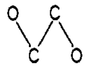
2.6 Å[3,14] so diffusion into the interior is effectively blocked. However, with solids of low crystallinity the interlayer spacing may be larger as the state of hydration is greater.[11,20] Furthermore, the forces holding the layers together are weaker and thus less energy is required to expand the layers. This combination of circumstances allows ethylene oxide to diffuse into the interior, resulting in extensive reaction.

The ion-exchange reactions of crystalline α-ZrP are known to occur at the surface of the crystal and proceed by a diffusion mechanism.[21] The ions form a new phase at the periphery of the crystal and diffuse with advancing phase boundary. Thus, the exchanged phase coexists in the same crystal or particle with the unexchanged phase. One would expect that the esterification proceeds simiarly. That is, the surface phosphate groups tend to create a barrier toward diffusion to the interior. However, the resulting P–OCH_2CH_2OH groups are hydrophilic so that some additional swelling might be expected. The swelling allows further diffusion of ethylene oxide inward with concomitant reaction at the interior sites. This mechanism explains why mixtures of unreacted α-ZrP and the esterified phase occur together. Since diffusion is slow and proceeds from the surface inward, portions of the interior may remain totally unesterified even when the uptake approaches 2 mol.

Yamanaka has explained the interlayer distances observed in ethylene oxide esterified γ-ZrP on the basis of fully extended chains, i.e., a distance of 3.5 Å for the oxygen–oxygen trans–trans



length. A plot of interlayer distance as a function of ethylene oxide content for α-ZrP is shown in Figure 2. The slope of the line for the anhydrous products is 2.79 Å and for the hydrated (average 1 mol of H_2O) is 2.95 Å. Thus the chains are not fully extended. This may result from the fact that the distance between chains in α-ZrP, 5.3 Å, is probably larger than in γ-ZrP, since it is known from density considerations that the metal atoms are more densely packed in the latter compound.[22]

The direct interaction of ethylene oxide with α-ZrP, θ-ZrP, and γ-ZrP did not yield products with chain lengths greater than 2. This is inferred from the low values of n and the interlayer spacings. Presumably the large amount of energy required to expand the layers precludes extensive polymerization from occurring. Thus, we were led to the indirect route of preparing polyether phosphates from which the α-layered polyether complexes precipitate on contact with soluble Zr(IV) salts. These derivatives become more hydrophilic as the chain length of the polyether increases. This is shown by the greater degree of swelling on contact with water culminating in the colloidal dispersion of the complex when $n = 9$. However, the colloidal particles could be recovered by centrifugation or filtration through fine Millipore filters, showing their colloidal nature.

The ready uptake of electrolytes and coordination complexes by the zirconium polyether derivatives presages some exciting applications in electrochemistry, heterogenization of soluble catalysts, and novel separation procedures.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE81-14613 and the Robert A. Welch Foundation under Grant No. A-673, for which grateful acknowledgment is made.

Registry No. 1, 112-60-7; $POCl_3$, 10025-87-3; $BaO_3PO(CH_2CH_2O)_4H$, 96194-46-6; $ZrOCl_2$, 7699-43-6; $Zr[O_3PO(CH_2CH_2O)_4H]_2$, 96194-47-7.

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[20] Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117.
[21] Alberti, G. *Acc. Chem. Res.* **1978**, *11*, 1633.
[22] Yamanaka, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1979**, *40*, 45.

Contribution from Xerox Webster Research Center,
Webster, New York 14580

Synthesis and Properties of *tert*-Butyl-Substituted Vanadylphthalocyanine Dyes

KOCK-YEE LAW

Received August 13, 1984

Soluble vanadylphthalocyanine dyes of various degree of *tert*-butyl substitution, $(t\text{-Bu})_n$VOPc, have been synthesized by reacting varying amounts of 4-*tert*-butylphthalonitrile and phthalonitrile with vanadium trichloride. The number of *tert*-butyl substituents on the VOPc ring is calculated from the elemental analysis results, which are in good agreement with the ^{1}H NMR data and are compatible with the mass spectrometric results. The solid-state properties of $(t\text{-Bu})_n$VOPc were studied by absorption spectroscopy and the X-ray powder diffraction technique, and results show that, at $n = 4.0$, the dye molecules form a non-IR-absorbing, amorphous VOPc phase I in the solid state and that, at $n = 1.4$, the crystalline, IR-absorbing VOPc phase II is formed. These results are discussed in terms of a steric effect on the packing of $(t\text{-Bu})_n$VOPc molecules into the phase II of VOPc in the solid state.

