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Temperature Dependence of the Lanthanide-Induced Shifts, Structure, and Dynamics of Adducts of Quinuclidine and $Ln(fod)_3$ Chelates As Studied by Variable-Temperature NMR Shift and Relaxation Measurements

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Abstract: $Yb(fod)_3$ (L) and quinuclidine (S) form 1:1 adducts (LS). In the 300-MHz ^1H NMR spectra slow exchange of S between the free and bound state takes place via an associative mechanism: $S^* + LS \rightarrow S^*LS \rightarrow LS^* + S$. From the average lifetimes of S and LS as a function of temperature the activation enthalpy and entropy for this process were determined to be $\Delta H^* = +23.9$ kJ mol^{-1} and $\Delta S^* = -64$ J mol^{-1} K^{-1}. Besides Bleaney's T^{-2} term, considerable contributions of higher order T^{-n} ($n \geq 3$) terms are needed to describe the temperature dependence of the experimental pseudocontact shifts. It is shown that in order to get structural information, shifts obtained from the slow-exchange region are more reliable than those obtained from the fast-exchange region. The Yb–N distance determined from the shifts (in the slow-exchange region), 2.63 Å, agrees well with literature data and also with the Gd–N distance determined from ^1H (2.56 Å) and ^{13}C (2.50 Å) longitudinal relaxation measurements.

Lanthanide shift reagents (L) have become valuable tools in NMR spectroscopy.[1] First of all these reagents have found widespread use in the separation of overlapping multiplets in NMR spectra of organic compounds, S, able to act as ligands. In addition, information on molecular structure in solution can be obtained by fitting the pseudocontact contribution to the shift of S nuclei in a LS complex to the McConnell–Robertson equation.[2] Usually one deals with the fast-exchange region, where the measured shift is the weighted average of the shifts of S in the free and complexed states. Therefore, the evaluation of bound shifts (the shift of S in the LS complex relative to free S) requires knowledge of the equilibria involved in the complexation of S with L. For example, for $Ln(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) shift reagents several complexes L_mS_n should be envisaged with $m \geq 1$ and $n \geq 0$.[3,4] It is rather difficult to extract reliable values for the bound shifts and equilibrium constants from measured shift data as a function of the ratio L_0/S_0 (the molar ratio of added L and S) if two or more equilibria are involved.[5-7] If, e.g., only LS and LS_2 adducts are formed, already shift measurements over a large L_0/S_0 range are needed.[7] As a consequence it is difficult to circumvent measurements at high $Ln(fod)_3$ concentrations. At these concentrations complex exchange and self-association phenomena of $Ln(fod)_3$ may take place.[5] On the other hand, the use of relative bound shifts, which usually are obtained from data at low L_0/S_0 ratios, may lead to other compolications.[8] Probably the best way to determine bound shifts is a direct measurement of these shifts in the slow-exchhange region. There the measurements can be performed under conditions where the self-association of L can be neglected (low L_0/S_0 ratio). An additional advantage is that in the slow-exchange region usually the separation of the various signals in the LS/LS_2 part of the ^1H NMR spectrum is optimal. Molecules S with internal motions may form adducts which may occur as several rotamers. This would complicate the analysis. Therefore quinuclidine, see Figure 1, was chosen as the substrate S: it is a rigid molecule with a threefold symmetry axis. Moreover, it forms very stable complexes with $Ln(fod)_3$.

In the present study first the exchange process of S between free S and LS will be investigated. The activation parameters concerned are determined. Then the bound shift and its temperature dependence are discussed. In the literature[9-13] still some controversy exists about the temperature dependence of the shifts, and so there is a need of experimental data to check the theory. In the slow-exchange region this dependence is not influenced by the temperature dependence of the equilibrium constants involved, so one gets more reliable data.

Finally, the Gd–N distance is determined from relaxation time measurements and compared with the Yb–N distance obtained from the bound shifts.

