

Compound (5)*Crystal data*

C₁₁H₁₆O₃
M_r = 196.24
 Monoclinic
*P*2₁/*n*
a = 6.675 (6) Å
b = 20.767 (19) Å
c = 7.109 (7) Å
 β = 106.08 (6)°
V = 946.9 (15) Å³
Z = 4
D_x = 1.377 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 17 reflections
 θ = 7.55–17.97°
 μ = 0.099 mm⁻¹
T = 293 (2) K
 Irregular plate
 0.50 × 0.30 × 0.05 mm
 Colorless

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 3130 measured reflections
 1856 independent reflections
 969 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.0664

θ_{\max} = 26.01°
 h = -8 → 6
 k = -19 → 25
 l = -8 → 8
 3 standard reflections
 every 97 reflections
 intensity decay: 3.82%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.0650
wR(*F*²) = 0.1473
S = 1.051
 1818 reflections
 135 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.1598P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.163 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.185 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (5)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O1	0.6823 (4)	0.02272 (12)	1.3418 (3)	0.0558 (7)
O2	0.0439 (4)	0.05938 (12)	0.7716 (3)	0.0479 (7)
O3	0.7011 (4)	0.10522 (13)	1.5351 (4)	0.0641 (9)
C1	0.4258 (4)	0.10552 (14)	1.2473 (4)	0.0292 (7)
C2	0.3296 (4)	0.06444 (15)	1.0677 (4)	0.0347 (8)
C3	0.1420 (4)	0.09863 (15)	0.9379 (4)	0.0323 (8)
C4	-0.0178 (5)	0.1101 (2)	1.0465 (5)	0.0398 (9)
C5	0.0766 (5)	0.1517 (2)	1.2245 (5)	0.0395 (8)
C6	0.1425 (5)	0.2148 (2)	1.1602 (5)	0.0444 (9)
C7	0.3020 (5)	0.2037 (2)	1.0503 (5)	0.0406 (9)
C8	0.4902 (5)	0.17021 (14)	1.1812 (5)	0.0360 (8)
C9	0.2087 (5)	0.1617 (2)	0.8726 (4)	0.0401 (8)
C10	0.2647 (5)	0.1171 (2)	1.3577 (4)	0.0393 (8)
C11	0.6143 (5)	0.0728 (2)	1.3773 (4)	0.0368 (8)

Table 4. Selected geometric parameters (Å, °) for (5)

O1—C11	1.190 (4)	O3—C11	1.299 (4)
O2—C3	1.436 (4)	C1—C11	1.501 (4)
O1—C11—O3	122.1 (3)	O3—C11—C1	113.3 (3)
O1—C11—C1	124.7 (3)		

The title structures were solved by direct methods and refined successfully in space groups *Pnma* and *P*2₁/*n* for (4) and (5), respectively. Full-matrix least-squares refinement was carried

out by minimizing $w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. H atoms were refined freely for (4) and only the H atoms connected to O were refined for (5). The other H atoms were treated using appropriate riding models.

For both compounds, data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: SHELXTL-Plus (Sheldrick, 1995); software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1307). Services for accessing these data are described at the back of the journal.

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Three *trans*-Diphenylperfluorotrienes

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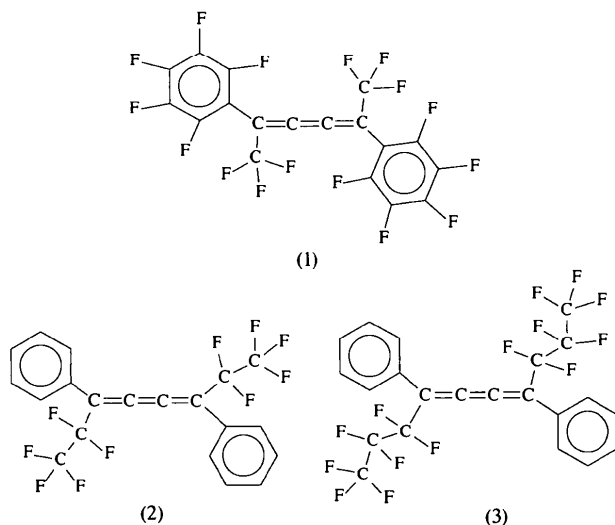
Abstract

