found no measurable reflections. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976). H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter. Fig. 1 was produced using *SCHAKAL* (Keller, 1988).

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 71086 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1038]

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Keller, E. (1988). *SCHAKAL*88. *A Fortran Program for the Graphical Representation of Molecular and Crystallographic Models*. Albert-Ludwigs Univ., Freiburg, Germany.

Lai, L.-L. (1990). MSc thesis, Univ. of the Witwatersrand, Johannesburg, South Africa.

Lai, L.-L. (1992). PhD thesis, Univ. of the Witwatersrand, Johannesburg, South Africa.

Lai, L.-L. & Reid, D. H. (1989). Abstracts of the 12th International Congress of Heterocyclic Chemistry, Jerusalem, 13–17 August, 1989, p. A4.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

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6,6a,7,11b-Tetrahydro-6a-methyl-5-phenyl-5,7-methano-5*H*-benzo[*c*]fluorene and 9-Methyl-1,3,9-triphenylfluorene

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Abstract

The two crystalline products of the non-steam volatile fraction from the reaction of acetophenone and methanesulfonic acid have been identified, by single-crystal strucure analysis, as 6,6a,7,11b-tetrahydro-6a-methyl-5-phenyl-5,7-methano-5*H*-benzo[*c*]fluorene and 9-methyl-1,3,9-triphenylfluorene. The mechanism leading to their formation is not obvious.

Comment

Treatment of acetophenone with hot neat methanesulfonic acid at 383 K (3 h) yields a complex product mixture. Steam distillation of the product mixture followed by chromatography on silica yielded 1,1,3-trimethyl-3-phenylindan, 3-methyl-3-phenyl-1-indanone, 1-methyl-3-phenylnaphthalene and 3,3,3′,3′-tetramethyl-1,1′-spirobiindan. Chromatography on silica of the steam distillation residue gave 1,3,5-triphenylbenzene, 9-methyl-1,3,9-triphenylfluorene, 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene and 6,6a,7,11b-tetrahydro-6a-methyl-5-phenyl-5,7-methano-5*H*-benzo[*c*]fluorene. 9-Methyl-1,3,9-triphenylfluorene was isolated previously among

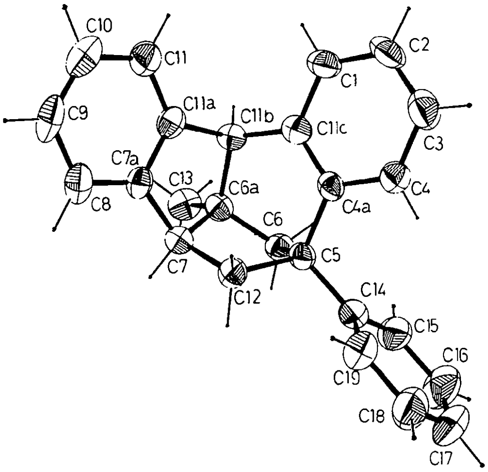

Fig. 1. Projection view of 6,6a,7,11b-tetrahydro-6a-methyl-5-phenyl-5,7-methano-5*H*-benzo[*c*]fluorene.

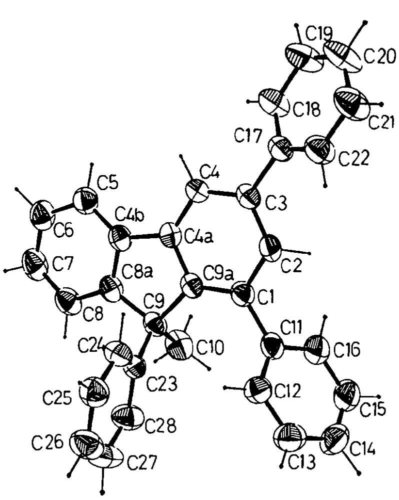

Fig. 2. Projection view of 9-methyl-1,3,9-triphenylfluorene.

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the products of the reaction of phenyl acetylene with anhydrous hydrogen chloride (Griesbaum, Rao & Leifker, 1982). The single-crystal structure of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene has been reported previously (Carrondo & Rogers, 1984).

