Volume 16 | Number 29 | 7 August 2014 | Pages 6493–6804

CrystEngComm

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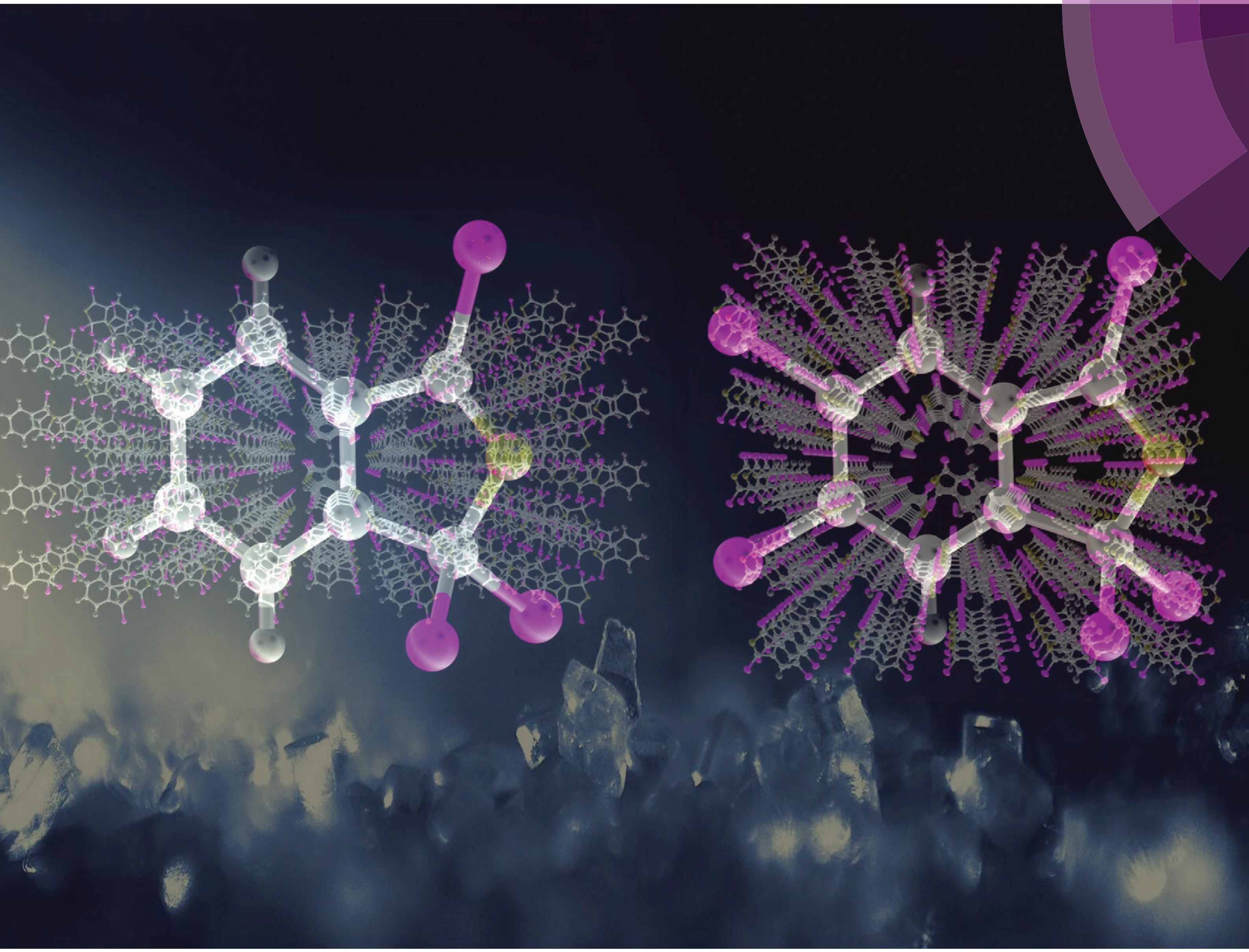

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PAPER

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Optimized synthesis and crystal growth by sublimation of 1,3,3-trichloroisoindolenines, key building blocks for crosswise phthalocyanines

CrystEngComm

PAPER

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Cite this: *CrystEngComm*, 2014, **16**, 6556

Optimized synthesis and crystal growth by sublimation of 1,3,3-trichloroisoindolenines, key building blocks for crosswise phthalocyanines†‡

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Received 24th January 2014,
Accepted 31st March 2014

DOI: 10.1039/c4ce00189c

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Among possible asymmetrically substituted phthalocyanines, ABAB derivatives remain rare. Their selective synthesis is based on the use of trichloroisoindolenines, so far remaining tedious to obtain. An optimized synthesis of 1,3,3-trichloroisoindolenine **1** and 1,3,3,6,7-pentachloroisoindolenine **2** is reported. An original crystallization method based on crystal growth by sublimation was eminently suitable regarding the air-sensitivity of these derivatives and allowed their thorough crystallographic characterization.

