

The structures of several modified isoindolines, the building blocks of phthalocyanines

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Dedicated to Professor Evgeny Luk'yanets on the occasion of his 75th birthday

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ABSTRACT: This report presents the single crystal X-ray structures of several substituted isoindolines that have been frequently used as starting materials for phthalocyanines, phthalocyanine analogs and related chelates. The structures of 1,3-diiminoisoindoline (1), 1,3-bis(hydroxyimino)isoindoline (2), 1,4-diaminophthalazine (3), 1,1,3-trichloroisoindoline (4) and 3-imino-1-oxoisoindoline (5) are reported; compounds 2 and 3 are synthesized from diiminoisoindoline (1) and 4 and 5 are produced from phthalimide. All five compounds are planar macrocycles, and localization of double bonds can be readily determined. We elucidated one of the known structures of 1 at low temperature, and observed two additional new structures of 1. For the crystal forms of 1 and compounds 2, 3, and 5, hydrogen bonding in the solid state was observed. Compounds 1, 2 and 3 form extended hydrogen bonded arrays in the solid state, whereas 5 forms discrete hydrogen bonded dimers.

KEYWORDS: 1,3-diiminoisoindoline, 1,3-bis(hydroxyimino)isoindoline, 1,4-diaminophthalazine, 1,1,3-trichloroisoindoline, 3-imino-1-oxoisoindoline, X-ray structures.

INTRODUCTION

The importance of phthalocyanines as both bulk colorants as well as specialized materials has driven investigations into their synthesis from simple, readily available starting materials [1–4]. Although the phthalocyanines are typically synthesized from phthalonitriles, several other convenient reagents can be used to produce phthalocyanines and related dyes. Much of the pioneering work in this area was carried out by Linstead in the 1950s [5–9]. During this period, Linstead produced 1,3-diiminoisoindoline (DII, 1), a key reagent for the synthesis of phthalocyanines [5, 6, 10]. Compound 1 is a reactive species, and can be readily modified and derivatized to afford macrocycles, chelates and related heterocycles.

and similar derivatives has greatly advanced the development of peripherally substituted and asymmetric phthalocyanines. Notably, great strides in this area have been made by Prof. Eugenii Lukyanets, to whom this issue is being dedicated in celebration of his 75th birthday. Lukyanets' work in this field is extensive and has been recently reviewed [11, 12]. Isoindoline derivates have also been used with great frequency for the synthesis of compounds structurally related to phthalocyanines. For example, this reagent is also useful for the synthesis of phthalocyanine analogs, such as subphthalocyanine [13–15] and the hemiporphyrazines [16–18], and metal chelates such as the bis(iminopyridyl)isoindoline [18–21] and phthalazine ligands [22–25].

In particular, the syntheses of diiminoisoindoline

Although 1,3-diiminoisoindoline and related isoindoline derived heterocycles have been studied for decades, there has been essentially very little elucidation *via* X-ray methods on these compounds. In this report, we present a study into the structures of several isoindolines

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Scheme 1.

including diiminoisoindoline 1 and one phthalazine compound. The structures and syntheses of these compounds are shown in Scheme 1. The DII derived compounds include the 1,3-bis(hydroxyimino) isoindoline **2** and the 1,4-diaminophthalazine **3**. The two remaining modified isoindolines include 1,1,3-trichloroisoindoline 4 and 3-imino-1-oxoisoindoline 5, which can both be readily synthesized with phthalimide. There has been some structural work on these compounds in the literature. Three crystal forms of compound 1 were reported at room temperature [26], and compound 5 was reported as a molecule of co-crystallization with a nickel complex [27]. These structures show the presence of localized double and single bonds in the heterocycles, as well as extensive hydrogen bonding in the solid state for compounds 1–3 and 5.

