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STERICALLY CROWDED CYCLOHEXANES - 2[1]. SYNTHESIS, STRUCTURE AND DYNAMICS OF HEXASPIRO[2.0.3.0.2.0.3.0.2.0.3.0]HENEICOSANE

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Summary: The synthesis, structure and dynamics of hexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane 3 are described. 3 adopts a chair conformation in the crystal state but prefers a chair-to-twistboat equilibrium in solution. The activation parameters of the chair-to-chair interconversion of 3 and the closely related hexaspiro[2.0.2.0.2.0.2.0.2.0.2.0]octadecane ([6]rotane) 4 have been determined by DNMR. Some consequences appertaining to the conformation and dynamics of other fully (cyclo-)alkylated cyclohexanes are discussed.

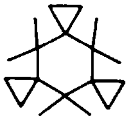
1. INTRODUCTION

The structure, conformation and dynamics of fully (cyclo-)alkylated cyclohexanes should largely be governed by strong nonbonding interactions. The synthesis and experimental evaluation of the structural and thermodynamic data of these unusual compounds should therefore be of considerable interest, especially in view of a future reparametrization of empirical force fields, some of which clearly deserve amelioration[2].

As part of a program devoted to the synthesis and investigation of the structure and dynamics of fully (cyclo-)alkylated cyclohexanes, we report here on the synthesis, structure and dynamics of the hitherto unknown hexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane 3, a reevaluation of the dynamics of the closely related hexaspiro[2.0.2.0.2.0.2.0.2.0.2.0]octadecane ([6]rotane) 4[3] and some consequences affecting the analysis of the conformation and dynamics of other fully (cyclo-)alkylated cyclohexanes.

As will be discussed later, the title compound 3 adopts a chair conformation in the crystal state but prefers a chair-to-twistboat equilibrium in solution.

Thus the structure of 3 leads to the interesting suggestion that fully (cyclo-)-alkylated cyclohexanes with substituents of identical opening angles, as in 4[3)], 5 and 6[1)], should retain the usual chair conformation whereas those with substituents of strongly alternating opening angles, as in 1[4)] and 2[4)], should adopt the unusual[5)] twistboat conformation. The former has been found for 4[3)] and 6[1)], the latter has yet to be proven[6)].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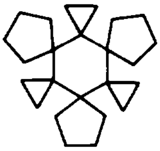
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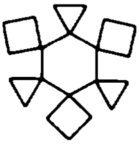
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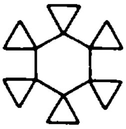
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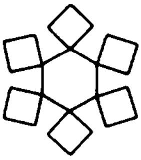
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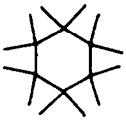
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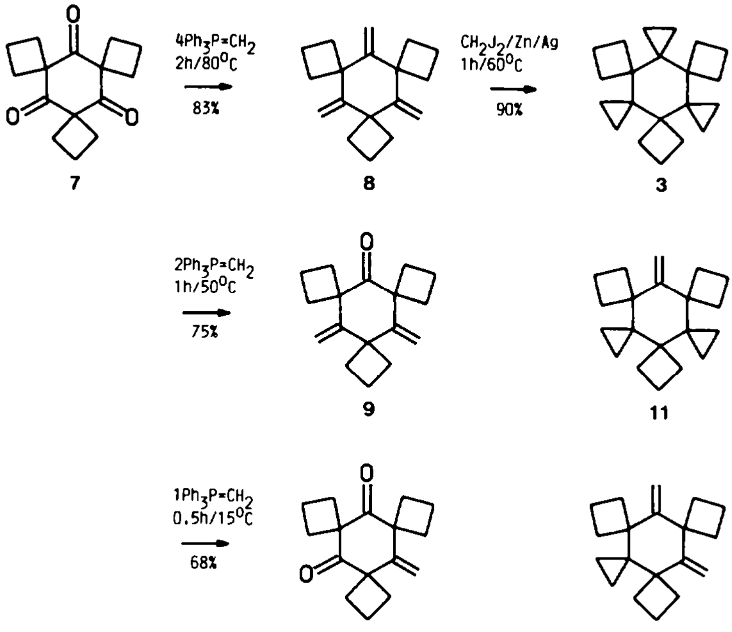
2. SYNTHESIS

Using the readily available trimethyleneketene-trimer 7[7)] we have found suitable conditions for its selective mono-, di-[8)] and trimethylenation yielding 10, 9[8)] and 8 respectively. Several methods were then checked for their usefulness in the exhaustive cyclopropanation of 8.



7 8 3

9 11

10 12

Method	Reaction Conditions	Relative Yields (%)			
		8	12	11	3
CH_2J_2/Zn/Ag	1h/60°C	-	-	-	100
CH_2J_2/Zn/Ag/ether[9]	2h/reflux	25	25	21	29
CH_2J_2/$(C_2H_5)_2$Zn/toluene[10]	11h/reflux	15	24	23	38
CH_2J_2/Cu/benzene[11]	70h/reflux	16	24	36	24

Table 1. Product distributions using different methods[9,10,11] for the cyclopropanation of 8.

As indicated in Table 1, diiodomethane/zinc/silver[9], diiodomethane/diethylzinc[10] and diiodomethane/copper[11] all yielded mixtures of all three possible cyclopropanation products (3, 11, 12) along with unreacted starting material. However, quantitative conversion of 8 to 3 could be achieved by use of a large excess of diiodomethane/zinc/silver[9] and nearly solvent-free conditions. The title compound 3 obtained in this way crystallized from acetone as colourless prisms (mp 125°C). Although analytically pure it showed ^{1}H- and ^{13}C-NMR-spectra which were only in part compatible with the expected fixed chair conformation. We therefore decided to determine its crystal structure.

