*Carbohydrate Research*, 192 (1989) 61–68
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# MOLECULAR DYNAMICS OF DERIVATIVES OF CYCLOMALTO-OLIGOSACCHARIDES AND THEIR COMPLEXES WITH AZO DYES*

MIYOKO SUZUKI[†]
*Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Suita, Osaka 565 (Japan)*

JOZSEF SZEJTLI, AND LAJOS SZENTE
*Chinoin Pharmaceutical and Chemical Works, To u. 1-5, H-1045 Budapest (Hungary)*
(Received March 21st, 1989; accepted for publication, June 19th, 1989)

## ABSTRACT

The molecular motions of the inclusion complexes of several cyclomalto-oligosaccharides (CDs) and azo dyes have been studied on the basis of $^{13}C$ relaxation times. The correlation times, estimated to be of the order of $10^{-10}$–$10^{-11}$ s by the isotropic model, increased as the host and guest molecules became large, long, and bulky, and the increase was larger for the azo dyes than for CDs on the formation of complexes. Azo dyes rotate up to twice as fast as CDs. The motion of the azo dye with respect to the cavity of the CD indicates that the longer and more bulky azo dyes rotate slower, and that lengthening of the cavity prevents their rotation. The internal rotations of the primary alcohol, methyl, and phenyl groups were preserved in the complexes.

## INTRODUCTION

Cyclomalto-oligosaccharides (cyclodextrins, CDs) form complexes with the hydrophobic residues of substrates that have a compatible size. They possess rigid structures and can be used as models for enzymes. We have synthesized CD derivatives which have different inner diameters and heights of the hydrophobic torus, namely, heptakis(2,6-di-*O*-methyl)cyclomaltoheptaose (DM-βCD) and heptakis-(2,3,6-*O*-trimethyl)cyclomaltoheptaose (TM-βCD), and water-soluble epichlorohydrin and ethyleneglycol-bis(epoxypropyl)ether derivatives of cyclomaltohexaose (αCD), -heptaose (βCD), and -octaose (γCD)[1,2]. The inclusion of Methyl Orange (**1**) in CDs has been studied using $^{1}H$- and $^{13}C$-n.m.r. spectroscopy[1,3] and circular dichroism[2]. The $^{13}C$ resonance of the hydrophobic moiety of **1** shifted to higher field with increase of the inner diameter of the CD. On alkylation of the hydroxyl

---

[*] Inclusion Compounds of Cyclodextrins and Azo Dyes, Part VII.
[†] Author for correspondence.

0008-6215/89/$ 03.50

groups of CDs, the hydrophobic interactions are enhanced and a closer resemblance of inclusion and solvent shifts was observed[1]. We now report on $^{13}$C-n.m.r. spin–lattice relaxation times ($T_1$). The correlation time obtained from the $T_1$ data gives information on the dynamic properties of substrates included in the cavities. Specific emphasis was placed on how the increase of the inner diameter of the CD, the lengthening of the hydrophobic torus by substituting CD with methyl groups, and the lengthening of the guest molecule affect the inclusion and the dynamic properties.

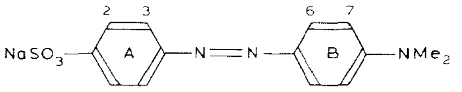
## EXPERIMENTAL

A JEOL JNM-GX 500 F.t.-n.m.r. spectrometer operating at 125 MHz was used. $^{13}$C–$T_1$ values were measured by the inversion–recovery method using a 180°–$t$–90°–$T$ pulse sequence[4] where $t$ is the time in s between 180° and 90° pulses, and the delay time $T$ was chosen to be at least five times that for the longest $^{13}$C-$T_1$ value measured.

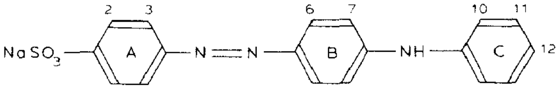
The substrates **1**, tropaeolin (**2**), and Metanil Yellow (**3**) studied have large association constants with $\alpha$CD, $\beta$CD, and $\gamma$CD ($10^4$–$10^5$ $\mathrm{M}^{-1}$)[5].The complexes were assumed to be 1:1, except the $\gamma$CD complexes which are mainly 2:1[5a,5b]. Unless otherwise stated, 0.1M host molecules were added to 0.1M guest molecules at 333 K. The mixtures were studied after agitating for 1 day. Assignments for each azo dye and CD have been reported[1,3].

