

indications of the formation of 9- and 15-membered rings, respectively.

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Geometry of the Pyridine-Iodine Complex from the Effect of an External Electronic Field on Absorption

Sir:

Molecular geometries of several donor-acceptor complexes have been determined in crystals by many investigators following the initial work of Hassel and collaborators.^{1,2} Since the enthalpies of formation of these complexes are small, there have been doubts in many peoples' minds whether forces other than those present in solution or vapor contribute to the observed conformations in crystals.³ If that were the case, the molecular geometry observed in crystals could be markedly different from that in solution or vapor. At present there are no available methods for the direct determination of molecular conformation of donor-acceptor complexes in solution or vapor. This is a great disadvantage, because the charge-transfer interactions are best studied in solution or vapor and not in crystals. The purpose of this communication is to suggest that studies of the effects of the external electric fields could provide a direct method of determining the geometry of donor-acceptor complexes in solution and to report the application of this method to the pyridine-iodine complex.

Figure 1 shows two of the many possible structures for the pyridine-iodine complex. It is suggested by analogy to the crystal structure of pyridine-iodine monochloride complex.¹ II is the structure proposed by Reid and Mulliken on theoretical grounds.⁴ It should be pointed out that I or some modification of it is favored by indirect evidence. Mulliken⁵ has recently shown that the shape of the charge-transfer absorption of the pyridine-iodine complex gives strong support for I. This system is considered here mainly to illustrate the power of electric dichroism studies in structure determination. Figure 1 also gives the expected directions of dipole moment and transition moments for the 4200-Å band and the charge-transfer absorption of the complex. The 4200-Å band of the complex is assigned as a transition mainly localized on iodine⁶ and its moment is expected to be along the iodine-iodine bond. It can be seen from Figure 1 that the dipole moment and the 4200-Å absorption are oriented along the same molecular axis for structure I. Therefore, if I were the correct structure, the component of absorption polarized parallel to the external field should be larger than the one perpendicular to the external

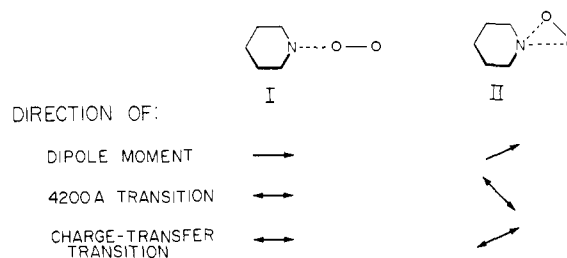


Figure 1. Two possible molecular conformations for the pyridine-iodine complex and the orientation of some moments for each conformation. These two cases are chosen for the sake of illustration only, and other possible conformations are not excluded in the interpretation of the results.

field. Exactly opposite results should be found if II were the correct structure. Thus, in the case of the pyridine-iodine complex, a qualitative study of the effects of electric fields on 4200-Å absorption should lead to the correct choice between structures I and II. If the geometry were to be intermediate between these two cases, a quantitative study should lead to its determination. In general, by a quantitative study of field effects on a sufficient number of local and charge-transfer transitions in a complex, it should be possible to uniquely determine the structure of donor-acceptor complexes.

We have determined the changes in absorption in the 4200-Å band of the pyridine-iodine complex due to an external electric field with the aid of the phase-sensitive technique.⁷ A half-wave rectified electric field of approximately 570 Hz was obtained from a high-voltage silicon rectifier (Varo VF25-15) and the secondary of a 12-kV transformer, the primary of which was connected to a power amplifier and audiooscillator. The cell consisted of two stainless-steel plates (48 mm in length and 25 mm high) suspended in a solution of 50-mm optical path. The separation between the electrodes was 1.5 mm. The change in the photocurrent induced by the electric field (for the electric vector of the light parallel and perpendicular to the field) was determined by an EMI 9558 photomultiplier tube and a Princeton Applied Research HR-8 lock-in amplifier.

Figure 2 shows the change in the photocurrent caused by the external electric field for one of the solutions investigated. Liptay^{8,9} has given a fairly complete theory of all the effects of external electric fields on dipolar molecules in solution. These effects can be classified as (i) wavelength-dependent effects which are mainly related to the change in dipole moment upon excitation and (ii) wavelength-independent effects which are related to (a) orientation of molecules by virtue of their ground-state dipole moment and (b) electrochromism (or change of the transition probability in the external electric field). At the maximum of absorption only (ii) contributes to the observed changes. Figure 2 shows that the change at the maximum is such that the absorption parallel to the field is greater

(1) O. Hassel and C. Romming, *Acta Chem. Scand.*, **10**, 696 (1956).

