	121.3(5)	C8	C7	C11	105.5(6)
C2	C1	H2	105(5)	C8	C7	H5	115(4)
C6	C1	C11	90.8(5)	C11	C7	H5	118(4)
C6	C1	H2	109(5)	C7	C8	C9	105.1(7)
C11	C1	H2	115(5)	C7	C8	H6	103(5)
O1	C2	C1	107.6(5)	C7	C8	H7	128(6)
O1	C2	C3	113.5(5)	C9	C8	H6	108(6)
C1	C2	C3	110.4(5)	C9	C8	H7	103(5)
O2	C3	C2	113.1(6)	H6	C8	H7	108(7)
O2	C3	C4	126.6(7)	C8	C9	C10	101.2(8)
C2	C3	C4	119.9(6)	C8	C9	H8	110(4)
C3	C4	C5	120.7(7)	C8	C9	H9	113(5)
C3	C4	H3	120(4)	C10	C9	H8	110(4)
C5	C4	H3	119(4)	C10	C9	H9	117(4)
O3	C5	C4	122.0(7)	H8	C9	H9	105(6)
O3	C5	C6	118.4(7)	C9	C10	C11	105.6(7)
C4	C5	C6	119.4(7)	C9	C10	H10	107(4)
C1	C6	C5	114.2(6)	C9	C10	H11	118(4)
C1	C6	C7	89.3(5)	C11	C10	H10	109(4)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
C11	C10	H11	106(4)	O4	C18	H16	108.3(9)
H10	C10	H11	110(6)	O4	C18	H17	107(1)
C1	C11	C7	88.8(5)	O4	C18	H18	107.6(9)
C1	C11	C10	111.2(6)	H16	C18	H17	110(1)
C1	C11	C12	118.1(5)	H16	C18	H18	111(1)
C7	C11	C10	105.0(6)	H17	C18	H18	112(1)
C7	C11	C12	120.2(5)	O2	C19	H19	105.4(7)
C10	C11	C12	111.3(6)	O2	C19	H20	113.5(9)
C11	C12	C13	123.3(6)	O2	C19	H21	110.1(8)
C11	C12	C17	120.4(6)	H19	C19	H20	108.1(9)
C13	C12	C17	116.3(6)	H19	C19	H21	104.3(9)
C12	C13	C14	121.9(7)	H20	C19	H21	114.6(9)
C12	C13	H12	115(4)	O1	C20	O5	123.4(7)
C14	C13	H12	123(4)	O1	C20	N1	109.8(6)
C13	C14	C15	118.8(7)	O5	C20	N1	126.7(7)
C13	C14	H13	118(4)	N1	C21	C22	117.6(6)
C15	C14	H13	123(4)	N1	C21	C26	123.2(6)
O4	C15	C14	123.5(7)	C22	C21	C26	119.1(6)
O4	C15	C16	115.9(6)	C21	C22	C23	121.4(8)
C14	C15	C16	120.6(7)	C21	C22	H22	118(6)
C15	C16	C17	119.5(7)	C23	C22	H22	120(6)
C15	C16	H14	111(4)	C22	C23	C24	118.7(7)
C17	C16	H14	129(4)	C22	C23	H23	123(5)
C12	C17	C16	122.8(7)	C24	C23	H23	117(5)
C12	C17	H15	119(5)	BR1	C24	C23	119.8(6)
C16	C17	H15	118(5)	BR1	C24	C25	119.4(6)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
C23	C24	C25	120.7(7)				
C24	C25	C26	119.9(8)				
C24	C25	H24	118(5)				
C26	C25	H24	122(5)				
C21	C26	C25	119.8(7)				
C21	C26	H25	119(4)				
C25	C26	H25	121(4)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
BR1	C24	C23	C22	172.9(6)	C1	C11	C10	C9	-71.4(9)
BR1	C24	C25	C26	-174.4(5)	C1	C11	C12	C13	97.5(7)
O1	C2	C1	C6	171.0(5)	C1	C11	C12	C17	-86.2(8)
O1	C2	C1	C11	63.6(8)	C2	C1	C6	C5	-18.6(8)
O1	C2	C3	O2	21.6(8)	C2	C1	C6	C7	-129.4(6)
O1	C2	C3	C4	-164.9(6)	C2	C1	C11	C7	124.1(7)
O1	C20	N1	C21	-165.9(6)	C2	C1	C11	C10	-130.2(7)
O2	C3	C2	C1	142.5(5)	C2	C1	C11	C12	0.2(9)
O2	C3	C4	C5	-178.1(7)	C2	C3	O2	C19	179.0(6)
O3	C5	C4	C3	-162.2(7)	C2	C3	C4	C5	9(1)
O3	C5	C6	C1	167.9(6)	C3	C2	O1	C20	-84.5(7)
O3	C5	C6	C7	-93.9(7)	C3	C2	C1	C6	46.7(7)
O4	C15	C14	C13	-176.8(6)	C3	C2	C1	C11	-60.8(8)
O4	C15	C16	C17	177.0(6)	C3	C4	C5	C6	23(1)
O5	C20	O1	C2	3(1)	C4	C3	O2	C19	6(1)
O5	C20	N1	C21	16(1)	C4	C5	C6	C7	81.5(8)
N1	C20	O1	C2	-175.1(5)	C5	C6	C1	C11	106.8(6)
N1	C21	C22	C23	-173.2(7)	C5	C6	C7	C8	140.8(7)
N1	C21	C26	C25	171.6(7)	C5	C6	C7	C11	-111.4(6)
C1	C2	O1	C20	153.0(6)	C6	C1	C11	C7	4.1(6)
C1	C2	C3	C4	-44.0(8)	C6	C1	C11	C10	109.7(6)
C1	C6	C5	C4	-16.7(9)	C6	C1	C11	C12	-119.9(6)
C1	C6	C7	C8	-103.7(7)	C6	C7	C8	C9	72.0(9)
C1	C6	C7	C11	4.1(6)	C6	C7	C11	C10	-115.7(6)
C1	C11	C7	C6	-4.0(5)	C6	C7	C11	C12	118.1(6)
C1	C11	C7	C8	113.9(7)	C7	C6	C1	C11	-4.1(6)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

