

dimension. Furthermore, SQMBC line widths are narrower in F_1 than their HMBC counterparts since the line width of a heteronuclear multiple-quantum coherence giving rise to a multiple bond correlation will effectively be equal to the sum of the line-widths of its active spins; although mutual dipolar relaxation vanishes in the slow tumbling limit, this will not be the major source of relaxation for either spin. Since the SQMBC experiment relies on the initial generation of amide proton magnetization, the experiment must be performed in H_2O ; for the same reason presaturation will not eliminate correlations to spins underneath the solvent signal. Another possible disadvantage is that the greater number of pulses in the SQMBC experiment will make it more difficult to obtain artifact-free spectra.

The two experiments are demonstrated and compared in Figure 2 on a uniformly ^{15}N labeled sample of the 79-residue c subunit of the ATP-synthase of *Escherichia coli*. In the case of the SQMBC experiment, the soft pulse was set up to invert the α -protons, thus channeling coherence to this region of the spectrum. The SQMBC spectrum is clearly superior since its peaks are better resolved and are pure absorption; it also exhibits a much more uniform distribution of intensity among peaks, although some individual HMBC peaks are more intense than their SQMBC counterparts. It should be noted that since the SQMBC experiment incorporates more pulses than HMBC, it will be more sensitive to rf inhomogeneity and pulse miss-setting. Although correlations to the C_α protons were chosen for the current study, others, for example, β -protons, could have been chosen as easily.

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New Route to Unsymmetrical Phthalocyanine Analogues by the Use of Structurally Distorted Subphthalocyanines

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In addition to traditional uses as dyes and in photocopying devices,¹ phthalocyanines (Pcs) are now rapidly growing in importance in many fields such as chemical sensors, electrochromism, batteries, photodynamic cancer therapy, molecular metals, photochemical hole burning, and liquid crystals.² Although symmetrical tetra-, octa-, and hexadecasubstituted Pcs are well documented, there have been few reports on Pc analogues with lower symmetry mainly because of their preparative difficulty. These compounds are also important in applications and in understanding the nature of Pcs. For example, fine tuning of the position of the absorption band of Pcs can be achieved by the stepwise introduction of peripheral substituent groups³ or by the

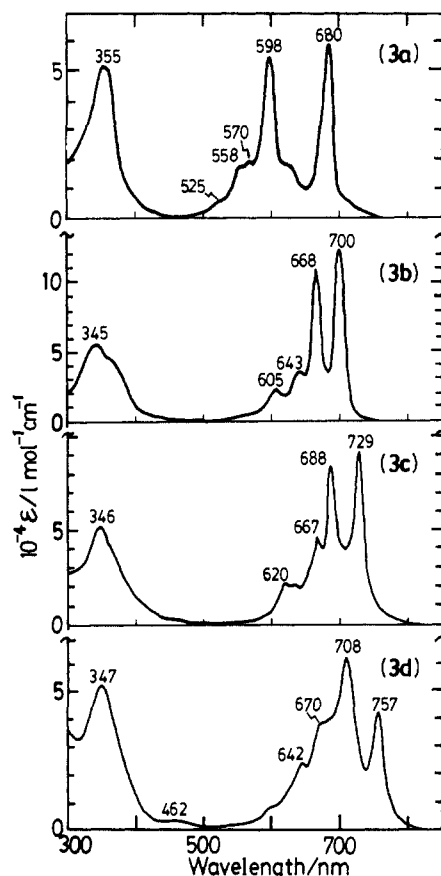
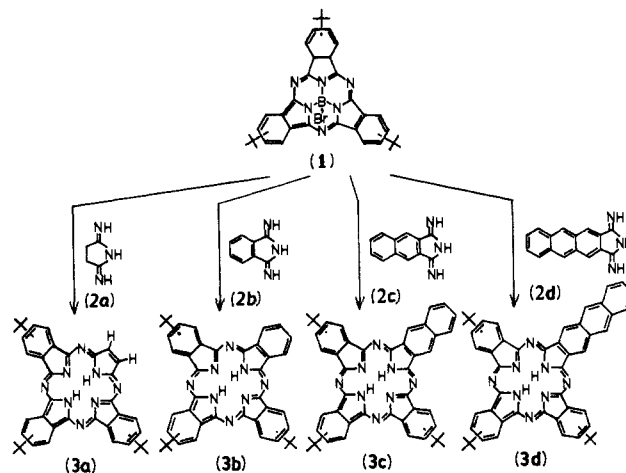


Figure 1. UV-visible-near IR absorption spectra of 3a-d in *o*-dichlorobenzene.

