References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441-451.

Burdon, J., Hayes, M. H. B. & Pick, M. E. (1977). *J. Environ. Sci. Health*, **B12**, 37-51.

Clemenson, P. I. (1990). *Coord. Chem. Rev.* **106**, 171-203.

Domingos, A., Henriques, R. T., Gama, V., Ameida, M., Lopes Vieira, A. & Alcacer, L. (1988). *Synth. Met.* **27**, B411-416.

Hofmann, H. J., Cimiraglia, R. & Tomasi, J. (1986). *J. Mol. Struct. (Theochem)*, **139**, 213-219.

Kisch, H., Dümler, W., Nüsslein, F., Zenn, I., Chiorboli, C., Scandola, F., Albrecht, W. & Meier, H. (1991). *Z. Phys. Chem. (Frankfurt am Main)*, **170**, 117-127.

Kisch, H., Fernandez, A., Wakatsuki, Y. & Yamazaki, H. (1985). *Z. Naturforsch. Teil B*, **40**, 292-297.

Kobayashi, A. & Yukiyoshi, S. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2650-2656.

McCleverty, J. A. (1968). *Prog. Inorg. Chem.* **10**, 84-85.

Russell, J. H. & Wallwork, S. C. (1972). *Acta Cryst.* **B28**, 1527-1533.

Schrauzer, G. N. (1968). *Transition Met. Chem.* **4**, 299-335.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Willner, I., Eichen, Y., Rabinovitz, M., Hoffman, R. & Cohen, S. (1992). *J. Am. Chem. Soc.* **114**, 637-644.

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The Optical Resolution of Bicyclo[2.2.1]-hept-5-ene-2-cyanohydrins Using Brucine – a Crystallographic and Molecular-Mechanics Study

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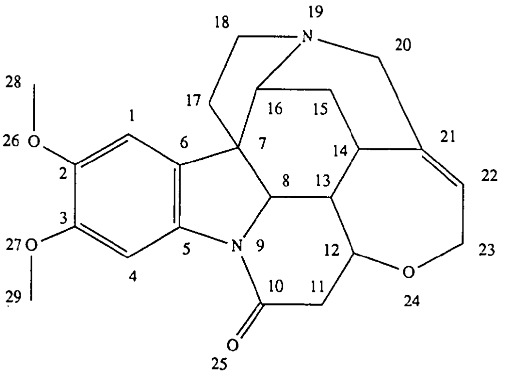
Abstract

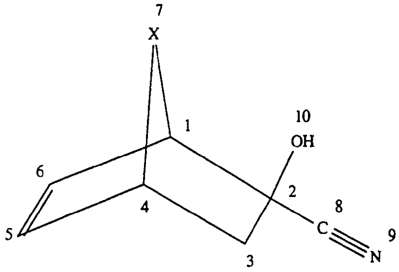
The structures of the brucine complexes with (+)-(1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-cyanohydrin and (+)-(1*R*,2*R*,4*R*)-7-oxabicyclo[2.2.1]hept-5-ene-2-cyanohydrin {(6) 2,3-dimethoxystrychnidine-2-hydroxybicyclo[2.2.1]hept-5-ene-2-carbonitrile (1/1) and (7) 2,3-dimethoxystrychnidine-2-hydroxy-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile (1/1)} have been determined. The primary interaction in the complexes is a hydrogen bond between the OH group of the cyanohydrin and the most basic N atom of brucine. Molecular-mechanics calculations on the 7-oxa derivative indicate that the enantiomeric cyanohydrin will fit into the same cavity in the brucine matrix at the cost of *ca* 71 kJ mol^{-1}.

Comment

There is current interest in understanding the mechanism of molecular recognition (Schneider, 1991) and in the resolution of racemic mixtures. The use of naturally occurring optically pure bases to form diastereomeric salts of differing solubility from racemic acids has been employed for over a century (Pasteur, 1853). More recently, brucine (1) was used to resolve some tertiary acetylenic alcohols by fractional crystallization of the diastereomeric complexes. For one of the complexes, the primary interaction was shown to be formation of a hydrogen bond between the OH group of the alcohol and N19 of brucine (Toda, Tanaka & Ueda, 1981; Toda, Tanaka, Ueda & Oshima, 1985). Applying this technique to the cyanohydrin mixture, (2)/(3), formed by (±)-bicyclo[2.2.1]hept-5-en-2-one (4) and (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one (5), we have been able to prepare optically pure (+)-(4) and (+)-(5), and also to use the resolved brucine/cyanohydrin complexes directly as synthons for the preparation of natural compounds (Black & Vogel, 1984; Warm & Vogel, 1986*a*,*b*, 1987; Vogel, Fattori, Gasparini & LeDrian, 1990; LeDrian & Greene, 1982). We have thus determined the structures of the brucine complexes (6) and (7) of the cyanohydrins derived from (+)-(4) and (+)-(5) to investigate the nature of the interaction in the complex and to gain insight into the determining factors in optical



