

Oxidation Reaction of Bis-Quinolizidine System: Synthesis of New 2-Methyl-17-Oxosparteine and 2-Methyl- α -Isosparteine

Beata Jasiewicz* and Władysław Boczon

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received October 21, 2006; Revised December 21, 2006; Accepted January 04, 2007

Abstract: Susceptibilities of two bis-quinolizidine systems: 2-methylsparteine and 2-phenylsparteine to oxidation reaction using $K_3Fe(CN)_6$, $KMnO_4$ and $Hg(CH_3COO)_2$ have been determined. Of these two derivatives only 2-methylsparteine has been found to undergo oxidation giving new 2-methyl-17-oxosparteine and 2-methyl- α -isosparteine. The structures of the new compounds have been established by IR, MS and NMR spectroscopies. The experimental evidence has been supported by DFT calculations.

Keywords: Sparteine derivatives, oxidation reaction, IR, MS, 1H and ^{13}C NMR spectroscopy, DFT calculations.

INTRODUCTION

The natural diamine (-)-sparteine has surfaced as one of the most robust external chiral ligands for asymmetric transformations because of its metal coordination ability and commercial availability [1,2]. Development of diamine surrogates complementary or superior to sparteine is of current interest [3]. We have obtained new compounds: 2-methyl-17-oxosparteine and 2-methyl- α -isosparteine via oxidation reaction of bis-quinolizidine system. Attempts at oxidation of sparteine and its derivatives have been made for many years. In the 1960s, Edwards, Clarc and Douglas studied the behaviour of some alkaloids of the sparteine type with Ag_2O [4], Marion and Leonard used NBS as oxidant [5]. Wiewiórowski and Legocki studied oxidation of the bis-quinolizidine alkaloids with a mercuric acetate/EDTA complex [6]. There is also a number of short reports on oxidation of bis-quinolizidine systems with $K_3Fe(CN)_6$ or $KMnO_4$ [7,8]. As a continuation of our earlier study on oxidation of sparteine derivatives [9,10], we decided to determine the susceptibility of 2-substituted sparteine derivatives: 2-methylsparteine (**1**) and 2-phenylsparteine (**2**) to oxidation with potassium ferricyanide, potassium permanganate and mercuric acetate.

EXPERIMENTAL SECTION

General Techniques

IR spectra were recorded with an FT-IR Bruker 113v spectrometer (KBr pellets or $CDCl_3$ for free bases and CD_3CN for salts). EI mass spectra were taken on an AMD 402 spectrometer. The 1H NMR, ^{13}C NMR, 1H - 1H COSY, ^{13}C - 1H COSY and DEPT spectra were measured on a Varian 300 Mercury spectrometer at 300 MHz and at ambient temperature, using ~0.5 M solutions in $CDCl_3$ (free base) and DMSO (salts) with TMS as internal reference. The conditions of the spectra recording: ^{13}C NMR: acquisition time 1.5 s, spectral width 23 000 Hz, number of points 69

000. 1H NMR: acquisition time 3.0 s, spectral width 9000 Hz, number of points 54 016. 1H - 1H Cosy 90-90: relax. delay 1.0 s, acquisition time 0.173 s, spectral width 2 954.2 Hz, 2D width 2 954.2 Hz, 16 repetitions, 256 increments. ^{13}C - 1H COSY: relax. delay 0.9 s, acquisition time 0.183 s, spectral width 3 258 Hz, 2D width 2 2630.8 Hz, 32 repetitions, 2 x 256 increments.

DFT Calculations

Information on the geometry of new 2-methyl-17-oxosparteine (**3**) and 2-methyl- α -isosparteine (**4**) were obtained using quantum-chemical calculations. The calculations were carried out by the density functional theory method (DFT) at the B3LYP/(6)6-311+G(2d,p) level implemented in the Gaussian 03 program package. The ^{13}C NMR absolute shielding constants (σ values) were calculated at the B3LYP/DFT level with the method of continuous set of gauge transformations (CSGT) using the (6)6-311+G(2d,p) basis set. The calculated magnetic shieldings were converted into the chemical shifts using the calculated ^{13}C absolute shieldings in TMS (177.3) at the same level of theory [11].

Synthesis

2-Methylsparteine and 2-phenylsparteine were prepared following the procedure described previously [12] by lithiation of the lactam carbonyl group of lupanine with methylolithium (or phenyllithium) followed by a reduction with $NaBH_4$.

