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Modification of channel structures by fluorination†

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Two perfluorinated triazines [2,4,6-tris(*p*-bromotetrafluorophenoxy)-1,3,5-triazine (**2**) and 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (**3**)] were synthesised to study their crystal structure and inclusion character. Compound **3** forms channel inclusions with the solvents *p*-xylene and *p*-chlorotoluene, showing a stoichiometry of 2:1 (host:guest). The channels have dimensions of 7.6×3 Å^2. The host-guest interactions, perfluorophenyl-phenyl stacking, F···H- and CH···π(perfluorophenyl) contacts, were revealed by the crystallographic and solid state NMR spectroscopy studies. The reversibility of the sorption process through the gas phase could be demonstrated by X-ray diffraction. In contrast to the pentafluorinated compound **3**, the tetrafluorinated one (**2**) showed no inclusions with a number of typical solvents.

Introduction

Channel-type inclusion compounds providing a fluorinated pore surface are still exceptions among the wide variety of supramolecular structures. A few known examples stem from coordination polymers[1] and the chemistry of heterocycles.[2] In the case of coordination polymers, perfluorinated ligands are connected by cadmium, building up flexible cavities. The walls of these cavities partly contain fluorine, whereas in the structure of 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine NF_2 fragments generate a circular channel with a diameter of 4.6 Å.

Perfluorination of channels in known channel-type inclusion compounds rises some basic questions: can channels still form, which host-host interactions stabilise channel formation and what are typical host-guest interactions?

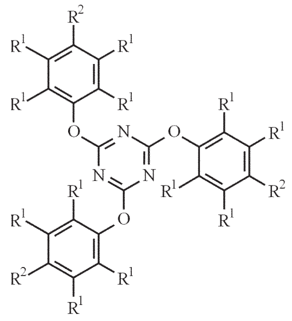
Characteristic non-fluorinated channel-type inclusions show that for a topologically homogeneous and electronically non-specific channel surface one-dimensional close packing of guests is favoured. In perhydrotriphenylene (PHTP),[3] for example, the channel wall is formed by the equatorial H atoms of six-membered rings. In this case, many known inclusions crystallise in close packing of guest molecules showing no specific host-guest interactions. In contrast to PHTP, guest molecules in tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP),[4] in which phenyl groups form the inner surface, seem to form much more specific interactions with the channel wall, so that the close packing is not typical. Another well-known channel-type inclusion compound is 2,4,6-tris(*p*-bromophenoxy)-1,3,5-triazine (BrPOT; **1**), showing inclusions with C_{60} and C_{70}, for example.[5] However, here also no close packing of guests was observed.

Summarising, we are interested in a comparison of inclusion properties of channel inclusions with their perfluorinated forms, particularly with respect to close packing of guests or specific host-guest interactions.

Results and discussion

Inclusion properties and X-ray structure analyses

Here we report on the inclusion properties of BrPOT, **1** [(Fig. 1)], as compared to the tetrafluorinated compound



1: $R^1 = H$, $R^2 = Br$

2: $R^1 = F$, $R^2 = Br$

3: $R^1 = R^2 = F$

Fig. 1 Molecular structure of phenoxy substituted triazines.

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† Electronic supplementary information (ESI) available: colour versions of Figs. 2–5. See http://www.rsc.org/suppdata/nj/b3/b311028a/

2,4,6-tris(*p*-bromotetrafluorophenoxy)-1,3,5-triazine (BrTFPOT; **2**). In contrast to the guest-free crystal structure of **1** [Fig. 2(a)], triazine molecules of **2** [Fig. 2(b)] show stacking along the *a* axis, featuring a distance of 6.3 Å. The typical Piedfort units (PUs; centre-to-centre distance: 3.7 Å), which stabilise molecules in **1** along the *c* axis, cannot be observed in **2**, where perfluorophenyl stacking is the dominant interaction. The significant distance of 6.3 Å between the rings is caused by a repulsion of electron-rich centres (nitrogen and oxygen, according to calculation of the electron density distribution [PC Spartan]).

In the guest-free structure of **1** [Fig. 2(a)] the triazine molecules are stabilised by PUs, π···π and Br···π interactions. The function of the para bromo atoms is the formation of X_3 synthons[6] in the channel structure of compound **1** to organise host molecules into stacked layers. However, in the structure of **2** [Fig. 2(b)] the Br atoms are involved in three different Br···Br-interactions, which constitute a three-dimensional connection between triazines. Corresponding to the definition of X···X interactions,[7] two of these contacts belong to type II (Br2···Br23, Br3···Br22) and one to type I (Br1···Br21).