Scheme I



stepwise adjustment of the size of the π -conjugated macrocyclic systems. Strategies of synthesis, based on using statistical condensation reactions of two different *ortho* dinitriles of aromatic compounds, give mixtures of products^{4a} that cannot be readily separated by chromatographic methods, although a polymer support method can be used.^{4b} In this communication, we present a completely new method for the preparation of monosubstituted type unsymmetrical Pcs and Pc analogues, which utilizes the so-called subphthalocyanines (SubPcs).⁵

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Tri-*tert*-butylated SubPc **1** (Scheme I) prepared by a literature method^{5a} at ca. 50% yield and succinimidine (**2a**)⁶ or diiminoisoindoline analogues **2a–d**⁷ (ca. 7 equiv) were reacted at 80–90 °C in a mixture of *N,N*-dimethyl sulfoxide and either chlorobenzene, *o*-dichlorobenzene, 1-chloronaphthalene, or 2-chloronaphthalene (2–1:1 v/v) for 5–27 h (reaction time and solvent ratio depend mainly on the solubility of **2**). After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel with methylene chloride as eluent. The blue-green fraction was collected, and this fraction was further purified by gel permeation chromatography using Bio-beads SX-8 (Bio-rad) and methylene chloride or tetrahydrofuran to give a very dark blue, shining solid in 8–20% yield depending on the system.⁸ Consistent with the structure (**3a–d**), parent ion peaks were observed at 632, 682, 732, and 782, respectively, using the fast atom bombardment technique, and **3a–d** were fully characterized by IR, NMR, and elemental analysis.⁸ The inner two pyrrole protons of these compounds generally gave three broad absorption peaks due to the presence of isomers and the difference of the attached position at fields as high as –1.7 to –4.4 ppm typical of Pcs.^{9,9}

Figure 1 shows the absorption spectra of these compounds. The spectrum of **3a** is similar to that of tribenzotetraazaporphine without peripheral substituent groups,¹⁰ and the spectrum of **3b** is typical of nonmetalated phthalocyanines.^{3a} The position of the Q-band peaks shifts to longer wavelength with the enlargement of the π -conjugated system, particularly that of the longest wavelength band, which shifts 20–30 nm (420–530 cm⁻¹) per benzene unit. The absorption coefficients (ϵ) of the Q bands decrease generally with decreasing symmetry of the molecules, i.e., **3b** > **3c** > **3d** > **3a**, while the ratio of the actual absorption intensity (the oscillator strength) at 500–800 nm is 0.75:1.00:1.03:0.88 for **3a:3b:3c:3d**. On the other hand, neither the ϵ values nor the positions of the Soret bands differ significantly among the compounds. Thus, fine tuning of the position of the intense Q band was realized by the removal or displacement of one benzene ring in Pcs.

The present method has several advantages over hitherto known mixed condensation methods. (i) The yield is relatively high. (ii) Purification is easy as column chromatography exhibits two easily separated colored bands. One is the blue fraction of the desired compound, and the other is the reddish purple fraction of unreacted **1**. (iii) No Pc analogue containing more than one **2** unit is obtained. If we collect the blue fraction in the purification process (column), it always gives Pc analogues that contain only one **2** unit.

In spite of being aromatic compounds, SubPcs are known to have a cone-shaped structure.^{5c} Such distorted bent aromatic

compounds appear structurally strained and unstable, and since structurally highly strained compounds such as cyclobutenes¹¹ and epoxides have successfully been applied in organic synthesis, this character of SubPcs appears to enable their above ring-expansion reaction to occur.

