

Crystal Structure of a Highly Efficient Clarifying Agent for Isotactic Polypropylene

Marko Schmidt,[†] Johannes J. Wittmann,[†] Roman Kress,[‡] Denis Schneider,[§] Stefan Steuernagel,[§] Hans-Werner Schmidt,^{*,‡} and Jürgen Senker^{*,†}

[†]Inorganic Chemistry III, University of Bayreuth, 95440 Bayreuth, Germany

[‡]Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

[§]Bruker Biospin GmbH, Silberstreifen 4, 76287 Rheinstetten, Germany

Supporting Information

ABSTRACT: Using a combined approach based on X-ray powder diffraction and solid-state NMR spectroscopy, we were able to determine the crystal structure of 1,3,5-tris(2,2-dimethylpropionylamino)benzene, an efficient clarifying agent for isotactic polypropylene. The XPRD data and 1D solid-state NMR experiments allowed to exclude most of the possible primitive orthorhombic space groups with the exception of 11. The structure solution was carried out using real space methods including a close-contact penalty. Four space groups lead to reasonable *w*Rp values below 10%. ¹³C¹³C double quantum (DQ) experiments of the labeled carbonyl group were measured with a supercycled symmetry based



dipolar recoupling sequence. Taking into account the wRp values after Rietveld refinement as well as simulations of DQ build-up curves based on nine spin systems, the space group $P2_12_12_1$ is clearly favored. The largest dipolar coupling within these spin systems was about 60 Hz corresponding to a distance of 5 Å. 1,3,5-Tris(2,2-dimethylpropionylamino)benzene crystallizes in an orthorhombic metric (a = 14.91(5) Å, b = 24.05(8) Å, c = 6.80(2) Å). The molecules are arranged in a pseudohexagonal rod packing with medium-strong hydrogen bonds and π -stacking. The antiferroelectric arrangement of neighbored rods leads to an averaging of the net dipolar moment in the whole crystal.

1. INTRODUCTION

The class of 1,3,5-benzenetrisamides (BTAs) has evolved to one of the most versatile motifs in supramolecular chemistry. First, Matsunaga et al. reported on thermotropic liquid crystalline behavior of alkyl substituted BTAs.^{1,2} Experimental studies on self-assembly $^{3-9}$ revealed the preferred formation of supramolecular columnar aggregates. Stabilized by strong hydrogen bonds between three amide groups per molecule the formed nanofibers are able to build up hydrogels^{10,11} and organogels,^{12–15} depending on the nature of the substituents. BTAs were used to study concepts of chiral amplification in helical self-assembly.^{3,16-19} Kreger et al. showed that azobenzene substituted BTAs are interesting for holographic volume gratings.²⁰ They are applied successfully as additives to improve the electret performance of polypropylene^{21,22} and as nucleating agents for polyvinylidenfluoride²³ and isotactic polypropylene (i-PP).^{23–26} In this regard, the significantly shorter cycle times in injection molding caused by the increased crystallization temperature of nucleated *i*-PP are of highly economic interest. New subclasses are the so-called "clarifying agents" which render the normally turbid *i*-PP highly transparent and thus opens the application for transparent packaging. These additives are capable of providing an ultrahigh

density of nucleation sites and inducing crystallization of low light-scattering rod-like crystals.²⁷ A detailed insight into the state of the art of nucleation and clarification of *i*-PP is published by Gahleitner et al.²⁸ Among the different classes of nucleating and clarifying agents the class of 1,3,5-benzene-trisamide attracts more and more attention.^{23–26}

Most important for the nucleation and clarification is the epitaxial matching to induce crystallization and growth of the crystal lamellae in the mesoscale regime. Nevertheless, only a few studies exist with respect to the crystallographic structure of BTAs. Lightfoot et al. described the columnar structure of a 2-methoxyethyl substituted BTA,²⁹ Jiménez et al. reported on n-alkyl substituted BTAs,³⁰ and Kristiansen et al. solved the structure of a *tert*-butyl substituted BTA (all based on trimesic acid).³¹ In the publication of Blomenhofer et al. the best reported clarifying agent is 1,3,5-tris(2,2-dimethyl-propionylamino)benzene (Figure 1).²⁴ The optical properties of a 1.1 mm thick sample of an *i*-PP homopolymer were improved from 79% clarity to 98% and from a haze of 64% to

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Figure 1. Left: Chemical structure of 1,3,5-tris(2,2dimethylpropionylamino)benzene 1 (if 13 C labeled at all three carbonyl groups, the compound will then be shorten as 1*). Right: Section of compound 1 highlighting the main motional degrees of freedom; the black arrows assign the structure directing torsion angles $C_{Ar}C_{Ar}N_{H}C_{O}$ (left) and $C_{Me}C_{q}C_{O}O$ (right).

10%. In the present work we focus on elucidating the structure of 1,3,5-tris(2,2-dimethylpropionylamino)benzene **1** by means of NMR crystallographic strategies.

