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Structure, polymorphism and thermal properties of phenyliminoisoindolines

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ABSTRACT: The crystal and molecular structures of (a) 1-imino-3-phenyliminoisoindoline (**2**), (b) two polymorphs (**3Mono** and **3Tric**) and a hexane solvate (**3Hex**) of 1,3-bis(phenylimino)isoindoline (**3**) and (c) 3-phenyliminoisoindolinone (**4**) were determined via single-crystal x-ray diffraction. The two polymorphs and solvate of **3** were all obtained by crystallization from hexane. In the solid state, **2** is found as the *anti* isomer of the amino tautomer, and all forms of **3** exist as either the *syn,anti* or *anti,anti* isomers of the diimino tautomer. The **3Tric** and **3Mono** polymorphs represent a rare example in which the phenomena of conformational polymorphism and conformational isomorphism occur for the same substance. Compound **4** crystallizes as the *anti* isomer of the keto form. Differential scanning calorimetry and thermogravimetric analysis were performed to characterize the thermal properties of samples of **2**–**4**. X-ray powder diffraction studies on **2**, **3** and **4** reveal that, whereas specimens of **2** are a single phase, none of the samples of **3** and **4** crystallize as single phases under the conditions of the experiments. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: aryliminoisoindolines; crystal structure; molecular structure; tautomers

INTRODUCTION

This paper reports the isolation and characterization of the structural and thermal properties of phenyl derivatives of diiminoisoindoline (**1**), namely phenyliminoisoindoline (**2**) and stereoisomers of 1,3-bis(phenylimino)isoindoline (**3**). There is a longstanding interest in isoindoline rings owing to their presence in the phthalocyanines[1] and proposed presence[2] in related linear conjugated polymers. They are also of interest[3] as intermediates for the synthesis of hemiporphyrazines. The linear cyclopolymerization of 2-benzylidene-4, 5-dicyano-1,3-dithiole to a related structure has been reported recently[4] and Sn(II) reagents[5] and unmodified sugars[6] bring about the linear oligomerization and polymerization of phthalonitriles and certain dicyanoalkenes to structures related to polyisoindolines.

Pursuant to our interests in solid-state reactions, especially a suitable precursor for a solid-state polymerization leading to a polyisoindoline,[7] the solid-state reactivity of **2**[8] attracted our attention. It was found that heating of **2** at 150 °C, well below its reported[8] decomposition temperature (203 °C), led to decomposition, possibly initiated by dissociation of **2** to aniline and phthalonitrile.[7] This process ultimately destroys the lattice of **2** and leads to the formation of **3**, ammonia and phthalocyanine (0.25% yield). Following a report[8] of its synthesis and thermal decomposition, **2** has been the subject of NMR studies[9] intended to deduce its preferred tautomeric structure. We were interested in the crystal structure of **2** for insights into the thermal decomposition process and for definitive identification of the preferred tautomer in the solid state.

Compound **3** was initially described[8] as yellow needles with a melting-point of 129 °C. Subsequently, **3** was studied[10] to learn about its preferred tautomeric structure and possible stereoisomers associated with stereomutation of the phenylimino group. Based on model Schiff bases,[11] such isomerization should be facile in solution at room temperature or in a liquid phase. Our observations of the thermal properties of different specimens of **3** reported here are consistent with this perspective. In this paper, we report the crystal structure of **2** and identify the preferred solid-state tautomer. In the course of our isolation and characterization of **3** and its solid-state reactivity, we discovered two polymorphs of **3**, one of which has two stereoisomers of **3** in the same unit cell, whereas the other contains only a single stereoisomer. This is a very rare example of the occurrence of both conformational polymorphism and conformational isomorphism for a single substance.[12]

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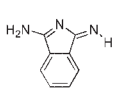
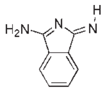


1a



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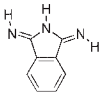

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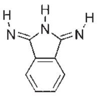

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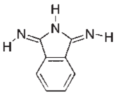

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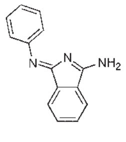

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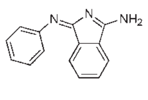

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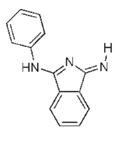

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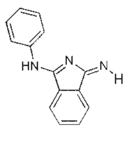

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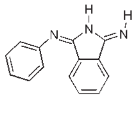

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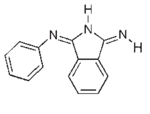

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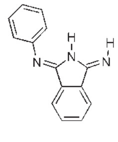
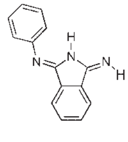


2g



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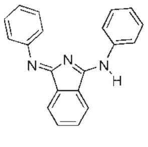
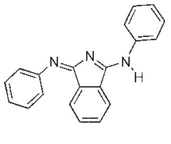


3a



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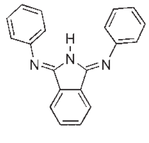

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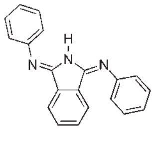

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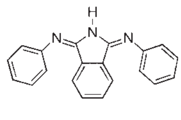
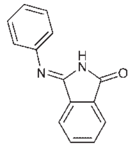
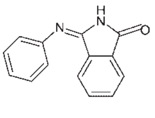


3e

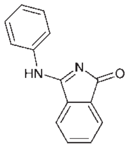
In the course of attempting to dope **2** into phthalonitrile in ethyl acetate solution, we isolated the known compound 3-phenyliminoisoindolinone (**4**). Its crystal structure is reported here.