BrPOT (**1**) is known to form inclusions with a number of typical solvents.[6] In this respect we were surprised to observe that the compound F4Br (**2**) showed no tendency for inclusion formation.

In contrast, the pentafluorophenyl substituted compound, 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (PFPOT; **3**),[8] showed channel-type inclusions with *p*-xylene [**3**·(*p*-xylene)$_{0.5}$; Fig. 3] and *p*-chlorotoluene [**3**·(*p*-chlorotoluene)$_{0.5}$]. Thermogravimetry, X-ray and elemental analysis confirmed a host:guest ratio of 2:1. Triazines are arranged in layers, in which four host molecules surround one guest. These layers are stacked in the direction of the *a* axis with a period of 6 Å, giving rise to channels with dimensions of about 7.6 × 3 Å^2 (Fig. 4). In these channels solvent molecules are stacked and kept at a distance of 6 Å, resulting in no close packing of the guests. Here the channel wall is mainly made up by stacked perfluorophenyl groups (Fig. 4).

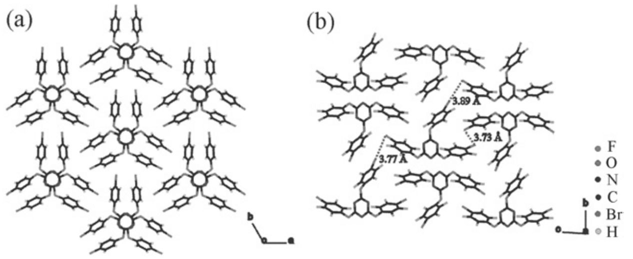


Fig. 2 Crystal structures of (a) **1** and (b) **2** (Br···Br interactions are emphasized by broken lines).

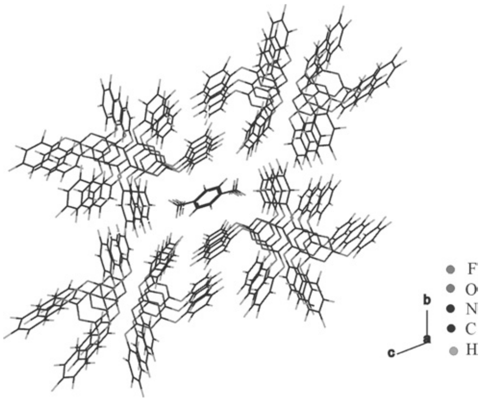


Fig. 3 Crystal structure of **3**·(*p*-xylene)$_{0.5}$.

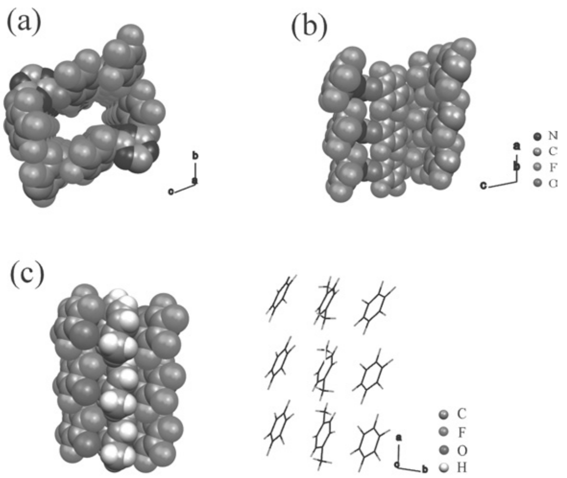


Fig. 4 Channel wall of **3**·(*p*-xylene)$_{0.5}$: (a) view along the channels (*a* axis); (b) view onto the channel wall (*b* axis); (c) host-guest packing.

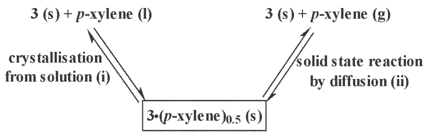
The guest molecules interact with the host *via* phenyl-perfluorophenyl interactions[9] [shortest distance: 3.86 Å (C4···C31); Fig. 4(c)] as well as F···H interactions. These F···H distances range from 2.6 to 2.9 Å (Table 1). Additional CH···π(perfluorphenyl) interactions were revealed by solid state NMR spectroscopy.