The main problem with solving the crystal structure of 1,3,5tris(2,2-dimethylpropionylamino)benzene is its microcrystallinity. As a consequence, all attempts to prepare suitable single crystals failed which is often the case also for many other substance classes like pharmaceuticals, dyes and pigments, biochemical macromolecules, or inorganic network compounds.^{32–34} Coping with powder data only complicates *ab initio* structure solutions.^{35–38} NMR crystallographic strategies help to overcome this problem by complementing powder diffraction data with solid-state NMR experiments at various steps of the crystal structure determination.³⁹ Many of these experiments are based on the three main interactions in solidstate NMR, namely the chemical shift, the dipolar interaction, and the quadrupolar splitting.^{40,41} The chemical shift and the quadrupolar splitting help to determine the correct space group, the asymmetric unit, the local symmetry of molecular units in the crystal structure, and dynamical disorder of individual building units.^{39,42-51} Furthermore, using adequate pulse sequences, the dipolar coupling allows to extract distances^{52–59} between homo- and heteronuclear nuclei or even torsion angles. Thus, it is possible to validate or falsify structure models, and the structure determination of ambivalent diffraction data becomes less difficult. However, it is hardly possible to get sufficient structural information based on nuclei with a low natural abundance. Therefore, isotope enrichment, for example ¹³C or ¹⁵N, is often inevitable. During the past years, these complementary methods have shown that NMR crystallography is a powerful tool to solve substructures and even complete crystal structures of molecular compounds and inorganic network compounds, respectively.^{60–69}

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization of 1*. All solvents were purified and dried using standard procedures. ¹H NMR spectra were recorded on a Bruker AC250 spectrometer at room temperature and referenced on TMS. Mass spectra were recorded on a VARIAN MAT 7 instrument with direct probe inlet and electron impact ionization. The labeled Ba¹³CO₃ was purchased from Deutero GmbH and used without further purification. 3,5-Dinitroaniline was obtained from Aldrich and used as received.

The ¹³C enriched 2,2-dimethylpropanoyl chloride (labeled at the carbonyl group) was synthesized from $Ba^{13}CO_3$.⁷⁰ A 15 mL portion of concentrated sulfuric acid was dropped slowly to 5 g of enriched barium carbonate (0.025 mol). The generated ¹³CO₂ was caught in a second flask that was cooled with a mixture of acetone, dry ice, and liquid nitrogen to a temperature of roughly –120 °C. To 0.99 g of

 $^{13}\mathrm{CO}_2$ (0.0225 mol) was added 30 mL of dried and cold $\mathrm{Et_2O}$ dropwise, followed by 0.04 mol of t-butyl magnesium chloride (2.0 M in Et₂O; used in excess due to the age of the solution). The mixture was stirred for several hours at -80 °C (acetone/dry ice) and defrosted overnight. Et₂O was evaporated under reduced pressure, and a white solid precipitated. This solid (3.62 g, 0.0225 mol) was solved in 35 mL of dichloromethane (DCM) and 3.9 mL of oxalyl chloride (0.04 mol, equimolar to t-butyl magnesium chloride) to gain ¹³C enriched 2,2-dimethylpropanoyl chloride and MgCl₂. The solids were solved in 80 mL of N-methyl-2-pyrrolidone (NMP), and potassium stearate was added dropwise (to react excess oxalyl chloride) until no further gas evolution was observed. The ¹³C labeled product was used without further purification. All resonances in the ¹H NMR could be unequivocally assigned to the solvents used during the synthesis and the ¹³C labeled acid chloride. Yield: 1.6 g (13 mmol, 51.8%). ¹H NMR (250 MHz, CDCl₃): $\delta = 1.14$ ppm (s, 9H, -CH₃).

1,3,5-Triaminobenzene was freshly synthesized by hydrogenation of the nitro compound: 3,5-dinitroaniline (8.0 g, 44 mmol) was stirred in a mixture of THF (400 mL), MeOH (50 mL), and palladium (0.6 g, 10% on activated carbon) in an autoclave at 35 °C for 12 h using a H₂ pressure of 3.5 bar. The palladium catalyst was filtered off under argon with Alox N, the solvents were evaporated under reduced pressure, and the product was subsequently dried under high vacuum. Yield: 5.3 g (43.1 mmol, 98%). ¹H NMR (250 MHz, [d⁶]DMSO): δ = 4.30 ppm (s, 6H, -NH); 5.13 ppm (s, 3H, Ar–H).

Compound 1* was synthesized by dropping ¹³C enriched acid chloride (0.46 g, 3.8 mmol) to a mixture of 1,3,5-triaminobenzene (0.15 g, 1.2 mmol), NMP (30 mL), pyridine (5 mL), and LiCl (0.05 g) at 0 °C under argon atmosphere. The reaction was stirred overnight at 60° C, and the reaction mixture was precipitated into an excess of ice water. The precipitate was filtered off, dried, and recrystallized from methanol. Yield: 0.174 g (0.46 mmol, 38%). ¹H NMR (250 MHz, [*d*⁶]DMSO): δ = 1.21 ppm (d, ³*J*(¹H,¹³C) = 3.5 Hz, 27H, -CH₃); 7.62 ppm (s, 3H, Ar–H); 9.2 ppm (d, ²*J*(¹H,¹³C) = 3 Hz, 3H, -NH). MS (70 eV), *m/z* (%): 378 (M+, 67); 321 (8); 293 (63); 236 (7); 208 (16); 123 (6); 57 (100).