Alkaline $K_3Fe(CN)_6$

10 ml aqueous 1M $K_3Fe(CN)_6$ was mixed with 4 ml of 20 % water solution of KOH; 1 ml of such a solution contains 0.7 mmol $K_3Fe(CN)_6$.

Oxidation of 2-methylsparteine to 2-methyl-17-oxosparteine with $K_3Fe(CN)_6$

To compound **1** (248 mg, 1 mmol), portions of 1 ml H_2O , 2 ml dioxane and 7 ml of alkaline $K_3Fe(CN)_6$ (5 mmol) were added. The mixture was stirred for 24 h. The reaction progress was controlled by TLC. If no **1** was

*Address correspondence to this author at the Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland; Tel: +48-61-829-1354; Fax: +48-61-865-8008; E-mail: beatakoz@amu.edu.pl

detected, the reaction mixture was basified with aqueous KOH (50% w/v), mixed with diatomaceous earth and transferred into a column. The column was eluted with diethyl ether (Dragendorff test). The ethereal eluate was dried with KOH pellets and evaporated to dryness. **3** (204 mg, 93%) was obtained as oil. EI-MS, m/z: 262 [M⁺]. IR (KBr): = 2937, 2859, 2791, 2765, 2230, 1617 (C=O), cm⁻¹. ¹³C NMR (CDCl₃): see Table 1. Anal. Calcd. for C₁₆H₂₆ON₂: C, 73.22; H, 10.01; N, 10.63. Found: C, 72.82; H, 9.91; N, 10.62. pK_a (CH₃CN) = 11.35 [¹J₂₀ = -0.010⁰ (c 1, CH₃OH).

2-Methyl-17-oxosparteine monoperchlorate

Compound **3** (262 mg, 1 mmol) was dissolved in MeOH (10 ml) and a 60% perchloric acid solution in methanol (1:4 v/v) was added until a slightly acidic pH was obtained. Recrystallization of a white powder from methanol gave white crystals of monoperchlorate salt of **3** (228 mg, 63%), m.p. 210 °C (with decomposition). EI-MS, m/z: 363 (M⁺). IR (CD₃CN): = 3056 (N⁺-H), 2117, 1656 (C=O), cm⁻¹. ¹³C NMR (DMSO): see Table 1. Anal. Calcd. for C₁₆H₂₇O₅N₂Cl: C, 52.95; H, 7.51; N, 7.72. Found: C, 53.32; H, 7.54; N, 7.68.

Isomerisation of 2-methylsparteine to 2-methyl- α -isoparteine

To a solution of **1** (248 mg, 1 mmol) in 5% acetic acid (10 ml) a portion of 2.52 g Hg(CH₃COO)₂ (8 fold excess) was added. The contents was heated under reflux for 4 hours. The reaction progress was controlled by TLC. If no **1** was detected, the reaction mixture was cooled down and the Hg(CH₃COO)₂ precipitate was filtered off. To the filtrate 5 ml 30% H₃PO₃ was added in portions and the content was heated under reflux for 15 minutes at the solution boiling point. After cooling down the mixture was filtrated and the filtrate was concentrated on an evaporator. The oil obtained (60 mg) was dissolved in MeOH (10 ml). After cooling, NaBH₄ (20 mg, 0.5 mmol) was added portionwise. The mixture was heated at 45⁰ C for 40 min, a few drops of AcOH were added to decompose the excess of reducing agent, and than, MeOH was evaporated under reduced pressure. The oil obtained was alkalized with 50% KOH and extracted with diethyl ether. The ether solution was dried with KOH pellets and evaporated to dryness. A yellowish oil of **4** was obtained (50 mg, 20%). EI-MS, m/z: 248 [M⁺]. ¹³C NMR (CDCl₃): see Table 1. Anal. Calcd. for C₁₆H₂₈N₂: C, 77.42; H, 11.29; N, 11.29. Found: C, 77.39; H, 11.34; N, 11.30.

RESULTS AND DISCUSSION

Oxidation of 2-Methylsparteine and 2-Phenylsparteine with KMnO₄ and K₃Fe(CN)₆

The oxidation reaction of sparteine derivatives substituted at the C2 position (Fig. 1) with KMnO₄ or K₃Fe(CN)₆ was performed under the same conditions as the oxidation of sparteine (**5**) and lupanine (**6**): for K₃Fe(CN)₆, a five-fold excess of oxidant was used, while for KMnO₄ only 40% excess. We assumed that the oxidation reaction, similarly as in **5** and **6**, would proceed at C17 leading through the intermediate state of 17-hydroxy-derivative (which could be isolated from the reaction mixture) to 17-oxo-compound. Only 2-methylsparteine underwent oxidation to 2-methyl-17-oxosparteine. We failed, however, to isolate the 17-hydroxy-2-methylsparteine.