Experimental

$C_{25}H_{22}$

Crystal data

$C_{25}H_{22}$
M_r = 322.4
Monoclinic
$P2_1/n$
a = 12.478 (1) Å
b = 6.223 (1) Å
c = 23.024 (11) Å
β = 96.36 (3)°
V = 1776.8 (12) Å^3
Z = 4

D_x = 1.20 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 10 reflections
θ = 6.76–10.70°
μ = 0.068 mm^{-1}
T = 298 K
Rhombohedron
0.20 × 0.15 × 0.10 mm
Colorless

Data collection

Syntex *P*3 automated diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3819 measured reflections
3819 independent reflections
1707 observed reflections [$I > 3.0\sigma(I)$]

θ_{max} = 27.0°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 23$
3 standard reflections monitored every 97 reflections
intensity variation: <5%

Refinement

Refinement on F
Final R = 0.052
wR = 0.051
S = 1.12
1707 reflections
315 parameters
H-atom positional parameters and isotropic thermal parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.93
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $C_{25}H_{22}$

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

	x	y	z	U_{eq}
C1	0.3076 (3)	0.9641 (7)	0.2012 (2)	4.5
C2	0.1987 (3)	0.9537 (7)	0.2066 (2)	5.5
C3	0.1346 (3)	0.8123 (8)	0.1724 (2)	5.5
C4	0.1787 (3)	0.6830 (7)	0.1323 (2)	4.4
C4a	0.2883 (3)	0.6932 (6)	0.1257 (2)	3.3
C5	0.3390 (3)	0.5682 (6)	0.0783 (1)	3.1
C6	0.4147 (3)	0.7288 (6)	0.0522 (2)	3.8
C6a	0.5086 (3)	0.7459 (6)	0.1005 (2)	3.6
C7	0.5307 (3)	0.5088 (6)	0.1186 (2)	3.6
C7a	0.5693 (3)	0.5228 (6)	0.1829 (2)	3.6
C8	0.6271 (3)	0.3725 (7)	0.2188 (2)	4.9
C9	0.6506 (3)	0.4201 (8)	0.2780 (2)	5.4
C10	0.6168 (3)	0.6096 (8)	0.3002 (2)	5.4
C11	0.5595 (3)	0.7615 (8)	0.2646 (2)	4.9
C11a	0.5363 (3)	0.7144 (6)	0.2055 (2)	3.6
C11b	0.4740 (3)	0.8484 (6)	0.1577 (2)	3.5
C11c	0.3533 (3)	0.8338 (6)	0.1613 (2)	3.5
C12	0.4208 (3)	0.3943 (6)	0.1049 (2)	3.6
C13	0.6066 (3)	0.8635 (7)	0.0817 (2)	5.1
C14	0.2538 (3)	0.4645 (6)	0.0347 (2)	3.8
C15	0.2157 (4)	0.5684 (7)	−0.0172 (2)	5.1
C16	0.1378 (4)	0.4686 (10)	−0.0564 (2)	6.9
C17	0.0985 (4)	0.2695 (10)	−0.0451 (2)	6.7
C18	0.1349 (4)	0.1658 (8)	0.0061 (2)	6.1
C19	0.2120 (3)	0.2630 (8)	0.0457 (2)	5.0

