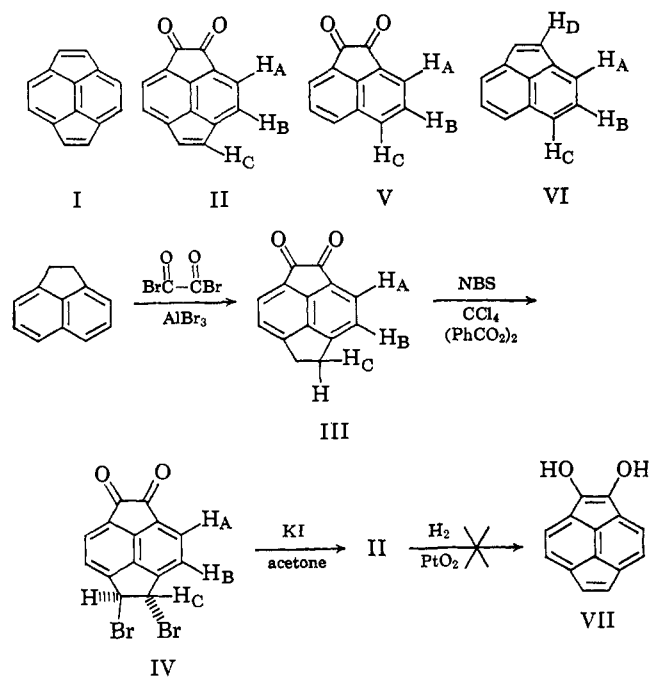


have a resonance energy of  $5.4156\beta$ ; Dauben<sup>2</sup> estimated a strain energy of about 52 kcal/mole. The unique feature of the electronic structure of this molecule is the prediction that it will have an empty non-bonding molecular orbital—the simplest hydrocarbon predicted to have this electronic configuration.<sup>1,3</sup> Stubbs and Tucker<sup>4</sup> synthesized dibenzpyracylene; Anderson<sup>5</sup> has failed in many attempts to synthesize the parent hydrocarbon. There have been no reports of simple naphthalene derivatives in which both *peri* positions are bridged by two  $sp^2$  carbons. We wish to report the synthesis of such a system, the quinone (II) derived from pyracylene.

1,2-Diketopyracene (III), mp 305–308°, was pre-



pared by the method of Richter and Stocker<sup>6,7</sup> [ $\nu_{\max}^{\text{KBr}}$  ( $\text{cm}^{-1}$ ) 3050, 2925, 1735, and 1660;  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  ( $m\mu$  ( $\epsilon$ )) 213 (43,000), 238 (52,500), 246 (48,200), 318 (sh, 4950), 332 (6400), 354 (6700), and 364 (sh, 5600)]. Its nmr spectrum (see Table I) supports the symmetrical substitution of the naphthalene ring. N-Bromosuccinimide converted III into 1,2-diketo-5,6-dibromopyracene,<sup>8</sup> yellow flakes, mp 189–191° dec, in approximately 60% yield [ $\nu_{\max}^{\text{CHCl}_3}$  ( $\text{cm}^{-1}$ ) 1740 and 1660;  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  ( $m\mu$  ( $\epsilon$ )) 225 (33,200), 231 (34,200), 243 (sh, 18,600), 324 (7700), and 332 (7800)]. Dehalogenation proceeded in 90–95% yield utilizing powdered potassium iodide in refluxing

(2) H. J. Dauben, Abstracts, 130th National Meeting of the American Chemical Society, New York, N. Y., 1956, p 37D.

(3) (a) B. M. Trost, unpublished calculations; (b) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of  $\pi$  Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(4) H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

(5) A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1958), and references therein.

(6) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 366 (1959).

