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Two Different Cyclization Modes in the Formation of Silylhydrazines

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The reactions of 1,2-bis(bromosilyl)ethane and 1,3-bis(bromosilyl)propane with anhydrous hydrazine lead to the two bicyclic silylhydrazines 1,6-diaza-2,5,7,10-tetrasila[4.4.0]bicyclodecane (1) and bis(1-aza-2,6-disila-1-cyclohexyl) (2), respectively. For compound 1, a distillable liquid with mp 7 °C, the low-temperature crystal structure determination has shown a bicyclic configuration with the N–N unit shared by two slightly twisted, chair-formed heterocycles. The N–NSi_2 units are virtually planar but not orthogonal relative to each other owing to conformational restraints. In crystals of compound 2, mp 57 °C, two six-membered rings each in a half-chair conformation are linked solely through the hydrazine N–N bond. The two planar $NNSi_2$ units are at right angles as expected for a nonforced tetrasilylhydrazine geometry. The N–N bond is longer in 1 than in 2. Variable-temperature ^{1}H ^{13}C, ^{15}N, and ^{29}Si NMR spectra of both hydrazines have been measured, and the barrier of ring inversion of 1 has been determined.

Introduction

Although several decades have elapsed since the first silylated hydrazines have been prepared, there is still a lack of structural data for this class of compounds. For more than 20 years the gas-phase structure (by electron diffraction) of tetrasilylhydrazine, $(H_3Si)_2NN(SiH_3)_2$ prepared by Aylett in 1956,[1] was the only example with an open-chain structure reported in the literature.[2] We have recently prepared tetrakis(phenylsilyl)hydrazine,[3] and determined its crystal structure, the first solid-state structure of this series. However, there are a few studies on cyclic silylhydrazines.[4–6] In continuation of our work we now present the syntheses and crystal structures of two bicyclic hydridosilylhydrazines. Previous work on cyclic silylhydrazines has been directed exclusively to compounds with the silicon atoms bearing a variety of non-hydrogen substituents.[7–10] It was the goal of our current studies to elucidate the ground-state structures of prototypes bearing only hydrogen as the substituent to silicon and thus to eliminate both steric and electronic effects of side groups. This concept should also lead to the most volatile compounds of the series with a very low carbon content, which would be ideal prerequisites for vapor deposition of silicon nitride from those single-source precursors.

Results and Discussion

1,4-Diaza-2,5,7,10-tetrasila[4.4.0]bicyclodecane (1) and bis(1-aza-2,6-disila-1-cyclohexyl) (2) result as the sole products from the base-assisted condensation reaction of hydrazine with the bifunctional α,ω-bis(bromosilyl)alkanes,[11] which are readily available through the bromination of the corresponding α,ω-disilylalkanes with elemental bromine.

Compound 1 is isolated as a colorless distillable liquid (mp 7 °C); compound 2 is a colorless solid (mp 57 °C), which also distills under reduced pressure. The characteristic odor of 1 and 2 is reminescent of the smell of related aza heterocycles without silicon. Both compounds can be exposed for a short time to dry air but are readily hydrolyzed by moisture or aqueous acid or base.

The two syntheses shown in eqs 1 and 2 yield one uniform product each, which are not readily distinguished from their possible isomers, ring compounds 3 (isomeric to 1) and 4 (isomeric to 2), respectively.

From the results of the structure determinations (below) it appears, that the ring size is obviously determining the nature of the isomers obtained in a thermodynamically controlled process in both cases.

By spectroscopic methods only, it is extremely difficult to determine unambiguously which isomers are actually produced. In the NMR spectra the spin systems for the equivalent nuclei are similar for both pairs of structural isomers, and there are no data available to determine the ring size from chemical shift values of the ring atoms. Although the mass spectra should show the mass peaks of the monocycles resulting from cleavage of the N–N bond in the isomers 2 and 3, such a finding does not rigorously exclude the presence of the other isomers. In fact the mass spectrum of 1 contains indeed a peak at 102 mass units (equal to half the molecular mass), and the spectrum of 2 shows a peak of very low intensity at the corresponding value of m/z = 116. Similar problems of structural assignment have been reported in the literature for some

