Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Molecular Behaviour of Six-Membered Ring Guests in Cyclophosphazene Inclusion Compounds

Ansgar Liebelt [a] , Ioannis Tiritiris [a] & Klaus Müller [a]

[a] Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569, Stuttgart, Germany

Version of record first published: 24 Sep 2006

To cite this article: Ansgar Liebelt, Ioannis Tiritiris & Klaus Müller (2001): The Molecular Behaviour of Six-Membered Ring Guests in Cyclophosphazene Inclusion Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 527-537

To link to this article: http://dx.doi.org/10.1080/10587250108023731

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 527-537
Reprints available directly from the publisher
Photocopying permitted by license only

The Molecular Behaviour of Six-Membered Ring Guests in Cyclophosphazene Inclusion Compounds

ANSGAR LIEBELT, IOANNIS TIRITIRIS and KLAUS MÜLLER

Institut für Physikalische Chemie, Universität Stuttgart Pfaffenwaldring 55, D-70569 Stuttgart, Germany

The molecular behaviour of six-membered ring compounds in cyclophosphazene inclusion compounds is studied by dynamic ^{2}H NMR spectroscopy. The analysis of the variable temperature NMR experiments provides a detailed picture about the guest mobility as well as the ordering behaviour of the guest species in such systems. It is found that the guest dynamics is rather complex with various intramolecular and intermolecular motional contributions, both of which giving rise to dynamic guest disorder. The intermolecular motions are found to depend strongly on the particular guest compound and dominate the experimental NMR data in the low temperature range beyond 150 K.

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

INTRODUCTION

Cyclophosphazene derivatives are known to form inclusion compounds in the presence of suitable guest molecules and can be compared with the well-known urea and thiourea inclusion compounds.[1,2] On the one hand, cyclophosphazene inclusion compounds also build up hexagonal channel structures, as shown by various X-ray studies. On the other hand, the cyclophosphazene channels possess a greater flexibility than the urea channels in the sense that guest molecules of quite different chemical structure or constitution can be incorporated. In the following we report on an ongoing solid state ^2H NMR study that is addressed to the evaluation of the molecular properties of six-membered ring guests

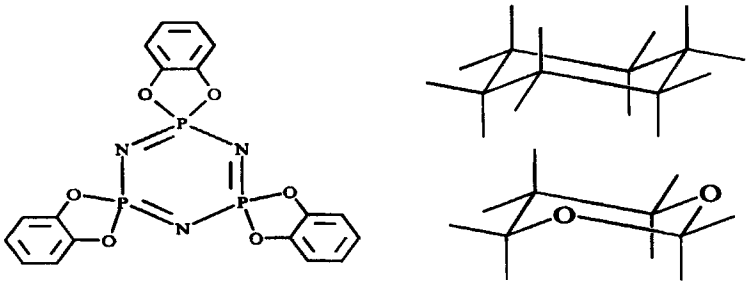

FIGURE 1 Chemical structures of the guest and host components.

in cyclophosphazene inclusion compounds.[3] It is shown that there exists a close relationship between the guest mobility and the actual structure of the guest molecules.

EXPERIMENTAL

Inclusion compounds of tris-(1,2-dioxyphenyl)-cyclotriphosphazene (see Fig. 1) with various guest components, cyclohexane-d_{12}, 1,3-dioxane-(2,2)-d_2 and 1,3-dioxane-(4,4)-d_2, were prepared by standard procedures.[2] ^{2}H NMR measurements were performed on a Bruker CXP 300 spectrometer operating at a frequency of 46.07 MHz for deuterium. The ^{2}H NMR experiments above 90 K were done using a 5 mm home-built probe employing the quadrupole echo sequence (lineshapes, spin-spin relaxation studies) with $\pi/2$-pulses of 2.2 μs width. The spectra were acquired at a fixed delay between the pulses of 20 μs. For the low temperature measurements a commercial Bruker low temperature probe has been used. Here, the $\pi/2$-pulse width varied with temperature between 5.2 and 4 μs. Computer simulations have been done with appropriate FORTRAN programs that consider various types of guest motions. In the theoretical spectra the finite pulse widths – in particular during the low temperature experiments – has been taken into account by a correction described in Ref. [4].

RESULTS AND DISCUSSION

In the following we present dynamic ^{2}H NMR investigations on polycrystalline samples with deuterated cyclohexane and 1,3-dioxane. In Fig. 2 variable temperature ^{2}H NMR spectra of cyclohexane-d_{12}/cyclophosphazene are given between 38 K and 128 K which display characteristic lineshape changes.

