¹H-NMR Spectroscopic Elucidation of Stereochemical Effects of Substituted Cerium Porphyrin Double-Deckers

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Introduction

Closely spaced porphyrinic macrocycles play an important role in such diverse systems as photosynthetic proteins[1] and organic conductors.[2] The best known example, the primary electron donor in the photosynthetic reaction center, consists of a special pair of bacteriochlorophyll molecules.[3–5] Strong electronic interactions between molecules within these natural and synthetic aggregates impart unique electron transfer and/or conductivity properties to the systems.[2,6] In this regard, an investigation of π–π interactions in the lanthanide porphyrin sandwich complexes, $Ce^{IV}(OEP)_2$ and $Ce^{IV}(TPP)_2$ (OEP = octaethylporphyrin; TPP = tetraphenyl porphyrin), as well as their corresponding π cation radicals,[7] has been reported. These complexes are of particular interest because of the two macrocycles which are in very close proximity.[8]

One approach to extend the inter-ring separation with the same metal is to change the position of substituent groups on the phenyl groups on the macrocycle, as we present in this work. Besides the change of the inter-ring distance, we have also observed the existence of equal population of two conformations for the peripheral groups.
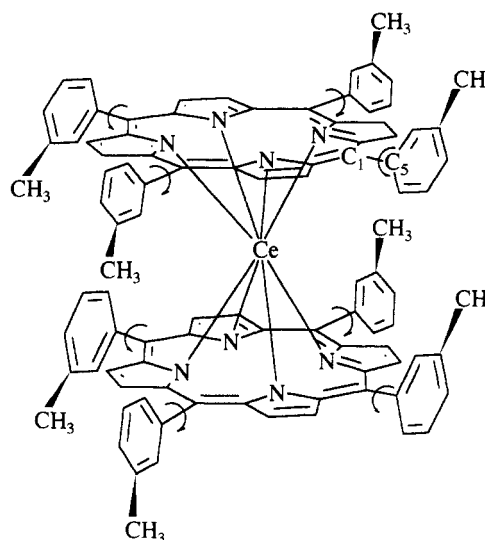
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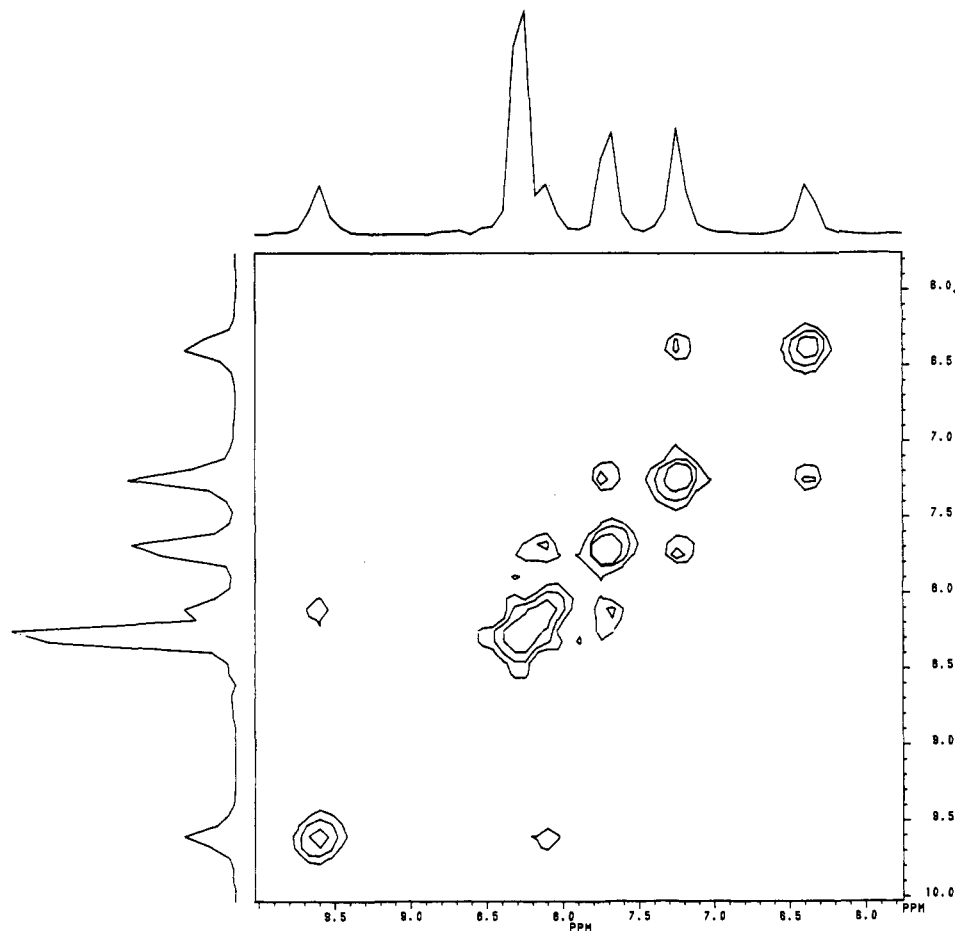**Figure 1.** Stereochemistry of the molecule and rotation positions for the phenyl groups.

