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COMMUNICATION

New symmetrically substituted 1,3,5-triazines as host compounds for channel-type inclusion formation†

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A new synthetic procedure for the production of symmetrically substituted 1,3,5-triazines by cyclization from aromatic nitriles in the molten state with zinc chloride as a catalyst has been developed and applied for a number of aromatic and fluoro aromatic nitriles. The new triazine 8 [2,4,6-tris(4′-bromobiphenylyl)-1,3,5-triazine] is shown to form channel-type inclusion compounds with several aromatic solvents, featuring two different channels in the same crystal.

Organic porous materials that survive the removal of guest molecules ("organic zeolites")[1] and are capable of selective guest inclusion have been widely examined in recent years. They provide possible applications in gas storage,[2] catalysis, molecular separation,[3] sorption,[4] sensing, and the implementation of physical properties.[5]

Symmetrically substituted 1,3,5-triazines offer many opportunities for interesting solid state supramolecular applications: molecules of this type form crystalline inclusion compounds[6] providing a van der Waals channel diameter of 10–12 Å,[7] thus allowing the accommodation of rather large molecules as guests.[8] For example 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (BrPOT) gives rise to the inclusion of fullerenes,[9] bucky-ferrocene[10] and decamethylferrocene-type molecules.[11] Moreover, the same triazine features zeolite properties, as micrometre sized crystals retain the open pore structure after removal of the guest up to a temperature of 80 °C,[12] and fluorinated derivatives resulted in a further enhancement of the thermal stability of the channel structure up to 110 °C.[13] With a channel size of 11 Å, BrPOT species are among organic zeolites stabilized by weak bonding which provide rather large open pores.[1] It has also been shown that variation of the linkage group connecting the triazine ring with the aryl substituent is a crucial parameter for the formation of inclusions, while the exchange of O with N or S resulted in less exciting inclusion properties.[14]

Symmetrically substituted 1,3,5-triazines have been synthesized by various methods, such as nucleophilic substitution of cyanuric chloride[15] or cyclization of nitriles catalyzed by very strong acids (*e.g.* chlorosulfonic acid or triflic acid).[16] Others involve weak bases combined with high pressures,[17] SmI_2 in the presence of amines,[18] *n*-BuLi[19] or lanthanide(III) ions.[20] All of these methods have severe disadvantages regarding either the rigidity of the reaction conditions, the need for additional reagents or co-catalysts and the occurrence of side reactions.

Zinc chloride ($ZnCl_2$) is a hygroscopic solid with a melting point of 327 °C[21] that acts as a Lewis-acid and is known to catalyze some electrophilic aromatic substitution reactions[22] as well as cyclizations of alkenes.[23] Moreover, $ZnCl_2$-coated silica has been used as a heterogeneous catalyst in cyclization reactions, such as asymmetric Diels–Alder reactions[24] and the cyclization of nitriles to give triazines.[25] However, the yields of phenyl-substituted triazines proved to be poor (13%) and a co-catalyst was needed.

Recently, Kuhn *et al.*[26] reported on $ZnCl_2$ catalyzed polymerization of aromatic dinitriles to form polymeric triazine frameworks with a regular or non-regular porosity. For the synthesis, one equivalent of $ZnCl_2$ and rather high temperatures of approximately 400 °C were used, producing a black, polymeric product. The resulting microporous materials are regarded as potential hydrogen storage materials that can compete with most MOFs, zeolites and mesoporous carbon materials. They provide high chemical, thermal and mechanical stability and thus also exhibit potential applications as sorption materials, sensors, or catalyst supports.

Here, we demonstrate the effectiveness of using pure $ZnCl_2$ as a catalyst for the cyclization reaction of a variety of substituted aromatic nitriles leading to monomeric 1,3,5-triazines (Fig. 1). Therefore, lower concentrations of $ZnCl_2$ and lower temperatures were used.

The reaction takes place in the liquid state without extra solvents or co-catalysts. The respective nitrile and $ZnCl_2$ are heated to the reaction temperature (between 250 and 300 °C) in a closed ampoule. Because of eutectic liquefaction, the reaction takes place far below the

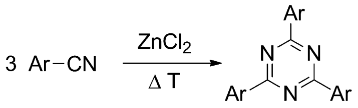

Fig. 1 Cyclization of aromatic nitriles with zinc chloride as a catalyst.