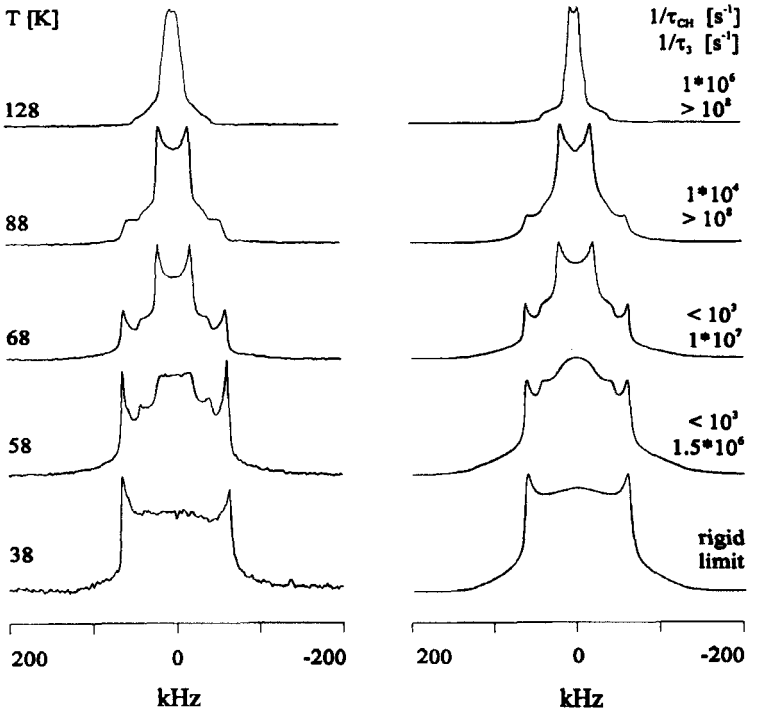

FIGURE 2 Experimental and simulated ^2H NMR spectra of cyclohexane-d_{12} in cyclophosphazene. The simulations were obtained, as described in the text (τ_3: correlation time for rotation around C_3 axis, τ_{CH}: correlation time for rotation around channel axis).

Thus, the spectrum at 38 K is typical for a "rigid limit" spectrum, where all molecular motions are frozen in on the NMR time scale. Attempts have been made to understand the spectral changes above 38 K by the examination of potential motional models for the guest

species. Eventually, it was found that the experimental NMR spectra and spin-spin ralaxation times (data not shown) at best can be reproduced on the basis of the following model assumptions for guest motions: (i) rotation about the molecular C_3 symmetry axis, (ii) rotation about the cyclophosphazene channel main axis and (iii) very fast overall molecular fluctuations of small amplitude (opening angle 10°). It should be noted that the two symmetry axes for rotation form an angle of 90°, i.e. the molecular C_3 axes of the guests are oriented perpendicular to the channel long axis. The theoretical ^2H NMR spectra, obtained on the basis of this motional model, are given in Fig. 2. They generally are in good agreement with their experimental counterparts. From this, the correlation times of the two rotational motions have been derived which follow the Arrhenius law. It is found that both rotational motions are characterized by rather low activation energies of 6.1 and 8.4 kJ/mol for rotation around the molecular C_3 symmetry axis and the channel axis, respectively. It should be noted that for the present case both rotational motions at best can be described by the model of three-fold jumps (120° jumps) between equally populated sites. This result is different from that reported for the 1,3,5-trioxane-d_6/cyclophosphazene inclusion compound, where for the C_3-axis rotation of the guests a rotational diffusion mechanism has been discussed.[3] Moreover, it should be noted that in the present case, the time scales of the two types of rotational motions differ by more than two orders of magnitude, i.e. the molecular C_3 rotational motion starts up at much lower temperatures than the rotation about the channel long axis. Again, this is different from the situation in 1,3,5-

trioxane-d_6/cyclophosphazene[3] where both rotational motions occured on a similar time scale.

Above 130 K these overall guest motions are in the fast exchange limit. As a result, the experimental ^2H NMR spectra are given as a superposition of two subspectra that originate from the fact that the C-^2H bonds of the axial and equatorial deuterons possess different orientations with respect to the molecular C_3-axis, i.e. motional symmetry axis. The observed subspectrum with a smaller quadrupolar splitting can be attributed to the equatorial deuterons (angle θ between C-^2H bond and motional axis: 108.0°) while the one with a larger splitting stems from the axial deuterons (angle θ: 0°).