Introduction

Vanadylphthalocyanine (VOPc), like the parent phthalocyanine and many of its metal derivatives, possesses photoconductive and semiconductive properties. It has been shown that VOPc is a photosensitive pigment useful in photoelectrophoretic[1] and xerographic[2,3] imagings and more recently ablative optical recording.[4] The polymorphic behavior of VOPc has been studied by Griffiths, Walker, and Goldstein.[5] These authors show that in the solid state VOPc may exist in three different morphological forms, namely phases I–III. Among the three phases, phase II is a thermodynamically stable, crystalline material and exhibits strong near-IR absorption ($\lambda_{max} \sim 840$ nm). This near-IR absorptivity makes VOPc a very attractive photoreceptor candidate for diode laser scanned xerographic applications.[3] As a pigment, VOPc has limited solubility in organic solvents. Established purification procedure for VOPc, which involves dissolution of VOPc in concentrated sulfuric acid and reprecipitation of VOPc by discharging the resulting sulfuric acid solution into ice water, is very tedious and labor intensive.[6]

It was felt that this difficult purification process could be avoided by modification of VOPc with various solubilizing groups. The resulting VOPc dye, being highly soluble in organic solvents, could thus be purified by conventional solution recrystallization. Among various substituent groups, *tert*-butyl,[7–9] trimethylsilyl,[9] and sulfamide[10] groups seem to give the highest solubilizing effect

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[1] U.S. Patents 3 825 422, 4 032 339, and 4 076 527.
[2] U.S. Patent 4 181 772.
[3] Grammatica, S.; Mort, J. *Appl. Phys. Lett.* **1981**, *38*, 445.
[4] Kivits, P.; DeBout, R.; VanDerVeen, J. *Appl. Phys.* **1981**, *A26*, 101.
[5] Griffiths, C. H.; Walker, M. S.; Goldstein, P. *Mol. Cryst. Liq. Cryst.* **1976**, *33*, 149.
[6] Germano, N. J.; Nealey, R. H. *Xerox Disclosure Journal* **1978**, *3*, 377.
[7] Mikhalenko, S. A.; Barkanova, S. V.; Lebedev, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1971**, *41*, 2735.
[8] British Patent 1 212 289.
[9] U.S. Patent 3 759 947.

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Table I. Characterization of (t-Bu)$_n$VOPc Dyes

reactant molar ratio t-BPN:PN:VCl$_3$	elemental anal. C, H, N.	calcd^a n	^{1}H NMR anal. t-Bu/aromatic protons	mol ion m/z (rel intens)
1:0:1.1	71.07, 5.88, 13.84 70.92, 5.90, 13.76	4.0	3.6	803 (100)
1:1:2.1	69.41, 4.82, 15.17	2.5 ± 0.3	2.7	803 (20.6), 747 (62.5), 691 (100), 635 (42.2)
1:3:4.2	68.88, 4.99, 15.59	2.0 ± 0.7	2.1	747 (21.8), 691 (59.1), 635 (100)
1:6:7.5	68.20, 4.04, 16.32	1.6 ± 0.3	2.0	747 (13.8), 691 (48), 635 (100)
1:11:12.5	67.75, 4.05, 16.96	1.4 ± 0.7	1.4_5	747 (7.4), 691 (35.4), 635 (100)

^{a}Calculated from elemental analysis.

on phthalocyanine materials. We choose *tert*-butyl groups in the present work because alkyl groups are known to have very little effect on the electronic properties of a chromophore.