Experimental Section

The synthesis of $Ln(fod)_3$, sample preparation, and measurement of the ^1H and ^{13}C relaxation rates are described elsewhere.[6] For the temperature-dependent shift and exchange rates, for the ^1H T_1, for the ^{13}C T_1, and for the exchange rate measurements as a function of the L_0/S_0 ratio samples were prepared with the following quinuclidine concentration and L_0/S_0 ratio: 0.23 M and $L_0/S_0 = 0.514$; 0.25 M and $L_0/S_0 = 3 \times 10^{-4}$; 2.75 M and $L_0/S_0 = 1 \times 10^{-4}$; 0.17 M with $L_0/S_0 = 0.19$, 0.33, and 0.57, respectively. The solvent was $CDCl_3$ (Uvasol, Merck). Quinuclidine (Aldrich) was purified by sublimation (110 °C (760mmHg)). Bicyclo[2.2.2]octane was synthesized by hydrogenation of bicyclo-[2.2.2]octene[14] at 1 atm and 40 °C with 5% Pt/C as the catalyst and ethyl acetate as solvent. After the hydrogen uptake ceased, the catalyst was filtered off, and from the filtrate the solvent was distilled off to yield the desired compound quantitatively. Further purification was achieved by sublimation at 70 °C (17mmHg).

The temperature was determined by methanol and ethylene glycol samples, using the graphs of van Geet.[15] The accuracy is ±1 °C.

The NMR measurements were performed on a Varian XL-100, a Varian CFT-20, and a home-built 300-MHz spectrometer.[16] The

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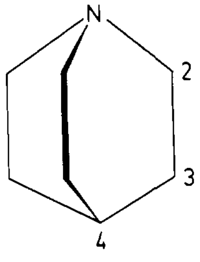

Figure 1. Quinuclidine.

chemical shifts of free quinuclidine, 2.79, 1.47, and 1.64 ppm for the 2, 3, and 4 protons, respectively, were temperature independent in the range studied (207–324 K). Over this whole range the 300-MHz spectra were in the slow-exchange region as to the exchange of quinuclidine between the free and complexed state. It was checked at the highest temperature (324 K) with an exchange simulation program that for the absolute bound shift could be taken the distance between the signals of complexed and free S in the spectrum. In this way only at the highest temperatures are small, negligible errors introduced in the bound shifts, due to the fact that the free and complexed S signals come closer to each other as a result of exchange upon approaching the intermediate-exchange region. Peak areas were determined with a planimeter. Exchange rates were determined by means of transient magnetization transfer[17] and line-broadening measurements. In the first method a selective π pulse is given to either free or bound S. The relaxation following the pulse is bi-exponential.[17] From the combined recovery data of the 2 and 3 protons the relaxation times, T_1, in the absence of exchange and the average lifetimes of free and bound S were determined. As in the case of the line width measurements only the signals of protons 2 and 3 were used, because the signal of proton 4 is relatively weak. Determination of lifetimes from line widths gave some problems. At higher temperatures the free S protons overlapped due to strong line broadening, at lower temperatures they gave rise to partially resolved multiplet spectra (AA′XX′Y spin system) which complicated the determination of the line broadening due to exchange. For the bound S protons these problems did not occur because their chemical shift differences were much larger and because the multiplet structure was washed out due to the short relaxation times. The latter dominated now the line width in the absence of exchange, and because they were known from the transient magnetization transfer experiments, they were used to calculate the line broadening due to exchange using eq 5 (see next section). As shown before[6] it is very important to get a good estimate of the intermolecular contribution to the relaxation, T_1^{-1} (inter), when the Gd–N distance is to be determined from relaxation rate enhancement (RE) measurements, using Gd(fod)$_3$ as a relaxation reagent. For the ^{13}C experiments T_1^{-1} (inter) was found by measuring the RE value of the reference compound bicyclo[2.2.2]octane (which resembles quinuclidine very much in shape and size) upon addition of Gd(fod)$_3$. In the proton experiments the small CHCl$_3$ peak (isotopic impurity in the solvent) was used for this purpose. Moreover, T_1^{-1} (inter) was determined by fitting calculated relaxation rates to experimental relaxation rates, using eq 7 (see next section) with T_1^{-1} (inter) and the Gd–N distance as variables. The T_1^{-1} (inter) value found in this way (0.07 s^{-1}) was used in further calculations and agreed reasonably well with the RE value of the CHCl$_3$ peak (0.06 s^{-1}).