(1)



(2) $X = CH_2$

(3) $X = O$

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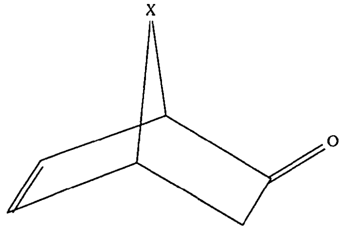
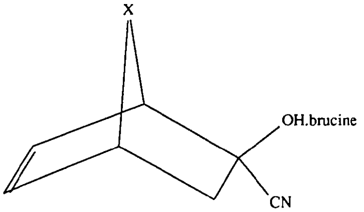


(4) $X = CH_2$
(5) $X = O$



(6) $X = CH_2$
(7) $X = O$

resolution by this technique. The structural study is complemented by molecular-mechanics calculations.

The primary interaction in both complexes is a hydrogen bond between the alcohol functionality of the cyanohydrin and the tertiary amine N atom N19 (Fig. 1). This is in agreement with the work described above on acetylenic alcohols and with the structure of brucine ethanol water solvate (Glover, Gould & Walkinshaw, 1985). The hydrogen-bond formation is in contrast to the observed salt formation when using brucine to resolve racemic acids (Gould, Taylor & Walkinshaw, 1984; Gould & Walkinshaw, 1984; Quinkert, Schmalz, Dzierzynski, Durner & Bats, 1986). The packing of the molecules is similar to that observed for brucine ethanol water solvate (Glover, Gould & Walkinshaw, 1985) and for the acetylenic alcohol complexes (Toda, Tanaka & Ueda, 1981; Toda, Tanaka, Ueda & Oshima, 1985). The cyanohydrin guest molecules spiral around the 2_1 axes parallel to **a** (Fig. 2), thus filling the channels formed by the brucine molecules (Fig. 3)

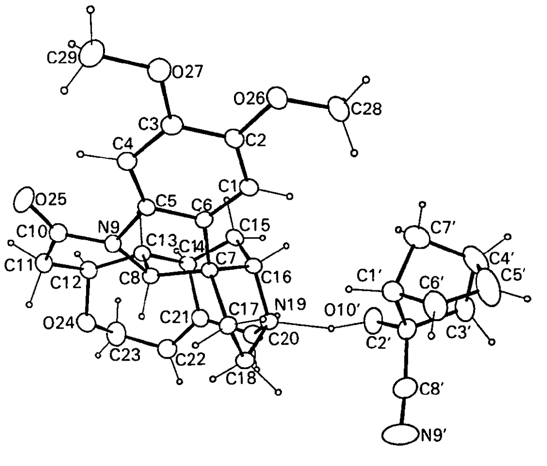


Fig. 1. *ORTEP* representation of the hydrogen-bonded complex (6). Complex (7) is essentially identical.

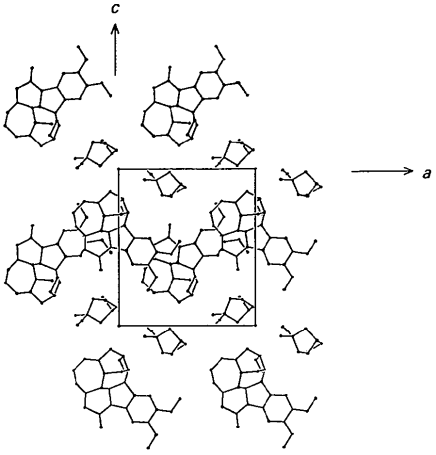


Fig. 2. Section of (6) parallel to the *ac* plane at $y = \frac{1}{4}$ (molecules included for $y = 0 - \frac{1}{2}$) showing the channel occupied by guest molecules.