It is known in the literature that metallophthalocyanines do not absorb in the near-IR region (750–900 nm) in the dissolved (monomer and dimer) state.[11-13] Some metallophthalocyanines are, however, known to shown near-IR absorption in the solid state due to exciton interaction, e.g., x-form of H$_2$PC,[14] phase II of VOPc,[5,13] AlClPc,[15] SnPc,[16] SnPc$_2$,[17] etc. Although it still remains to be established that the phase II of VOPc is more photoconductive than its phase I, the IR absorptivity of phase II makes it a necessity for IR-photoreceptor applications. Thus, the ability of soluble VOPc dyes to form the phase II of VOPc is of technological importance. To date, no information is available in the literature regarding the effect of solubilizing groups on the solid-state properties (packing) of crystalline metallophthalocyanines. It is thus not certain that the VOPc phase II packing can be retained upon substitution.

We describe here the synthesis and the characterization of *tert*-butyl-substituted VOPc dyes, (t-Bu)$_n$VOPc. All of these (t-Bu)$_n$*VOPc* dyes are highly soluble in organic solvents as compared with VOPc. The solid-state properties of (t-Bu)$_n$VOPc are studied, and results reveal that substituent groups can destroy the VOPc phase II packing. We are able to retain the VOPc phase II packing, while maintaining a high dye solubility, by reducing the steric hindrance between individual (t-Bu)$_n$VOPc molecules in the solid state using lightly substituted materials.

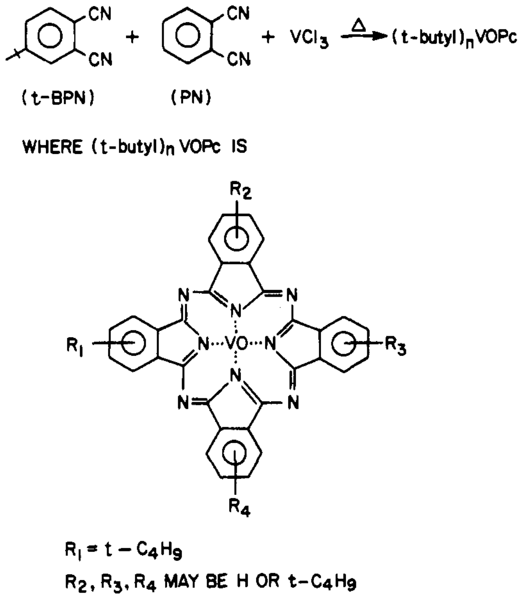
Experimental Section

Materials. 4-*tert*-Butylphthalonitrile was synthesized according to the procedures of Mikhalenko and co-workers.[7] Phthalonitrile was bought from Fisher and was recrystallized from water before use. Vanadium trichloride (Aldrich), methylene chloride, and chloroform (Baker analyzed reagent) were used as received. Solvents for absorption spectra were either spectral grade or analytical grade; they were used without further purification.

General Techniques. Infrared spectra were determined on a Beckman IR 4250 spectrophotometer. ^{1}H NMR spectra were recorded in CD$_2$Cl$_2$ (Aldrich) on a Bruker WP-80 spectrometer. Absorption spectra were taken on a Cary 17 spectrophotometer. Mass spectra were recorded on a Nuclide 12-90 GCMS single-focusing magnetic sector spectrometer with an electron energy of 70 eV. X-ray data were collected from a Norelco powder diffractometer. Elemental analysis was performed by Galbraith Laboratories.

Tetra-*tert*-butylvanadylphthalocyanine.[18] 4-*tert*-Butylphthalonitrile (0.72 g) and vanadium trichloride (0.74 g) were reacted at the melt at 240–260 °C for 2 h. The product mixture was cooled down to room temperature and was boiled successively with 30 mL of 5% aqueous HCl solution and 30 mL of 5% aqueous NaOH solution. The blue solid obtained was washed thoroughly with water and methanol. TLC analysis (on Al$_2$O$_3$, using CHCl$_3$ as eluent) indicated the absence of unreacted 4-*tert*-butylphthalonitrile and byproduct, tetra-*tert*-butyl metal-free phthalocyanine. The product was purified by column chromatography on Al$_2$O$_3$ (neutral, activity 1) using CHCl$_3$ as eluent. The blue fraction was collected and dried, yielding purple reflective blue crystals, 0.36 g (~46%).

