ol and (2S,3R)-exo-3-propylsulfonyl-1,3,7,7-tetra-methylbicyclo[2.2.1]heptan-2-ol (Declercq, Feneau-Dupont, Huart & Nemery, 1991, and references cited therein) are closely related to the title compound.

References

DECLERCQ, J.-P., FENEAU-DUPONT, J., HUART, C. & NEMERY, I. (1991). *Acta Cryst.* C47, 2234–2236.

DE LOMBAERT, S., NEMERY, I., ROEKENS, B., CARRETERO, J. C., KIMMEL, T. & GHOSEZ, L. (1986). *Tetrahedron Lett.* **27**, 5099–5102.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRUGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

Acta Cryst. (1992). C48, 404–406

N-{2-[(1-Cyanocyclohexyl)(*tert*-butyldimethylsilyloxy)amino]propionyl}-2,5-bis(methoxymethyl)pyrrolidine and N-(2-Anilinopropionyl)-2,5-bis(methoxymethyl)pyrrolidine

BY B. TINANT AND J.-P. DECLERCQ

Laboratoire de chimie physique et de cristallographie, Université Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

AND P. HENDERSON

Laboratoire de chimie organique de synthèse, Unversité Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

Abstract. (1): $C_{24}H_{45}N_3O_4Si$, $M_r = 467.73$, monoclinic, $P2_1/c$, $a = 12.947$ (3), $b = 13.814$ (4), $c = 16.186$ (5) Å, $\beta = 108.61$ (3)°, $V = 2744$ (1) Å³, $Z = 4$, $D_x = 1.13$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 9.90$ cm⁻¹, $F(000) = 1024$, $T = 291$ K, $R = 0.058$ for 4276 observed reflections. (2): $C_{17}H_{26}N_2O_3$, $M_r = 306.41$, monoclinic, $P2_1/c$, $a = 9.579$ (2), $b = 9.601$ (1), $c = 18.826$ (2) Å, $\beta = 103.25$ (2)°, $V = 1685.3$ (4) Å³, $Z = 4$, $D_x = 1.21$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.89$ cm⁻¹, $F(000) = 664$, $T = 291$ K, $R = 0.042$ for 2361 observed reflections. The relative configuration of the propionyl asymmetric carbon is inverse with respect to that of the pyrrolidine ring carbon atoms (*i.e.* one is R and the other S). The conformation of the pyrrolidine is different in the two compounds: in (1), it is an envelope with torsion angles of 23.0 (6), -36.0 (6), 36.5 (6), -22.2 (6) and 0.0 (6)°; in (2), it adopts a half-chair conformation with the twofold axis through N, the endocyclic torsion angles being 8.8 (5), -27.7 (5), 36.5 (5), -30.3 (5) and 13.4 (5)°. In (2), an intermolecular hydrogen bond between the N—H and the carbonyl O is observed: N—H···O, N···O = 3.098 (3), H···O = 2.24 (2) Å, N—H···O = 175 (1)° (O: $1 - x$, $-y$, $1 - z$).

Experimental. Crystals were obtained by evaporation from pentane–methanol, 1:1, for (1) and from hexane for (2). D_m not measured. Lattice parameters refined using 20 reflections in the range $5 \le 2\theta \le 50°$ for (1) and 30 reflections in the range $5 \le 2\theta \le 25°$ for (2). Huber four-circle diffractometer, monochromatized Cu $K\alpha$ for (1), Mo $K\alpha$ radiation for (2).
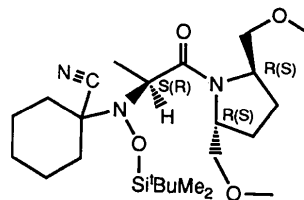
(1)
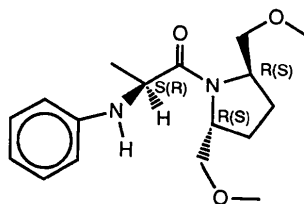
(2)