Results and Discussion

The shift and lifetime measurements as a function of temperature were performed at 300 MHz on the degassed sample of quinuclidine and Yb(fod)$_3$ with the L_0/S_0 ratio of 0.514. Below about 320 K only two sets of quinuclidine signals were observable, one set of free S, and at a lower field one set of S complexed to the shift reagent L. The latter signals may arise from LS, or LS$_2$, or the narrow exchange signal of a fast LS/LS$_2$ equilibrium. From the temperature dependence of the line widths of these signals and from the ratios of the peak areas in the spectrum and the L_0/S_0 value, it was concluded that besides free S mainly the 1:1 complex LS was present. Most times LS$_2$ complexes are observed for lanthanide shift reagents with fod as ligands.[18] The presence of a 1:1 complex is, however, in agreement with results of Evans et al.[18] who reported a 1:1 adduct between Eu(fod)$_3$ and triethylamine. The steric demands of the latter compound with respect to adduct formation are comparable with those of quinuclidine. Only one set of L signals was present (L complexed as LS), so self-association of L, which may occur at higher concentrations,[5] was not observable. Moreover, the association constant for LS formation, *K*, is so large that only a lower limit for *K* can be determined from the spectrum. If it is assumed that the peak areas can be measured with an accuracy of 5%, it follows that *K* is at least 86 L mol^{-1}.

The Exchange Process. The line width of the S and LS signals increases with temperature, which means that exchange of S takes place between the free and complexed state. At 320 K the spectrum is still in the slow-exchange region (at 300 MHz), but at higher temperatures the lines become so broad that reliable measurements of peak positions and line widths can hardly be performed. The two most likely mechanisms expected for the exchange process[18-20] are the associative

$$S^* + LS \underset{k}{\overset{k_-}{\rightleftharpoons}} S^*LS \underset{k_-}{\overset{k}{\rightleftharpoons}} LS^* + S \qquad (1)$$

$$k_- \gg k$$

and the dissociative mechanisms

$$LS \underset{k_1}{\overset{k_{1-}}{\rightleftharpoons}} L + S\ (+S^*) \underset{k_{1-}}{\overset{k_1}{\rightleftharpoons}} LS^*\ (+S) \qquad (2)$$

$$k_{1-} \gg k_1$$

By determining the average lifetime of S and LS, τ_S and τ_{LS}, respectively, as a function of the quantities L_0 and S_0, it is possible to differentiate between these two mechanisms.[20] From eq 1 and 2 immediately follows

associative mechanism:

$$\tau_S^{-1} = k[LS] \quad \tau_{LS}^{-1} = k[S] \qquad (3)$$

dissociative mechanism:

$$\tau_S^{-1} = k_{1-}[L] \quad \tau_{LS}^{-1} = k_1 \qquad (4)$$

If the slow-exchange region holds for the line width $\Delta\nu_{1/2}$

$$\Delta\nu_{1/2} = \Delta\nu_{1/2}(0) + \frac{1}{\pi\tau} \qquad (5)$$

$\Delta\nu_{1/2}(0)$ is the line width in the absence of exchange. Since $K \gg 1$, $[LS] \simeq [L_0]$, $[S] \simeq [S_0] - [L_0]$, and $[L] \simeq 0$, in the range where $L_0/S_0 < 1$. A plot of the line broadening vs. $[L_0]$ will therefore give a straight line with slope k, $-k$ and $-k$ for the quinuclidine signals of S and LS and for the Yb(fod)$_3$ signals of LS, respectively, in the case of an associative mechanism. For a dissociative mechanism the line widths of S and L in the LS complex are indepent of $[L_0]$, while the broadening of free S due to exchange is very small. Measurements of the line widths at 100 MHz and 233 K showed that in the region where $\Delta\nu_{1/2}$ is dominated by exchange (exchange rate larger than 100 s^{-1}, $L_0/S_0 < 0.6$), and not by splittings due to *J* coupling the line broadening of free S and of S and L in LS varies linearly with $[L_0]$. So it can be concluded that an associative mechanism is mainly dealt with. Of course it is possible that at higher L_0/S_0 ratios the dissociative mechanism becomes also important, but due to self-association of L, measurements in this range were not possible. Since we are dealing with an associative mechanism, the average lifetimes of S in the free and complexed state are given by eq 3. These lifetimes were determined in the temperature range 207–324 K at 300 MHz by means of a transient magnetization transfer experiment and from line width measurements, as described in the Experimental Section. Activation parameters for the reaction rate constant *k* were determined by fitting all data, using eq 3, to Eyring equation. A plot is given in Figure 2. Because over the whole temperature range studied the ratios of the peak areas in the spectrum indicated that $K \gg 1$, $[L_0]$ and $[S_0] - [L_0]$ respectively, were used in place of [LS] and [S], in eq 3. Possible