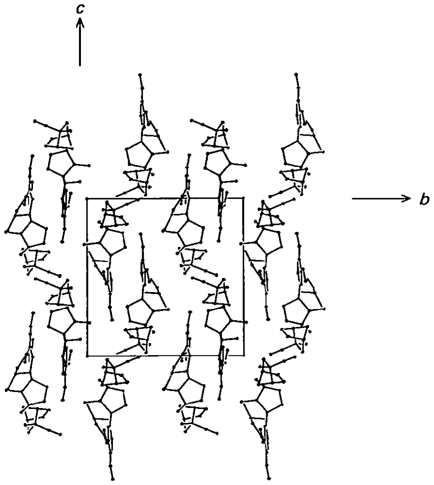


Fig. 3. Projection of structure (6) on the *bc* plane showing the screw-related guest molecules in channels formed by brucine molecular packing.

To obtain insight into the selectivity of the molecular recognition in these systems, we have carried out molecular-mechanics calculations on complex (7). First, a cluster of brucine molecules was built using the *CRYSIN* module of the *SYBYL* software (Tripos Associates, 1991) and symmetry operations generated by the space group. For the calculations, we retained only 17 brucine molecules belonging to a sphere of radius 8 Å around the bicyclic molecule. Two types of calculations were performed, one with the standard Tripos (Tripos Associates, 1991) force field without the electrostatic term and another including the electrostatic term calculated with Gasteiger & Marsili (1980) atomic charges. During the minimizations, the brucine molecules were kept constant (as an aggregate). In the first calculation, the bicyclic part was totally optimized, starting from the crystallographic coordinates, and compared with the crystal structure. The main difference between the two geometries results from the change in the description of the hydrogen bond [the interatomic distance O10′···N19 is 2.711 (3) Å in the crystal structure and 3.014 Å in the model]. Then, the chirality of the bicyclic moiety was inverted, the hydrogen bond held constant at the calculated value (3.014 Å), and the bicyclic part optimized again. An energy difference of *ca* 63 kJ mol^{-1} (without the electrostatic term) and *ca* 71 kJ mol^{-1} (with the electrostatic term) was calculated, the model with the original chirality being the most stable.

Other calculations with the hydrogen bond between the brucine and the cyanohydrin fixed, as measured in the crystal [2.711 (3) Å], for the two models were also carried out. The energy difference between the two enantiomers was calculated to be even greater (*ca* 109 kJ mol^{-1}).

The calculated lower energy of the observed crystallized form may explain its preferential crystallization; however, this does make the assumption that the complex formed between the enantiomer cyanohydrin and brucine would crystallize with the brucine molecules packed in the same way. The large difference in calculated energy suggests that this is unlikely; however, all reported structures for brucine complexes have similar packing (Glover, Gould & Walkinshaw, 1985). We have not been able to obtain suitable crystals of the other diastereomer to confirm or refute this assumption.

The molecular structure of brucine is comparable in (6) and (7) and also to that previously reported (Glover, Gould & Walkinshaw, 1985; Toda, Tanaka & Ueda, 1981; Toda, Tanaka, Ueda & Oshima, 1985). The two cyanohydrin molecules are similar and unremarkable. The main difference between them arises from the smaller size of the bridging O atom in (7).

Experimental

Compound (6)

Crystal data

$C_{23}H_{26}N_2O_4.C_8H_9NO$
$M_r = 529.64$
Orthorhombic
$P2_12_12_1$
$a = 12.519$ (2) Å
$b = 14.286$ (1) Å
$c = 14.607$ (2) Å
$V = 2612$ (1) Å^3
$Z = 4$
$D_x = 1.35$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$13°$
$\mu = 0.086$ mm^{-1}
$T = 294$ K
Extended plate
0.28 × 0.25 × 0.18 mm
Colorless
Crystal source: crystallized from methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined empirical (Walker & Stuart, 1983)
$T_{\min} = 0.9770$, $T_{\max} = 0.9999$
5951 measured reflections
4605 independent reflections
2879 observed reflections [$I > 3.0\sigma(I)$]
$R_{\rm int} = 0.027$
$\theta_{\max} = 24.97°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 50 min
intensity variation: −7.02%