3. CRYSTAL STRUCTURE

In the solid state, 3 exhibits exact mirror symmetry with two opposite substituent rings in the mirror plane (Fig. 1). The central ring adopts a chair conformation with bond lengths (Table 2) and torsion angles (Table 4) similar to those observed for 4[12]. However, the bond angles within the cyclohexane ring alternate by about 7°, the larger ones being centred at the atoms which form part of a cyclopropane (Table 3). There are striking differences between the bond lengths within the four-membered rings: those to the spiro carbon atoms (opening angles: 86.8 and 86.7°) are considerably elongated (average: 1.57 Å). One cyclobutane ring is slightly puckered (torsion angle: 5°) while the second is forced to be planar by crystallographic symmetry.

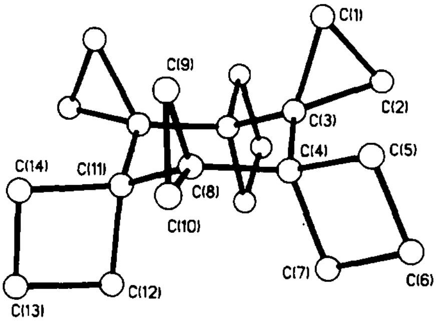


Fig.1. Perspective view of the carbon skeleton of 3 with the atom numbering

C(1)-C(2)	1.498(5)	C(4)-C(8)	1.528(3)	C(9)-C(10)	1.506(4)
C(1)-C(3)	1.520(4)	C(5)-C(6)	1.516(4)	C(11)-C(12)	1.570(4)
C(2)-C(3)	1.515(4)	C(6)-C(7)	1.510(4)	C(11)-C(14)	1.561(4)
C(3)-C(4)	1.526(2)	C(8)-C(9)	1.509(3)	C(11)-C(8')	1.524(2)
C(3)-C(4')	1.526(2)	C(8)-C(10)	1.512(3)	C(12)-C(13)	1.496(5)
C(4)-C(5)	1.570(3)	C(8)-C(11)	1.524(2)	C(13)-C(14)	1.495(6)
C(4)-C(7)	1.576(3)				

Table 2. Bond lengths [Å] for <u>3</u> with estimated standard deviations in parentheses

C(2)-C(1)-C(3)	60.3(2)	C(1)-C(2)-C(3)	60.6(2)
C(1)-C(3)-C(2)	59.1(2)	C(1)-C(3)-C(4)	116.8(1)
C(2)-C(3)-C(4)	118.1(1)	C(1)-C(3)-C(4')	116.8(1)
C(2)-C(3)-C(4')	118.1(1)	C(4)-C(3)-C(4')	116.0(2)
C(3)-C(4)-C(5)	114.6(2)	C(3)-C(4)-C(7)	115.6(2)
C(5)-C(4)-C(7)	86.8(2)	C(3)-C(4)-C(8)	108.6(2)
C(5)-C(4)-C(8)	115.4(2)	C(7)-C(4)-C(8)	114.7(2)
C(4)-C(5)-C(6)	90.8(2)	C(5)-C(6)-C(7)	91.2(2)
C(4)-C(7)-C(6)	90.8(2)	C(4)-C(8)-C(9)	117.0(2)
C(4)-C(8)-C(10)	118.5(2)	C(9)-C(8)-C(10)	59.8(2)
C(4)-C(8)-C(11)	115.1(2)	C(9)-C(8)-C(11)	117.1(2)
C(10)-C(8)-C(11)	118.2(2)	C(8)-C(9)-C(10)	60.2(2)
C(8)-C(10)-C(9)	60.0(2)	C(8)-C(11)-C(12)	115.2(1)
C(8)-C(11)-C(14)	115.2(1)	C(12)-C(11)-C(14)	86.7(2)
C(8)-C(11)-C(8')	108.3(2)	C(12)-C(11)-C(8')	115.2(1)
C(14)-C(11)-C(8')	115.2(1)	C(11)-C(12)-C(13)	90.6(3)
C(12)-C(13)-C(14)	91.9(3)	C(11)-C(14)-C(13)	90.9(3)

Table 3. Bond angles [°] for <u>3</u> with estimated standard deviations in parentheses

C(1)-C(3)-C(4)-C(5)	-38.7(3)	C(5)-C(4)-C(8)-C(10)	-28.3(3)
C(1)-C(3)-C(4)-C(8)	91.9(2)	C(5)-C(4)-C(8)-C(11)	-176.4(2)
C(2)-C(3)-C(4)-C(5)	28.8(3)	C(4)-C(5)-C(6)-C(7)	-5.1(2)
C(2)-C(3)-C(4)-C(8)	159.5(2)	C(4)-C(8)-C(11)-C(14)	174.5(2)
C(4')-C(3)-C(4)-C(5)	177.3(2)	C(4)-C(8)-C(11)-C(8')	-54.8(3)
C(4')-C(3)-C(4)-C(8)	-52.1(3)	C(9)-C(8)-C(11)-C(14)	-42.2(3)
C(3)-C(4)-C(8)-C(9)	-90.0(2)	C(9)-C(8)-C(11)-C(8')	88.5(2)
C(3)-C(4)-C(8)-C(10)	-158.6(2)	C(10)-C(8)-C(11)-C(14)	26.3(3)
C(3)-C(4)-C(8)-C(11)	53.4(2)	C(10)-C(8)-C(11)-C(8')	157.0(2)
C(5)-C(4)-C(8)-C(9)	40.2(2)	C(11)-C(12)-C(13)-C(14)	0

Table 4. Selected torsion angles [°] for <u>3</u> with estimated standard deviations in parentheses

4. CONFORMATION AND DYNAMICS

When crystallographically pure <u>3</u> was dissolved in chloroform-d and its ^{1}H-NMR-spectrum (200 MHz) measured at 23.6°C, an AA'BB'-system centered at δ = 0.39 ppm (12H, cyclopropane-H) and multiplets at δ = 1.15-1.25, 1.50-1.70 and 2.30-2.50 ppm (6H each, cyclobutane-H) expected for a chair conformation within the slow exchange limit, were observed (Fig. 2). A slight but significant extra intensity of the multiplet at δ = 1.50-1.70 ppm and an additional singlet at δ = 0.49 ppm indicated, however, that a second conformation was present, apparently a rapidly interconverting twistboat conformation. This was confirmed by inspection of the