Introduction

Phthalocyanines are one of the most attractive high-technological molecular materials,[1] appearing promising in the last years in the fields of dye sensitised solar cells,[2] non-linear optics,[3] electron-transfer based technologies,[4] as well as photodynamic,[5] catalytic[6] or sensing[7] applications. Their related spectroscopic, optic, electronic or electrical properties, among others, can be tailored by fine structural variations, either by varying the central metal or by playing with the number, position and nature of the substituents.[8] In addition, asymmetrically substituted phthalocyanines offer additional functionalization possibilities and geometrical variations. The four isoindole subunits of the phthalocyanine macrocycle can bear substituents A or B, and the different possible asymmetric substitution patterns are summarized in Fig. 1. If the A3B type is now quite common and easy to prepare by a statistical method or subphthalocyanine ring expansion selective method, the AABB and the ABAB derivatives remain tedious to obtain.

Only a few number of crosswise ABAB phthalocyanines are described,[9] despite their interest again confirmed by our recent studies.[10] As an alternative to statistical phthalonitriles condensation implying numerous chromatographic separations, a selective method is based on the cross condensation of two precursors of different types: a trichloroisoindolenine with a diiminoisoindoline. This method offers the advantage to lead, in theory, exclusively to the desired crosswise phthalocyanine, as trichloroisoindolenines can not react on themselves, as can phthalonitriles and diiminoisoindolines which are the most common phthalocyanine precursors. Anyway, formation of A3B derivatives during the crosswise condensation is sometimes observed.[9b] This is due to the reactivity of diiminoisoindolines, likely to react faster on themselves than with the trichloroisoindolenine. This method allowed in addition to prepare the unique ABAC phthalocyanine reported so far.[11]

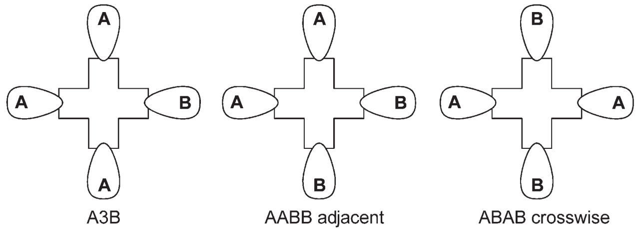
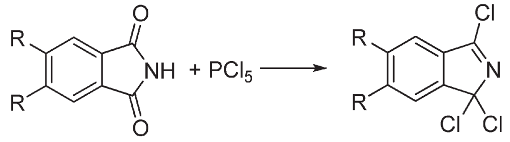


Fig. 1 The different types of asymmetric substitution patterns.



1 R = H
2 R = Cl

Scheme 1 Preparation of trichloroisoindolenines **1** and **2** from corresponding phthalimides.

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† In the memory of Christian Claessens.

‡ Electronic supplementary information (ESI) available: Intermolecular interactions in 1 and 2 (Table S1), are available. CCDC 876241 and 913163. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00189c

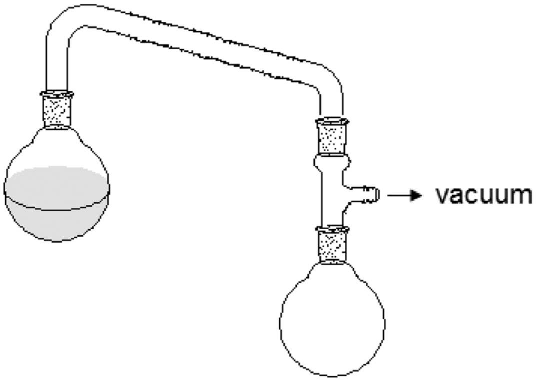

Fig. 2 Schematic representation of the distillation glassware.

Given the importance of the introduction of substituents on ABAB derivatives, and since the description of trichloroisoindolenine **1** remains incomplete, **1** was selected together with the new 6,7-dichlorinated substituted derivative **2** to report an optimized method to obtain trichloroisoindolenines in excellent yields, including the use of sublimation as a crystallization method allowing their thorough crystallographic structural characterization.