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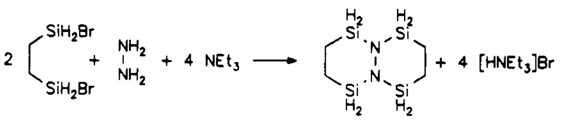

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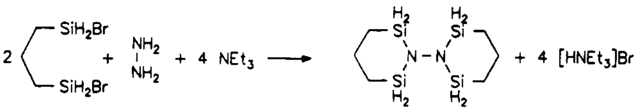
(1)



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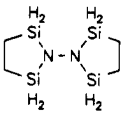
(2)



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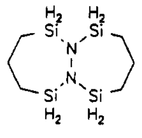

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cyclic methylsilylhydrazines[4,9] and for the condensation products of succinic anhydride with hydrazine.[12] In the latter case the erroneously assigned structures had to be corrected later on the basis of UV data.[13] Crystallography was therefore the method of choice to clarify this point for 1 and 2.

Crystal Structures of 1 and 2. Suitable solvent free crystals of 1 were grown from a concentrated pentane solution at −20 °C as monoclinic plates (space group $P2_1/n$, No. 14). 2 crystallizes without solvent in the monoclinic space group $C2/c$ (No. 15) by cooling a warm concentrated hexane solution slowly to ambient temperature. The crystal data of 1 and 2 are listed in Table I. The results of the structure determinations are shown in Figure 1 (1) and Figure 2 (2).

Molecule 1 shows no crystallographic symmetry. Both N atoms are in a trigonal planar environment (angle sums: 360.0 (4)° at N1, 359.7 (4)° at N(2)), but the Si–N–Si angles are clearly expanded (at the expense of the N–N–Si angles) to an average value of 134.1°. The situation is similar to that already observed for tetrasilylhydrazine[2] and tetrakis(phenylsilyl)hydrazine.[3] The average Si–N bond length of 1.722 (2) Å may be compared with 1.731 (4) Å found for tetrasilylhydrazine, and 1.728 (2) Å for tetrakis(phenylsilyl)hydrazine. The values of silylamines[14,15] are very similar, and it seems that the Si–N distances are not significantly affected by the oxidation state of the nitrogen atoms or by effects of sterical crowding.[16]

Molecule 2 has a crystallographic 2-fold axis, which transforms one six-membered ring into the other. Like in molecule 1, the nitrogen atoms have a trigonal planar configuration with an expanded Si–N–Si angle (134.05°) and Si–N bond lengths in the expected range (1.730 Å, average). The dihedral angle for 1 enclosed by the two Si_2N planes (Figure 3) amounts to only 64.5 (1)° owing to conformational restraints imposed by the conformational pressure exerted on the endocyclic Si–N–N–Si skeleton. By contrast, 2 shows an interplanar angle of 86.3 (1)°. With no conformative directionality placed on the N–N bond, the repulsive interaction of the nitrogen lone pairs of electrons which reaches minimum energy in the orthogonal position (in 2), determines the orthogonal orientation and allows an N–N bond shortening of 0.023 Å in 2 as compared with 1, where nonorthogonal orientation requires a longer N–N bond. In a bicyclic molecule with two five-membered rings sharing an N–N edge, reported by Klingebiel et al.,[4] the larger twist leads to a similar lengthening of 0.022 Å for the N–N bond as compared

Table I. Crystal Data and Structure Solution for Compounds 1 and 2

	1	2
formula	$C_4H_{16}N_2Si_4$	$C_6H_{20}N_2Si_4$
mol mass (g·mol^{-1})	204.530	232.584
temp (°C)	−60	−50
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a (Å)	9.734 (1)	11.105 (1)
b (Å)	10.241 (1)	12.541 (2)
c (Å)	12.072 (1)	10.052 (1)
β (deg)	105.33 (1)	110.15 (1)
V (Å^3)	1160.6	1314.15
ρ_{calc} (g·cm^{-3})	1.170	1.175
Z	4	4
$F(000)$ (e)	440	504
μ(Mo Kα) (cm^{-1})	4.5	4.1
radiation (λ = 0.710 69 Å, graphite monochromator)	Mo Kα	Mo Kα
diffractometer	Syntex P2$_1$	CAD4
scan	ω	θ-2θ
scan range (θ) (deg)	2–25	2–27
hkl range	±11,+12,+14	±13,+15,+12
no. of measd reflns	3355	1416
no. of unique reflns	1964	1294
R_{int}	0.045	0.011
no. of obsd reflns	1808	1187
$F_o \geq$	2σ(F$_o$)	2σ(F$_o$)
no. of refined params	147	71
weighting scheme	$w = 1/\sigma(F_o)$	
weighting param l	2.2147	1.0000
H atoms (found/calcd)	14/2	4/6
R	0.042	0.038
R_w	0.042	0.043
(shift/error)$_{max}$	0.000	0.001
$\Delta\rho_{fin}$ (max/min) (e·Å^{-3})	+0.43/−0.29	+0.24/−0.33