4a



4b



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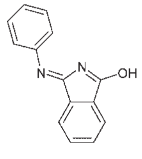

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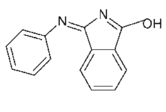

4e

Using x-ray powder diffraction, we observed that, with the exception of **2**, all samples studied in this work involve more than one crystalline phase by comparison of the observed powder reflections with those calculated from the lattice constants for a given crystal. While we recognize that observation of melting behavior is an important part of the characterization of an organic molecular compound, we will be unable to give definitive thermal properties for each crystalline phase found in this work. Nevertheless, we have made some noteworthy attempts along these lines.

EXPERIMENTAL

General

Melting-points taken in a capillary tube are uncorrected. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were made on DuPont DSC 2910 and TA 2950 instruments, respectively, at a rate of 10 °C min^{-1} under N_2. X-ray powder diffraction was recorded from $2\theta = 2$ to 60° using a Cu Kα source on a Phillips vertical diffractometer with a graphite monochromator. Calculated x-ray powder patterns were generated by MICRO-Dspace (Materials Data, Livermore, CA, USA). ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker 250 MHz spectrometer or a Varian 400 MHz spectrometer.

X-ray structure determinations

X-ray crystal structure analyses were performed at Brandeis University on an Enraf-Nonius CAD-4U diffractometer using graphite-monochromated Cu Kα radiation (**2**, **3Hex**, **3Tric**, **4**) and on a CAD-4 Turbo diffractometer using graphite-monochromated Mo Kα radiation (**3Mono**).[13] Each structure was solved by direct methods (SIR92).[14] Full-matrix least-squares refinement was carried out using the Oxford University Crystals for Windows system.[15] All ordered non-hydrogen atoms were refined by using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and updated after each least-squares cycle. Hydrogen atoms attached to N were refined by using isotropic displacement parameters. Drawings were prepared using the Oxford University CAMERON program.[16] In **3Hex**, the occupancy of a disordered hexane solvate was also refined, leading to a value of 0.193(2). A set of CIF files is available as Supplementary material (available in Wiley Interscience).

1-amino-3-phenyliminoisoindoline (2)[7]

A solution of 1,3-diiminoisoindoline (**1**) (2.5 g, 17 mmol) and aniline (1.6 ml, 18 mmol) in ethanol (15 ml) was refluxed for 2 h and allowed to cool to 5 °C. The yellow precipitate obtained was suction filtered, triturated with cold ethanol and recrystallized from ethanol with a total

Table 1. Crystallographic data

	2	**3Hex**	**3Mono**	**3Tric**	**4**
Chemical formula	$C_{14}H_{11}N_3$	$C_{20}H_{15}N_3 \cdot$ 0.1925 (C_6H_{14})	$C_{20}H_{15}N_3$	$C_{20}H_{15}N_3$	$C_{14}H_{10}N_2O$
Formula weight	221.263	311.235	297.361	297.361	222.248
Crystal system	Tetragonal	Hexagonal	Monoclinic	Triclinic	Monoclinic
Space group	$P4_12_12$	$R\bar{3}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Temperature (K)	294	294	294	294	294
a (Å)	9.5328 (18)	25.475 (8)	11.3341 (4)	13.1134 (12)	11.1873 (15)
b (Å)	9.5328 (18)	25.475 (8)	14.926 (1)	14.252 (2)	5.0576 (7)
c (Å)	25.9609 (12)	13.610 (2)	9.2767 (5)	18.331 (3)	19.985 (3)
α (°)	90	90	90	79.190 (13)	90
β (°)	90	90	90.431 (4)	73.781 (9)	101.713 (11)
γ (°)	90	120	90	75.565 (9)	90
V (Å^3)	2359.2 (6)	7649 (4)	1569.3 (15)	3160.0 (8)	1107.2 (3)
Z	8	18	4	8	4
ρ_{calcd} (g cm^{-3})	1.246	1.227	1.259	1.250	1.333
ρ_{obsd} (g cm^{-3})	1.22 (1)	1.19 (2)			1.31 (1)
λ (Å)	1.54178	1.54178	0.71073	1.54178	1.54178
μ (mm^{-1})	0.605	0.572	0.076	0.589	0.692
Trans. coeff. (empirical corr.)	0.76–0.92	0.89–0.94	0.96–0.98	0.76–0.81	0.80–0.86
Unique reflections; No. obsd.	1522; 1440	3589; 2818	3177; 1965	13293; 8914	2322; 1774
R_{merge}	0.021	0.024	0.014	0.010	0.043
R	0.0366	0.0472	0.0365	0.0416	0.0400
R_w	0.0545	0.0639	0.0421	0.0528	0.0527
SDU	0.89	1.01	1.10	1.04	1.03

yield of 2.89 g (77%); m.p. 203 °C (decomp.) [lit.[8] m.p. 203 °C (decomp.)]. A yellow single crystal obtained from ethyl acetate was determined to be **2**. The observed density was 1.22 g cm^{-3} (calc. 1.246 g cm^{-3}) determined by neutral buoyancy in carbon tetrachloride–cyclohexane. TGA: a 28.9% weight loss at 170 °C, an additional 31.6% weight loss at 260 °C and a further 20.3% weight loss at 321 °C. Observed x-ray powder pattern, d (Å): 9.0, 5.4, 4.8, 4.48, 4.21, 4.18, 4.07, 3.98, 3.16, 3.13, 3.09, 2.73, 2.50, 2.24 and 2.12.