## RESULTS AND DISCUSSION

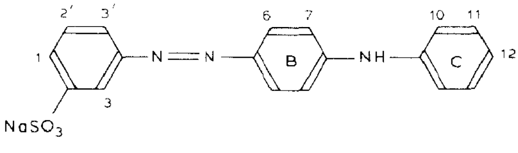
*Relaxation and correlation times.* — In the rapid exchange process of the sub-



**1** Methyl Orange



**2** Tropaeolin



**3** Metanil Yellow

strate, CD, and complex, and when the formation constant is large enough, the $T_1$ values are equal to those for a spin in the complex. For most organic molecules in the extreme narrowing condition, protonated carbon atoms are those that relax most easily and the dipole–dipole mechanism usually dominates the process. If the overall molecular re-orientation is isotropic, $^{13}C\text{-}T_1$ is given by

$$1/NT_1 = \hbar^2 \cdot \gamma_C^2 \cdot \gamma_H^2 \cdot r_{CH}^{-6} \cdot \tau_{eff} = \text{const} \cdot \tau_{eff}, \qquad (1)$$

where $N$ is the number of directly bonded protons, $\gamma_H$ and $\gamma_C$ are the gyromagnetic ratios of $^1H$ and $^{13}C$ nuclei, respectively, $r_{CH}$ is the length of the C–H bond, and $\tau_{eff}$ is the effective isotropic correlation time for overall molecular re-orientation[6]. Moreover,

$$\tau_{eff} = V_m \cdot \eta \cdot fr/kT, \qquad (2)$$

where $V_m$ is the molecular volume, $\eta$ is the viscosity of the solution in poise, $fr$ is a microviscosity factor, $k$ is Boltzmann's constant, and $T$ is the absolute temperature[7]. Equation *1* can be used for the analysis of the overall molecular re-orientation of CD and the substrate in the free state and might be applicable to the analysis of their molecular motions in the complexes[8].

An isotropic model which simplifies the molecular motion is useful for analysing $T_1$ and obtaining $\tau_{eff}$. Moreover, in the present work, as judged from the shape of the molecule and the experimental data, an azo dye is not expected to be isotropic, and an anisotropic system ought to be better. For monosubstituted benzenes, it is not usually possible to distinguish between rapid overall rotation around the $C_2$ molecular axis and internal spinning of the phenyl group around the carbon–substituent bond[9a]. For **1**–**3**, the above two motions can be distinguished. For an anisotropically overall-tumbling azo dye and for the groups undergoing additional internal motion, such as the phenyl group in azo dyes and the primary alcohol group in the CD, the $NT_1$ value of a carbon atom with $N$ directly bonded hydrogen atoms is given[6,10] by

$$1/NT_1 = \text{const} \cdot \tau_{eff}\,[A + B \cdot 6\tau_{II}/(6\tau_{II} + \tau_{eff}) + C \cdot 3\tau_{II}/(3\tau_{II} + 2\tau_{eff})] \qquad (3)$$

and

$$1/NT_1 = \text{const} \cdot \tau_{eff}\,[A + B \cdot 6\tau_G/(6\tau_G + \tau_{eff}) + C \cdot 3\tau_G/(3\tau_G + 2\tau_{eff})], \qquad (4)$$

where $\tau_{II}$ is the correlation time for the rotation around the long molecular axis, $\tau_G$ is the correlation time for additional internal motion, and

$$A = 1/4(3\cos^2\theta - 1)^2,\ B = 3\sin^2\theta\cos^2\theta,\ \text{and}\ C = 3/4\sin^4\theta,$$

TABLE I

$^{13}$C RELAXATION TIMES ($T_1$) FOR CDs, AZO DYES, AND THEIR COMPLEXES AT 333 K (125 MHz)