(1)	(2)	(3)	(4)	angle
C7	C8	C9	C10	41(1)
C7	C11	C10	C9	23.2(9)
C7	C11	C12	C13	-8.9(9)
C7	C11	C12	C17	167.4(6)
C8	C7	C11	C10	2.3(9)
C8	C7	C11	C12	-123.9(7)
C8	C9	C10	C11	-39.3(9)
C9	C8	C7	C11	-27(1)
C9	C10	C11	C12	154.7(7)
C10	C11	C12	C13	-132.1(7)
C10	C11	C12	C17	44.2(8)
C11	C12	C13	C14	175.7(6)
C11	C12	C17	C16	-175.5(6)
C12	C13	C14	C15	-2(1)
C12	C17	C16	C15	1(1)
C13	C12	C17	C16	1(1)
C13	C14	C15	C16	4(1)
C14	C13	C12	C17	-0.7(9)
C14	C15	O4	C18	5(1)
C14	C15	C16	C17	-4(1)
C16	C15	O4	C18	-175.7(8)
C20	N1	C21	C22	-170.5(7)
C20	N1	C21	C26	12(1)
C21	C22	C23	C24	1(1)
C21	C26	C25	C24	2(1)
C22	C21	C26	C25	-6(1)
C22	C23	C24	C25	-5(1)
C23	C22	C21	C26	5(1)
C23	C24	C25	C26	3(1)

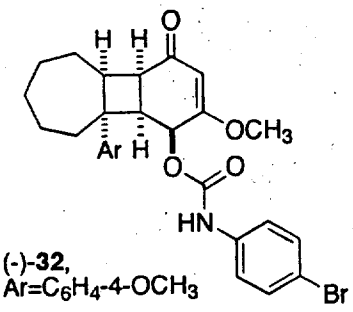
The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Ref. No.: Crystal-212