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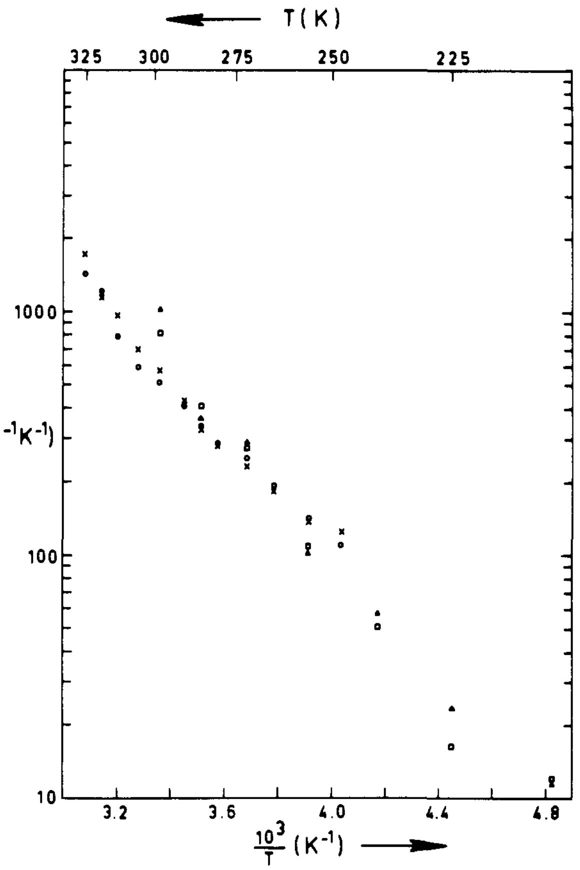

Figure 2. The average lifetime τ of free and bound quinuclidine, S and LS, respectively, as a function of temperature: × and ○, τ of proton 2 and 3 of LS, respectively, as determined from the line widths; △ and □, τ of LS and S, respectively, as determined from the magnetization transfer experiments on protons 2 and 3 of S and LS.

errors introduced in this way are much smaller than the uncertainties in the experimental τ values. The latter vary from 7 to 35%. The fit to the Eyring equation gave the following activation parameters

$$\Delta H^{\ddagger} = +23.9 \pm 2.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\ddagger} = -64 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$$

The negative $\Delta S^{\ddagger}$ value is in agreement with the associative mechanism, the loss of disorder upon association of two particles to the SLS intermediate.

Temperature Dependence of and Yb–N Distance from the Pseudocontact Shifts. In Figure 3 the bound shifts are given as a function of temperature. In general the shift consists of a diamagnetic and a scalar and dipolar (pseudoscalar) paramagnetic part. Measurements with the diamagnetic La^{3+} ion on similar compounds (see, e.g., ref 6) showed that the diamagnetic shift is in the range 0.0–0.3 ppm, so it can be neglected. The scalar part can also be neglected for Yb.[1] The good agreement found between the Yb–N distance determined from the shift and other Ln–N distances (vide infra) indicates that these approximations are justified.

X-ray[21] analysis of the adduct between quinuclidine and Eu(dpm)$_3$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dionate) shows that the adduct has threefold symmetry around the Eu–N bond. Since the chelating parts of dpm and fod are identical, the immediate surrounding of the Yb ion is the same in the Yb(fod)$_3$ and Yb(dpm)$_3$ quinuclidine adduct. Therefore we assume that, as to the susceptibility tensor, the Yb(fod)$_3$ quinuclidine complex also has threefold symmetry around the Yb–N bond. Anyway, if this is not the case, the complex will have effective axial symmetry due to internal reorientations.[22,23] The measured shifts of the combined quinuclidine protons two, three, and four are in perfect agreement with an axially symmetric model,[24] so this model is assumed here. According to Bleaney[9] the dipolar shift is given in this case by

