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2D-NMR: Part VI*. 2D-INADEQUATE Spectral Analysis and Crystal Structure of Tricyclo[7.3.1.0^{2,7}]tridecane

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2-Hydroxy-13-oxo-tricyclo[7.3.1.0^{2,7}]tridecane derivatives can be obtained by reaction of cyclohexanone with alcohols under alkaline conditions. The unambiguous assignment of all signals of the ^{1}H-NMR- and ^{13}C-NMR-spectrum is possible by 2D-^{1}H-^{13}C-shift correlation and 2D-INADEQUATE. Compound **1** crystallizes in space group $P2_1/n$ with $a = 8.518\ (1)$, $b = 14.789\ (2)$, $c = 19.321\ (2)$ Å, $\gamma = 94.91\ (1)°$, $Z = 8$, $D_c = 1.22\ \mathrm{Mg\,cm^{-3}}$. The structure refined to $R = 0.100$ and $R_w = 0.097$ for 1719 observed reflections. Two independent molecules form centrosymmetric hydrogen-bonded dimers.

(Keywords: 2-Hydroxy-13-oxo-tricyclo[7.3.1.0^{2,7}]tridecane; 2D-NMR; ^{1}H-^{13}C-*Shiftcorrelation; INADEQUATE; Crystal structure)*

2D-NMR, 6. Mitt.: 2D-INADEQUATE Spektrum und Kristallstruktur von einem Tricyclo[7.3.1.0^{2,7}]tridecanderivat

Das ^{13}C-NMR-Spektrum von 2-Hydroxy-13-oxo-tricyclo[7.3.1.0^{2,7}] tridecan kann mit Hilfe eines INADEQUATE Experimentes eindeutig zugeordnet werden. Die Kristallstrukturdaten dieser Verbindung werden beschrieben.

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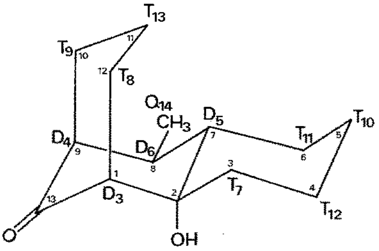
* Part V: *Haslinger E., Kalchhauser H., Robien W., Steindl H.*, Monatsh. Chem. **115**, 597 (1984).

Introduction

Continuing earlier NMR-studies of alicyclic ringsystems[3–8] we have analyzed the ^{1}H-, the ^{13}C-NMR-spectrum and done a crystal structure determination of 2-hydroxy-8-methyltricyclo[7.3.1.$0^{2,7}$]tridecan-13-one (**1**). **1** can be obtained by condensation of acetaldehyde with cyclohexanone under alkaline conditions[9,10]. Its structure was determined by chemical methods as well as by spectroscopic investigations[9–17]. IR-measurements show that in chloroform and also in cyclohexane solutions intramolecular hydrogen bonding exists[18]. We have unambiguously assigned the ^{1}H- and ^{13}C-resonances and tried to gain information about hydrogen bonding in the solid state by x-ray measurements.



Results and Discussion

1. NMR-Spectra

Neither in the proton- nor in the carbon NMR-spectrum of **1** the assignments of the signals can be made straightforward. This is due to the fact that the signals of the aliphatic hydrogens are overlapping strongly even at 250 MHz. Only the dublett of the CH_3-group at $\delta = 0{,}9$ ppm can be assigned immediately (Fig. 1). Fig. 1 shows the ^{13}C-NMR-spectrum of **1** which reveals a similar situation, although the CO-signal and the resonances at 15,26 (CH_3) and 59,4 ppm (C_1) can be assigned by chemical shift considerations and by their multiplicity obtained from an off-resonance decoupled spectrum. The only way to get an unambiguous assignment of the ^{13}C signals, even when the structure of the compound is not known, is via a 2D-INADEQUATE-experiment[19–23], which yields the carbon—carbon-connectivity. During this experiment the double-quantum frequency of directly bonded (thus coupled) ^{13}C—^{13}C-pairs is used to identify adjacent carbons. The assignments of the ^{1}H- and ^{13}C-resonances are given in Table 1, the ^{13}C—^{13}C-coupling constants in Table 2. Fig. 2 shows the 2D-INADEQUATE of **1**. Parallel to the frequency coordinate F2, the conventional proton decoupled ^{13}C-spectrum is shown. The signals 1 and