| *Compound*[a] | $NT_l(s)$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *C-1* | *C-2* | *C-3* | *C-4* | *C-5* | *C-6* | $\langle NT_l\rangle_{1/5}$[b] | *MeO-2* | *MeO-3* | *MeO-6* |
| αCD | 0.37 | 0.38 | 0.38 | 0.36 | 0.37 | 0.53 | 0.37 | | | |
| **2**-αCD | 0.31 | 0.30 | 0.31 | 0.34 | 0.38 | 0.36 | 0.33 | | | |
| **3**-αCD | 0.28 | 0.32 | 0.25 | 0.31 | 0.31 | 0.30 | 0.29 | | | |
| βCD[c] | 0.33 | 0.34 | 0.35 | 0.36 | 0.34 | 0.42 | 0.34 | | | |
| **1**-βCD | 0.25 | 0.30 | 0.30 | 0.29 | 0.31 | 0.40 | 0.29 | | | |
| **2**-βCD | 0.28 | 0.30 | 0.31 | 0.31 | 0.31 | 0.34 | 0.30 | | | |
| DM-βCD[d] | 0.33 | 0.34 | 0.33 | 0.30 | 0.32 | 0.38 | 0.32 | 4.38 | | 4.44 |
| **1**-DM-βCD | 0.28 | 0.29 | 0.26 | 0.27 | 0.29 | 0.34 | 0.28 | 3.99 | | 4.47 |
| **2**-DM-βCD | 0.26 | 0.27 | 0.29 | 0.28 | 0.24 | 0.32 | 0.27 | 3.48 | | 3.93 |
| TM-βCD[e] | 0.23 | 0.28 | 0.25 | 0.24 | 0.25 | 0.28 | 0.25 | 3.06 | 2.85 | 3.30 |
| **1**-TM-βCD | 0.25 | 0.31 | 0.27 | 0.25 | 0.27 | 0.32 | 0.27 | 3.51 | 3.09 | 3.87 |
| γCD | 0.33 | 0.35 | 0.35 | 0.34 | 0.34 | 0.40 | 0.34 | | | |
| **1**-γCD | 0.28 | 0.30 | 0.28 | 0.27 | 0.25 | 0.30 | 0.28 | | | |
| | | *C-2* | *C-3* | | | *C-6* | *C-7* | *Me* | | |
| **1**[f] | | 0.76 | 0.74 | | | 0.58 | 0.59 | 6.81 | | |
| **1**-βCD | | 0.53 | 0.56 | | | 0.49 | 0.51 | 6.30 | | |
| **1**-DM-βCD | | 0.54 | 0.54 | | | 0.42 | 0.45 | 6.69 | | |
| **1**-TM-βCD | | 0.43 | 0.40 | | | 0.33 | 0.33 | 5.31 | | |
| **1**-γCD | | 0.34 | 0.37 | | | 0.33 | 0.35 | 3.87 | | |
| | | *C-2* | *C-3* | | | *C-6* | *C-7* | *C-10* | *C-11* | *C-12* |
| **2**-αCD | | 0.65 | 0.61 | | | 0.60 | 0.64 | 1.42 | 1.32 | 0.62 |
| **2**-βCD | | 0.72 | 0.69 | | | 0.48 | 0.50 | 0.88 | 0.80 | 0.46 |
| **2**-DM-βCD | | 0.41 | 0.41 | | | 0.29 | 0.33 | 0.45 | 0.45 | 0.22 |
| | *C-1* | *C-3* | *C-2'* | *C-3'* | | *C-6* | *C-7* | *C-10* | *C-11* | *C-12* |
| **3**[g] | 0.23 | 0.33 | 0.31 | 0.26[i] | | 0.30 | 0.31 | 0.50 | 0.51 | 0.31 |
| **3**-αCD | 0.26 | 0.37 | 0.71[h] | 0.33[i] | | 0.37 | 0.40 | 0.77 | 0.71 | —[j] |

[a] See formulae for the numbering of **1**–**3**; **2** is solubilised only on the formation of complexes. [b] Mean values for C-1/5. [c] Measured at 0.05M. [d] Measured at 307 K. [e] Measured at 0.07M and 307 K. [f] When D-glucose was added instead of the CD, the $NT_1$ values of the azo dyes did not change. [g] 0.3M Solutions were used in order to obtain the best S/N ratio, because higher accuracy of the $T_1$ values was required in order to compare the correlation times by the isotropic and anisotropic models. [h] Overlapped with C-11. [i] The $T_1$ values become less because this position is *para* to the $SO_3Na$ group. [j] Too broad to measure the $T_1$ value.

