*Chem. Mater.* **1998,** *10,* 3589−3596

# $^{13}$C and $^{31}$P Magic-Angle Spinning Nuclear Magnetic Resonance Spectroscopy of Tris(2,3-naphthalenedioxy)cyclotriphosphazene Inclusion Compounds

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*Received May 12, 1998. Revised Manuscript Received July 22, 1998*

The inclusion compounds of tris(2,3-naphthalenedioxy)cyclotriphosphazene (TNP) with several small molecules have been studied, for the first time, by $^{13}$C magic-angle spinning (MAS) NMR. The channel-type structure of TNP inclusion compounds (ICs) with benzene (and tetrahydrofuran, THF), and the cage-type structure of TNP ICs with *p*-xylene has been associated with the multiplicity of the $^{13}$C signals due to each carbon atom in the unit cell. Bending of the large paddles of the TNP matrix was established on the basis of the chemical shifts. The release of the guest molecules has been followed by differential scanning calorimetry and by solid-state NMR. The $^{13}$C cross-polarization (CP) MAS spectrum of guest-free TNP structure has been interpreted in accordance with the formation of the monoclinic cell. $^{31}$P CP MAS spectra reflect the symmetry of the crystal cell. A residual dipolar coupling with $^{14}$N is also observed. The dynamic behavior of the guest and host molecules has been studied by the measument of $^{13}$C $T_1$ relaxation times. The high mobility of benzene molecules is transferred to the host structure, which presents shorter relaxation times than the guest-free TNP system. The triethylammonium tris(2,3-naphthalenedioxy)phosphate obtained as a byproduct from the synthesis has also been characterized by $^{13}$C and $^{31}$P CP MAS.

## Introduction

Tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP) and tris(2,3-naphthalenedioxy)cyclotriphosphazene (TNP) (Figure 1, top) form inclusion compounds (ICs) with several molecules such as benzene, xylene, cyclohexane, linear alkanes, etc.[1,2] Inclusion and polymerization[3,4] and, recently, the formation of adducts between TPP and some polymers has also been presented.[5] The selectivity with respect to some guests makes them good materials as separation agents.[6,7]

The ICs were mainly characterized by X-ray diffraction techniques: most of the TPP and TNP inclusion compounds present a hexagonal crystalline cell (Figure 1, bottom) a channel-type structure with 4−5 and 10 Å diameter, respectively.[1,2] In some cases a cage-type structure was found, e.g., in TNP/*p*-xylene IC.[8]

The dynamic behavior of guest molecules such as benzene and *p*-xylene were examined by $^{1}$H solid-state NMR of TPP and TNP ICs.[7,9,10]

In recent years particular attention has been dedicated to the characterization of the guest-free TPP[11] and TNP host matrix. The guest-free TNP molecule forms a monoclinic crystal structure and can be obtained by a sublimation process under high vacuum.[12]

The TPP molecule results from the reaction of hexachlorocyclotriphosphazene with *o*-dioxophenylene in a basic solution of triethylamine in tetrahydrofuran. In the synthesis proposed by Allcock, a byproduct is also quantitatively obtained.[13] A triethylammonium tris(*o*-phenylenedioxy)phosphate is formed in which the phosphorus atom is bonded octahedrally to six oxygen atoms (in the solid state).[14,15] The synthesis of TNP molecule is similar, but the byproduct is less characterized.

Till now only limited solid-state NMR characterization has been performed on these molecules. This paper presents the characterization by $^{13}$C and $^{31}$P cross-polarization magic-angle spinning (CP MAS) of the

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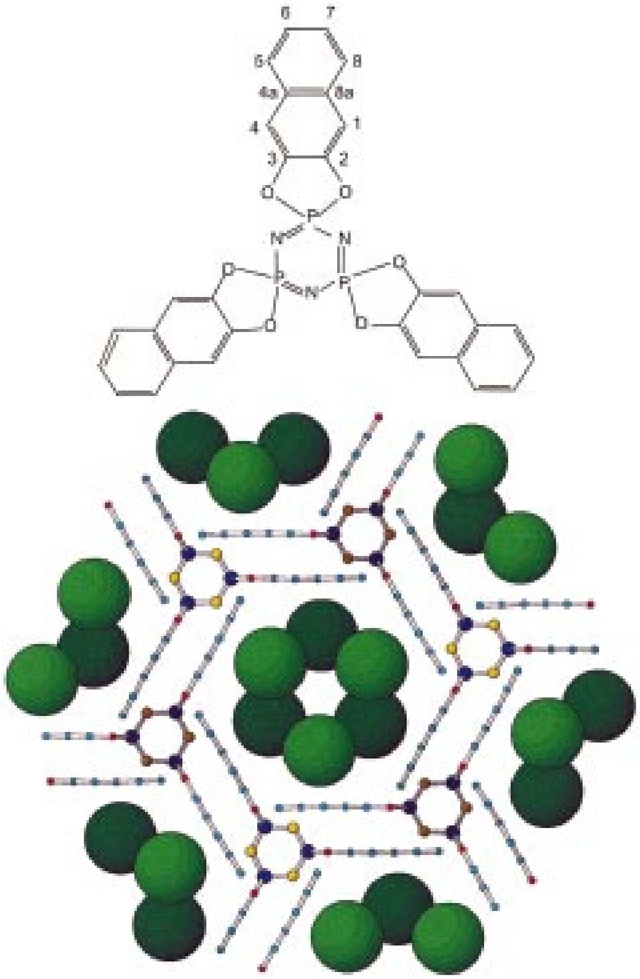

