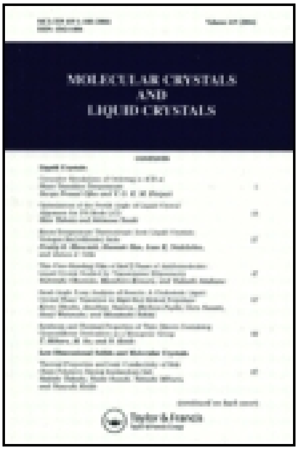

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The Preparation, Spectral Properties, and X-Ray Structural Features of 2,3-Naphthalocyanines

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The Preparation, Spectral Properties, and X-Ray Structural Features of 2,3-Naphthalocyanines

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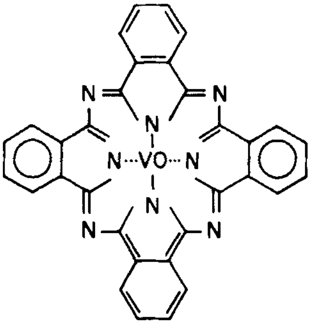
We have prepared a series of 2,3-naphthalocyanine (H_2NPc) compounds and examined their spectroscopic properties. All of them can be vacuum sublimed as thin films which absorb strongly in the near infrared and thus make them potentially useful as optical data recording media. In addition, we have measured the electrical resistivities, at room temperature, of several of the compacted 2,3-naphthalocyanines and find them to be semiconductors. Doping with bromine vapor enhances the conductivities only slightly (H_2NPc actually becomes more resistive).

INTRODUCTION

Since the discovery of phthalocyanines[1] in the early 1930's a rich and varied chemistry and technology has developed around these interesting materials. There are literally thousands of publications and patents concerned with phthalocyanine (Pc) and related compounds.[2,3] Of recent interest, in the burgeoning world of computers and information storage, is the application of Pc's as optical data recording (ODR) media.[4,5,6,7]

The properties of Pc's that make them reasonable candidates for ODR applications are: their very good thermal, hydrolytic and oxidative stabilities; their ability to be prepared as thin films by vacuum sublimation techniques and their intense long wavelength absorption bands. This latter property becomes even more significant when it is realized that one of the goals of modern-day optical storage instrument design is to use solid state semiconductor lasers for writing purposes.[8] These solid state lasers (e.g. GaAlAs) emit at wavelengths greater than 800 nm. Vanadyl Pc (VOPc) (I) has been of particular interest in this regard,[4] since it has an absorption maximum at 810 nm. We have recently found that the parent compound, H_2Pc (II), has certain other advantages for ODR purposes but without the necessary long wavelength absorption.[9] Therefore, we decided to pursue the synthesis of other Pc materials having strong absorption bands in the near IR. Naphthalocyanines (NPc's), because of their larger aromatic π-systems, should have the requisite spectral properties, and these became our target molecules.



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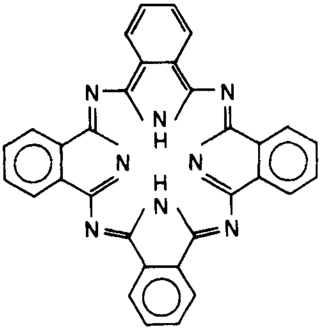
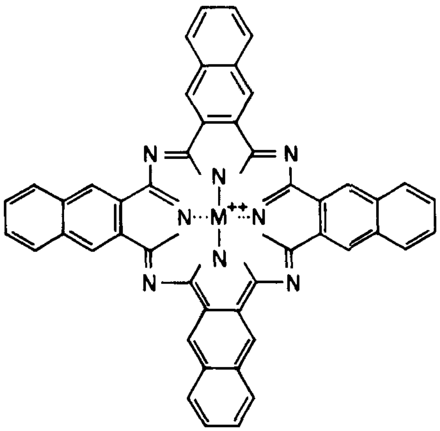


II

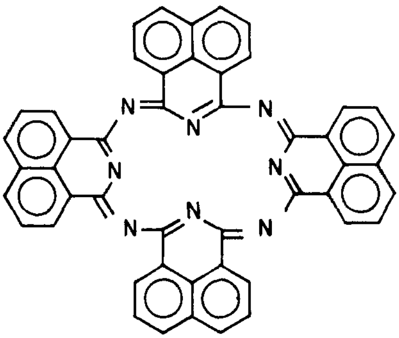
Another area of interest, in addition to their optical properties, are the electrical properties of the NPc's. Much has been written concerning the semiconducting Pc's[2,3] and the large increase in conductivity that occurs on doping. We report here preliminary measurements on conductivities of doped NPc's.