where $\theta$ is the angle between the C–H vector and the axis of the rotation. For a methyl group undergoing an additional internal motion on an isotropic overall motion, the $NT_1$ value of a carbon with 3 directly bonded hydrogen atoms is given[11] by

$$1/NT_1 = \text{const}\,[\mathrm{A}/6D + \mathrm{B}/(6D + R_{\text{int}}) + \mathrm{C}/(6D + 4R_{\text{int}})], \tag{5}$$

where $D$ and $R_{\mathrm{int}}$ are the isotropic and internal rotational diffusion constants, respectively. For a methyl group undergoing free rotation where $R_{\mathrm{int}}$ greatly exceeds $D$, $1/T_1$ is reduced to 1/9 of the value for a rigidly attached methyl group (*i.e.*, for methyl group geometry, A becomes 0.111 in equation *5*). For rapid motion, $1/T_1$ is proportional to $0.111/6D$, and, for no rotation, $1/T_1$ is proportional to $1/6D$.

Table I shows the $^{13}$C-$NT_1$ values for CDs, azo dyes, and the complexes. For free and complexed CDs, the $NT_1$ values for the ring carbon atoms (C-1/5) are nearly equal in each system, indicating the absence of specific rapid internal motion in the pyranose ring. Thus, the mean value $\langle T_1\rangle_{1/5}$ can be used to calculate the effective correlation time for isotropic overall molecular re-orientation of a CD, using equation *1*. The larger $NT_1$ values indicate rapid internal rotation of the $CH_2OH$ group of the CD and all of the MeO groups of DM-βCD and TM-βCD. The $\tau_G$ value for the internal rotation of the $CH_2OH$ group was estimated from $\tau_{\mathrm{eff}}$ for the mean value of $T_1$ of C-1/5 of the pyranose ring and the $T_1$ value of the $CH_2OH$ group, using equation *4*. The $NT_1$ values of the MeO groups in TM-βCD are in the order MeO-6>MeO-2>MeO-3. That of MeO-3 is always the lowest, suggesting that it is situated in the crowded interior of the cavity.

**1**, the average $T_1$ value of the carbon atoms in ring A is 1.1–1.3 times greater than that of carbon atoms in ring B. In **2** and **3**, the average $T_1$ value of C-10 and C-11 in ring C is 1.5–2.0 times greater than that of the carbon atoms in ring B. In **3**, the $T_1$ value of C-1 in ring A is smaller than the average $T_1$ values of C-2′ and C-3 in ring A and of the carbon atoms in ring B[9b]. This situation arises because the azo dyes can be approximated to rod-shaped molecules which, in solution, tumble anisotropically overall with additional internal motions. In order to estimate the anisotropic overall molecular motion of **3**, equation *3* was used. The long molecular axis was approximated to coincide with the (C-1)–H bond. Rotation does not modulate the $T_1$ value of C-1, since $\theta$ is zero and equation *3* is reduced to equation *1*. The $\tau_{\mathrm{II}}$ value of **3** was estimated to be $20 \times 10^{-11}$ s from $\tau_{\mathrm{eff}}$ for C-1 and the average $T_1$ value of C-2′ and C-3 in ring A and of the carbon atoms in ring B[10b]. On the other hand, when **3** was assumed to be pseudoisotropic, $\tau_{\mathrm{eff}}$ was calculated from equation *1* to be $16 \times 10^{-11}$ s by adopting the average $T_1$ value of the carbon atoms in ring B (the smallest $T_1$ values in each azo dye) as representative of the overall molecular reorientation having little contribution from internal rotation. Both $\tau$ values for **3**–αCD were the same ($13 \times 10^{-11}$ s). For **1** and **2**, C-1 does not have an attached proton and a more elaborate model has to be used. Finally, all azo dyes were assumed to be pseudo-isotropic and $\tau_{\mathrm{eff}}$ was used instead of $\tau_{\mathrm{II}}$. For ring C in **2** and **3**, the $T_1$ values of C-10 and C-11 are 1.6–2.0 times greater than that of C-12. This fact also suggests the existence of anisotropic internal rotation of the phenyl residue, and the $\tau_G$ value was estimated from the $\tau_{\mathrm{eff}}$ value for C-12 and the average $T_1$ value of C-10 and C-11, using equation *4*.