The structures of (*E*)-1,1,1,6,6,6-hexafluoro-2,5-bis-(pentafluorophenyl)-2,3,4-hexatriene, (1), C₁₈F₁₆, (*E*)-1,1,1,2,2,7,7,8,8,8-decafluoro-3,6-diphenyl-3,4,5-octatriene, (2), C₂₀H₁₀F₁₀, and (*E*)-1,1,1,2,2,3,3,8,8,9,9,10,10,10-

tetradecafluoro-4,7-diphenyl-4,5,6-decatriene, (3), $C_{22}H_{10}F_{14}$, confirm the *trans* conformation assigned by spectrophotometric methods. These trienes exhibit the central double-bond shortening observed in cumulenes. The phenyl rings are rotated slightly from the triene plane in (2) and (3) and are nearly perpendicular to the triene plane in (1). The large rotation of the perfluorophenyl rings from the triene plane is due to intramolecular steric interactions with the *ortho*-F atoms.

Comment

(*R1*)(*R2*)C=C(ZnBr)(Br) (where *R1* is CF_3 , C_2F_5 or C_3F_7 and *R2* is C_6H_5 or C_6F_5) dimerizes in the presence of catalytic amounts of CuBr to give the *E* and *Z* isomers of (*R1*)(*R2*)C=C=C=C(*R1*)(*R2*) in high yields (Morken, Bachand, Swenson & Burton, 1993). The isomers were separated by chromatography and/or fractional recrystallization and tentatively assigned by spectrophotometric methods. The isomers that exhibited λ_{max} at longer wavelengths with a larger extinction coefficient, ϵ , were assigned the *trans* conformation. These assignments were confirmed by the structures of (1), (2) and (3).



Each of the triene molecules is on a crystallographic center of symmetry. The middle ($C1=C1'$) double bond for each of the trienes is significantly shorter than the outside ($C1=C2$) double bond. This situation has been noted in previous studies (Berkovitch-Yellin & Leiserowitz, 1977; Tinant, Declercq, Bouvy, Janousek & Viehe, 1993; Morken *et al.*, 1991). The plane of the phenyl ring ($C3-C8$) is rotated somewhat from the triene plane ($C1-C3$, $C9$) for (2) and (3). The dihedral angles are $16.9(2)^\circ$ for (2) and $7.4(6)^\circ$ for (3). The dihedral angle between the perfluorophenyl ring and the triene plane for (1) is $90.4(2)^\circ$. The intramolecular steric interactions between the *ortho*-F atoms and the

C9-methyl F atoms [$F4-F9C = 3.132(4) \text{ \AA}$, $F8-F9B = 3.067(4) \text{ \AA}$] and between the triene *C2* atom and the *ortho*-F atoms [$C2-F4 = 2.826(4) \text{ \AA}$ and $C2-F8 = 2.816(4) \text{ \AA}$] force the phenyl ring to be perpendicular to the plane of the triene atoms.