(7) Although these workers confirmed the structure of III by chemical degradation, they reported no spectral properties. These data, presented here, fully confirm this assignment. The shift to higher frequency of the carbonyl absorption in the infrared spectrum of III compared to V ( $\nu_{\max}^{\text{KBr}}$  1720  $\text{cm}^{-1}$ ) exemplifies the increased strain. When naphthalene is bridged by two carbons in the 1,8 positions, the aromatic ring shortens this distance by increasing the distance between the opposite *peri* positions. This method to release strain is no longer available in III.

(8) Satisfactory elemental analyses were obtained for all new compounds.

Table I. Nmr Spectra<sup>a</sup> of Acenaphthalene Derivatives

Compd	H <sub>A</sub>	H <sub>B</sub>	H <sub>C</sub>	H <sub>D</sub>	J <sub>A,B</sub>	J <sub>B,C</sub>	J <sub>A,C</sub>
II <sup>b,e</sup>	8.26	8.26	7.69				
III <sup>c,f</sup>	8.12	7.72	3.76		8.0		
IV <sup>c,g</sup>	8.25	7.91	6.09		7.5		
V <sup>d,f</sup>	7.95	7.12	7.75		7.5	7.0	1.0
VI <sup>d,e</sup>	7.90	7.58	7.79	7.15	7.5	7.5	1.0

<sup>a</sup> Chemical shifts are in parts per million relative to TMS as an internal standard. <sup>b</sup> The naphthalene ring protons collapsed to an A<sub>2</sub> system. <sup>c</sup> AB spectrum. <sup>d</sup> ABC spectrum. <sup>e</sup> DMSO-*d*<sub>6</sub> solvent. <sup>f</sup> CF<sub>3</sub>CO<sub>2</sub>H solvent. <sup>g</sup> CDCl<sub>3</sub> solvent.

acetone. The product,<sup>8</sup> orange flakes, did not melt up to 350° although some decomposition was noted at about 300°. Its spectral data fully support structure II, for which we propose the name pyracyoquinone [ $\nu_{\max}^{\text{CHCl}_3}$  ( $\text{cm}^{-1}$ ) 1735 and 1685;  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  ( $m\mu$  ( $\epsilon$ )) 230 (28,500), 245 (17,900), 307 (17,500), 314 (17,000), and 346 (7120)]. Its nmr spectrum (see Table I) showed a considerable deshielding<sup>9</sup> of both H<sub>B</sub> and H<sub>C</sub> relative to the comparable protons in compounds III, V, and VI. This observation indicates an appreciable ring current effect in pyracyoquinone.

Further confirmation of the structure was provided by its catalytic hydrogenation. Compound II almost instantaneously absorbs 1 mole of hydrogen to produce III in quantitative yield. The reactivity of the double bond accentuates the high degree of strain involved in bridging naphthalene with two  $sp^2$  carbons in both *peri* positions. The lack of any reduction of the quinoid grouping<sup>10</sup> suggests that the delocalization energy of the pyracylene system may not be sufficient to overcome the large amount of strain energy—contrary to predictions based on molecular orbital theory.

**Acknowledgment.** We wish to thank the Petroleum Research Foundation (Grant No. 539-G1) and the Wisconsin Alumni Research Foundation for partial support of this work.

(9) The deshielding of these protons relative to the model compounds becomes more striking when corrections for solvent differences are applied.

(10) Treatment of II with other reducing agents such as zinc, sodium, and triethyl phosphite, which should attack at the quinoid system, will be reported in a future communication.

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## Unusual Metalloporphyrins. I. Preparation of Chromium Mesoporphyrin IX Dimethyl Ester<sup>1</sup>

Sir:

To our knowledge a chromium porphyrin has never been prepared by the application of any of the standard synthetic methods.<sup>2</sup> Recently, Elvidge and Lever<sup>3</sup> isolated a chromium phthalocyanine complex which has a structure similar to a metalloporphyrin. This indicates that the preparation of chromium porphyrin was feasible if a fresh synthetic approach could be found.

(1) Elemental Organic Compounds. XVII.