Results and discussion

Optimized synthetic procedure

From a synthetic method point of view, one of the key points is the use of freshly sublimed phosphorus pentachloride, as

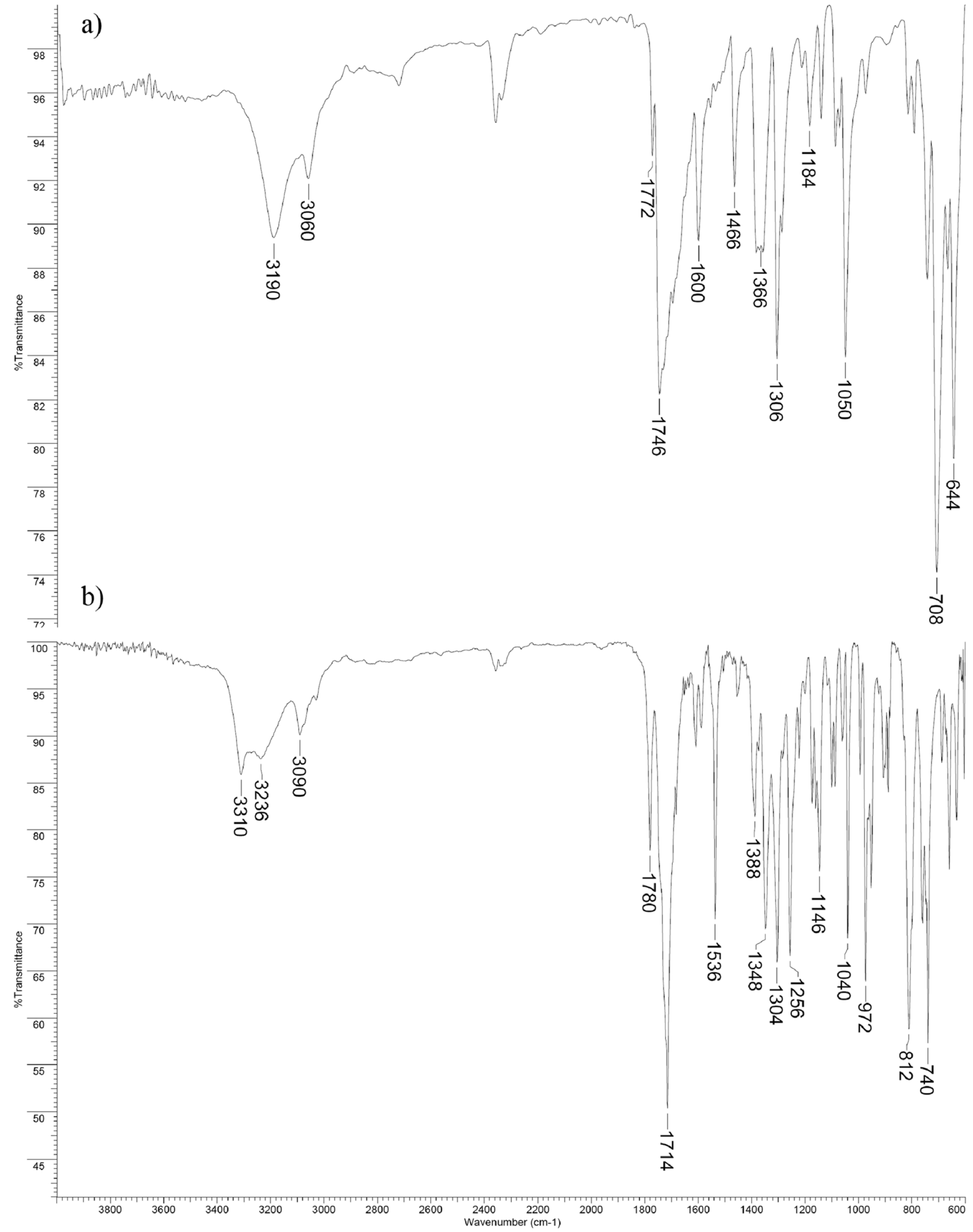

Fig. 3 ATR-IR spectra of trichloroisoindolenines **1** (a) and **2** (b).

