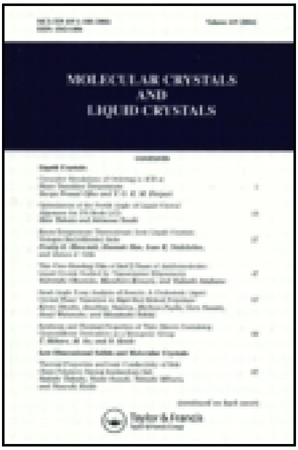

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Solid State Reactions of Phthalonitrile and Related Compounds

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Solid State Reactions of Phthalonitrile and Related Compounds

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The strategy of rendering an unreactive molecular solid reactive by doping is illustrated for the case of phthalonitrile doped with diiminoiso-indoline. The doped solid undergoes thermal reaction, and the product of the reaction is identified as phthalocyanine by solution spectrophotometry. The possible crystal chemistry associated with this new reaction is discussed. X-ray powder diffraction of phthalonitrile and its doped phases indicates the presence of multiple crystalline phases. The solid state decomposition of phenyliminoisoindoline has been studied, and some of the reaction products were identified.

Keywords: phthalonitrile reactivity; dopant-induced reactivity; phthalonitrile phases; phenyliminoisoindoline decomposition; tautomerism

INTRODUCTION

We have recently made initial reports[1] of the synthesis and unexpected polymerization of 2-benzylidene-4,5-dicyano-1,3-dithiole(1). The polymerization(Figure 1) was unexpected because all previous reports of reactions of dicyanoalkenes and -arenes with alkoxides in alcohol lead to molecular tetrazaporphines.[2] While the backbone structure of the conjugated polymer in Scheme 1 had been earlier proposed for relatively intractable materials from phthalonitrile(PN), diphenylmaleonitrile, and succinonitrile[3], we are the first to offer a modern structure proof based on observation[1] of the backbone C=N carbon resonances near 170 ppm. The polymer, obtained in 55% purified yield, is soluble and processable, and it has intense visible absorption with a broad maximum near 550 nm that tails past 1000 nm as well as interesting photoluminescence and semiconducting electrical properties. Since conjugated

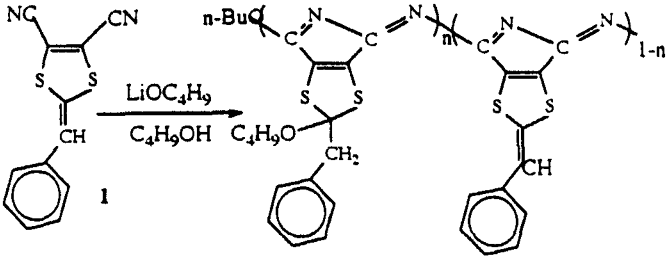


Figure 1. Polymerization of 2-benzylidene- 4,5-dicyano-1,3-dithiole(1); n = 0.5

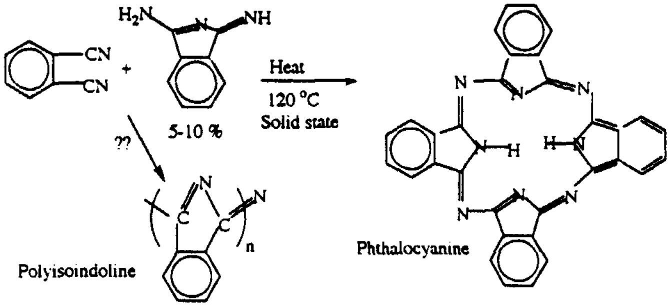


Figure 2. Solid state synthesis of phthalocyanine by doping of phthalonitrile; possible approach to polyisoindoline.

polymers are of considerable current interest for their electrical and optical properties[4], the synthesis of a new processable class of such materials, as in Scheme 1, is most noteworthy. Our observation of the unprecedented polymerization of **1** has motivated us to develop a comprehensive program involving novel approaches to the synthesis, processing, and materials properties of polymers, cyclotetramers, and oligomers derivable from dicyanoalkenes and -arenes. In this article, we focus on solid state reactions that are related to this objective.