2.2. Powder X-ray Diffraction. The powder pattern was recorded in transmission using a STOE StadiP with a germanium (111) monochromator (Cu K α_1 radiation, 1.5406 Å). The sample was filled in a capillary tube with a diameter of 0.7 mm and measured in the 2θ range 5-40° at room temperature. The data were fully handled using the module Reflex Plus of the program package Accelerys MS $Modeling^{71}$ (version 5.0). The structure solution step was performed by real-space methods using the simulated annealing algorithm including a close-contact penalty. As starting model four molecules were placed into the unit cell which were geometry optimized before using DFT methods (see section 2.5). During the structure solution these molecules were allowed to rotate and translate freely as rigid bodies with two torsion angles in each side chain as additional degrees of freedom. The first Rietveld refinement step was performed including energy considerations using the COMPASS forcefield where each atom was allowed to relax freely. The additional energy weighting was set to 50%, and for the energy window the default value of 40 kcal/mol was used.

2.3. Solid-State NMR. ¹H and ¹³C shifts are reported with respect to TMS, ¹⁵N shifts were referenced on liquid NH₃. Compared to nitromethane all values are shifted by 380.5 ppm. ¹H spectra of compound 1 were recorded on a Bruker Avance III spectrometer operating at a proton frequency of 500 MHz. The sample was filled in a 1.3 mm ZrO_2 MAS rotor. The MAS frequency and the 90° pulse length were set to 65 kHz and 2.5 μ s, respectively. The ¹⁵N and ¹³C spectra of the nonlabeled compound were recorded on a Bruker Avance II 300 spectrometer using triple resonance probes (7 mm and 4 mm) at a MAS frequency of 5 kHz and 12.5 kHz, respectively. Cross-polarization (CP) from proton to nitrogen and carbon was used to enhance the signal-to-noise ratio. The 90° pulse on the proton channel was set to 4.8 μ s (3.0 μ s), and the contact time was adjusted to 2 and 5 ms, respectively. ¹³C 1D spectra and double quantum buildup curves of compound 1* were recorded on a Bruker Avance III 700 in a 3.2 mm ZrO₂ rotor. For 1D spectra, cross-polarization

Scheme 1. Synthetic Route to ¹³C Labeled 1,3,5-Tris(2,2-dimethylpropionylamino)benzene 1*^a



^aPrecursors are numbered with I and II. The asterisk marks the ¹³C labeled carbonyl groups.

experiments at a MAS frequency of 12.5 kHz were performed. The ¹H 90° pulse length was adjusted to 3.0 μ s by applying a contact pulse of 5 ms. The recycle delay was set to 5 s (not fully relaxed for the –NH and aromatic protons). For the double quantum build-up curves, the symmetry-based pulse sequence SR26¹¹₄ was used.⁷² The performance of this sequence was checked by recording and evaluating DQ build-up curves for ¹³C labeled glycine (γ -polymorph). Here, the intermolecular ¹³C–¹³C distances could be reproduced with high accuracy possessing rms values below 0.2 (compare to section 2.4).

The MAS frequency was set to 5.5 kHz corresponding to a nutation frequency of roughly 36 kHz. The R-block was implemented as a 90°–270° composite pulse. The filtering corresponding coherence pathway 0 \pm 2 0 –1 was performed with the conventional 16-fold phase cycle.⁵² Additionally, a standardization experiment was collected with the coherence pathway 0 0 0 –1. The number of repetitions for each 1D experiment was set to 32. Cross-polarization from proton to ¹³C with a ¹H 90° pulse length of 3.0 μ s and a contact time of 5 ms was used. The read-out 90° pulse on ¹³C was set to 3.0 μ s. During excitation and reconversion CW decoupling with a nutation frequency of roughly 105 kHz was performed. For all experiments, a broadband SPINAL64 proton decoupling with a nutation frequency of about 85 kHz was used during data collection.

2.4. Solid-State NMR Simulations. Simulations for ¹³C¹³C buildup curves with the SR26 experiments were performed with the simulation package SIMPSON.⁷³ Magnitude and relative orientation of the carbon–carbon dipole tensors were extracted from the structure solutions after Rietveld refinement. The parameters for the ¹³C chemical shift tensors were estimated from a static 1D spectrum and included in the spin system. We first performed the simulations within a seven spin system and completed in a nine spin system to reduce finite size effects. The Euler angles for the CSA were found to have only a minor contribution to the shape of the build-up curves. Due to strong proton decoupling in the experiments, the influence of further proton interactions could be neglected. The simulations were carried out using a crystal file of 144 orientations and seven γ angles.

For each simulated build-up curve of the four space groups the rootmean-square deviation (rms) was calculated with MATLAB 74 according to

$$rms = \frac{\sum_{i} (sim_{i} - exp_{i})^{2}}{\sum_{i} exp_{i}^{2}}$$
(1)

where sim_i are the simulated and exp_i the experimental data points. The choice of the correct space group was then made based on the minimal rms values.

