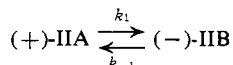


time gave, in this case, values for the initial rotation of $[\alpha]_{435}^{32.8} -561$ to -590° . Evidently the crystalline forms of (+)-IIA and (-)-IIB arise by second-order asymmetric transformations; the separation of the crystalline phase displaces the equilibrium between the two diastereomers in the supernate. The same equilibrium rotation ($[\alpha]_{435}^{32.8} \sim +25^\circ$) is obtained starting with either diastereomer.

The equilibrium rotation is temperature dependent and becomes negative above *ca.* 60° . Assuming the reasonable values⁴ of $\pm 570^\circ$ for $[\alpha]_{435}$ of the pure diastereomers, equilibrium constants may be calculated from the temperature dependence of the equilibrium rotation, whence ΔH° is *ca.* 0.9 kcal./mole and ΔS° is *ca.* 2.7 e.u. for the equilibrium in toluene



Given these values of ΔH° and ΔS° , the temperature dependence of the rate constant of mutarotation ($k_1 + k_{-1}$) yields $k_1 = 10^{12.4} \exp(-22.7/RT) \text{ sec.}^{-1}$ and $k_{-1} = 10^{11.8} \exp(-21.8/RT) \text{ sec.}^{-1}$. The values of these rate constants are in consonance with the value of $k_{\text{inv}} = 10^{12.5} \exp(-23.1/RT) \text{ sec.}^{-1}$ which was found for the configurational inversion ($k_{\text{inv}} = 0.5k_{\text{rac}}$) of 9,10-dihydro-4,5-dimethylphenanthrene (III).²

The rotations of the diastereomers of II are effectively equal and opposite. It may therefore be concluded that the contribution of the asymmetric C-9 atom is essentially negligible and that the chirality of the inherently dissymmetric biphenyl moiety is the dominating factor determining sign and magnitude of the optical rotation. It has been shown that 2,2'-bridged biphenyls which lack extraneous chromophores and which have the (*S*) configuration have strong positive rotations in the visible.⁵ The configurations of the biphenyl components in (+)-IIA and (-)-IIB are therefore (*S*) and (*R*), respectively. These conclusions are supported by preliminary o.r.d. results on (-)-IIB which

(4) Variations of less than 10% in the values assumed for $[\alpha]_{435}$ do not significantly alter the calculated thermodynamic constants.

(5) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

are typical for such compounds:^{2,6} the sign of rotation in the visible is dominated by the background rotation originating in an intense negative Cotton effect centered at short wave lengths (*ca.* 225 $m\mu$); a positive Cotton effect is interposed at the biphenyl conjugation band (near 260 $m\mu$). The absolute configuration at C-9 (arbitrarily shown as (*R*) in the drawing) is not yet firmly established and we are investigating this interesting problem which has direct bearing on the mechanism of the Stevens rearrangement. It should be noted at this time however that the transfer of dissymmetry (from biphenyl I to C-9 in II) appears to be essentially complete and that the reaction is therefore highly stereospecific.

Wittig and Zimmermann reported¹ that reaction of I with potassium amide in liquid ammonia gives an amine of structure II, and that this amine does not deaminate under the conditions of the reaction. In contrast we have found that the major products are 4,5-dimethylphenanthrene (IV) and III, the ratio of III:IV increasing with increasing reaction time (III:IV = 0.012 after 1 hr. and 17.6 after 1 week. After 8 months only III is observed). With weaker bases (potassium hydroxide) II is produced; this material is identical in every respect with the product of the phenyllithium reactions.

(6) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

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The Structure of Porphine¹

Sir:

The crystal structures of several tetraphenylporphines have been determined recently by X-ray methods.²⁻⁴ The space groups of these porphyrins all require some molecular symmetry. The structure of porphine is of interest because it is unaffected by phenyl substituents and has no molecular symmetry required by the space group. The results of an X-ray structure determination of this molecule are given here.