The **3**·(*p*-xylene)$_{0.5}$ inclusion compound was obtained by (*i*) crystallisation and by (*ii*) a solid state reaction providing xylene from the gas phase (Scheme 1). For an investigation of the sorption/desorption equilibrium crystals were exposed to vacuum at 60 °C for 3 days, leading to a complete desorption of the solvent. As confirmed by powder X-ray measurements the channel-type structure was replaced by the guest-free phase of **3**.

In the structure of **3** (Fig. 5) the triazine molecules show two different geometries depending on the C–O–C angle, whereby molecules of the same geometry are arranged in a congruent stacking along the *a* axis (distance: 6 Å) caused by the perfluorophenyl stacking interactions.

Table 1 F···H interactions: bond lengths (Å) and angles (°)

H(31)···F(1)	2.63	C(32)–H(31)···F(1)	152.9
H(31)···F(2)	2.80	C(32)–H(31)···F(2)	133.9
H(34a)···F(9)	2.68	C(30)–H(34a)···F(9)	150.8
H(34c)···F(14)	2.90	C(30)–H(34c)···F(14)	133.8



Scheme 1 Different routes to form the inclusion compound **3**·(*p*-xylene)$_{0.5}$.

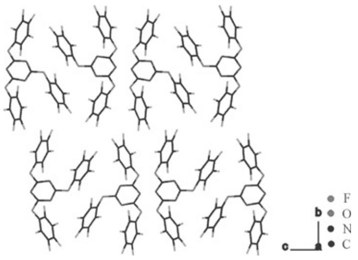


Fig. 5 Crystal structure of **3**.

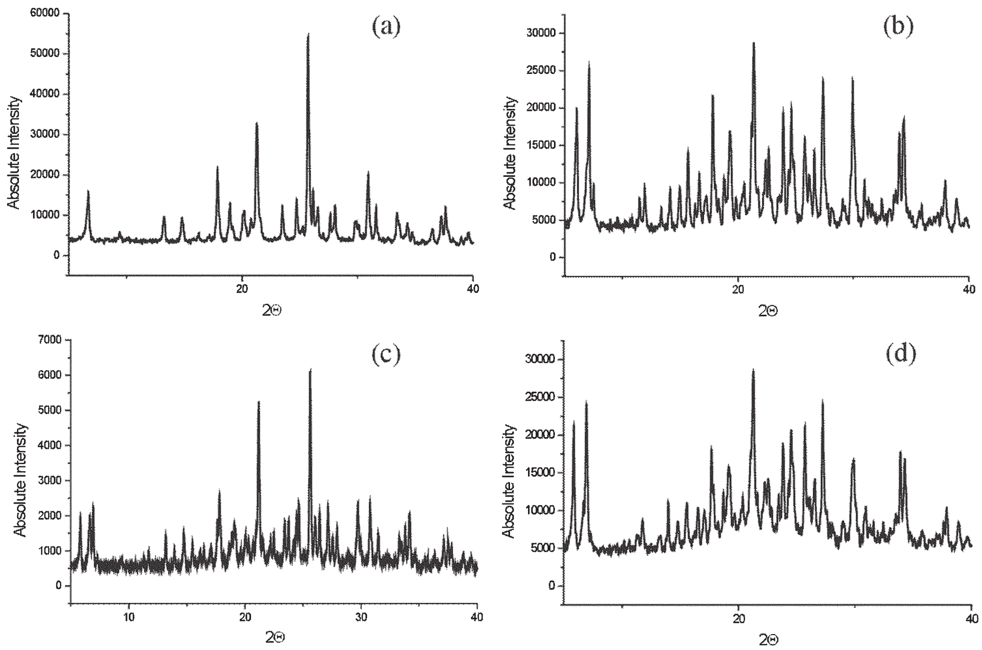


Fig. 6 Powder X-ray diffraction patterns of (a) **3**; (b) the inclusion compound **3**·(*p*-xylene)$_{0.5}$; and of the equilibrium state of the inclusion compound (c) at 100 °C and (d) after cooling to room temperature.‡

As the reversibility of the desorption of guests was observed for TPP by Allcock and Siegel in 1964,[10] we also tested our inclusion compound for this property (Fig. 6). Accordingly, two sealed ampoules filled with a fine powder of **3**·(*p*-xylene)$_{0.5}$ were heated up to 100 °C for 3 days and one was cooled down to room temperature at a rate of 1 °C h^{-1}. The powder of the ampoule opened for powder X-ray analysis at 100 °C contained a mixture of inclusion compound and guest-free phase [Fig. 6(c)]. The second ampoule, which was opened after returning to room temperature, showed only crystals of **3**·(*p*-xylene)$_{0.5}$ [Fig. 6(d)]. In view of these results we have shown the reversibility of the sorption of guest molecules to form a channel-type inclusion compound.