RESULTS AND DISCUSSION

The syntheses of the compounds investigated in this report have all been previously reported and are shown in Scheme 1. Diiminoisoindoline **1** is produced *via* the reaction of anhydrous ammonia with phthalonitrile in methanol and the presence of a catalytic amount of sodium methoxide, a method first developed by Linstead [5]. We used compound **1** to make two additional derivatives: the bis-oxime substituted isoindoline **2** [5, 6, 10] and the diaminophthalazine **3** [22]. Two additional substituted isoindolines can be produced from the starting material phthalimide. The reaction of phthalimide with PCl₅ in *o*-dichlorobenzene results in the halide substituted variant

trichloroisoindoline **4** [28, 29]. If phthalamide is reacted with ammonium hydroxide followed by dehydration with acetic anhydride, *o*-cyanobenzamide is produced, which then can be sublimed to produce the 3-imino-1oxoisoindoline species **5** [30]. For all five compounds, we were able to elucidate their structures *via* single crystal X-ray methods. The structures of all five compounds are shown in Figs 1 and 3, and the X-ray data collection and structure parameters are provided in Table 1.

In 2004, Zhang et al. reported on three crystal forms of diiminoisoindoline 1 [26]. All three structures were collected at room temperature, and only the two nonsolvated forms were presented with atom positions, denoted as forms A and B. In our discussion, we shall refer to these compounds as 1a and 1b for the two fully presented structures and form 1c for the methanol solvate form presented without atom positions. We were able to obtain a low temperature structure of form 1a (from methylene chloride solution) where the molecule crystallizes in the P(2)1/c space group with two equivalents in the asymmetric unit. The structure of one of these two equivalents of **1a** is shown in Fig. 1. This compound has three ionizable protons present on the imine and isoindoline nitrogen atoms. We observed that the location of these ionizable hydrogen atoms is different than how this molecule was originally described by Linstead. In agreement with the observation by Zhang et al., the difference map shows that the hydrogen atoms asymmetrically reside on the imine nitrogen atom positions and not on the central isoindoline nitrogen position. These hydrogen atoms were located on the

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Table 1. X-ray data collection and structure parameters for compounds 1-5

Compound	1a	1d	1 e	7	3	4	Ŋ
Empirical formula	$C_{16}H_{14}N_{6}$	$C_8H_7N_3$	$C_{80}H_{94}N_{30}O_{11}$	$C_8H_7N_3O_2$	$C_8H_{10}N_4O$	$C_8H_4Cl_3N$	$C_8H_6N_2O$
Formula weight	290.33	145.17	1651.85	177.17	178.2	220.47	146.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/c	P2(1)/n	C2/m	Pmna	C2/c	Pmna	P2(1)/n
Unit cell dimensions	a = 10.8050(12) Å	a = 3.7258(17) Å	a = 15.419(5) Å	a = 12.214(3) Å	a = 8.7526(3) Å	a = 15.8928(15) Å	a = 3.7240(7) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	b = 7.0574(8) Å $B = 1005777(3)^{\circ}$	b = 7.650(3) Å $B = 00.337(5)^{\circ}$	b = 18.724(6) Å $R = 106.300(1)^{\circ}$	b = 14.172(4) Å R – a∩°	b = 13.3593(5) Å $B = 107.759(2)^{\circ}$	b = 6.8909(7) Å B- an°	b = 7.6577(14) Å $B = 00.262(2)^{\circ}$
	p = 102.577(2) c = 19.436(2) Å	c = 22.637(10) Å	c = 14.685(5) Å	p = 30 c = 4.5983(12) Å	c = 7.2839(4) Å	c = 7.8036(7) Å	p = 22.618(4) Å
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	1446.5(3) Å ³	$(645.2(5) \text{ Å}^3)$	4069(2) Å ³	$796.0(4) \text{ Å}^3$	$811.11(6) \text{ Å}^3$	854.62(14) Å ³	$645.0(2) \text{ Å}^3$
Ζ	4	4	2	4	4	4	4
Density (calculated)	1.333 mg/m^3	1.495 mg/m^3	1.348 mg/m^3	1.478 mg/m^3	1.459 mg/m^3	1.714 mg/m^3	1.505 mg/m^3
Absorption coefficient	0.086 mm^{-1}	0.096 mm^{-1}	0.095 mm^{-1}	0.111 mm^{-1}	0.103 mm^{-1}	1.005 mm^{-1}	0.104 mm^{-1}
F(000)	608	304	1744	368	376	440	304
Crystal size (mm)	$0.11 \times 0.10 \times 0.08$	$0.30\times0.13\times0.10$	$0.21 \times 0.13 \times 0.04$	$0.18 \times 0.11 \times 0.07$	$0.33 \times 0.22 \times 0.19$	$0.19\times0.14\times0.08$	$0.30\times0.10\times0.04$
Theta range for data collection	2.15° to 27.25°	1.80° to 26.99°	1.75° to 25.14°	2.87° to 27.14°	2.88° to 27.25°	2.56° to 27.14°	1.80° to 27.49°
Index ranges	-13<=h<=13,	-4<=h<=4,	-18<=h<=18,	-15<=h<=15,	-11<=h<=11,	-20<=h<=19,	-4<=h<=4,
	-9<=K<=9, -25<=l<=24	-9<=k<=9, -28<=l<=28	-21<=K<=21, -17<=l<=17	-10<=K<=17, -5<=l<=5	-1 /<=k<=14, -9<=1<=9	-o<=k<=o, -10<=l<=9	-9<=k<=9, -28<=l<=29
Reflections collected	11404	4869	14038	5950	3307	6826	5340
Independent reflections	3193	1390	3676	914	912	1027	1468
	[R(int) = 0.0328]	[R(int) = 0.0362]	[R(int) = 0.0649]	[R(int) = 0.0387]	[R(int) = 0.0165]	[R(int) = 0.0249]	[R(int) = 0.0162]
Completeness to theta	98.9%	98.7%	97.1%	%6.66	99.3%	100.0%	99.7%