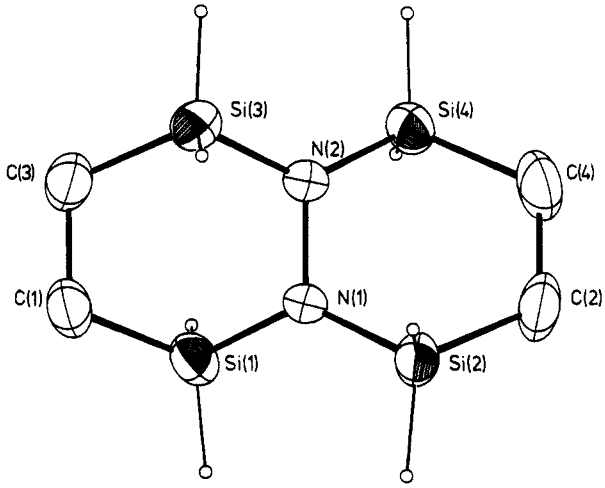

Figure 1. Structure of 1 in the crystal. H atoms bound to carbon are omitted for clarity. Selected distances (Å) and angles (deg), esd's in parentheses: Si(1)–N(1), 1.724 (2); N(1)–N(2), 1.497 (2); Si(1)–C(1), 1.851 (3); C(1)–C(3), 1.544 (4); Si(1)–N(1)–N(2), 113.5 (2); Si(1)–N(1)–Si(2), 133.4 (1); N(1)–Si(1)–C(1), 108.4 (1); Si(1)–C(1)–C(3), 111.4 (3).

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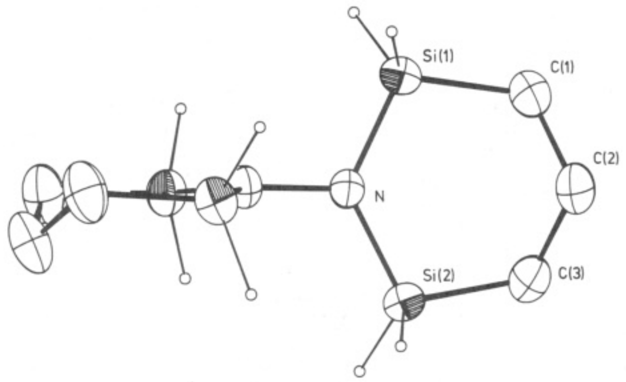


Figure 2. Structure of 2 in the crystal. H atoms bound to carbon are omitted for clarity. Selected distances (Å) and angles (deg), esd's in parentheses: N–N', 1.474 (3); Si(1)–N, 1.723 (2); Si(1)–C(1), 1.864 (3); C(1)–C(2), 1.520 (4); N–Si(1)–C(1), 108.0 (1); Si(1)–N–Si(2), 126.8 (2); Si(1)–N–N', 115.0 (1); Si(1)–C(1)–C(2), 113.2 (3); C(1)–C(2)–C(3), 113.2 (2).