NMR results

Further details of host-guest interactions in the **3**·(*p*-xylene)$_{0.5}$ inclusion compound were analysed by solid state NMR. The ^{13}C CP-MAS NMR spectra of the inclusion with long and short contact times are shown in Fig. 7. The signals of the host and the guest can be assigned by choosing appropriate contact times that select carbons at different distances from the hydrogens. In fact, in the cross-polarised spectra the hydrogens of the guests are the only magnetisation source of the system and host carbons receive magnetisation through-space in a time as long as a few milliseconds. In the CP spectrum of Fig. 7(a) (long contact times) the downfield signal at about 173 ppm is assigned to the carbons bonded to two nitrogens in the N–C=N system of the host.[11] The peculiar lineshape, rarely observed, derives from the ^{14}N–^{13}C dipolar interaction that cannot be effectively averaged out by fast magic angle spinning, giving rise to the characteristic doublet.[12] The broad signal centred at 140 ppm corresponds to the aromatic carbons of the host coupled to ^{19}F. The high natural abundance of the spin-active ^{19}F causes the broadening of the signal, because no fluorine decoupling was applied during the acquisition time. The C–O carbon of the fluorinated ring gives rise to the peak at 125.8 ppm because of the balance of two strong contrasting effects generated by fluorine and oxygen substitution.

The guest can be separately observed in the spectrum of Fig. 7(b): the host resonances were filtered out by performing a CP experiment with short contact times (1 ms). In this case only the carbons of the guest at short distances from the hydrogens (within 2.5–3 Å) are observed. The signals are assigned as follows: the peak at 134.8 ppm to quaternary carbon, the peaks at 129.8 and 127.8 ppm to the CH and the peak at 18.8 ppm to the CH$_3$ group. No shift is observed with respect to the solution spectrum for the quaternary carbon, whilst an upfield shift of 2.1 ppm with respect to *p*-xylene in CDCl$_3$ solution is observed for the methyl, suggesting that the magnetic susceptibility of the ring current of the aromatic host is experienced by the guest as already observed in other aromatic hosts forming inclusion compounds with *p*-xylene.[13] An upfield shift requires that the methyl of the *p*-xylene be placed perpendicularly to the plane of the host aromatic ring at a short distance. The topological information from the NMR data is in agreement with the single crystal structure (CH$_3$ to ring centre distance of 4.1 Å) and demonstrates the strong CH···π(perfluorophenyl) interaction between guest and host. In addition, the 1:1 splitting of the CH aromatic carbons of the guest as compared to the single signal in the solution spectrum of *p*-xylene indicates the lower symmetry of the molecule in the crystal structure. The presence of an inversion centre in the molecule is in agreement with the observed signal multiplicity as predicted by the $P\bar{1}$ space group of the unit cell.

The 2D ^{1}H–^{13}C heterocorrelated spectrum of the **3**·(*p*-xylene)$_{0.5}$ inclusion compound recorded at high spinning rate with application of the Lee–Goldburg sequence is depicted in Fig. 8 together with its projections in the carbon and hydrogen dimensions. Under the applied experimental conditions the hydrogens can be detected with very high resolution in the solid state. In this way, the aliphatic and aromatic hydrogens can be detected separately. The hydrogen-to-carbon correlations indicate short distances. Two types of signals are present, which are associated to intramolecular and intermolecular interactions. In particular, guest hydrogens of the CH$_3$ group communicate through space with all six carbons of the host aromatic rings bearing either fluorine or oxygen, confirming thus the guest-to-host CH···π(perfluorophenyl) interaction. The remaining signals correspond to the intramolecular interactions between the guest hydrogens and the host carbon.

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‡ Powder X-ray diffraction patterns were recorded on a Stoe STADIP diffractometer with CuK$_{\alpha1}$ radiation at room temperature.