Bis(phenylimino)isoindoline (3)

Method A[8]. A mixture of **1** (1.51 g, 10 mmol), aniline (2 ml, 20 mmol) and ethanol (15 ml) was refluxed for 24 h. After evaporation of the ethanol, the residue was purified by column chromatography [silica gel, elution with CH_3OH–CH_2Cl_2(5:95)] to give a yellow solid (1.80 g, 58%). Repeated recrystallizations from hexane yielded four different kinds of crystals, yellow needles, light-orange plates and two yellow single crystals.

Yellow needle crystals with m.p. 129–130.5 °C are a major product from the recrystallization. However, these were of unsatisfactory quality and size for further study. FT-IR (mineral oil): 3440, 1662, 1587, 1458, 1376, 1233, 1100, 690 cm^{-1}. The crystals exhibited an irreversible melt and did not resolidify until cooled to −25 °C. Observed x-ray powder pattern (d, Å): 17.3, 15.6, 14.7, 13.8, 12.3, 9.0, 7.2, 7.1, 6.8, 5.7, 5.5, 5.2, 4.9, 4.81, 4.63, 4.50, 4.33, 4.21, 3.68, 3.58, 3.50, 3.43, 3.37, 3.14.

A yellow single crystal **3Mono** with m.p. 122–125 °C was determined to be isomer **3c**. Crystallographic data are given in Table 1. The ^{1}H NMR spectrum ($CDCl_3$) exhibited δ 8.09–8.07 (m, 2H), 7.75 (m, 2H), 7.4–7.3 (m, 4H), 7.16–7.12 (m, 2H), 7.08–7.02 (m, 4H), 2.0 (s, broad, 1H). This spectrum is representative of those observed for all specimens of **3** in the present work.

A yellow single crystal **3Tric** with m.p. 128–130 °C was determined to be a mixture of isomers of **3c** and **3d**. Crystallographic data are given in Table 1.

Method B (catalyzed by $CaCl_2$)[17]. A mixture of phthalonitrile (1.28 g, 10 mmol), aniline (1.9 ml, 21 mmol), $CaCl_2$ (0.11 g, 1 mmol) and *n*-butanol (20 ml) was refluxed for 48 h. After evaporating the *n*-butanol under reduced pressure, the residue was purified by column chromatography [silica gel, CH_3OH–CH_2Cl_2 (5:95)] to yield orange crystals (1.80 g, 61% yield) with m.p. 125–127 °C.

The hexane-solvated single crystals **3Hex** were recrystallized from hexane and the structure was determined to be isomer **3d**. Crystallographic data are given in Table 1. The observed density was 1.19 g cm^{-3} determined by neutral buoyancy in carbon tetrachloride–cyclohexane. TGA: a 5% weight loss at 100 °C with a further 95% weight loss at 160 °C. No DSC exotherm or endotherm was observed. The crystal exhibited an irreversible melt. On cooling, a yellow solid was found at −13 °C. Observed x-ray powder pattern, d (Å) (before melt): 15.5, 14.2, 13.2, 12.9, 11.6, 9.1, 8.9, 8.7, 8.6, 6.3, 5.6, 5.3, 5.1, 4.3, 4.2, 4.0, 3.9, 3.8, 3.6, 3.5, 3.4, 3.3, 3.2, 3.1, 3.0, 2.92

and 2.81. Observed x-ray powder pattern: *d* (Å) (after melt): 4.3 and 3.2. The observed reflections at $d = 15.5$, 14.2, 13.2, 9.1, 8.9, 8.7, 8.6, 5.3 and 5.1 Å are not found in the calculated pattern for **3Hex**.

3-Phenyliminoisoindolinone (4)

Method A. Reaction of phthalonitrile and **2**: a mixture of phthalonitrile (1.54 g, 0.012 mmol), **2** (0.75 g, 0.003 mmol) and 25 ml of ethyl acetate was refluxed overnight to yield an orange solution. After evaporation of the ethyl acetate, the residue was triturated with hot hexane, purified by column chromatography [silica gel, CH_3OH–CH_2Cl_2(1:99)] to yield an orange solid. Orange single crystals was recrystallized from ethyl acetate–hexane (1:3, v/v) and determined to be 3-phenyliminoisoindolinone and the isomeric form **4a** with m.p. 162–164 °C (lit. m.p. 167–169 °C[18] and 170–171 °C.[19] Crystallographic data are given in Table 1. The observed density was 1.31 g cm^{-3} determined by neutral buoyancy in carbon tetrachloride–cyclohexane. IR (Nujol): 1735, 1677, 1579, 1258, 1165, 1087 cm^{-1}.

Method B[18]. A solution of 3-iminoisoindolinone (0.5 g, 3.4 mmol) and aniline (1 ml, 11 mmol) in a mixture of ethanol (20 ml) and acetic acid (0.67 ml) was heated under reflux for 30 min to yield a yellow solution. After cooling, the solution was poured into water (34 ml) to give a yellow precipitate. The precipitate was filtered by suction, dried in vacuum and recrystallized from ethanol to give yellow crystals, 0.56 g (73%), m.p. 167–169 °C (lit.[18] m.p. 167–169 °C). The yellow crystals were found to have the same crystal structure as the orange crystals obtained by method A. The isomer form was **4a**. Crystallographic data are given in Table 1. The observed density was 1.33 g cm^{-3} determined by neutral buoyancy in carbon tetrachloride–cyclohexane. Observed x-ray powder pattern, *d* (Å): 20.3, 19.8, 14.7, 10.2, 8.3, 6.8, 5.5, 5.3, 4.9, 4.44, 4.19, 3.67, 3.48, 3.34, 3.28 and 3.10. The observed reflections at $d = 20.3$, 19.8, 14.7, 6.8 and 4.19 Å are not in the calculated pattern.