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			Table 1. (Continu	(pə			
Compound	1a	1d	1e	2	3	4	ъ N
Max. and min. transmission	0.9932 and 0.9906	0.9904 and 0.9717	0.9962 and 0.9804	0.9923 and 0.9804	0.9803 and 0.9672	0.9239 and 0.8319	0.9959 and 0.9695
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²				
Data/restraints/ parameters	3193/0/207	1390/7/109	3676/5/322	914/0/62	912/0/64	1027/0/70	1468/0/100
Goodness-of-fit on F2	1.103	1.035	0.937	0.993	0.983	1.036	1.373
Final R indices [I > 2sigma(I)]	R1 = 0.0495, w $R2 = 0.1439$	R1 = 0.0641, w $R2 = 0.1778$	R1 = 0.0595, w $R2 = 0.1495$	R1 = 0.0391, w $R2 = 0.0935$	R1 = 0.0501, w $R2 = 0.1528$	R1 = 0.0251, w $R2 = 0.0689$	R1 = 0.0639, w $R2 = 0.1948$
R indices (all data)	R1 = 0.0589, w $R2 = 0.1531$	R1 = 0.0782, w $R2 = 0.1974$	R1 = 0.0956, w $R2 = 0.1774$	R1 = 0.0493, w $R2 = 0.1019$	R1 = 0.0530, w $R2 = 0.1565$	R1 = 0.0272, w $R2 = 0.0710$	R1 = 0.0683, w $R2 = 0.2021$
Largest diff. peak and hole	0.385 and -0.187 e.Å ⁻³	0.529 and -0.336 e.Å ⁻³	0.918 and -0.212 e.Å ⁻³	0.320 and -0.224 e.Å ⁻³	0.589 and -0.671 e.Å ⁻³	0.503 and -0.193 e.Å ⁻³	0.878 and -0.972 e.Å ⁻³

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Fig. 1. The structures of 1a (top left), 1d (top right) and 1e (bottom) with 35% thermal ellipsoids. The asymmetric unit in 1e has 5 1/2 water solvent molecules. Non-ionizable hydrogen atoms and the solvent water molecule hydrogen atoms in 1e have been omitted

difference map, but the assignment can also be made on the basis of the C–N bond distances of the imine groups. The C–NH distances for each of the two molecules in the asymmetric unit are 1.2847(18) and 1.2834(19) Å, whereas the C–NH₂ distances are longer, at 1.3180(18)and 1.3226(17) Å. Accordingly, the C–N bonds to the isoindoline nitrogen atom are asymmetric as well, with lengths of 1.3319(18) and 1.3440(19) Å for the shorter bonds and 1.4039(17) and 1.396(2) Å for the longer of the two. Additionally, as seen by Zhang *et al.*, each equivalent of **1a** presents a different stereochemistry of the imine hydrogen atom, with one *syn* and one *anti* conformation, as shown in Scheme 2.