The IR spectra of sparteine and its derivatives show a characteristic absorption in the range 2840-2600 cm⁻¹ (Bohlman *trans*-band). The *trans*-band of 2-methyl-17-oxosparteine consists of two absorption maxima at about 2791 and 2765 cm⁻¹. The IR spectrum of **3**, taken in CDCl₃, at ca. 2230 cm⁻¹ reveals an absorption peak related to the stretching vibrations of CDCl₃ molecules associated with the carbonyl oxygen atom, while there is no band at ca. 2170 cm⁻¹ (appearing in the IR spectrum of 2-methylsparteine) assigned to the association of the nitrogen atom N16 with the solvent molecule. The monoprotonated cation of **3** occurs in the "transoidal" form with ring C in the sofa conformation. In the IR spectra of **3**-HClO₄ the *trans*-band disappears, the band assigned to Cl-O of the ClO₄⁻ group appears at 1100 cm⁻¹.

In the NMR spectrum of **3** we found chemical shifts very close to those of sparteine [13], except for those in the nearest vicinity of the substituents, and, consequently almost the same conformation with ring C in a sofa (i.e. a flattened boat) conformation. The most symptomatic ¹³C NMR chemical shifts of **3** are those of carbonyl carbon atom, which are highly deshielded (= 169.8 ppm). Another distinctive NMR spectroscopic property of sparteine derivatives is the position of the apex carbon signal (C8) which is indicative of the conformation of the two internal B/C rings in the sparteine skeleton. According to the criterion of Bohlmann and Zeisberg [14] for the one-carbon bridge in the bicyclo[3.3.1] moiety, this resonance is expected to move downfield in the sequence boat/boat – chair/boat – chair/chair [15]. For the unsubstituted (chair/boat) sparteine this resonance occurs at = 27.4 ppm [13]. In compound **3** rings B/C have chair/sofa conformation

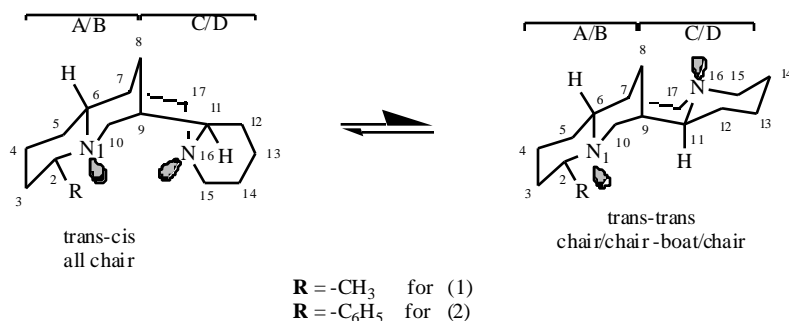


Fig. (1). Conformation and atom numbering of 2-methylsparteine (**1**) and 2-phenylsparteine (**2**).

Table 1. NMR Spectroscopic data of **3** (in CDCl₃), its Monoperchlorate salt 3-HClO₄ (in DMSO) and **4** (in CDCl₃).