Table 2. *Geometric parameters* (Å, °) *for* $C_{25}H_{22}$

C1—C2	1.380 (6)	C7a—C8	1.396 (6)
C2—C3	1.375 (6)	C7a—C11a	1.382 (6)
C3—C4	1.384 (6)	C8—C9	1.393 (6)
C4—C4a	1.394 (5)	C9—C10	1.370 (7)
C4a—C11c	1.396 (5)	C10—C11	1.394 (6)
C4a—C5	1.533 (5)	C11—C11a	1.393 (6)
C5—C6	1.542 (5)	C11a—C11b	1.524 (5)
C5—C12	1.565 (5)	C11b—C11c	1.519 (5)
C5—C14	1.523 (5)	C11c—C1	1.393 (6)
C6—C6a	1.526 (5)	C14—C15	1.395 (6)
C6a—C11b	1.567 (5)	C15—C16	1.396 (7)
C6a—C7	1.549 (5)	C16—C17	1.368 (8)
C6a—C13	1.529 (6)	C17—C18	1.376 (7)
C7—C12	1.547 (5)	C18—C19	1.389 (6)
C7—C7a	1.508 (5)	C19—C14	1.392 (6)
C1—C2—C3	119.6 (4)	C8—C7a—C11a	120.7 (3)
C2—C3—C4	120.3 (4)	C7a—C8—C9	118.4 (4)
C3—C4—C4a	120.8 (4)	C8—C9—C10	120.5 (4)
C4—C4a—C5	122.8 (3)	C9—C10—C11	121.6 (4)
C4—C4a—C11c	118.6 (3)	C10—C11—C11a	117.9 (4)
C5—C4a—C11c	118.5 (3)	C11—C11a—C11b	128.7 (4)
C4a—C5—C6	105.5 (3)	C11—C11a—C7a	120.8 (4)
C4a—C5—C12	112.0 (3)	C7a—C11a—C11b	110.5 (3)
C4a—C5—C14	111.8 (3)	C11a—C11b—C6a	102.6 (3)
C6—C5—C12	101.5 (3)	C11a—C11b—C11c	111.0 (3)
C6—C5—C14	115.5 (3)	C6a—C11b—C11c	112.9 (3)
C12—C5—C14	110.0 (3)	C11b—C11c—C1	118.8 (3)
C5—C6—C6a	102.4 (3)	C11b—C11c—C4a	121.4 (3)
C6—C6a—C7	103.2 (3)	C4a—C11c—C1	119.8 (4)
C6—C6a—C11b	112.3 (3)	C11c—C1—C2	120.8 (4)
C6—C6a—C13	113.6 (3)	C5—C14—C15	121.0 (4)
C7—C6a—C11b	102.6 (3)	C5—C14—C19	120.7 (3)
C7—C6a—C13	114.1 (3)	C15—C14—C19	118.3 (4)
C11b—C6a—C13	110.3 (3)	C14—C15—C16	119.6 (4)
C6a—C7—C7a	103.7 (3)	C15—C16—C17	121.2 (4)
C6a—C7—C12	104.8 (3)	C16—C17—C18	119.8 (4)
C7a—C7—C12	114.0 (3)	C17—C18—C19	119.8 (5)
C7—C7a—C8	129.2 (4)	C18—C19—C14	121.3 (4)
C7—C7a—C11a	110.1 (3)		

$C_{32}H_{24}$

Crystal data

$C_{32}H_{24}$
M_r = 408.5
Triclinic
$P\bar{1}$
a = 10.543 (3) Å
b = 11.400 (3) Å
c = 10.444 (3) Å
α = 106.90 (2)°
β = 77.24 (2)°
γ = 107.96 (2)°
V = 1130.6 (5) Å^3
Z = 2

D_x = 1.20 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 13 reflections
θ = 8.42–13.66°
μ = 0.079 mm^{-1}
T = 298 K
Rhombohedron
0.20 × 0.20 × 0.20 mm
Colorless

Data collection

Syntex *P*3 automated diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5072 measured reflections
5072 independent reflections
2613 observed reflections [$I > 3.0\sigma(I)$]
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 97 reflections intensity variation: <5%

Refinement

Refinement on *F*
Final $R = 0.048$
$wR = 0.045$
$S = 0.61$
2613 reflections
386 parameters
H-atom positional parameters refined with isotropic thermal parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 2.24$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $C_{32}H_{24}$