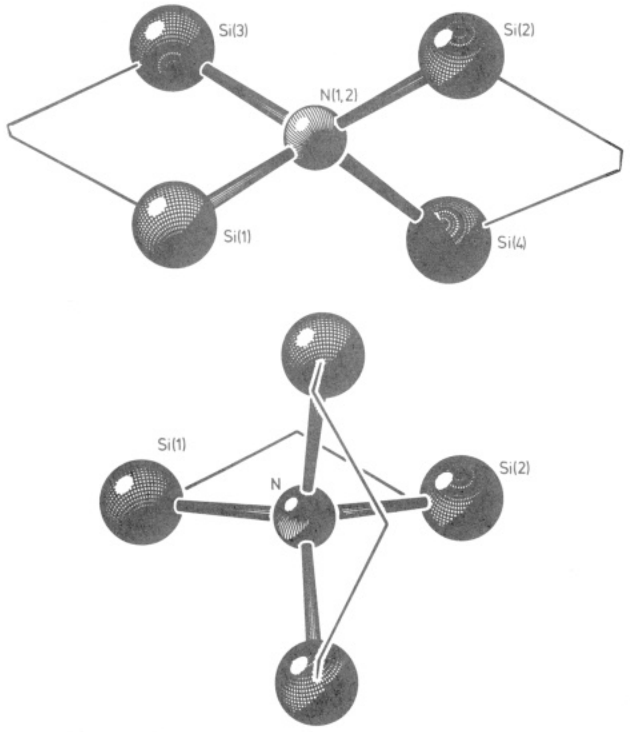
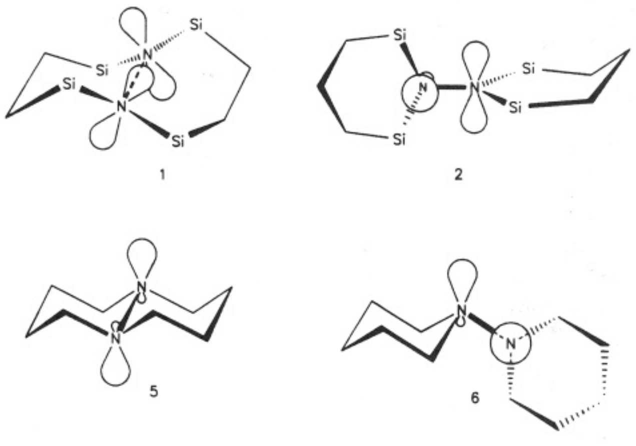


Figure 3. Comparison of the dihedral angles enclosed by the two Si_2N planes in (top) 1 (64.5 (1)°) and (bottom) 2 (86.3 (1)°), respectively. Shown is in each case the view along the N–N bond, the carbon skeleton is drawn as lines and H atoms are omitted for clarity.

Chart I. Conformations and Different Lone Pair–Lone Pair Angles (Values in Parentheses) of the Molecules 1 (64.5°) and 2 (86.3°) and Their Carbon Analogues 5 (180°) and 6 (90°)



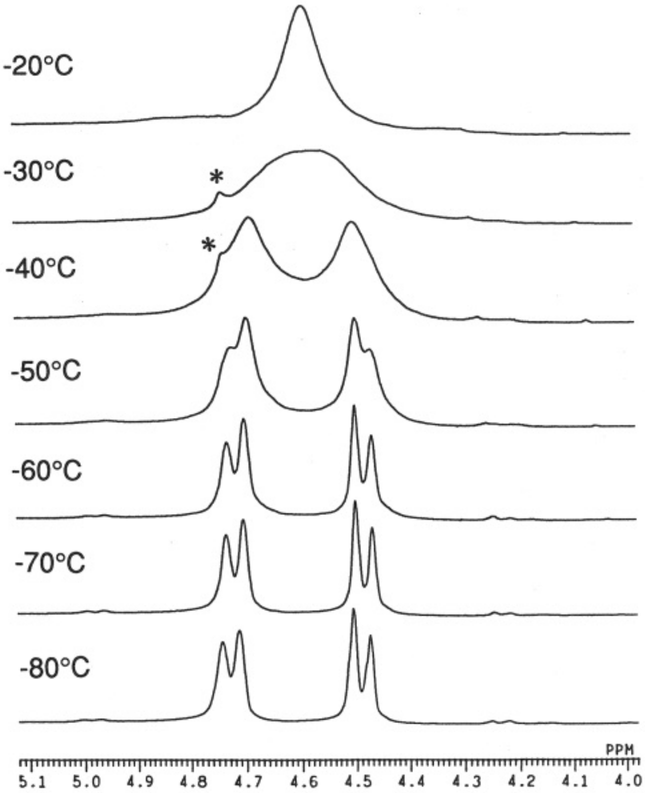


Figure 4. Variable-temperature ^1H NMR spectra of 1 recorded at 399.78 MHz. Only the region of the H–Si proton resonances is shown. * marks the resonance of an impurity.