In this work, we report the characterization of the $Ce^{IV}(T-m-MePP)_2$ and the absorption spectra of all $Ce^{IV}(Por)_2$ complexes. These data are compared with those of other $Ln(Por)_2$ or $Ln(Por)X$ complexes. The ¹H-NMR spectra of all of the complexes have been studied and a 2D-NMR study of $Ce^{IV}(T-p-MePP)_2$ has been performed in order to define the position of all protons in the complex.

Experimental Procedures

The complexes $Ce^{IV}(Por)_2$ (were Por = TPP, T-m-MePP and T-p-MePP) were prepared by a literature procedure,[8b,d,e] by refluxing $PorH_2$ and $Ce^{III}(acetylacetonate)_3·xH_2O$ in 1,2,4-trichlorobenzene (Aldrich, 99+%) under an inert atmosphere. Purification of all the complexes was performed by the Buchler procedure[8b–e] modified as follows: After reflux, the reaction mixture was passed through a Al_2O_3 column (type Basic I) activated at 150 °C overnight without evaporation of 1,2,4-tcb. With toluene as eluent, traces of free base were observed in the first fraction, and as second fraction the metalated compound was obtained (yield 50%). Anal. Calcd for $Ce(T-m-MePP)_2$, $C_{96}H_{72}N_8Ce$ (mol wt 1477.81): C, 78.02; N, 7.15; H, 4.91. Found: C, 78.41; N, 7.15; H, 5.13.

Absorption spectra were collected on a Perkin-Elmer Lamda 6 grating spectrophotometer. Spectra for ε measurements were recorded by using dichloromethane or toluene (Riedel-de Häen spectral grade) as solvents (solutions of 0.068 × 10⁻³M). UV–visible data for $Ce(T-m-MePP)_2$: {λ/nm [log(10⁻³ ε/dm³ mol⁻¹ cm⁻¹)]}, 399 (5.24), 484 (4.08), 543 (3.97), 629 (3.23) in toluene.

Infrared spectra of CsI pellets or Nujol mulls of the samples were acquired with a Perkin-Elmer FT-IR 1760 instrument. Characteristic vibrations (cm⁻¹) of cerium^{IV} double-deckers by IR spectroscopy: Ce-$(TPP)_2$, 1327, 1180, 980, 800, 720; Ce($T-p-MePP)_2$, 1325, 1182, 979, 796, 722; Ce($T-m-MPP)_2$, 1331, 1182, 982, 802, 722.

¹H-NMR spectra were recorded on a Bruker AC spectrometer (200 MHz for ¹H) in $CDCl_3$ solutions of 2 × 10⁻³ M. Also, ¹H-NMR spectra at different temperatures were recorded in $C_2D_2Cl_4$ from 298 to 393 K.

The 2D homonuclear-correlated experiments were carried out with the following parameters: spectral width 1900 Hz in both dimensions, four transients for each FID; 256 t_1 increments; recycling delay 1 s; and a 1024 × 1024 data matrix for processing. The phase sensitive NOESY experiment was obtained with t_m = 0.5 s and a recycling delay of 1.2 s. The other parameters used were as follows: spectral width 1800 Hz in both dimensions, 128 t_1 increments, a 512 × 512 data matrix, and 16 transients for each FID.

Results

A. Absorption and Infrared Spectra. UV–visible spectroscopy was the tool for monitoring the reaction mixture. So, before we

Figure 2. COSY spectrum of Ce^{IV}(TPP)$_2$.