2.5. Computational Methods. The geometry optimization of the molecule before the *ab initio* structure solution was performed by DFT methods with the module DMol3 from MS Modeling.⁷¹ Within the DNP (double numerical plus polarization) basis set the GGA minimization was performed using the PW91 functional. The SCF (self-consistent field) density convergence was set to $1.0e^{-6}$ eV per atom.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of ¹³C Labeled 1,3,5-Tris(2,2-dimethylpropionylamino)benzene. The synthesis we here present is well established,²⁶ and the starting material, 3,5-dinitroaniline (I), is commercially available. The first step is the reduction of I in order to gain 1,3,5triaminobenzene (II) in almost quantitative yields of 98%. The formation of II was characterized by ¹H solution-state NMR spectroscopy. The spectrum displayed two singlets at δ = 4.30 and 5.13 ppm. The signal at δ = 4.30 ppm can be assigned to the amino groups while the signal at δ = 5.13 ppm belongs to the aromatic protons. The upfield shift of the aromatic resonance is caused by a strong decreasing of the shielding of the protons due to the electronegativity of the three nitrogen atoms of the NH2-groups. The expected intensity ratio of 2:1 clearly shows the complete formation as well as the purity of the product. For the formation of the target molecule $(1^*)^{13}$ C labeled 2,2-dimethylpropanoyl chloride was synthesized from commercialized Ba¹³CO₃ as described by Parnes et al.⁷⁰ with a yield of 51.8%. The product was characterized by ¹H solutionstate NMR where only one signal corresponding to the methyl group of the enriched acid chloride was observed reflecting the complete conversion to the labeled product. In a third step, the conversion of II with an excess of ¹³C labeled 2,2dimethylpropanoyl chloride gives the product with a yield of 38% after recrystallization from MeOH (Scheme 1). The ¹³C labeled product 1* was characterized by ¹H solution-state NMR, solid-state NMR, mass spectrometry, and powder X-ray diffraction.

The formation of compound 1* leads to three signal groups in the ¹H solution-state NMR spectrum. The resonances at δ = 1.209 ppm and δ = 9.205 ppm show an additional doublet splitting while the signal at δ = 7.625 ppm occurs only as singlet which can be assigned as the aromatic resonance. The signal at δ = 1.209 ppm belongs to the CH₃-group, and the signal at δ = 9.205 ppm can be assigned to the NH-group. Both proton resonances show a splitting due to the coupling to the neighbored ¹³C labeled carbonyl group over three bonds and two bonds, respectively. The corresponding coupling constants amount to 3.5 Hz for the methyl protons (³*J*-coupling) and 3.0 Hz (²*J*-coupling) for the amide protons. All three signal groups show an integral ratio of 1:1:8.99 which fits very well to the theoretical exception of a ratio of 1:1:9 resulting in a high purity of the product.

3.2. Symmetry Considerations from 1D Solid-State NMR Spectra. The ¹H, ¹⁵N, and the ¹³C solid-state NMR spectra of compound 1 are shown in Figure 2a–c. The proton spectrum displays three different signal groups at roughly δ = 2.0, 6.5, and 9.5 ppm clearly corresponding to the methyl protons, the aromatic protons, and the protons of the amide



Figure 2. 1D MAS spectra of 1,3,5-tris(2,2-dimethylpropionylamino)benzene: (a) ¹H spectrum ($\nu_{rot} = 65$ kHz, $B_0 = 11.7$ T), with signal assignment for **1** given in Figure 1, the asterisk marks an impurity; (b) ¹⁵N CP-MAS spectrum ($\nu_{rot} = 5$ kHz); (c) ¹³C CP-MAS spectrum ($\nu_{rot} = 12.5$ kHz, with signal assignment on top).

groups. In comparison to the isotropic chemical shift in solution-state, the resonance of the amide protons is shifted downfield of about 0.3 ppm. The aromatic protons, on the other hand, show an upfield shift of roughly 1 ppm (Figure 2a). Both aspects indicate the existence of packing effects like hydrogen bonds and $\pi-\pi$ interactions due to aromatic ring currents.⁹ Furthermore, the single sharp ¹H resonance of the NH-group suggests a quite narrow distribution of the hydrogen bond lengths. For similar systems, i.e., symmetric 1,3,5-benzenetrisamides ("N-centered"- based on 1,3,5-triaminobenzene and "C-centered" - based on trimesic acid), such effects have recently been reported and verified with solid-state NMR⁹ and quantum chemical calculations⁹ as well as temperature depending infrared spectroscopy.⁷⁵

The upfield shift of the aromatic protons of 1.2 ppm is in the same range as the ¹H chemical shift presented in ref 9 for the aromatic protons which points to a parallel arrangement of benzene rings within a columnar packing. The $\pi - \pi$ stacking within these columns with intermolecular distances of roughly 3.5 Å leads to an additional shielding of the protons due to strong ring currents of neighboring molecules. In our ¹H spectrum, we find one resonance for the aromatic protons. Therefore, compound 1 seems to possess a coplanar arrangement of the benzene rings, ideally with a helical rod stacking which would maintain C_3 symmetry of the molecules including a high symmetry within the crystal structure. However, this is in contrast to the N-centered tricarboxamide recently investigated by Wegner and co-workers.9 Indeed, they reported about significant upfield shifts for the aromatic proton signals due to the ring current effect like in our case, but in contrast, they observed three distinct signals for the aromatic resonances for N-BTA 3 (N-centered benzene-1,3,5-tricarboxamide with (S)-2,6-dimethylheptyl side chains). They explain their observance with a symmetry-breaking within the local packing motif. For their system it is possible that one carbonyl group of a molecule points in the opposite direction. This new stacking order can be

described as quasihelical structure accompanying with a partial loss of the coplanarity leading to a splitting of the aromatic protons.

