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Structure and Dynamics of Guest Molecules in Cyclophosphazene Inclusion Compounds

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^{2}H NMR techniques are employed to study the structure and dynamics of guest molecules in cyclophosphazene inclusion compounds. A detailed analysis of the variable temperature NMR experiments provides quantitative information about the molecular mobility of the guest components within the cyclophosphazene channels. It is shown that the guest species are highly mobile displaying internal conformational motions and overall reorientational processes along with a considerable amount of dynamic disorder. For the overall motions a strong influence by the actual structure (or symmetry) of the organic guest molecules is registered.

Keywords: cyclophosphazene inclusion compounds; ^{2}H NMR spectroscopy

INTRODUCTION

Inclusion compounds can be formed by a variety of host compounds. Among these, cyclophosphazene derivatives have shown a particular potential to include organic guest molecules of quite different chemical structure.[1,2] X-ray investigations have proven that these systems - in analogy with urea and thiourea inclusion compounds - mainly build up hexagonal channel structures. Although cyclophosphazene inclusion compounds are known for years, so far little is

known about the specific molecular properties of the guest components in these systems.[1–3] Here, we report on a comprehensive ^2H NMR study on cyclophosphazene inclusion compounds which is addressed to the motional and ordering characteristics of the molecular guests over a large temperature range. The guest species examined here are selectively deuterated six-membered rings which are distinguished by their molecular symmetry. The analysis of the dynamic ^2H

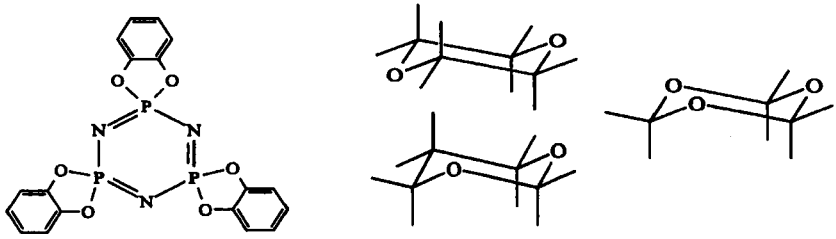

FIGURE 1 Chemical structures of the host and the guest components.

NMR experiments - comprising lineshape and relaxation measurements as well as 2D exchange experiments - provides a detailed picture about the molecular features of such guest components in cyclophosphazene inclusion compounds.

EXPERIMENTAL

Inclusion compounds of tris-(1,2-dioxyphenyl)-cyclotriphosphazene with various guest components, 1,3-dioxane-(2,2)-d_2, 1,4-dioxane-d_8 and 1,3,5-trioxane-d_6 (see Fig. 1), were prepared by standard procedures.[2,4] NMR measurements were performed on a Bruker CXP 300 spectrometer operating at a frequency of 46.07 MHz for deuterium. The ^2H NMR experiments above 90 K were done using a 5 mm home-built probe employing the quadrupole echo sequence with $\pi/2$-pulses of 2.7 μs width and a time interval between the pulses of 20 μs. For the low temperature ^2H NMR experiments ($T < 90$ K) a home-built NMR spectrometer (^2H frequency: 70 MHz) was used. Simulations have been performed using a FORTRAN simulation package developed to simulate the various types of dynamic NMR experiments.

RESULTS AND DISCUSSION

In the following we present dynamic ^2H NMR investigations on polycrystalline samples with deuterated 1,3-dioxane-(2,2)-d_2, 1,4-dioxane-d_8 and 1,3,5-trioxane-d_6 in cyclophosphazene inclusion compounds. Calorimetric measurements have shown that between 110 K and 370 K there are no solid-solid phase transitions. Fig. 2 presents ^2H NMR spectra of various cyclophosphazene inclusion com-