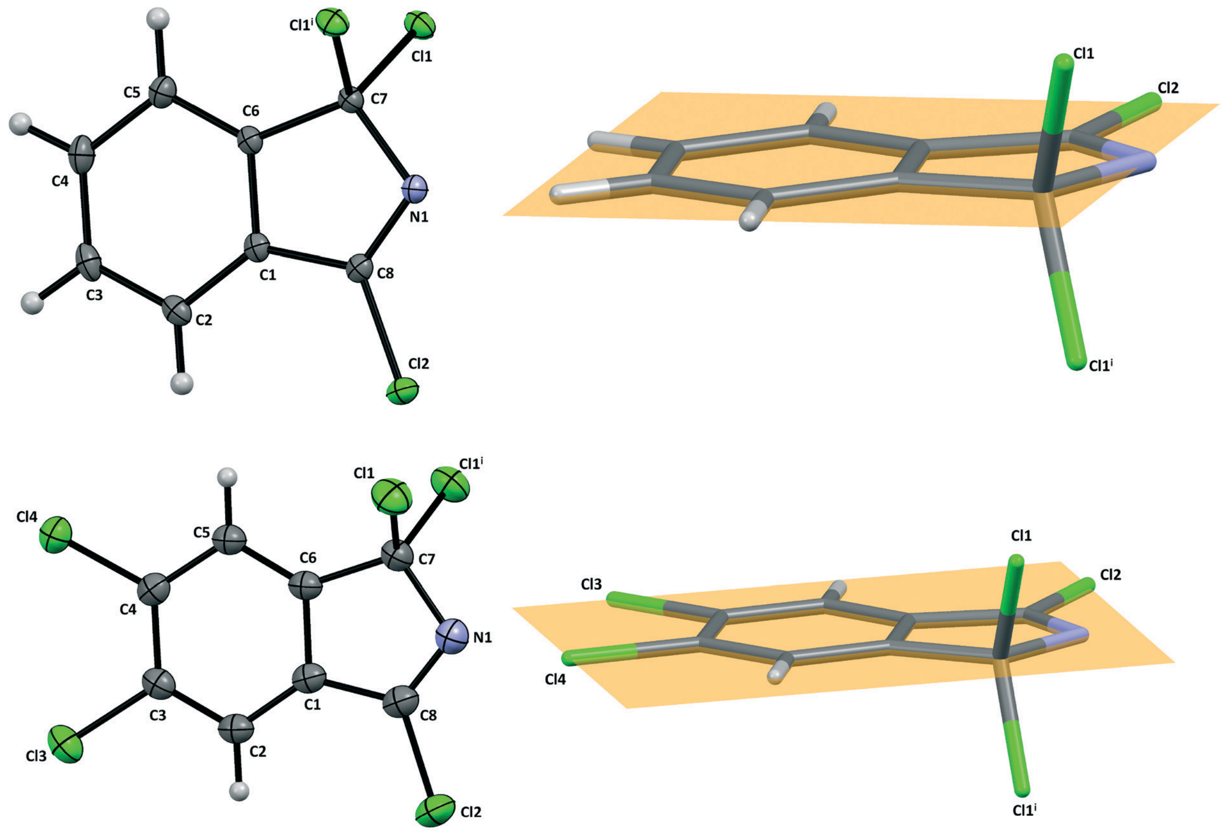

Fig. 4 Left handside: molecular structures of **1** (top) and of **2** (bottom). Displacement ellipsoids are drawn at the 30% probability level. H-atoms are shown as small spheres of arbitrary radii. Symmetry transformations used to generate equivalent atoms: (i) x, $-y + 1/2$, z; right handside: side view of **1** (top) and of **2** (bottom).

previously mentioned by Hanack,[9b] to react on relevant phthalimide (Scheme 1).

Substitutive chlorination appeared to be optimal when performed during one week, in dry *o*-dichlorobenzene, under a continuous flux of argon. The importance of this argon flux is crucial, as it allows to remove the hydrochloric acid formed during the course of the reaction and to make the reaction much more complete than under closed conditions. This method was satisfying enough not to test other options to neutralize the hydrochloric acid, such as the use of a proton sponge. After distillation of the solvent and of $POCl_3$ using a classical horizontal distillation set-up with a horizontal condenser, this condenser is replaced by a special piece of glassware, consisting of a horizontal tube equipped at each extremity by a male cone shaped NS joint to distil the trichloroisoindolenine under high vacuum (Fig. 2). The whole system (remaining crude compound in the reaction round bottom-flask + horizontal tube) is heated with a heat gun. **1** and **2** are obtained in the excellent respective yields of 84 and 60%, **2** being far less easy to collect due to its heavier and less volatile structure.

This optimized synthetic procedure was applied as well to the preparation of 6-nitro-1,3,3-trichloroisoindolenine, previously described by Young and Onyebuagu. The yield was optimized as well, from 35% (literature report)[9a] to 72%, demonstrating the scope of our method. Unfortunately, it was not possible to obtain the compound under a crystalline form.

Crystal growth and sublimation advantages

Attempts to further purify trichloroisoindolenine **1** following reported recrystallization in cyclohexane[12] failed, the product turning back to the corresponding starting phthalimide. Such trichloroisoindolenine derivatives are indeed reported to be highly unstable to air and moisture, and no set-up allowed the recrystallization of the trichloroisoindolenines. All other recrystallization attempts resulted in the conversion of the trichloroisoindolenine into the starting phthalimide.

The use of solvents was not further considered and therefore classical crystallization means were not conceivable anymore.[13] Nevertheless, in order to complete the best possible characterization of the compounds, we were keen on obtaining crystals. Sublimation appeared to be a possible method, and indeed trichloroisoindolenine **1** was successfully obtained. If no major difference was observed in the yields of ABAB phthalocyanine when using distilled or sublimated trichloroisoindolenines, the major advantage of the sublimation, in addition to the structural investigation reported here, is the longer stability of the compound, which can be stored without degradation for much longer periods.