RESULTS AND DISCUSSION

The stereoisomers and tautomers of **1** and its derivatives have been of interest since 1945.[20] Here we report our observations from structural determinations for **2**, **3** and **4**.

Structural characterization of phenyliminoisoindoline (2)

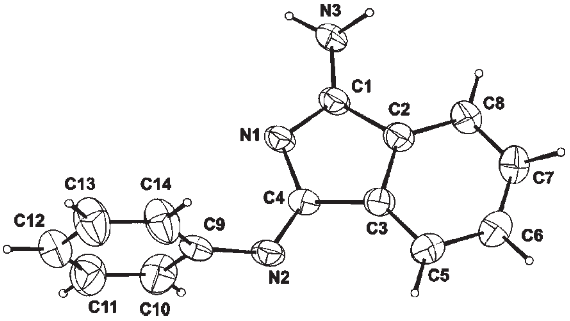

Figure 1. Molecular structure of **2**. Selected bond distances: N1—C1, 1.331(2); N1—C4, 1.395(1); C4—N2, 1.288(1); N2—C9, 1.425(2); C1—N3, 1.317(2) Å

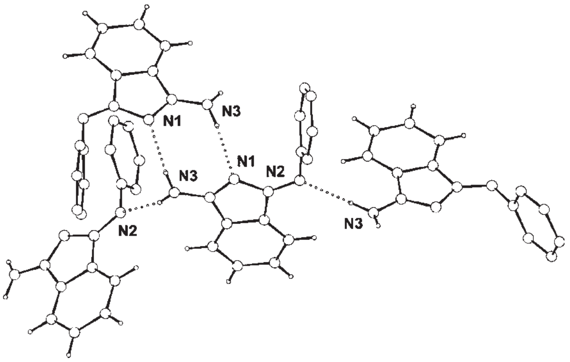

Figure 2. Hydrogen bonding in **2**

As shown in Fig. 1, **2**, which can exist in several isomeric forms, crystallizes as the *anti* isomer **2a** of the amino tautomeric form. Bond lengths (Fig. 1) and angles are in normal ranges, in good agreement with those of the similar compounds 3-amino-5,6-dicyano-1-phenylimino-1*H*-isoindole[21] and 5-(1-aminoisoindol-3-ylideneamino)-1,3,4-thiadiazol-2(3*H*)-thione dimethylformamide solvate monohydrate.[22] The C4—N2—C9—C14 torsion angle is 84.1°, a likely result of packing forces. Figure 2 shows a portion of the infinite hydrogen-bonding

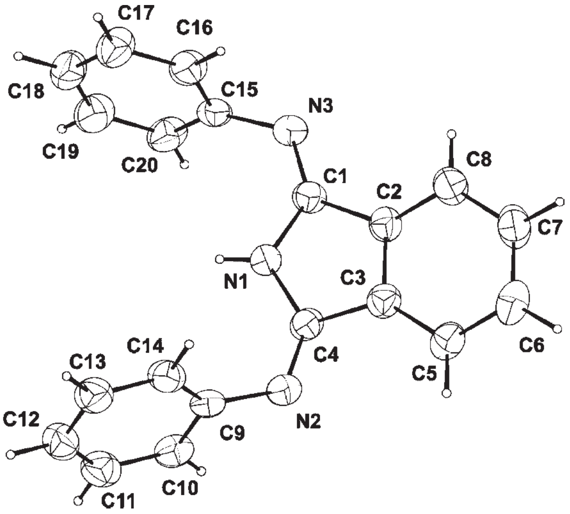

Figure 3. Molecular structure of **3Mono**. Selected bond distances: N1—C1, 1.395(2); N1—C4, 1.393(2); C4—N2, 1.276(2); N2—C9, 1.415(2); C1—N3, 1.270(2); N3—C15, 1.420(2) Å

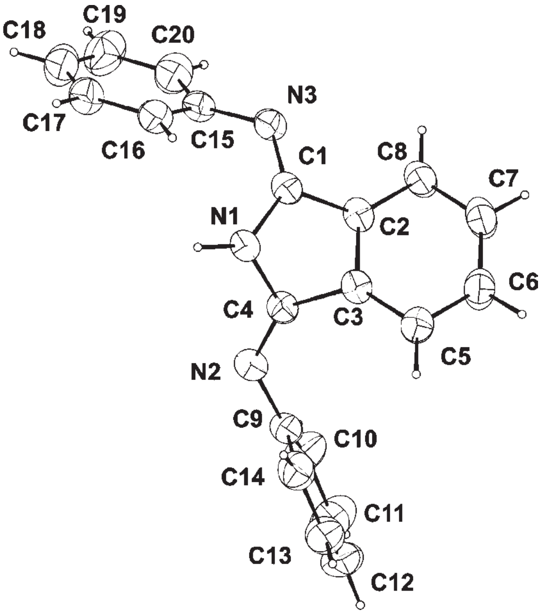

Figure 4. Molecular structure of **3Hex**. Selected bond distances: N1—C1, 1.378(2); N1—C4, 1.397(2); C4—N2, 1.265(2); N2—C9, 1.412(2); C1—N3, 1.276(2); N3—C15, 1.424(2) Å

network. One hydrogen bond, N3—H1···N1($1+y$, $x-1$, $-z$; N···N, 2.96 Å; N—H···N, 156°) forms an $\boldsymbol{R_2^2(8)}$ ring, whereas the other, N3—H2···N2($\frac{1}{2}+y$, $\frac{1}{2}-x$, $z-\frac{1}{4}$; N···N, 2.95 Å; N—H···N, 166°), is part of an infinite chain, **C(6)**.[23] Tautomer **2** was indicated in a solution NMR study in the literature.[10] If the solid-state decomposition of **2**[7,8] to aniline and phthalonitrile is an intramolecular process, it cannot proceed through the observed tautomer.