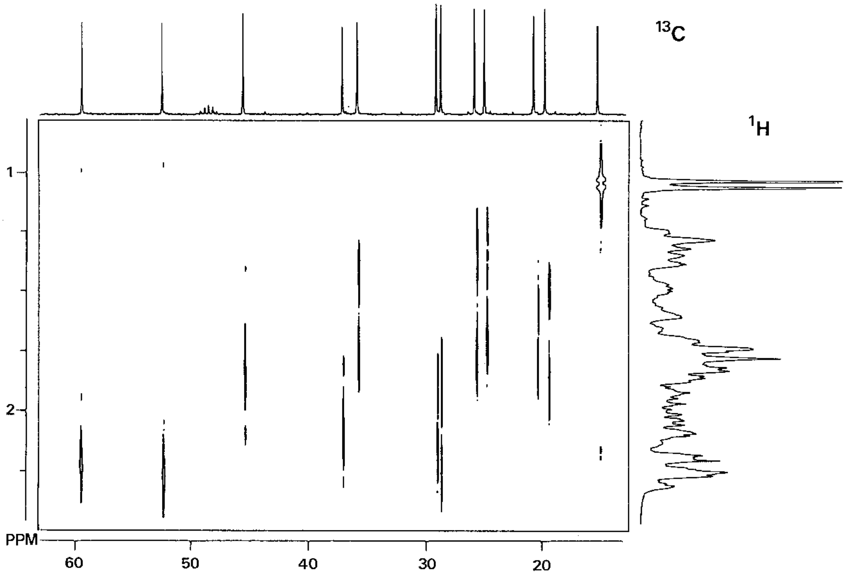


Fig. 1. 2D-^1H—^{13}C-Shift correlation of **1**

Table 1. *Chemical shifts of* **1** *in ppm.* The proton chemical shift values are taken from cross sections of the 2D-shift correlation

^{13}C	ppm	multiplicity	^1H	ppm
1	59.36	d	1	2.21
2	77.41	s	2	—
3	35.80	t	3	1.40/1.75
4	20.68	t	4	1.59/1.77
5	25.82	t	5	1.31/1.80
6	24.95	t	6	1.30/1.71
7	45.48	d	7	1.81
8	37.06	d	8	2.08
9	52.40	d	9	2.25
10	28.72	t	10	1.81/2.27
11	19.71	t	11	1.52/1.86
12	29.11	t	12	1.90/2.11
13	220.78	s	13	—
14	15.26	q	14	1.04

2 are outside the spectral region. The assignment is clear and starts with signal 14, a quartett which belongs to the methyl group of **1**, which leads to two connecting sequences, shown in Scheme 1. The multiplicities of the carbon signals are indicated by capital letters (Q = quartett, T = triplett, D = dublett).

Table 2. $^{13}C-^{13}C$-*coupling constants of* **1** ($\pm$0,5 Hz). The coupling constants are taken from a 1D-INADEQUATE experiment

1–2	31.9 Hz	8–9	30.6 Hz
2–3	34.5 Hz	9–10	30.3 Hz
3–4	33.3 Hz	10–11	32.4 Hz
4–5	33.1 Hz	11–12	32.6 Hz
5–6	30.4 Hz	12–1	30.2 Hz
6–7	34.1 Hz	8–14	36.1 Hz
7–8	34.1 Hz	2–7	34.1 Hz

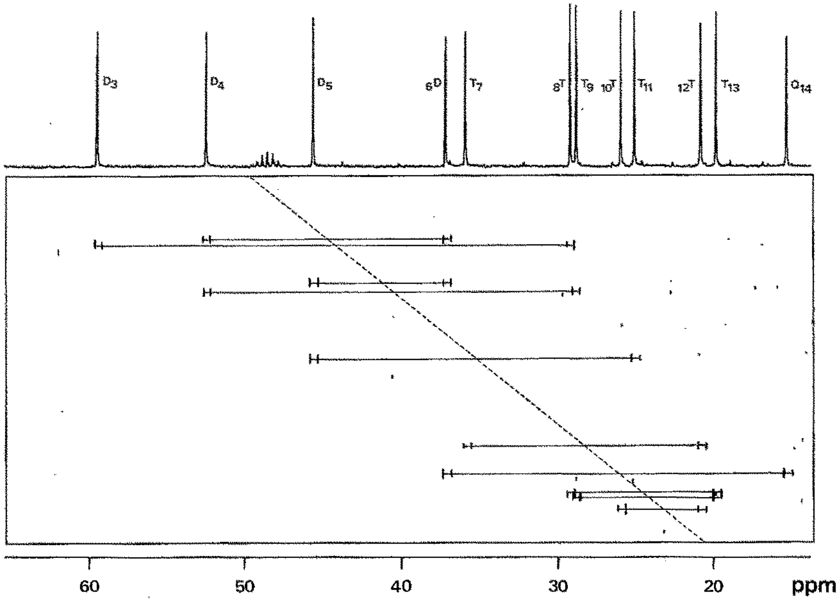
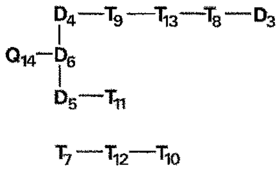