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

	x	y	z	$U_{\rm eq}$
C1	0.3730 (3)	0.3182 (2)	0.2678 (3)	4.2
C2	0.4756 (3)	0.2728 (3)	0.1742 (3)	4.4
C3	0.5504 (3)	0.2047 (3)	0.2032 (3)	4.1
C4	0.5223 (3)	0.1803 (3)	0.3311 (3)	4.1
C4a	0.4215 (3)	0.2246 (2)	0.4256 (3)	3.9
C4b	0.3784 (3)	0.2148 (3)	0.5668 (3)	4.2
C5	0.4202 (3)	0.1557 (3)	0.6429 (3)	5.1
C6	0.3593 (3)	0.1605 (3)	0.7763 (3)	6.0
C7	0.2612 (3)	0.2255 (3)	0.8327 (3)	6.4
C8	0.2203 (3)	0.2859 (3)	0.7577 (3)	5.6
C8a	0.2790 (3)	0.2797 (3)	0.6239 (3)	4.4
C9	0.2485 (3)	0.3360 (3)	0.5212 (3)	4.1
C9a	0.3467 (3)	0.2928 (2)	0.3951 (3)	3.9
C10	0.2867 (3)	0.4829 (3)	0.5679 (3)	5.9
C11	0.3054 (3)	0.3948 (3)	0.2240 (3)	4.4
C12	0.1697 (3)	0.3543 (3)	0.2103 (3)	5.2
C13	0.1135 (4)	0.4239 (4)	0.1594 (3)	6.4
C14	0.1906 (4)	0.5328 (4)	0.1221 (4)	7.0
C15	0.3252 (4)	0.5740 (3)	0.1365 (4)	7.2
C16	0.3830 (3)	0.5055 (3)	0.1864 (3)	6.1
C17	0.6593 (3)	0.1602 (3)	0.0999 (3)	4.3
C18	0.7763 (3)	0.1575 (3)	0.1385 (3)	5.8
C19	0.8770 (3)	0.1151 (4)	0.0416 (4)	7.3
C20	0.8618 (4)	0.0759 (4)	−0.0925 (4)	7.7
C21	0.7468 (4)	0.0781 (4)	−0.1331 (3)	7.3
C22	0.6457 (3)	0.1193 (3)	−0.0368 (3)	5.5
C23	0.1005 (3)	0.2764 (3)	0.5024 (3)	4.1
C24	0.0588 (3)	0.1490 (3)	0.4387 (3)	4.8
C25	−0.0752 (3)	0.0884 (3)	0.4268 (3)	5.8
C26	−0.1711 (3)	0.1550 (4)	0.4804 (4)	6.8
C27	−0.1323 (4)	0.2810 (4)	0.5431 (4)	7.6
C28	0.0026 (3)	0.3433 (3)	0.5540 (3)	6.0