TABLE II

ROTATIONAL CORRELATION TIMES ($\tau_{eff}$ AND $\tau_G$) OF CDs, AZO DYES, AND THEIR COMPLEXES[a], AND MOTIONAL STATES OF AZO DYES IN CDs

| *Compound*[b] | *Correlation times* ($10^{-11}$ *s*) | |
|---|---|---|
| | *CD overall* ($\tau_{eff}$)[c] | *$CH_2OH$ internal* ($\tau_G$) |
| αCD | 13 | 12 |
| **2**–αCD | 15 (1.2) | 65 (5.4) |
| **3**–αCD | 17 (1.3) | — |
| βCD | 14 | 30 |
| **1**–βCD | 17 (1.2)[d] | 21 (0.7)[d] |
| **2**–βCD | 16 (1.1)[d] | 64 (2.1)[d] |
| DM-βCD | 14[e] | 36[e] |
| **1**–DM-βCD | 18 (1.3) | 30 (0.8) |
| **2**–DM-βCD | 18 (1.3) | 44 (1.2) |
| TM-βCD | 18[e] | 56[e] |
| **1**–TM-βCD | 18 (1.0) | 44 (0.8) |
| γCD | 14 | 42 |
| **1**–γCD | 18 (1.3) | 78 (1.9) |

| *Compound*[f] | *Substrate overall* ($\tau_{eff}$)[g] | *Phenyl internal* ($\tau_G$) | $\tau_{CD\text{-}dye}/\tau_{CD\text{-}dye}$ |
|---|---|---|---|
| **1** | 8 | | |
| **1**–βCD | 10 (1.3) | | 0.6 |
| **1**–DM-βCD | 11 (1.4) | | 0.6 |
| **1**–TM-βCD | 15 (1.9) | | 0.8 |
| **1**–γCD | 14 (1.8) | | 0.8 |
| **2**–αCD | 8 | 2 | 0.5 |
| **2**–βCD | 10 | 4 | 0.6 |
| **2**–DM-βCD | 16 | 6 | 0.9 |
| **3** | 16 | 7 | |
| **3**–αCD | 13 (0.8) | 4[h] | 0.8 |

[a]The values in parentheses are the ratios of the correlation times of the complexed and free states. [b]The calculated values correspond to the CDs. [c]Calculated by using the mean values of $T_1$ for C-1/5. [d]The concentration of βCD was 0.05M (saturated) and that of the complex was 0.1M. [e]Values were estimated at 333 K, using equation *2*. [f]The calculated values correspond to **1**–**3**. [g]Calculated by using the mean values of $T_1$ for the carbon atoms of ring B in Table I. [h]The signal of C-12 was too broad to obtain a $T_1$ value. The average $T_1$ value of C-6 and C-7 was estimated instead of that of C-12.

*Effects of the formation of complexes on the molecular motion of CDs and azo dyes.* — The rotational correlation times of CDs, azo dyes, and the complexes, the ratios of the complex and free states, and the motional states of azo dyes in CDs are shown in Table II. Most $\tau$ values for CDs and azo dyes increase on the formation of complexes, which is due to increases in apparent molecular volumes as expected from equation *2*.

Increases in the molecular volume of CDs do not cause a large change in $\tau_{eff}$ ($13–18 \times 10^{-11}$ s), but increase $\tau_G$ ($12–56 \times 10^{-11}$ s) of the $CH_2OH$ (Me) group.

The ratios of the complex to the free states are 1.0–1.3 for $\tau_{eff}$ and 0.7–5.4 for $\tau_G$. A detailed investigation of $\tau_G$ values indicated that the formation of complexes reduces the internal rotation of the $CH_2OH$ groups, but not that of the $CH_2OMe$ group. In azo dyes, the formation of complexes increases $\tau_{eff}$ except in the case of the **3**-series.

In the **1**-series, **1** rotates 1.3–1.9 times slower in the complex than in the free state. The $\tau_{eff}$ values are in the order TM-βCD~γCD>DM-βCD~βCD ($15 \sim 14 > 11 \sim 10 \times 10^{-11}$ s), which reflects the crowded conditions in the interior of the cavities of **1**–TM-βCD and **1**–γCD.

The $NT_1$ values of the methyl group in **1** in the free and the complexed states are 11~15 times larger than those of the carbon atoms in ring B. The $NT_1$ values are in the order γCD < TM-βCD < βCD~DM-βCD~**1** ($3.9 < 5.3 < 6.3 \sim 6.7 \sim 6.8 \times 10^{-11}$ s) and give the same information as the $\tau_{eff}$ values. The methyl group is always decoupled from the aromatic ring and has free internal rotation as judged from equation 5. Molecular models show that the magnitude and the shape of **1** are most suited to the cavity of αCD (the $T_1$ values of this complex could not be determined because of precipitation). The $^{13}C$ chemical shift data suggested that **1** is included in the CD from the hydrophobic *N,N*-dimethylaniline side[1]. The $NMe_2$ group in the complexes of βCD and DM-βCD has the same $T_1$ value as that of free **1** and may extrude from the cavity.