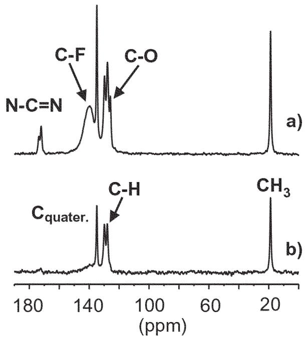

Fig. 7 ^{13}C CP-MAS NMR of the **3**·(*p*-xylene)$_{0.5}$ inclusion compound with a spinning speed of 12.5 KHz: (a) a contact time of 10 ms was applied to detect the resonances of both host and guest carbons; (b) a contact time of 1 ms was applied; the carbon resonances of the *p*-xylene guest were selectively recorded.

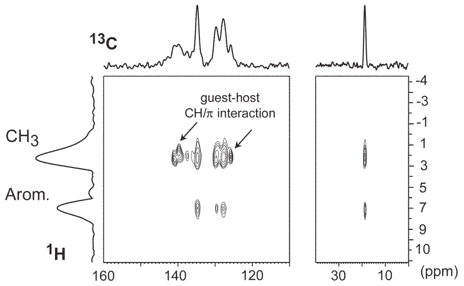

Fig. 8 2D ^{1}H–^{13}C HETCOR NMR spectrum of the **3**·(*p*-xylene)$_{0.5}$ inclusion compound performed under fast magic angle spinning and conditions of a Lee–Goldburg experiment.

Conclusions

As compared to 2,4,6-tris(*p*-bromophenoxy)-1,3,5-triazine (**1**) the perfluorinated compound 2,4,6-tris(*p*-bromotetrafluorophen-oxy)-1,3,5-triazine (**2**) showed no tendency for inclusion formation for a number of typical solvents.

Surprisingly, 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (**3**) forms channel inclusions with *p*-xylene and *p*-chlorotoluene. The phenyl-perfluorophenyl interactions between host and guest seem to prevent close packing of guest molecules. Weak host-guest interactions such as CH···π with the perfluorinated aromatic system were revealed by solid state NMR. The transition from the channel inclusion to the structure of **3** upon desorption of the guests demonstrates the importance of the host-guest interactions for stabilising the present channel structure.

Experimental

Methods

^{13}C-NMR spectra were recorded on a Bruker spectrometer DPX 400 (internal standard: tetramethylsilane [TMS]). FT-IR-spectra were measured on a Perkin Elmer model 1600.

Synthesis of triazines

Cyanuric chloride and phenol were mixed in a ratio of 1:5 and stirred with 5 ml *n*-decane (dry) at 180 °C for 13 h under nitrogen. The mixture was than washed with hot methanol and purified by chromatography (silica gel 60, eluent: CHCl$_3$–*n*-hexane 1:1).

$C_{21}Br_3F_{12}N_3O_3$ (2). F_p 209–210 °C, yield: 80.7%, ^{13}C-NMR (300 MHz, acetone-d6): $\delta = 98.69$ ppm (C4, t, $^1J_{CF} = 22.74$ Hz), 128.75 ppm (C1, t, $^2J_{CF} = 13.84$ Hz), 139.44/141.88 ppm (C2, d, $^1J_{CF} = (-)245.52$ Hz), 143.84/146.35 ppm (C3, d, $^1J_{CF} = (-)252.57$ Hz), 172.55 ppm (N–C–N, s), FT-IR: 1639/1505 (perfluorophenyl), 1595/1376 (triazine), 1142 (C–F), 983 (C–O), 837 (C–Br) cm^{-1}.

$C_{21}F_{15}N_3O_3$ (3). $F_p = 158$–159 °C, yield: 79.1%, ^{13}C-NMR (acetone-d6): $\delta = 126.15$ ppm (C1, t, $^2J_{CF} = 14.14$ Hz), 137.13/139.62 ppm (C2, d, $^1J_{CF} = (-)250.55$ Hz), 140.26/142.71 ppm (C3, d, $^1J_{CF} = (-)246.53$ Hz), 139.28/141.79 ppm (C4, d, $^1J_{CF} = 252.54$ Hz), 173.19 ppm (N–C–N, s), FT-IR: 1657/1526 (perfluorophenyl), 1615/1574/1377 (triazine), 1169/1156 (C–F), 1001 (C–O–C) cm^{-1}.