Refinement

Refinement on F
Final $R = 0.036$
$wR = 0.043$
$S = 1.189$
2879 reflections
461 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\max} = 0.169$
$\Delta\rho_{\max} = 0.218$ e Å^{-3}
$\Delta\rho_{\min} = -0.110$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (6)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7753 (2)	0.6316 (2)	−0.0525 (2)	0.0367 (7)
C2	0.7259 (2)	0.6308 (2)	0.0319 (2)	0.0367 (7)
C3	0.7868 (2)	0.6437 (2)	0.1115 (2)	0.0415 (8)
C4	0.8971 (2)	0.6543 (2)	0.1077 (2)	0.0387 (7)
C5	0.9443 (2)	0.6521 (2)	0.0220 (2)	0.0341 (7)
C6	0.8858 (2)	0.6414 (2)	−0.0570 (2)	0.0334 (7)
C7	0.9561 (2)	0.6491 (2)	−0.1404 (2)	0.0326 (7)
C8	1.0701 (2)	0.6381 (2)	−0.0992 (2)	0.0331 (7)
N9	1.0554 (2)	0.6560 (2)	0.0003 (1)	0.0359 (6)
C10	1.1376 (2)	0.6371 (2)	0.0595 (2)	0.0431 (8)
C11	1.2419 (2)	0.6127 (2)	0.0143 (2)	0.0445 (8)
C12	1.2384 (2)	0.5538 (2)	−0.0738 (2)	0.0442 (8)
C13	1.1234 (2)	0.5428 (2)	−0.1067 (2)	0.0368 (7)
C14	1.1030 (2)	0.4961 (2)	−0.1999 (2)	0.0407 (8)
C15	0.9822 (2)	0.4839 (2)	−0.2088 (2)	0.0403 (8)
C16	0.9316 (2)	0.5802 (2)	−0.2191 (2)	0.0356 (7)
C17	0.9462 (2)	0.7440 (2)	−0.1895 (2)	0.0384 (7)
C18	0.9969 (2)	0.7266 (2)	−0.2819 (2)	0.0440 (8)
N19	0.9692 (2)	0.6278 (2)	−0.3056 (1)	0.0394 (6)
C20	1.0599 (2)	0.5785 (2)	−0.3497 (2)	0.0485 (9)
C21	1.1438 (2)	0.5504 (2)	−0.2823 (2)	0.0429 (8)
C22	1.2455 (2)	0.5736 (2)	−0.2902 (2)	0.0555 (9)
C23	1.3268 (3)	0.5525 (3)	−0.2199 (2)	0.071 (1)
O24	1.3072 (1)	0.6014 (2)	−0.1360 (1)	0.0547 (6)
O25	1.1270 (2)	0.6393 (2)	0.1421 (1)	0.0669 (7)
O26	0.6183 (1)	0.6205 (1)	0.0452 (1)	0.0484 (5)
O27	0.7296 (1)	0.6427 (2)	0.1921 (1)	0.0562 (6)
C28	0.5561 (2)	0.6034 (2)	−0.0337 (2)	0.061 (1)
C29	0.7870 (3)	0.6581 (3)	0.2740 (2)	0.071 (1)
C1′	0.6819 (3)	0.6841 (2)	−0.3285 (2)	0.057 (1)
C2′	0.7274 (2)	0.6682 (2)	−0.4264 (2)	0.0467 (8)
C3′	0.6297 (2)	0.6252 (3)	−0.4775 (2)	0.066 (1)
C4′	0.5472 (3)	0.6179 (3)	−0.4007 (3)	0.089 (1)
C5′	0.5154 (3)	0.7174 (3)	−0.3805 (3)	0.105 (1)
C6′	0.5969 (3)	0.7556 (3)	−0.3357 (2)	0.070 (1)
C7′	0.6170 (3)	0.5938 (3)	−0.3195 (3)	0.084 (1)
C8′	0.7644 (3)	0.7572 (2)	−0.4645 (2)	0.062 (1)
N9′	0.7981 (3)	0.8259 (2)	−0.4911 (2)	0.100 (1)
O10′	0.8114 (2)	0.6031 (1)	−0.4301 (1)	0.0660 (7)

Table 2. *Geometric parameters* (Å, °) *for* (6)