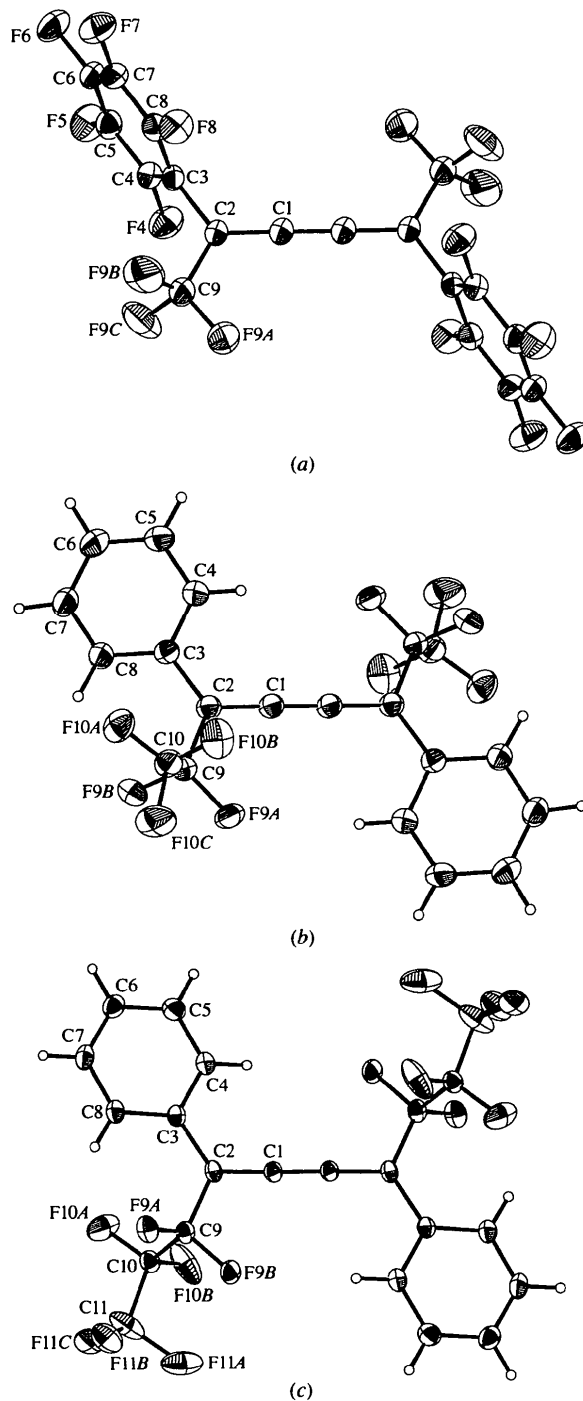


Fig. 1. ORTEP (Johnson, 1976) diagrams of the title compounds with displacement ellipsoids drawn at the 35% level: (a) compound (1), (b) compound (2), (c) compound (3).