Table 2 Crystal data and experimental details for **1**, **2**, **3**, **3**·(*p*-xylene)$_{0.5}$ and **3**·(*p*-chlorotoluene)$_{0.5}$

	1	**2**	**3**	**3**·(*p*-xylene)$_{0.5}$	**3**·(*p*-chlorotoluene)$_{0.5}$
Empirical formula	$C_{21}Br_3H_{12}N_3O_3$	$C_{21}Br_3F_{12}N_3O_3$	$C_{21}F_{15}N_3O_3$	$C_{25}H_5F_{15}N_3O_3$	$C_{24.5}H_{3.5}Cl_{0.5}F_{15}N_3O_3$
Formula weight/g mol^{-1}	594.07	809.97	627.24	680.32	690.53
T/K	253(2)	293(2)	293(2)	153(2)	153
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Rhombohedral	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$R3c$	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P\bar{1}$
a/Å	23.869(2)	6.2648(6)	5.9960(5)	5.9555(5)	5.9681(4)
b/Å	23.869(2)	17.8465(17)	26.5650(15)	13.5912(12)	13.6038(12)
c/Å	6.4684(5)	20.782(2)	13.5330(10)	16.1207(14)	16.0136(13)
α/°	90	86.114(12)	90	111.055(10)	111.029(9)
β/°	90	84.699(12)	99.315(9)	91.871(10)	91.527(9)
γ/°	120	88.033(11)	90	95.776(10)	96.390(10)
U/Å^3	3191.5(5)	2307.3(4)	2127.2(3)	1208.22(18)	1202.88(17)
Z	6	4	4	2	2
ρ/g cm^{-3}	1.855	2.332	1.959	1.87	1.906
μ(Mo$_{K\alpha}$)/mm^{-1}	5.716	5.377	0.22	0.202	0.258
Meas. reflect.	4839	18124	16928	9569	9466
Indep. reflect.	1090	8348	8089	4379	4330
R_{int}	0.0925	0.0553	0.0598	0.0558	0.0494
R_1 [$I > 2\sigma(I)$]	0.0343	0.0658	0.0457	0.0382	0.0352
wR_2 [$I > 2\sigma(I)$]	0.056	0.1004	0.085	0.0904	0.0824
CCDC	198 640	198 643	198 644	198 642	198 641

X-Ray structure determination

Single crystals of **1**, **2** and **3** were obtained by sublimation in a closed ampoule. Crystals of **3**·(p-xylene)$_{0.5}$ and **3**·(p-chlorotoluene)$_{0.5}$ were obtained by crystallisation of **3** from p-xylene and p-chlorotoluene at a concentration of 1 g l^{-1}. The solutions were heated up to 110 °C and than cooled to room temperature at a rate of 1 °C h^{-1}. The intensity data were recorded on a Stoe IPDS diffractometer. The structures were solved by direct methods using the programme SHELXS-97.[14] The refinement and all further calculations were carried out using SHELXL-97.[15] The corresponding crystallographic data are shown in Table 2.§

Solid state NMR spectroscopy

The solid state NMR spectra were run at 75.5 MHz on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with 4 mm double resonance magic angle spinning (MAS) probes. The sample was spun at a spinning speed of 12.5 kHz and the 90° pulse for protons was 2.9 μs. Cross polarisation (CP) MAS experiments were performed using a recycle delay of 10 s and contact times of 10 and 1 ms. Ramped-amplitude cross polarisation (RAMP-CP) transfer was applied.[16] A phase-modulated Lee–Goldburg (PMLG) heteronucler ^{1}H–^{13}C correlation (HETCOR) experiment under fast magic angle spinning permitted the recording of 2D spectra with high resolution both in the proton and carbon dimensions.[17] The 2D HETCOR experiment was performed with an LG period of 18.9 μs and an efficient transfer of magnetisation from the protons to the carbon nuclei was achieved by the RAMP-CP sequence. A contact time of 10 ms allows the intermolecular proximity between guest hydrogens and host carbons to be observed, in this specific case, within a distance of about 0.5 nm.[18] Quadrature detection in t_1 was achieved by the time proportional phase increment method. Carbon signals were acquired during t_2 under proton decoupling applying a two-pulse phase modulation scheme (TPPM).

Acknowledgements

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§ CCDC reference numbers 198 640–644. See http://www.rsc.org/suppdata/nj/b3/b311028a/ for crystallographic data in .cif or other electronic format.