**Figure 1.** Schematic representation of the TNP molecule (top) and channel-type structure (bottom) of inclusion compound with benzene, as reported by Allcock et al.[2]

guest-free TNP matrix and of ICs with some guests, e.g., benzene, tetrahydrofuran, and *p*-xylene. The multiplicity of the $^{13}$C peaks associated with each carbon atom is compared to those of the nonequivalent carbon atoms in the crystal cell. Carbon relaxation times were performed to study the motion mechanism of the guests in the inclusion compounds. The $^{31}$P CP MAS spectra are particularly informative regarding the symmetry of the phosphazene ring and are diagnostic of the byproducts formed during the reactions.

This work is part of a general project started some years ago for the NMR characterization of conformations and mobility of molecules of high and low molecular weight when confined to nanotubes in the crystal state.[16] Perhydrotriphenylene (PHTP) was found to be a host suitable for those studies, because it could include, in particular, *n*-alkanes and polymers.[17] Stereospecific polymerization reactions were also performed and the dynamics of the polymer motion within the channel were explored by $^{13}$C relaxation times and deuterium NMR.[18]

## Experimental Section

**Synthesis.** The synthesis of TNP was carried out by the original method proposed by Allcock.[13] Under $N_2$ atmosphere a solution of 15.74 g of 2,3-dihydroxynaphthalene in 27.5 mL of triethylamine and 90 mL of anhydrous tetrahydrofuran (THF) distilled from metal sodium solution was added dropwise under stirring and refluxing to sublimated hexachlorophosphazene (11.53 g) dissolved in 175 mL of THF. The triethylamine had first been dried over calcium hydride for 1 h and then filtered. Stirring and refluxing was continued for 40 h at 60 °C. The white precipitate was filtered off and washed with THF and then distilled water (3 L). The product was dried under vacuum ($10^{-2}$ Torr) until it reached constant weight. A prolonged extraction with benzene in a Kumagawa apparatus and then crystallization in benzene yielded the TNP/benzene inclusion compound. Mass spectrometry identified the white residue as triethylammonium tris(2,3-naphthalenedioxy)phosphate.[15]

The TNP inclusion compounds and the byproduct were identified by $^{31}$P CP MAS NMR.

The TNP monoclinic structure was obtained following two methods: (a) thermal treatment of TNP/benzene IC at 135 °C under vacuum ($10^{-1}$ mmHg) for 30 min or (b) crystallization of TNP/benzene IC with *o*-xylene.

The TNP/*p*-xylene IC was prepared from the TNP monoclinic structure by crystallization in *p*-xylene solvent.

**Mass Spectrometry.** Electron impact mass spectra were run with a VG7070E instrument.

**Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) traces were performed on a Mettler Toledo Star thermal analysis system equipped with a $N_2$ cooling apparatus. The experiments were run under $N_2$ atmosphere from −100 to 400 °C.

**Solid-State NMR.** High-resolution $^{13}$C and $^{31}$P MAS NMR spectra were run at 75.5 and 121.5 MHz, respectively, on a MSL300 Bruker instrument operating at a static field of 7.4 T. A MAS Bruker probe head was used with 7 mm $ZrO_2$ rotors spinning at a standard speed of 4−6 kHz. All the experiments were made using a high-power proton decoupling (DD) field; 90° pulse for carbon was 4 $\mu$s, 90° pulse for phosphorus was 5 $\mu$s, and 90° pulse for proton was 4 $\mu$s; CP MAS experiments were performed by applying a delay time of 6 s and a contact time ranging from 3 to 12 ms. The pulse sequence to suppress signals from protoned carbons was also applied with a delay of 50 $\mu$s.[19]

The resolution for carbon was checked on glycine (width at half-height = 22 Hz). Crystalline polyethylene (PE) was taken as an external reference at 33.63 ppm from tetramethylsilane (TMS).[20] The resolution for phosphorus was checked on a $NH_2(H_2PO_4)$ sample. It was used as the second standard, assigning the $^{31}$P chemical shift of $NH_4(H_2PO_4)$ to +1 ppm with respect to 85% $H_3PO_4$;[21] $^{13}$C $T_1$ values were obtained using the method developed by Torchia.[22] Spectra were acquired at 9−14 $\tau$ values.

## Results and Discussion

The DSC analysis of TNP ICs with benzene and THF show an endotherm at the melting point of TNP matrix (338 °C) and a sharp endotherm at 124 °C (Figure 2b). The latter peak is associated with the presence of two