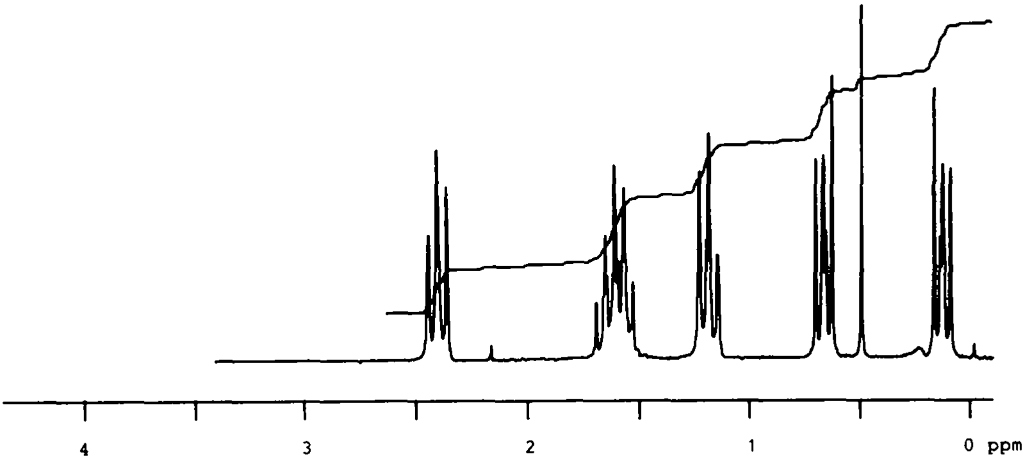


Fig.2. ^{1}H-NMR-spectrum (200 MHz, $CDCl_3$, 23.6°C) of hexaspiro[2.0.3.0.2.0.3.0.2.0.-3.0]heneicosane 3.

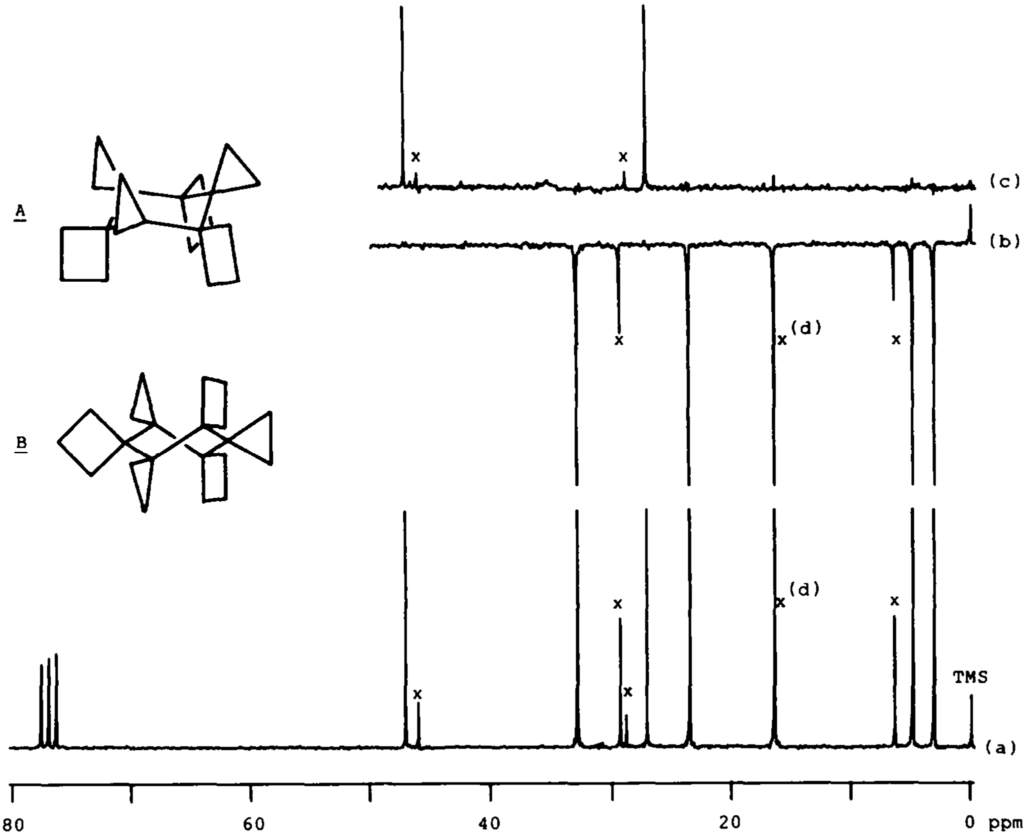


Fig.3. ^{13}C-NMR-spectra (50.3 MHz, $CDCl_3$, TMS int, 20°C) of hexaspiro[2.0.3.0.2.0.-3.0.2.0.3.0]heneicosane 3; (a) normal spectrum; (b) DEPT-spectrum[13]: CH3/CH pos, CH2 neg, Cq suppressed; Cq-spectrum[13]: Cq pos, CH3/CH2/CH suppressed; (d) two lines ($\Delta\nu$ = 1Hz). For clarity, the resonance lines in (a) and (b) were cut at 50 and 25% respectively of the hight of the most intense line (δ = 16.45).

^{13}C-NMR-spectrum (50.3 MHz, $CDCl_3$, Fig. 3): seven high intensity lines at δ = 3.11, 4.91, 16.47, 23.58 (CH_2), 27.15 (C_q), 32.92 (CH_2) and 47.19 (C_q) showed once again that 3 exists in solution predominantly in a fixed chair conformation A, but five additional low intensity lines (x) at δ = 6.43, 16.45 (CH_2), 28.99 (C_q), 29.35 (CH_2) and 46.25 (C_q) now unequivocally established a rapidly interconverting twistboat B as second albeit minor conformation. Careful integration of the AA'BB'-system centered at δ = 0.39 ppm vs. the A_4-singlet at δ = 0.49 ppm revealed a population ratio of 1.00:0.12 at 23.6°C and hence a difference in the free enthalpies of ΔG^o = 5.3 kJ/mol (1.3 kcal/mol) in favour of the chair conformation.