C1—C2	1.379 (4)	C15—C16	1.522 (4)
C1—C6	1.392 (3)	C16—N19	1.510 (3)
C2—C3	1.403 (4)	C17—C18	1.511 (4)
C2—O26	1.369 (3)	C18—N19	1.493 (4)
C3—C4	1.390 (4)	N19—C20	1.483 (4)
C3—O27	1.378 (3)	N19—H9′	1.70 (4)
C4—C5	1.385 (4)	C20—C21	1.494 (4)
C5—C6	1.375 (3)	C21—C22	1.321 (4)
C5—N9	1.427 (3)	C22—C23	1.477 (4)
C6—C7	1.506 (3)	C23—O24	1.432 (4)
C7—C8	1.557 (3)	O26—C28	1.411 (4)
C7—C16	1.545 (4)	O27—C29	1.414 (4)
C7—C17	1.539 (4)	C1′—C2′	1.557 (4)
C8—N9	1.486 (3)	C1′—C6′	1.478 (5)
C8—C13	1.520 (4)	C1′—C7′	1.531 (5)
N9—C10	1.371 (3)	C2′—C3′	1.559 (4)
C10—C11	1.504 (4)	C2′—C8′	1.463 (5)
C10—O25	1.215 (3)	C2′—O10′	1.405 (4)
C11—C12	1.538 (4)	C3′—C4′	1.528 (5)
C12—C13	1.526 (4)	C4′—C5′	1.506 (6)
C12—O24	1.425 (3)	C4′—C7′	1.513 (6)
C13—C14	1.538 (4)	C5′—C6′	1.329 (5)
C14—C15	1.527 (4)	C8′—N9′	1.137 (5)
C14—C21	1.520 (4)	O10′—H9′	1.09 (4)
C2—C1—C6	119.3 (2)	C15—C14—C21	108.9 (2)
C1—C2—C3	119.8 (2)	C14—C15—C16	108.5 (2)
C1—C2—O26	124.6 (2)	C7—C16—C15	114.8 (2)
C3—C2—O26	115.6 (2)	C7—C16—N19	105.9 (2)
C2—C3—C4	121.4 (2)	C15—C16—N19	111.2 (2)
C2—C3—O27	115.1 (2)	C7—C17—C18	103.7 (2)
C4—C3—O27	123.6 (2)	C17—C18—N19	105.4 (2)
C3—C4—C5	117.3 (2)	C16—N19—C18	107.7 (2)
C4—C5—C6	122.3 (2)	C16—N19—C20	112.8 (2)
C4—C5—N9	128.0 (2)	C18—N19—C20	111.9 (2)
C6—C5—N9	109.7 (2)	N19—C20—C21	112.3 (2)
C1—C6—C5	120.0 (2)	C14—C21—C20	115.0 (2)
C1—C6—C7	128.8 (2)	C14—C21—C22	121.4 (3)
C5—C6—C7	111.0 (2)	C20—C21—C22	123.5 (3)
C6—C7—C8	102.4 (2)	C21—C22—C23	123.5 (3)
C6—C7—C16	116.1 (2)	C22—C23—O24	112.2 (3)
C6—C7—C17	113.2 (2)	C12—O24—C23	114.6 (2)
C8—C7—C16	113.9 (2)	C2—O26—C28	116.5 (2)
C8—C7—C17	110.0 (2)	C3—O27—C29	117.2 (2)
C16—C7—C17	101.4 (2)	C2′—C1′—C6′	107.4 (3)
C7—C8—N9	104.3 (2)	C2′—C1′—C7′	98.6 (3)
C7—C8—C13	117.7 (2)	C6′—C1′—C7′	101.9 (3)
N9—C8—C13	106.2 (2)	C1′—C2′—C3′	102.1 (2)
C5—N9—C8	109.3 (2)	C1′—C2′—C8′	109.8 (3)
C5—N9—C10	125.7 (2)	C1′—C2′—O10′	114.0 (2)
C8—N9—C10	119.3 (2)	C3′—C2′—C8′	114.1 (3)
N9—C10—C11	114.9 (2)	C3′—C2′—O10′	107.9 (2)
N9—C10—O25	122.7 (2)	C8′—C2′—O10′	108.9 (2)
C11—C10—O25	122.4 (2)	C2′—C3′—C4′	101.9 (3)
C10—C11—C12	118.0 (2)	C3′—C4′—C5′	104.9 (3)
C11—C12—C13	110.3 (2)	C3′—C4′—C7′	101.6 (3)
C11—C12—O24	104.8 (2)	C5′—C4′—C7′	102.3 (3)
C13—C12—O24	114.7 (2)	C4′—C5′—C6′	106.3 (3)
C8—C13—C12	107.4 (2)	C1′—C6′—C5′	107.8 (3)
C8—C13—C14	112.3 (2)	C1′—C7′—C4′	92.8 (3)
C12—C13—C14	118.7 (2)	C2′—C8′—N9′	176.2 (4)
C13—C14—C15	106.8 (2)	C2′—O10′—H9′	100 (1)
C13—C14—C21	115.1 (2)	N19—H9′—O10′	151 (3)