Table 1. ^{1}H-NMR Data for Cerium(IV) Bis(porphyrinates) and Corresponding Free Bases (Non-metallo-complexed Porphyrins) [δ in ppm, TMS, 200 MHz, CDCl$_3$]

	ortho		meta			Me		
complexes	endo	exo	endo	exo	para	endo	exo	pyrrolic
(TPP)H$_2$[a]	8.21		7.77		7.77			8.88
Ce(TPP)$_2$[a]	9.60	6.37	8.01	7.25	7.69			8.30
(T-p-MePP)H$_2$[a]	8.1		7.56			2.7		8.87
Ce(T-p-MePP)$_2$[a]	9.39	6.24	7.89	6.96		2.57		8.12
(T-m-MePP)H$_2$[a]	8.06		7.67		7.67	2.68		8.89
Ce(T-m-MePP)$_2$	9.39	6.21/6.36	8.05	7.22	7.53	3.04	2.18	8.30

[a] Spectra recorded under the same conditions for the purpose of this study see also refs 7a, 8a, 15, and 17.

Table 2. Induced Chemical Shifts $\Delta\delta$ in Complexes Ce(TPP)$_2$, Ce(T-p-MePP)$_2$, Ce(T-m-MePP)$_2$

	$\Delta\delta$[a]							
	ortho		meta			Me		
complexes	endo	exo	endo	exo	para	endo	exo	pyrrolic
Ce(TPP)$_2$[a]	+1.39	−1.84	0.24	−0.52	−0.08			−0.58
Ce(T-p-MePP)$_2$[a]	+1.29	−1.86	0.33	−0.6		−0.13		−0.75
Ce(T-m-MePP)$_2$	+1.33	−1.85/1.9	0.38	−0.45	−0.14	0.36	−0.5	−0.59

[a] $\Delta\delta$ calculated as $\Delta\delta = \delta_{complex} - \delta_{free\ base}$. A more rigorous estimation of this shift due to the ring current effect could be made if we considered the chemical shift of a monomeric metal porphyrin, but ^{1}H-NMR spectra of Zn(TPP)[16] are the same as the free base, which indicates that the presence of the metal is not significant.

discuss the UV–visible data of the three tetraphenyl-substituted, or not, double-deckers some comments on the above-mentioned UV–visible process are indispensable. During the metallation reaction observed by UV–visible spectroscopy the following changes; the appearence of one band in the Soret region (~448 nm), probably due to the "acid form" of the porphyrin ring, while 2 days later this band disappeared and when the Soret band of the formed complex appeared in the reaction mixture the metallation reaction was completed. As it has been observed by UV–visible control of the reaction mixture, there was not a clear formation of the final compound.

The only direct information for the metal insertion reaction by infrared spectroscopy was the disappearance of the N–H band of the free base at about 3300 cm^{-1}.

B. ^{1}H-NMR Spectra. The ^{1}H-NMR spectra can be interpreted on the basis of the distinction of the phenyl group protons to endo and exo, as has already been proposed for the Ce(TPP)$_2$ and Ce(p-MeTPP)$_2$ complexes (Figure 1).

In these complexes the diastereotopic endo and exo o-H give two distinct NMR signals and the same is true for the exo m-H.

These complexes give broad, structureless NMR signals due to the flipping motion of the rings as previously reported.[8a] An unambiguous assignment of the complexes spectra was obtained via a COSY experiment.

In Ce(p-MeTPP)$_2$ the –CH$_3$ proton resonance can be easily recognized at high field. The COSY spectrum shows connectivities between o- and m-protons which clearly indicates the two pairs of endo- end exo-protons. From the COSY spectrum of the Ce(TPP)$_2$ we can distinguish between o- and m- protons (Figure 2). The two m-protons at 8.01 and 7.29 ppm (endo- and exo-) correlate with the p-proton at 7.69 ppm. The assignment of the three complexes is given in Table 1. We also reinvestigated ^{1}H-NMR data given in the literature for the complex Ce(p-MeTPP)$_2$.