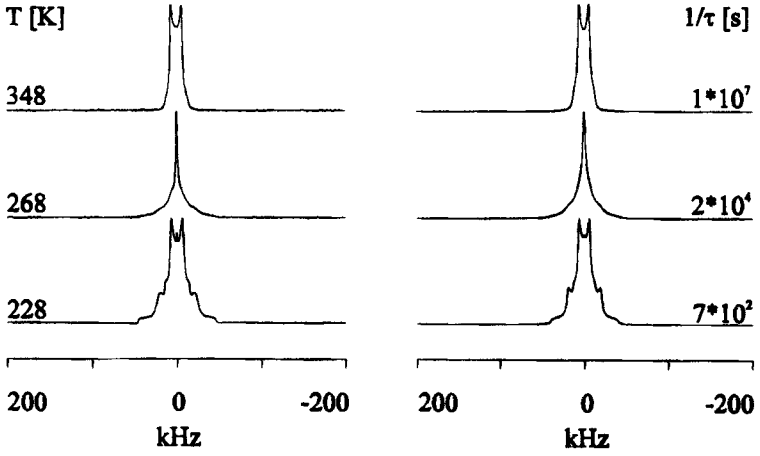

FIGURE 3 Experimental and theoretical ^2H NMR spectra of cyclohexane-d_{12} in cyclophosphazene reflecting the influence of the ring inversion process ($1/\tau$: rate constant for exchange process).

Above 220 K again spectral changes can be observed (see Fig. 3) which – as found before in other inclusion compounds with cyclohexane[5,6] – can be attributed to the ring interconversion process of the cyclohexane guests. This internal process can be understood by a chemical exchange process between the axial and equatorial deuterons. As a result, the motionally averaged ^{2}H NMR spectrum at 350 K is given by a single axially symmetric powder pattern. From the theoretical spectra, also given in Fig. 3, a much higher activation energy of 40 kJ/mol has been obtained. This value, however, is very close to that reported from former dynamic NMR measurements in solution.[7] In a similar way we have studied cyclophosphazene inclusion compounds with 1,3-dioxane, deuterated either at position C-2 or C-4. As before, experiments have been performed between 40 K and 360 K that can be subdivided into a low temperature range up to 150 K and a high temperature region above 200 K. In the low temperature range the ^{2}H NMR spectra and relaxation data were found to be determined by overall motional processes of the guest molecules, while in the high temperature range again the ring inversion is dominant. Representative ^{2}H NMR spectra of 1,3-dioxane-(2,2)-d_2, referring to the low temperature range, are given in Fig. 4 along with their theoretical counterparts. It should be noted that the ^{2}H NMR spectra of 1,3-dioxane-(4,4)-d_2 in cyclophosphazene (not shown) are almost identical. The best reproduction of the experimental data (spectra, spin-spin relaxation data) has been achieved with the assumption that the 1,3-dioxane molecules undergo a rotation around a preferential long axis. This motional symmetry axis is aligned parallel to the cyclophosphazene channel axis and exhibits additional fluctuations within an ordering

potential. The rotational motion is described by three-fold jumps (120° jumps). The relative populations of the jump sites, however, vary with temperature.

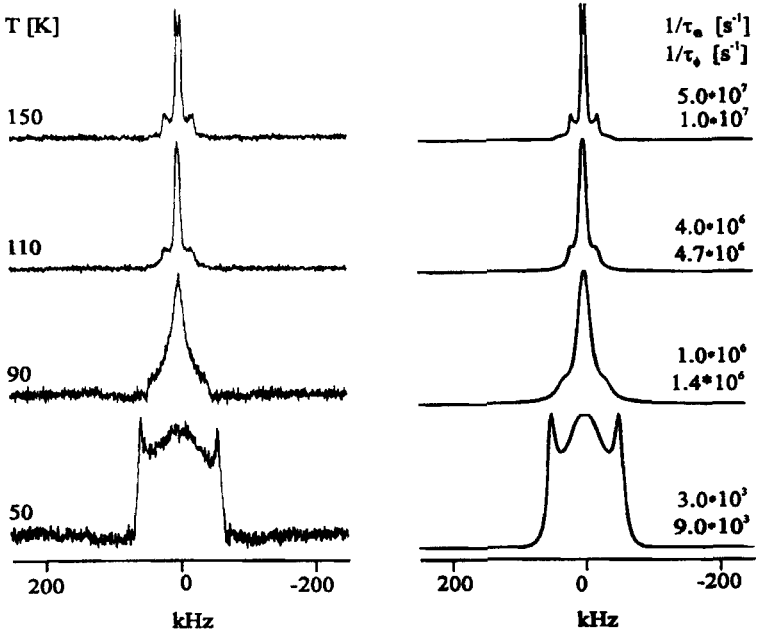

FIGURE 4 Experimental and simulated ^2H NMR spectra of 1,3-dioxane-(2,2)-d_2 in cyclophosphazene reflecting the overall motions in the low temperature range (τ_ϕ: correlation time for rotation, τ_θ: correlation time for fluctuation).