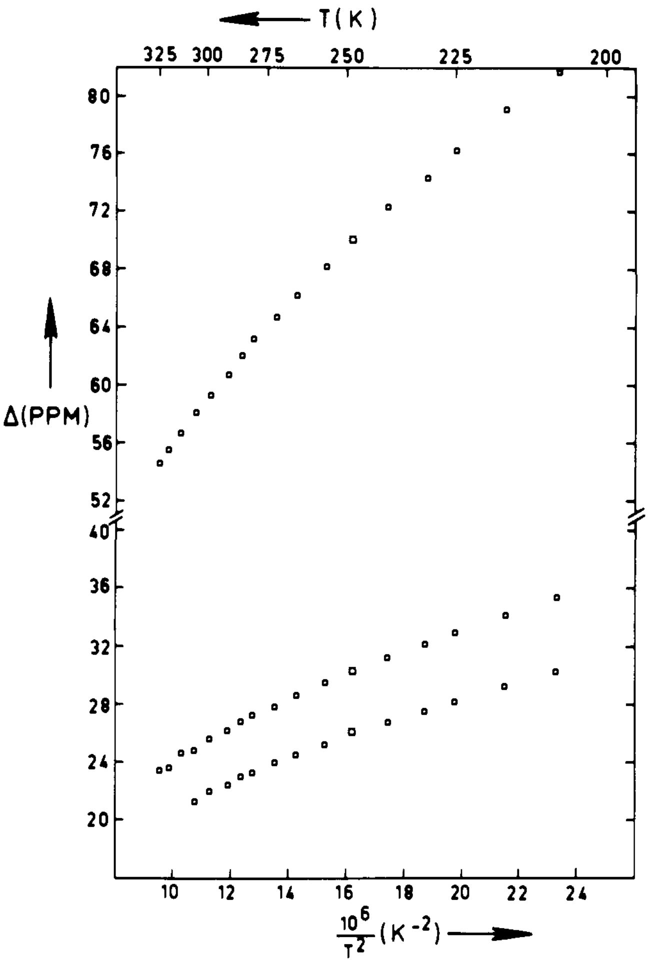

Figure 3. The pseudocontact shift, Δ, as a function of $1/T^2$ (K^{-2}). The shift decreases in the order of protons 2, 3, and 4.

$$\frac{\Delta\nu}{\nu} = \left[\frac{-\beta^2 J(J+1)(g_{\parallel}{}^2 - g_{\perp}{}^2)}{9kT} + \frac{g^2\beta^2 J(J+1)(2J-1)(2J+3)D_z}{60(kT)^2}\right]\frac{3\cos^2\theta - 1}{r^3} \quad (6)$$

β, J, g, $g_{\parallel}$, $g_{\perp}$, and k have their usual meaning, D_z is one of the principle values of the ligand field interaction tensor,[9] r is the internuclear distance between the Yb nucleus and the proton concerned, and θ is the angle between the Yb–N direction and the vector $\vec{r}$. The value of g and J can be calculated from the $^2F_{7/2}$ ground state of the Yb^{3+} ion. For the lanthanide ions except Sm^{3+} and Eu^{3+} the first term in eq 6 is zero,[9] because these ions, having high lying excited states, are in the ground state, resulting in an isotropic **g** tensor. A plot of the shift versus T^{-2} for Yb^{3+} should also be a straight line with intercept zero. Figure 3 shows that the experimental data are certainly not in agreement with this. A plot of the shifts vs. T^{-1}, however, is almost perfectly linear, in agreement with the results of other investigators.[1,3] Horrocks et al.[10] and Golding et al.[11] remarked that a considerable apparent T^{-1} dependence may occur, due to a composite of terms in T^{-2},

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(24) At 280 K, e.g., the experimental shifts are 63.22, 27.29, and 23.47 and the calculated ones 63.22, 27.17, and 23.43 ppm, respectively.