The activation parameters of the chair-to-chair interconversion were then determined by bandshape analysis of the cyclopropane part (δ= 0.0-0.8 ppm) of exchange broadened ^1H-NMR-spectra (79.6 MHz, HMPT-d_{18}) using the computer program DNMR 5[14]. The spectra were taken at 62.5°C and seven further temperatures ranging from 144.1 to 195.9°C (Fig. 4). The low temperature spectrum was used to determine the static parameters of the AA'BB'-system of the chair conformation. Starting parameters were taken from the literature[15] and then refined by an iterative calculation to yield δ-H_a(chair) = 0.120 ppm, δ-H_e(chair) = 0.661 ppm, $^2J_{ee}$ = $^2J_{aa}$ = -5.49 Hz, $^3J_{cis}$ = 9.15 Hz, $^3J_{trans}$ = 5.56 Hz and δ-H(twist) = 0.488 ppm. These values were assumed to be independent of temperature and used in the computational analysis of the high temperature spectra throughout. Experimental and computed bandshapes and the corresponding rate constants are shown in Fig. 4.

A weighted least squares adjustment of the rate data to the Eyring equation, shown graphically in Fig. 6, then yielded the activation parameters and their standard deviations as $\Delta H^{\ddagger}$ = 88.1 ± 0.4 kJ/mol and $\Delta S^{\ddagger}$ = -13.1 ± 1.0 J/mol·grd. The free energy of activation was then calculated from the equation $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ to give $\Delta G^{\ddagger}_{298}$ = 92.0 ± 1.0 kJ/mol.

Clearly an experimental determination of the twistboat-to-twistboat interconversion barrier was also desirable. Orientational ^1H-NMR-measurements (200 MHz, CF_2Cl_2, acetone-d_6) within the temperature range of -75°C to -120°C revealed, however, that the static parameters of the AA'BB'-system (4H) and the ABCD-system (8H) to be expected for the cyclopropane part of the fixed twistboat conformation of 3 were inaccessible because of partial to full overlap with the AA'BB'-system of the cyclopropane part of the fixed chair conformation. An experimental determination of the activation parameters of the twistboat-to-twistboat interconversion must therefore await for a bandshape analysis of exchange broadened ^{13}C-NMR-spectra of specifically labelled 3, preferentially of 1-^{13}C-3.

Having determined the activation parameters of the chair-to-chair interconversion of 3, we reexamined the dynamics of the closely related hexaspiro[2.0.2.0.2.0.2.0.2.0.2.0]octadecane ([6]rotane) 4[3], which exists both in the crystal state[12] and in solution[3] in a pure chair conformation and whose inversion barrier had previously been determined by the coalescence method to give $\Delta G^{\ddagger}_{450}$ = 92.5 kJ/mol[3].

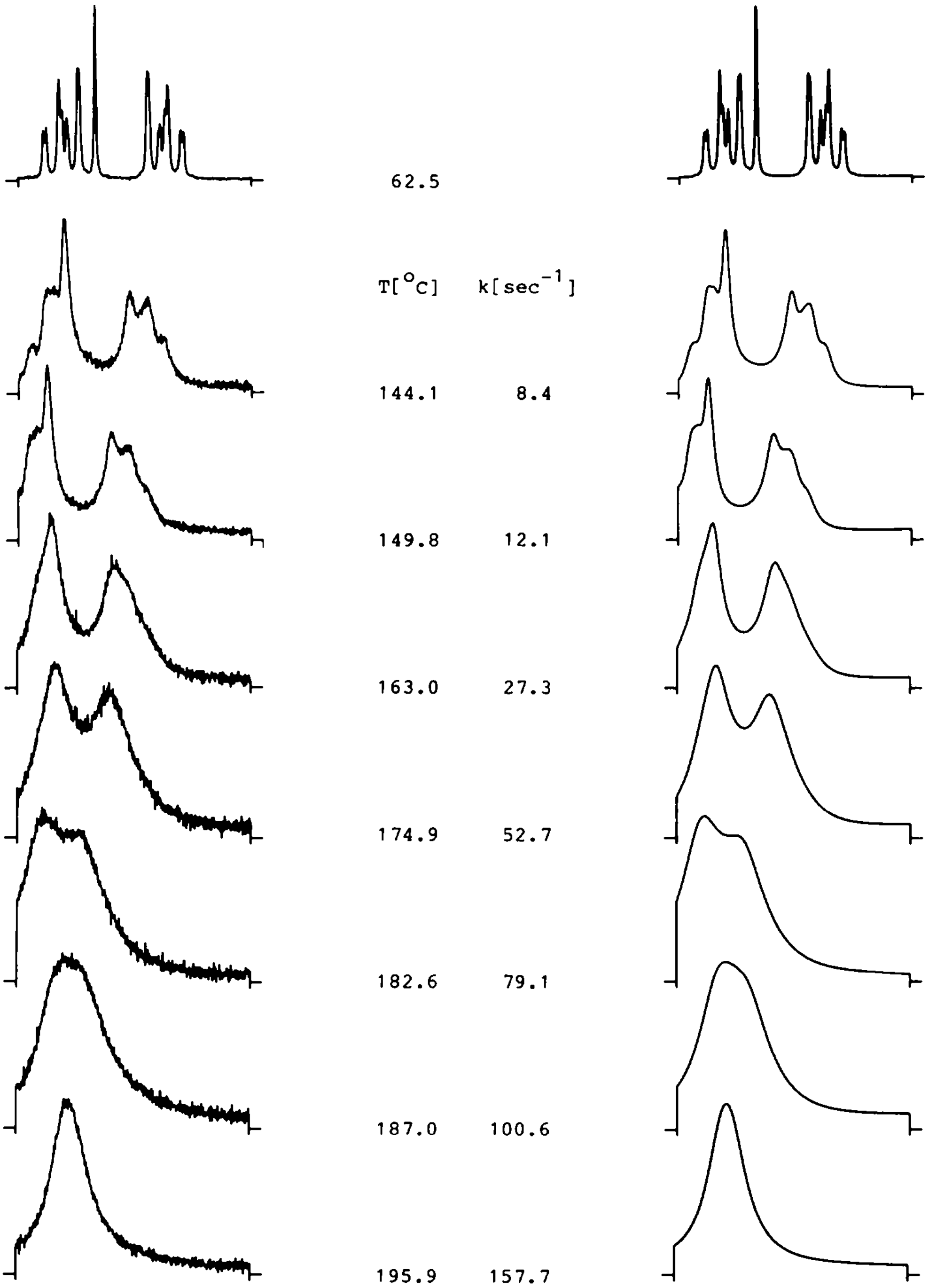


Fig.4. Experimental and computed bandshapes of the cyclopropane part of $\underline{3}$ at different temperatures and corresponding rate constants derived therefrom.