RESULTS AND DISCUSSION

One of the more attractive approaches to near IR absorbing materials, at least on paper, is the preparation of 2,3-naphthalocyanines (NPc) (III). Instead of the basic unit being the isoindole structure, as in Pc, we have benzoisoindole. The additional electronic delocalization afforded by the larger aromatic system should lead to longer wavelength absorption.



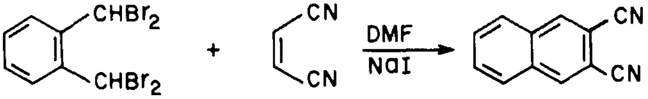
III



VIII

The original Pc compounds were available through the reaction of *o*-cyanobenzamide, phthalimide, or phthalonitrile with metals or inorganic compounds of metals.[10,11] Phthalonitrile seems to be most accessible and appears to be the compound of choice in these reactions.

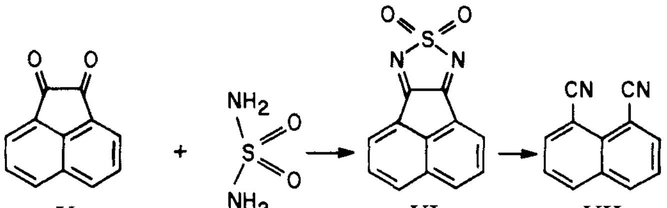
The routes to the analogous NPc precursor, 2, 3-dicyanonaphthalene, that appear in the nonpatent literature[12] are not practicable since starting materials are unavailable. A Russian patent did, however, give us a different approach.[13] This procedure was one-step and involved the reaction of $\alpha, \alpha, \alpha', \alpha'$-tetrabromo-*o*-xylene with fumaronitrile in dimethylformamide containing sodium iodide.



IV

Presumably this reaction proceeds through an intermediate dibromo-o-quinodimethane,[14] with subsequent aromatization occurring through loss of hydrogen bromide. This reaction, in our hands, results in a 66% yield of the desired 2, 3-dicyanonaphthalene (IV).

Another dicyanonaphthalene which might give a symmetrical NPc is the 1, 8-derivative. This was reported not to give NPc's under the usual reaction conditions. We prepared 1, 8-dicyanonaphthalene (VII) by the thermal decomposition of acenaphtho[1, 2-C] (1, 2, 5) thiadiazole-8, 8-dioxide (VI).[15] The thiadiazole dioxide (VI) was in turn derived from acenaphthoquinone (V) and sulfamide.[16] When VI is heated with copper-bronze no NPc is obtained, thus confirming previous workers' observations. The reason for this failure is related to the fact that no structural formulae can be written that incorporate a metal ion. In VIII it can be seen that the only reasonable structure is one which is electrically neutral without a metal ion. Further, examination of space filling molecular models indicates that severe steric interactions of the hydrogens at the 2-positions would prevent a planar molecule from being formed. Even if the NPc-like molecule were formed, it could not easily adopt an aromatic structure and thus would tend towards instability.



V VI VII

Only a few test tube reactions with 2, 3-dicyanonaphthalene were undertaken by Linstead and coworkers.[17] Most of their studies were done with 1, 2-dicyanonaphthalene, a much more accessible material. Unfortunately, the resultant 1, 2-naphthalocyanines proved to be a mixture of several structural isomers that were difficult to separate and characterize. The 2, 3-naphthalene derivatives would, of course, yield only a single isomer. The syntheses of the metal NPc's generally followed standard procedures,[17] whereby 2, 3-dicyanonaphthalene was heated with the appropriate metal or metal compound. Two variations were tried, one in which the reaction was carried out in a sealed, evacuated tube and the other, in an open tube under N_2. Table I presents a summary of reaction conditions which were used.