Compound **1a** exhibits a significant degree of hydrogen bonding in the solid state, forming a three dimensional network of isoindoline dimers. The hydrogen bonding network array of **1a** is shown in Fig. 2. Compound **1a** arranges in hydrogen bonded pairs, forming symmetric reciprocal hydrogen bonds of ~2.93 Å. These hydrogen bonds are similar in appearance to those seen in the base pair hydrogen bonding interaction between purine and pyrimidine nucleotides. The hydrogen bonded dimers link together *via* NH₂...NH interactions that measure ~2.93 and ~2.99 Å, forming layers composed of nearly orthogonal pairs of **1**.

We also isolated two additional forms of compound **1** which we shall describe as **1d** and **1e**. Crystal form **1d** is also a monoclinic form without solvent molecules, and the asymmetric unit is shown in Fig. 1. In this form, we observe a different tautomerization for DII, with one





Fig. 2. Hydrogen bonding formed between DII units for 1a, (left) 1d and 1e (right). 1d and 1e have identical hydrogen bonding between equivalents of DII in the solid



Fig. 3. The structures of 2–5 with 35% thermal ellipsoids. Non-ionizable hydrogen atoms and the solvent water molecule in 3 have been omitted for clarity

ionizable proton on each of the nitrogen atom positions. This assignment, which assumes an imine bond to the external nitrogen atom positions, is supported by the observed bond lengths. In **1d**, the C–N bonds with the central nitrogen atom are longer than in **1a**, measuring 1.387(3) and 1.391(3) Å, and the C–N bonds to the external nitrogen atom positions are clearly imine in character, measuring 1.214(3) and 1.218(3) Å. The imine hydrogen atom positions, although not readily observed on the difference map, can be inferred to be in the *syn* configuration, oriented toward the phenyl ring of the DII. The imine hydrogen atoms must be in the syn orientation since the DII units in **1d** form hydrogen bonded dimers,

as shown in Fig. 3. The N–H…N interactions measure ~ 2.88 Å. In the solid state, **1d** exhibits stacks of these hydrogen bonded dimers, spaced at ~ 3.37 Å, in an alternating herringbone fashion.

We isolated a fifth crystal form of DII, 1e, upon recrystallization of **1** from wet ethanol. This crystal form, which adopts the C2/m space group, has three equivalents of DII in the asymmetric unit, as well as 11 equivalents of water solvent molecules per unit cell. Four of the five solvent water molecules found in the asymmetric unit are fully occupied, while the remaining water molecule is disordered over two positions with 50% occupancy. In 1e, two of the equivalents of DII adopt an asymmetric tautomeric state, with two ionizable protons on one external nitrogen atom and one syn hydrogen atom on the opposite external nitrogen atom. The C-N bond lengths in these two equivalents support the proton assignment. The NH imine bonds exhibit lengths of 1.255(3) and 1.283(4) Å, the C- NH_2 bonds are longer (1.302(3)) and 1.304(3) Å) and the internal C-N bonds exhibit single and double bond character (1.334(3))and 1.379(3) Å; 1.330(4) and 1.382(4) Å). The remaining equivalent of DII was modeled with a disordered hydrogen atom with 50% occupancy on the central nitrogen atom position and 50% on one of the two external nitrogen atom positions. The nitrogen atom position is

not disordered. This disordered tautomerization is based on observed differences in bond lengths. The C–N bond (1.274(3) Å) for this disordered tautomer is intermediate between the amine and imine bonds seen in the other forms of **1**. Additionally, the internal C–N bonds are longer as well (1.361(3) and 1.374(3)) implying some degree of single bond character, but not as long as that seen in similar bonds in **1d**.