Carbon atom	2-methyl-17-oxosparteine (3)		Monoperchlorate salt of 2-methyl-17-oxosparteine (3-HClO ₄)		2-methyl- α -isoparteine (4)
	δ_C	δ_H , multiplicity, J	δ_C	δ_H , multiplicity, J	δ_C
2	58.7 ^a +1.7	1.87ax	59.8 ^b +1.1	3.27ax	59.2 ^c +1.2
3	34.8 +9.2	*1.42ax *1.22eq	32.0a -2.8		33.8 -1.5
4	24.5 0.0	*1.61 *1.61	22.2b -2.3		25.2 +0.7
5	31.0 +0.9	*1.59ax *1.25eq	24.7 -6.3		31.6 +1.4
6	64.7 -1.6	1.98 ax	65.0 +0.3	3.29ax	68.4 +2.2
7	44.6 11.9	2.32eq	41.6 -3.0	2.55eq	36.5 +2.7
8	27.3 -0.1	1.54ax 2.03eq	28.2 +0.9		34.4 +6.9
9	35.2 -0.7	1.76eq	32.2 -3.0	2.10eq	35.7 -0.7
10	58.7 -3.1	1.94ax J=11.1; 2.4 3.16eq J=11.1; 2.8; 2.2	55.4 -3.3	3.08ax 3.68eq J=12.1	54.4 -2.9
11	61.5 -2.7	3.10ax J=11.1; 2.9	63.9 +2.4	3.21ax	66.2 +1.8
12	33.5 -1.0	*1.50 *1.50	31.1a -2.4		32.5 -2.2
13	25.3 +0.7	*1.61 *1.61	23.9b -1.4		24.7 -0.2
14	25.5 -0.3	*1.35ax J=12.3; 3.9; 3.9 *1.60eq	24.5b -1.0	1.21ax J=13.1; 3.1 1.59eq	26.2 +0.2
15	42.4 -12.8	2.45ax J=12.9; 12.9; 2.8 4.76eq J=13.1; 4.0; 2.1	42.7 +0.3	2.46ax J=12.9; 2.4 4.52eq J=12.9; 3.8; 1.9	56.4 +1.1
17	169.8 116.4		164.9 -4.9		54.6 +1.1
-CH ₃	21.2	1.01 J=6.0	16.6 -4.6	1.01 J=6.0	21.5 +0.2

(*) - δ_H values extracted from the HET-COR spectrum;

^aSubstituent effects were calculated by subtracting the chemical shifts of individual carbon atoms of sparteine from the values of the chemical shifts of the corresponding carbon atoms of **3**.

^bProtonation effects were calculated by subtracting the chemical shifts at individual carbon atoms of **3** base from the values of the chemical shifts of the corresponding carbon atoms in the spectrum of perchlorate salt **3-H⁺**.

^cIsomerization effects were calculated by subtracting the chemical shifts of individual carbon atoms of 2-methylsparteine from the chemical shifts of the corresponding carbon atoms of **4**.

and the resonance of C8 is slightly displaced downfield ($\delta = 27.3$ ppm). Because of the presence of oxygen atom at C17, an upfield shift is observed at C15 (-12.8 ppm) and a downfield shift is observed at C7 (+11.9 ppm). The ¹H NMR spectra of 17-oxosparteine and 2-methyl-17-oxosparteine show a downfield shift of the signal assigned to H5ax, which is much greater for 17-oxosparteine (2.09 ppm) [16] than for 2-methyl-17-oxosparteine (1.59 ppm). This low-field far range shift caused by the presence of a carbonyl group has been known for a long time. It is explained by the fact that H5ax is in the plane of the proximal lactam carbonyl group [17]. Deformation of ring C

must be assumed in order to account for the strong deshielding H15eq of 4.76 ppm which is by 2.13 ppm different from that of H15eq of sparteine and by 1.88 ppm from that of H15 of 2-methylsparteine [18]. For 17-oxosparteine this value is 5.11 ppm [17]. It is known that in 2-methylsparteine, after introducing one proton, both amino groups adopt cisoidal arrangement, which permits formation of an intramolecular hydrogen bond stabilizing this conformation and hindering the inversion of the N16 atom [18]. The situation is different for 2-methyl-17-oxosparteine, in which the protonation site is N1 in the rigid part of *trans*-quinolizidine (A/B rings), and conformational changes -

possible only in the *cis*-quinolizidine part (C/D rings) - cannot occur because of the presence of the lactam group [19]. The chemical shifts in the spectrum of monoperochlorate salt of **3** are very close to those of its free base. No *-gauche* effects which usually accompany a change in the conformation from boat-chair to all-chair are observed at carbon atoms C12 and C14. When analysing protonation effects (Table 1), it is necessary to take into account the fact that a contribution to these effects comes also from the solvent change. The protonation of N1 atom is manifested by low-field shifts of the proton signals at C2, C6 and C10 (above 3.0 ppm).