The ¹⁵N CP spectrum (Figure 2b) displays one single resonance at $\delta = 127.5$ ppm corresponding to the amide nitrogen atom. The appearance of only one signal, on one hand, indicates the entire conversion from 1,3,5-triaminobenzene to the product due to an absence of the resonance being typical for an amino group. On the other hand, the single resonance suggests that all amide groups depict similar torsion angles with respect to the aromatic core and the *t*-butyl groups. This in turn suggests that only one molecule or one-third is located in the asymmetric unit. Both aspects display useful hints with regard to the structure solution which will be discussed at a later point. Finally, the narrow signal in the ¹⁵N CP spectrum is in very good agreement with the results from the proton signal of the amide group with respect to the hydrogen bonding situation.

Complementary results can be obtained from the ¹³C CP spectrum of 1 (not labeled, Figure 2c) where five signal groups can be obtained. At roughly $\delta = 27$ ppm the resonance for the methyl carbon atoms occurs. Interestingly, two different chemical shifts can be identified in an integral ratio of 2:1 suggesting a staggered conformation of the methyl groups concerning the adjacent OC–NH bond. The resonance at $\delta = 39$ ppm belongs to the quaternary carbon atom of the *t*-butyl group, and the two aromatic carbon atoms are located at $\delta = 112$ ppm and $\delta = 138$ ppm, respectively, whereas the carbon atom of the carbonyl group has a chemical shift of $\delta = 177$ ppm. The existence of only five resonances shows the high purity of 1,3,5-tris(2,2-dimethylpropionylamino)benzene without any residual educts as well as high order within the structure.

Moreover, the narrow line shape of the signals of the quaternary carbon atom and the upfield shifted aromatic carbon atom indicates a high symmetry in the packing of the molecules with uniformly distributed C-C distances between the benzene rings in the packing pattern. In the case of a tilted conformation of the benzene rings, more signals with a broader distribution of chemical shifts are expected. The ¹³C CP signal of the carbonyl group for the enriched BTA measured at a high external magnetic field ($B_0 = 16.4$ T), where the ¹⁴N interaction (I = 1) is eliminated due to its ω^{-2} dependence, depicts a marginally structured resonance due to the slightly different environment of the carbonyl atoms within one molecule. The signal was deconvoluted into three resonances ($\delta = 176.6$, 177.0, and 177.2 ppm) possessing equal FWHM with an intensity ratio 1.02(2):1:00(2):1.01(2) (Figure 3). The FWHM of roughly 0.5 ppm pictures a typical value for an α -carbon signal of ¹³Cenriched amino acids. This clearly shows that only one molecule is arranged within the asymmetric unit.

3.3. Crystal Structure of 1,3,5-Tris(2,2-dimethylpropionylamino)benzene. For developing a structure model, compound 1 was investigated by X-ray powder diffraction and solid-state NMR. Indexing of the powder pattern leads unequivocally to an orthorhombic metric which could subsequently be refined using the Pawley algorithm (a =14.79(3) Å, b = 23.85(5) Å, c = 6.75(1) Å, V = 2381(13) Å³, wRp = 2.6%). Assuming that carbon, nitrogen, and oxygen atoms possess a volume of roughly 18 Å³, the molecular volume of compound 1 can be estimated to 490 Å³. Including the hydrogen atoms would even increase this volume. This size restriction just allows at maximum four molecules within the unit cell. The reflection conditions, however, provide



Figure 3. ¹³C CP-MAS signal of the carbonyl group of ¹³C enriched 1,3,5-tris(2,2-dimethylpropionylamino)benzene (ν_{rot} = 12.5 kHz; B_0 = 16.4 T) with deconvolution into three distinct ¹³C resonances with an intensity ratio of 1.02(2):1.00(2):1.01(2). For all three resonances the same restriction for the FWHM was used.

reasonable results for 19 primitive and six body-centered space groups. On the basis of the nonplanarity of the molecule itself and the absence of an intrinsic C_2 symmetry, they cannot be placed on special positions in the unit cell. Therefore, only space groups possessing a multiplicity of 4 on general positions have to be taken into consideration for a further investigation. Nevertheless, 11 primitive space groups remain for a possible structure elucidation.