Compound (7)

Crystal data

$C_{23}H_{26}N_2O_4.C_7H_7NO_2$
M_r = 531.61
Orthorhombic
$P2_12_12_1$
a = 12.378 (2) Å
b = 14.088 (2) Å
c = 14.582 (3) Å
V = 2542 (1) Å^3
Z = 4
D_x = 1.39 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 25 reflections
θ = 12–14°
μ = 0.091 mm^{-1}
T = 294 K
Elongated plate
0.35 × 0.20 × 0.15 mm
Colorless
Crystal source: crystallized from methanol

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{\min}$ = 0.9631, $T_{\max}$ = 0.9994
3154 measured reflections
2873 independent reflections

2514 observed reflections [$I > 3.0\sigma(I)$]
$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 25.95°
h = 0 → 15
k = 0 → 16
l = −17 → 17
3 standard reflections
frequency: 50 min
intensity variation: −1.86%

Refinement

Refinement on F
Final R = 0.036
wR = 0.043
S = 1.195
2514 reflections
456 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\max}$ = 0.039
$\Delta\rho_{\max}$ = 0.1953 e Å^{-3}

$\Delta\rho_{\min}$ = −0.1135 e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.30 × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (7)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7744 (2)	0.6260 (2)	−0.0549 (2)	0.0326 (8)
C2	0.7239 (2)	0.6232 (2)	0.0303 (2)	0.0360 (8)
C3	0.7845 (2)	0.6311 (2)	0.1104 (2)	0.0372 (8)
C4	0.8957 (2)	0.6434 (2)	0.1072 (2)	0.0331 (8)
C5	0.9440 (2)	0.6458 (2)	0.0213 (2)	0.0313 (8)
C6	0.8862 (2)	0.6373 (2)	−0.0579 (2)	0.0297 (8)
C7	0.9575 (2)	0.6497 (2)	−0.1419 (2)	0.0284 (8)
C8	1.0726 (2)	0.6404 (2)	−0.0987 (2)	0.0280 (7)
N9	1.0565 (2)	0.6548 (2)	0.0010 (2)	0.0301 (6)
C10	1.1391 (2)	0.6357 (2)	0.0591 (2)	0.0386 (8)
C11	1.2474 (2)	0.6150 (2)	0.0147 (2)	0.0396 (9)
C12	1.2463 (2)	0.5600 (2)	−0.0748 (2)	0.0378 (9)
C13	1.1307 (2)	0.5463 (2)	−0.1106 (2)	0.0311 (8)
C14	1.1134 (2)	0.5002 (2)	−0.2042 (2)	0.0366 (9)
C15	0.9904 (2)	0.4850 (2)	−0.2134 (2)	0.0359 (9)
C16	0.9364 (2)	0.5811 (2)	−0.2207 (2)	0.0312 (8)
C17	0.9423 (2)	0.7464 (2)	−0.1888 (2)	0.0330 (8)
C18	0.9966 (3)	0.7320 (2)	−0.2801 (2)	0.0402 (9)
N19	0.9720 (2)	0.6321 (2)	−0.3061 (2)	0.0361 (7)
C20	1.0651 (3)	0.5863 (2)	−0.3531 (2)	0.0427 (9)
C21	1.1510 (3)	0.5598 (2)	−0.2848 (2)	0.0392 (9)
C22	1.2525 (3)	0.5881 (3)	−0.2924 (2)	0.049 (1)
C23	1.3372 (3)	0.5679 (3)	−0.2216 (2)	0.057 (1)
O24	1.3135 (2)	0.6136 (2)	−0.1360 (1)	0.0455 (6)
O25	1.1294 (2)	0.6367 (2)	0.1428 (1)	0.0622 (8)
O26	0.6145 (2)	0.6119 (2)	0.0418 (1)	0.0457 (6)
O27	0.7266 (2)	0.6267 (2)	0.1899 (1)	0.0499 (7)
C28	0.5520 (3)	0.5985 (3)	−0.0382 (3)	0.059 (1)
C29	0.7842 (3)	0.6254 (3)	0.2722 (3)	0.074 (1)
C1′	0.6677 (3)	0.6790 (3)	−0.3258 (2)	0.061 (1)