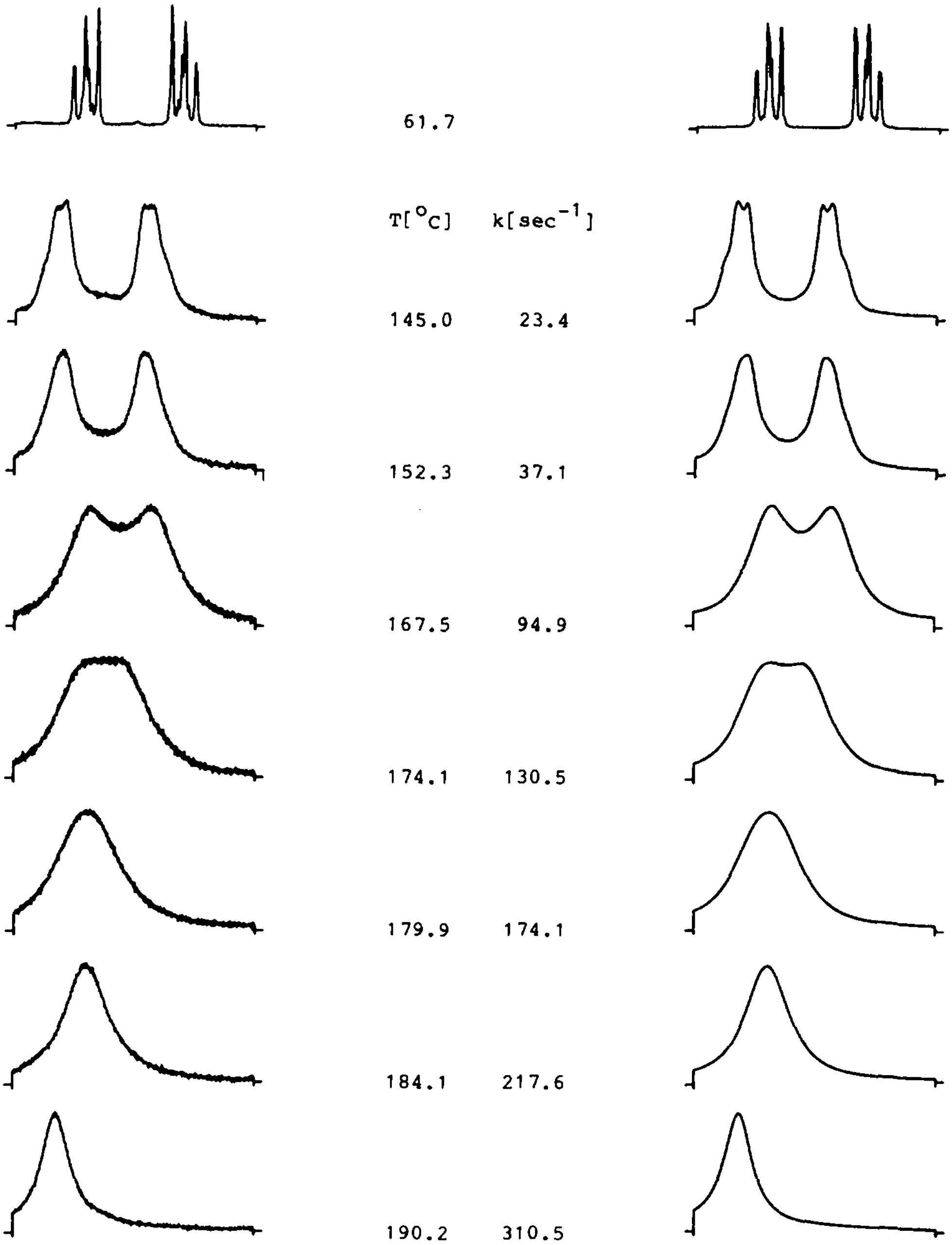


Fig.5. Experimental and computed bandshapes of the cyclopropane part of <u>4</u> at different temperatures and corresponding rate constants derived therefrom.

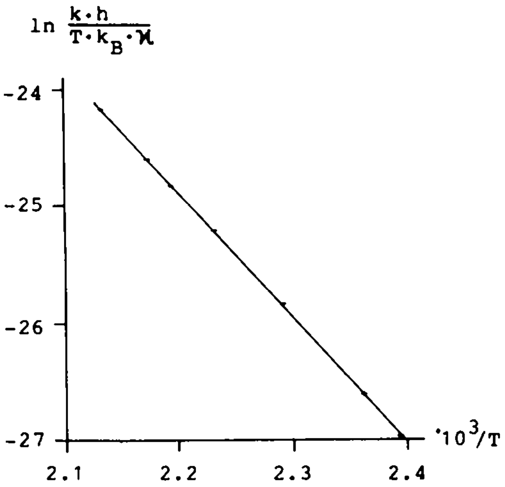


Fig.6. Eyring plot for the rate data of 3.