Once the reactions were completed, purification of the products was accomplished by exhaustive washing with halogenated hydrocarbon solvents, and/or sublimation *in vacuo* of the more volatile impurities. The greenish solids were not amenable to recrystallization in ordinary solvents and were used, directly as produced, for spectroscopic measurements.

Mass spectroscopic studies of several selected NPc's confirmed that the synthetic route did result in the desired compounds. Solids probe

TABLE I

Reaction conditions for preparation of 2, 3-naphthalocyanines.[a]

Metal or Compound used	Amount of Metal or Compound	Temp. °C	Time	Tube P
Copper-Bronze	0.2 g	260–270°	1 hr.	0.02 Torr
PbO	0.38 g	275°	30 min	0.02 Torr
PbO	0.5 g	280°	30 min	1 atm. N_2
V_2O_5	0.5 g	280°	1 hr.	1 atm. N_2
Mg	0.1 g	370°	80 min	0.02 Torr

[a] 1.0 g of 2, 3-dicyanonaphthalene was used in all cases.

mass spectroscopy of CuNPc, PbNPc and H_2NPc gave molecular ions of the three compounds and, in addition, fragmentation patterns with several common peaks. A summary of the mass spectral data appears in Table II. The following are assignments of common fragments: M/e 208, $C_{13}H_{10}N_3^+$; M/e 178, $C_{12}H_6N_2^+$; M/e 179, $C_{12}H_6N_2H^+$; M/e 163, $C_{12}H_5N^+$.

Infrared spectra were taken of solid samples prepared in CsI pellets. These spectra are shown in Figure 1. The most obvious feature, common to all the spectra, is the very strong line at 1081–1085 cm^{-1}. Generally, it is the strongest absorption, and we attribute it to ring breathing modes in the phthalocyanine portion of the molecules. Other apparent similarities are the strong multiplets near 1360 cm^{-1}, the doublets centered near 875 cm^{-1} and 730 cm^{-1} respectively and the singlet at 470 cm^{-1}.

In phthalocyanines, several bands in the IR have been attributed to the nature of the metal, and to metal-ligand vibrations.[18] Specifically,

TABLE II

Mass spectral data for selected 2, 3-naphthalocyanines.[a]

Compound	Nominal mass peaks (relative intensity)
CuNPc	776(64.6), 209(25.7), 208(32.5), 179(27.9),
	178(100.0), 163(38.8), 161(30.8), 157(21.0), 153(35.8)
PbNPc	923(59.8), 208(100.0), 207(45.7), 206(37.2), 193(21.3),
	179(27.1), 178(33.9), 165(24.2), 163(31.2)
H_2NPc	714(100.0), 209(67), 208(60), 180(50),
	179(83), 178(100), 153(75)

[a] Only the strongest lines are given.