C2′	0.7224 (3)	0.6669 (2)	−0.4220 (2)	0.046 (1)
C3′	0.6268 (3)	0.6274 (3)	−0.4787 (2)	0.055 (1)
C4′	0.5383 (3)	0.6240 (3)	−0.4030 (3)	0.072 (1)
C5′	0.5097 (3)	0.7244 (3)	−0.3819 (3)	0.083 (1)
C6′	0.5882 (3)	0.7584 (3)	−0.3336 (3)	0.069 (1)
O7′	0.6006 (2)	0.5974 (2)	−0.3251 (2)	0.083 (1)
C8′	0.7634 (3)	0.7578 (3)	−0.4552 (2)	0.053 (1)
N9′	0.8011 (3)	0.8276 (3)	−0.4770 (2)	0.079 (1)
O10′	0.8069 (2)	0.6005 (2)	−0.4243 (2)	0.0644 (8)

Table 4. *Geometric parameters* (Å, °) *for* (7)

C1—C2	1.392 (4)	C15—C16	1.513 (4)
C1—C6	1.394 (4)	C16—N19	1.504 (4)
C2—C3	1.392 (4)	C17—C18	1.505 (4)
C2—O26	1.375 (3)	C18—N19	1.489 (4)
C3—C4	1.387 (4)	N19—C20	1.489 (4)
C3—O27	1.365 (4)	N19—H7′	1.54 (4)
C4—C5	1.389 (4)	C20—C21	1.504 (4)
C5—C6	1.365 (4)	C21—C22	1.322 (5)
C5—N9	1.430 (4)	C22—C23	1.499 (5)
C6—C7	1.520 (4)	C23—O24	1.434 (4)
C7—C8	1.564 (4)	O26—C28	1.412 (4)
C7—C16	1.523 (4)	O27—C29	1.395 (4)
C7—C17	1.536 (4)	C1′—C2′	1.567 (5)
C8—N9	1.481 (4)	C1′—C6′	1.494 (6)
C8—C13	1.518 (4)	C1′—O7′	1.417 (5)
N9—C10	1.355 (4)	C2′—C3′	1.548 (5)
C10—C11	1.517 (4)	C2′—C8′	1.460 (5)
C10—O25	1.226 (4)	C2′—O10′	1.403 (4)
C11—C12	1.519 (4)	C3′—C4′	1.556 (5)
C12—C13	1.534 (4)	C4′—C5′	1.491 (7)
C12—O24	1.435 (4)	C4′—O7′	1.422 (5)
C13—C14	1.527 (4)	C5′—C6′	1.292 (6)
C14—C15	1.543 (4)	C8′—N9′	1.134 (5)
C14—C21	1.518 (4)	O10′—H7′	1.23 (4)
C2—C1—C6	118.5 (3)	C15—C14—C21	108.2 (3)
C1—C2—C3	120.3 (3)	C14—C15—C16	108.5 (2)
C1—C2—O26	123.7 (3)	C7—C16—C15	116.1 (2)
C3—C2—O26	116.0 (3)	C7—C16—N19	105.7 (2)
C2—C3—C4	121.1 (3)	C15—C16—N19	110.9 (2)
C2—C3—O27	115.2 (2)	C7—C17—C18	102.7 (2)
C4—C3—O27	123.7 (3)	C17—C18—N19	105.1 (3)
C3—C4—C5	117.4 (3)	C16—N19—C18	107.5 (2)
C4—C5—C6	122.4 (3)	C16—N19—C20	113.6 (2)
C4—C5—N9	127.5 (3)	C18—N19—C20	111.7 (2)
C6—C5—N9	110.1 (2)	N19—C20—C21	110.5 (3)
C1—C6—C5	120.3 (3)	C14—C21—C20	115.6 (3)
C1—C6—C7	127.9 (3)	C14—C21—C22	121.5 (3)
C5—C6—C7	111.6 (2)	C20—C21—C22	122.8 (3)
C6—C7—C8	101.2 (2)	C21—C22—C23	123.3 (3)
C6—C7—C16	115.8 (2)	C22—C23—O24	111.8 (3)
C6—C7—C17	112.9 (2)	C12—O24—C23	115.1 (3)
C8—C7—C16	114.0 (2)	C2—O26—C28	117.0 (2)
C8—C7—C17	111.4 (2)	C3—O27—C29	117.6 (2)
C16—C7—C17	101.9 (2)	C2′—C1′—C6′	107.4 (3)
C7—C8—N9	105.2 (2)	C2′—C1′—O7′	99.9 (3)
C7—C8—C13	117.3 (2)	C6′—C1′—O7′	102.8 (3)
N9—C8—C13	107.2 (2)	C1′—C2′—C3′	100.8 (3)
C5—N9—C8	108.8 (2)	C1′—C2′—C8′	110.6 (3)
C5—N9—C10	126.0 (2)	C1′—C2′—O10′	114.6 (3)
C8—N9—C10	119.0 (2)	C3′—C2′—C8′	113.7 (3)
N9—C10—C11	116.0 (2)	C3′—C2′—O10′	108.5 (3)
N9—C10—O25	123.1 (3)	C8′—C2′—O10′	108.5 (3)
C11—C10—O25	120.9 (3)	C2′—C3′—C4′	99.8 (3)
C10—C11—C12	117.2 (3)	C3′—C4′—C5′	106.5 (3)
C11—C12—C13	111.4 (2)	C3′—C4′—O7′	101.2 (3)
C11—C12—O24	105.1 (2)	C5′—C4′—O7′	102.3 (3)
C13—C12—O24	113.3 (2)	C4′—C5′—C6′	106.5 (4)
C8—C13—C12	107.0 (2)	C1′—C6′—C5′	105.1 (4)
C8—C13—C14	114.0 (2)	C1′—O7′—C4′	95.7 (3)
C12—C13—C14	119.2 (2)	C2′—C8′—N9′	175.2 (4)
C13—C14—C15	106.0 (2)	C2′—O10′—H7′	105 (1)
C13—C14—C21	114.4 (3)	N19—H7′—O10′	154 (3)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Similar H atoms were constrained to have the same isotropic thermal parameter. Molecular-mechanics calculations were carried out using *SYBYL* (Tripos Associates, 1991). Starting coordinates for complex (7) were taken from (6) and refined. Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program used to solve structure (direct methods): *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Program used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *CIF* in *MolEN*.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71150 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1047]