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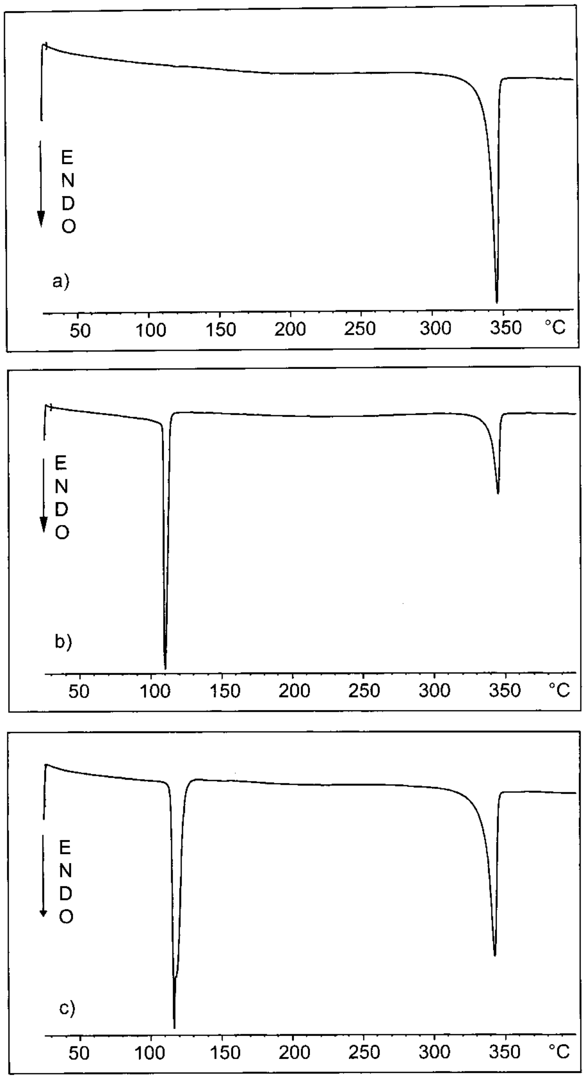

**Figure 2.** Differential scanning calorimetry trace from 25 to 400 °C: (a) TNP guest free after thermal treatment; (b) TNP/benzene IC; (c) TNP/*p*-xylene IC.

phenomena: the guest removal and the collapse of the channel structure of the IC. The temperature at which the latter endotherm peak drops is 110−120 °C, independent of the guest molecules (benzene or THF), indicating that the transition is driven by the TNP crystal packing. Therefore, the TNP/benzene IC sample was subjected to thermal treatment at 135 °C (see Experimental Section) in order to free the matrix from the guest. The DSC trace of the guest-free TNP shows only the endotherm at the melting point (Figure 2a).

The TNP/*p*-xylene IC presents, in the DSC trace (Figure 2c), two first-order endotherm transitions; one at 118 °C associated with the release of the *p*-xylene and the other at a high temperature, corresponding to the melting of the TNP structure. The former first-order transition is observed at the same temperature as benzene leaving in the TNP/benzene IC, suggesting that, at about 120 °C, the bending of the naphthalenedioxy unit toward a less constrained conformation occurs independently of the crystal packing.

Solid-state NMR spectra were performed at room temperature on the TNP ICs and on the product obtained after the heating process. The $^{13}C$ CP MAS spectra of the TNP/benzene IC were also run at variable temperature in order to follow in situ the release of the guest molecules and the formation of the guest-free TNP structure.

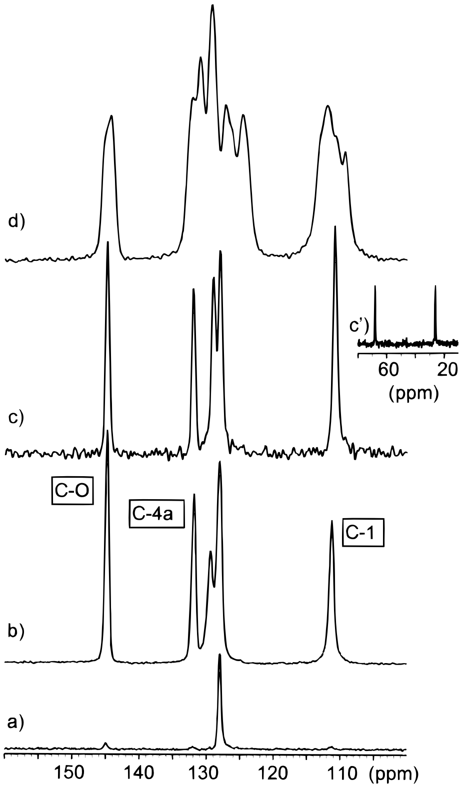

**Figure 3.** $^{13}C$ MAS NMR spectra of TNP/benzene IC, spinning speed of 5530 Hz: (a) single pulse sequence (SPE) with a delay of 10 s; (b) cross-polarization sequence with a contact time of 8 ms. $^{13}C$ MAS NMR spectra of TNP/THF IC, spinning speed of 4000 Hz: (c) cross-polarization sequence with a contact time of 3 ms; (c′) single pulse sequence with a delay of 8 s; (d) $^{13}C$ CP MAS NMR spectra of TNP after thermal treatment with a contact time of 1 ms.

**$^{13}$C CP MAS NMR.** The $^{13}C$ CP MAS spectrum of TNP/THF IC shows five peaks in the aromatic chemical shift region (Figure 3, trace c); thus, there is a single peak for each type of aromatic carbon atom, in accordance with the high symmetry of the hexagonal crystalline phase.[2] The single paddles are perpendicular to the phosphazene ring. Table 1 summarizes the assignments made on the basis of solution data. The $^{13}C$ MAS single pulse sequence with short recycle delay revealed two upfield resonances associated with the THF guest (Figure 3, trace c′). In fact, the $^{13}C$ $T_1$ of THF are short due to a considerable mobility.