Scheme I



Anal. Calcd for C$_{48}$H$_{48}$N$_8$VO: C, 71.72; H, 6.02; N, 13.94; V, 6.33. Found: C, 71.07 and 70.92; H, 5.88 and 5.90; N, 13.84 and 13.76; V, 5.97 and 6.18.

IR (KBr, cm^{-1}): 3060, 2960, 2910, 2870, 1615, 1475, 1390, 1365, 1330, 1283, 1266, 1192, 1148, 1080, 1050, 1000, 922, 890, 747, 688, 665.

Synthesis of (t-Bu)$_n$VOPc Dyes ($n \neq 4$). A mixture of 4-*tert*-butylphthalonitrile, phthalonitrile, and vanadium trichloride (molar ratios specified in Table I) was heated to 240–260 °C for ~2 h. The resulting mixture was boiled successively with 5% aqueous HCl solution and 5% NaOH aqueous solution. The blue solid obtained consisted of a mixture of VOPc and (t-Bu)$_n$VOPc. The soluble product was isolated by extracting the blue solid with methylene chloride and was purified by column chromatography (on Al$_2$O$_3$) using CHCl$_3$ as eluent, affording purple reflective blue crystals of (t-Bu)$_n$VOPc, in ~40–50% yield (based on 4-*tert*-butylphthalonitrile).

Results and Discussion

Synthesis and Characterization. *tert*-Butyl-substituted vanadylphthalocyanine dyes, (t-Bu)$_n$VOPc, were prepared by reacting vanadium trichloride with a mixture of 4-*tert*-butylphthalonitrile (t-BPN) and phthalonitrile (PN) at the melt. The general reaction scheme is shown in Scheme I. The number of *tert*-butyl groups, n, substituting on the VOPc ring is calculated from the elemental analysis results. Results in Table I show that n decreases from 4.0 to 2.5 to 2.0 to 1.6 to 1.4 as the molar ratio of t-BPN to PN decreases from 1:0 to 1:1 to 1:3 to 1:6 to 1:11.

Solubility. All (t-Bu)$_n$VOPc samples exhibit excellent solubility in organic solvents such as methylene chloride, chloroform, tet-

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(10) U.S. Patents 3 853 783 and 4 039 467.

(11) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292.

(12) Monahan, A. R.; Brado, J. A.; DeLuca, A. F. *J. Phys. Chem.* **1972**, *76*, 1994.

(13) Huang, T. H.; Sharp, J. H.; Wagner, H. J. *Chem. Phys.* **1982**, *65*, 205.

(14) Sharp, J. H.; Lardon, M. *J. Phys. Chem.* **1968**, *72*, 3230.

(15) Arishima, K.; Hiratsuka, H.; Tate, A.; Okada, T. *Appl. Phys. Lett.* **1982**, *40*, 279.

(16) Vartanyan, A. T.; Meshkova, G. N.; Sidorov, A. N. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1976**, *50*, 1597.

(17) Morita, M. *J. Phys. Soc. Jpn.* **1972**, *33*, 863.

(18) The formal redox potentials of tetra-*tert*-butylvanadylphthalocyanine were reported by Lever and co-workers[19] at the completion of the present work. However, neither the synthesis nor the analytical data of this compound was reported.

(19) Lever, A. B. P.; Licoccia, S.; Ramaswamy, B. S.; Kandil, S. A.; Stynes, D. V. *Inorg. Chim. Acta* **1981**, *51*, 169.

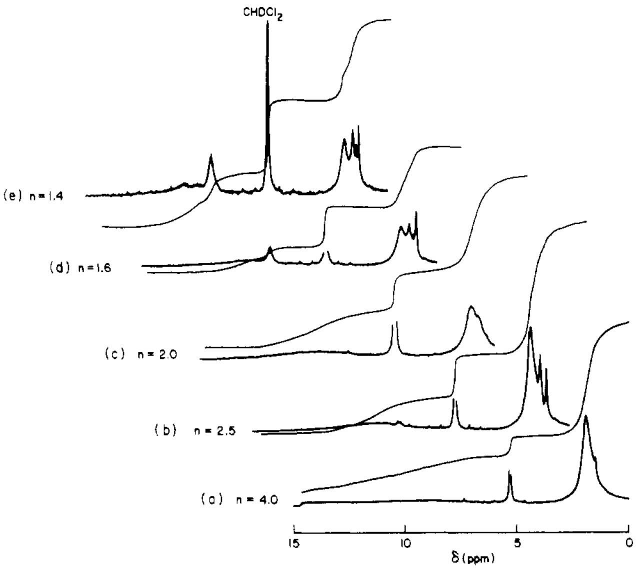

Figure 1. ^{1}H NMR spectra of $(t\text{-Bu})_n$VOPc.