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Direct Observation and Retro-Ene Reaction of a Propargylic Diazene. Stereochemical Assignment of Monoalkyl Diazenes

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Allylic and propargylic diazenes and their rearrangement by [3,3]-sigmatropic elimination of dinitrogen (retro-ene reaction) have been invoked in numerous organic transformations.^{1,2} As rearrangement uniformly occurs under the conditions of diazene formation, these hypothetical intermediates have not previously been observed, and fundamental questions regarding their stereochemistry (*E* vs *Z*) and reactivity remain. Employing a new method for diazene generation,² we have been able to produce and study such an intermediate at low temperature and thereby address these issues of structure and mechanism, as described below.

The reaction of (3-phenyl-2-propynyl)hydrazine (**1**) with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) in tetrahydrofuran produces 1,2-propadienylbenzene (**2**) in 70% yield after chromatographic isolation.² Through the use of variable-temperature NMR spectroscopy, we have learned that two pathways operate in the formation of **2** from **1**. A sealed, evacuated NMR tube containing solid MTAD (1 equiv) layered upon a frozen solution of hydrazine **1** and vinylidene chloride (internal reference) in deoxygenated tetrahydrofuran-*d*₈ was agitated in a –100 °C bath so as to mix the thawing components and was quickly loaded into the probe of a high-field NMR spectrometer, precooled to –95 °C. Three products were formed cleanly and reproducibly: 4-methylurazole (85%), allene **2** (44%), and as evidenced by the low-field resonance at δ 15.9 ppm, the propargylic diazene **3** (40%).³ These products were stable at –95 °C, and their ratio did not vary appreciably from run to run, nor was the product distribution altered when the sample was prepared by allowing the frozen mixture to thaw within the probe (as monitored by the appearance and sharpening of the deuterium lock signal). Upon warming to –70 °C, signals for **3** underwent first-order decay ($k = (8 \pm 2) \times 10^{-5} \text{ s}^{-1}$, four determinations, $t_{1/2} = 2.5 \text{ h}$) while those for **2** grew correspondingly ($k = (7 \pm 4) \times 10^{-5} \text{ s}^{-1}$).⁴ The data

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(8) The yields and analytical data of the products are as follows (reaction was carried out in a DMSO/1-chloronaphthalene 2:1 v/v mixture for **3a–c** and a 1:1 mixture for **3d**). **3a**: 13%. Anal. Calcd for C₄₀H₄₀N₈: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.70; H, 6.06; N, 17.96. **3b**: 20%. Anal. Calcd for C₄₄H₄₂N₈: C, 77.39; H, 6.20; N, 16.41. Found: C, 77.07; H, 6.02; N, 16.70. **3c**: 11%. Anal. Calcd for C₄₈H₄₄N₈: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.39; H, 5.87; N, 15.55. **3d**: 8%. Anal. Calcd for C₅₂H₄₆N₈: C, 79.77; H, 5.92; N, 14.31. Found: C, 79.54; H, 5.67; N, 14.64. The 500-MHz ¹H NMR data in CDCl₃ are as follows. **3a**: 8.35–9.05 (m, 9 H), 7.92–7.97 (m, 2 H), 1.76–1.87 (m, 27 H), –1.73 to –1.97 (3 br s at –1.78, –1.83, and –1.94, in total 2 H). **3b**: 8.3–9.1 (m, 8 H), 8.0–8.2 (m, 3 H), 1.81–1.92 (m, 27 H), –2.7 to –4.1 (3 br s at –2.86, –3.36, and –3.97, in total 2 H). **3c**: 7.4–9.3 (m, 15 H), 1.81–1.93 (m, 27 H), –2.35 to –3.2 (3 br s at –2.55, –2.76, and –3.03, in total 2 H). **3d**: 9.38 (s, 2 H), 7.4–9.2 (m, 15 H), 1.70–1.80 (m, 27 H), –1.8 to –4.4 (3 br s at –2.15, –3.00, and –3.36, in total 2 H).

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(4) Without proper care in purification of reagents, the decomposition of **3** to form **2** is more rapid and irreproducible, though always strictly first order in **3**. Values cited in the text were obtained with carefully purified materials and were the slowest decompositions observed. It is reasonable to propose that impurities catalyze the decomposition of **3**, perhaps by trans → cis isomerization (vide infra).