Table 4. *Geometric parameters* (Å, °) *for* $C_{32}H_{24}$

C1—C2	1.406 (4)	C11—C12	1.387 (4)
C1—C9a	1.392 (4)	C12—C13	1.392 (6)
C1—C11	1.498 (5)	C13—C14	1.368 (5)
C2—C3	1.391 (5)	C14—C15	1.378 (6)
C3—C17	1.495 (4)	C15—C16	1.386 (7)
C3—C4	1.392 (4)	C11—C16	1.388 (4)
C4—C4a	1.392 (4)	C17—C18	1.391 (5)
C4a—C4b	1.470 (4)	C18—C19	1.394 (5)
C4a—C9a	1.401 (5)	C19—C20	1.371 (5)
C4b—C8a	1.395 (4)	C20—C21	1.379 (6)
C4b—C5	1.390 (5)	C21—C22	1.389 (5)
C5—C6	1.392 (4)	C22—C17	1.392 (4)
C6—C7	1.384 (5)	C23—C24	1.385 (4)
C7—C8	1.385 (6)	C24—C25	1.384 (4)
C8—C8a	1.388 (4)	C25—C26	1.374 (6)
C8a—C9	1.531 (5)	C26—C27	1.367 (6)
C9—C9a	1.544 (4)	C27—C28	1.394 (5)
C9—C10	1.550 (4)	C28—C23	1.392 (5)
C9—C23	1.530 (4)		
C9A—C1—C2	117.4 (3)	C9—C9a—C4a	110.0 (2)
C11—C1—C2	117.0 (2)	C9—C9a—C1	130.0 (3)
C9A—C1—C11	125.5 (2)	C4a—C9a—C1	120.0 (2)
C1—C2—C3	123.2 (3)	C1—C11—C12	122.2 (3)
C2—C3—C4	118.4 (2)	C1—C11—C16	118.9 (3)
C2—C3—C17	120.6 (3)	C12—C11—C16	118.7 (3)
C4—C3—C17	120.9 (3)	C11—C12—C13	120.2 (3)
C3—C4—C4a	119.5 (3)	C12—C13—C14	120.8 (4)
C4—C4a—C9a	121.5 (3)	C13—C14—C15	119.2 (4)
C4—C4a—C4b	129.0 (3)	C14—C15—C16	120.7 (3)
C4b—C4a—C9a	109.4 (2)	C15—C16—C11	120.3 (3)
C4a—C4b—C8a	108.3 (3)	C3—C17—C18	120.6 (2)
C4a—C4b—C5	131.2 (3)	C3—C17—C22	120.9 (3)
C5—C4b—C8a	120.5 (2)	C18—C17—C22	118.4 (3)
C4b—C5—C6	118.7 (3)	C17—C18—C19	120.3 (3)
C5—C6—C7	120.6 (4)	C18—C19—C20	120.3 (4)
C6—C7—C8	120.9 (3)	C19—C20—C21	120.4 (3)
C7—C8—C8a	118.8 (3)	C20—C21—C22	119.5 (3)
C8—C8a—C4b	120.4 (3)	C21—C22—C17	121.1 (3)
C8—C8a—C9	128.3 (3)	C9—C23—C24	119.6 (3)
C4b—C8a—C9	111.3 (2)	C9—C23—C28	122.5 (2)
C8a—C9—C9a	101.0 (2)	C24—C23—C28	117.7 (2)
C8a—C9—C10	109.9 (2)	C23—C24—C25	122.0 (3)
C8a—C9—C23	108.1 (2)	C24—C25—C26	119.7 (3)
C9a—C9—C10	110.0 (2)	C25—C26—C27	119.4 (3)
C9a—C9—C23	113.0 (2)	C26—C27—C28	121.3 (4)
C10—C9—C23	114.0 (3)	C27—C28—C23	119.8 (3)

To methanesulfonic acid (100 ml) at 383 K was added (12.0 g, 0.10 mol) of acetophenone and the resulting dark green solution was stirred for 3 h at 383 K. The mixture was cooled, poured into ice water and extracted with ether. The ether layer was washed with water and with saturated aqueous $NaHCO_3$. The material of the ether layer was steam distilled. High-pressure liquid chromatography (Waters prep LC500 system, silica, hexane) of the non-steam volatile material allowed separation of 6,6a,7,11b-tetrahydro-6a-methyl-5-phenyl-5,7-methano-5*H*-benzo[*c*]fluorene and 9-methyl-1,3,9-triphenylfluorene in addition to other products. Data collection: Syntex-Nicolet *P*3 data collection package; θ-2θ scans of variable rate and width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to maximum $2\theta = 60°$. Cell refinement: Syntex-Nicolet *P*3 data collection package. Data reduction: *DREAM* (Blessing, 1986). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *XRAY80* (Stewart, 1980) (full-matrix least squares). Molecular graphics: *CHEM3D* (Rubenstein & Rubenstein, 1987).

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 71174 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1040]

References

Blessing, R. H. (1986). *Crystallogr. Rev.* **1**, 3-58.
Carrondo, M. A. A. F. C. T. & Rogers, D. (1984). *J. Organomet. Chem.* **276**, 219-230.

Griesbaum, K., Rao, V. V. R. & Leifker, G. (1982). *J. Org. Chem.* **47**, 4975–4981.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Rubenstein, M. & Rubenstein, S. (1987). *CHEM3D. The Molecular Modelling System*. Cambridge Scientific Computing, Inc., Cambridge, Massachusetts, USA.
Stewart, J. M. (1980). Editor. *The XRAY System of Crystallographic Programs*. Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

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X-ray Diffraction Analysis of Two Hexahydropyrido[2,1-*b*][1,3,4]oxadiazines: Evidence for the Effect of Steric Congestion on Anion Formation at the Aminonitrile Centre