Hydrogen bonding is extensive in crystal form 1e. The equivalents of DII form hydrogen bonded dimers essentially identical to that seen in 1d (~2.89, ~2.89 and ~3.02 Å). Additionally, all of the water molecules in 1e form eight hydrogen bonds with the external nitrogen atom positions, ranging in N…O lengths from ~2.73 to ~3.07 Å. There is also hydrogen bonding between water molecules in the solid state, ranging from ~2.68 to ~2.76 Å. The presence of this extended hydrogen bond network of water molecules affects how the hydrogen bonded dimers pack in the solid state in 1e. The dimers pack in two ways in the unit cell: pairs of dimers form stacks spaced by ~3.70 Å, and these stacks are separated by monolayers of dimers that are orthogonal to the plane of the stacked layers, in contrast to the herringbone pattern in 1d.

The reaction of hydroxylamine hydrochloride with compound **1** results in the bis-oxime derivative of DII **2**. Compound **2** crystallizes in the orthorhombic space group Pmna, and the asymmetric unit is comprised of one half of the molecule. The structure of this compound is shown in Fig. 3. The molecule is also planar, with the oxime units occupying the same plane as the isoindoline and the entire molecule exhibiting a mean deviation from planarity of ~0.01 Å. Accordingly, unlike compound **1**, inspection of the bond distances shows the more expected symmetric structure. The oxime unit exhibits a clear C–N double bond at 1.2870(18) Å, whereas the C–N bond to the isoindoline central nitrogen atom is longer at 1.3840(17) Å. The oxime N–O distance measures 1.4132(16), which is clearly a single bond.

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There are three ionizable protons on compound 2, with one on each oxime oxygen and one on the central nitrogen atom of the isoindoline. This compound exhibits hydrogen bonding between the oxime OH units and oxime nitrogen atoms on neighboring equivalents of 2, however there is no observed hydrogen bonding to the central NH group of the isoindoline. The hydrogen bonding interactions in 2 are shown in Fig. 4. The OH…N heteroatom distances



Fig. 4. Hydrogen bonding networks formed by compounds 2 and 3

measure ~2.74 Å, and result in herringbone-like layers of **2** in the solid state. The herringbone layers are comprised of stacks of compound **2**, with isoindoline–isoindoline spacings of 3.30 Å.

When diiminoisoindoline **1** is reacted with hydrazine, a nitrogen atom inserts into the isoindoline heterocycle to afford a diaminophthalazine, compound 3. The structure of **3** is shown in Fig. 3. The molecule crystallizes in the C2/c space group, and as in compound 2 the asymmetric unit is comprised of one half of the heterocycle. As in the above compounds, this molecule is also planar, with an average deviation of ~0.01 Å. The aromaticity in phthalazine extends over the heterocycle portion of the compound, however the presence of heteroatoms does induce some bond alternation effects. The phthalazine portion of the macrocycle clearly shows localized double bond character between the nitrogen atoms and carbon atoms, with a length of 1.306(2) Å. The phthalazine N-N distance is longer, with a distance of 1.384(2) Å.; The C-N bonds to the exocyclic nitrogen atoms are clearly single, with lengths of 1.3906(19) Å.

Compound **3** engages in hydrogen bonding with itself, *via* NH···N interactions as well as to an equivalent of solvent water found in the asymmetric unit, as shown in Fig. 4. The diaminophthalazine NH···N hydrogen bonds (~3.01 Å) form nearly co-planar linear arrays, forming a total of four such bonds per diaminophthalazine. The hydrogen bonds to the solvent water, which bridge between the linear arrays of compound **3**, are slightly shorter, measuring ~2.96 and ~2.83 Å. The linear arrays of **3** form π stacks with distances of ~3.52 Å.