In the TNP/benzene IC five peaks can still be detected at the same chemical shifts in the aromatic region (Figure 3, trace b) but, in this case, the benzene chemical shift overlaps the peak at 128.1 ppm, as selectively recorded in the $^{13}C$ MAS NMR spectrum obtained with a short recycle time (Figure 3, trace a).

The $^{13}C$ CP MAS spectrum of guest free TNP shows more signals for each type of carbon atom (Figure 3, trace d). This is because the conversion to the monoclinic guest free TNP structure[12] occurs after the thermal treatment. The lower symmetry of the monoclinic guest-free cell is reflected in the signal multiplicity. The monoclinic cell is also obtained after recrystallization of TNP/benzene IC with *o*-xylene solvent, as

**Table 1. $^{13}$C Isotropic Chemical Shifts of TNP ICs, Guest-Free TNP, and Triethylammonium Tris(2,3-naphthalenedioxy)phosphate in the Solid State**

| $^{13}$C CP MAS | TNP/THF IC | | TNP/benzene IC | | TNP guest-free, matrix | TNP/*p*-xylene IC | | triethylammonium tris(2,3-naphthalenedioxy)-phosphate |
|---|---|---|---|---|---|---|---|---|
| | host | guest | host | guest | | host | guest | |
| C-2/C-3 | 144.9 | | 144.8 | | 145.0 | 145.3 | | 147.0 |
| | | | | | 144.1 | 144.2 | | |
| | | | | | | 143.5 | | |
| *p*-xylene | | | | | | | 135.0$^d$ | |
| C-4a/C-8a | 132.1 | | 131.9 | | 132.0 | 132.1 | | |
| | | | | | 130.9 | 130.6 | | 130.6 |
| | | | | | | 129.6 | | 130.1 |
| | | | | | | 130.1 | | 129.5$^a$ |
| C-5/C-8 | 129.1$^b$ | | 129.4$^b$ | | 129.1 | 129.1 | | 128.5$^a$ |
| C-6/C-7 | 128.1$^b$ | | 128.1$^b$ | | 127.1 | 128.6 | | |
| | | | | | 126.4 | 126.8 | | |
| | | | | | 124.6 | 124.4 | | 124.5$^a$ |
| | | | | | | | | 124.2$^a$ |
| C-1/C-4 | | | | | 112.9 | | | |
| | 110.9 | | 111.3 | | 111.9 | 111.3 | | |
| | | | | | 110.6 | 110.2 | | |
| | | | | | 109.3 | 108.6 | | 107.4 |
| | | | | | | | | 106.5 |
| benzene | | | | 128.0$^c$ | | | | |
| -$CH_2$-O | | 67.8 | | | | | | |
| -$CH_2$-NH | | | | | | | | 49.2 |
| -$CH_2$- | | 26.0 | | | | | | |
| $CH_3$- | | | | | | | 19.7$^d$ | |

[a] The assignment was based on the chemical shifts of TNP ICs. [b] The assignment was based on the $^{13}$C chemical shifts of the 2,3-naphthalenediamine of DMSO-$d_6$. [c] The $^{13}$C solution NMR chemical shift is 128.4 ppm (0.5 mL of $C_6H_6$, 1.5 mL of $CDCl_3$). [d] The $^{13}$C solution NMR chemical shifts of *p*-xylene (16% in $CDCl_3$) are 134.7, 129.0, and 20.9 ppm for quaternary, C-H, and methyl carbons, respectively.

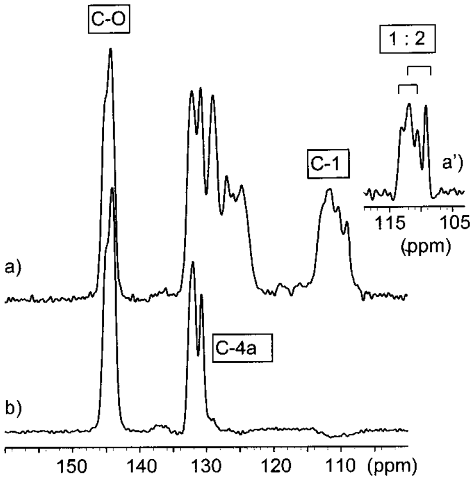

**Figure 4.** (a) $^{13}$C CP MAS NMR spectra with a contact time of 8 ms, spinning speed of 5550 Hz of the guest-free TNP, sample after *o*-xylene crystallization. (b) Protonated carbon suppression pulse sequence with a delay of 50 $\mu$s. (b′) C-1 signals obtained by applying the resolution enhancement: line broadening = −40 Hz, Gaussian broadening = 50%.

confirmed by $^{13}$C CP NMR spectrum (Figure 4, trace a). When the protonated carbon suppression pulse sequence with a delay of 50 $\mu$s (Figure 4, trace b) is applied, only the quaternary carbon peaks survive, corresponding to the C-2 and C-4a carbon atoms. This pulse sequence is particularly useful as the chemical shift overlaps some carbon atoms in the region, at about 130 ppm. It is possible to detect the multiplicity of the quaternary carbon atoms and to distinguish two peaks for C-4a atoms (intensity ratio of 2:1). Also visible is a splitting in the C-2 carbon region, with an intensity ratio of 1:2. The multiplicity of the C-2 and C-4a carbon peaks reflects the symmetry of the TNP molecule