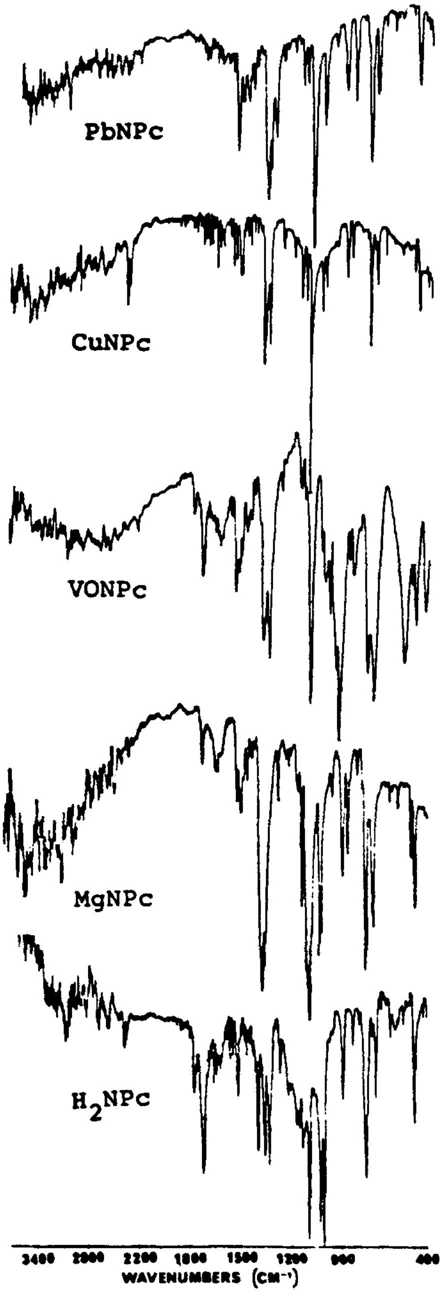


FIGURE 1 Transmission infrared spectra taken in CsI pellets of H_2NPc, MgNPc, VONPc, CuNPc and PbNPc.

the region between 850–950 cm^{-1} contains absorption peaks only in metal derivatives of Pc. The H_2Pc samples had no corresponding peaks and thus these lines were attributed to metal-ligand vibrations. No such correlation could be made on the basis of our NPc spectra, probably because the region of interest was obscured by absorptions due to the naphthalene portion of the molecule. Consistent with our NPc spectra, the Pc spectra also exhibit very strong lines at about 1085 cm^{-1}. This strengthens our belief that this line, which appears in all NPc's and Pc's, is a characteristic of the central ring structure.

One complicating factor which we have not discussed, because of the dearth of information on the subject, is the role of various polymorphs on the spectroscopic behavior of the NPc's. Certainly, for the Pc's, it has been shown that different polymorphic forms exist and contribute to various lines in their IR spectra.[18] The problem of the existence of various polymorphs of the NPc's must await careful single crystal x-ray crystallographic analyses, of which none presently exist. Some of the data, spectroscopic and x-ray, which we present here may undergo some modification as more is learned about the different crystalline types of NPc's that may be found.

Electronic spectra were recorded for various 2,3-NPc's. Film samples for these measurements were prepared, by standard vacuum evaporation techniques, on glass microscope slide substrates. Since we have no information on densities for these substances we chose 1.3 g/cc as an approximate number to use in our quartz crystal monitor so that an estimate could be made of film thickness. This thickness estimate was in good agreement with values determined using Nomarski interferometry. Using these values we could then calculate absorption coefficients for the various NPc's (Table III). It is apparent that the long wavelength absorption maxima occur at about 80–100 nm higher wavelength than those of similar compounds in the phthalocyanine series.[20,21] As mentioned above, this was to be expected from the larger aromatic system of the NPc's. Sublimed thin films of CuPc exhibit long wavelength absorption maxima at 691, 626 and 580 (sh.) nm[21] and H_2Pc has bands at 635 and 700 (sh) nm,[9] and the comparable NPc's show maxima at 785 nm for Cu and 800 nm for the H_2 compounds respectively (Table III).

The absorptivities that we show in Table III are calculated based on a number of assumptions including NPc densities, which have not been reported, and molecular volumes based on examination of molecular models. No crystal structures are known for NPc's. We note that, except for VONPc all absorptivities, including H_2Pc, are about 10^5. Unexpectedly, the VONPc absorption spectrum in the

TABLE III

Absorption maxima of evaporated thin films of various 2, 3-naphthalocyanines

Compound	Color and nominal thickness[a]	λ_{max}(O.D.)	a[b]
CuNPc	Green 160 Å	712 nm (0.136), 785 (0.10)	1.1×10^5
PbNPc	Green 1000 A°	sh 770 nm (0.40), 846 (0.54)	9.8×10^4
VONPc	Green 235 A°	sh 770 nm (0.19), 846 (0.56)	4.3×10^5
MgNPc	Green 500 Å	720 nm (0.25), 788 (0.35)	1.3×10^5
H_2NPc	Green 1000 Å[d]	715 nm (0.19), 800 (0.17)	3.1×10^4
H_2Pc[c]	Blue 600 Å	635 nm (0.58), sh 700 (0.42)	2.4×10^4

[a] Film thicknesses were determined by using a quartz crystal thickness monitor during the evaporation and assuming densities of 1.3 g/cc. (For PbNPc we assumed 1.5 g/cc.)