For all these space groups an *ab initio* structure solution with real-space methods was performed using a combination of a close-contact penalty and *w*Rp as cost functions. The DFT geometry optimized molecule was taken as rigid body with the rotational and translational degrees of freedom during the solution step. Additionally, the six most important and structure directing torsion angles (two in each side chain, see Figure 1, right) were refined during the optimization process. At the end, only four space groups remain possessing a comparable low *w*Rp value well below 10% (see Table 1), whereas all other

Table 1. wRp Values of the Four Most Probable Space Groups after the Powder Solution Step and Rietveld Refinement

space group	solution wRp/%	refinement wRp/%
$P2_{1}2_{1}2_{1}$	5.73	4.18
$Pna2_1$	5.96	4.57
P2an	7.49	5.19
P2 ₁ cn	7.16	4.37

structure solutions possess *w*Rp values far above 10%. An initial Rietveld refinement of these space groups leads to similar *w*Rp values which are listed in Table 1. Exemplarily, the Rietveld plot for space group $P2_12_12_1$ is depicted in Figure 4.

Selecting the correct structure model just from the observed structures from the powder data is difficult since the *w*Rp values are almost equal. All four structures show a similar behavior concerning their topology where the molecules build a pseudohexagonal rod packing along the *c*-axis. The major difference is the arrangement of the molecules within the packing pattern that can be distinguished in hydrogen-bonding $(P2_12_12_1 \text{ and } Pna2_1)$ and non-hydrogen-bonding $(P2_1cn)$ patterns (see Figure 5).

To further distinguish the structure models the intermolecular distances between the ¹³C labeled carbon atoms of the



Figure 4. Rietveld profile plot of the X-ray powder diffraction pattern for the solution in space group $P2_12_12_1$ collected at room temperature in a 2θ range 5–40°.

carbonyl groups were taken into consideration (see Table 2). While the intramolecular distances for all four space groups essentially show the same values, the intermolecular ones can



Figure 5. Top view on one rod of the different packing patterns where the NH-protons are emphasized. Top: pattern for the space groups P2an and $P2_1cn$ without hydrogen bonding. Bottom: pattern for the space groups $P2_12_12_1$ and $Pna2_1$ with a hydrogen bonding network. All other protons are omitted for clarity.

Table 2. Intramolecular and Intermolecular ¹³C-¹³C Distances between Labeled Carbonyl Groups from a Nine Spin System Used as Input for the Simulations

distance/Å	$P2_{1}2_{1}2_{1}$	$Pna2_1$	$P2_1cn$	P2an
intramolecular	6.622-6.628	6.586-6.601	6.634-6.715	6.633-6.654
intermolecular	4.927-5.259	4.983-5.229	4.616-5.740	4.189-6.105

clearly be distinguished. For the space groups possessing a hydrogen bond network the minimum and maximum distances are almost equal (~ 4.9 and ~ 5.2 Å), and moreover, the length distribution is quite narrow. On the other hand, both space groups without H-bonds show a significantly different behavior. The minimum distances amount to 4.19 and 4.62 Å, respectively, while the maximum distance is drastically extended up to 6.1 Å. Thus, the length distribution is much broader than in the first case.

To support the structure selection we therefore performed quantitative solid-state NMR experiments. For this purpose we carried out ${}^{13}C{}^{13}C$ DQ experiments taking advantage of the dipolar coupling between the carbonyl atoms using the SR26¹¹₄ pulse sequence (see section 2.3). The constant thereby is proportional to r^{-3} where *r* represents the ${}^{13}C{}^{-13}C$ distance. The normalized experimental build-up curve of the carbonyl resonance is depicted in Figure 6b.

It shows a very slow increase with a quite broad maximum at about $\tau = 17$ ms, and the double quantum efficiency reaches roughly 50%. For simulating the experimental build-up curve we cut out a characteristic element of one rod of each crystal structure after the Rietveld refinements. Hence, the generated spin system had to be sufficiently large to avoid finite size effects and small enough to be handled with reasonable computation time. A nine spin system (Figure 6c) turned out to be the best choice. Here, each triangle represents one molecule within one rod of the structure, while the black circles illustrate the labeled carbonyl groups. The nine spin system used for our simulations is hence spanned by the three carbonyl spins of each molecule.

In Figure 6a, the root-mean-square errors (rms) between experiment and simulation (see section 2.4) are given for the four remaining space groups. It can be distinguished between space groups containing hydrogen bonds and without hydrogen bonds. While the latter possess rms values of 1.1 and 2.9, respectively, the former shows significantly lower values of 0.25 and 0.35. The simulated build-up curves for P2an and $P2_1cn$

therefore badly reproduce the experiment. Due to the shorter intermolecular distances (see Table 2) the slope of the simulated curves is stronger leading to a maximum excitation time of roughly $\tau = 14$ ms. In fact, the simulated curves for $P2_12_12_1$ and $Pna2_1$ match the experimental build-up curve very well on the basis of the longer ${}^{13}C-{}^{13}C$ distances and the narrower distribution of the distances between the ${}^{13}C$ atoms in the spin system. However, the best fit could be achieved for space group $P2_12_12_1$ (see rms values, Figure 6a). On the basis of the higher *w*Rp and rms values as well as the fact that peculiar gliding planes (like in $Pna2_1$) are uncommon for molecular compounds which prefer crystallizing in rather simple lattices and point groups, the structure model in space group $Pna2_1$ can definitely be excluded.