Table 1 Crystal data and refinement parameters for **1** and **2**

Crystal parameters	1	2
Empirical formula	$C_8H_4Cl_3N$	$C_8H_2Cl_5N$
Formula weight (g mol^{-1})	220.47	289.36
Temperature (K)	170(2)	299(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/m$
a (Å)	15.9288(3)	7.8916(7)
b (Å)	6.9261(2)	7.1079(7)
c (Å)	7.8324(2)	9.4988(11)
β (°)	90	97.514(7)
Crystal size (mm)	0.17 × 0.20 × 0.24	0.06 × 0.11 × 0.17
V (Å^3)	864.11(4)	528.24(9)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.695	1.819
μ (mm^{-1})	0.994	1.326
$F(000)$	440	284
θ range for data collection (°)	2.56–25.02	2.16–25.01
$h/k/l$	−18/18, −8/6, −9/9	−9/9, −7/8, −11/11
Reflections collected	4573	3948
Independent reflections	834	1015
T_{min} and T_{max}	0.78 and 0.85	0.81 and 0.93
Data/restraints/parameters	834/0/70	1015/0/82
Goodness-of-fit on F^2 (S)	1.138	1.143
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0221$, $wR_2 = 0.0624$	$R_1 = 0.0322$, $wR_2 = 0.0946$
R indices (all data)	$R_1 = 0.0231$, $wR_2 = 0.0632$	$R_1 = 0.0376$, $wR_2 = 0.0984$
Largest diff. peak and hole (e Å^{-3})	0.184 and −0.354	0.282 and −0.258

During sublimation, the best crystal quality was obtained by a slow heating of the compound. Trichloroisoindolenine was quantitatively sublimated, but the need to quickly transfer the crystals into a vessel under argon allowed to recover usually ~90% of the product.

Structural characterizations

As mentioned above, such derivatives are highly unstable in the presence of moisture, and more especially in solution. This prevented us to complete NMR analyses as all attempts lead to the degradation of the compounds, due to unavoidable presence of moisture in the deuterated solvents we have at our disposition, even when preparing the samples under argon. Conversely, analyses in the solid state, such as ATR-IR spectroscopy, melting points determination and crystallographic structure elucidation could be performed. The melting point of **1** is in accordance with the previously reported (106–107 °C),[14] and the presence of the two chlorine atoms in **2** slightly increases it (110–111 °C). The ATR-IR spectrum (Fig. 3) showed stretching vibrations of Csp^2–H bonds at respectively 3060 and 3090 cm^{-1} for **1** and **2**. Additional broad bands at 3190 cm^{-1} for **1** and 3236 and 3310 cm^{-1} for **2** are observed. These bands are quite unexpectedly shifted but can be likely attributed to an effect of the presence of the chlorine atoms on Csp^2–H bonds vibration. Other characteristic peaks in the 1700–1800 cm^{-1} area of the spectrum are due to concomitant vibrations of the C–Cl bonds (1772 cm^{-1} for **1** and 1780 cm^{-1} for **2**) and of the C═N bonds (1746 cm^{-1} for **1** and 1714 cm^{-1} for **2**). Once again, the presence of the chlorine atoms explains the shifted position of the C═N bonds vibration, more commonly centered at 1600 cm^{-1}.

Molecular structures of trichloroisoindolenines **1** and **2** are represented on Fig. 4, with the atomic numbering system. Crystallographic data and refinement details of the data collection for **1** and **2** are provided in Table 1. To highlight similarities between **1** and **2**, some selected equivalent bond lengths, angles and torsion angles are tabulated in Table 2. Intermolecular interactions are listed in Table S1.‡

Table 2 Selected bond lengths, bond angles and torsion angles for **1** and **2**

	1	2
Bond lengths (Å)		
C7–Cl1	1.7853(12)	1.7821(18)
C7–Cl1^i	1.7853(12)	1.7821(18)
C8–Cl2	1.706(2)	1.706(3)
C7–N1	1.469(3)	1.467(4)
C8–N1	1.279(3)	1.274(4)
C3–Cl3	—	1.729(3)
C4–Cl4	—	1.718(3)
Bond angles (°)		
Cl1^i–C7–Cl1	108.52(11)	108.39(16)
N1–C7–Cl1^i	108.87(15)	108.40(8)
C8–N1–C7	105.22(16)	105.4(3)
N1–C8–Cl2	122.02(16)	122.7(3)
Torsion angles (°)		
C5–C6–C7–Cl1	−61.12(11)	60.82(16)
C5–C6–C7–Cl1^i	61.12(11)	−60.82(16)
C5–C6–C7–N1	180.00	−180.00(1)
C2–C1–C8–Cl2	0.00(1)	0.00(1)

Symmetry transformations used to generate equivalent atoms: (i) x, $-y + 1/2$, z.

As shown in Table 2, there are no significant differences in the conformations of the two molecules. For both compounds, the isoindole moiety, consisting of a six-membered benzene ring fused to a pyrrole ring, coincides with the mirror symmetry (Fig. 4, right handside).

