The above results provide evidence for facile [4 + 2] cycloaddition of 1,3-butadiene with ethyne and propyne mediated by atomic Fe^+ in the gas phase. We are exploring the scope of this novel cycloaddition process by varying the diene, dienophile, and the ligand environment on Fe^+ as well as studying other transition metals. In particular, the electronic structure of both diene and dienophile will be varied in order to address the electronic requirements for cycloaddition.

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Rosarin: A New, Easily Prepared Hexapyrrolic Expanded Porphyrin

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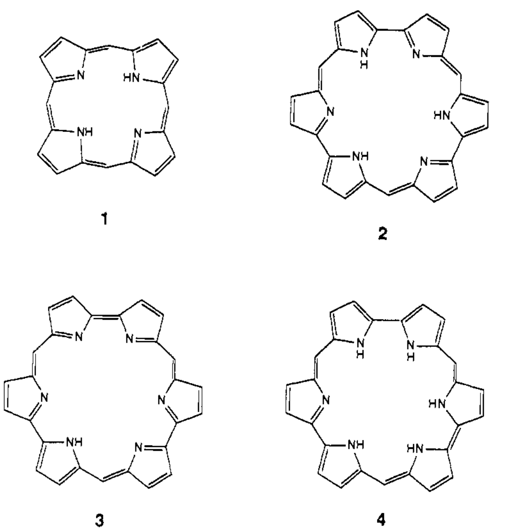
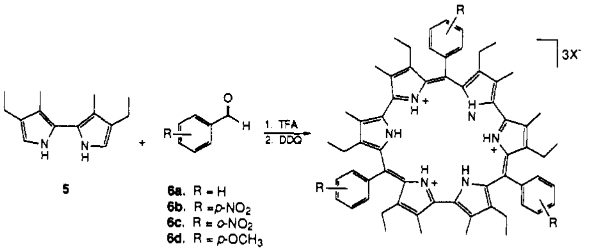
The porphyrins (e.g., porphine, **1**) are of ubiquitous biological importance and remain among the most widely studied of all known macrocycles. Increasingly, however, attention is being devoted to the study of larger pyrrole-containing macrocycles. Such larger systems, the so-called "expanded porphyrins",[1] appear attractive with regard to a variety of biomedical applications ranging from magnetic resonance imaging (MRI)[1-3] and photodynamic therapy (PDT)[1,4,5] to anion chelation and drug delivery.[1,6] While there are now a number of expanded porphyrins known,[1] including penta- and hexapyrrolic macrocycles such as sapphyrin,[7] pentaphyrin,[8] hexaphyrin,[9] and rubyrin,[10] none is easy to prepare.

Chart I. Porphine and Generalized 22π-, 24π-, and 26π-Electron Rosarins



Scheme I. Synthesis of Protonated Rosarins **7a,b–10**



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6a. R = H
6b. R = *p*-NO$_2$
6c. R = *o*-NO$_2$
6d. R = *p*-OCH$_3$

7a. R = H, X = TFA$^-$
7b. R = H, X = Cl$^-$

8. R = *p*-NO$_2$, X = TFA$^-$
9. R = *o*-NO$_2$, X = TFA$^-$
10. R = *p*-OCH$_3$, X = TFA$^-$

Thus, there remains a need for a general and facile synthesis of expanded porphyrins. We now wish to report such a synthesis and, also, present the first member of a new class of alkyltris(bipyrrole)trimethine-derived expanded porphyrins of generalized structure **2**.[11] On the basis of the bright-red-to-purple color of the triprotonated derivatives, we have assigned the trivial name rosarin (from the Latin *rosa*) to this new class of molecules (Chart I).

The synthesis of the protonated form of the title molecule, 4,9,13,18,22,27-hexaethyl-5,8,14,17,23,26-hexamethyl-2,11,20-triphenylrosarin (**7**), is shown in Scheme I. The reaction is based on a general synthesis of tetra-meso-substituted porphyrins first reported by Rothemund in 1936[12] and subsequently optimized by others.[13-16] In this approach, a 2,5-unsubstituted pyrrole is condensed with an aromatic aldehyde under acidic, oxidative conditions. In the present synthesis, the pyrrolic starting material is replaced by an alkyl-substituted bipyrrole subunit, such as **5**[7c] (Scheme I). Thus, the preparation of triphenylrosarin **7** bears a formal resemblance to recent syntheses of highly strained tet-

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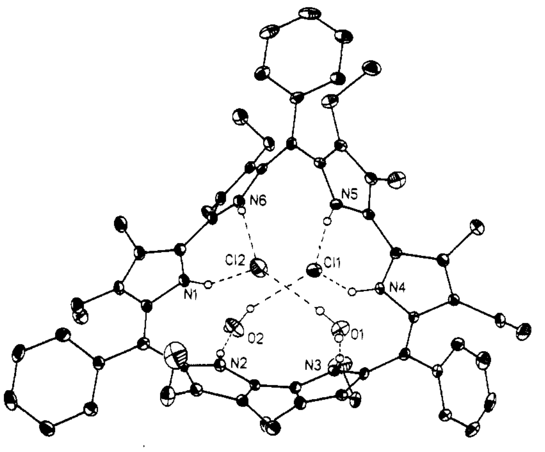