The distinction between the endo- and exo-pair of o- and m-protons can be revealed from the comparison of the proton chemical shifts of these double decker complexes with the chemical
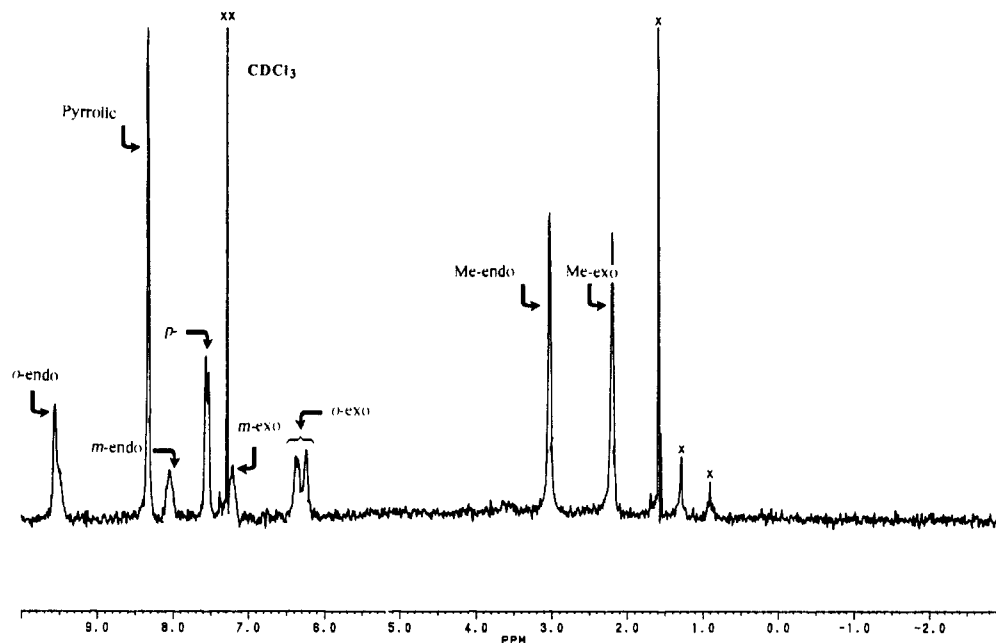
Figure 3. ^{1}H-NMR spectrum of $Ce^{IV}(T\text{-}m\text{-}MeTP)_2$, xx = $CDCl_3$, x = impurities.

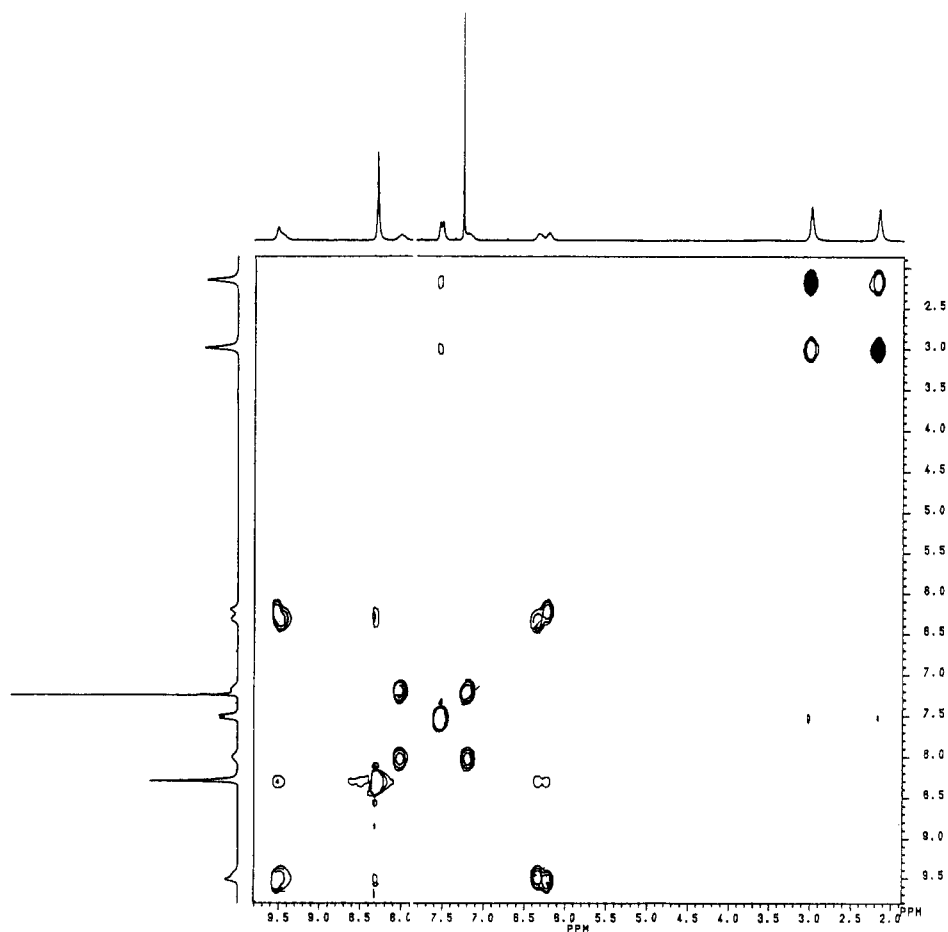**Figure 4.** NOESY spectrum of $Ce^{IV}(T\text{-}m\text{-}MeTP)_2$.