with 1. The known silicon–carbon analogues to 1 and 2 (1,6-diaza[4,4,0]bicyclodecane (5) and bis(1-pyrrolidinyl) (6), respectively) show quite different geometries at the nitrogen atoms as suggested by photoelectron spectroscopy and comparative NMR studies.[17] The unforced configuration of such alkylated hydrazines shows pyramidal coordinated nitrogen atoms with electon lone pairs oriented orthogonally to each other. This geometry is realized in 6, but 5 exhibits the double-chair conformation of *trans*-decaline, where the nitrogen lone pairs are placed in trans positions with a dihedral angle of 180° (Chart I).

NMR Spectra of the Compounds and Structure in Solution. NMR data for compounds 1 and 2 (^1H, ^{13}C, ^{15}N, and ^{29}Si) are summarized in the Experimental Section. Most of the values do not depart significantly from the expected values.[3] The spectra of 2 in toluene show no major temperature dependence (to −95 °C), and for 1 important changes were only observed on cooling of the samples. The variable-temperature data can be used to determine the barriers of the ring inversions in 1. This ring inversion process is accompanied by partial rotation around the N–N bond, whereby the energy maximum of the repulsion of the nitrogen lone pairs (in parallel orientation) has to be crossed. For toluene solutions a coalescence temperature of −30 °C was observed for the H–Si protons (Figure 4). For the parameters associated with this coalescence, the free energy of activation for ring inversion is calculated to be approximately 52 ± 3 kJ mol^{-1}

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using the Eyring equation.[18] This value is lower than in comparable open-chain silylhydrazines like $(PhH_2Si)(Me_2HSi)NN(SiHMe_2)_2$[3] (75 ± 4 kJ mol^{-1}). This indicates that the NN bond rotation associated with ring inversion in 1 departs from a higher ground state, which is caused by the conformationally imposed, nonorthogonal orientation of the $NNSi_2$ planes at the N–N bond shared by both six-membered rings.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen. The solvents and triethylamine were dried over CaH_2 and distilled prior to use. All glassware was heated to 160 °C and evacuated and filled with dry nitrogen several times. NMR: JEOL JNM GX-400, NMR spectra are taken from solutions in C_6D_6 at 25 °C with internal TMS (^1H, ^{13}C, ^{29}Si) and external CH_3NO_2 (^{15}N) as standards. IR: Perkin-Elmer 1650 FT-IR. GC–MS: Hewlett Packard HP 5890 with mass-selective detector 5971A.

Materials. Anhydrous hydrazine was obtained by drying concentrated hydrazine (95%) over BaO followed by distillation in vacuo. 1,2-Bis(bromosilyl)ethane and 1,3-bis(bromosilyl)propane were prepared as described in the literature.[19]

1,6-Diaza-2,5,7,10-tetrasila[4.4.0]bicyclodecane (1). A 3.06-mL aliquot of anhydrous hydrazine (96.4 mmol) is added to a solution of 53.5 mL of triethylamine (386 mmol) in 700 mL of hexane and emulsified by vigorous stirring. A 47.85-g sample of 1,2-bis(bromosilyl)ethane dissolved in 40 mL of hexane is then dropped into the emulsion with stirring. The whole mixture is refluxed for 3 h, slowly cooled to ambient temperature and filtered. The solvent is removed by distillation, and the residue is fractionally distilled in vacuo to yield 12.48 g (63%) of 1, bp 62 °C (2 mbar), mp 7 °C. ^1H NMR (399.78 MHz): δ 0.75 (m, 8 H, H_2C), 4.58 (m, 8 H, H_2Si). $^{13}C\{^1H\}$ NMR (100.54 MHz): δ 5.54 (s). $^{15}N\{^1H\}$ NMR (INEPT, 40.51 MHz): δ −337.73 (s, $^1J(NSi)$ = 13.7 Hz). ^{29}Si NMR (INEPT, 79.43 MHz): δ −27.57 (tm, $^1J(SiH)$ = 205.1 Hz). MS (GC-coupled): *m/z* (relative intensity) 204 (100, M$^+$), 175, 147, 117, 115, 102, 72. IR (film): 2131 (vs, $\nu(SiH)$), 1025 (vs, $\nu_{as}(SiNSi)$), 926 (s) cm^{-1}.