Cl2 is coplanar to the isoindole ring, whereas Cl1 and Cl1^{i} are both out of this plane (Table 2). Bond lengths of C8–N1 and C7–N1 in compound **1** are 1.279(3) Å and 1.469(3) Å respectively, and 1.274(4) Å and 1.467(4) Å in compound **2**.

In both compounds, in the pyrrole ring, the two C(sp^3)–Cl bond lengths vary within the range of 1.7821(18)–1.7853(12) Å, while the C(sp^2)–Cl bond lengths vary within the range of 1.706(2)–1.706(3) Å. This is reasonable when compared to corresponding distances reported previously.[15] In the case of **2**, the C(sp^2)–Cl on the benzene ring are significantly longer compared to the C(sp^2)–Cl on the pyrrole ring of **1** and **2**, C3–Cl3 being 1.729(3) Å and C4–Cl4 being 1.718(3) Å long.

The crystal lattice of each compound is illustrated on each unit cell view. It appears that Cl⋯Cl interactions ($d_{\mathrm{Cl1\cdots Cl2}}{}^{\mathrm{i}}$ = 3.4623(6) Å, i = x, $-y + 1/2$, z) play a major role in the crystallographic arrangement of **1**. These interactions lead to the formation of one-dimensional chains along the *c*-axis, for **1** (Fig. 5a). In the case of **2**, the intermolecular C═N⋯Cl interactions ($d_{\mathrm{N1\cdots Cl4}}{}^{\mathrm{i}}$ = 3.170(3) Å, i = x, y, $-1 + z$)