Figure 1. X-ray structure of complex **7b** showing partial atom labeling scheme. The third chloride anion (not shown) makes up part of the general lattice structure and is not proximate to the macrocycle. One bipyrrole is twisted (dihedral angle = 123.3°) so that the two NH groups (N2 and N3) are oriented in nearly opposite directions. Dashed lines indicate short N—H···X contacts with relevant distances and angles: Cl2···N1 3.105 Å, Cl···H—H 156°; O2···N2 2.747 Å, O···H—N 166°; O1···N3, 2.854 Å, O···H—N 169°; Cl1···N4, 3.112 Å, Cl···H—N 132°; Cl1···N5 3.186 Å, Cl···H—N 170°; Cl2···N6, 3.175 Å, Cl···H—N 151°. Thermal ellipsoids are scaled to the 30% probability level; most H atoms have been omitted for clarity.

raaryloctaalkylporphyrins[17] as well as to simplified procedures used to prepare octaalkylporphyrins.[18]

In our hands, the rosarin-forming reaction of Scheme I is best performed in dry CH_2Cl_2 containing a catalytic amount of TFA (12 h, room temperature, exclusion of light and air) followed by oxidation with 3 equiv of DDQ. After filtration through Celite, the product is purified by column chromatography on silica gel (3% MeOH in CH_2Cl_2, eluent) followed by recrystallization from $CHCl_3$/hexane to give a green metallic solid (**7a**) in surprisingly high yield (≥70%!). This material, which is red-purple in solution, can be converted to the free-base form (corresponding to **2**) by treating it with 10% aqueous NaOH; treatment with aqueous HCl generates the hydrochloride salt (**7b**). This free-base, like the starting salt, appears to be stable under normal laboratory conditions.

Three different oxidation states, represented by structures **2**–**4**, can be formulated for the cyclic, hexapyrrolic products formed from the oxidative condensation of bipyrrole **5** with benzaldehyde. While two of these (i.e., **3** and **4**) correspond to formal $4n + 2$ aromatic species, we believe that it is actually the nonaromatic, *but fully conjugated*, 24π-electron species **7** (corresponding to structure **2**) that is formed under the reaction conditions. This assignment is based on the observation of a considerably red-shifted Soret-like transition in the UV/vis absorption spectrum of **7b** (λ_{max} = 552.5 nm; ϵ = 192 000 M^{-1} cm^{-1}), which would be expected for a deformed, nonplanar structure,[17] as well as an absence of any substantial ring current effects in the ^1H NMR spectrum. Moreover, as would be expected for such a 24π-electron formulation, the mass spectrum of the fully protonated macrocycle **7b** is consistent with a free-base structure containing three imine-type C–N bonds and three pyrrolic protons within the core.

Confirmation of the above assignment came from single-crystal X-ray diffraction analysis of the hydrochloride salt **7b**.[19] The structure obtained (Figure 1) revealed the presence of three chloride counteranions. This counteranion count is only consistent with an overall +3 charge on the macrocycle and hence serves to confirm inter alia the proposed 24π-electron formulation. In addition, as expected, the molecule was found to be nonplanar. Nonetheless, the system appears conjugated with the hybridization, in particular, of the three "meso-like" carbons being best assigned as sp^2 (as judged from bond angles). Thus, compound **7** and its free-base derivative bear closer analogy to the 20π-electron isophlorins[20] than to the 18π-electron porphyrins in the tetrapyrrolic series.

The procedure reported here appears to be quite general. In fact, we have found that a range of aryl aldehydes may be used in place of benzaldehyde **6a**. In all cases, however, it is the nonaromatic products (e.g., compounds **8**–**10**[21]) that are produced. This result, which could reflect unfavorable ethyl–phenyl interactions about the mesolike positions and/or destabilizing methyl–methyl interactions within the bipyrrole subunits, leads us to predict that it may be possible to prepare aromatic analogues of compounds **7**–**10** (corresponding to structures **3** and **4**) by the judicious choice of bipyrrole and/or aldehyde precursor. We are exploring this possibility.

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Supplementary Material Available: Listings of synthetic experimental data for compounds **7**–**10** and their corresponding free-base derivatives, details of the X-ray experiment and tables of atomic thermal factors, positional parameters, bond distances, and angles for **7b**, atom labeling scheme for **7b**, side view of **7b**, and a unit cell packing diagram (29 pages); table of observed and calculated structure factor amplitudes for **7b** (44 pages). Ordering information is given on any current masthead page.

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(21) Satisfactory ^1H and ^{13}C NMR and high-resolution mass spectrometric data were obtained.

High-Resolution Chemical Shift and Chemical Shift Anisotropy Correlation in Solids Using Slow Magic Angle Spinning

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In this communication, a new and simple two-dimensional NMR method is presented to obtain high-resolution chemical shift and chemical shift anisotropy correlation spectra of solids. This method can be easily implemented without additional hardware on normal magic angle spinning probes using very low spinning rates.

Magic angle spinning (MAS) has been used as the standard method to obtain high-resolution NMR spectra of solids.[1] When the chemical shift anisotropy (CSA) is large compared with the spinning rate, MAS spectra are often crowded with spinning sidebands which make the line assignments and the quantitative analysis of the spectra difficult. This problem is further intensified on high-field NMR spectrometers because of the increased magnitude of the CSA.

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