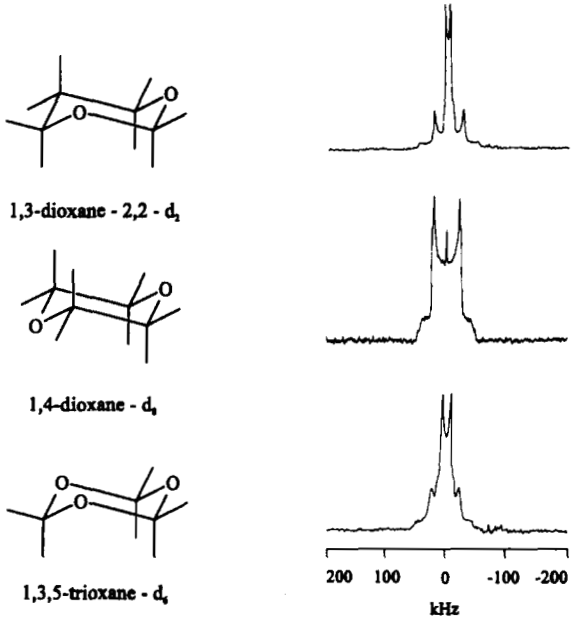

FIGURE 2 ^2H NMR spectra of three guest molecules in cyclophosphazene inclusion compounds.

pounds. At first sight the spectra recorded at about 200 K seem to be rather complex. They vary with the sample and appear as a superposition of two powder pattern. Moreover, the widths of the subspectra are rather small and indicate the presence of highly mobile guest molecules even at such low temperatures. Thus, for 1,3,5-trioxane-d_6 the splittings between the perpendicular singularities are found to 45 and 15 kHz while a completely rigid sample should show a splitting of about 120 kHz. It turned out that each spectrum reflects a single component system with fast overall reorientational motions ("fast motional

limit") of the guest species. At the same time, internal motions like the ring inversion process are on the slow NMR time-scale (rate constant $k < 10^3\ s^{-1}$). The highly anisotropic overall motions therefore give rise to a different averaging of the axial and equatorial deuterons along with a substantial degree of dynamic disorder. As a result, two subspectra are visible for all guest species at

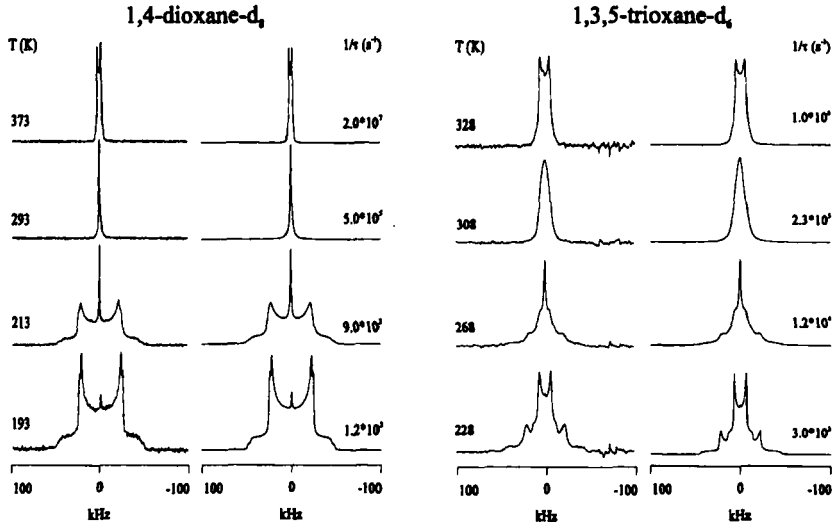

FIGURE 3 Experimental and theoretical ^2H NMR spectra of 1,3,5-trioxane-d_6 and 1,4-dioxane-d_8 in cyclophosphazene reflecting the influence of the ring inversion process ($1/\tau$: rate constant).

about 200 K. For the case of 1,3,5-trioxane-d_6 the larger splitting refers to the axial deuterons while the smaller splitting is due to the equatorial deuterons. It is interesting to note that the type of reorientational process varies with the guest molecule. Obviously, there is a close relationship between the type of overall motion and the actual symmetry of the guest component. Above 200 K a further thermally activated process sets in along with characteristic changes of the NMR lineshapes (see Fig. 3). This motion - assigned to the ring inversion process - is accompanied by a further averaging of the two subspectra. At higher temperature therefore only a single powder pattern remains. As can be taken from Fig. 3, a very good agreement between experimental and theoretical spectra

could be achieved on the basis of this motional process. A further independent proof for the model assumption can be taken from the 2D exchange experiments shown in Fig. 4. Here, characteristic exchange pattern (straight lines at distinct angles with respect to the diagonal) are observed which are typical for a chemical exchange process, i.e. mutual exchange between axial and equatorial