Table I. The Coefficients a_i and b_i of the Polynomial Expansion of the Temperature Dependence of the Pseudocontact Shift Δ^a

	proton number		
	2	3	4
a_1	13.96	5.79	4.63
$10^{-3}a_2$	−3.55	−1.43	−1.07
$10^{-6}a_3$	0.287	0.113	0.078
b_1	12.32	7.28	1.34
$10^{-3}b_2$	−2.30	−2.57	1.45
$10^{-6}b_3$	−0.027	0.399	--0.553
$10^{-9}b_4$	0.026	−0.023	0.052

[a] $\Delta = a_1/T^2 + a_2/T^3 + a_3/T^4$ and $\Delta = b_1/T^2 + b_2/T^3 + b_3/T^4 + b_4/T^5$.

T^{-3}, T^{-4}, ··· Therefore the experimental shift data were fitted to (1) $a_1T^{-2} + a_2T^{-3} + a_3T^{-4}$ and (2) $b_1T^{-2} + b_2T^{-3} + b_3T^{-4} + b_4T^{-5}$. The coefficients a_i and b_i are given in Table I (they depend except on the ligand field parameters also on the position of protons 2, 3, and 4 with respect to the Yb^{3+} nucleus in the LS complex). It is seen terms with $n \geq 3$ give considerable contributions to the shift, much larger than the 10–20% which are expected and reported in the literature.[1,9-12] For the 2 proton at 320 K, e.g., the contributions of the T^{-n} terms ($n \geq 3$) in the two cases mentioned above are (1) −80 and 21% and (2) −59, −2, and 7% of the T^{-2} term. With decreasing temperature these contributions strongly increase. From the coefficients a_1 and b_1 of the polynomial expansion for the shift of proton 2 values of 35.3 an 31.2 cm^{-1} were calculated for the ligand field splitting parameter D_z. These values are in the range of what is usually reported for D_z.[25] If the shift data are fitted to both terms of eq 6, the result is $g_\parallel^2 - g_\perp^2 = -0.75 \pm 0.05$ (it should be zero[9]) and $D_z = 0.016$ cm^{-1} which is 3 orders of magnitude too small.[25] So it can be concluded that Bleaney's theory describes the temperature dependence of our pseudocontact shift data reasonable if higher order terms T^{-n} ($n \geq 3$) are taken into account. The apparent T^{-1} dependence of the shifts is due to considerable contributions of these higher order terms. Possible causes for the larger contribution of higher order terms as compared to the expected 10–20% mentioned above are as follows. (1) Bleaney's relation with only the T^{-2} term is very aproximate. More complete calculational procedures[10,11] than the one used by Bleaney, However, showed it to be a very good approximation. (2) The ligand field parameter D_z is temperature dependent. This is very likely but probably not to such an extent as to be able to explain the differences. (3) Our experiments have been performed in the slow-exchange region as to the exchange of S, so the temperature dependence of the L–S association should not play a role. However, the fod ligands in the Yb(fod)$_3$ complex are still rapidly rearranging intramolecularly.[5] This may make the shift and also D_z temperature dependent. From the relative bound shifts (all the data of Figure 3 were used) the Yb–N distance was calculated by using the X-ray analysis data of Bye[21] on the structure of quinuclidine. A value of 2.633 Å ± 0.27% was found.[26] The quoted error is the 90% confidence interval of the F test. This value will be compared with Ln–N distances determined in other ways below. As shown above it is important to get reliable shifts in order to check, e.g., their temperature dependence. In general shifts determined from spectra in the fast-exchange region depend on ligand-exchange phenomena and stoichiometric equilibria. These facts may obscure the temperature dependence of the shifts. Processes in the slow-exchange region will not do so, and if only these kind of processes are present, the correct temperature dependence will be obtained. Therefore it is advisable to do shift measurements in this region. A second reason to do this is the fact that the relative bound shifts, which are important to get information about the geometry of the adduct, can be unrealistic in the fast-exchange region, as will be illustrated now. In the present 300-MHz study the spectra were in the slow-exchange region over the whole temperature range. Except for the four points at the highest temperature in Figure 3, the ratio of the shifts of protons two and three was 0.4326 ± 0.0010 over the whole range, resulting in a very reasonable Yb–N distance, *r*, of 2.63 Å. This ratio is in good agreement with the value of 0.424 obtained by Beautê et al.[27] in the fast-exchange region, using Yb(dpm)$_3$ and a 10% solution of quinuclidine in CCl$_4$. In a different[5] fast-exchange study (Yb(fod)$_3$, 2 M quinuclidine solution in CCl$_4$) a value of 0.38 was obtained, which gave an approximate solution for *r* of 3.6 Å. So as we have shown before,[5,6] great care is needed when fast exchange bound shifts are used to determine molecular geometries. If possible, slow-exchange data should be used. A possible reason for the different bound shift ratios in the three studies just mentioned will now be given. Several kinds of adducts L_mS_n ($m \geq 1$, $n \geq 0$) may be found in solution.[5] As one observes only one averaged signal in the fast-exchange region, the measured shift will be the weighted average of the shifts of the L_mS_n adducts. This may lead to wrong shift ratios if only a 1:1 LS adduct is taken into account. On the other hand, in the slow-exchange region this problem does not exist in principle because one can determine the bound shifts of each kind of adduct if its signals in the spectrum are visible and have been assigned. In our study only a 1:1 adduct was observable. In the two fast-exchange studies, however, the concentrations were about 10 times larger than in our case, favoring the formation of complexes L_mS_n ($m \geq 1$, $n \geq 0$). Beautê et al. used as a shift reagent Yb(dpm)$_3$, instead of Yb(fod)$_3$, which was used in the other two studies. The electron-donating character of the Yb ligands in the former compound is different from that in the latter one, resulting in less self-association. This may be the reason why Beautê's shift ratio is very close to the results in the present investigation.