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melting point of zinc chloride (327 °C). This new mode of cyclization was applied to several aromatic nitriles. Depending on the reactivity and susceptibility of the nitriles towards decomposition, the reaction conditions (molar ratio of benzonitrile *vs.* ZnCl$_2$, reaction temperature and reaction time) and the yields vary (Table 1).

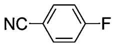
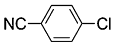
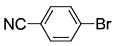
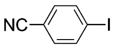
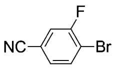
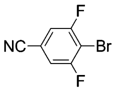
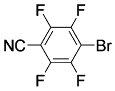
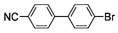
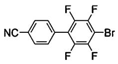
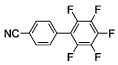
A potential mechanism for the ZnCl$_2$-catalyzed cyclization is given in Fig. 2. The reaction is initiated *via* polarization of the C≡N triple bond by Zn^{2+} ions, being present in the ionic melt. As a result, a nucleophilic attack of a cyano group on the positively polarized carbon atom is facilitated, producing a carbenium ion which undergoes a subsequent attack by a third nitrile group yielding the triazine ring.

The rather low yields of triazines from fluorinated benzonitriles might be due to the electronic effects of the fluorine substituents, which probably attract electron density from the nitrile group. This will lower the nucleophilic power of the nitrile and slow down the reaction.

The substances obtained are new channel forming host compounds featuring diverse channel diameters. They provide several van der Waals binding sites, offering opportunities to create new functional host–guest structures. As an example, compound **8** has been crystallized from various organic solvents and was found to include toluene, chlorobenzene, *p*-xylene and mesitylene in channel-type cavities. The inclusions of toluene and *p*-xylene are isomorphous (see Notes and references), the one with *p*-xylene is shown in Fig. 3. The guest is included into two different channels along the crystallographic *b*-axis (4 × 6 Å and 6 × 9 Å), accommodating *p*-xylene along its axis (in the small channel) and approximately perpendicular to it (in the large one). This is a rare example of a channel system allowing for two packing modes of guests in one crystal (compare Lit. ref. 27). In the wide channel, the π-rings of the *p*-xylene overlap partly (Fig. 4), and the molecules are inclined about 24° with reference to the (*a*,*c*)-plane. This is, to our knowledge, the first time that π-overlap of guest molecules could be achieved in channels. As the stacking period of *p*-xylene defined by the van der Waals length (about 9.1 Å) is incommensurable with the *b*-axis (3.87 Å), the guest molecules are disordered along this axis and the host–guest ratio amounts to 1.46 : 1. The inclusion structure is stabilized mainly by $\pi\cdots\pi$ stacking,[30] C–H···Br hydrogen bonds,[31] a C–H···π and a C–Br···π[32] contact. It is interesting to note that the walls of the bigger channels are lined with hydrogen atoms, whereas the narrow channels also comprise bromine atoms at the channel walls.

If crystallized from mesitylene, the host **8** forms a channel-type inclusion compound with a very wide channel comprising a cross-

Table 1 Cyclization of aromatic nitriles

Product	Benzonitrile	Molar ratio[a]	*T*/°C	*t*/h	Yield (%)
1		2 : 1	270	64	40
2		2 : 1	300	60	71
3		5 : 1	270	60	69
4		2 : 1	270	20	61
5		2 : 1	250	20	6
6		2 : 1	250	20	9
7		2 : 1	270	60	3
8		2 : 1	270	60	49
9		2 : 1	250	50	40
10		2 : 1	270	60	45

[a] Molar ratio of benzonitrile *vs.* ZnCl$_2$.

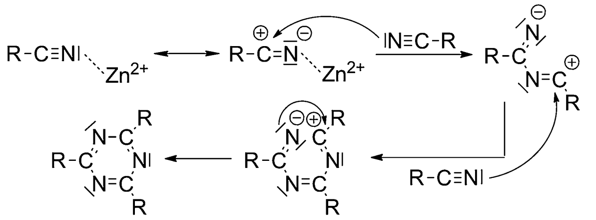


Fig. 2 Potential mechanism for the ZnCl$_2$ catalyzed cyclization of aromatic nitriles.