REACTIVITY OF PHTHALONITRILE

Phthalonitrile, the key precursor to phthalocyanines and their metal derivatives, exhibits reversible melting behavior. In 1994[5], it was exposed to ^{60}Co gamma radiation(50 Mrad) and found to be unreactive. Also in 1994[5], aware that solid diiminoisoindoline thermally decomposes to ammonia and phthalocyanine, diiminoisoindoline(5-10 mole %) was crystallized with phthalonitrile in a benzene-ethanol mixture. It was anticipated that, if the dopant occupied a lattice site in a manner analogous to phthalonitrile, such a doped solid could lead to either the cyclotetramer phthalocyanine (from a centrosymmetric structure) or to the linear polyisoindoline(from a noncentrosymmetric structure) from a thermal reaction. Heating of the doped solid at 120°C for two hours (below the phthalonitrile m.p., 144-145°C) turned the white solid greenish blue. The electronic spectrum of the resultant solid in o-dichlorobenzene revealed the solution to contain phthalocyanine. This reaction is illustrated in Figure 2.

In these experiments, the nominally unreactive phthalonitrile was rendered reactive by our doping experiment. We have earlier noted[6] that, while vacuum sublimed crystals of propiolamide and the semicarbazone of propiolaldehyde are relatively inert to radiation, the presence of traces of chlorinated solvents(1 molecule of solvent per 250 molecules) in these crystals of monoacetylenes renders these crystals reactive to ^{60}Co gamma radiation. Similar observations were reported[7] earlier concerning solid state polymerization of trithiane. It was recently published[8] that the solid state polymerization of hexaphenylcyclotrisiloxane was initiated by spreading KOH and oligo (methylphenylsiloxanolate) uniformly over the surface of the crystals.

A crystal structure of phthalonitrile was reported[9] in 1995. The paper presented an orthorhombic structure in the noncentrosymmetric space group *Pmn*2_1. If the diiminoisoindoline dopant had been substituted at the site of a phthalonitrile in this structure, phthalocyanine could not form via a topochemical reaction. Reaction leading to phthalocyanine in the solid would then take place near vacancies or defects.

We have studied the X-ray powder diffraction patterns of phthalonitrile, diiminoisoindoline, and the solids obtained by doping. Doped single crystals that were greenish in color, indicating that the reaction had initiated, were studied by Professor Bruce Foxman (Brandeis University) who solved the structure for the known[9] phase of phthalonitrile! One possibility is that reaction takes place at vacancies or defects in such crystals. This is also the case for 4-methoxyphthalonitrile doped with diiminoisoindoline. Table 1 lists the powder patterns of phthalonitrile and two doped phases. In the phthalonitrile pattern, the (300) reflection should not be observed in the space group $Pmn2_1$. Hence the phthalonitrile sample is not a single phase. The (210), (400), and (202) reflections of the $Pmn2_1$ phase of phthalonitrile are not present in the material crystallized from ethanol, suggesting its absence, but are present in the sample from benzene/ ethanol. We conclude that all samples of phthalonitrile and its diiminoisoindoline doped forms consist of multiple crystalline phases. Studies of phthalonitrile with additional dopants are in progress.

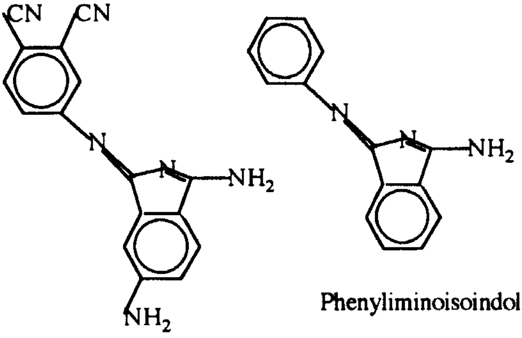
SOLID STATE REACTION OF PHENYLIMINOISOINDOLINE

We have also sought additional monomeric structures that are bifunctional and could serve as precursors to polymers analogous to polyisoindoline or as dopants for phthalonitrile and its derivatives. 4-Aminophthalonitrile[10] has both the *o* -dicyano and amino groups, but exhibits reversible melting behavior[11]. In the course of our characterization of a dimer of 4-aminophthalonitrile[11], phenyliminoisoindoline, the adduct of phthalonitrile and aniline, came to our attention as a simpler molecular structure. These molecular structures are shown in Figure 3. This compound was reported[12] to undergo a thermal decomposition at 203°C, but the products of the

TABLE 1. X-ray powder diffraction patterns of phthalonitrile and phthalonitrile doped with diiminoisoindoline.