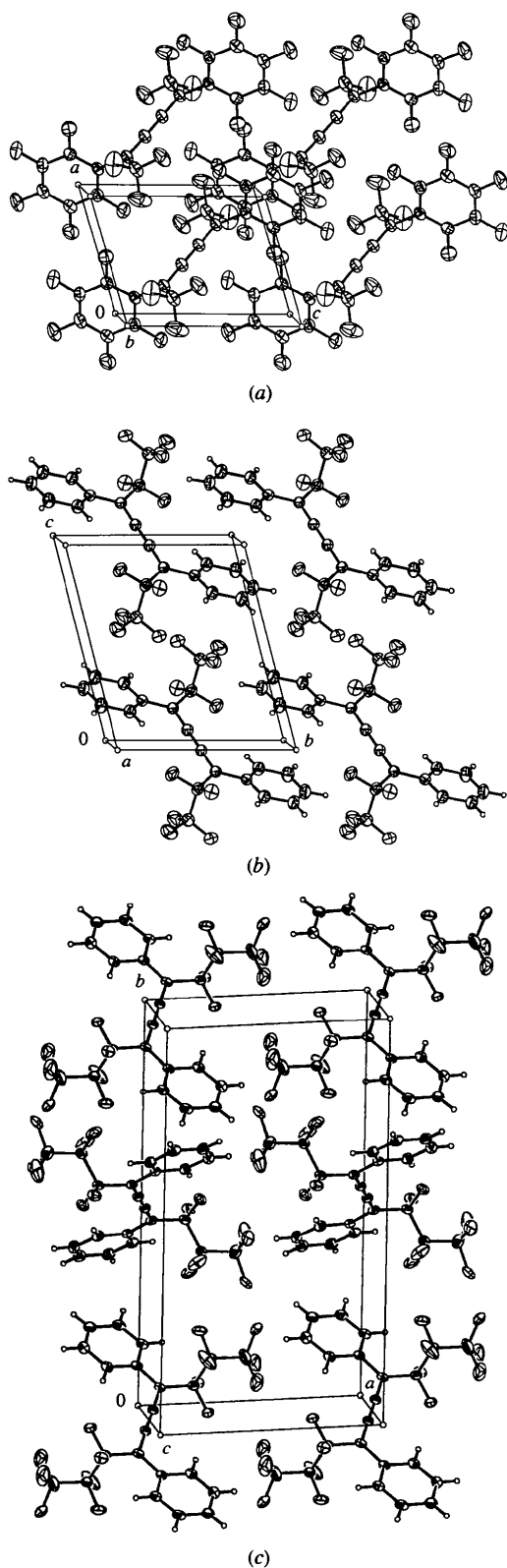


Fig. 2. Packing diagrams of the title compounds: (a) compound (1), (b) compound (2), (c) compound (3).

Molecules of compounds (2) and (3) pack similarly in the solid state. These molecules stack in a tilted manner to form columns along the *a* direction for (2) and along the *c* direction for (3) (these are the short dimensions in each case). The tilt of the molecules alternates in a herringbone fashion for (3). The molecules of (1) form stacks of molecules along the *b* direction. The phenyl rings from adjacent stacks overlap in an alternating fashion to interleave the stacks.

The C11—CF₃ group is rotationally disordered. The occupancy of the major site (F11A, F11B, F11C) refined to 0.62 (2). The occupancy of the minor site (F11D, F11E, F11F) is 0.38. C11 is common to both sites.

Experimental

The details of compound preparation and crystallization are given in Morken, Bachand, Swenson & Burton (1993).

Compound (1)

Crystal data

C₁₈F₁₆

M_r = 520.18

Triclinic

P $\bar{1}$

a = 5.7009 (8) Å

b = 10.509 (2) Å

c = 9.420 (2) Å

α = 123.78 (1)°

β = 102.66 (1)°

γ = 94.08 (1)°

V = 444.5 (4) Å³

Z = 1

D_x = 1.94 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 10–17°

μ = 0.223 mm⁻¹

T = 293 K

Prism

0.42 × 0.30 × 0.25 mm

Colorless

Data collection

Enraf–Nonius CAD-4

diffractometer

$\theta/2\theta$ scans

Absorption correction: none

7799 measured reflections

3900 independent reflections

1395 reflections with

$I > 2\sigma(I)$

R_{int} = 0.031

θ_{\max} = 35°

h = -9 → 9

k = -16 → 16

l = -15 → 15

4 standard reflections

frequency: 240 min

intensity decay: 9.06%

[linear correction, *MolEN*
(Fair, 1990)]

Refinement

Refinement on *F*

R = 0.053

wR = 0.061

S = 1.031

1395 reflections

154 parameters

Weighting scheme based

on measured e.s.d.'s

(Killean & Lawrence,

1969)

$(\Delta/\sigma)_{\max}$ = 0.003

$\Delta\rho_{\max}$ = 0.28 e Å⁻³

$\Delta\rho_{\min}$ = 0.05 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (1)

C1—C1 ¹	1.252 (6)	C2—C3	1.486 (4)
C1—C2	1.316 (4)	C2—C9	1.494 (4)
C1 ¹ —C1—C2	179.4 (4)	C1—C2—C9	120.2 (3)
C1—C2—C3	122.5 (3)	C3—C2—C9	117.2 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.**Compound (2)***Crystal data* $\text{C}_{20}\text{H}_{10}\text{F}_{10}$ $M_r = 440.29$

Triclinic

 $P\bar{1}$ $a = 5.8990$ (7) \AA $b = 9.509$ (1) \AA $c = 9.304$ (1) \AA $\alpha = 102.75$ (1) $^\circ$ $\beta = 94.62$ (1) $^\circ$ $\gamma = 115.92$ (1) $^\circ$ $V = 448.4$ (3) \AA^3 $Z = 1$ $D_x = 1.63$ Mg m^{-3} D_m not measured*Data collection*