Porphine crystals are monoclinic, space group $P2_1/a$. Since there are four molecules per unit cell, there is no required molecular symmetry. The cell dimensions are $a = 12.36 \pm 0.01$, $b = 12.12 \pm 0.02$, $c = 10.272 \pm 0.002$ Å.; $\beta = 102.1 \pm 0.1^\circ$. Cu $K\alpha$ radiation was used to obtain 2421 nonzero structure factors, and the structure was solved by the probability methods of Hauptman and Karle.^{5,6} The final conventional *R* factor including all 2421 reflections was 4.9%.

Twelve hydrogens at reasonable positions on the outside of the porphine ring and four "half-hydrogens"

(1) This research was supported by a grant from the Public Health Service.

(2) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964).

(3) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

(4) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

(5) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," A.C.A. Monograph, No. 3., Polycrystal Book Service, Brooklyn, N. Y., 1953.

(6) J. Karle and H. Hauptman, *Acta Cryst.*, **12**, 404 (1959).

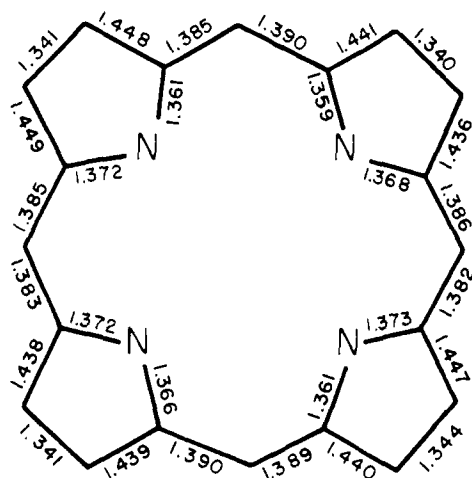


Figure 1. Bond distances of porphine.

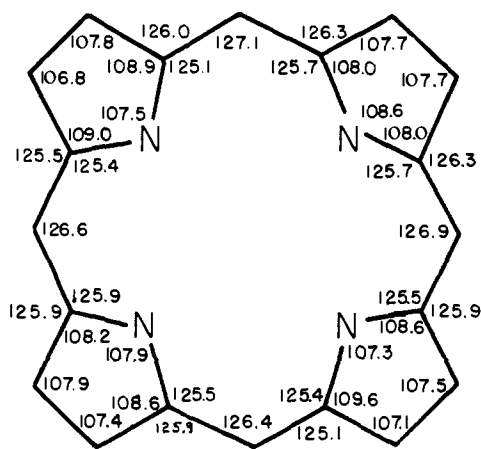


Figure 2. Bond angles of porphine.

each attached to a nitrogen were indicated by well-defined peaks on difference maps. Possible explanations for the half-hydrogens are (1) static molecular disorder within the crystal, and (2) a rapid interconversion of N-H tautomers, first suggested by Becker, Bradley, and Watson on the basis of n.m.r. evidence.⁷ The single β -pyrrole hydrogen peak that we find in the n.m.r. spectrum of *meso*-tetraphenylporphine⁸ is consistent with this possible interpretation. The single peak can be attributed to an averaging of the properties of the pyrrole rings caused by the rapid tautomerism.

Least-squares refinement which includes the hydrogens and anisotropic temperature factors gives the bond distances and bond angles shown in Figures 1 and 2. Estimated standard deviations in bond parameters that do not include hydrogens are 0.003 to 0.004 Å. for bond lengths and about 0.3° for bond angles. The least-squares refinement is the source of these estimates of the standard deviations. The nitrogen to half-hydrogen distances are about 0.9 Å. The bond parameters given for each pyrrole ring are actually an average of the parameters of pyrrole rings with and without hydrogen attached to nitrogen. The relatively long bonds between α - and β -carbons of the pyrroles and the short bonds between pyrrole β -carbons con-

(7) E. D. Becker, R. B. Bradley, and J. C. Watson, *J. Am. Chem. Soc.*, **83**, 3743 (1961).

(8) Unpublished results.