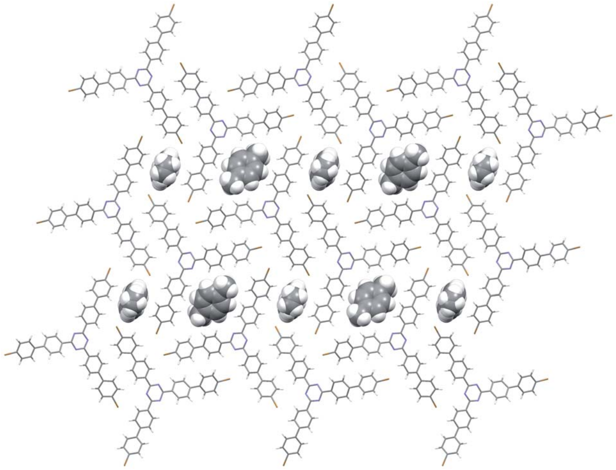


Fig. 3 View along the *b*-axis of an inclusion crystal of **8** with *p*-xylene.

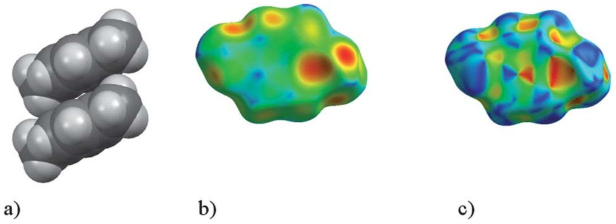
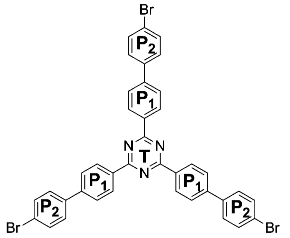


Fig. 4 π-Stacking of guest molecules within the channels of **8**·*p*-xylene; (a) van der Waals surface;[28] (b) d_e (distance to the external), the blue hexagonal feature is typical of benzene ring $\pi\cdots\pi$ stacking; (c) shape index, the face-to-face red and blue triangles are again typical of $\pi\cdots\pi$ stacking.[29]

Table 2 Angles between triazine/phenyl ring and two phenyl rings in the inclusion structures of **8** with *p*-xylene and mesitylene

Angles	**8**·*p*-xylene	**8**·mesitylene
T–P$_{\mathbf{1a}}$	3.49°	5.46°
T–P$_{\mathbf{1b}}$	4.05°	4.12°
T–P$_{\mathbf{1c}}$	20.04°	3.42°
P$_{\mathbf{1a}}$**–P**$_{\mathbf{2a}}$	38.85°	34.41°
P$_{\mathbf{1b}}$**–P**$_{\mathbf{2b}}$	33.35°	33.30°
P$_{\mathbf{1c}}$**–P**$_{\mathbf{2c}}$	35.90°	43.34°



section of 10 × 18 Å. Due to the width of the channel, the guest molecules are disordered. The remaining difference in electron density suggests an orientation of mesitylene along the channel axis and was treated by the SQUEEZE[33] technique. The solvent accessible void volume of 708 Å^3 leaves space for about four guest molecules per unit cell, *i.e.* a host–guest ratio of 1 : 2. Here, the host structure is mainly stabilized by π···π stacking. Furthermore, one C–H···Br hydrogen bond can be found. Contrary to what the symmetric structure of the host molecule suggests, it does not show a trigonal symmetry in the crystal structures. The angles between triazine and phenyl rings deviate from each other up to 16° and those between the phenyl rings in the substituents up to 10° (Table 2). This proves that trigonal crystal symmetry is not a prerequisite for the formation of channel-type inclusion compounds.

A series of crystallizations of other compounds of Table 1 with numerous solvents were performed and analyzed by ^{1}H NMR spectroscopy and/or thermogravimetric analysis (TG). It was shown that compounds **1** to **7** and **10** do not include any common solvents, whereas **9** seems to include the aromatic solvents toluene, *p*-xylene and mesitylene.

We have elaborated a new synthesis for symmetrically substituted 1,3,5-triazines from aromatic nitriles, showing good yields in most cases. The reaction can be implemented in the synthesis of a variety of symmetrical 1,3,5-triazines, being substituted with aromatic groups. The procedure is also useful for the synthesis of partly fluorinated 1,3,5-triazines, although the yields might be lower in particular cases. Further work to promote the range of application of the present reaction to a wide field of aromatic and heteroaromatic nitriles is in progress.

The new triazines form inclusions featuring channels. However, depending on the template, either two channels of different packing geometry or one particularly large channel-type (without interpenetration) is formed: inclusion of slightly elongated aromatics, such as toluene and *p*-xylene, gives two channels of different sizes existing both in one crystal, whereas the inclusion of rather big molecules, such as mesitylene, results in rather big channels with cross-sections of up to 18 Å.

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