shift of the corresponding free base protons (Tables 1 and 2). We observe a downfield shift for the one pair of *o*- and *m*-protons while the other two *o*- and *m*-protons are shifted upfield. We also observe an upfield shift for the pyrrolic protons, but no significant shift is noted for the *p*-methyl protons. These data can be interpreted on the basis of the ring current effect of the TPP macrocycle. The endo *o*- and *m*-protons are shifted downfield because they are close to the porphyrin plane and they

experience the deshielding effect of the ring current. The other pair, the exo *o*- and *m*-protons, are situated above the ring plane and they experience the shielding effect of the ring current.

This is in good agreement with the crystal structure of analoguous lanthanoid complexes[9] where the two porphyrin rings

(9) Girolami, G. S.; Milam, S. N.; Suslick, K. N. *Inorg. Chem.* **1987**, *122*, 343–344.
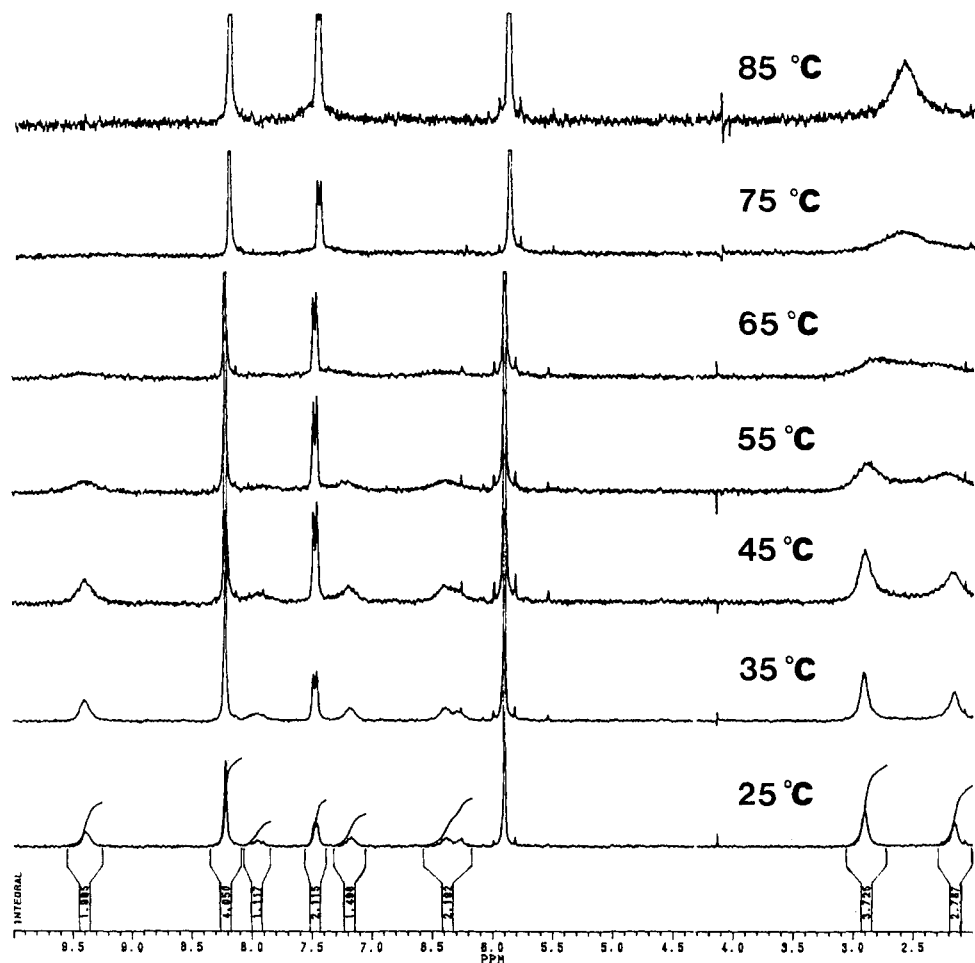
Figure 5. ¹H-NMR spectrum of Ce(T-*m*-MePP)₂ at variable temperatures in C₂D₂Cl₄, with coalescence temperature at 65 °C.