Structural characterization of bis(phenylimino)isoindoline (3)

The specimens obtained from synthetic methods A or B given in the Experimental Section are a mixture of phases as revealed by x-ray powder diffraction, and single crystals were selected from the mixtures. Three different single crystals, **3Mono, 3Tric** and **3Hex**, were obtained by modifying the literature procedures and recrystallizing the products from hexane. During various attempts, two or more polymorphs and/or solvates crystallized concomitantly,[24] without strong reproducibility.

After melting, all specimens of **3** remain viscous liquids when cooled to ambient temperature. As stated in the Experimental section, they do not resolidify until cooled significantly below 0 °C. These resolidified materials are not homogeneous crystalline phases and have significant amorphous character, as revealed by x-ray powder diffraction. This melting behavior of the various forms of **3** is a likely consequence of the low barrier to stereomutation[11] of the phenylimino groups. The result is a mixture of stereoisomers that does not crystallize readily upon cooling to ambient temperature.

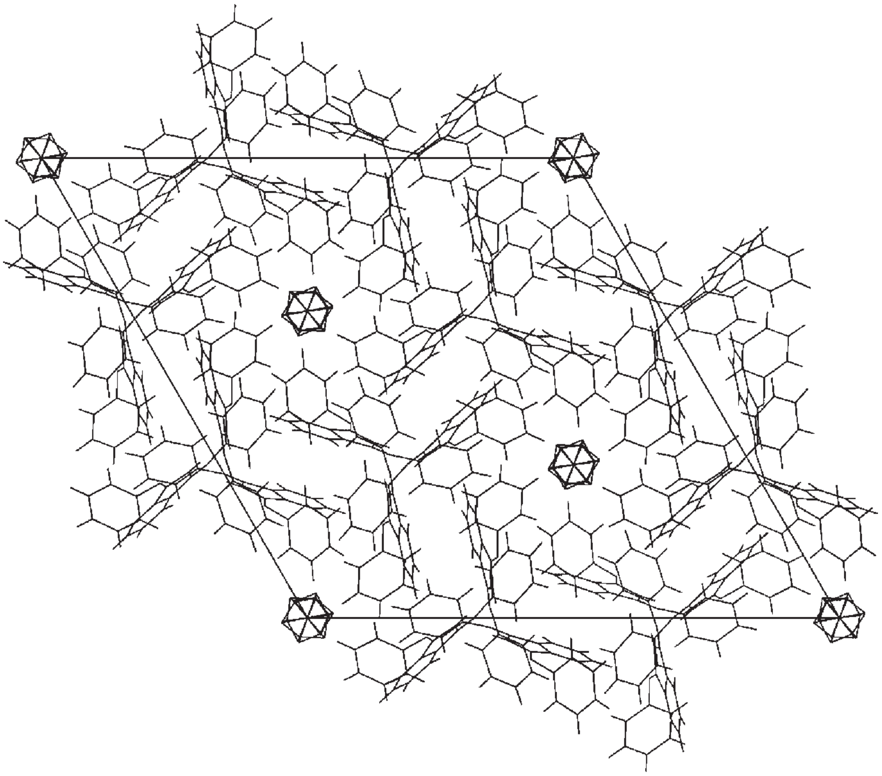

Figure 5. Packing diagram of **3Hex** projected down the *c*-axis; the hexagonal motifs represent disordered hexane with average S_6 symmetry

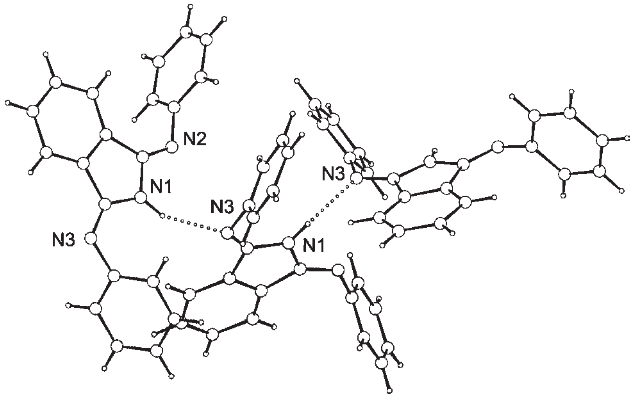

Figure 6. Hydrogen bonding **C(4)** chain in **3Hex**

The crystal structure of **3Mono** (Fig. 3) reveals it to be the *anti,anti* isomer **3c**. Bond lengths and angles are in good agreement with the structures discussed above, and also that of 2-trimethylsilyl-1,3-bis(trimethylsilylimino)-1,3-dihydroisoindole.[25] The C4—N2—C9—C14 and C1—N3—C15—C20 torsion angles are 61.0 and 59.5°, respectively, which isolates the NH group and precludes intermolecular hydrogen bonding. There are therefore no N—H···N hydrogen bonds; inspection of the crystal structure reveals only two weak intermolecular C—H···N interactions (not shown), C5—H51···N3($1-x, \frac{1}{2}+y, \frac{1}{2}-z$; C···N, 3.65 Å; C—H···N, 152°) and C20—H201···N2($x, \frac{1}{2}-y, \frac{1}{2}+z$; C···N, 3.50 Å; C—H···N, 138°). The lack of N—H hydrogen bonding is confirmed in the FT-IR spectrum of **3Mono**, which exhibits a sharp peak at 3446 cm^{-1}, an appropriate frequency for a NH group not involved in hydrogen bonding. The ^{1}H NMR spectrum of the sample obtained from isolated crystals of **3Mono** (see Experimental section) is similar to that obtained in an earlier NMR study (at 263 K),[9] which suggested that a mixture of both stereoisomers **3c** and **3d** was observed in $\mathrm{CDCl_3}$.