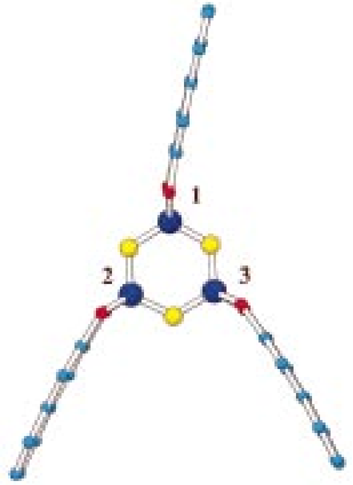

**Figure 5.** Geometry of the TNP molecule in the monoclinic crystal cell. The geometry is calculated by the atomic coordinates reported by Kubono et al.[12]

and, in particular, the bending of the five-membered hexocyclic rings (Figure 5). In the TNP molecule, there are two naphathalendioxy residues bonded to phosphorus atoms 2 and 3 that show a considerable deviation from the mean plane and give rise to peaks with double intensity. The $^{13}$C signals of C-2 and C-4a atoms of intensity equal to 1 are associated with the third residue (bonded to phosphorus 1) which deviates from the mean plane slightly.[12] The signal of intensity 1 resonates at the same chemical shift as ICs with benzene and THF, consistent with the symmetry of the paddles (hereafter described as perpendicular).

The interpretation of the C-1 carbon atom is more complex as it is particularly sensitive to the dihedral angle C(1)−C(2)−P−O. In the TNP ICs, this dihedral angle is close to 180° and therefore the C-1 atoms

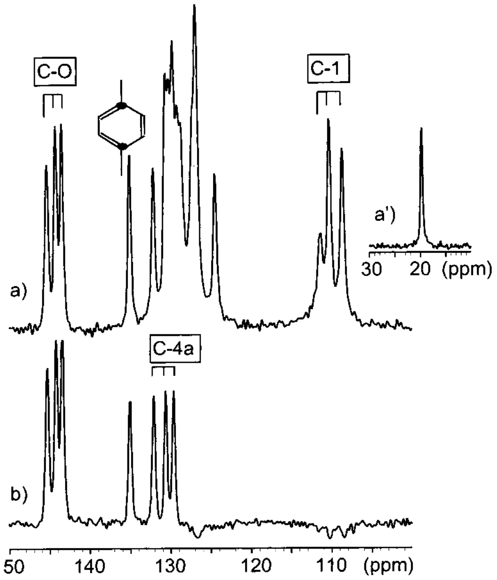

**Figure 6.** (a) $^{13}$C CP MAS NMR spectra with a contact time of 4 ms, spinning speed of 5476 Hz of the TNP/*p*-xylene. (a′) $^{13}$C MAS single pulse sequence with a recycle delay of 10 s. (b) Protonated carbon suppression pulse sequence with a delay of 50 $\mu$s.

resonate upfield like the *ortho* carbon of 1,4-dimethoxybenzene in the trans conformation to the methoxy side group.[23] In the TNP guest-free matrix, the C-1 carbon atom presents a high multiplicity, but it is possible to distinguish two groups of signals of intensity 1:2. Each group is split further, giving rise to a doublet that presents an intensity ratio of 1:1 (Figure 4, trace a′). The distribution of the 1:2 intensity ratio reflects the bending distortion of the exocyclic rings, as shown before for the quaternary carbon atoms. The reason for the further multiplicity might be the loss of symmetry on the cyclophosphazene ring, justifying the 1:1 splitting.

The high multiplicity of the *ortho* carbons (C-1 carbon atom), related to the dihedral angle of the naphthalenic ring with respect to the O−P bond [C(1)−C(2)−O−P], is mainly due to electric field shielding of the O−P bond.[23] This shielding effect is the major contribution to the chemical shift, compared to the steric hindrance and the ring current chemical shift effects when the dihedral angles are close to 0° or 180°.[23] A deviation of about 15° for the C-1 in the TNP matrix causes a considerable shift downfield in agreement with the trend predicted by Clayden.

$^{13}$C CP MAS spectra of the TNP/*p*-xylene IC are shown in Figure 6, trace a. The high crystallinity of the sample is indicated by the sharpness of the signals. Quite striking is the high multiplicity of the carbon atoms, compared to the spectra of the ICs with benzene (or THF); each C-2 and C-1 carbon atom gives rise to three peaks. The quaternary carbon atoms can also be observed separately by the nonquaternary carbon suppression pulse sequence as shown in Figure 6, trace b. With this specific pulse sequence we can selectively detect the 135 ppm resonance, corresponding to the quaternary carbons of the *p*-xylene guest and the three peaks assigned to C-4a carbon atoms, which, in the conventional CP MAS spectrum, overlap other signals.