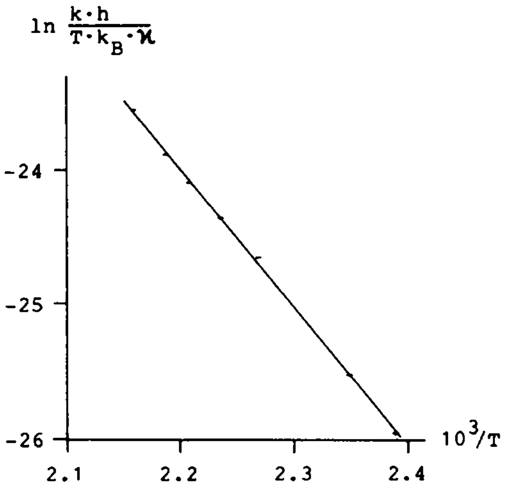


Fig.7. Eyring plot for the rate data of 4.

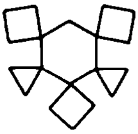
^{1}H-NMR-spectra (79.6 MHz, HMPT-d_{18}) were taken at 61.7°C and seven further temperatures ranging from 145.0 to 190.2°C (Fig. 5). Bandshape analysis of the low temperature spectrum yielded the static parameters of the AA'BB'-system δ-H_a (chair) = 0.450 ppm, δ-H_e(chair) = -0.297 ppm, $^2J_{ee} = {}^2J_{aa}$ = -1.67 Hz, $^3J_{cis}$ = 8.75 Hz, $^3J_{trans}$ = 6.57 Hz which were then used in the analysis of the high temperature spectra throughout. Experimental and computed bandshapes are shown in Fig.5, together with the corresponding rate constants. A weighted least-squares adjustment of the rate data to the Eyring equation shown graphically in Fig.7 yielded the activation parameters of the chair-to-chair interconversion of 4 as $\Delta H^{\ddagger}$ = 87.4 ± 1.2 kJ/mol and $\Delta S^{\ddagger}$ = -6.6 ± 2.8 J/mol·grd. The free energy of activation was calculated as above to give $\Delta G^{\ddagger}_{298}$ = 89.4 ± 1.0 kJ/mol.

5. DISCUSSION

The most critical distinctions in the structures of the per(cyclo-)alkylated cyclohexanes 1-6 are the opening angles of their substituents. These vary from strongly alternating (1,2) over moderately alternating (3) to identical (4,5, 6). Given this fact, the preference for a chair conformation in 4 and the preference for a chair-to-twistboat equilibrium in 3 leads to the interesting suggestion that 3 may represent a borderline case where the preferred conformation switches from chair (4,5,6) to twistboat (1,2). According to this suggestion, the inversion barriers of 4,5 and 6 should be extremely high, and those of 1 and 2 should be extremely low. The former has been found for 4 and 6$^{1)}$, the latter has yet to be proven$^{6)}$.

Another interesting result concerns the activation entropies of the chair-to-chair interconversions of 3 and 4. Whereas positive activation entropies are generally found in less substituted cyclohexanes[16] and cyclohexane itself[17], those related to the inversion processes of 4 ($\Delta S^{\ddagger}$ = -6.6 ± 2.8 J/mol·grd) and 3 ($\Delta S^{\ddagger}$ = -13.1 ± 1.0 J/mol·grd) are clearly negative. This means that the ground states of 4 and 3 are more flexible than the corresponding transition states. We feel that this is due to the high degree of substitution in 4 and 3 rendering a pseudorotating transition state less favourable than in lower substituted cyclohexanes. We would therefore expect negative activation entropies for 5 and 6 too.

As to the unknown hexaspirane 5, we have already mentioned that its inversion barrier should be high. A current study of the structure, conformation and dynamics of the pentaspiranes 13, 14 and 15 along with a correlation of their structural and thermodynamic data with those of the hexaspiranes 3 and 4 will certainly allow a more precise prediction.



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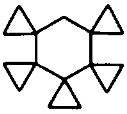

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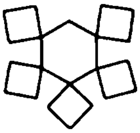

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6. EXPERIMENTAL

Analytical and preparative gas chromatography was carried out on a Varian Aerograph Model 920 instrument employing a thermal conductivity detector and hydrogen as carrier gas. Product ratios were not corrected for relative response. IR-spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^{1}H- and ^{13}C-NMR-spectra were measured on Varian Associates FT 80A, XL100 or XL200 spectrometers. Mass spectra were obtained with a Varian MAT 731 operated at 70 eV. Boiling and melting points are not corrected.

5,10,15-Trimethylenetrispiro[3.1.3.1.3.1]pentadecane 8: To a stirred suspension of 27.4 g (0.25 mol) of potassium t-butoxide in 160 ml of dry benzene under nitrogen was added 87.4 g (0.25 mol) methyltriphenylphosphonium bromide and the mixture heated to reflux. After 1 h a solution of 15.0 g (0.061 mol) of trispiro-[3.1.3.1.3.1]pentadecane-5,10,15-trione 7[7] in 50 ml of dry benzene was added and after additional 2 h of reflux the formation of 8 was complete according to glpc analysis [2m x 1/4" steel, 15% FFAP on chromosorb P AW/DMCS, 45/60 mesh, 190°C; rel. retention times: 1.00 (8), 1.55 (9), 2.20 (10), 2.50 (7)] of a hydrolysed sample. The mixture was cooled, diluted with 150 ml of benzene and hydrolysed with 150 ml of water. The layers were seperated, the aqueous phase extracted with 50 ml of pentane, the combined organic layers washed with 150 ml of water, dried ($MgSO_4$) and concentrated on a rotary evaporator to yield a brown oil which was continuously extracted with 300 ml of pentane for 4 h. The pentane extract was filtered, the solvent distilled off and the residual oil fractionated to yield 12.1 g (83%) of 8 as colourless liquid (bp 110°C/0.2 mm) which crystallized on cooling (mp 47°C). - IR (KBr): 3080, 2980, 2940, 2860 (CH), 1627 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.[18]): δ = 1.80-2.05 (m, 6H), 2.10-2.25 (m, 12H), 5.10 (s, 6H). - ^{13}C-NMR (25.2 MHz, $CDCl_3$, TMS int.): δ = 15.52, 34.46, 50.25, 102.56, 159.50. - MS (70 eV): m/e = 240 (4%, M^+), 225 (5%), 212 (30%), 197 (100%). - $C_{18}H_{24}$ requires C, 89.94; H, 10.06. Found: C, 90.03; H, 10.10.

