

NEGATIVE IONS OF PORPHIN METAL COMPLEXES¹

Sir:

The study of physical and chemical properties of negative ions of porphin metal complexes and related compounds (*e.g.* chlorins) promises to be of value in developing adequate theories for the electron distributions and absorption spectra of the porphin system.² Furthermore, such information may be of interest in connection with the primary step in photosynthesis where the intermediacy of similar ions has been postulated.³ We wish to report the preparations and characterizations of negative ions of porphin metal complexes in which the excess electrons appear to be distributed in the π -system of the organic ligand.

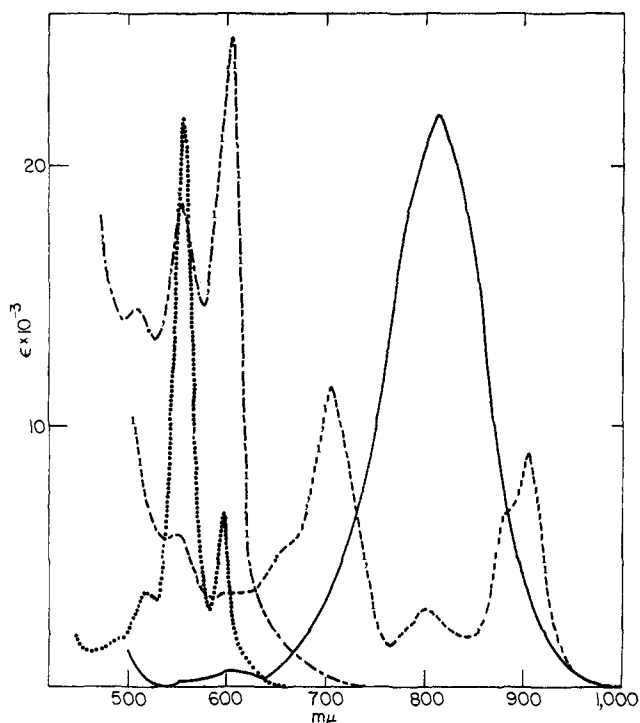


Fig. 1.—Part of absorption spectra of (.....) TPP-Zn, I; (----) [TPP-Zn]⁻Na⁺, II; (-·-·-) [TPP-Zn]²⁻Na₂⁺, III; (—) [TPPhlorin-Zn]⁻Na⁺, IV.

The reaction of sodium benzophenone ketyl with the zinc complex of tetraphenylporphin (TPP-Zn, I) in tetrahydrofuran gave the sodium salt of TPP-Zn mononegative ion (II). With anthracene negative ion a two-electron reduction product III was formed. Both compounds were obtained crystalline and were purified by recrystallizations.⁴ The reduction equivalents of II and III were established through these transformations: Iodine titrations of II were in agreement with the proposed stoichiometry as were titrations of the alkali liberated on air oxidations of both II and III. Under these conditions I was regenerated quantitatively. Protonation of III with methanol produced in instantaneous reaction the phlorin zinc complex salt IV, which with excess methanol rearranged slowly to the tetraphenylchlorin zinc complex (V) in excellent yield. Reaction of the dinegative species with one equivalent of I gave II, while the latter disproportionated upon protonation to I and IV, respectively. Finally, a strong electron spin resonance signal was

(1) Supported in part by a research grant from the National Institutes of Health (USPHS-RG5841).

(2) For a discussion of porphin absorption spectra see: M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959), and references cited therein.

(3) M. Calvin and G. M. Andros, *Science*, **138**, 867 (1962).

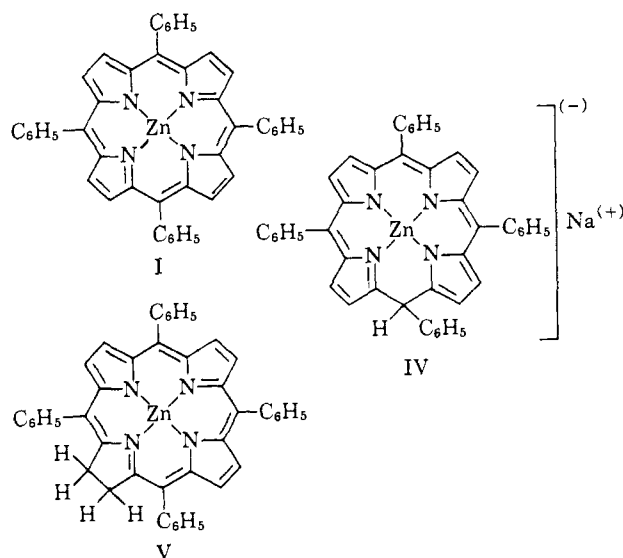
(4) Infrared analysis after reoxidation of II and III showed that both precipitates were free of benzophenone and anthracene, respectively.