[b] Molar absorptivities for the longest wavelength band were estimated assuming a molecular volume of NPc of 3.0×10^{-21} cm^3. This number was obtained from examinations of molecular models.

[c] Reference 9 (1 molecule contains 1/2 abc sinβ or 5.82×10^{-22} cm^3)[23].

[d] The thickness measurement for H_2NPc is questionable because the film of H_2NPc includes some decomposition products.

visible is, except for intensity, the same as that found for PbNPc. Both have a near infrared absorption peak at 846 nm. The absorption coefficients of thin films of several phthalocyanines have been reported.[22] Those values, about 3×10^5, are similar to our findings for NPc films, even though our measurements did not incorporate the more rigorous corrections used by the other authors. The literature contains only scant references to 2, 3-NPc electronic spectroscopy, and those only to solution measurements. The most recent paper[23] reports the long wavelength maximum for ZnNPc is 767 nm ($\epsilon = 1.6 \times 10^5$). In addition, maxima from solution spectra[24] of CuNPc, VONPc, MgNPc and H_2NPc were given as 776, 820, 776 and 780 nm respectively. As might be expected, these values are somewhat lower than those from the solid state spectra given in Table III.

In order to obtain structural information, x-ray diffractograms of powdered samples were recorded. The results are shown in Figure 2, which also includes the diffraction pattern from gradient-sublimed crystals of H_2Pc for comparison purposes. Of the four naphthalocyanines, the Pb compound appears to have the highest degree of crystallinity, while the broadened diffraction peaks of the others suggest disordered and/or very fine grained crystalline structures. The anomalously sharp lines at high angles for VONPc have been identified as belonging to V_2O_5 and other vanadium oxides (Fig. 2), so that the experimentally produced VONPc is substantially disordered. Superficially, there appear to be reflections common to all the materials, e.g. in the vicinity of 6°, 9°, 13°, 18°, 22°, and $27° = 2\theta$. However, despite the common features, the unit cells of the naphthalocyanines are not simply congruently expanded versions of the H_2Pc unit cell.[25] For example, the two strongest reflections in the $5° - 15°$ 2θ region of the NPc's are not simply consecutive $00l$ orders as they are in H_2Pc. If they were, then using the PbNPc diffractogram (which is the best resolved of the four) would yield *c*-axis repeats of 16.9 Å and 15.7 Å, respectively, from the hypothetical 001 and 002 reflections. Similarly, the two intermediate peaks in this region could not be $20\bar{1}$ and $20\bar{2}$ as in H_2Pc, because that would imply *a*-axis repeats of 20.6 Å from the first and 16.8 Å from the second, assuming $c = 16.9$ Å and the same monoclinic angle as for H_2Pc.[26] Therefore, a full structural determination must await the preparation of single crystals of these naphthalocyanines.

The electrical properties of 2,3-NPc's have not, to our knowledge, been examined. Some very sketchy data have been published for 1,2-NPc's. For example, the activation energy for conductivity in Cu 1,2-NPc is reported to be 0.72 eV, while its resistivity (ρ) at room temperature exceeds 10^{11} Ω-cm.[27] Also, the sensitivity of the conductivity of 1,2-NPc's to the surrounding atmosphere was determined.[28] Finally, a study of the conductivity of amorphous Cu 1,2-NPc (presumably the 1,2-isomer, but not specified), grown directly on brass substrates, was published.[29] From this work, the carrier density and mobility at 300°K were found to be 3×10^{12} cm^{-3} and 0.5 $cm^2v^{-1}s^{-1}$ respectively. Conclusions were drawn implicating polarons as the charge carriers.

In our own work, we have measured the room temperature resistivities of several compacted NPc's together with the resistivity of H_2Pc for comparison. These data are presented in Table IV. The resistivity of H_2NPc is significantly lower than that of either PbNPc or VONPc.