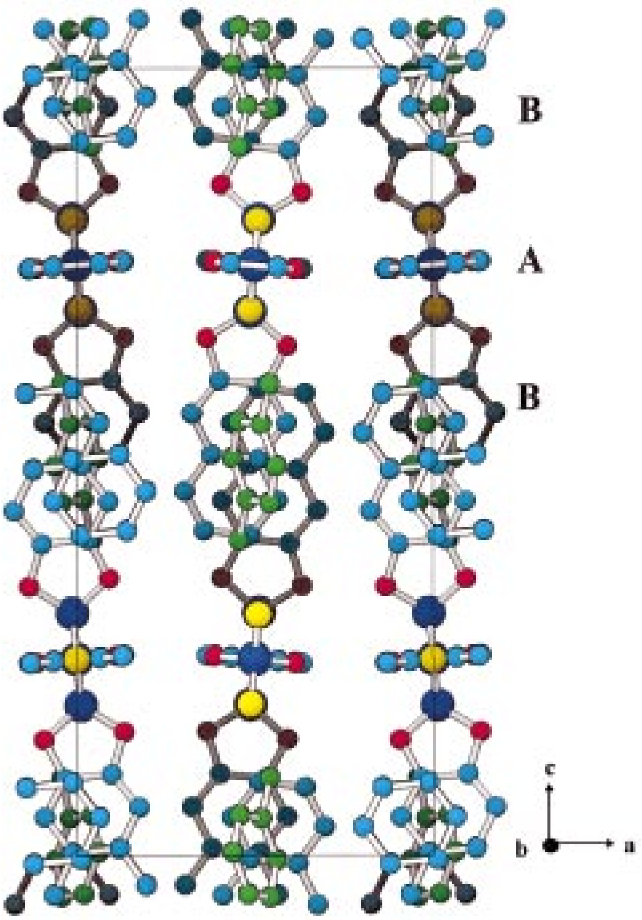

**Figure 7.** Crystal structure of TNP/*p*-xylene IC. Paddle A lies in the plane **a**−**b**. The crystal structure derives from the atomic coordinates reported by Kubono et al.[8]

The intensity ratio of 1 for the *p*-xylene peak, compared with the C-4a carbon signals (three peaks with intensity 1:1:1), leads to a guest-to-host ratio of 1:1. This result is consistent with the crystal structure suggested by Kubono.[8] The authors propose a cage-type structure with the *p*-xylene and the TNP molecule in the 1:1 ratio.

Three peak multiplicity of C-4a atoms (and of C-2 and C-1 atoms) suggest, at first sight, a different environment for each paddle (with the maintenance of the symmetry plane within the molecule). This is not the case: in fact, one of the three signals (downfield signal in each group) is assigned to a naphthalenedioxyphosphole unit lying close to the plane **a**−**b** (paddle A, Figure 7), this unit bisects the N−P−N angle as for the paddles of TNP inclusion compounds with THF and benzene. The intensity of each downfield signal is thus due to two carbon atoms. This is consistent with the proposed crystal structure, containing a paddle (A) lying on a mirror plane of the TNP molecule. The remaining two paddles (B) are equivalent and form an angle of 140°, one with respect to the other.[24] Therefore, the two remaining signals of each group (hereafter called "doublet") cannot be explained by a different geometry of the two paddles. However, in this conformation, the mirror

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[23] Clayden, N. J. *Magn. Reson. Chem.* **1989**, *27*, 692.

[24] The angles between the paddles in TNP/*p*-xylene IC are 140°, 110°, 110° instead of 120°, 120°, 120° as in the TNP hexagonal structure; thus a 10° tilt is consistent with the former geometry.

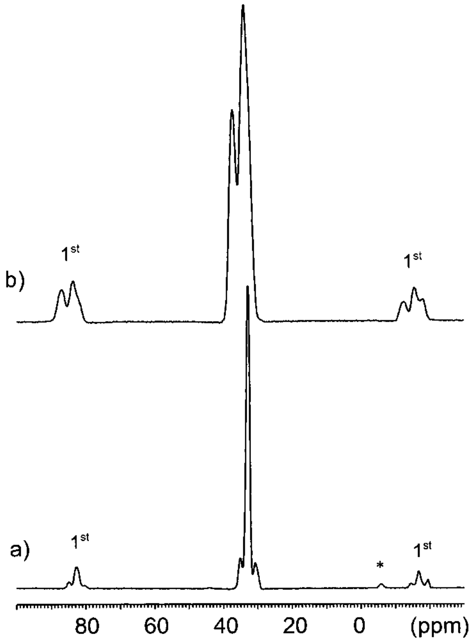

**Figure 8.** $^{31}$P CP MAS NMR spectra of TNP/benzene IC (a) and monoclinic TNP structure (b); contact time of 2 ms, spinning speed of 6000 Hz, recycle delay of 10 s.

plane of the TNP molecule lying on the phosphazene ring is retained, but the mirror plane is lost in the crystal cell. Because of the tilt of the mean plane of the phosphazene ring around the **b** axis, the carbon atoms of the paddles B are tilted (Figure 6). Each doublet is due to two carbon atoms in the same paddles. The tilt produces a large displacement of these paddles, whereas on the single one which is perpendicular to **c** axis, it is much less.

After thermal treatment the TNP/*p*-xylene sample yields the monoclinic TNP matrix, as characterized by $^{13}$C CP MAS at room temperature.