Table II. Relaxation Rate Enhancements Relative to Proton and Carbon 2^a

	protons		carbon-13	
	exptl	calcd	exptl	calcd
2	1	1	1	1
3	0.0652	0.0652	0.111	0.113
4	0.0291	0.0287	0.080	0.078

[a] The calculated values were obtained by substituting the optimal Gd–N distance in eq 7.

Gd–N Distance from Proton and Carbon-13 Longitudinal Relaxation Times. Besides from the bound shifts, information about the geometry of the adduct can also be obtained from the longitudinal relaxation times, T_1, using Gd(fod)$_3$ as a relaxation reagent.[28] From the experimental relaxation rates it can be calculated that the T_1 value of proton 2, the quinuclidine proton with the smallest relaxation time in the Gd(fod)$_3$ quinuclidine adduct, is about 1.5×10^{-4} s. At the temperature where the relaxation experiments were performed, the average lifetime of the Yb(fod)$_3$ quinclidine adduct is about 5×10^{-4} s. In general the lifetime of lanthanide adducts decreases in the range Yb to La. Lenkinski et al.[29] e.g., showed that a Gd^{3+} complex with bleomycin has about a 50 times shorter lifetime than the Yb complex. Moreover, the concentration of free S was 2.3 and 26 (for ^1H and ^{13}C, respectively) times larger in the relaxation experiments as compared to the shift measurements, resulting according to eq 3 in corresponding shorter lifetimes for the Gd(fod)$_3$ quinuclidine adduct. So we may assume that the average life time

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(26) The distance was calculated by using the Yb–N distance, *r*, as the variable, while the Yb–N direction coincided with the C_4–N direction. If the Yb–N distance is calculated as described in ref 31, a sharp minimum in the plot of the crystallographic agreement factor, AF, vs. *r* should be an indication that *r* is determined accurately. Performing this calculation we found a minimum for $r = 2.6$ Å, while the slope at the AF vs. *r* plot is very steep for $r < 2.6$ Å and more flat for $r > 2.6$ Å. So the under bound of *r* seems to be determined accurately by means of the LIS measurements.

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of this adduct will be much smaller than the ^1H and ^{13}C T_1 values of quinuclidine in this adduct. Under these circumstances the relaxation rate enhancement, RE_i, of a certain quinuclidine nucleus i is given by[30]

$$RE_i = T_1{}^{-1}{}_i - T_1{}^{-1}(0)_i - T_1{}^{-1}(\mathrm{inter}) = K/R_i{}^6 \qquad (7)$$