are close to each other (the reported distance is 3.4 Å) and the endo and exo *o*-protons are situated in quite different distances from the macrocycles because of the orthogonal disposition of the phenyl groups with respect to the porphyrin nucleus.

According to the magnetic anisotropy of the TPP macrocycle proposed by Abraham et al.,[10] the observed induced chemical shift $\Delta\delta$ (Table 2) indicates a vertical tilting of the phenyl and the pyrrole rings, which are oriented to the opposite direction of the second porphyrin ring. These deformations of the macrocycle are also in agreement with the macrocycle conformations observed in crystal structures.[9,11]

In the case of Ce(*m*-MeTTP)₂ we observe two methyl signals of equal intensity (12 protons each): one, at 3.04 ppm, deshielded and the second, at 2.18 ppm, shielded in comparison with the corresponding free base. We also observe two distinct signals for the *m*-protons (corresponding to four protons each) at 8.05 and 7.22 ppm. This suggests that the *m*-methyl substituents (and the whole tolyl group) are partly exo and partly endo oriented (see Figure 1). Accordingly four different signals are expected for the *o*-protons: two for the endo *o*-H and two for the exo *o*-H (depending in each case on whether the *o*-H is in the vicinity of the methyl substituent or not). Indeed the exo *o*-protons appear as two superimposed broad multiplets (corresponding to a total of 8 protons) at 6.21 and 6.36 ppm (see Figure 3). The endo *o*-proton signals are not resolved but appear as a broad signal at 9.6 ppm (corresponding to 8 protons).

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(11) Buchler, J. W.; DeCian, A.; Fischer, J.; Hammerschmith, P.; Löffler, J.; Scharbert, B.; Weiss, R. *Chem. Ber.* **1989**, *122*, 2219–2228.

The phase-sensitive NOESY spectum of this complex shows correlation between the endo and exo *o*-protons, the endo and exo *m*-protons and the endo and exo methyl protons, Figure 4. The observed cross-peaks are of the same sign as the diagonal ones, suggesting that the magnetization is transfered via an exchange process and not by NOE enhancement since the complex is considered to be a relatively small molecule. This indicates a slow (on the NMR time scale) exchange process between two conformations of the phenyl group with respect to the porphyrin ring, of equal population: one with the methyl substituent endo oriented and the other with the methyl group exo oriented, as proven by integration.

In order to explore more closely the exchange process suggested from the NOESY data we carried out a temperature dependence study of Ce(T-*m*-MePP)₂. The ¹H-NMR spectrum of this complexe in 1,1,2,2-C₂D₂Cl₄ (solvent with a higher boiling point) is different from the one in chloroform as seen in Figure 5. Thus at room temperature the integrals of the endo- and exo-methyl protons are no longer equal: the ratio of the two integrals shows that 57% of the methyl groups are endo-oriented and 43% are exo-oriented. Consistenly the integrals of the *m*-protons show an endo/exo ratio equal to 3:4. When the temperature is increased the rate of rotation of the *m*-tolyl group around the sites are obtained. Coalescence is observed at 65 °C.

These NMR data show that the rotation of the *m*-tolyl groups is influenced by the solvent. In the case of CDCl₃ solution the rotation is not hindered and the different methyl groups have the same probability to be in the endo- or in the exo-position. In the C₂D₂Cl₄ solution the presence of the solvent molecules hinders the rotation and the equilibrium between the different atropi-somers shifts toward isomers that have more endo- than exo-

oriented methyl groups. This is in agreement with the observation that the resonance at 2.18 ppm (exo-methyl group) is broader than the one at 3.04 ppm (endo-methyl group). This is probably due to the fact that the exo-posistion has a shorter life time, and there is a larger contribution of endo-oriented methyl groups. The data available are not suficient to suggest a preference for any particular isomer.