Unlike compounds 2 and 3, the trichloroisoindoline 4, shown in Fig. 3, is produced via the reaction of phthalimide with PCl₅. This compound crystallizes in the orthorhombic space group Pnma and the heterocycle lies on a reflection plane (*i.e.* the asymmetric unit is half of the macrocycle). As in diiminoisoindoline 1, compound 4 has asymmetric bonding around the central nitrogen atom, with a C-N double bond (1.278(2) Å) and a C-N single bond (1.472(2) Å). The C-Cl bonds also differ; the C-Cl bond on the sp² hybridized carbon measures 1.706(2) Å whereas the sp³ C–Cl bonds are 1.7848(11) Å. Since there are no heteroatom-bound hydrogen atoms in the structure, there is no hydrogen bonding in the solid state structure of 4. The molecules pack in a head-to-tail fashion, and stack in anti-parallel sheets with a distance of ~3.45 Å.

The oxygen substituted analog of diiminoisoindoline, 3-imino-1-oxoisoindoline **5** can be produced *via* a three step reaction from phthalimide, and the final thermal cyclization and sublimation steps produces single crystals that can be readily structurally elucidated. Previously, this compound was observed as a co-crystallizing molecule with bis(dithiobiureto)nickel(II) [27]. In this structure, the 3-imino-1-oxoisoindoline forms a strongly hydrogen bonded interaction with the back end of the dithiobiurea ligand. The 3-imino-1-oxoisoindoline engages in its hydrogen bonding interaction *via* the internal N–H group of the isoindoline and *via* an anti-configuration of the imine N–H unit, which acts as a hydrogen bond acceptor. Additionally, the acyl oxygen of the previously elucidated compound interacts with an N–H unit from the dithiobiurea ligand to form a hydrogen bond.

The compound presented herein crystallizes in the P2(1)/n space group, and the asymmetric unit is comprised of a single equivalent of the molecule, also shown in Fig. 3. The C-O length is clearly double bond in character (1.212(2)Å) and the exocyclic C-N bond is clearly an imine, with a length of 1.218(2) Å. The C-N bonds to the indoline nitrogen atom are longer, measuring 1.401(2) and 1.383(2) Å in length, with the shorter bond observed with the imine carbon atom. The observation of these bond lengths is counterintuitive, since one might expect there to be a greater degree of resonance with the acyl carbon atom than the imine carbon atom. There are two ionizable hydrogen atoms present in compound 5, with one present on each of the nitrogen atom positions. The imine N–H group is oriented syn to the aromatic ring of the isoindoline.

In the solid state, compound **5** forms discrete hydrogen bonded dimers *via* the isoindoline N–H group and the imine nitrogen atom position, as shown in Fig. 5. Thus, the hydrogen bonding is symmetric, with N–H…N lengths of ~2.88 Å. There are no observed extended



Fig. 5. Hydrogen bonded dimer structure formed in compound 5

hydrogen bonding linear arrays in the solid state, as seen in compounds **1–3**. This hydrogen bonding is also very similar to that seen in the co-crystallized structure with bis(dithiobiureto)nickel(II). The hydrogen bonded dimers form slipped stacked arrays, with distances of ~3.37 Å between the planes of the isoindolines, and these stacked arrays form a herringbone pattern in the solid state.

EXPERIMENTAL

General methods

Unless otherwise stated, all reagents and solvents were purchased from Sigma, Aldrich, Acros Organics, or Strem and used without further purification. Solution NMR spectroscopy was performed with Varian VXR 300 MHz and Varian 500 MHz NMR instruments. Elemental analyses were carried out at the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. Mass spectrometric analyses were carried out at the Mass Spectrometry and Proteomics Facility at The Ohio State University in Columbus, OH or at the University of Akron in Akron, OH.

Synthesis

1,3-diiminoisoindoline (1). This compound was synthesized according to a modified literature procedure [2a]. Crystals suitable for single crystal X-ray diffraction were grown from dichloromethane solution, affording crystal form **1a**. Crystals were also obtained from butanol solution (form **1d**) and from wet ethanol (form **1e**).

1,3-bis(hydroxyimino)isoindoline (2). We used a modification of Linstead's procedure to synthesize compound **2** [2a, 2b, 3]. 1,3-diiminoisoindoline (100 mg, 0.68 mmol) was dissolved in 10 mL of methanol with gentle heating. Three equivalents of hydroxylamine hydrochloride (144 mg) was also dissolved in 10 mL of methanol and the two solutions were mixed. The mixture was then allowed to sit at room temperature and slowly evaporate until crystals of the product formed, which were then collected by filtration. These crystals were suitable for X-ray structure elucidation. Yield: 117 mg (96%).