1,3,5-Tris(2,2-dimethylpropionylamino)benzene therefore crystallizes in the orthorhombic noncentrosymmetric space group $P2_12_12_1$ (a = 14.91(5) Å, b = 24.05(8) Å, c = 6.80(2) Å) containing four molecules in the unit cell, all on general positions. The *w*Rp of 4.18% is a very good value for an *ab initio* structure solution picturing the high order of the sample despite the presence of only light atoms leading to weak scattering.

The molecular structure after the Rietveld refinement can be seen in Figure 7. The CArCArN_HCO torsion angles seem to play a major role for the formation of the structure. Two side arms exhibit almost identical values for this torsion angle (31.36° and 31.46° , respectively), while the third one is a little bit higher (34.56°). This fact in addition to the deconvoluted ${}^{13}C=O$ signal of 1* (Figure 3) slightly breaks the perfect regularity; however, a pseudo- C_3 symmetry remains as assumed from ¹H and ¹⁵N solid-state NMR experiments. The HNCO torsion angles picturing the amide bonds are 178.78°, 178.93°, and 179.66°. This is in very good agreement with the expected value of 180° due to the behavior as partial double bonds. The oxygen atoms of the three carbonyl groups in one molecule point in the same direction out of the plane of the central aromatic ring system which is a precondition to form hydrogen bond patterns within the structure (Figure 8).

In 2009, Jiménez et al. reported the structure of a "C-centered" BTA (connected with the carbonyl carbon atom to the benzene ring) carrying a propyl moiety in each side arm instead of a *t*-butyl group.³⁰ The molecules within the crystal packing build up a supramolecular 3D H-bond network within a primitive cubic metric. However, in contrast to 1, π -stackings are avoided with the linear side arms. Also in 2009, Kristiansen



Figure 6. (a) Histogram with root-mean-square deviation between experimental and simulated symmetric build-up curve of all four space groups. (b) Experimental (orange plus) and simulated (solid lines) symmetric ${}^{13}C{}^{13}C$ SR26 build-up curves of 1* after Rietveld refinement. (c) Scheme of a nine spin system for all simulations where each triangle represents one molecule within the packing of the structures. The ${}^{13}C$ spins (three in each molecule) are marked as circles; intermolecular distances are highlighted with dotted lines.



Figure 7. Molecular structure of 1,3,5-tris(2,2-dimethylpropionylamino)benzene with distances in angstroms as derived from the X-ray powder diffraction experiment.



Figure 8. Section of the crystal structure of 1,3,5-tris(2,2dimethylpropionylamino)benzene with view along the *c*-axis. The unit cell contains four molecules on general positions.

et al. reported about the crystal structure of a similar 1,3,5benzenetrisamide (compared to compound 1) on the basis of transmission electron microscopy and electron and X-ray diffraction studies,³¹ carrying the same moieties in the side arms (*t*-butyl), but, in contrast, with a "C-centering" of the amide group. Here the molecules are reported to possess a complete C_3 symmetry, and moreover, all three oxygen atoms of the carbonyl groups show in one direction with $C_{Ar}C_{Ar}N_HC_O$ torsion angles of 53.21° each of which is roughly 20° higher than for our benzene based trisamide.

The crystal structure of 1 can be described as hexagonal rodpacking where the molecules build long rods parallel to the *c*axis (see Figure 8). Due to the 2_1 screw axis and the additional pseudo- C_3 symmetry, the molecules are twisted around 60° within one rod leading to a helical arrangement which has also been reported for similar benzene based supramolecular systems.³¹ An extensive hydrogen bond network is built between the amide protons and the oxygen atoms of the neighboring molecules in one rod. The NH···O distances with 2.04–2.14 Å, picturing medium strong H-bonds, are narrowly distributed which is in very good agreement with the results from ¹H and ¹⁵N solid-state NMR. The corresponding N–O distances account for 2.97–3.06 Å. In addition to the H-bond network the helical structure is characterized by sandwich stacked π -systems within one rod. The aromatic rings and therefore the molecules are stacked in a coplanar arrangement where the aromatic rings are tilted less than 1°. Typical distances of the benzene carbon atoms of two molecules are between 3.37 and 3.42 Å which is similar to the distances in π -stacked discotic liquid crystals.⁷⁶

In comparison, the structure presented in ref 31 crystallizes in a hexagonal unit cell where two molecules are sited on special positions. The structure is also characterized by an extensive hydrogen bonding network within the rod packing as well as a helical arrangement. The N–O distance with 2.65 Å is roughly 0.3 Å shorter than for compound 1 indicating stronger hydrogen bonds. This is also supported by the increased jut of the oxygen atoms from the aromatic ring system in comparison to compound 1. Due to the 6_3 screw axis the molecules are also twisted around 60°. The sandwich-like $\pi - \pi$ contacts picture the second structure directing interaction whereupon the distances between two benzene rings amount to 3.45 and 3.47 Å, respectively, which is in the same range as that observed for compound 1. Surprisingly, the synchrotron X-ray pattern of this "C-centered" trisamide reveals an immense diffuse scattering. This pictures a structural disorder where the two rods within the unit cell can be slid against each other. For the "N-centered" trisamide, on the other hand, no diffuse scattering was observed during investigation indicating a high order within the crystal structure.