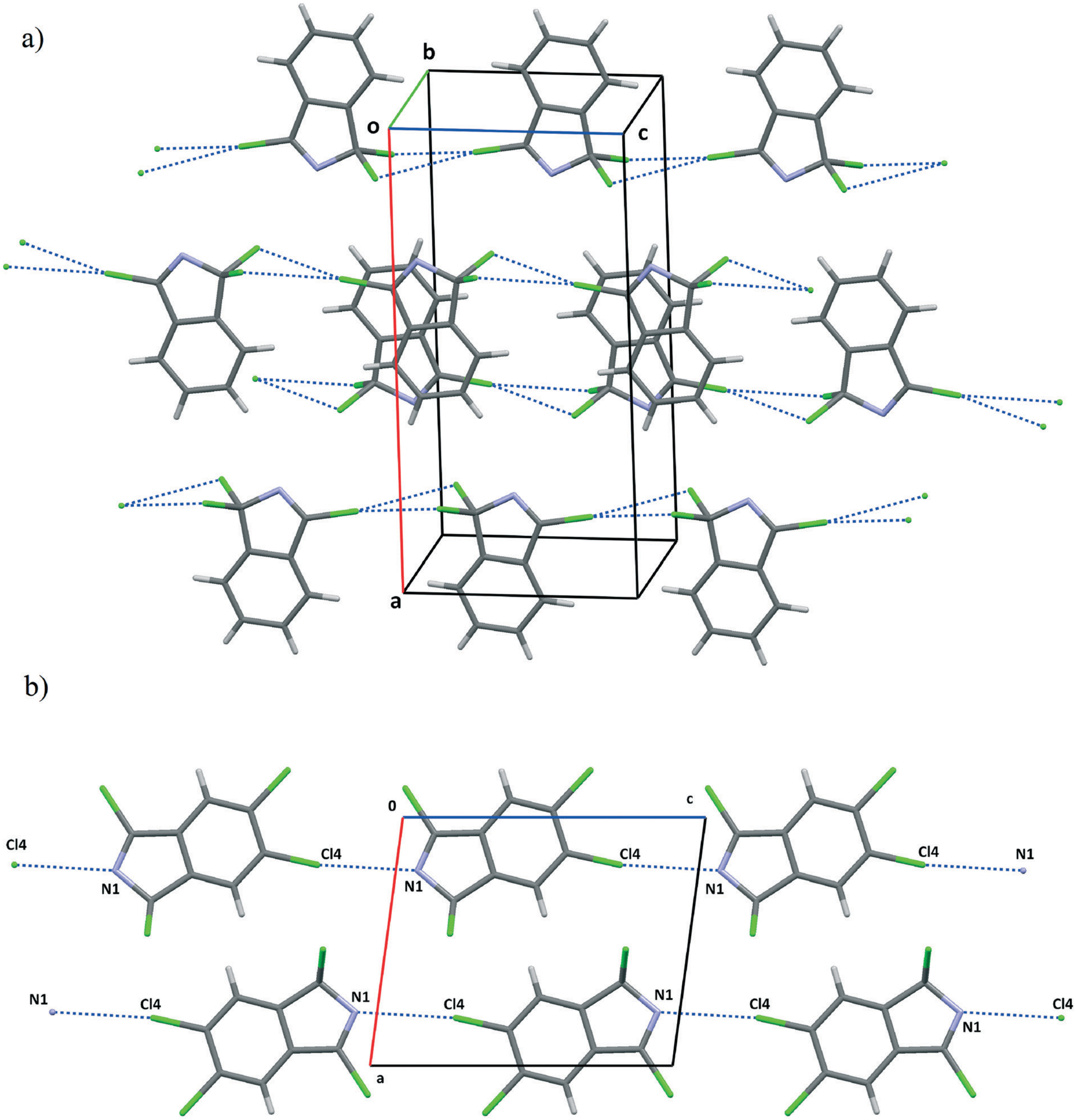

Fig. 5 (a) The unit cell view of **1** showing the intermolecular Cl⋯Cl interactions; (b) the unit cell view of **2** showing the intermolecular C═N⋯Cl interactions.

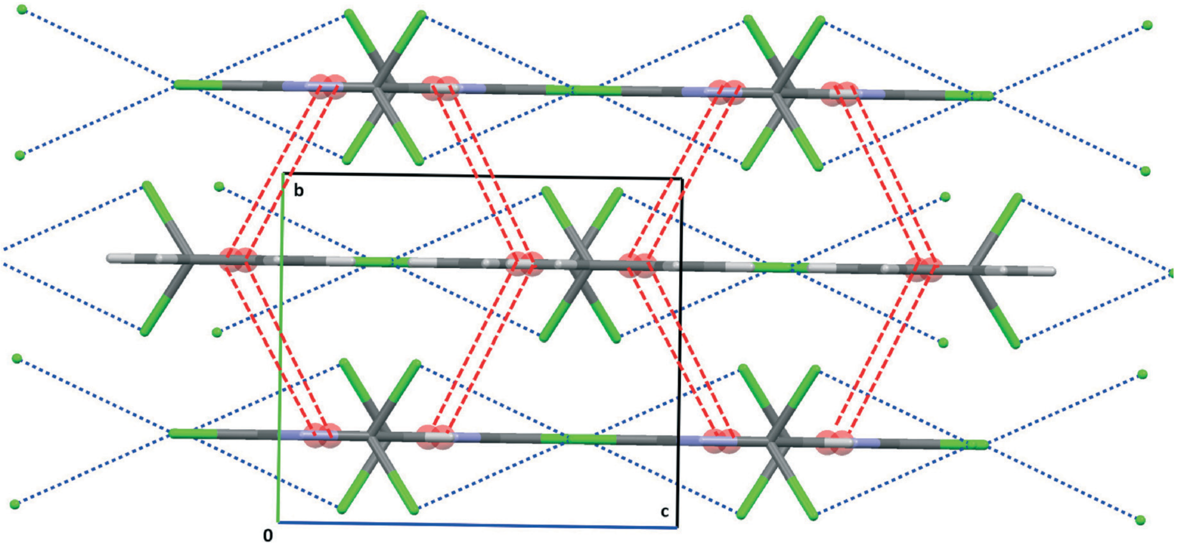

Fig. 6 A perspective view of 2D network generating from π···π (red dashed lines) and Cl···Cl interactions in **1** (blue dotted lines). Ring centroids of the isoindole are shown by red ball.