obtained from solutions of II ($g = 2$, signal width at points of maximum slope 26 oersteds), whereas III was found to be diamagnetic. Essentially identical results were obtained for the reduction of the magnesium complex of TPP. Preliminary experiments on reductions with sodium metal indicate that higher negative ions can be formed from TPP-Zn and TPP-Mg; however, pure species have not yet been isolated.⁵

Figure 1 shows part of the spectra of compounds I-IV. In addition to these low energy, medium intensity transitions more intense absorption bands are found at shorter wave length (I, 422 $m\mu$, ϵ 600,000; II, 455 $m\mu$, ϵ 160,000; III, 437 $m\mu$, ϵ 76,000; IV, 457 $m\mu$, ϵ 157,000).⁷ Particular striking is the spectrum of the dinegative species which, with the exceptions of considerable increase in intensity of the O-O band and general band broadening, is almost unchanged from the spectrum of the neutral TPP-Zn.⁸ Reversible line shape changes of the infrared bands of II upon dilution (increase in intensity of the peak at 905 $m\mu$ on expense of the shoulder at 885 $m\mu$) indicate association with the sodium ion.⁹ The spectra of the negative ions of TPP-Mg have the same appearances and show only minor bathochromic shifts.

Approximate ranges for the potentials of II and III were obtained by utilizing different sodium ketyls and sodium aromatics. The ranges deduced this way were -1.0 to -1.2 volts for II and -1.5 to -1.8 volts for III. Polarographic half wave potentials in dimethylformamide were found to occur at -1.30, -1.75 and -2.43 volts (*vs.* s.c.e.).

The n.m.r. spectrum of the phlorin IV is in agreement with expectations. The chemical shifts of the peripheral protons (0.3 to 0.5 p.p.m. to high field of internal benzene) indicates the absence of the macrocyclic ring current. Furthermore the observed multiplet structure of the resonances of these protons is evidence for the loss of D_{4h} symmetry. Due to ex-



(5) Simple LCAO MO calculations⁶ indicate the lowest non-occupied MO in TPP-Zn to be doubly degenerate, thus allowing the addition of four electrons.

(6) G. R. Seely, *J. Chem. Phys.*, **27**, 125 (1957).

(7) When the intensities of the high energy transitions are integrated ($\int \epsilon d\nu$) much smaller differences among the spectra of compounds I-IV result.

(8) It cannot be ruled out with certainty that very weak absorptions do occur at longer wave length in the spectrum of compound III. Employing the circular box model for porphin metal complexes⁹ one would expect forbidden transitions to occur in the very near infrared.

(9) It is only reasonable to expect ion association for the dinegative species as well. We were unable to detect any changes of the spectrum with dilution; however, a different solvent might produce such changes.

tremely low solubility no unambiguous spectrum for III was obtained.¹⁰

Finally, it should be mentioned that the observed facile conversion of the phlorin zinc complex (IV) to the chlorin V is the first of its kind and is in striking contrast to the failure of certain phlorin hydrochlorides to undergo this transformation.¹¹

Acknowledgment.—We are indebted to Dr. Mendel Friedman for determining the polarographic half waves and for participating in some of the preliminary work that led to this study.

(10) The only signal recorded besides the solvent spectrum and its C-13 satellites was a sharp line at 1.95 p.p.m. at the high field side of internal benzene. The signal to noise ratio was so low that the phenyl protons would not have shown up if they exhibited the same type of splitting as they do in I. TPP-Mg dinegative ion showed the same resonance at 1.96 p.p.m. If these signals are indeed due to the identical 8 protons in III, their high shielding compared to the equivalent protons in I (-1.55 p.p.m. from benzene) must indicate a substantial loss of delocalization of the pi electrons in the dinegative ions.

(11) R. B. Woodward, *Angew. Chemie*, **72**, 651 (1960).

(12) A. P. Sloan Foundation Fellow.

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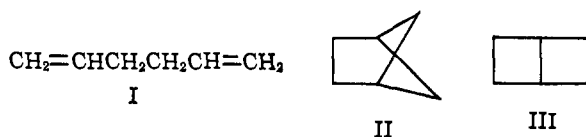
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MERCURY PHOTSENSITIZED ISOMERIZATION OF 1,5-CYCLOOCTADIENE TO TRICYCLO[3.3.0.0^{2,6}]OCTANE

Sir:

The intramolecular addition of one olefinic group to another under the influence of light to yield an isomeric product which contains a cyclobutane ring is well known. In molecules in which the two olefinic groups have freedom to twist with respect to each other, the addition appears to be *trans* rather than *cis*. As examples, one may cite the photoisomerization of carvone to carvone camphor¹ and the mercury photosensitized isomerization of 1,5-hexadiene (I) to bicyclo[2.1.1]hexane (II).² The preferential formation of II from 1,5-hexadiene rather than bicyclo[2.2.0]hexane (III) which may also be formed by the addition of the double



bonds led to the present investigation of the mercury photosensitized isomerization of 1,5-cyclooctadiene.

