710 *J. Org. Chem.* **1987**, *52*, 710-711

nylogous urethanes deserves some comment. Single-crystal X-ray analysis of 4, mp 87–89 °C, confirmed the minimum energy conformation suggested by molecular models for this material to be that depicted by structure **22** (Scheme I, Figure 1). Assuming some correlation between the conformation of 4 in solution and in the condensed phase, it becomes clear that nucleophilic attack can reasonably occur only via the vector indicated in **22**. This vector requirement seems insensitive to the steric bulk carried at C-6, since changing from methyl to *tert*-butyl does not influence diastereoselectivity. The same effect holds for those acylated products derived from the vinylogous urethane 17, where in these cases the absolute configuration of the lactone products is determined in the acylation step. Applications of these convenient and effective threo-selective processess to problems of total synthesis are currently being examined.

Acknowledgment. We gratefully acknowledge financial support from the NIH and the Merck Corp. We also acknowledge Dr. Alan D. Adams and Mr. Edwin J. Iwanowicz for valuable help and discussion during the course of this work.

Supplementary Material Available: X-ray crystallographic data for 4 and experimental data for **2**, **5**, **18**, and **4** (10 pages). Ordering information is given on any current masthead page.

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[17] Sherman Clarke Fellow.

Richard Schlessinger,* James R. Tata[17]
Department of Chemistry
University of Rochester
Rochester, New York 14627

James P. Springer*
Merck, Sharp, and Dohme Research Laboratories
Rahway, New Jersey 07065

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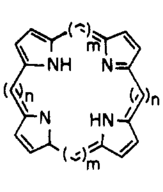
Synthesis of a [1,5,1,5]Platyrin, a 26 π-Electron Tetrapyrrolic Annulene

Summary: The synthesis of the strongly diatropic, highly reactive tetraazaannulene **2** is reported.



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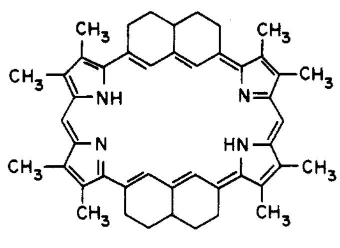
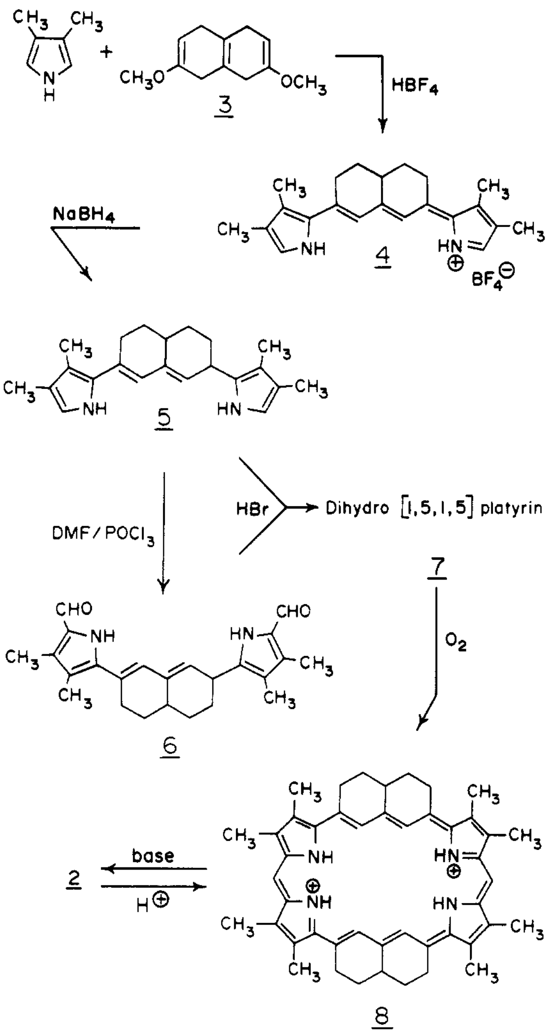


2

Sir: Expansion of the azaannulene, porphyrin, by inserting odd numbers of carbon alternatively between the pyrrolic rings, **1**, gives rise to a family of coplanar porphyrin vinylogues, to which we have given the name "platyrins".[1] Like the porphyrins, the platyrins are conjugated azaannulenes containing $(4n + 2)$ π-electrons. The synthesis of the first member of this new series, a [1,3,1,3]platyrin, has been reported by us.[2] We now report the synthesis of the next member, the [1,5,1,5]platyrin, **2**.