Oxidation of 2-Methylsparteine and 2-Phenylsparteine with $\text{Hg}(\text{CH}_3\text{COO})_2$

The oxidation procedure was that of Leonard and co-workers [20] used for isomerisation of sparteine. Similarly as when KMnO_4 and $\text{K}_3\text{Fe}(\text{CN})_6$ were used as oxidising agents, only 2-methylsparteine underwent oxidation, while 2-phenylsparteine was left unreacted despite a few attempts of carrying out the reaction with greater amount of the oxidising agent and extended reaction time. As the product of the oxidation was very unstable and decomposing on contact with the air, the compound (5,11-didehydro-derivative) was reduced by sodium borohydride to give saturated 2-methyl-*-*isosparteine (**4**). In contrast to the isomerisation reaction of sparteine that of isomerisation of 2-methylsparteine ran with a low yield (~ 20 %) giving an oily product. Compound **4** was identified on the basis of analysis of its IR and NMR spectra and their comparison with the corresponding spectra of the initial 2-methylsparteine and *-*isosparteine. The *trans*-band of *-*isosparteine consists of three sharp peaks at 2793, 2758 and 2735 cm^{-1} [21]. The presence of a methyl group at C2 in the newly obtained compound **4** results in impoverishment of the *trans*-band which consists of two absorption maxima at about 2780 and 2752 cm^{-1} . As a result of 2-methylsparteine isomerisation, the conformation of ring C changes from boat to chair. The ^{13}C NMR spectrum of **4** (Table 1) confirms our suppositions about the all-chair structure of the new compound. This spectrum has been analysed by comparison with those of **1** and *-*isosparteine [18]. The ^{13}C NMR spectrum of *-*isosparteine being a symmetric compound gives only 8 signals. The presence of the methyl substituent at the carbon atom C2 disturbs the symmetry. The bridge carbon atom C8 resonates at 34.4 ppm, which indicates the chair/chair conformation of the two fused B/C rings. At this carbon atom the changes in the chemical shift resulting from

isomerisation are the greatest (+6.9 ppm). The other values are in the range from -2.9 ppm (C10) to +2.7 ppm (C7). Assignment of chemical shifts to particular protons was impossible because of too much overlapping of the signals in the ^1H NMR spectrum.

DFT Calculations

The structures of the newly obtained compounds **3** and **4** were fully optimized by using the Gaussian03 package at the B3LYP level with the 6-311+G(2d,p) basis set (see Fig. 2).

For **3** the calculated N1-N16 distance is 3.140 Å; i.e. it is shorter than that obtained for 17-oxosparteine [22]. Characteristic angles of inclination of one quinolizidine skeleton to the other are: C6-C7-C17 = 111.1, C10-C9-C11 = 111.1 and C7-C8-C9 = 107.2. The C17-N16 bond length in the lactam group is 1.380 Å, and the C17=O bond length is 1.240 Å; this indicates a slightly conjugated bond system. Because the crystal structure of 2-methylsparteine has not been determined, the structure of **4** was compared with the known structure of *-*isosparteine monohydrate [23]. Because of the symmetry of its molecules the latter compound has the same lengths of the following bonds: N1-C6 and N16-C11 (1.45 Å); N1-C2 and N16-C15 (1.35 Å), N1-C10 and N16-C17 (1.46 Å). For **4** the calculated N1-N16 and N1-C2 distances are longer than those calculated for N16-C11 and N16-C15, respectively. The calculated C2-CH₃ distance is 1.528 Å. The difference in the computed energy between the new 2-methyl-17-oxosparteine ($E = -810.33489$ H) and the parent 2-methylsparteine ($E = -736.26187$ H) is a result of the presence of oxygen atom at C17. On the other hand, isomerisation of 2-methylsparteine to 2-methyl-*-*isosparteine ($E = -810.33489$ H) causes changes in energy by only ca. 0.3 H (Hartrees [H] = 627.51 kcal/mol).

The conformation assignment of the new compounds was achieved also by comparison of the experimental ^{13}C NMR chemical shifts with those predicted by DFT/CSGT shielding calculations. The results of these calculations for the optimized structure together with the experimental values are listed in Table 2. The correlation coefficient (R^2) for carbon chemical shifts is 0.986 and 0.969 for **3** and **4**, respectively. The results suggest that the structures of the new compounds in CDCl_3 solution are as proposed by us. The differences observed between the calculated and experimental values (Table 2) stem from the fact that the chemical shifts in solution are subject to solvent, concentration and temperature effects.



Fig. (2). The optimized structures of 2-methyl-17-oxosparteine (a) and 2-methyl-*-*isosparteine (b).