Fig. 2. 2D-INADEQUATE-spectrum of **1**

Scheme 1



In sequence 1, the quartett Q 14 and the doublett D 3 have already been assigned to the CH_3-group and the C_1 by multiplicity resp. chemical shift arguments. With this information the connectivity sequence 1 can be unambiguously assigned to the appropriate structural fragment in the molecule (Scheme 1). No connectivity information about C_2 and C_{13} could be obtained because their frequencies are beyond the spectral width of the experiment. The symmetrical sequence 2 contains T 7 with a chemical shift of 35.8 ppm indicating the neighborhood of a OH-group in β-position. T 7 can therefore be assigned to CH_2 in position 3 and both sequences can be put together as shown in Scheme 1. We could not get a connectivity signal for T 11 and T 10. This may be explained by the small chemical shift difference of the carbon signals leading to an AB- rather than an AX-spin system and to signal distortions in the INADEQUATE experiment. Having obtained the unambiguous assignment of all ^{13}C-signals a 2D-^1H-^{13}C-shift correlation experiment[24] was made (Fig. 1). The chemical shifts obtained for all protons are given in Table 1.

2. *Crystal Structure Determination*

A single crystal of compound **1** (0.15 × 0.15 × 0.30 mm) was analysed on a Philips PW 1 100 four-circle diffractometer at ambient temperature. The cell dimensions in Table 3 were determined by a least squares fit to the positions of 74 centered reflections. Data collection was carried out by the ω-2θ scan technique between 2 and 22° in ω with graphite-monochromated $MoK\alpha$ radiation. The data were corrected for variation in reference reflections and *Lorentz* and polarisation effects but not for absorption. 1719 unique reflections with $F > 3\sigma(F)$ were retained for use in the analysis; 1257 were considered unobserved. The structure was solved by direct methods (MULTAN[25]) and refined by full-matrix least squares (SHELX[26]) with isotropic temperature factors for the non-hydrogen atoms. All H atoms bonded to carbon were included in the structure factor calculation at idealized positions (C—H = 1.08 Å) sharing two common temperature factors in the refinement [U (CH, CH_2) = 0.066 (4) and U (CH_3) = 0.080 (10)]. The positional parameters of the hydroxy H atoms were refined freely and are included in Table 4. The terminal value of R was 0.100 with $R_w = 0.097$ for the 1719 observed reflections. Weights were given by $w = k[\sigma(F_0) + 0.0006(F_0^2)]^{-1}$ and scattering factors were taken from the International Tables for X-ray Crystallography[27]. The final parameters are listed in Table 4*, bond lengths and angles in Table 5.

The two independent molecules in the unit cell are linked together by two hydrogen bonds, O(1)—H(1)...O(22) and O(2)...H(21)—O(21), building up pseudo centric dimers. The two molecules itself are identical within limits of error, which can be recognized by comparing column I and II in Table 5. The carbon framework can be considered to consist of three cyclohexane rings, two forming *trans*-decaline and the third connected in an adamantane-like configuration (Fig. 3).

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* Copies of the list of structure factors may be obtained through one of the authors (*H.V.*).

Table 3. *Crystal data*

Formula $C_{14}H_{22}O_2$
$M_r = 222.33$
Space group $P2_1/n$
$a = 8.518\,(1)$ Å
$b = 14.789\,(2)$
$c = 19.231\,(2)$
$\gamma = 94.91\,(1)°$

$V = 2425$ Å^3
$F(000) = 976$
$Z = 8$
$D_c = 1.22$ Mg cm^{-3}
μ(Mo Kα) $= 0.044$ mm^{-1}