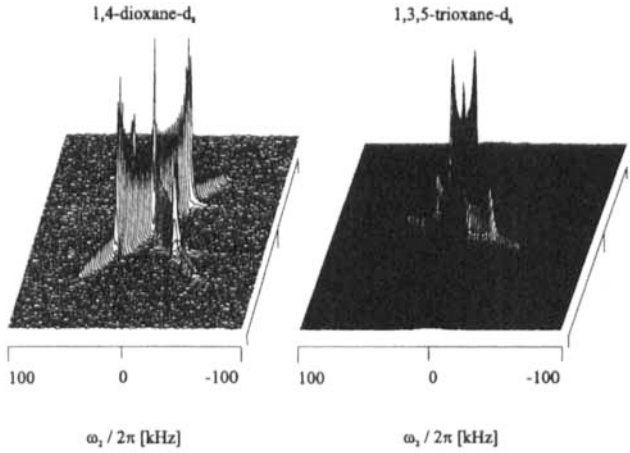

FIGURE 4 Experimental 2D exchange spectra of 1,3,5-trioxane-d_6 (208 K , τ_m = 30 ms) and 1,4-dioxane-d_8 (183 K, τ_m = 50 ms) in cyclophosphazene (τ_m: mixing time).

deuterons. The simulations of the temperature dependent lineshapes provided the rate constants of the ring inversion process. From this, the corresponding activation parameters have been calculated which were found to be very close the values reported from solution studies. For example, for 1,3,5-trioxane-d_6 in cyclophosphazene an activation energy of 49.9 kJ/mol is found while in solution the value is given to 48.9 kJ/mol.[5] A similar behaviour has been observed for the other guest components as well. These results imply that obviously the internal ring inversion process is less affected by the cyclophosphazene host matrix. The low temperature range (T < 180 K) again will be exemplarily discussed for the 1,3,5-trioxane-d_6/cyclophosphazene complex. In Fig. 5 representative spectra of this sample are given between 50 K and 120 K. The observed spectral changes can be traced back to three superimposed molecular processes: (i) rotation of the trioxane molecules about their C_3-symmetry axes which are oriented perpen-

dicular to the cyclophosphazene channel long axis, (ii) rotation of the molecules about the channel long axis, (iii) fast wobble motions of the molecules within the channels which give rise to some orientational disorder. Model simulations have shown that for the former process a rotational diffusion process is appropriate.

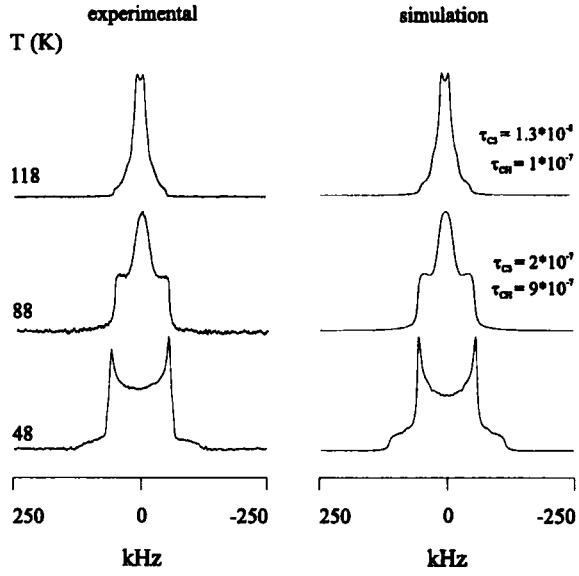

FIGURE 5 Experimental and simulated ^{2}H NMR spectra of 1,3,5-trioxane-d_6 in cyclophosphazene ($1/\tau_{C3}$ and $1/\tau_{CH}$ are rate constants for rotation about the molecular C_3- and channel axis, respectively).