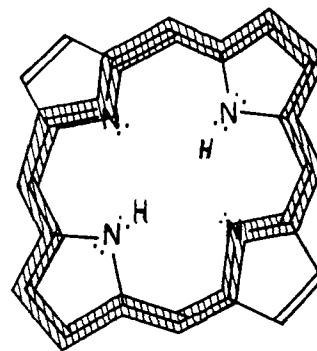


Figure 3. Usual representation of porphine electronic structure.

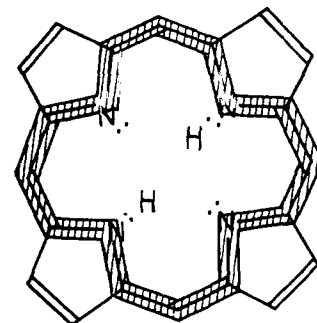


Figure 4. Alternative representation of porphine electronic structure.

trast with the bonds of intermediate length, which are in the ring outlined in Figure 4. The average length of the C_{β} - C_{β} bonds is 1.342 Å., which is very close to the 1.337-Å. distance given for a double bond.⁹ Thus the β -pyrrole carbons are apparently not coupled to the interior resonant system.

The molecule was found to be nearly planar. Distances of carbon and nitrogen atoms from the nuclear least-squares plane calculated from the four nitrogen atoms varied from 0.01 to 0.04 Å. Apart from the slight deviations from planarity, the statistical symmetry of the molecule in the crystal is D_{4h} , whereas the symmetry of individual molecules is D_{2h} within experimental error.

The electronic structure of porphine is usually represented by resonance structures consistent with an eighteen-membered conjugated ring of alternating single and double bonds. The path of this ring is shown in Figure 3. Resonance structures of this type always impart some single bond character to the bonds between β -pyrrole carbons; the bond order given by the proportion of Kekulé structures in which these bonds are double is $7/4$.

We wish to suggest another possible way of representing the electronic structure which is more consistent with our findings on the similarity of the pyrroles and the lengths of the bonds between β -pyrrole carbons. As shown in Figure 4., we represent all four of these bonds as double bonds. The inner ring π -cloud has 16 atoms. Each atom in the ring contributes one electron to the π -system of this ring. However, we know that porphine with no protons or

(9) "International Tables for X-Ray Crystallography. Vol. III. Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962.

metal ions bonded to the nitrogens is a dianion so we add two more electrons to the π -system of the sixteen-membered ring. This makes 18 electrons, which is consistent with the $4n + 2$ electrons required by Hückel's rule for a stable aromatic system. The inner ring is similar to the cyclooctatetraene dianion, which has ten electrons. Two protons or a dipositive metal ion added to the center of the dianion ring create a neutral species. The bonding around each nitrogen is similar to the bonding around nitrogen in pyridine. Each nitrogen has a lone pair of electrons, and it may be that two of these lone pairs form N-H bonds as in the pyridinium ion. This would help explain the N-H stretch found in the infrared. Alternatively, the protons may be bound ionically in some fashion. In any case, the molecule can be represented as the sixteen-membered ring with perturbations due to β -pyrrole carbons and the protons or metal atom in the center.

The above argument relies heavily on the observation that the $C_\beta-C_\beta$ bond is a double bond. Our argument also predicts that the $C_\alpha-C_\beta$ bond should be a single bond and that the $C_\alpha-N$ and the $C_\alpha-C$ (methine) bonds should have the same bond order. The observed $C_\alpha-C_\beta$ bond length is a little short for a pure trigonally hybridized C-C σ -bond. A better description of the molecule may be a combination of the two electronic structures shown in Figures 3 and 4.¹⁰

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(10) We wish to thank a referee for bringing the seitemts to our attention.