Acid-catalyzed condensation (HBF$_4$/C$_2$H$_5$OH) of 3,4-dimethylpyrrole with 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene (**3**),[3] gave a 97% yield of the green pentamethine salt **4** [mp >300 °C; ^{1}H NMR (Me$_2$SO-d_6) δ 11.73 (br, 2 H, N*H*), 7.20 (m, 2 H, pyrrole-C*H*), 6.74 (s, 2 H, vinyl-C*H*), 3.2–1.4 (m, 9 H, -C*H*$_2$-), 2.18 (s, 6 H, C*H*$_3$), 1.85 (s, 6 H, C*H*$_3$); vis $\lambda_{\max}$ (HCCl$_3$) 658 nm; mass spectrum, m/z (relative intensity) 318 (24, M − HBF$_4$), 94 (100)]. Partial reduction of **4** (NaBH$_4$ in CH$_3$CN) afforded a near quantitative yield of **5**, a pale yellow, oxygen-sensitive oil [^{1}H NMR (DCCl$_3$) δ 7.66 (br, 1 H, N*H*), 7.44 (br, 1 H, N*H*), 6.35 (d, 2 H, pyrrole-C*H*), 6.10 (s, 1 H, pyrrole-C*H*), 5.42 (d, 1 H, vinyl-C*H*), 3.58 (br, 1 H, -C*H*-), 2.7–1.1 (m, 9 H, -C*H*$_2$-), 2.13 (s, 3 H, C*H*$_3$), 2.02 (s, 9 H, C*H*$_3$)]. Reaction of **5** with dimethylformamide and phosphorus oxychloride gave a 71% yield of the bis-formylated product **6** [^{1}H NMR (DCCl$_3$) δ 9.60 (br, 2 H, N*H*), 9.30 (s, 1 H, C*H*O), 9.25 (s,



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[1] To fill the need for a simple name, we have coined the word "platyrin", a word derived from the Greek "πλατυς" (platys) meaning "wide or broad" and the suffix "-rin" from the ending of porphy*rin*, hence, a wide or broad porphyrin. A bracket indicating the number of methine carbons may be prefixed to the name, e.g., a porphyrin would also be a [1,1,1,1]platyrin, 1.

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Table I. Comparison of Platyrin ^1H NMR Spectra (δ)

compound	[1,5,1,5]platyrin 2	[1,3,1,3]platyrin ref 5	OMP[a]
internal =C*H*—	−14.26	−8.97	
meso =C*H*—	11.75	11.64	10.98
CH_3	4.51	4.22	3.76
	4.43	4.17	
>N*H*	−10.58	−5.6	−4.82

[a] Octamethylporphyrin in trifluoroacetic acid.

1 H, C*H*O), 5.98 (s, 1 H, -C*H*-), 3.64 (d, 1 H, -C*H*-), 3.5–1.1 (br, -CH_2-), 2.24 (s, 6 H, CH_3), 2.05 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3); IR ($HCCl_3$) 1710 (C=O); mass spectrum, m/z (relative intensity) 376 (4, M^+), 117 (100)]. Coupling of **5** with **6** to give a dihydro[1,5,1,5]platyrin, **7**, was accomplished by simultaneous addition of separate methanol/dichloromethane solutions of **5** and **6** to a hot, oxygen-free solution of hydrobromic acid in methanol. Oxidation with oxygen, followed by rapid chromatographic workup gave a 2% yield of the dark purple platyrin **2** [mp > 350 °C; vis (CH_2Cl_2) λ_{max} (ϵ) 495 (123 000), 536 (144 000), 651 (15 700), 705 (12 300), 718 (13 500), 780 (9400); **8** (diprotonated **2**) ^1H NMR (Me_2SO-d_6/CF_3CO_2H): δ 11.75 (s, 2 H, meso-C*H*), 4.51 (s, 12 H, CH_3), 4.43 (s, 12 H, CH_3), 2.70–1.0 (m, 18 H, CH_2, -C*H*-), −10.58 (s, 4 H, N*H*), −14.26 (s, 4 H, =C*H*—); λ_{max} (ϵ) (bis-tetrafluoroborate salt **8**): 495 (171 000), 536 (376 000), 651 (47 000), 703 (32 000), 719 (34 000), 780 (24 000), 830 (19 000)].