Thus, at temperatures below 90 K the populations are given by $p_1 = 0.6$, $p_2 = p_3 = 0.2$, while at 90 K and above a good reproduction of the experimental ^2H NMR spectra is achieved with three-fold jumps between equally populated sites.

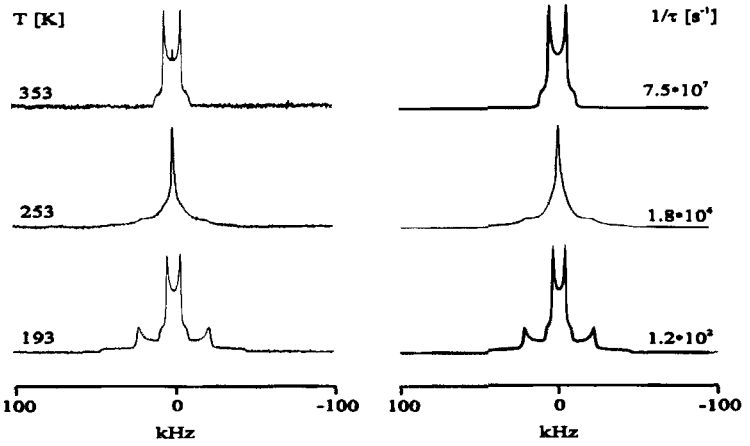

FIGURE 5 Experimental and theoretical ^2H NMR spectra of 1,3-dioxane-(2,2)-d_2 in cyclophosphazene reflecting the influence of the ring inversion process ($1/\tau$: rate constant for exchange process).

The motional symmetry axis for rotational motion is located in the symmetry plane of 1,3-dioxane and inclined at an angle of 10° with respect to the equatorial C-^{2}H bond. These findings indicate that here the hexagonal symmetry of the cyclophosphazene channels, that usually is encountered at room temperature, might be distorted at temperatures below 90 K. Recent NMR investigations on cyclophosphazene inclusion compounds with other guests point to the same direction.[8] As before, the reorientational motions exhibit low activation energies with values of 3.9 kJ/mol (rotation) and 5.7 kJ/mol (fluctuations). Finally, from the simulations in the high temperature region, shown in Fig. 5, the correlation times for the ring inversion process have been derived. For this process an activation energy of 36

kJ/mol has been found which can be compared to 41.9 kJ/mol from measurements in isotropic solution.[9]

CONCLUSIONS

The motional characteristics of cyclohexane and 1,3-dioxane in cyclophosphazene inclusion compounds have been determined employing dynamic ^2H NMR techniques. The experimental analysis has shown that the guest molecules are highly mobile exhibiting both conformational (ring inversion) and reorientational motions. The actual type and time scale for overall motion were found to depend strongly on the particular guest component. In addition, such overall motions represent the fastest molecular processes being characterized by a rather small temperature dependence. The ring inversion only sets in at elevated temperature and is accompanied by a higher activation energy. In general, such local conformational motions seem to remain almost unaffected by the incorporation of the guest molecules into the cyclophosphazene host channels.

Acknowledgment

We thank Mrs. D. Zauser and Mrs. H. Seidel for the synthesis of the compounds used in the present study. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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] A. Liebelt and K. Müller, *Mol. Cryst. Liq. Cryst.* **313,** 145 (1998).

[4] M. Bloom, J.H. Davis and M.I. Valic, *Can. J. Phys.* **58,** 1510 (1980).
[5] R. Poupko, E. Furman, K. Müller and Z. Luz, *J. Phys. Chem.* **95,**407 (1991).
[6] S. Nishikiori, C.I. Ratcliffe and J.A. Ripmeester, *J. Phys. Chem.* **94,** 8098 (1990).
[7] F.A.L. Anet and A.J.R. Bourne, *J. Am. Chem. Soc.* **98,** 760 (1967).
[8] A. Liebelt and K. Müller, in preparation.
[9] B. Pedersen and J. Schaug, *Acta Chem. Scand.* **22,** 1705 (1968).