Table 1. *Data collection and refinement parameters*

	Compound (1)	Compound (2)
Approx. crystal size (mm)	0.28 × 0.25 × 0.20	0.36 × 0.32 × 0.20
Collection range $(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.60	0.59
Range of hkl	$-15 \le h \le 15$	$0 \le h \le 12$
	$0 \le k \le 16$	$0 \le k \le 12$
	$0 \le l \le 19$	$-22 \le l \le 22$
Scans	ω	θ–2θ
Indices of standard reflection	533	$\overline{1}18$
No. of measured reflections	5409	3881
No. of observed reflections $[I > 2.5\sigma(I)]$	4276	2361
No. of parameters	290	278
R	0.058	0.042
wR	0.060	0.042
$w = 1/(\sigma^2 + gF^2)$, $g =$	0.00017	0
S	3.75	0.66
(Δ/σ)	0.48	0.04
$\Delta\rho$(max., min.) (e Å^{-3})	0.37, −0.39	0.19, −0.14

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

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

	x	y	z	U_{eq}
Compound (1)				
N1	7558 (1)	2511 (1)	5468 (1)	42 (1)
C2	6491 (2)	2887 (2)	5513 (1)	44 (1)
C3	6436 (2)	4003 (2)	5456 (1)	45 (1)
O4	6305 (1)	4475 (1)	6060 (1)	59 (1)
N5	6520 (1)	4439 (1)	4737 (1)	47 (1)
C6	6412 (2)	3992 (2)	3885 (1)	50 (1)
C7	6883 (2)	4770 (2)	3441 (2)	61 (1)
C8	6518 (2)	5712 (2)	3754 (2)	64 (1)
C9	6582 (2)	5507 (2)	4697 (2)	55 (1)
O10	7397 (1)	1465 (1)	5379 (1)	47 (1)
Si11	7210 (1)	895 (1)	4435 (1)	50 (1)
C12	5834 (3)	1087 (2)	3641 (2)	77 (1)
C13	8203 (3)	1266 (3)	3886 (2)	86 (1)
C14	7379 (2)	−397 (2)	4817 (2)	64 (1)
C15	8518 (3)	−592 (3)	5393 (3)	124 (1)
C16	7102 (4)	−1072 (2)	4025 (2)	112 (1)
C17	6605 (4)	−622 (3)	5313 (3)	130 (2)
C18	8549 (2)	2612 (2)	6245 (1)	46 (1)
C19	8714 (2)	3661 (2)	6562 (2)	53 (1)
C20	9807 (2)	3824 (2)	7279 (2)	68 (1)
C21	10759 (2)	3515 (3)	6977 (2)	83 (1)
C22	10624 (2)	2463 (2)	6689 (2)	85 (1)
C23	9535 (2)	2291 (2)	5973 (2)	64 (1)
C24	8503 (2)	1973 (2)	6976 (2)	61 (1)
N25	8535 (2)	1493 (2)	7546 (2)	96 (1)
C26	6128 (2)	2524 (2)	6264 (2)	58 (1)
C27	5226 (2)	3820 (2)	3337 (2)	54 (1)
O28	4691 (1)	3191 (1)	3760 (1)	56 (1)
C29	3627 (2)	2963 (2)	3215 (2)	72 (1)
C30	7619 (2)	5905 (2)	5347 (2)	64 (1)
O31	8537 (2)	5625 (1)	5115 (1)	82 (1)
C32	9511 (3)	6032 (3)	5686 (2)	92 (1)
Compound (2)				
N1	5181 (2)	2151 (2)	5003 (1)	45 (1)
C2	4289 (2)	2068 (2)	4271 (1)	38 (1)
C3	2814 (2)	1419 (2)	4265 (1)	36 (1)
O4	2746 (2)	357 (2)	4624 (1)	51 (1)
N5	1617 (2)	2031 (2)	3864 (1)	34 (1)
C6	189 (2)	1443 (2)	3879 (1)	40 (1)
C7	−812 (2)	2163 (2)	3234 (1)	48 (1)
C8	−89 (2)	3543 (3)	3152 (1)	44 (1)
C9	1517 (2)	3191 (2)	3338 (1)	37 (1)
C10	4919 (2)	3023 (2)	5535 (1)	41 (1)
C11	5843 (2)	3007 (3)	6232 (1)	52 (1)
C12	5634 (3)	3894 (3)	6771 (2)	61 (1)
C13	4506 (3)	4826 (3)	6648 (2)	61 (1)
C14	3585 (3)	4860 (3)	5969 (1)	54 (1)
C15	3786 (2)	3978 (3)	5415 (1)	46 (1)
C16	5070 (3)	1142 (3)	3830 (1)	52 (1)
C17	−197 (3)	1691 (2)	4605 (1)	43 (1)
O18	−360 (2)	3132 (2)	4719 (1)	52 (1)
C19	−782 (4)	3402 (4)	5373 (2)	67 (1)
C20	2023 (3)	2725 (3)	2668 (1)	47 (1)
O21	1785 (2)	3814 (2)	2152 (1)	53 (1)
C22	2555 (3)	3625 (3)	1608 (1)	55 (1)