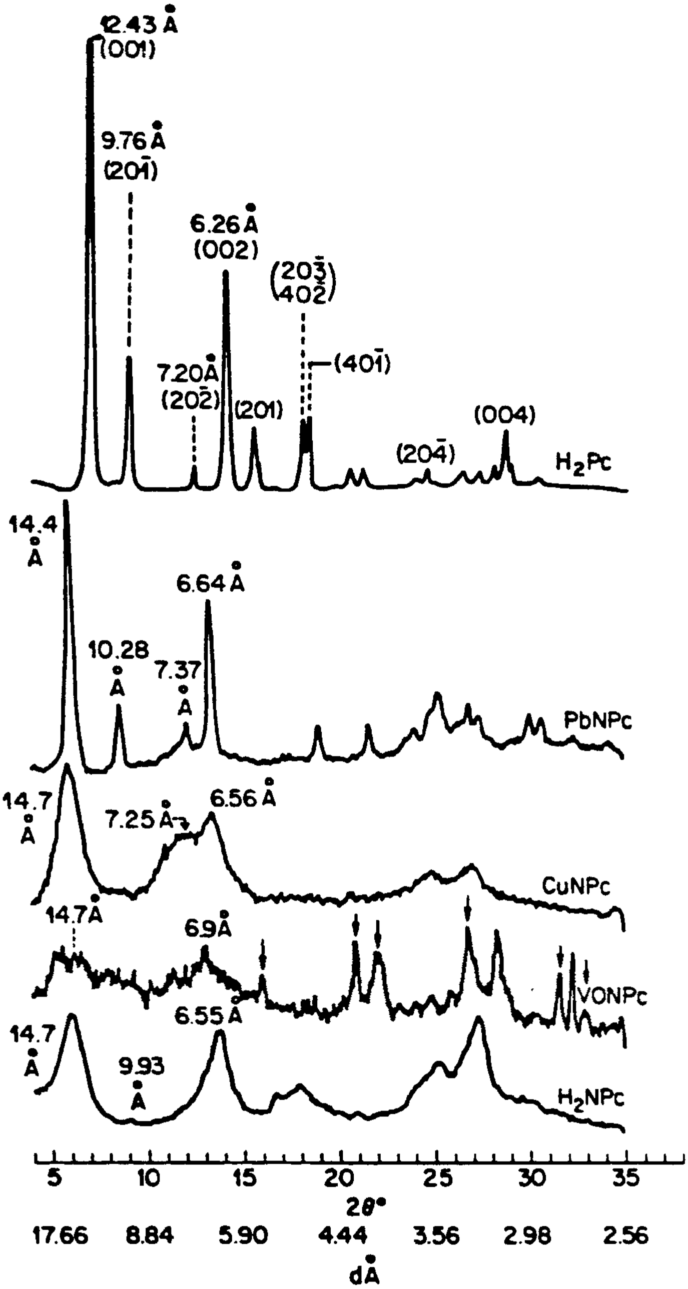


FIGURE 2 Powder x-ray diffractograms of H_2NPc, VONPc, CuNPc and PbNPc with H_2Pc as a comparison. Single arrows on the VONPc diffractogram identify V_2O_5 reflections, and other sharp lines are associated with other stoichiometric oxides.

TABLE IV

Room temperature resistivities of compressed pellets of 2, 3-naphthalocyanines

MATERIAL	RESISTIVITY[a] (UNDOPED)	RESISTIVITY[a] (Br_2 VAPOR DOPED)
H_2NPc	$1.6 \times 10^4 \Omega cm$	$1.9 \times 10^5 \Omega cm$
PbNPc	9.4×10^6	6.3×10^5
VONPc	2.5×10^6	4.7×10^5
H_2Pc[b]	Insulator	9.4×10^4

[a] Sample sizes were approximately 0.01 cm^2 × 0.001 cm.
[b] Gradient sublimed crystals were compacted.