15-Methylenetrispiro[3.1.3.1.3.1]pentadecane-5,10-dione 10: To a stirred suspension of 0.36 g (3.2 mmol) potassium t-butoxide in 10 ml of dry benzene under nitrogen was added 1.15 g (3.2 mmol) methyltriphenylphosphonium bromide and the mixture heated to reflux. After 1 h the mixture was cooled to 20°C and a solution of 0.40 g (1.6 mmol) of trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione 7[7] in 10 ml of dry benzene was added. The reaction temperature was maintained at 20°C and after 30 min 68% of dione 10 had formed according to glpc analysis [2.6m x 1/4" all-glass system, 15% OV 210 on chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (10), 1.20 (7)] of a hydrolysed sample. The mixture was hydrolysed with 10 ml of water, the organic layer washed with another 10 ml of water, dried ($MgSO_4$) and concentrated on a rotary evaporator to yield 0.42 g of a yellow oil part of which was subjected to preparative glpc to give a pure sample of 10 as colourless oil. - IR (film): 3090, 3000-2840 (CH), 1720, 1690 (C=O), 1635 cm^{-1} (C=C). - ^{1}H-NMR (60 MHz, $CDCl_3$, $CHCl_3$ int.[18]): δ = 1.50-2.50 (m, 18H), 5.20 (s, 2H). - ^{13}C-NMR (25.2 MHz, $CDCl_3$, TMS int.): δ = 15.50, 15.67, 27.91, 30.88, 55.12, 61.01, 109.02, 149.71, 207.00. - MS (70 eV): m/e = 244 (19%, M^+), 216 (100%, $M^+-C_2H_4$). - $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25. Found: C, 78.81; H, 8.33.

Hexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane 3: 20.0 g of freshly prepared zinc-silver couple[9] were just covered with anhydrous ether and then, under nitrogen and stirring, 2.0 g (8.3 mmol) 8 and 41.9 g (153 mmol) of diiodomethane were added dropwise. After the initially vigorous exothermic reaction subsided, the reaction temperature was held by external heating at 60°C until glpc analysis [2m x 1/4" all-glass system, 15% OV 210 on Varaport 30, 60/80 mesh, 210°C; rel. retention times: 1.00 (8), 4.07 (3)] indicated that the formation of 3 was complete (1h). The mixture was hydrolysed with saturated NH_4Cl_{aq}, exhaustively extracted with pentane, the pentane extract dried ($MgSO_4$), the solvent distilled off and the remaining solid (2.5 g) purified by chromatography on silica gel (0.05-0.20 mm; column 20 x 5 cm) in pentane. Crystallisation from acetone yielded 2.1 g (90%) of analytically pure 3 as colourless prisms (mp 125°C). - IR (KBr): 3070, 3000, 2980, 2940, 2850 cm^{-1} (CH). - ^{1}H-NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.[18], 23.6°C): chair: δ = 0.39 (AA'BB', 12H), 1.15-1.25 (m, 6H), 1.50-1.70 (m, 6H), 2.30-2.50 (m, 6H); twistboat: δ = 0.49 (s, 12H), 1.50-1.70 (m, 18H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$[18]): chair: δ = 3.11, 4.91, 16.47, 13.58 (CH_2), 27.15 (C_q), 32.92 (CH_2), 47.19 (C_q); twistboat: δ = 6.43, 16.45 (CH_2), 28.99 (C_q), 29.35 (CH_2), 46.25 (C_q). - MS (70 eV): m/e = 254 (1%, $M^+-C_2H_4$), 239 (4%), 226 (20%), 211 (15%), 198 (100%). - $C_{21}H_{30}$ requires C, 89.29; H, 10.71. Found: C, 89.23; H, 10.68.

Hexaspiro[2.0.3.0.2.0.3.0.2.0.3.0]heneicosane 3, 8,13-Dimethylenetetraspiro[2.0.3.1.3.1.3.0]heptadecane 12 and 8-Methylenepentaspiro[2.0.3.1.3.0.2.0.3.0]nonadecane 11: (a) by reaction of 8 with diiodomethane/zinc/silver/ether[9] : To a stirred suspension of 5.9 freshly prepared zinc-silver couple in 20 ml of anhydrous ether under nitrogen were added 0.36 g (1.5 mmol) 8 and 4.0 g (15 mmol) diiodomethane. After the exothermic reaction subsided, the mixture was heated to reflux until glpc analysis [2.2m x 1/4" all-glass system, 15% OV 210 on chromosorb W AW/DMCS, 60/80 mesh, 180°C; relative retention times: 1.00 (3), 1.75 (12), 2.83 (11), 4.83 (8)] revealed that no further change in the product distribution (25% 8, 25% 12, 21% 11, 29% 3) had occurred (2h). The mixture was hydrolysed with saturated NH_4Cl_{aq}, the layers separated, the aqueous phase extracted with pentane, the combined organic layers dried ($MgSO_4$), concentrated and subjected to preparative glpc. 3 and 8 were identified by comparision (IR, ^{1}H-NMR) with authentic material, 12 and 11 were fully characterized.

12: colourless solid (mp 42°C). - IR (KBr): 3080, 3070, 2970, 2940, 2860 (CH), 1630, 1620 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, C_6H_6int.[18]): δ = 0.44 (s, 4H), 1.50-2.00 (m, 14H), 2.12-2.24 (m, 4H), 5.02 (s, 2H), 5.12 (s, 2H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 7.18, 15.86, 16.03, 29.04, 31.88, 34.12, 48.04, 51.19, 103.35, 160.14. - MS (70 eV): m/e = 254 (5%, M^+), 226 (18%), 211 (33%), 198 (99%), 183 (100%). - $C_{19}H_{26}$ requires C, 89.70; H, 10.30. Found: C, 89.70; H, 10.11.