**$^{31}$P CP MAS.** $^{31}$P CP MAS of TNP/benzene IC is shown in Figure 8, trace a. We can observe an asymmetric triplet at 35.1, 32.8 (main peak), and 30.7 ppm, which resonates in the chemical shift region of spirocyclophosphazene and therefore is diagnostic of the formation of the cyclophosphazene molecules. The asymmetric triplet derives from the dipolar coupling between $^{14}$N and $^{31}$P not completely suppressed by magic-angle spinning.[25] The $^{31}$P line shape is influenced by many factors, which include the $^{14}$N quadrupole coupling tensor, the orientation of the internuclear vector in the principal axis system of the electric field gradient, the internuclear distance, and the magnitude of the applied magnetic field.[26-28] The spectrum is also complicated by the dipolar coupling to two $^{14}$N atoms. A detailed analysis of the line shape is in progress. The $^{31}$P spectrum contains information about the crystal cell; in fact, the presence of one main peak agrees with the high symmetry of the hexagonal cell where all the phosphorus atoms are equivalent in the crystal cell.

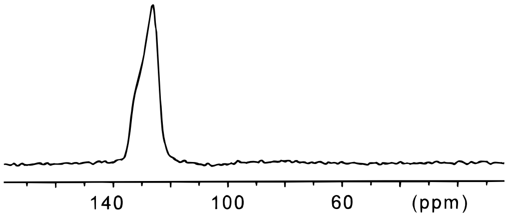

**Figure 9.** $^{13}$C SPE static sample of TNP/benzene IC, delay time = 5 s.

The $^{31}$P CP MAS of the guest-free TNP monoclinic structure presents two signals broader than the asymmetric triplet of TNP ICs with an intensity ratio of 1:2 that resonate at 37.2 and 33.7 ppm (Figure 8, trace ,b). The broadening may be caused by the nonequivalence of the phosphorus nuclei in the TNP molecule, the phosphorus−phosphorus coupling *J*(PP) of the order of 50 Hz,[29] and the crystal packing effect, which cannot be resolved at this field strength. The dipolar coupling with $^{14}$N must also be taken into account in the overall line shape analysis.

The symmetry loss of TNP molecule generates nonequivalent phosphorus atoms, and at first sight, we can expect that phosphorus atom 1 has a different resonance with respect to resonances of phosphorus atoms 2 and 3. The presence of the doublet with an intensity ratio of 1:2 agrees with the geometry of the TNP molecule in the monoclinic cell (Figure 5).

**Dynamics of TNP Crystal Structures.** The dynamic behavior of the TNP/benzene IC can be determined by a few complementary perspectives with the application of specific pulse sequences: $^{13}$C cross-polarization (CP) and the $^{13}$C single pulse experiment with proton decoupling (SPE). The CP technique, which can collect the response essentially from the crystalline and rigid phases, highlights the matrix signals. The selective detection of the benzene signals (Figure 3, trace a) in the $^{13}$C SPE spectrum with short recycle delay is indicative of the higher mobility of the guest molecules than those of the TNP matrix. The short $^{13}$C $T_1$ relaxation times of the benzene molecules (12 s) confirms the presence of relatively fast motions at room temperature. The matrix signals for spin−lattice relaxation times ($T_1$) of the inclusion compound show, respectively, 69, 66, 56, 57, and 54 s for carbons C-4a, C−O, C-1, C-5, and C-6. The measurements suggest a crystalline rigid system, but not so rigid as the pure host monoclinic crystal structure, where values of more than 1000 s are estimated for each carbon atom. The drastic reduction of the matrix relaxation times in the IC derives from the high mobility of the guest molecules and by a looser crystal packing that must be taken into account. The static $^{13}$C SPE spectrum of the TNP/benzene IC, performed with a short recycle delay (Figure 9), presents a chemical shift anisotropy (CSA) of about 1000 Hz for benzene carbons. Taking into account the principal components of the carbon CSA in solid benzene ($\sigma_{11} = -88.2$, $\sigma_{22} = -12.0$, and $\sigma_{33} = 127.7$ ppm),[30] the small residual chemical shift anisotropy indicates the fast range of motions experienced by the guest mol-

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ecules, even though an isotropic dynamics has not yet been reached.[31]

In the TNP/*p*-xylene IC the cross-polarization phenomenon is effective for the signal matrix as well as for the *p*-xylene peaks. In fact, we can detect the nonquaternary peak of *p*-xylene under CP conditions (Figure 6, trace b). This result indicates the marked constriction experienced by the guest molecule in the cage cavity. In fact each cavity contains one *p*-xylene molecule surrounded by naphthalene rings showing long $^{13}$C relaxation times. The long relaxation times of both the matrix (600−1000 s) and the guest molecule (about 500 s) confirm that, at room temperature, the degrees of freedom explored by the *p*-xylene molecules are not so many as found by benzene in the channel-type structure.[7] The relaxation times of methyl groups (15 s) represent an exception because of the intrinsic relaxation mechanism.

**Triethylammonium Tris(2,3-naphthalenedioxy)-phosphate.** The triethylammonium tris(2,3-naphthalenedioxy)phosphate is a byproduct of the synthesis and if not identified may affect the data. We isolated the pure compound and characterized it by DSC and NMR.