Table 2. Comparison of CSGT Chemical Shifts (δ , in ppm) Calculated at the DFT Level of Theory for 2-Methyl-17-Oxosparteine and 2-Methyl- α -Isosparteine

Carbons	2-methyl-17-oxosparteine			2-methyl- α -isosparteine		
	δ exper.	δ theor.	$\Delta\delta$	δ exper.	δ theor.	$\Delta\delta$
C2	58.7	52.1	-6.6	59.2	58.4	-0.8
C3	34.8	35.0	0.2	33.8	31.5	-2.3
C4	24.5	26.4	1.9	25.2	23.8	-1.4
C5	31.0	31.0	0.0	31.6	29.2	-2.4
C6	64.7	56.3	-8.4	68.4	72.7	4.3
C7	44.6	37.8	-6.8	36.5	34.8	-1.7
C8	27.3	29.0	1.7	34.4	41.4	7.0
C9	35.2	32.0	-3.2	35.7	34.9	-0.8
C10	58.7	57.6	-1.1	54.4	56.9	2.5
C11	61.5	56.2	-5.3	66.2	63.7	-2.5
C12	33.5	34.1	0.6	32.5	33.0	0.5
C13	25.3	27.5	2.2	24.7	24.8	0.1
C14	25.5	27.0	1.5	26.2	25.3	-0.9
C15	42.4	43.3	0.9	56.4	54.1	-2.3
C17	169.8	173.3	3.5	54.6	52.2	-2.4
-CH ₃	21.2	28.5	7.3	21.5	24.9	3.4

REFERENCES

- [1] Gallagher, D.J.; Wu, S.; Nikolic, N.A.; Beak, P. *J. Org. Chem.*, **1995**, *60*, 8148.
- [2] Resek, J.E.; Beak, P. *J. Am. Chem. Soc.*, **1994**, *116*, 405.
- [3] Dearden, M.J.; Firkin, C.R.; Hermet, J.-P.R.; O'Brien, P. *J. Am. Chem. Soc.*, **2002**, *124*, 11870.
- [4] Edwards, O.E.; Clarke, F.H.; Douglas, B. *Can. J. Chem.*, **1954**, *32*, 235.
- [5] Marion, L.; Leonard, N.J. *Can. J. Chem.*, **1951**, *29*, 355.
- [6] Wiewiórowski, M.; Legocki, A.B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **1963**, *11*, 5.
- [7] Clemo, G.R.; Leitch, G.C. *J. Chem. Soc.*, **1928**, 1811.
- [8] Gołebiewski, W.M.; Spencer, I.D. *Can. J. Chem.*, **1985**, *63*, 716.
- [9] Boczon, W.; Kozioł, B. *Pol. J. Chem.*, **2000**, *74*, 1249.
- [10] Thiel, J.; Boczon, W.; Fiedorow, P.; Jasiewicz, B.; Knychala, M. *J. Mol. Struct.*, **2002**, *642*, 15.
- [11] Galasso, V.; Asaro, F.; Berti, F.; Kovač, B.; Habus, I.; Schetti, A. *Chem. Phys.*, **2003**, *294*, 155.
- [12] Boczon, W. *Pol. J. Chem.*, **1981**, *55*, 339.
- [13] Duddeck, H.; Skolik, J.; Majchrzak-Kuczynska, U. *Khim. Geterotsykl. Soedin.*, **1995**, *8*, 1026.
- [14] Bohlmann, F.; Zeisberg, R. *Chem. Ber.*, **1975**, *108*, 1043.
- [15] Schneider, H.-J.; Lonsdorfer, M.; Weigand, E.F. *Org. Magn. Reson.*, **1976**, *8*, 363.
- [16] Galasso, V.; Asaro, F.; Berti, F.; Habus, I.; Kovač, B.; De Risi, C. *Chem. Phys.*, **2004**, *301*, 33.
- [17] Gołebiewski, W.M. *Magn. Reson. Chem.*, **1986**, *24*, 105.
- [18] Jasiewicz, B.; Boczon, W. *J. Mol. Struct.*, **2005**, *752*, 115.
- [19] Perkowska, A.; Wiewiórowski, M. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **1980**, *28*, 249.
- [20] Leonard, N.J.; Thomas, P.D.; Gash, P.D. *J. Am. Chem. Soc.*, **1955**, *77*, 1552.
- [21] Skolik, J.; Kruger, P.J. *Tetrahedron*, **1968**, *24*, 5439.
- [22] Katrusiak, A.; Hoser, A.; Grzesiak, E.; Kałuski, Z. *Acta Cryst.*, **1980**, *B36*, 2442.
- [23] Przybylska, M.; Barnes, W.H. *Acta Cryst.*, **1953**, *6*, 377.