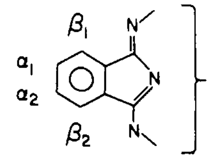

Figure 2. Aromatic protons on phthalocyanine ring.

rahydrofuran, 3-pentanone, etc. There is an observable, but slight, decrease in solubility as *n* decreases. For example, the solubility of $(t\text{-Bu})_4$VOPc is ~20 mg in 1 mL of CH_2Cl_2 (~2×10^{-2} M) whereas the solubility of $(t\text{-Bu})_{1.4}$VOPc decreases to ~12 mg in 1 mL of CH_2Cl_2 (~1.2×10^{-2} M). The dramatic increase in solubility of $(t\text{-Bu})_n$VOPc dyes as compared with VOPc, which has a saturated concentration of ~10^{-6} M in CH_2Cl_2, may be attributed to the steric hindrance produced by the bulky *tert*-butyl groups in the solid state that reduces the intermolecular interaction in the solid state and increases the solubility of $(t\text{-Bu})_n$VOPc in organic solvents.

^{1}H NMR Studies. Figure 1 shows the ^{1}H NMR spectra of $(t\text{-Bu})_n$VOPc dyes in CD_2Cl_2. Because of the presence of the paramagnetic vanadium atom and the possible aggregation of $(t\text{-Bu})_n$VOPc molecules in CD_2Cl_2 solution under the recording condition, the ^{1}H NMR spectra are extremely broad.

The chemical shifts of the *tert*-butyl protons and the aromatic protons of $(t\text{-Bu})_4H_2Pc$ (in CD_2Cl_2) are at δ 1.8–2.0 and 7.9–9.5, respectively. As shown in Figure 2, *tert*-butyl group can either locate at the α_1 or the α_2 position on the benzene ring. This generates four geometric isomers and eight magnetically nonequivalent protons for $(t\text{-Bu})_4H_2Pc$. Indeed, in a recent study of $(t\text{-Bu})_4H_2Pc$, Duff, Branston, and Hamer were able to resolve all four geometric isomers and all eight magnetically nonequivalent *tert*-butyl protons by high-resolution ^{1}H NMR spectroscopy.[20]

Owing to the broad ^{1}H NMR spectrum of $(t\text{-Bu})_4$VOPc (Figure 1a), isomers are not expected to be resolved. The chemical shifts of the *tert*-butyl protons and the aromatic protons of $(t\text{-Bu})_4$VOPc are in the region of δ 0.8–3.0 and ~5–12, respectively, which are comparable to those of $(t\text{-Bu})_4H_2Pc$. Very similar ^{1}H NMR spectra are obtained for other $(t\text{-Bu})_n$VOPc ($n \neq 4$) dyes (Figure 1b–e), except that the relative intensity of the peak at δ ~8.0 increases as *n* decreases. ^{1}H NMR spectra of metallophthalocyanines, namely zinc phthalocyanine, dilithium phthalocyanine, and tetramethylzinc phthalocyanine have been reported by Mark and Stojakovic, who have shown that the chemical shifts of the α and the β protons are at δ ~8.0 and ~9-9.5, respectively.[21] The increase in proton intensity at δ ~8.0 as *n* decreases indicates that the *tert*-butyl groups are indeed at the α positions of the VOPc ring and the chemical shifts observed in $(t\text{-Bu})_n$VOPc are very comparable to the literature data.