Table 4. *Positional parameters* ($\times 10^4$ *for* O *and* C, $\times 10^3$ *for* H) *and isotropic temperature parameters* (Å$^2 \times 10^3$) *for refined atoms*

	x	y	z	U
O(1)	6910 (6)	8673 (3)	8285 (3)	47 (2)
O(2)	6401 (6)	6555 (4)	8841 (3)	52 (2)
C(1)	5890 (9)	7276 (5)	7764 (4)	38 (2)
C(2)	6746 (9)	8231 (5)	7621 (4)	37 (2)
C(3)	5777 (9)	8773 (5)	7134 (4)	45 (2)
C(4)	6576 (9)	9727 (5)	7001 (4)	55 (3)
C(5)	8252 (9)	9678 (6)	6746 (4)	52 (2)
C(6)	9222 (9)	9131 (5)	7229 (4)	47 (2)
C(7)	8425 (8)	8176 (5)	7339 (4)	35 (2)
C(8)	9368 (9)	7586 (5)	7812 (4)	39 (2)
C(9)	8477 (9)	6667 (5)	8012 (4)	43 (2)
C(10)	8183 (10)	5965 (6)	7412 (4)	52 (2)
C(11)	7061 (9)	6220 (6)	6851 (4)	50 (2)
C(12)	5589 (9)	6633 (5)	7138 (4)	49 (2)
C(13)	6888 (9)	6817 (5)	8268 (4)	41 (2)
C(14)	11010 (9)	7445 (5)	7530 (4)	53 (3)
H(1)	582 (9)	872 (5)	837 (4)	70 (17)
O(21)	3271 (6)	6807 (4)	9240 (3)	47 (2)
O(22)	3800 (6)	8965 (4)	8800 (3)	61 (2)
C(21)	4218 (9)	8149 (5)	9850 (4)	39 (2)
C(22)	3392 (9)	7178 (5)	9927 (4)	36 (2)
C(23)	4318 (9)	6582 (5)	10382 (4)	42 (2)
C(24)	3529 (9)	5617 (5)	10434 (4)	50 (2)
C(25)	1840 (9)	5621 (5)	10677 (4)	52 (2)
C(26)	0908 (9)	6204 (5)	10219 (4)	45 (2)
C(27)	1673 (8)	7180 (5)	10175 (4)	36 (2)
C(28)	0765 (9)	7811 (5)	9725 (4)	45 (2)
C(29)	1640 (9)	8759 (5)	9599 (4)	50 (2)
C(210)	1840 (10)	9388 (6)	10234 (4)	59 (3)
C(211)	2918 (10)	9093 (6)	10797 (4)	59 (4)
C(212)	4427 (9)	8743 (5)	10502 (4)	50 (2)
C(213)	3252 (9)	8636 (5)	9352 (4)	47 (2)
C(214)	−0930 (10)	7897 (6)	9988 (4)	61 (3)
H(21)	439 (9)	673 (5)	911 (4)	70 (17)

Table 5. *Bond lengths (Å) and angles (°); the e.s.d.'s for non-hydrogen atoms are typically 0.008–0.010 Å and 0.4–0.7°, for values involving H atoms 0.07 Å and 5°*

	I	II
O(1)–C(2)	1.441	1.435
O(1)–H(1)	0.945	1.000
O(2)–C(13)	1.233	1.246
C(1)–C(2)	1.558	1.552
C(1)–C(12)	1.546	1.537
C(1)–C(13)	1.492	1.490
C(2)–C(3)	1.523	1.514
C(2)–C(7)	1.539	1.541
C(3)–C(4)	1.534	1.528
C(4)–C(5)	1.518	1.515
C(5)–C(6)	1.524	1.509
C(6)–C(7)	1.529	1.535
C(7)–C(8)	1.537	1.533
C(8)–C(9)	1.548	1.550
C(8)–C(14)	1.532	1.546
C(9)–C(10)	1.562	1.541
C(9)–C(13)	1.475	1.479
C(10)–C(11)	1.514	1.512
C(11)–C(12)	1.543	1.536
O(1)...O(22)	2.897	2.830
H(1)–O(1)–C(2)	97	104
C(2)–C(1)–C(12)	117.3	118.2
C(2)–C(1)–C(13)	106.7	106.5
C(12)–C(1)–C(13)	107.5	107.2
O(1)–C(2)–C(1)	105.9	106.1
O(1)–C(2)–C(3)	110.2	109.8
O(1)–C(2)–C(7)	106.5	104.6
C(1)–C(2)–C(3)	110.2	112.1
C(1)–C(2)–C(7)	112.3	112.5
C(3)–C(2)–C(7)	111.0	111.3
C(2)–C(3)–C(4)	111.7	111.8
C(3)–C(4)–C(5)	110.9	111.0
C(4)–C(5)–C(6)	112.4	111.5
C(5)–C(6)–C(7)	111.0	111.6
C(2)–C(7)–C(6)	110.0	110.0
C(2)–C(7)–C(8)	110.7	110.7
C(6)–C(7)–C(8)	113.3	114.1
C(7)–C(8)–C(9)	113.9	114.3
C(7)–C(8)–C(14)	113.2	112.8
C(9)–C(8)–C(14)	110.7	110.9
C(8)–C(9)–C(10)	115.9	116.1
C(8)–C(9)–C(13)	109.8	108.6
C(10)–C(9)–C(13)	104.6	106.0
C(9)–C(10)–C(11)	115.7	115.9
C(10)–C(11)–C(12)	113.2	112.2
C(11)–C(12)–C(1)	115.2	115.9
O(2)–C(13)–C(1)	122.6	122.5
O(2)–C(13)–C(9)	122.8	123.3
C(1)–C(13)–C(9)	114.5	114.1
O(1)–H(1)...O(22)	163	177