This > 2-orders of magnitude difference may possibly be accounted for by the way the H_2NPc is made. The preparation of H_2NPc requires that MgNPc be dissolved in concentrated sulfuric acid. During that step some oxidation must occur, and these species remain in the H_2NPc product acting as an impurity dopant to enhance conductivity. Nevertheless, when additional dopant is added, in the form of Br_2 vapor (Table IV), the H_2NPc resistivity does not decrease, but increases by about a factor of 10.

The resistivities of the PbNPc and VONPc both decrease on bromine treatment, but not anywhere near as much as the change observed for H_2Pc where the drop in resistivity is many orders of magnitude. This could be accounted for by the highly crystalline nature of the H_2Pc as compared to the NPc's.

CONCLUSION

Starting with 2,3-dicyanonaphthalene, a number of 2, 3-naphthalocyanines have been prepared. These include H_2NPc, MgNPc, CuNPc, VONPc and PbNPc. Infrared absorption spectra of the various compounds, obtained in CsI pellets, had common features. Thin films of the NPc's were prepared by standard evaporation techniques and optical absorption spectra were recorded and compared to absorption spectra of the related Pc compounds. As expected, the absorption maxima for the NPc's occurred in the near infrared, about 80–100 nm longer wavelength than the maxima for the Pc's. Powder x-ray diffractograms of the NPc's were taken to obtain some structural information. No simple correlation with the known crystal structures of Pc's was discerned. Several reflections were found common to all the NPc's. The electrical resistivities of several NPc's have been measured as room temperature compactions. All seem to exhibit semiconducting behavior. Treatment of the compacted samples with bromine vapor does not change the resistivities very much, only about an order of magnitude. In the case of H_2NPc the bromine treated material actually develops a higher resistivity.

EXPERIMENTAL

2, 3-Dicyanonaphthalene

A mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (16.88 g, 0.04 moles), NaI (dried 3 hrs. at 110°C, 40.0 g, 0.27 mole) and fumaronitrile (3.12 g, 0.04 moles) in N, N-dimethylformamide 150 mL (dried over 4A molecular sieves) was heated in a N_2 atmosphere at 65° for 48 hours. After cooling to room temperature, the brown mixture solidified and was then stirred with 500 mL of cold water. A solution of sodium thiosulfate was added until the brown iodine color was dispelled. The pale yellow mixture was filtered to collect a beige solid. After air drying, the solid was recrystallized from 1, 2-dichloroethane/hexane (2 : 1) and afforded 4.69 g (66%) of cream colored needles with m.p. 253–255°C (Lit. 251°C[12]).

2, 3-Naphthalocyanines

Table I summarizes the experimental conditions used in the various preparations. Purification of the products was effected by exhaustive washing and/or vacuum sublimation to remove impurities.

The dihydrogen compound, H_2NPc, was prepared by dissolving the MgNPc in concentrated H_2SO_4, filtering, and pouring the solution over ice. The precipitate was collected by centrifugation, washed and then dried.

Film preparation

A vacuum bell jar station, turbine-pumped to $\sim 5 \times 10^{-5}$ Torr, was used. Glass microscope slides, used as substrates, were held in place approximately 15 cm above a resistively heated tantalum cup containing the NPc. Clamped next to the glass substrate was a quartz-crystal thickness monitor. The organic material was heated (> 500°C) until a reasonable deposition rate was observed (~3 Å/s). Heating too long resulted in decomposition of the NPc's, with a concomitant reduction in the deposition rate.

Characterization

Infrared spectra were obtained on CsI pellet samples using a Fourier Transform IR spectrophotometer.

Electronic spectra were measured on a Perkin-Elmer Model 330 spectrophotometer using evaporated film samples.

Solids-probe mass spectrometry was performed on the PbNPc and CuNPc. The samples were heated to 500°C before any significant spectrum could be seen. Nominal, uncalibrated masses were observed at M/e 776 (CuNPc) and M/e 923 (PbNPc). The calculated masses for the molecular ions of the CuNPc and PbNPc are 776 and 920, respectively.

X-ray diffractometry was performed in the reflection geometry scanning at 2° 2θ/min using Ni-filtered CuKα radiation.

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