Table 3. *Selected bond distances* (Å) *and angles* (°) *for compounds* (1) *and* (2)

	(1)		(2)
C2—N1	1.500 (3)		1.446 (3)
O10—N1	1.460 (2)	C10—N1	1.373 (3)
C18—N1	1.488 (2)		
C3—C2	1.546 (3)		1.542 (3)
C26—C2	1.521 (3)	C16—C2	1.526 (3)
O4—C3	1.229 (2)		1.233 (2)
N5—C3	1.346 (3)		1.353 (2)
C6—N5	1.475 (3)		1.486 (2)
C9—N5	1.480 (3)		1.479 (2)
C7—C6	1.523 (3)		1.529 (3)
C8—C7	1.525 (4)		1.520 (3)
C9—C8	1.528 (3)		1.535 (3)
Si11—O10	1.667 (1)		
C24—C18	1.494 (3)		
N25—C24	1.126 (3)		

|	(1)		(2)
O10—N1—C2	104.0 (1)	C10—N1—C2	124.2 (2)
C18—N1—C2	119.0 (2)		
C18—N1—O10	103.5 (1)		
C3—C2—N1	111.6 (2)		111.7 (2)
C26—C2—N1	116.7 (2)	C16—C2—N1	107.1 (2)
C26—C2—C3	110.8 (2)	C16—C2—C3	108.9 (2)
O4—C3—C2	119.8 (2)		119.6 (2)
N5—C3—C2	118.9 (2)		119.1 (2)
N5—C3—O4	121.4 (2)		121.3 (2)
C6—N5—C3	127.7 (2)		119.4 (2)
C9—N5—C3	120.2 (2)		128.1 (2)
C9—N5—C6	111.5 (2)		112.3 (2)
C7—C6—N5	102.3 (2)		103.0 (2)
C8—C7—C6	103.4 (2)		104.9 (2)
C9—C8—C7	104.5 (2)		104.0 (2)
C8—C9—N5	104.0 (2)		103.1 (2)
Si11—O10—N1	122.2 (1)	C11—C10—N1	119.6 (2)
		C15—C10—N1	123.2 (2)
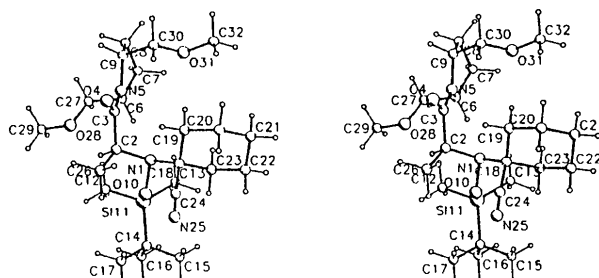
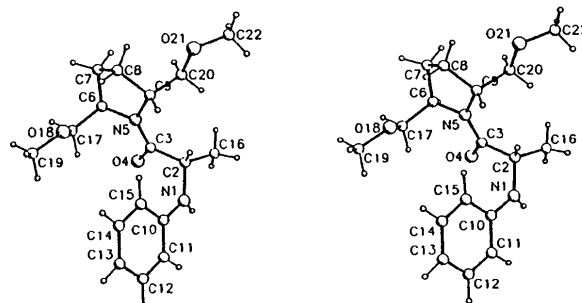Fig. 1. Stereoscopic view of molecule (1).