In the **2**-series, $\tau_{eff}$ and $\tau_G$ of **2** in CDs are in the order DM-βCD>βCD~αCD ($16 > 10 \sim 8$ and $6 > 4 > 2 \times 10^{-11}$ s). The values are influenced more by the lengthening of the CD than by the inner diameter of the cavity. The $\tau_{eff}$ value is correlated with the viscosity of the solution by equation 2. The intrinsic viscosity of the CD increases with increasing volume and methyl substitution (αCD, 1.7; βCD, 2.2; γCD, 2.4; DM-βCD = TM-βCD = 3.0 [mL/mol]). Even when the above viscosities, approximated to those of their complexes, are taken into account, the $\tau$ values of **2** keep the same order. Moreover, in the αCD complexes, the $T_1$ values of the carbons of rings A and B have almost the same values and each ring is coupled. In the other complexes, the rings are not necessarily coupled. αCD may include **2** in a particular manner. All the $\tau_G$ values of ring C are always smaller than $\tau_{eff}$, indicating retention of rapid internal rotation even in the complex.

In the **3**-series, $\tau_{eff}$ for **3** is larger than that for the complex with αCD, suggesting strong self-association of **3** in solution in $D_2O$. This view is supported by the marked concentration-dependence of the observed $T_1$ values.

In the complexes, $\tau_{eff}$ values for azo dyes are smaller than those for the CDs; the ratios for azo dyes to CDs were 0.5–0.9; the azo dyes rotate up to twice as fast as the CDs. Lehn *et al.*[12] obtained ratios of 0.16–0.26 for the complexes of αCD with monosubstituted benzenes. The larger values noted above suggest restricted motion of the longer azo dyes included tightly in the CDs. The CDs and azo dyes rotate at almost the same speed when (*a*) the CD and azo-dye molecules are long, (*b*) the inside of the CD is substituted, (*c*) more than one azo dye is included in the cavity, and (*d*) the azo dye has the substituent *meta* and/or *ortho* to the azo group.

## REFERENCES

1 M. Suzuki, Y. Sasaki, J. Szejtli, and E. Fenyvesi, *J. Incl. Phenom.*, 5 (1987) 459–468.

2 M. Suzuki, E. Fenyvesi, M. Szilasi, J. Szejtli, M. Kajtar, B. Zsadon, and Y. Sasaki, *J. Incl. Phenom.*, 2 (1984) 715–724.

3 M. Suzuki and Y. Sasaki, *Chem. Pharm. Bull.*, 27 (1979) 609–619.

4 F. Freeman and H. D. W. Hill, *J. Chem. Phys.*, 53 (1970) 4103–4105.

5 (*a*) H. Hirai, N. Toshima, and S. Uenoyama, *Polym. J.*, 13 (1981) 607–610; (*b*) R. J. Clarke, J. H. Coates, and S. Lincoln, *Carbohydr. Res.*, 127 (1984) 181–191; (*c*) M. Komiyama, E. Hirai, and K. Kobayashi, *Proc. Symp. Cyclodextrins, 5th, Kyoto,* 1986, p. 12; (*d*) J. Pitha, L. Szente, and J. Szejtli, in S. D. Bruck (Ed.), *Controlled Drug Delivery,* Vol. 1, CRC Press, Boca Raton, FL, 1983, p. 124.

6 A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 55 (1971) 189–198.

7 U. Edlung, C. Holloway, and G. C. Levy, *J. Am. Chem. Soc.*, 98 (1976) 5069–5073.

8 Y. Inoue, Y. Katono, and R. Chujo, *Bull. Chem. Soc. Jpn.*, 52 (1979) 1692–1697.

9 G. C. Levy, *Topics in $^{13}C$ NMR Spectroscopy,* Wiley–Interscience, New York, 1974 (*a*) p. 116, (*b*) p. 115.

10 D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, 56 (1972) 3683–3689.

11 D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *J. Chem. Phys.*, 50 (1969) 719–721.

12 J. P. Behr and J. M. Lehn, *J. Am. Chem. Soc.*, 98 (1975) 1743–1747.