11: colourless solid (mp 55°C). - IR (KBr): 3070, 2980, 2940, 2860 (CH), 1623 cm^{-1} (C=C). - ^1H-NMR (100 MHz, $CDCl_3$, C_6H_6int.[18]): δ = 0.45 (s, 8H), 1.6-2.2 (m, 18H), 4.96 (s, 2H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$[18]): δ = 5.72, 16.20, 16.54 28.17, 29.64, 31.25, 46.25, 49.91, 103.72, 157.95. - MS (70 eV): m/e = 240 (5%, $M^+-C_2H_4$), 225 (6%), 212 (39%), 197 (29%), 184 (100%). - $C_{20}H_{28}$ requires C,89.49; H, 10.51. Found: C, 89.38; H, 10.46

(b) by reaction of 8 with diiodomethane/diethylzinc in toluene[10]: To a stirred solution of 3.6 g (7.3 mmol) of 15% (w/w) diethylzinc in toluene under nitrogen was added at 60°C 0.30 g (1.2 mmol) 8 and, within 6 h, 2.8 g (10 mmol) of diiodomethane. The reaction was monitored by glpc analysis [2m x 1/4" all-glass system, 15% OV 101 on Varaport 30, 60/80 mesh, 205°C; rel.retention times: 1.00 (3), 1.56 (12), 2.54 (11), 4.12 (8)] and stopped, after no further change in the product distribution (15% 8, 24% 12, 23% 11, 38% 3) was observed (11h). The cooled mixture was slowly poured into 50 ml of 10% (v/v) HCl, the organic layer washed with saturated $NaHCO_3$ and water, dried ($MgSO_4$), concentrated and subjected to preparative glpc. 3, 8, 11 and 12 were then identified by comparision of their IR- and ^1H-NMR-spectra with those of authentic material.

(c) by reaction of 8 with diiodomethane/copper in benzene[11]: To a stirred suspension of 2.05 g (32 mmol) of copper powder in 6.0 ml of dry benzene was added a trace of iodine. After the brown colour of iodine had disappeared, 0.40 g (1.67 mmol) 8 and 4.5 g (16 mmol) of diiodomethane were added and the mixture heated to reflux. The reaction was monitored as described above and stopped, after no further change in the product distribution (16% 8, 24% 12, 36% 11, 24% 3) was observed (70h). The mixture was filtered, concentrated and subjected to preparative glpc. IR- and ^1H-NMR-spectra of 3, 8, 11 and 12 all proved identical with those of authentic material.

Crystal structure analysis of 3: 3 (molecular formula: $C_{21}H_{30}$, M = 282.5) was crystallized from acetone as colourless prisms, space group $P2_1/m$, $a = 7.190(1)$, $b = 13.912(2)$, $c = 8.094(1)$ Å, $\beta = 96.74(1)°$, $V = 804.0$ Å^3, $Z = 2$, $D_c = 1.167$ g·cm^{-3}. 2421 reflections with $2\theta < 60°$ were measured on a Stoe four-circle diffractometer using graphite-monochromated Mo-K_α radiation; of these, 1542 with $|F| > 3\sigma_F$ were used for the structure determination and refinement. The structure was solved by direct methods and refined isotropically to $R = 0.199$, which dropped to 0.129 with inclusion of anisotropic temperature factors. At this stage all H atoms were located by a difference electron-density synthesis. Weights $w = (\sigma_F^2 + 0.0008 \cdot F^2)^{-1}$ were introduced, and further refinement with fixed individual H atom temperature factors finally converged at $R = 0.080$ ($R_w = 0.077$). C atom parameters are listed in Table 5. All calculations were performed with the program SHELXTL (written by G.M.S.).

	x	y	z	U		x	y	z	U
C(1)	5816(4)	2500	3404(5)	66(1)	C(8)	2410(3)	3388(1)	603(2)	35(1)
C(2)	4739(5)	2500	4879(4)	75(2)	C(9)	3950(3)	3773(2)	-327(3)	53(1)
C(3)	3687(4)	2500	3143(3)	42(1)	C(10)	2140(4)	4320(2)	-353(4)	63(1)
C(4)	2736(3)	3430(2)	2502(2)	40(1)	C(11)	1368(4)	2500	-113(3)	35(1)
C(5)	3699(4)	4372(2)	3251(4)	67(1)	C(12)	-798(4)	2500	-5(4)	49(1)
C(6)	2032(4)	4583(2)	4178(4)	67(1)	C(13)	-1179(6)	2500	-1862(5)	87(2)
C(7)	971(3)	3738(2)	3362(3)	47(1)	C(14)	867(5)	2500	-2044(4)	58(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 5. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic parameters (Å$^2 \cdot 10^3$) for 3 with estimated standard deviations in parentheses*

Variable-temperature NMR measurements: Spectra were recorded on a Varian FT 80A spectrometer equipped with a variable temperature probe. Precision 5mm o.d. NMR tubes (Wilmad Glass Co.) were filled with solutions of 5 mg of 3 and 4 respectively in 450 µl of HMPT-d_{18} and then a temperature sensor consisting of a 1.8-mm-diameter high precision Pt 100 resistor (1/5 DIN; accuracy ± 0.05° from 0°C to +200°C) at the end of a glass rod was introduced such, that the active zone (15 mm length) was positioned 10 mm above the height of the receiver coil but was still immersed into the solution. Immediately before and immediately after taking a spectrum, the sensor was moved precisely to the height of the receiver coil, connected to a dual channel digital temperature measuring-instrument (Model S 1220, Systemteknik, Sweden; resolution 0.01°) and the temperature measured against molten ice. Spectra for which the temperatures from these two measurements differed by more than 0.3°K were discarded and rerun.

Calculations: The calculations of the static and dynamic spectra and the weighted least-squares adjustments of the rate data to the Eyring equation were performed on the Sperry Univac 1100 computer of the Gesellschaft für Wissenschaftliche Datenverarbeitung at Göttingen, employing the computer programs DNMR 5[14] and ACTPAR[19] respectively.

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Dedicated to Professor Wolfgang Lüttke on the occasion of his sixtyfifth birthday.

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