X-RAY STRUCTURE REPORT

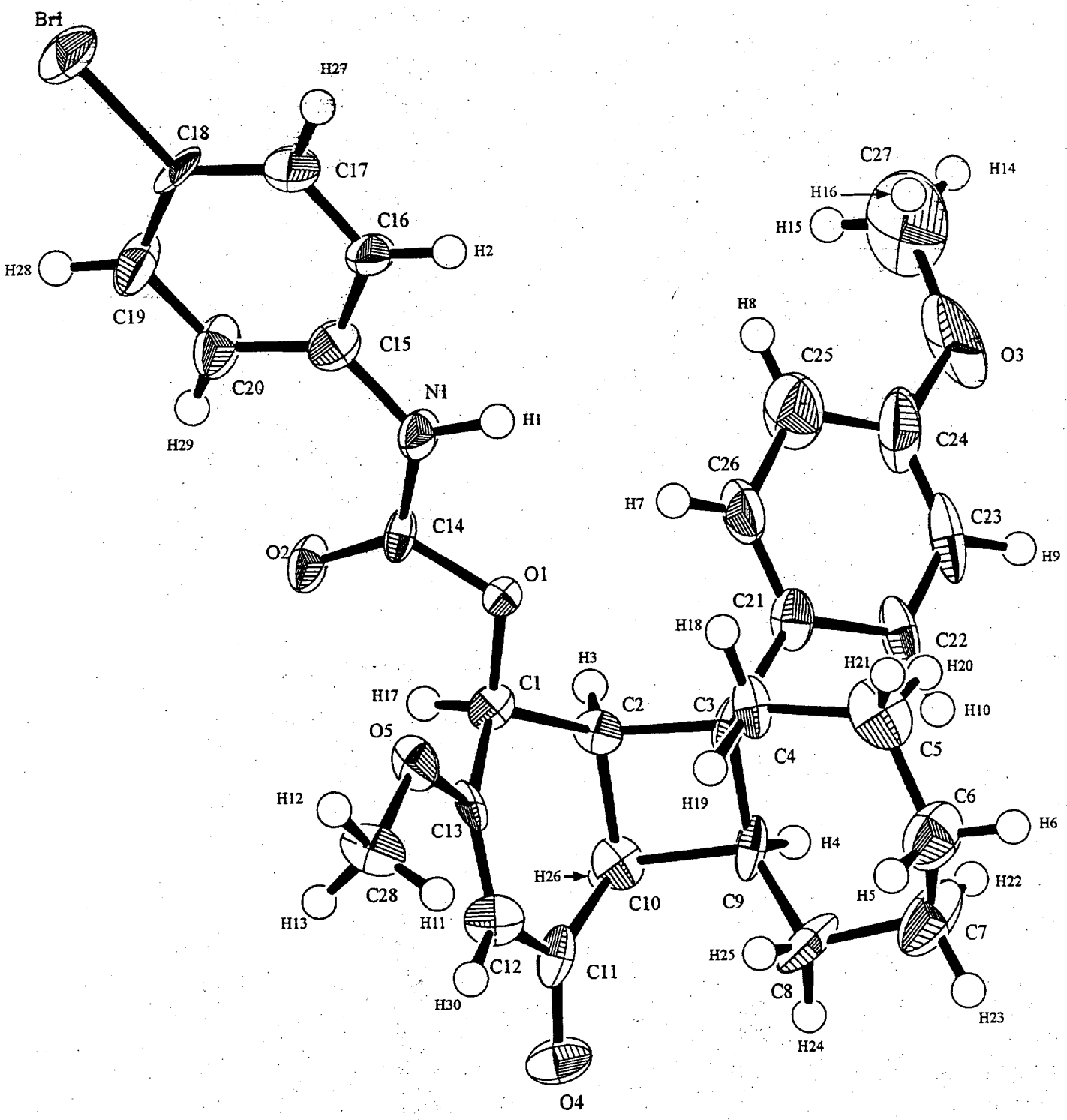
for

Prof. Tom Engler



(-)-**32**,
Ar=C_6H_4-4-OCH_3

19-NOV-96



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INTRODUCTION

EXPERIMENTAL

DATA COLLECTION

A colorless needle crystal of $BrO_5NC_{28}H_{30}$ having approximate dimensions of 0.300 X 0.300 X 0.600 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Cu Kα radiation and a 12KW 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 49.18 < 2θ < 49.79° corresponded to an orthorhombic cell with dimensions:

a = 25.488 (2)Å
b = 11.376 (2)Å
c = 12.763 (2)Å
V = 3701 (2)Å^3

For Z = 4 and F.W. = 540.45, the calculated density is 0.970 g/cm^3. Based on the systematic absences of:

h00: h ≠ 2n
0k0: k ≠ 2n

and the successful solution and refinement of the structure, the space group was determined to be:

$P2_12_12$ (#18)

The data were collected at a temperature of -140 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 100.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.37° with a take-off angle of 6.0°. Scans of (1.78 + 0.30 tan θ)° were made at a speed of 32.0°/min (in omega). The weak reflections (I < 10.0σ(I)) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure 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 0.5 mm and the crystal to detector distance was 400.0 mm.

DATA REDUCTION

A total of 2287 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Cu Kα is 17.3 cm^{-1}. An empirical absorption correction, using the program DIFABS[3], was applied which resulted in transmission factors ranging from 0.91 to 1.07. The data were corrected for Lorentz and polarization effects.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods[4]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[5] was based on 1941 observed reflections ($I > 3.00\sigma(I)$) and 346 variable parameters and converged (largest parameter shift was 2.50 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.074$$

$$R_w = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.106$$

The standard deviation of an observation of unit weight[6] was 2.32. The weighting scheme was based on counting statistics and included a factor ($p = 0.08$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, 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 1.00 and -0.44 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[7]. Anomalous dispersion effects were included in Fcalc[8]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer[9]. All calculations were performed using the TEXSAN[10] crystallographic software package of Molecular Structure Corporation.

References

(1) PLUTO:
Motherwell,S. & Clegg,W.; PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England (1978).

(2) ORTEP:
Johnson,C.K.; ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

(3) DIFABS:
Walker & Stuart, Acta Cryst. A39, 158-166, (1983).

(4) Structure Solution Methods:
MITHRIL
Gilmore,C.J.; MITHRIL - an integrated direct methods computer program. J. Appl. Cryst. 17, 42-46, Univ. of Glasgow, Scotland, (1984).
DIRDIF
Beurskens,P.T.; DIRDIF: Direct Methods for Difference Structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(5) Least-Squares:
Function minimized: $\Sigma\, w\,(|Fo| - |Fc|)^2$
where: $w = 4Fo^2/\sigma^2(Fo^2)$
$\sigma^2(Fo^2) = [S^2(C+R^2B) + (pFo^2)^2]/Lp^2$
S = Scan rate
C = Total Integrated Peak Count
R = Ratio of Scan Time to background counting time.
B = Total Background Count
Lp = Lorentz-polarization factor
p = p-factor

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

$$[\Sigma\, w(|Fo| - |Fc|)^2/(No - Nv)]^{1/2}$$

where: No = number of observations
Nv = number of variables

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

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

(9) D.T. Cromer, "International Tables for X-ray

Crystallography", Vol/ IV, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).

(10) TEXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$BrO_5NC_{28}H_{31}$ ~~30~~
Formula Weight	~~541.46~~ 540.45
Crystal Color, Habit	colorless, needle
Crystal Dimensions (mm)	0.300 X 0.300 X 0.600
Crystal System	orthorhombic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (49.2 - 49.8°)
Omega Scan Peak Width at Half-height	0.37
Lattice Parameters:	a = 25.488 (2)Å b = 11.376 (2)Å c = 12.763 (2)Å V = 3701 (2)Å^3
Space Group	$P2_12_12$ (#18)
Z value	4
D_{calc}	~~0.972~~ g/cm^3 0.970 g/cm^3
F_{000}	1124
μ(CuKα)	17.28 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5S
Radiation	CuKα (λ = 1.54178 Å)
Temperature	-140°C
Attenuators	Zr foil (factors: 4.1, 14.5, 51.4)
Take-off Angle	6.0°

Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	40 cm
Scan Type	ω-2θ
Scan Rate	32.0°/min (in omega) (2 rescans)
Scan Width	$(1.78 + 0.30 \tan\theta)°$
$2\theta_{max}$	100.0°
No. of Reflections Measured	Total: 2287
Corrections	Lorentz-polarization Absorption (trans. factors: 0.91 - 1.07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\ w\ (\|Fo\| - \|Fc\|)^2$
Least-squares Weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.08
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	1941
No. Variables	346
Reflection/Parameter Ratio	5.61
Residuals: R; R_w	0.074; 0.106
Goodness of Fit Indicator	2.32
Max Shift/Error in Final Cycle	2.50
Maximum Peak in Final Diff. Map	1.00 $e^-/Å^3$
Minimum Peak in Final Diff. Map	-0.44 $e^-/Å^3$

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

atom	x	y	z	B_{eq}
Br(1)	0.82088(5)	0.02419(13)	-0.24075(9)	4.45(4)
O(1)	0.7463(2)	0.2447(6)	0.3548(5)	1.6(2)
O(2)	0.8008(3)	0.3268(6)	0.2342(6)	2.2(2)
O(3)	0.4762(3)	0.3610(10)	0.3631(10)	5.8(3)
O(4)	0.8040(3)	0.4628(6)	0.7183(6)	2.5(2)
O(5)	0.8339(2)	0.1932(6)	0.4443(6)	2.3(2)
N(1)	0.7529(3)	0.1610(7)	0.1981(6)	2.1(2)
C(1)	0.7638(4)	0.3292(8)	0.4285(8)	1.6(2)
C(2)	0.7189(4)	0.3763(8)	0.4931(8)	1.5(2)
C(3)	0.6776(4)	0.2994(9)	0.5533(8)	1.9(2)
C(4)	0.6892(4)	0.1638(8)	0.5594(9)	1.9(2)
C(5)	0.6511(5)	0.0955(9)	0.6283(10)	3.1(3)
C(6)	0.6603(5)	0.0999(10)	0.7444(10)	3.5(3)
C(7)	0.6598(6)	0.2241(10)	0.7968(9)	3.9(3)
C(8)	0.7019(5)	0.3031(10)	0.7550(9)	3.3(3)
C(9)	0.6882(4)	0.3675(9)	0.6520(8)	2.1(2)
C(10)	0.7337(4)	0.4363(9)	0.5970(9)	2.0(2)
C(11)	0.7872(4)	0.4112(9)	0.6406(9)	1.9(2)
C(12)	0.8196(4)	0.3188(9)	0.5908(8)	2.2(2)
C(13)	0.8070(4)	0.2770(8)	0.4960(8)	1.5(2)

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

atom	x	y	z	B_{eq}
C(14)	0.7704(4)	0.2506(9)	0.2600(8)	1.7(2)
C(15)	0.7690(4)	0.1356(9)	0.0938(8)	2.1(2)
C(16)	0.7492(4)	0.0356(10)	0.0485(8)	2.5(3)
C(17)	0.7642(5)	0.0032(11)	-0.0508(8)	2.9(3)
C(18)	0.7981(5)	0.0711(10)	-0.1064(8)	2.4(3)
C(19)	0.8198(5)	0.1730(10)	-0.0611(8)	2.9(3)
C(20)	0.8035(5)	0.2044(9)	0.0369(9)	2.6(3)
C(21)	0.6223(4)	0.3138(9)	0.5017(9)	2.2(3)
C(22)	0.5770(4)	0.3444(9)	0.5605(10)	2.7(3)
C(23)	0.5306(4)	0.3566(11)	0.5085(11)	3.6(3)
C(24)	0.5246(5)	0.3428(13)	0.4064(11)	4.2(4)
C(25)	0.5681(5)	0.312(1)	0.3449(11)	4.3(3)
C(26)	0.6178(4)	0.2956(12)	0.3980(10)	3.5(3)
C(27)	0.4687(6)	0.342(3)	0.254(2)	11.2(7)
C(28)	0.8812(4)	0.1500(9)	0.4920(9)	2.3(6)
H(1)	0.7274	0.1101	0.2278	4(3)
H(2)	0.7249	-0.0117	0.0861	4(3)
H(3)	0.7003	0.4317	0.4516	2(2)
H(4)	0.6598	0.4197	0.6644	4(3)
H(5)	0.6936	0.0656	0.7577	1(2)