Phthalonitrile d, Å(hkl)	**Doped phase (ethanol), d, Å**	**Doped phase (benzene/ethanol) d, Å**
6.27(200)	12.8	9.5
4.17(300) ??	9.4	7.5
3.93(010)	7.4	6.9
3.75(110)	6.27	6.41
3.62(301)	5.57	6.21
3.49(002)	4.67	6.11
3.42(011)	4.55	5.63
3.31(210)	4.17	4.70
3.17(400)	3.88	3.91
3.06(202)	3.81	3.77
3.01	3.67	3.70
2.86	3.62	3.63
	3.52	3.60
	3.40	3.51
	3.02	3.43
	2.96	3.32
	2.86	3.18
		3.07
		3.02
		2.96
		2.95
		2.87

decomposition were not specified. Since the capillary tube melting behavior of any thermally reactive diacetylene monomer(in optimal cases, these lead to a topochemical, topotactic solid state polymerization), for example, might be reported as a decomposition reaction, we deemed it of



Phenyliminoisoindoline

Figure 3. Molecular structures of a dimer of 4-aminophthalonitrile and phenyliminoisoindoline.

interest to specify the reaction products of phenyliminoisoindoline.

When phenyliminoisoindoline is heated at about 150°C for 24 hours, the material darkens and a 5-8% weight loss is noted. Ammonia is identified as a volatile product of the reaction. 1,3-Bis-phenyliminoisoindoline and phthalonitrile are identified by authentic sample comparison in thin layer chromatography, and the latter compound sometimes sublimes away from the bulk reactant. From its solution electronic spectrum, phthalocyanine is detected in 0.25% yield. Our tentative reaction pathway for this decomposition involves conversion of phenyliminoisoindoline to aniline and phthalonitrile as first step and is shown in Figure 4.

Phenyliminoisoindoline can, in principle, exist in several tautomeric forms, as shown in Figure 5. An earlier[13] proton NMR study indicated that form A was preferred in solution, and this form is also found in our crystal structure(B.M. Foxman). Our modeling studies [11] (AM1 and MM) also favor tautomer A. If the first step in the decomposition of phenyliminoisoindoline involves intramolecular dissociation to aniline and phthalonitrile, then it may be required that tautomer A convert to a higher energy tautomer. This could involve a phase transition. However, our differential scanning calorimetry study

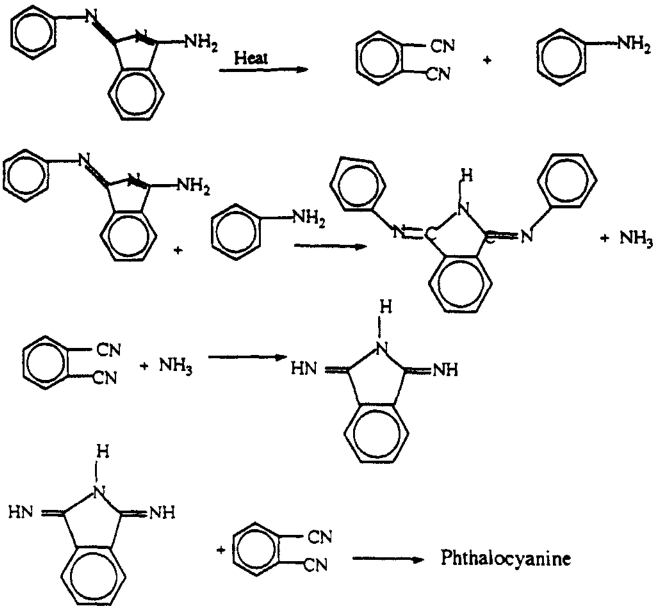


Figure 4. Tentative reaction scheme for the decomposition of phenyliminoisoindoline.

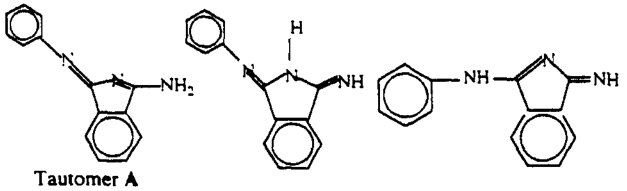


Figure 5. Possible tautomers of phenyliminoisoindoline.

of phenyliminoisoindoline does not reveal a phase transition below the thermal decomposition point.

Acknowledgments

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