$T_1{}^{-1}{}_i$ and $T_1{}^{-1}(0)_i$ are the relaxation rates of nucleus i in the presence and absence of $Gd(fod)_3$. $T_1{}^{-1}$(inter) is the contribution of Gd^{3+} ions to the relaxation of nucleus i, other than the intra $Gd(fod)_3$ quinuclidine adduct contributions. For the determination of this quantity see the Experimental Section. K is a constant containing gyromagnetic ratios and reduced spectral density functions,[30] R_i is the internuclear Gd–i distance. In Table II the relaxation rate enhancements relative to the enhancements of proton 2 or carbon 2 are given. After substituting the geometry of quinuclidine,[21] the Gd–N distance was found by determing the best fit of the calculated relaxation rates to the experimental ones, using eq 7. Gd–N distances of 2.56 and 2.50 Å were found from the ^1H and ^{13}C results, respectively. As show before[6] the Gd–N distance obtained is rather insensitive to random variations in the relaxation rate enhancements but very sensitive to the value of T_1(inter). A variation of 10% in T_1(inter) varied the Gd–N distance by 0.08 Å. Comparing the values of 2.50 and 2.56 Å with the Yb–N distance of 2.63 Å obtained from the bound shifts, the agreement is very good, contrary to what was found previously,[6] when shift measurements in the fast-exchange region were applied. The values of 2.50, 2.56, and 2.63 Å are also in very good agreement with the Eu–N distance of 2.50 Å in the $Eu(dpm)_3$ quinuclidine adduct as determined by x-ray analysis.[21] This once again emphasizes that bound shifts obtained in the slow-exchange region and relaxation rate enhancements give reliable structural information, whereas shifts obtained in the fast-exchange region might give unreasonable results. Unfortunately, it is often difficult or even impossible to reach the slow-exchange region. In these cases it may be useful to check structural data based on LIS measurements via measurements of ^1H and ^{13}C spin-lattice relaxation rate enhancements induced by $Gd(fod)_3$. These experiments can be performed under conditions where self-association is negligible ($L_0/S_0 < 10^{-2}$).

Conclusions

(1) Exchange of quinuclidine between the free and bound state takes place via an associative mechanism. (2) Except for Bleaney's T^{-2} term there are considerable contributions of higher order T^{-n} ($n \geq 3$) terms to the experimental pseudocontact shifts. (3) Pseudocontact shifts obtained from the slow-exchange region of NMR spectra are preferable to fast-exchange data in order to get structural information about the complex. (4) Ln–N distances determined from shift and ^1H and ^{13}C relaxation data agree well.

Registry No. S, 100-76-5; LS, 80327-79-3.

Supplementary Material Available: Tables with the bound shifts of the 2, 3, and 4 protons as a function of temperature, with the longitudinal relaxation and average lifetimes of free and bound quinuclidine as a function of temperature, and with the average lifetimes of bound quinuclidine as determined from the line widths of the 2 and 3 protons of bound S (3 pages). Ordering information is given on any current masthead page.

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Reaction of (9-Anthryl)arylmethyl Chlorides with Grignard and Lithium Reagents

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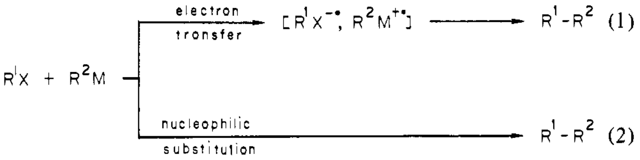
Abstract: We have investigated the reaction of (9-anthryl)arylmethyl chlorides **1a–d** (para substituent = MeO, Me, H, and Cl) with Grignard and lithium reagents. The variables are the structures of the alkyl group of Grignard and lithium reagents (alkyl group = *tert*-butyl, isopropyl, ethyl, methyl, and phenyl), solvent (diethyl ether and tetrahydrofuran), and presence or absence of additive (*p*-dinitrobenzene and $FeCl_3$). The products were a mixture of two alkylation products, **3** (coupling at C-α) and **4** (coupling at C-10), and three dimerization products, **5** (C_α–C_α coupling), **6** (C_α–C_{10} coupling), and **7** (C_{10}–C_{10} coupling), the composition being determined for each reaction.

Introduction

The reaction of alkyl halides with magnesium and lithium reagents has received attention lately with regard to mechanism.[1] Using stereochemistry and CIDNP as the most definitive indicators of mechanism, it has been confirmed that at least two reaction mechanisms, i.e., electron transfer (eq 1) and direct nucleophilic substitution (eq 2), are possible. Evidence is available for both mechanisms in individual cases. However, a delicate balance must exist between these mechanistic alternatives, and



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