The molecules of compound 1 and the ones from ref 31 remain nearly C_3 symmetric where all carbonyl groups point in one direction. Due to this out-plane arrangement of the oxygen atoms the molecules itself possess a quite large dipolar moment leading to the formation of macrodipoles for individual rods of the packing. One common mechanism of choice to reduce this moment within the unit cell and with it the potential energy is to form an antiferroelectric arrangement.⁷⁷ For compound 1, indeed, the molecules in neighbored columns show in the opposite direction (Figure 9) canceling out the net dipolar



Figure 9. Part of the crystal structure of **1** with view along the *b*-axis. The oxygen atoms of the carbonyl groups point in the opposite direction leading to an averaging of the net dipolar moment. All protons and the carbon atoms of the *t*-butyl groups were omitted for clarity.

moment. Due to avoid frustration while canceling the dipole moment, compound 1 undergoes an orthorhombic distortion ("pseudohexagonal") in contrast to the BTA reported by Kristiansen et al. where all rods are aligned parallel. Consequently, the net dipolar moment increases drastically leading to a complete ferroelectric arrangement. Interestingly, the structure of compound 1 in $P2_12_12_1$ could easily be transferred into the one of $Pna2_1$ by twisting the $C_{Ar}C_{Ar}N_HC_O$ torsion angle (see Figure 1) in each side chain of every second rod by roughly 60° leading also to a ferroelectric arrangement analogous to that of ref 31.

4. CONCLUSIONS

We have presented an approach for the determination of the crystal structure of 1,3,5-tris(2,2-dimethylpropionylamino)benzene, an efficient clarifying agent for isotactic polypropylene. The structure was solved in the orthorhombic space group P212121 using X-ray powder diffraction in combination with multinuclear solid-state NMR experiments and computer simulations. During structure elucidation, only four space groups led to reasonable structure models. DQ experiments allowed excluding the three remaining space groups. Using the symmetry-based SR26¹¹₄ pulse sequence, ¹³C-¹³C distances of nearly 5 Å could be reproduced with high precision. The simulation of the build-up curves fitted best for the space group $P2_12_12_1$ with a root-mean-square deviation of 0.25. The *c*-axis with a length 6.80(2) Å is in this connection in the similar range with the c-axis of the crystalline part of *i*-PP (\sim 6.50 Å) which possesses a helical structure as well.⁸¹ The additive crystallites within the polymer melt therefore might serve as a surface which allows the polymer to grow epitactically. This remarkable fact may cause *i*-PP to appear highly transparent. Therefore, further investigations in the additive/polymer composite systems are mandatory and will be discussed in a forthcoming publication.

The structure itself can be described as a hexagonal rod packing where the pseudo- C_3 symmetric molecules are twisted by 60° due to the 2_1 screw axis. The rods are stabilized via moderate hydrogen bonds with NH---O distances of roughly 2.0 Å and, moreover, via π -interactions due to a sandwich stacking of the aromatic cores with distances of about 3.4 Å. Each molecule possesses an intrinsic dipolar moment due to the fact that all oxygen atoms point in one direction. Therefore, the dipolar moment in one rod strongly increases. This H-bond mediated growth within one rod is in principle possible since the increasing potential energy is counterbalanced by the energy advantage based on the formation of hydrogen bonds. Moreover, the occurrence of such macrodipoles is not completely unknown within the BTA systems. Such phenomena have recently been demonstrated by Kulkarni et al.⁸⁰ on the basis of quantum chemical calculations. In addition, experimental proof was given by Sakamoto et al. where benzene-1,3,5-tricarboxamides with long side chains formed onedimensional macrodipoles in solution of n-decane leading to highly viscous liquids.⁷⁸ In thin films it was even possible to generate macrodipoles in a three-dimensional ordered system." However, a ferroelectric arrangement could not be achieved per se rather than by applying an external electrical field. Obtaining ferroelectricity by crystallization from solution seems to be improbable. Once a macrodipole in one rod is built, the second one must be arranged antiparallel since parallel formation strongly increases the potential energy of the system that cannot be compensated by the 1D H-bond network. In this case only small nanocrystals would be observed. Therefore, an antiferroelectric arrangement with antiparallel aligned rods as observed for compound 1 leading to a net dipolar moment of zero represents the driving force for the fast needlelike crystal growth of this class of materials.

ASSOCIATED CONTENT

S Supporting Information

Spin system extracted from the structure solution as input file for SIMPSON used for the simulation of the DQ build-up curve as well as a CIF file of **1** including the crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: (+49) 921-55-3206 (H.-W.-S.); (+49) 921-55-2788 (J.S.). E-mail: hans-werner.schmidt@uni-bayreuth.de (H.-W.S.); juergen.senker@uni-bayreuth.de (J.S.).

Notes

The authors declare no competing financial interest.

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