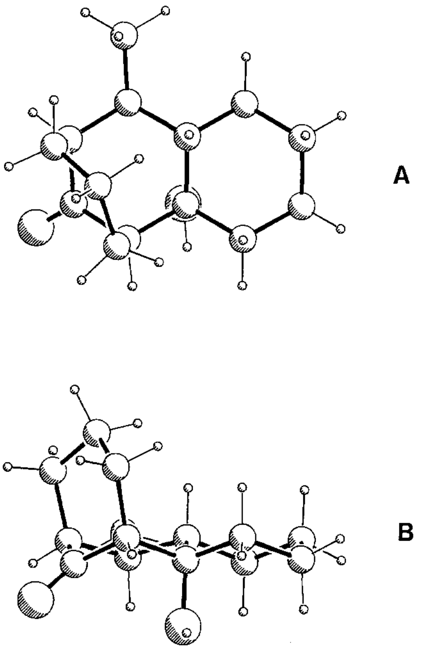

Fig. 3. Projection of **1** perpendicular (*A*) and parallel (*B*) to the decaline plane

Experimental

Melting points were determined on a "*Kofler*-Heiztisch-Mikroskop"; they are not corrected. GC-analysis have been done on a Carlo Erba gaschromatograph; column: 30 m SE 30, glas capillary; inject. temp. 250°, column temp. 140–280°/4° per minute. The recording of the mass spectra by Dr. *A. Nikiforov* (Institute of Organic Chemistry, University of Vienna) on a Varian MAT CH-7 (70 eV) is gratefully acknowledged. All NMR-spectra have been measured on a Bruker WM 250 spectrometer equipped with a 80 K ASPECT-2000 computer.

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2-Hydroxy-8-methyltricyclo[7.3.1.0^{2,7}]tridecan-13-one (**1**)

a) 30 g (0,3 mol) freshly distilled cyclohexanone have been added to a solution of sodium ethoxide in dry *Et*OH (13.8 g = 0.6 mol sodium and 580 ml = 10 mol dry *Et*OH) at room temperature. The mixture has been refluxed for a period of 12 h and then dispensed from the solvent. The residual liquid was neutralized with HCl and extracted with ether. After drying with Na_2SO_4 the solvent has been evaporated, the residue mixed with some acetone and cooled for crystallization. Yield: 8.0 g (35.3%); white crystals, m.p. 162 °C. $C_{14}H_{22}0_2$ (222.33).

MS (m/e; r. I.): 222 (M^+, 8); 125 (100); 124 (94); 98 (17). 2D-INADEQUATE: 680 mg **1** in 2 ml solvent (70% $CDCl_3$ + 30% $^{12}CD_3OD$), 10 mm tube. Parameters: 90°-pulse, ^{13}C: 26,5 μs, D1 = 6 s, D2 = 7,67 ms (1/4J for J = 32,6 Hz), DP = 2 W, NS = 192, SW_2 = 5000 Hz. Data matrix: 4 K × 128, *Fourier* transformation: 4 K × 512. Recording time: ~ 44 h.