Commercial 1,5-cyclooctadiene which is predominantly the *cis,cis* material³ was irradiated with the mercury resonance line at 2537 Å. in the presence of mercury vapor. The apparatus has been described before.⁴ From the volatile fraction of the photolyzate, a compound (b.p. 125°) which constituted about 30% of this fraction was isolated. Since its molecular formula was C₈H₁₂ it was isomeric to the starting material. (*Anal.*⁵ Calcd. for C₈H₁₂: C, 88.82; H, 11.19. Found: C, 88.46; H, 11.19; mol. wt. 108 (mass spectrum). It showed no unsaturation in either its infrared or ultraviolet spectrum, which indicated that it was tricyclic. Pyrolysis of the compound in the vapor phase in a static system at 360–390° gave 1,5-cyclooctadiene which in turn underwent further isomerization to give 4-vinyl cyclohexene. It was inferred that the photoproduct of 1,5-cyclooctadiene was a valence tautomer that was probably formed by the mutual

(1) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1909); G. Buchi and I. M. Goldmann, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

(2) R. Srinivasan, *J. Phys. Chem.*, in press.

(3) L. E. Craig, *Chem. Rev.*, **49**, 103 (1951).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4823 (1961).

(5) Microanalysis by Microtech Laboratories, Skokie, Illinois.

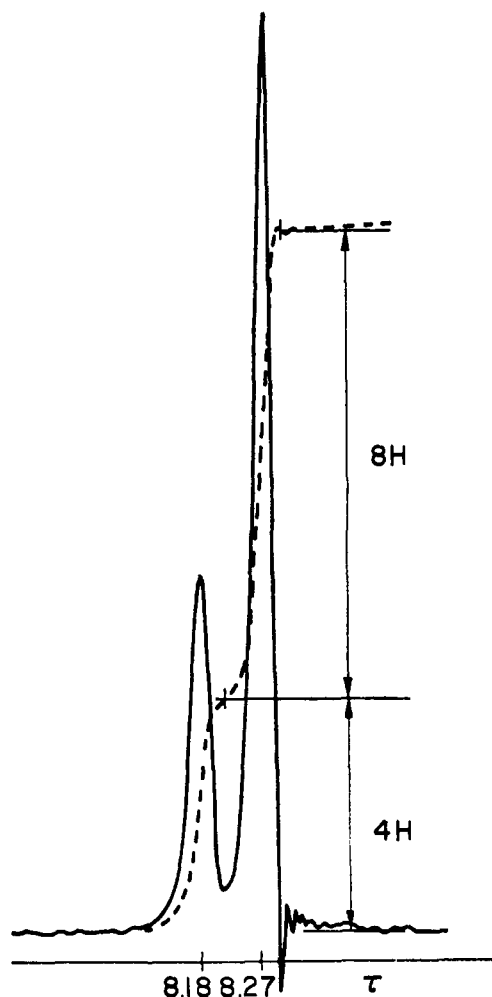
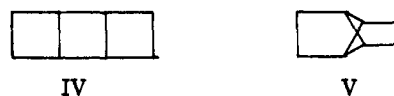


Fig. 1.—N.m.r. spectrum of tricyclo[3.3.0.0^{2,6}]octane; experimental conditions as described in text.

addition of the two double bonds in the molecule. Such an addition may give IV or V.



The n.m.r. spectrum of the product (carbon tetrachloride as solvent, concentration 15%; tetramethyl silane as internal standard)⁶ confirmed the absence of unsaturation and consisted of two unsplit peaks located at 8.18 and 8.27 τ , respectively. The areas under these peaks were in the ratio 1:2. If the product had the structure IV, its protons may be expected to occur at less than 8 τ in common with protons on cyclobutane derivatives⁷ and in bicyclo[2.2.0]hexane (III).^{4,8} Further, the protons in IV, whether the molecule has a "chair" or "tub" conformation, are of three kinds of four each, which also conflicts with the observed distribution. Structure V would fit the observed spectrum well. In this structure, the molecule has only two kinds of protons which are in the ratio 4:8. The eight protons on the four methylene groups occur at nearly the same position as the methylene protons on the two carbon bridge in bicyclo[2.2.1]hexane.⁴ The four tertiary protons can reasonably be expected to occur at lower τ values.

Apart from the intrinsic interest in the structure of the tricyclooctane (V), two aspects of its formation

(6) The author is deeply grateful to Drs. R. L. Hinman and E. B. Whipple of Union Carbide Research Institute, Tarrytown, N. Y., for their help in obtaining this spectrum.

(7) Catalog of NMR Spectra, Varian Associates, Palo Alto, Calif., 1962, pp. 128, 272.

(8) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, **21**, 24 (1960).