Table II. Isotropic Distribution of Molecular Ions of $(t\text{-Bu})_n$VOPc (n = 1–4)

molecule	*m/z*	found	calcd
$(t\text{-Bu})_4$VOPc	803 (M)	100	100
	804 (M + 1)	55.8	57.5
	805 (M + 2)	15.4	16.2
$(t\text{-Bu})_3$VOPc	747 (M)	100	100
	748 (M + 1)	50.8	52
	749 (M + 2)	11.2	13.7
$(t\text{-Bu})_2$VOPc	691 (M)	100	100
	692 (M + 1)	45.5	48.0
	593 (M + 2)	10.0	11.4
$(t\text{-Bu})$VOPc	635 (M)	100	100
	636 (M + 1)	43.4	43.7
	637 (M + 2)	8.5	9.3

Table III. Visible Absorption Spectral Data of $(t\text{-Bu})_n$VOPc in Chloroform

sample	λ_{max}[a] (log ε[b])
$(t\text{-Bu})_4$VOPc	700 (5.31), 670 (sh), 630 (4.54)
$(t\text{-Bu})_{2.5}$VOPc	697.4 (5.29), ~670 (sh), 628.5 (4.55)
$(t\text{-Bu})_{2.0}$VOPc	695.9 (5.23), ~668 (sh), 627.6 (4.51)
$(t\text{-Bu})_{1.6}$VOPc	694.7 (5.15), ~665 (sh), 627.3 (4.43)
$(t\text{-Bu})_{1.4}$VOPc	694.7 (5.13), ~665 (sh), 626.5 (4.43)
VOPc	691.2, 660 (sh), 622.4

[a] Absorption maximum wavelength, in nm. [b] Molar extinction coefficients, in cm^{-1} M^{-1}.

The ratios of the number of *tert*-butyl protons to the number of aromatic protons for $(t\text{-Bu})_n$VOPc dyes can be obtained from NMR integration and are listed in the fourth column of Table I. At *n* = 4, the ratio of *tert*-butyl protons to aromatic protons is 3.6, which is 20% higher than the expected value (3.0) calculated from its molecular formula. This discrepancy may be attributed to the broad aromatic signals that results in an underestimation of the number of aromatic protons during the integration. From the ratios of *tert*-butyl protons to aromatic protons, the *n* values of $(t\text{-Bu})_n$VOPc dyes are calculated to be 4.7, 3.7, 3.0, 2.9, and 2.2. Assuming that there exists a 20% underestimation of aromatic protons in all the samples and a correction is made, the corrected *n* values are 4.0, 3.0, 2.4, 2.3, and 1.7, respectively, which are in reasonable agreement with the *n* values calculated from the elemental analysis results.

Mass Spectrometric Analysis. The compositions of $(t\text{-Bu})_n$VOPc dye samples in this work were subjected to mass spectrometric analysis. The results are summarized in the fifth column of Table I. At *n* = 4.0, a molecular ion of $(t\text{-Bu})_4$VOPc at *m/z* 803 is observed. At *n* = 2.5, 2.0, 1.6, and 1.4, molecular ions of $(t\text{-Bu})_4$VOPc, $(t\text{-Bu})_3$VOPc, $(t\text{-Bu})_2$VOPc, and $(t\text{-Bu})$VOPc, which have *m/z* values at 803, 747, 691, and 635, respectively, are observed.[22] Their identities are further confirmed by their isotropic distributions, which are in good agreement with the calculated values (Table II). Also seen in Table I, all the $(t\text{-Bu})_n$VOPc samples (except *n* = 4) contain VOPc of varying *tert*-butyl substitution. From the relative intensity of each molecular ion, we find that the relative amount of $(t\text{-Bu})$VOPc increases as *n* decreases. The mass spectrometric analysis cannot be more quantitative because of the lack of volatility and fragmentation data of each individual molecule.

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(20) Duff, J.; Branston, R.; Hamer, G. Xerox Research Centre of Canada, unpublished results.

(21) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695.