The motion about the channel long axis can be best described by a three-fold jump process which also reflects the symmetry of the cyclophosphazene channels. The theoretical spectra obtained with these model assumptions (see Fig. 5) agree very well with their experimental counterparts. The same is true for the partially relaxed ^{2}H NMR spectra (quadrupole echo experiment), given in Fig. 6, which can be used as a further check for the underlying model assumptions. Such spectra are determined by the T_2-anisotropy and are very sensitive to both the type and time-scale of the responsible motional processes.[6] From the complete analysis of the available experimental data the rate constants for the overall

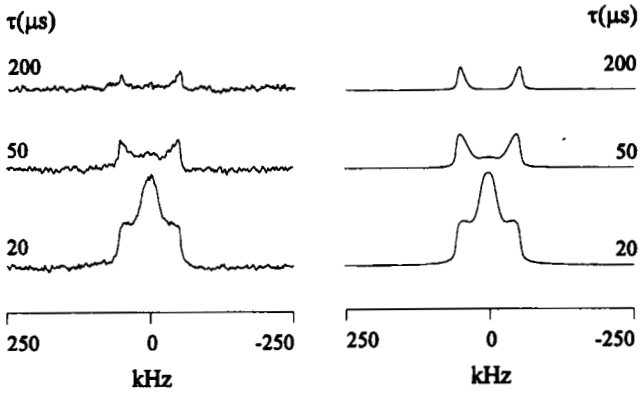

FIGURE 6 Partially relaxed ^2H NMR spectra of 1,3,5-trioxane-d_6 obtained with the quadrupole echo sequence at 88K (τ: delay time).

motions between 50 K and 120 K have been obtained which are summarized in the Arrhenius plot of Fig. 7. It can be seen that both rotational processes appear on a similar time-scale; their activation energies are found to be rather low with values of 7.2 kJ/mol (C_3-axis rotation) and 6.0 kJ/mol (rotation about the channel axis). This again suggests a low sterical hindrance of these overall motions by the cyclophosphazene host lattice. It should be noted that similar low activation energies for guest motions have been reported for other inclusion compounds as well.[7] In principle, the Arrhenius plot could be extended towards the faster range by analysing T_1-relaxation experiments. At present, such studies are under way along with the analysis of the low temperature data of other guest components.

CONCLUSIONS

The motional characteristics of six-membered rings in cyclophosphazene inclusion compounds have been determined employing ^2H NMR techniques. The experimental results gave evidence for the existence of both conformational and overall reorientational motions. The former process was found to be dominant in the high temperature range above 200 K while the latter determines spin relax-

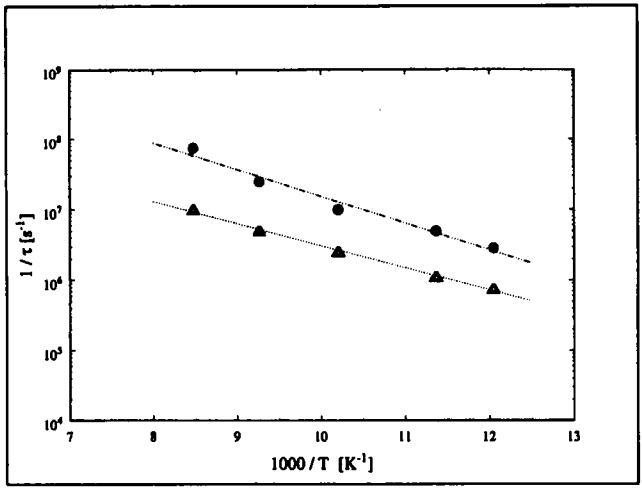

FIGURE 7 Arrhenius plot for the overall motions of 1,3,5-trioxane-d_6 in cyclophosphazene ($1/\tau_{C3}$ (•), $1/\tau_{CH}$ (△)).

ation below 200 K. Likewise, the data analysis provided information about the absolute orientation of the guests within the host channels. Further work along this line is in progress.

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References

[1.] J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds.) *Inclusion Compounds*, Vols. 1-3 Academic Press, New York (1984); Vols. 4 and 5 Oxford University Press, Oxford (1991).

[2.] H. R. Allcock, M. L. Levin and R. R. Whittle, *Inorg. Chem.*, **25**, 41 (1986).

[3.] E. Meirovitch, S. B. Ranavare, J. H. Freed, *J. Phys. Chem.*, **91**, 5014 (1987).

[4.] A. Liebelt and K. Müller, in preparation.

[5.] H. W. Spiess and H. Sillescu, *J. Magn. Reson.*, **42**, 381 (1982).

[6.] Z. Luz, R. Naor and E. Meirovitch, *J. Chem. Phys.*, **74**, 6621 (1981).

[7.] R. Poupko, E. Furman, K. Müller and Z. Luz, *J. Phys. Chem.*, **95**, 407 (1991).