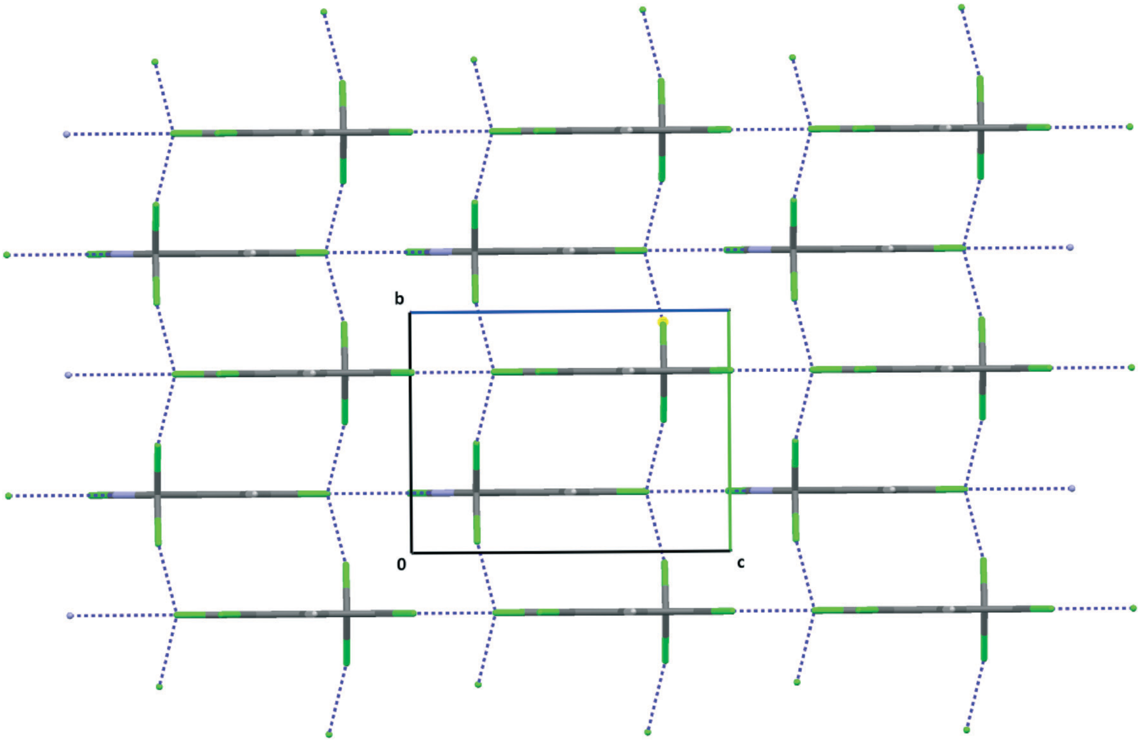

Fig. 7 A perspective view of 2D layer generating from C═N···Cl and Cl···Cl interactions in **2**.

are predominant and promote the formation of similar one-dimensional chains (Fig. 5b)

In the case of **1**, the adjacent infinite one dimensional chains lead to the formation of two dimensional network in the (*bc*) plane of the unit-cell through π···π interactions between two isoindole rings, helping to stabilize the packing lattice (Fig. 6, Table S1‡).

In the case of **2**, infinite one-dimensional chains are extended into a 2D network through Cl···Cl interactions (Fig. 7). Furthermore, π···π interactions between isoindole rings and C–Cl···π interactions between Cl atoms and the benzene ring contributed to the stabilization of the three-dimensional supramolecular network (Table S1‡).

Conclusion

As a conclusion, the above reported optimized preparation of trichloroisoindolenines **1** and **2** opens the way to a easier preparation of ABAB phthalocyanine derivatives, a class of asymmetric phthalocyanines still scarcely represented. These two derivatives were crystallized by sublimation, an uncommon method particularly suitable due to their air-moisture sensitivity. Their crystallographic structures were determined, a premiere for this class of compounds.

Experimental section

General

Phthalimide and dichlorophthalimide were prepared as described in the literature. *O*-dichlorobenzene was dried and purified as described in Perrin and Armarego.[16] PCl_5 was freshly sublimed. Melting points were measured with a Stuart melting point apparatus (SMP3). IR spectra were recorded between 4000 and 600 cm^{-1} using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal.

General procedure for the synthesis of trichloroisoindolenines 1 and 2. Phthalamide or 5,6-dichlorophthalimide (1 equiv.) and phosphorus pentachloride (4 equiv.) in *o*-dichlorobenzene (~1–2 mL per mmole of phthalimide) are heated one week at 120 °C under a continuous argon flow, the purged vapours being passed through a NaOH trap. Solvent and $POCl_3$ are distilled under vacuum, then the horizontal condenser is replaced by a suitable piece of glassware, consisting of a horizontal tube equipped at each extremity by a male cone shaped NS joint to collect the trichloroisoindolenines distilled under high vacuum. The whole system (remaining crude compound in the reaction round bottom-flask + horizontal tube) is heated with a heat gun to collect the desired compound.

Synthesis of 1,3,3-trichloroisoindolenine (1). Starting from phthalimide (10 g, 68 mol). White crystals (12.5 g, 57 mol, 84%). $C_8H_4Cl_3N$, MW 220.48. M. p.: 106–107 °C.[14] ATR-IR ν (cm^{-1}) 3190 (br, w), 3060 (w), 1772 (s), 1746 (s), 1600 (s), 1466 (s), 1366 (s).

Synthesis of 1,3,3,6,7-pentachloroisoindolenine (2). Starting from 5,6-dichlorophthalimide (20 g, 93 mmol). Pale yellow crystals (16 g, 60%). $C_8H_2Cl_5N$, MW 289.37. M. p.: 110–111 °C. ATR-IR ν (cm^{-1}) 3310 (br, w), 3236 (w), 3090 (w), 1780 (s), 1714 (s), 1536 (s), 1388 (s), 1348 (s), 1304 (s).

X-ray data collection and structure refinement

Unit cell measurements and intensity data collection was performed on an Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo Kα X-radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS).[17] Space groups were determined using XPREP implemented in APEX2.[18] The structure was solved using the direct methods procedure in SHELXS-97[19] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. The final geometrical calculations and the molecular drawings were carried out with PLATON[20] and MERCURY[21] programs.

Acknowledgements

The Scientific and Technological Research Council of Turkey (project 108 M034) is gratefully acknowledged.

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