Fig. 2. Stereoscopic view of molecule (2).

One standard reflection checked every 50 reflections: no significant deviation. Both structures solved by *SHELXS*86 (Sheldrick, 1985). For (1), all H atoms in idealized positions (C—H = 1.08 Å, H—C—H = 109.5°). For (2), all H atoms from difference Fourier

synthesis. Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Experimental details are summarized in Table 1. The atomic parameters are given in Table 2.* Selected bond lengths and bond angles are listed in Table 3. Figs. 1 and 2 are stereoscopic views of the molecules, showing the numbering of the atoms (*PLUTO*, Motherwell & Clegg, 1978).

Related literature. We have currently developed an asymmetric version of the electrophilic amination of

---

* Lists of structure factors, anisotropic thermal parameters, a complete list of bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54598 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0075]

silylketene acetals (Sasaki, Ishibashi & Ohno, 1983; Henderson, 1991). During the course of this investigation we were able to isolate compounds (1) and (2), the latter being obtained after reductive cleaving of the N—O bond of the phenyl analogue of (1). The configuration at the new asymmetric carbon (C2), as established by this study, provides useful information which should allow a model for asymmetric induction in these transformations to be proposed.

References

HENDERSON, PH. (1991). PhD thesis, Univ. of Louvain, Belgium.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SASAKI, T., ISHIBASHI, Y. & OHNO, M. (1983). *Chem. Lett.* pp. 863–866.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRUGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

REGULAR STRUCTURAL PAPERS

Dibromobis(ethyldiphenylphosphine)nickel(II)

JAN-OLLE MALM, VIVEKA ALFREDSSON, GÖRAN SVENSSON* AND JÖRGEN ALBERTSSON†

Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

Abstract

The asymmetric unit comprises two mononuclear complexes, one with a twofold and the other with a pseudo twofold axis passing through Ni. The coordination around Ni is tetrahedral with Ni—Br = 2.339 (2)–2.362 (2) Å and Ni—P = 2.306 (3)–2.316 (3) Å. The angles Br—Ni—Br = 122.7 (1) and 114.86 (7)° are greater and the angles P—Ni—P = 102.9 (2) and 98.7 (1)° smaller than the tetrahedral

---

† Present address: Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96, Göteborg, Sweden.

angle. The two ethyl groups are pointing in opposite directions in both complexes. The crystal is built up from discrete complexes stabilized by van der Waals interactions.

Comment

The title compound was prepared as described by Hayter & Humiec (1965). Square planar–tetrahedral isomerism for complexes of Ni^{II} was first observed for the title compound (Hayter & Humiec, 1962). Since then several other cases of this isomerism have been found for complexes of the type $[NiX_2(PR_3)_2]$. Tetrahedral coordination is favored in the sequences $X = I > Br > Cl$ and $PPh_3 > PR_2Ph > PR_3$ (Tolman, 1977). Crystal structure determinations of tetrahedral complexes in the solid state have been reported for $NiCl_2(PPh_3)_2$ (Garton, Henn, Powell & Venanzi, 1963) and $NiBr_2(PPh_3)_2$ (Jarvis, Mais & Owston, 1968). Square-planar complexes have, *e.g.*, been reported for $NiBr_2(PMe_3)_2$ (Mari, Gleizes, Dartiguenave & Dartiguenave, 1981), $NiCl_2[P(C_6H_{11})_3]_2$ (Bellon, Albano, Bianco, Pompa & Scatturin, 1963) and *trans*-dibromobis(5-methyl-5*H*-dibenzophosphole)nickel(II) (Watkin, 1976). In $NiBr_2[PPh_2(CH_2Ph)]_2$ (Kilbourn & Powell, 1970) the unit cell contains both isomers.