Crystal **3Hex** is a solvate, and contains ~0.2 mol of hexane per mole of *syn,anti* stereoisomer **3d** (Fig. 4). The results from the x-ray structure determination (5.3% hexane) are consistent with TGA analysis, which revealed an initial 5% weight loss. Crystalline **3Hex** has an irreversible melt; after resolidification, some of the original peaks reappeared, but additional peaks and evidence for an amorphous component were also present. Bond lengths (Fig. 4) and angles are again in good agreement with the structures discussed above. The C4—N2—C9—C10 and C1—N3—C15—C16 torsion angles are 86.2 and 65.8°, respectively, probably a reflection of packing forces. Compound **3Hex** crystallizes in the high-symmetry trigonal space group $R\bar{3}$; inspection of a packing diagram projected down the *c*-axis reveals the disordered hexane molecules in a site of crystallographic $\bar{3}(S_6)$ symmetry (Fig. 5). A single

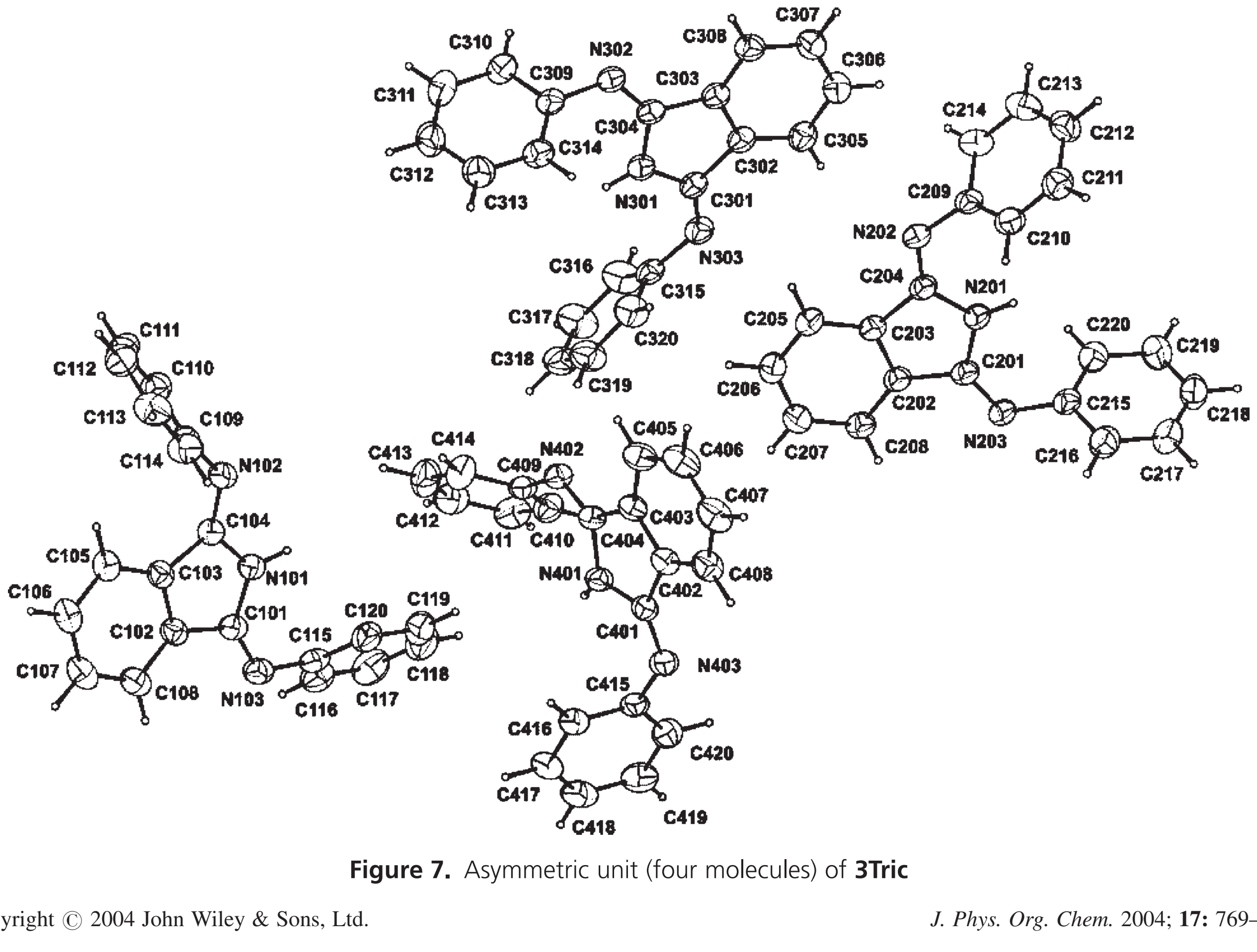

Figure 7. Asymmetric unit (four molecules) of **3Tric**

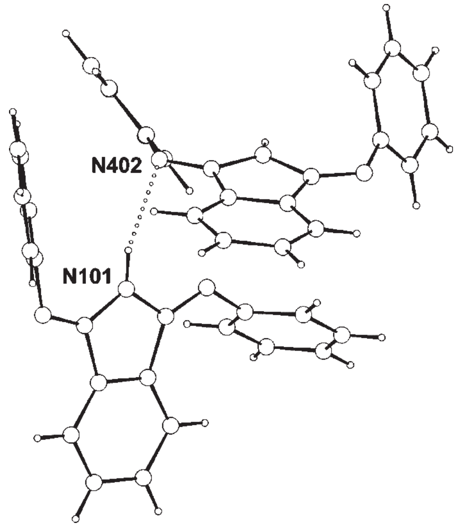

Figure 8. Discrete **D(4)** hydrogen bonding in **3Tric**

hydrogen bond, N1—H1···N3 $(\frac{4}{3} - y, x - y - \frac{1}{3}, z - \frac{1}{3}$; N···N, 3.01 Å; N—H···N, 154°), is part of an infinite chain, **C(4)**, as shown in Fig. 6.

Crystal **3Tric**, a second polymorph in the series, is a 3:1 mixture of the *anti,anti* and *anti,syn* stereoisomers **3c** and **3d** (Fig. 7). This is an example of conformational isomorphism (presence of different conformers in the same crystal). The **3Tric** and **3Mono** polymorphs represent another rare example[12] in which the phenomena of conformational polymorphism (presence of different conformers in different polymorphs) and conformational isomorphism (presence of different conformers in the same crystal) occur for the same substance. The density of **3Mono** is only slightly greater than that for **3Tric** (1.259 and 1.250 g cm^{-3}, respectively), which suggests