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Solvent-Separated Ion Pairs of Carbanions

Sir:

Ionic species are known to associate into ion pairs in low dielectric constant solvents. Two types of ion pairs may be visualized,¹ namely, contact (or intimate) ion pairs which are peripherally solvated, and solvent-separated ion pairs. The existence of such distinct species was invoked by Winstein, *et al.*,² to account for the observed salt effects in the solvolysis of certain arene sulfonates. A similar assumption was made by Cram and his co-workers to explain the stereochemical course of electrophilic substitution at saturated carbon.³ The concept of two chemically distinct ion pairs has also been proved useful in interpreting the absorption spectra of tetraalkylammonium iodide solutions.⁴

We have found direct evidence for the existence of the two kinds of ion pairs from the electronic spectra of fluorenyl carbanion (F^-). Figure 1 shows the spectrum of its sodium salt in tetrahydrofuran (THF) at three dif-

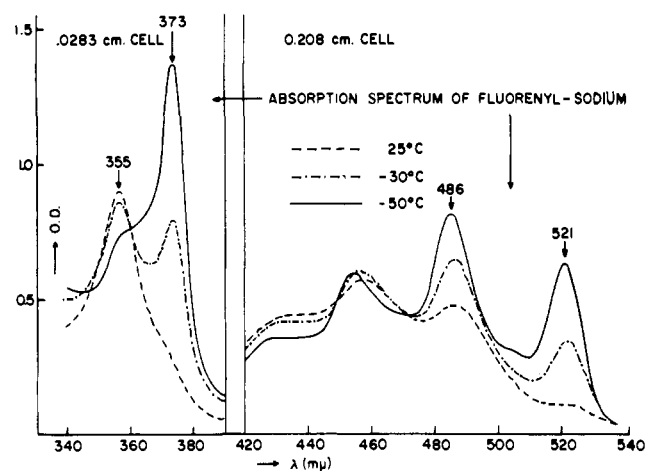


Figure 1.

ferent temperatures. A sharp absorption peak at 355 $m\mu$ ($\epsilon_m \sim 10,000$) is seen at room temperature in addition to some weaker bands in the visible region. On cooling, a new peak develops at 373 $m\mu$, while the 355 $m\mu$ peak decreases, and eventually only the 373 $m\mu$ absorption band remains below -50° . Simultaneously with this change, an additional peak develops at 521 $m\mu$. The process is reversible, indicating that this new species is in equilibrium with that existing at room temperature. The new entity is not the free fluorenyl ion, although its concentration, like that of the free ion, increases on lowering the temperature. This conclusion is based on the following observations: At any temperature, the relative heights of the two absorption bands (355 and 373 $m\mu$) are not affected by dilution or by the addition of $NaB(Ph)_4$, although the added salt is strongly ionized in THF.⁵ Moreover, the dissociation constants for F^-, Na^+ , calculated from conductivity data, vary from about $7 \times 10^{-7} M$ at 25° to about $4 \times 10^{-5} M$ at -70° . Hence, under our experimental conditions ($[F^-, Na]$ between 10^{-2} and $10^{-3} M$), only a small fraction of ion pairs dissociates into free ions, not sufficient to be seen in the spectrum.

These observations strongly suggest that the entity formed at low temperatures is a solvent-separated ion pair ($F^-||Na^+$). In the sequence $F^-, Na^+ \rightleftharpoons F^-||Na^+ \rightleftharpoons F^- + Na^+$, a large gain in solvation energy occurs in the first step, and indeed the temperature dependence of the ratio of the two absorption bands leads to ΔH of about -6 kcal. This value is confirmed by the results derived from the temperature dependence of the conductivity. In the range $+25^\circ$ to -20° , ΔH_{total} of the contact ion pair dissociation into free ions has been found to be about -8 kcal., but at very low temperatures ΔH decreases to about -1.5 kcal./mole, since then the ions are formed from solvent-separated ion pairs.

Bathochromic shifts were observed in absorption maxima of ion pairs on increasing the interionic distance.⁶ Hence, it is not surprising that $F^-||Na^+$ absorbs at higher wave length than F^-, Na^+ . Variation of counterion has a similar effect, as shown by the

(1) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(2) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

(3) D. J. Cram, *et al.*, *ibid.*, **81**, 5774 (1959).

(4) T. R. Griffiths and M. C. R. Symons, *Mol. Phys.*, **3**, 90 (1960).

(5) C. L. Lee, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, in press.

(6) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960); M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).