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

atom	x	y	z	B_{eq}
H(6)	0.6337	0.0541	0.7770	1(2)
H(7)	0.6476	0.2717	0.3589	4 (4)
H(8)	0.5650	0.3022	0.2713	6(4)
H(9)	0.5004	0.3765	0.5485	12(5)
H(10)	0.5789	0.3561	0.6341	1(2)
H(11)	0.8730	0.1149	0.5576	4(3)
H(12)	0.8969	0.0930	0.4475	21(7)
H(13)	0.9049	0.2133	0.5026	2(2)
H(14)	0.4336	0.3609	0.2357	7(4)
H(15)	0.4922	0.3897	0.2155	2(1)
H(16)	0.4752(4)	0.2613(9)	0.2384(9)	7(6)
H(17)	0.7784	0.3932	0.3905	1(2)
H(18)	0.6874	0.1324	0.4905	3(3)
H(19)	0.7235	0.1533	0.5866	2(3)
H(20)	0.6169	0.1255	0.6155	3(3)
H(21)	0.6526	0.0154	0.6075	11(6)
H(22)	0.6267	0.2597	0.7843	1(1)
H(23)	0.6648	0.2149	0.8701	2(2)
H(24)	0.7093	0.3608	0.8068	2(2)
H(25)	0.7323	0.2568	0.7430	3(3)

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

atom	x	y	z	B_{eq}
H(26)	0.7267	0.5183	0.5950	2(3)
H(27)	0.7508	-0.0671	-0.0807	5(4)
H(28)	0.8451	0.2186	-0.0977	3(3)
H(29)	0.8161	0.2755	0.0668	3(1)
H(30)	0.8495	0.2889	0.6263	3(3)

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

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	0.0671(10)	0.0784(11)	0.0234(8)	-0.0252(8)	0.0164(7)	-0.0213(7)
O(1)	0.019(4)	0.026(4)	0.016(4)	-0.002(3)	0.001(3)	0.001(3)
O(2)	0.038(4)	0.020(4)	0.026(4)	-0.010(4)	0.014(4)	-0.002(4)
O(3)	0.009(4)	0.098(8)	0.112(9)	0.008(5)	-0.006(5)	0.027(7)
O(4)	0.042(4)	0.029(4)	0.025(4)	0.009(4)	-0.004(4)	-0.011(4)
O(5)	0.017(4)	0.032(4)	0.037(5)	0.005(4)	0.007(4)	-0.015(4)
N(1)	0.035(5)	0.025(5)	0.021(5)	-0.012(5)	0.007(4)	0.002(5)
C(1)	0.026(6)	0.017(5)	0.019(6)	0.003(5)	0.001(5)	0.003(5)
C(2)	0.018(6)	0.014(5)	0.025(6)	0.008(5)	-0.002(5)	-0.004(5)
C(3)	0.027(6)	0.020(6)	0.024(6)	0.006(5)	0.017(6)	-0.001(5)
C(4)	0.020(6)	0.014(6)	0.039(7)	0.002(5)	0.009(5)	0.005(5)
C(5)	0.041(7)	0.016(6)	0.061(8)	-0.000(5)	0.000(7)	0.000(6)
C(6)	0.057(7)	0.039(7)	0.037(7)	-0.004(6)	0.009(7)	0.007(7)
C(7)	0.087(10)	0.027(6)	0.033(7)	-0.005(7)	0.021(7)	0.006(6)
C(8)	0.075(8)	0.035(7)	0.014(6)	-0.005(6)	0.012(7)	0.000(6)
C(9)	0.023(6)	0.028(6)	0.030(6)	0.007(5)	0.017(5)	0.006(6)
C(10)	0.029(6)	0.012(5)	0.033(7)	0.002(5)	-0.000(5)	0.000(5)
C(11)	0.031(6)	0.015(5)	0.026(7)	0.003(5)	0.011(6)	0.013(6)
C(12)	0.032(6)	0.021(6)	0.029(7)	0.008(5)	-0.007(6)	0.004(6)
C(13)	0.016(6)	0.010(5)	0.031(7)	-0.010(5)	0.004(5)	-0.001(5)