Both the platyrin **2** and its diprotonated form, **8**, prove to be unstable (chemically reactive). Solutions of **2** and **8**, as well as their solid forms, were observed to decompose in a few hours to a few days even at low temperatures. This high chemical reactivity suggests that there is little if any resonance stabilization[5] in this 26 π-electron annulene.

A comparison (Table I) of the ^1H nuclear magnetic resonance spectrum of the diprotonated platyrin **8** with the acyclic salt **4** reveals that a very substantial diamagnetic ring current is present in **8**. The internal vinyl protons of **8** are shifted some 21 ppm when compared to **4**. The ring current effects in **8** are even greater than those corresponding effects exhibited by the diatropic[4] [1,3,1,3]platyrin.[2]

Both of these properties, high chemical reactivity and a pronounced diamagnetic ring current, are consistent with the view that in the higher [$4n + 2$]annulenes, there will be little resonance stabilization (R.E. is inversely proportional to the number of π-electrons).[6] In contrast, these same annulenes will exhibit increasingly higher diamagnetic ring currents (ring currents increase linearly with the number of π-electrons[6]).

Thus, in the series porphyrin, [1,3,1,3]platyrin, and [1,5,1,5]platyrin, a consistent picture of reactivity and ring currents is emerging.

Supplementary Material Available: Experimental details for compounds **2–8** (4 pages). Ordering information is given on any current masthead page.

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E. LeGoff,* O. G. Weaver
Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

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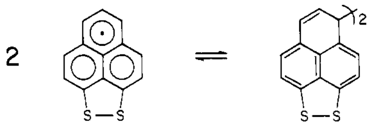
Perchloro-7*H*-cycloprop[*a*]acenaphthylene and the Perchlorophenalenyl System

Summary: Perchloro-7*H*-cycloprop[*a*]acenaphthylene (PCCPA) has been synthesized from the reaction of perchloroacenaphthylene with phenyl(bromodichloromethyl)mercury; PCCPA may be converted into perchlorophenalenyl (PCPLY) which has been detected by solution ESR spectroscopy.

Sir: Coplanar neutral radicals may exhibit interesting electronic properties in the solid state.[1] The primary obstacle to experimental test of this hypothesis is the propensity of such compounds to undergo σ-bond coupling to form a diamagnetic dimer in the condensed state.[1–8] Disulfide substitution in the phenalenyl (PLY) system has been shown to suppress the dimerization reaction (eq 1)



(1)

in the solution state[1c] but probably not in the solid form of 1,9-dithiophenalenyl (DTPLY).

In the present paper we report the synthesis and characterization of perchloro-7*H*-cycloprop[*a*]acenaphthylene (PCCPA) and our initial entry into the perchlorophenalenyl (PCPLY) system. A number of novel aromatic chlorocarbons have been previously reported,[9–12] and perchlorination has been shown to be particularly effective in enhancing the stability of the triphenylmethyl-type radicals.[12,13]

Perchloroacenaphthylene[14,15] (PCAN) is expected to be a poor substrate for carbenoid addition as the peri double bond conjugates quite strongly with the naphthalene ring system and the presence of eight chlorine atoms directly attached to the π-system further deactivates the double bond toward electrophilic attack. Nevertheless, we found the Seyfreth reagent, phenyl(bromodichloromethyl)mercury ($PhHgCCl_2Br$),[16] to be effective in transferring dichlorocarbene to perchloroacenaphthylene (although in low yield). Perchloroacenaphthylene was treated with 6 equiv

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