Enraf–Nonius CAD-4

diffractometer

 $\theta/2\theta$ scans

Absorption correction:

 ψ scans, *MolEN* (Fair, 1990) $T_{\min} = 0.651$, $T_{\max} = 0.719$

3681 measured reflections

1841 independent reflections

Cu $K\alpha$ radiation $\lambda = 1.54184$ \AA

Cell parameters from 25

reflections

 $\theta = 22$ – 44° $\mu = 1.499$ mm^{-1} $T = 293$ K

Prism

 $0.35 \times 0.29 \times 0.22$ mm

Pale yellow

1659 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.050$ $\theta_{\max} = 75.0^\circ$ $h = -7 \rightarrow 6$ $k = -11 \rightarrow 11$ $l = -11 \rightarrow 11$

4 standard reflections

frequency: 240 min

intensity decay: 0.01%

*Refinement*Refinement on F $R = 0.042$ $wR = 0.067$ $S = 1.194$

1659 reflections

156 parameters

All H-atom parameters

refined

Weighting scheme based

on measured e.s.d.'s

(Killean & Lawrence, 1969)

 $(\Delta/\sigma)_{\max} = 0.010$ $\Delta\rho_{\max} = 0.16$ e \AA^{-3} $\Delta\rho_{\min} = -0.12$ e \AA^{-3}

Extinction correction: none

Scattering factors from *Inter-**national Tables for X-ray**Crystallography* (Vol. IV)Table 2. Selected geometric parameters (\AA , $^\circ$) for (2)

C1—C1 ¹	1.245 (3)	C2—C3	1.478 (2)
C1—C2	1.334 (2)	C2—C9	1.517 (2)
C1 ¹ —C1—C2	178.9 (2)	C1—C2—C9	115.1 (1)
C1—C2—C3	122.2 (1)	C3—C2—C9	122.6 (1)

Symmetry code: (i) $-x, 1 - y, 2 - z$.**Compound (3)***Crystal data* $\text{C}_{22}\text{H}_{10}\text{F}_{14}$ $M_r = 540.3$ Mo $K\alpha$ radiation $\lambda = 0.71073$ \AA

Monoclinic

 $P2_1/c$ $a = 10.2071$ \AA $b = 17.6882$ \AA $c = 5.9376$ \AA $\beta = 97.52^\circ$ $V = 1062.78$ \AA^3 $Z = 2$ $D_x = 1.68$ Mg m^{-3} D_m not measured*Data collection*

Enraf–Nonius CAD-4

diffractometer

 $\theta/2\theta$ scans

Absorption correction: none

5445 measured reflections

1856 independent reflections

1238 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.090$

Cell parameters from 25

reflections

 $\theta = 5$ – 14° $\mu = 0.184$ mm^{-1} $T = 291$ K

Plate

 $0.31 \times 0.28 \times 0.09$ mm

Light green

*Refinement*Refinement on F $R = 0.052$ $wR = 0.065$ $S = 1.057$

1238 reflections

191 parameters

H atoms refined, $U = 1.3$ $\times U$ of bonding atom

Weighting scheme based

on measured e.s.d.'s

(Killean & Lawrence,

1969)

 $(\Delta/\sigma)_{\max} = 0.033$ $\Delta\rho_{\max} = 0.36$ e \AA^{-3} $\Delta\rho_{\min} = -0.09$ e \AA^{-3}

Extinction correction:

isotropic (Zachariasen, 1963)

Extinction coefficient: 0.74 $\times 10^{-6}$ Scattering factors from *Inter-**national Tables for X-ray**Crystallography* (Vol. IV)Table 3. Selected geometric parameters (\AA , $^\circ$) for (3)

C1—C1 ¹	1.253 (6)	C2—C3	1.474 (4)
C1—C2	1.329 (4)	C2—C9	1.523 (4)
C1 ¹ —C1—C2	178.5 (4)	C1—C2—C9	115.3 (3)
C1—C2—C3	122.1 (2)	C3—C2—C9	122.5 (2)

Symmetry code: (i) $2 - x, 1 - y, -z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974)

For all compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Software*; data reduction: *PROCESS MolEN* (Fair, 1990); program(s) used to solve structures: direct methods (*MULTAN*; Main *et al.*, 1980); program(s) used to refine structures: *LSFM MolEN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CIF VAX MolEN*.