(2) J. F. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(3) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, 1257 (1961).

We have now discovered a novel method of metal insertion into the porphyrin structure using metal carbonyls as metal sources and have succeeded in preparing a chromium mesoporphyrin IX dimethyl ester. Several other known metalloporphyrins have also been obtained by employing this new method. In the synthesis of the chromium porphyrins, mesoporphyrin IX dimethyl ester and an excess of chromium hexacarbonyl were heated in *n*-decane for 1.5 hr at a bath temperature of 170° under an atmosphere of nitrogen. After the reaction mixture<sup>4a</sup> was cooled to room temperature, solvent and unreacted chromium hexacarbonyl were evaporated and sublimed out under reduced pressure. The residue was dissolved in oxygen-free toluene and insoluble material, if any, was filtered off. The solution obtained was concentrated and reprecipitated by adding oxygen-free *n*-pentane, and the precipitate was collected by centrifugation. After drying for 8 hr at the boiling point of toluene, an apparently violet crystalline compound was obtained.<sup>4b</sup> *Anal.* Calcd for C<sub>36</sub>H<sub>40</sub>O<sub>4</sub>N<sub>4</sub>Cr: C, 67.06; H, 6.25; N, 8.69; Cr, 8.08. Found: C, 67.20; H, 6.11; N, 8.61; Cr, 7.88. The original N-H stretching vibration (~3300 cm<sup>-1</sup>), N-H deformation (~1630 cm<sup>-1</sup>), and N-H rocking vibration (~1100 cm<sup>-1</sup>) of mesoporphyrin IX dimethyl ester disappeared from the infrared spectrum of this new complex. In addition, no absorption band of a carbonyl group bound to metal was observed, but the sharp single band (~1750 cm<sup>-1</sup>) for an ester carbonyl group remained. The magnetic susceptibility of chromium mesoporphyrin IX dimethyl ester, measured by Gouy's method, was 2.84 BM.<sup>5</sup> These results indicate that the chromium ion in the new metalloporphyrin may be in the divalent state. Nickel protoporphyrin IX dimethyl ester and cobalt mesoporphyrin IX dimethyl ester were also prepared by the reaction of porphyrin with Ni(CO)<sub>4</sub> and Co<sub>2</sub>(CO)<sub>8</sub>, respectively. These two metalloporphyrins were identified by comparing their visible spectra with those of the authentic complexes.<sup>6,7</sup> Furthermore, iron insertion into protoporphyrin IX dimethyl ester was successful using iron pentacarbonyl and iodine in mesitylene for 4 hr at a bath temperature of 80° to form iron protoporphyrin IX dimethyl ester iodide. *Anal.* Calcd for C<sub>36</sub>H<sub>36</sub>O<sub>4</sub>N<sub>4</sub>FeI: Fe, 7.24. Found: Fe, 7.00.

During the investigation of the reaction between metal carbonyls and porphyrin as mentioned above, a significant observation has been made: the metal is oxidized and, in this oxidation state, the carbonyl