(22) Weak ion peak at *m/z* 579 is also observed for some $(t\text{-Bu})_n$VOPc (*n* = 2.0, 1.6, 1.4) samples. Since there is no correlation between the intensity of this *m/z* 579 peak with the amount of phthalonitrile used in the synthesis and since the properties of $(t\text{-Bu})_{1.4}$VOPc remain unchanged upon repetitive chromatographic purification, we feel that the existence of VOPc in these samples is unlikely. After all, since the dealkylation reaction is the only mass spectral reaction observed in the mass spectrum of $(t\text{-Bu})_4$VOPc, we attribute the *m/z* 579 peak to the dealkylation product of $(t\text{-Bu})_n$VOPc (*n* = 1–3).

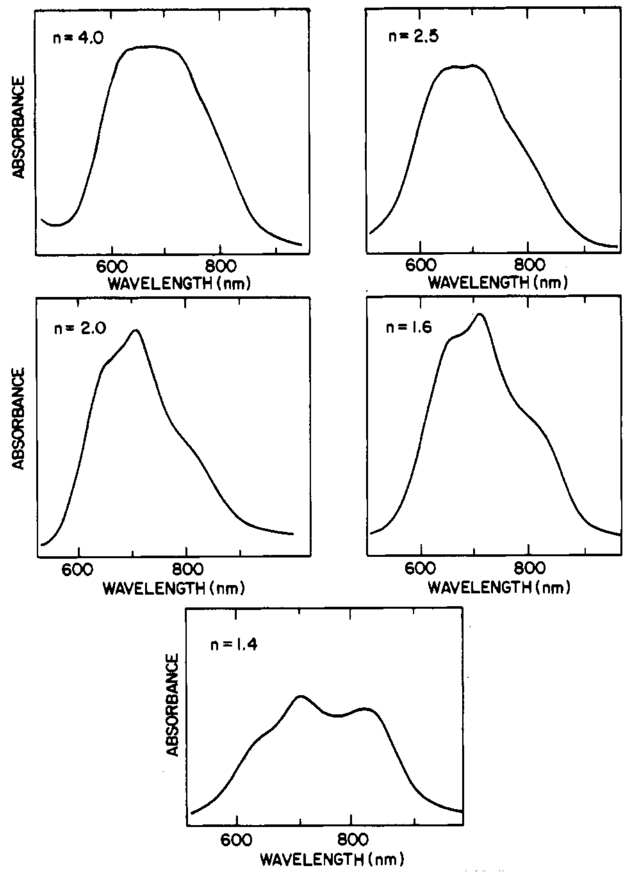

Figure 3. Solid-state absorption spectra of $(t\text{-Bu})_n\text{VOPc}$.

Optical Spectra. $(t\text{-Bu})_n\text{VOPc}$ dyes show intense absorption bands in both visible and near-UV regions. The low energy band and the high-energy band are attributed to the $\pi \rightarrow \pi^*$ Q-band and the $\pi \rightarrow \pi^*$ Soret band, respectively, according to the literature.[11] The visible absorption spectral data of $(t\text{-Bu})_n\text{VOPc}$ dyes are summarized in Table III. The molar extinction coefficient of the longest wavelength $\lambda_{\max}$ of $(t\text{-Bu})_4\text{VOPc}$ is $\sim 2 \times 10^5$ cm^{-1} M^{-1} and is in good agreement with literature data on other tetra-*tert*-butylmetallophthalocyanines.[7] However, it decreases as *n* decreases. Since a concomitant increase in absorption band band width is observed and since each dye sample contains dyes of various *n*, the decrease in molar extinction coefficient is therefore not due to any substituent effect, but rather due to the broadening effect produced by $(t\text{-Bu})_n\text{VOPc}$ dyes of various *n* where $\lambda_{\max}$ blue-shifts as *n* decreases (see next paragraph for discussion).

Careful inspection of the spectral data in Table III indicates that the longest wavelength $\lambda_{\max}$ of the Q-band shifts systematically to the red as *n* increases, e.g., $\lambda_{\max} = 691.2$ nm at $n = 0$, $\lambda_{\max} = 700$ nm at $n = 4.0$. The observed red-shift, which is in parallel with the increase in dye solubility, is attributable to the increase in solvation energy of the excited state as the number of solubilizing group increases.[23]