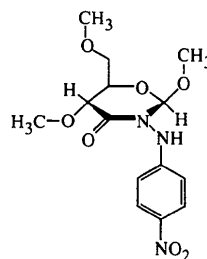
DJB thanks the National Science Foundation for support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: PA1195). Services for accessing these data are described at the back of the journal.

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Rey & Bernardinelli, 1988). The reaction proceeds generally regioselectively and the configuration of the existing asymmetric C atoms is preserved. These compounds are potential glycosidase inhibitors (Look, Fotsh & Wong, 1993). The title compound has been prepared (Tronchet, Tronchet, Barbalat-Rey & Bernardinelli, 1997) from methyl 2-deoxy-3,5-di-*O*-methyl-2-(*p*-nitrophenylhydrazono)- β -D-erythro-pentofuranoside which was oxidized (lead tetraacetate) to an epimeric mixture of azoacetates, which upon saponification of their ester function underwent a base-catalyzed ring enlargement. X-ray analysis was deemed necessary to assess the geometrical features of this new type of sugar analogue which has an anomeric center of the unusual orthoester type, particularly its solid-state conformation, and to confirm the configuration established by ¹H NMR. Despite numerous attempts at crystallization only very fine needle crystals could be obtained.



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Methyl 2-Aza-2-deoxy-4,6-di-*O*-methyl-2-*N*-(*p*-nitrophenylamino)- β -D-erythro-hexopyranosid-3-ulose

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Abstract

All asymmetric C atoms of the title compound, C₁₄H₁₉N₃O₇, are in the *R* configuration. The azapyranose ring adopts a half-chair conformation with substituents in equatorial and quasi-equatorial positions. The molecular packing is fixed by hydrogen bonds involving the amino group and one of the methoxy substituents.

Comment

Six-membered sugar lactams can be obtained by oxidative ring enlargement of furanose *p*-nitrophenyl hydrazones (Tronchet, Tronchet, Rachidzadeh, Barbalat-

Since the configuration at the C3 atom is known (*R*) and preserved during the regioselective synthesis, the absolute configuration of the molecule is well determined as 2*R*,3*R*,4*R*. The minimum value of the asymmetry parameters (Nardelli, 1983) shows that the azapyranose ring adopts a half-chair conformation with a pseudo-twofold axis passing through the O1—C3 bond [$\Delta C_2(O1—C3) = 0.012(5)$]. The substituents at C2 and C4 are located in quasi-equatorial positions whereas the methoxymethyl group at C3 is equatorial. In the crystal the molecules are associated in chains along the *b* axis by hydrogen-bond interactions involving the amino group and the anomeric methoxy group at C4 [N2...O5(*x*, *y* - 1, *z*) = 2.89(1) Å; N2—H02...O5 = 138.2(4)°].

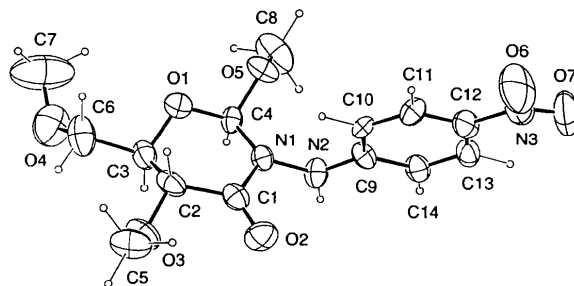


Fig. 1. View of the title compound with atomic labelling. Ellipsoids are represented at the 40% probability level.