similar packing efficiencies. For **3Tric**, the bond lengths and angles are again in normal ranges, in good agreement with the structures discussed above. The analogous C—N—C—C torsion angles, reflecting, as above, the twist angle between the phenyl and phthalic imidine molecular planes, lie in the narrow range 55.1–68.3°. As suggested by the crystal structure of the *anti,anti* isomer **3Mono**, hydrogen bonding may be expected to play only a minor role in the overall packing of the molecules. Figure 8 shows only a discrete N—H···N hydrogen bond, of graph set type **D(4)**, N101–H101···N402$(-x, 1 - y, 2 - z$; N···N, 3.10 Å; N—H···N, 158°).

Structural characterization of 3-phenyliminoisoindolinone (4)

Earlier studies[17,26] indicated that two isomers of **4** have been observed in CD_3OD whereby the *anti* isomer is the predominant structure in solution. An x-ray structure determination of a single crystal of **4** (Fig. 9) showed only the *anti* isomer to be present; the bond lengths (Fig. 9) and angles lie in normal ranges. The C4—N2—C9—C10 torsion angle is again typical at 57.4°. The crystal structure of **4** contains only an $R_2^2(8)$ hydrogen bond (Fig. 10), N1—H1···O1 $(1 - x, 1 - y, 1 - z$; N···O, 2.88 Å, N—H···O, 170°).

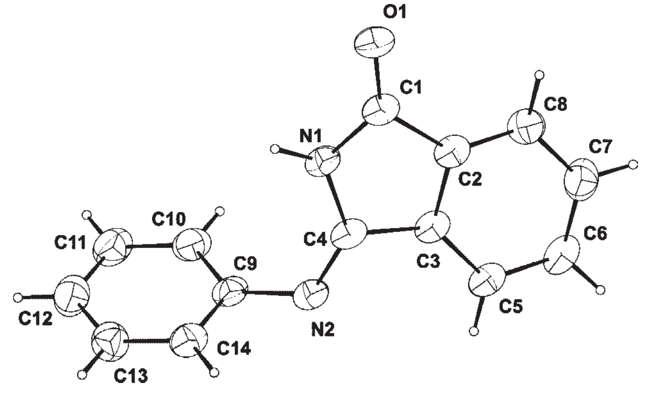

Figure 9. Molecular structure of **4**. Selected bond distances: N1—C1, 1.367(2); N1—C4, 1.402(2); C4—N2, 1.271(2); N2—C9, 1.419(2); C1—O1, 1.224(2) Å

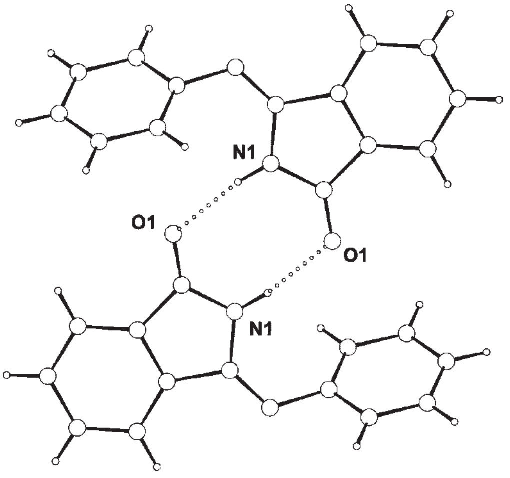

Figure 10. Hydrogen bonding in **4** [$R_2^2(8)$ ring shown]

Both yellow and orange crystals of **4** were obtained as described in the Experimental section. The yellow crystals had a slightly higher melting-point than the orange crystals, but both have the same unit cell constants within experimental error. A calculated powder x-ray pattern, using the unit cell data for **4**, did not correspond to the observed powder pattern from the bulk material, which therefore must not be a single phase.