The $^{31}$P CP MAS spectrum of the triethylammonium tris(2,3-naphthalenedioxy)phosphate shows a single peak at −83.2 ppm (Figure 10, trace a).[32,33] The spectrum does not contain relevant spinning sidebands, indicating a limited chemical shift anisotropy. In fact, the static $^{31}$P CP NMR spectrum is unusual: the chemical shift anisotropy covers a few parts per million at room temperature (Figure 10, trace a′). The line is narrow and appears to be Gaussian in shape. The small anisotropy agrees with the high symmetry around the phosphorus atom ($D_3$ symmetry) and confirms that, in the solid state, the hexacoordinate structure exists with the anion charge on the phosphorus and the cation charge on the nitrogen, as suggested by Allcock for the triethylammonium tris(*o*-phenylenedioxy)phosphate.[15] Comparison with the $^{31}$P NMR spectra of $PCl_6$ and $PF_6$ samples suggests that the line narrowing may also result from rapid motions; in fact, the estimated $^{13}$C $T_1$ relaxation times are less than 50 s.[34,35]

The $^{13}$C CP MAS spectrum of the triethylammonium tris(2,3-naphthalenedioxy)phosphate shows sharp peaks that indicate the high degree of crystallinity of the sample. In the aromatic region, it is possible to observe the single lowfield signal of the C-2 atoms and four doublets (intensity ratio of 1:1) for the four different constitutional carbon atoms (Figure 10, trace b). In the region at 130 ppm two doublets partially overlap, but from the analysis of the first order spinning sideband intensity (not shown) it can be seen that the downfield signals (at 131.2 and 130.6 ppm) exhibit the same chemical shift anisotropy, suggesting univocally that they belong to the quaternary carbon atoms. In the aliphatic region there are the two peaks that correspond to the triethylammonium methyl and methylene groups (Figure 10, trace b′). The assignment of the chemical shifts is shown in Table 1. With reference to the crystal structure of the corresponding triethylammonium tris(*o*-phenylenedioxy)phosphate,[15] the doublets with intensity 1:1 for most of the carbon atoms may be associated with the different chiral relationships of the anion and cation units in the solid state.[15]

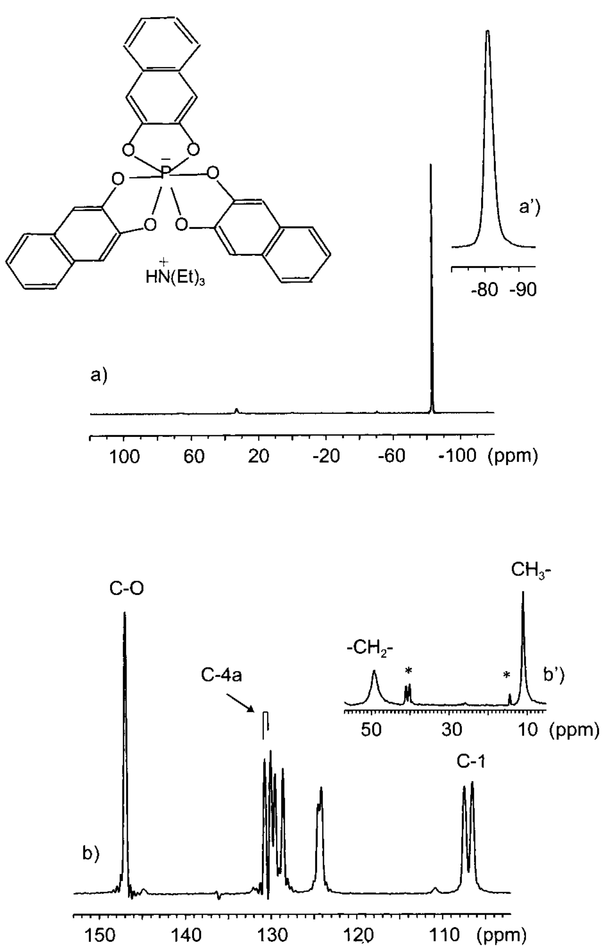

**Figure 10.** $^{31}$P CP MAS NMR spectra of triethylammonium tris(2,3-naphthalenedioxy)phosphate: (a) spinning speed of 4000 Hz, contact time of 2 ms, the small peak at 31.7 ppm is due to residual TNP/THF IC; (a′) $^{31}$P SPE of static triethylammonium tris(2,3-naphthalenedioxy)phosphate with a recycle delay of 100 s; (b) spinning speed of 5000 Hz; (b′) aliphatic region, where the peaks indicated with asterisks correspond to spinning sidebands of the aromatic signals.

## Conclusions

$^{13}$C and $^{31}$P MAS NMR spectra of TNP IC with benzene, THF, and *p*-xylene have been performed for the first time. It is possible to discriminate between the channel-type and cage-type structure from the multiplicity of the $^{13}$C and $^{31}$P signals. The polymorphic behavior of the guest-free TNP structure has been followed by DSC analysis and in situ by $^{13}$C CP MAS. The guest-free TNP strucure has also been formed from the crystallization with *o*-xylene and has been characterized by NMR. The dynamic behavior of both the guest and host molecules has been pointed out by $^{13}$C

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$T_1$ relaxation times. The short relaxation times of benzene molecules (12 s) and the small chemical shift anisotropy indicate that a fast regime of motions is experienced by the guests, which, in turn, make the host system less rigid than the TNP guest-free structure. The triethylammonium tris(2,3-naphthalenedioxy)phosphate is also formed during the reaction. The hexacoordinate structure with an anion charge on the phosphorus atom can be characterized by $^{31}$P CP MAS.

**Acknowledgment.** We thank MURST for financial support and G. M. Catel for help in the synthesis of the samples.

CM980338G