1,4-diaminophthalazine (3). This reaction was based on work first published by Fujii [22] and later successfully used by Lever to synthesize substituted phthalazines [24]. 3.5 mmol of 1,3-diiminoisoindoline (500 mg) was heated in methanol and allowed to dissolve. The reaction mixture was then removed from heat and while the reaction mixture was still hot, ~1.7 mL of hydrazine hydrate was added drop wise to the solution. The reaction mixture was allowed to sit for a few hours, during which time crystals of the product formed that were suitable for single crystal X-ray diffraction. Vacuum filtration of the mixture yielded yellow/orange crystals. Yield: 492 mg (92%).

1,1,3-trichloroisoindoline (4). The synthesis of this compound followed a modified literature procedure [28, 29]. PCl₅ (1.75g, 8.42 mmol) was dissolved in o-dichlorobenzene (1.63 mL, 11.1 mmol), then phthalimide (600 mg, 4.08 mmol) was added. The reaction mixture was heated to 95-100 °C under an argon atmosphere. After 2 h, a clear solution was formed and was heated for 3 more hours with no visible change. POCl₃ was distilled under aspirator pressure at 40 °C. After all of the POCl₃ was removed, the temperature was raised to 80 °C and o-dichlorobenzene distilled. While the temperature reached 105 °C, white crystals formed in the flask. The residue was recrystallized in cyclohexane to yield 368 mg (1.67 mmol, 40%) of a white solid. These crystals were suitable for structure elucidation via single crystal X-ray diffraction.

3-imino-1-oxoisoindoline (5). This compound was prepared via a three step process starting with phthalimide using the procedure presented by Murthy et al. [30]. Phthalimide (10.0 g, 0.07 mol) was suspended in 60 mL of ammonium hydroxide for 24h, and the resultant phthalamide was isolated by filtration and washed with water, affording 10.1 g (85% yield). After drying, 10 g of the phthalamide was dissolved in 70 mL of acetic anhydride and refluxed for 2h. Upon cooling of the reaction solution, a white solid formed (o-cyanobenzamide) that was collected and washed with cold ethanol, producing 3.0g of product (40%). The o-cyanobenzamide was simultaneously cyclized and sublimed under nitrogen gas at atmospheric pressure to afford crystals of 5 (1.0g, 33%) that were suitable for structure elucidation via single crystal X-ray diffraction.

X-ray crystallography

Single crystal X-ray diffraction data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 watts power. The detector was placed at a distance of 5.009 cm from the crystal. Integration and refinement of crystal data was done using Bruker SAINT software package and Bruker SHELXTL (version 6.1) software package, respectively. Absorption corrections were carried out using the SADABS program [31]. Crystals were placed in paratone oil upon removal from the mother liquor and mounted on a plastic loop in the oil. Data collection and structure parameters can be found in Table 1.

CONCLUSION

In conclusion, we have structurally elucidated five isoindoline derivatives that have been historically investigated as starting materials for phthalocyanines, phthalocyanine analogs and metal chelating ligands. As expected, all five compounds are planar, with the exception of the chlorine atoms on compound 4. The location of the double bonds in these compounds can be unambiguously determined from the elucidated structures. In compounds 1 and 3, we observed exocyclic amine groups, and in 1, 2 and 5 there are clear C-N double bonds to exocyclic nitrogen atoms. With the exception of compound 4, all of the compounds in this report engage in hydrogen bonding in the solid state, with most of the compounds (1, 2 and 3) forming hydrogen bond polymeric structures, and with 5 forming discrete dimers. We are continuing our work on the structure elucidation of isoindoline derived compounds, and hope that the current work will assist others in understanding the structural aspects of isoindoline-based macrocycles, as well as in related areas, such as the construction of hydrogen bond network solids.

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Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC-914960-914966. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/ data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam. ac.uk).

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