groups do not remain. In 1965, Fitch and Lagowski<sup>8</sup> obtained ferrous acetylacetonate by the reaction of Fe(CO)<sub>5</sub> and acetylacetonate under a nitrogen atmosphere. The reactions here described between metal carbonyls and porphyrins also gave the divalent metalloporphyrins except for the reaction between Fe(CO)<sub>5</sub> and protoporphyrin IX dimethyl ester in the presence of I<sub>2</sub> as an oxidizing agent. To accommodate the oxidation of the metal to the +2 state, the central imino hydrogens would seem the most likely reductants. Reduced porphyrin species, hydrogen, or formaldehyde would seem to be possible end products for these hydrogens. Chromium hexacarbonyl has six carbon monoxide molecules. A CO group occupies one coordinating site and is replaced by one monodentate ligand. Therefore, it is expected that two CO groups will remain on the chromium porphyrin because the ligand is quadridentate. However, chromium mesoporphyrin IX dimethyl ester has no CO group on it, as shown by the infrared spectrum. In chromium mesoporphyrin IX dimethyl ester it is probable that one electron, at least, occupies the d<sub>z<sup>2</sup></sub> orbital because divalent chromium has four d electrons and the magnetic data show the presence of two unpaired electrons. The existence of a d<sub>z<sup>2</sup></sub> electron weakens the bond between the metal and carbon monoxide perpendicular to the molecular plane because of the repulsion between the lone pair of electrons on C atom in CO and the d<sub>z<sup>2</sup></sub> electron. This is perhaps one of the reasons that the bond between the metal and carbon atoms of CO in chromium porphyrin should be very weak even if it forms. Another possibility is to replace CO by another chromium mesoporphyrin IX dimethyl ester to form an association complex (as suggested by Elvidge and Lever<sup>3</sup>) for chromium(II) phthalocyanine. This point becomes apparent as a result of the investigation of the structure of the chromium porphyrin.

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(8) J. W. Fitch, III, and J. J. Lagowski, *Inorg. Chem.*, **4**, 910 (1965).

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## The [1,1]Ferrocenophane System<sup>1</sup>

Sir:

In contrast to the active interest in cyclophane compounds generally, the [*m,n*]ferrocenophane system<sup>1</sup> has received little attention, the only compounds of this class which have been described being [4,4]ferrocenophane<sup>2</sup> and bis(*as*-indacenyliron).<sup>3</sup> We wish to report the synthesis and characterization of 1,12-dimethyl[1,1]-ferrocenophane (II).

Reduction of the bisfulvene (I)<sup>4</sup> with lithium aluminum hydride in tetrahydrofuran afforded a yellow

(1) The systematic nomenclature proposed by B. H. Smith in "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, has been adopted throughout.

(2) A. Lüttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

(3) T. J. Katz and J. Schulman, *J. Am. Chem. Soc.*, **86**, 3169 (1964).

(4) M. Furdik, S. Toma, and J. Suchy, *Chem. Zvesti*, **15**, 547 (1961).

(4) (a) The visible absorption bands of the mixture at this stage of the reaction are 573 (α) and 535 mμ (β) in toluene, and the relative intensities of these two bands are α > β. (b) This compound was sparingly soluble in toluene, but soluble in chloroform, methanol, and others. Both toluene and chloroform solutions showed a gradual change in their absorption spectra when they were kept in air. No variations, however, were observed in their absorption spectra after 24 hr. The initial and final absorption maxima and the order of intensity in toluene and chloroform solutions are as follows: λ(toluene, I<sub>max</sub> ~ 578 mμ) < λ(toluene, I<sub>max</sub> ~ 546 mμ), λ(toluene, F<sub>max</sub> ~ 573 mμ) > λ(toluene, F<sub>max</sub> ~ 535 mμ); λ(chloroform, I<sub>max</sub> ~ 573 mμ) (ε 2.42 × 10<sup>3</sup>) < λ(chloroform, I<sub>max</sub> ~ 540 mμ) (ε 3.09 × 10<sup>3</sup>), λ(chloroform, F<sub>max</sub> ~ 575 mμ) (ε 3.0 × 10<sup>3</sup>) < λ(chloroform, F<sub>max</sub> ~ 545 mμ) (ε 4.7 × 10<sup>3</sup>); I<sub>max</sub> is the initial maximum and F<sub>max</sub> is the final maximum.

The reason for the different behavior of the compound in toluene and chloroform solutions, will be discussed in a forthcoming paper.

(5) We thank Professor Harry B. Gray for the use of his apparatus.

(6) J. E. Falk "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Inc., New York, N. Y., 1964, p. 244.

(7) A. Stern and M. Deželić, *Z. Physik. Chem.*, **180**, 131 (1937).