Bis(1-aza-2,6-disila-1-cyclohexyl) (2). The procedure is the same as described for 1. Parent compounds: 4.64 mL of N_2H_4 (148 mmol), 81.2 mL of triethylamine (586 mmol), 76.77 g of 1,3-bis(bromosilyl)propane (293 mmol), 1000 mL of hexane. Fractional distillation yields 20.14 g (59%) of 2, bp 61–63 °C (0.1 mbar), mp 57 °C. ^1H NMR (399.78 MHz): δ 0.64 (m, 8 H, H_2CSi), 1.60 (m, 4 H, H_2CC_2), 4.85 (t, $^3J(HSiCH)$ = 2.4 Hz, 8 H, H_2Si). $^{13}C\{^1H\}$ NMR (100.54 MHz): δ 11.65 (s, $^1J(CSi)$ = 54.2 Hz, CSi), 18.51 (s, CC_2). $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz): δ −342.31 (s, $^1J(NSi)$ = 11.8 Hz). ^{29}Si NMR (INEPT, 79.43 MHz): δ −27.47 (ttt, $^1J(SiH)$ = 207.1 Hz, $^3J(SiNSiH)$ = 8.2 Hz, $^2J(SiCH)$ = 8.2 Hz). MS (GC-coupled): *m/z* (relative intensity) 232 (100, M$^+$). IR (film): 2129 (vs, $\nu(SiH)$), 1020 (vs, $\nu_{as}(SiNSi)$), 960 (s) cm^{-1}.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound 1[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Si1	−0.00389 (9)	0.19051 (7)	0.41281 (6)	0.042
Si2	0.28966 (9)	0.33982 (8)	0.45364 (6)	0.043
Si3	−0.08361 (9)	0.46353 (8)	0.26675 (6)	0.043
Si4	0.15378 (9)	0.32315 (8)	0.17216 (6)	0.042
N1	0.1175 (2)	0.2986 (2)	0.3831 (2)	0.035
N2	0.0635 (2)	0.3687 (2)	0.2713 (2)	0.035
C1	−0.1677 (3)	0.2818 (3)	0.4140 (2)	0.045
C2	0.4038 (4)	0.3047 (5)	0.3572 (3)	0.058
C3	−0.2239 (3)	0.3610 (4)	0.3023 (3)	0.047
C4	0.3458 (4)	0.3532 (4)	0.2363 (3)	0.057

[a] $U(eq) = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the $\mathbf{U}_{ij}$ matrix. (Estimated standard deviations in parentheses.)

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound 2[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Si1	0.13819 (7)	0.27080 (5)	0.18216 (7)	0.033
Si2	0.14858 (7)	0.44854 (6)	0.39918 (7)	0.034
N	0.0707 (2)	0.3522 (1)	0.2754 (2)	0.029
C1	0.3159 (3)	0.2845 (2)	0.2613 (3)	0.045
C2	0.3645 (3)	0.3934 (3)	0.3229 (3)	0.048
C3	0.3228 (3)	0.4237 (2)	0.4463 (3)	0.047

[a] See Table II.

Crystal Structure Determination. Crystals of 1 (2) were obtained from pentane (hexane), sealed in glass capillaries under argon at dry ice temperature, and mounted on the diffractometer. After a check for higher symmetry 3355 (1416), data were collected and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS 86).[20] After anisotropic refinement (SHELX 76)[21] of all non-H atoms several H atom positions could be located in difference Fourier maps. These were refined isotropically while the remaining H atoms were calculated in idealized positions and included into the refinement with fixed atomic contributions of $U_{iso(fix)}$ = 0.05 Å^2. Further detailed information, fractional atomic coordinates, and equivalent isotropic displacement parameters are listed in Tables I–III, respectively.

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Supplementary Material Available: Tables of the atom positions and thermal parameters for the hydrogen and nonhydrogen atoms and of bond distances and angles for each compound (7 pages). Ordering information is given on any current masthead page.

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