Solid-State Properties. Figure 3 shows the solid-state, visible absorption spectra of $(t\text{-Bu})_n\text{VOPc}$ dyes at various degree of *tert*-butyl substitution. The near-IR absorptivity (at ~800 nm) increases as *n* decreases. Griffiths, Walker, and Goldstein have shown that VOPc exists in three different phases in the solid state, namely a thermodynamically metastable phase I and two relatively stable phases II and III.[5] Since phase III has only been formed by quenching VOPc from the melt and since the near-IR absorption is the unique characteristic of phase II, the results in Figure 3 thus suggest that only the VOPc phase I is formed in the solid state of $(t\text{-Bu})_4\text{VOPc}$. As *n* decreases, the near-IR absorptivity increases, indicating that a gradual change in packing, from phase I to phase II, occurs as *n* decreases. The inability of $(t\text{-Bu})_4\text{VOPc}$ to form the VOPc phase II may be attributed to the steric repulsion produced by the bulky *tert*-butyl groups in the solid state, which prohibits the phase II packing where the interplanar distance between VOPc rings has been shown to be in the order of 3.4 Å.[24] We are, however, able to reduce this repulsive force by decreasing the degree of *tert*-butyl substitution and retain the phase II packing at $n = 1.4$.

The solid-state packing of $(t\text{-Bu})_n\text{VOPc}$ molecules was also studied by X-ray powder diffraction technique. At $n = 4.0$ and 2.5, the solid samples are basically amorphous, and no sharp diffraction line is discernible. Relatively sharp diffraction lines are observed at $n = 2.0$, 1.6, and 1.4, indicating that crystalline materials are obtained. These results confirm our absorption spectral data that the IR-absorbing VOPc phase II, a crystalline phase, can only be formed for samples of lower degree of *tert*-butyl substitution.

As shown in our mass spectrometric analysis, each dye sample contains a mixture of dye molecules of various degree of *tert*-butyl substitution. Together with the existence of geometrical isomers for each substitution, the solid state of $(t\text{-Bu})_n\text{VOPc}$ dyes is expected to be extremely disordered. However, assuming the packing of $(t\text{-Bu})_n\text{VOPc}$ is very similar to that of VOPc phase II, there would be two probable repeating units in the three-dimensional space. They are the V=O double bond and the phthalocyanine ring of VOPc. At $n = 2.0$ three diffraction lines corresponding to interplanar spacings of ~13, 3.1, and 3.4 Å are observed. At $n = 1.6$ and 1.4, two diffraction lines corresponding to interplanar spacings of ~13 and 3.23 Å are observed. The diffraction lines at ~13 and ~3.1–3.4 Å are attributable to the interplanar spacings between V=O double bonds and phthalocyanine rings, respectively. These assignments are compatible with the X-ray single-crystal data of VOPc phase II reported by Ziolo and coworkers where they found that the interplanar distance between V=O double bonds and phthalocyanine rings are 12.57 and 3.1–3.4 Å, respectively.[24]

Concluding Remarks. The work described here demonstrates that *tert*-butyl substitution of VOPc increases the solubility of the pigment, allowing it to be purified by conventional techniques. However, because of steric effects, substitution disturbs the VOPc phase II packing, which is a prerequisite for the IR sensitivity and is a probable requirement for the efficient photogeneration. We have shown by systematic variation of the degree of *tert*-butyl substitution that, at $n = 1.4$, the VOPc phase II packing is retained with a concomitant achievement of the high dye solubility in organic solvents.

Acknowledgment. The author thanks R. Crandall for the mass spectra and G. Fekete for the X-ray powder diffraction data.

Registry No. VCl_3, 7718-98-1; phthalonitrile, 91-15-6; 4-*tert*-butylphthalonitrile, 32703-80-3; di-*tert*-butylvanadylphthalocyanine, 95552-15-1; tetra-*tert*-butylvanadylphthalocyanine, 95865-59-1.

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(23) There is also a possibility that this alkyl substituent effect is due to an inductive stabilization of a charge-transfer π,π^* state by the electron-releasing *tert*-butyl groups. Extensive solvent effect study on the absorption spectra of $(t\text{-Bu})_4\text{VOPc}$, however, fails to support such a hypothesis: Law, K. Y., unpublished results.

(24) Ziolo, R. F.; Griffiths, C. H.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2300.