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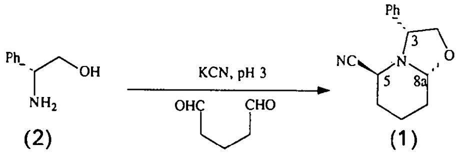
Abstract

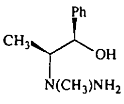
The X-ray crystal structures of (2*R*,3*S*,6*R*,9a*S*)- and (2*S*,3*S*,6*R*,9a*R*)-3,4-dimethyl-2-phenyl-3,4,7,8,9,9a-hexahydro-2*H*,6*H*-pyrido[2,1-*b*][1,3,4]oxadiazine-6-carbonitrile, (6) and (7), respectively, revealed that the six-membered rings are chair shaped and the ring junctions are *cis*. Furthermore, it was found that the C6 H atom is hindered by the axial methyl group substituted at C3 in (6) and that the C6 H atom in compound (7) is similarly protected by the presence of the equatorial methyl group on N4. These results provide insight into the reactivity of these molecules.

Comment

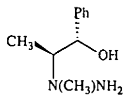
The versatility of 3-phenyl-2,3,6,7,8,8a-hexahydro-5*H*-oxazolo[3,2-*a*]pyridine-5-carbonitrile (1) as a monochiral 1,4-dihydropyridine equivalent is illustrated by the concise enantioselective synthesis of a variety of different piperidine alkaloids (Guerrier, Royer, Grierson & Husson, 1983; Yue, Royer & Husson, 1990; Lienard, Royer, Quirion & Husson, 1991; Rubiralta, Giralt & Diez, 1991). This compound is obtained as a crystalline solid in a high-yielding one-step procedure involving condensation of (−)-2-amino-2-phenylethanol (2) with glutaraldehyde (3) in the presence of KCN (Bonin, Grierson, Royer & Husson, 1991). An essential feature of the reactivity of (1) is that the N atom of aminophenylethanol is incorporated into the piperidine ring of the target molecule, and that once the role of the chiral benzylic carbon centre C3 has been fulfilled, the piperidine N atom can be liberated conveniently under hydrogenolysis conditions. An alternative strategy which permits both liberation of the piperidine N atom and recovery of the aminoalcohol component intact involves the use of the hydrazine based compounds (6) and (7). These monochiral compounds were prepared in an analogous fashion to (1) from the hydrazine derivatives (4) and (5) of (1*R*,2*S*)-(−)-ephedrine and (1*S*,2*S*)-(+)-pseudoephedrine, respectively (Takahashi, Senda & Higashiyama, 1991). Interestingly, problems were encountered during attempts to generate and alkylate the anion formed at C6 through reaction of (6) and (7) with alkyllithium bases or lithium diisopropylamide. To corroborate our view that the C6 position in these compounds is highly congested, thus prohibiting both efficient anion formation and subsequent approach of the electrophile to the anion centre, we have determined the structures of compounds (6) and (7) by X-ray diffraction.



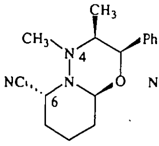
(2) (3) (1)



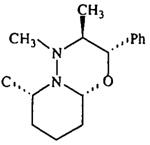
(4)



(5)



(6)



(7)

In the asymmetric unit of compound (7) there are two independent molecules which adopt identical conformations. A systematic comparison of all bond distances, bond angles and torsion angles gave r.m.s. deviations of 0.006 Å, 0.5 and 3.1°, respectively.

In the structures of (6) and (7), the six-membered rings are chair shaped and the junctions of these rings are *cis*. However, the conformations of the two molecules (6) and (7) are quite different. The H atom at C9a and the lone pair at N5 point in different directions, being below the general plane of the molecule in (6) and above this plane in (7). The phenyl group is equatorial in the two molecules while the position of the cyano group at C6 is equatorial in (6) and axial in (7). The methyl groups at N4 and C3 are axial in (6) and equatorial in (7). The steric environment of H6 in compounds (6) and (7) is clearly depicted in the figures. In compound (6) (Fig. 1), H6, which is in an axial position, is in close contact with the methyl group C17 (linked to C3); H6···C17 2.61 and H6···H17a 2.09 Å.