CONCLUSIONS

The crystal structures of 1-imino-3-phenyliminoisoindoline (**2**), three forms of bis(phenylimino)isoindoline (**3**) and 3-phenyliminoisoindolinone (**4**) have been solved. TGA and DSC were used to characterize their thermal properties. The **3Tric** and **3Mono** polymorphs represent a rare example in which the phenomena of conformational polymorphism and conformational isomorphism occur for the same substance. Specimens of **3** do not return to a solid phase unless cooled below −10 °C. This is a likely consequence of the facile stereoisomerization[11] of the Schiff base-like groups. Analysis of powder diffraction results suggests that samples of **3** and **4** are mixtures of at least two phases, whereas specimens of **2** were found to be a single phase.

During the course of this work, crystal structures were solved for polymorphs of **1**; these studies will be reported separately.[27]

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REFERENCES

1. (a) Leznoff CC, Lever ABP (eds). *Phthalocyanines: Properties and Applications*, vols 1–4. VCH: Weinheim, 1989–95; (b) Thomas AL. *Phthalocyanine Research and Applications*. CRC Press: Boca Raton, FL, 1990; (c) Moser FH, Thomas AL. *The Phthalocyanines*, vols. 1 and 2. CRC Press: Boca Raton, FL, 1983; (d) Matsuoka M. In *Infrared Absorbing Dyes*, Matsuoka M (ed.). Plenum Press: New York, 1990; Chapt. 5; (e) Löbbert G. In *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A20. VCH: Weinheim, 1992; 213–242; (f) McKeown NB. *Phthalocyanine Materials: Synthesis, Structure and Function*. Cambridge University Press: Cambridge, 1998.
2. (a) Butler GB. In *Encyclopedia of Polymer Science and Technology*, vol. 4 (2nd edn), Mark HF, Bikales NM, Overberger CG, Menges G (eds). Wiley-Interscience: New York, 1986; 566–568; (b) Wöhrle D. *Adv. Polym. Sci.* 1972; **10**: 35–107.
3. Fernández-Lázaro F, Torres T, Hauschel B, Hanack M. *Chem. Rev.* 1998; **98**: 563–576.
4. Rixman MA, Sandman DJ. *Macromolecules* 2000; **33**: 248–249.
5. (a) Sandman DJ, Rixman MA, Tsai Z-H. *Proc. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.* 1999; **80**: 112–113.
6. Sandman DJ, Kim I-B, Rixman MA, Njus J, Kim M. *Synthesis* 2002; 1147–1156.
7. Sandman DJ, Rixman MA, Daudelin C, Shah S, Zhang Z, Ellis NA. *Mol. Cryst. Liq. Cryst.* 2001; **356**: 91–98.
8. Clark P, Elvidge J, Linstead R. *J. Chem. Soc.* 1953; 3593–3601.
9. Spiessens LI, Arteunis MJO. *Bull. Soc. Chim. Belg.* 1984; **93**: 205–222.
10. Spiessens LI, Arteunis MJO. *Bull. Soc. Chim. Belg.* 1988; **97**: 431–451.
11. Eliel EL, Wilen SH, Mander LN. *Stereochemistry of Organic Compounds.* Wiley: New York, 1994; 550–555.
12. Bilton C, Howard JAK, Madhavi NNL, Nangia A, Desiraju GR, Allen FH, Wilson CC. *Chem. Commun.* 1999; 1675–1676.
13. Straver LH. *CAD4-EXPRESS*. Enraf-Nonius: Delft, 1992.
14. Altomare A, Cascarano G, Giacovazzo G, Guagliardi A, Burla MC, Polidori G, Camalli M. *J. Appl. Crystallogr.* 1994; **27**: 435.
15. Watkin DJ, Prout CK, Carruthers JR, Betteridge PW, Cooper RI. *CRYSTALS*, Issue 12. Chemical Crystallography Laboratory, University of Oxford: Oxford, 2003.
16. Watkin DJ, Prout CK, Pearce LJ. *CAMERON*. Chemical Crystallography Laboratory, University of Oxford: Oxford, 1996.
17. Siegl WO. *J. Org. Chem.* 1977; **42**: 1872–1878.
18. Spiessens LI, Arteunis MJO. *Bull. Soc. Chim. Belg.* 1982; **91**: 763–790.
19. Elvidge JA, Linstead RP. *J. Chem. Soc.* 1952; 5000–5007.
20. Kornilov MYu, Makovetskii VP. *Ukr. Khim. Zh.* 1945; **41**: 933–939.
21. Dahl T. *Acta Crystallogr., Sect. E* 2002; **58**: o139–o141.
22. Shishkin OV, Kudrik EV, Islyaikin MV, Lyubimtsev AV, Siling SA. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1998; 334.
23. Etter MC, MacDonald JC, Bernstein J. *Acta Crystallogr., Sect. B* 1990; **46**: 256–262.
24. Bernstein J, Davey RJ, Henck JO. *Angew. Chem., Int. Ed.* 1999; **38**: 3441–3461.
25. Weller F, Schmock F, Dehnicke K. *Z. Naturforsch., Teil B* 1989; **44**: 548–552.
26. Clark P, Elvidge J, Golden JH. *J. Chem. Soc.* 1956; 4135–4143.
27. Zhang Z-Q, Njus JM, Sandman DJ, Guo C, Foxman BM, Erk P, Van Gelder R. *Chem. Commun.* 2004; 886–889.