References

Black, K. A. & Vogel, P. (1984). *Helv. Chim. Acta*, **67**, 1612-1615.
Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488-492.
Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. An interactive intelligent system for crystal structure analysis. User's manual. Enraf-Nonius, Delft, The Netherlands.
Gasteiger, J. & Marsili, M. (1980). *Tetrahedron*, **36**, 3219-3222.
Glover, S. S. B., Gould, R. O. & Walkinshaw, M. D. (1985). *Acta Cryst.* C**41**, 990-994.
Gould, R. O., Taylor, P. & Walkinshaw, M. D. (1984). *Acta Cryst.* A**40**, C-85.
Gould, R. O. & Walkinshaw, M. D. (1984). *J. Am. Chem. Soc.* **106**, 7840-7842.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
LeDrian, C. & Greene, A. E. (1982). *J. Am. Chem. Soc.* **104**, 5473-5483.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Pasteur, L. (1853). *C. R. Acad. Sci.* **37**, 162-166.
Quinkert, G., Schmalz, H.-G., Dzierzynski, E. M., Durner, G. & Bats, J. W. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 992-993.
Schneider, H.-J. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1417-1436.
Toda, F., Tanaka, K. & Ueda, H. (1981). *Tetrahedron Lett.* **22**, 4669-4672.
Toda, F., Tanaka, K., Ueda, H. & Oshima, T. (1985). *Isr. J. Chem.* **25**, 338-345.
Tripos Associates (1991). *SYBYL*. Versions 5.41 and 5.5. Tripos Associates, St. Louis, Missouri, USA.
Vogel, P., Fattori, D., Gasparini, F. & LeDrian, C. (1990). *Synlett*, pp. 173-185.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158-166.
Warm, A. & Vogel, P. (1986*a*). *J. Org. Chem.* **51**, 5348-5353.
Warm, A. & Vogel, P. (1986*b*). *Tetrahedron Lett.* **27**, 5615-5616.
Warm, A. & Vogel, P. (1987). *Helv. Chim. Acta*, **70**, 690-700.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139-1144.