2D-^{1}H—^{13}C-shift correlation: 100 mg **1** in 0,5 ml solvent (vide supra), 5 mm tube. Parameters: 90°-pulse: ^{1}H: 19,5 μs, 90°-pulse ^{13}C: 18,1 μs. D1 = 3 s, D2 = 4 ms (1/2J for J = 125 Hz); D3 = 2 ms (1/4J for recording all multiplicities); DP: 2 W, SW_1 = 500 Hz, SW_2 = 3200 Hz. Data matrix: 2 K × 128.

b) 6 g (0.2 mol) sodium hydride (80% oily suspension) have been added to 720 g (10 mol) dry *THF* (drying procedure: boiling with KOH, then boiling with $LiAlH_4$ and distillation from $LiAlH_4$) and afterwards mixed with 19.6 g (0.2 mol) freshly distilled cyclohexanone. Upon this 4.4 g (0.1 mol) acetaldehyde in 160 ml dry *THF* have been added dropwise during 8 h with stirring at room temperature. After further 8 h reaction time the alkaline solution has been worked up in the manner described above. Yield: 1.45 g (6.5%).

References

[1] *Fischlmayr A.*, work for diploma, University of Vienna, 1983.

[2] *Wassmann C.*, work for diploma, University of Vienna, 1983.

[3] *Haslinger E.*, *Kalchhauser H.*, *Robien W.*, Monatsh. Chem. **113**, 805 (1982).

[4] *Buchbauer G.*, *Haslinger E.*, *Robien W.*, *Vitek R.*, Monatsh. Chem. **114**, 113 (1983).

[5] *Buchbauer G.*, Monatsh. Chem. **109**, 289 (1978).

[6] *Buchbauer G.*, *Wiedenhorn M.*, Monatsh. Chem. **111**, 1299 (1980).

[7] *Buchbauer G.*, *Hell I.*, *Schindler K.*, Monatsh. Chem. **112**, 841 (1981).

[8] *Spreitzer H.*, *Buchbauer G.*, in preparation.

[9] *Barbulescu N.*, Rev. Chim. (Bukarest) **7**, 45 (1956).

[10] *Plesek J.*, *Munk P.*, Coll. Czech. Chem. Comm. **22**, 1596 (1957); Chem. Listy **51**, 633 (1957).

[11] *Barbulescu N.*, Anal. Univ. "C. I. Parhon" Bukarest, Ser. Stiintelor Naturii **7**, Nr. 20, 79 (1958) and **6**, Nr. 13, 101 (1957); Chem. Zentralbl. **1960**, 11642.

[12] *Barbulescu N.*, *Leca-Minicuta M.*, *Stanescu Gr.*, Rev. Chim. (Bukarest) **16**, 76 (1965).

[13] *Barbulescu N.*, *Leca M.*, Rev. Roum. Chim. **19**, 233 (1974).

[14] *Barbulescu E.*, *Barbulescu N.*, *Tilicenko M. N.*, Rev. Chim. (Bukarest) **11**, 631 (1961).

[15] *Julia S.*, *Varech D.*, Bull. Soc. Chim. France **1959**, 1127.

[16] *Julia S.*, *Varech D.*, C. R. hebd. Seances Acad. Sci. **246**, 1559 (1958).

[17] *Julia S.*, *Varech D.*, *Bürer Th.*, *Günthard Hs. H.*, Helv. Chim. Acta **43**, 1623 (1960).

[18] *Pitha J.*, *Plesek J.*, *Horak M.*, Coll. Czech. Chem. Comm. **26**, 1209 (1961).

[19] *Bax A.*, *Freeman R.*, *Kempsell S. P.*, J. Amer. Chem. Soc. **102**, 4849 (1980).

[20] *Freeman R.*, *Bax A.*, *Frenkiel T. A.*, *Levitt M. H.*, J. Magn. Res. **43**, 478 (1981).

[21] *Bax A.*, *Freeman R.*, *Frenkiel T. A.*, J. Amer. Chem. Soc. **103**, 2101 (1981).

[22] *Benn R.*, *Günther H.*, Angew. Chem. Int. Ed. **22**, 350 (1983).

[23] *Freeman R.*, *Frenkiel T. A.*, *Rubin M. B.*, J. Amer. Chem. Soc. **104**, 5545 (1982).

[24] *Freeman R.*, *Bodenhausen G.*, J. Magn. Res. **28**, 471 (1977).

[25] *Main P.*, MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York, England, 1978.

[26] *Sheldrick G. M.*, SHELX. A Program for Crystal Structure Determination. Univ. of Cambridge, 1976.

[27] International Tables for X-ray Crystallography, Vol. IV. Birmingham: Kynoch Press. 1974.