(2) See R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapter 8, for a comprehensive citation.

(3) For example, see p 216, ref 2.

(4) C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 3869 (1954).

(5) R. S. Mulliken, *ibid.*, **91**, 1237 (1969); also see R. S. Mulliken and W. B. Person, *ibid.*, **91**, 3409 (1969).

(6) R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).

(7) The experimental arrangement is similar to the one described by H. Labbert, *Tetrahedron, Suppl.*, **No. 2**, 223 (1963), and W. Liptay, H. Eberlein, H. Weidenberg, and O. Elflein, *Ber. Bunsenges. Phys. Chem.*, **71**, 548 (1967).

(8) W. Liptay, *Z. Naturforsch. A*, **21**, 1605 (1966).

(9) W. Liptay in "Modern Quantum Chemistry Part III: Action Light and Organic Crystals," O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, pp 45-66.

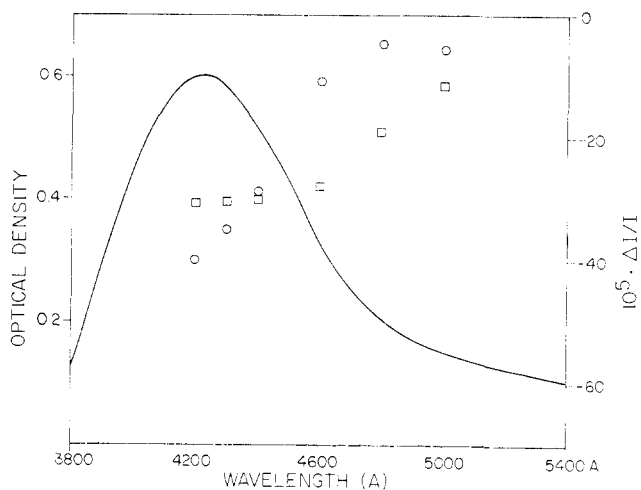


Figure 2. Absorption spectrum and the effects of external field. Circles correspond to the component parallel to the external field and squares to the perpendicular component. ΔI is the change in transmitted light induced by the external field. I is the optical transmission of the solution without the external field. The data between 4400 to 5000 Å are not discussed in the text. Concentrations: pyridine, $1.8 \times 10^{-2} M$; iodine, $1 \times 10^{-4} M$; solvent, cyclohexane; field strength, $6.8 \times 10^4 V/cm$ at peak value.

(lesser transmission) than the absorption perpendicular to the field. This result is consistent with structure I.¹⁰ Quantitative treatment of the data on several solutions of the pyridine-iodine complex show that the 4200-Å band is polarized very nearly parallel to the dipole moment of the complex and that the changes in transition probability induced by the electric field are not negligible. Data between 4400 and 5000 Å can also be explained satisfactorily by a consideration of changes in the dipole moment upon excitation.^{8,9}

These results conclusively show that studies of effects of electric fields on the absorption of donor-acceptor complexes can yield valuable information on the geometry in solution and the dipole moment in the excited state. Details of this work and work on other donor-acceptor complexes will be communicated in the near future.

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(10) A conformation in which the iodine molecule is located along an axis perpendicular to the plane of pyridine is also consistent with these data. Such a possibility can, however, be ruled out in the present case because pyridine is an n and not a π donor.

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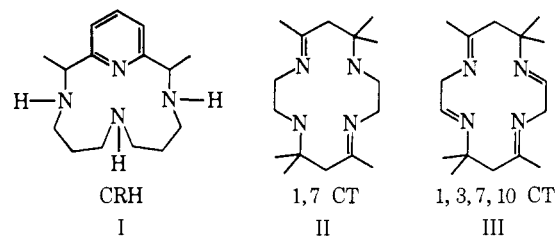
Five-Coordinate High-Spin Iron(II) Complexes of Synthetic Macrocyclic Ligands

Sir:

A new synthetic class of complexes having five-coordinate high-spin iron(II) bound to macrocyclic ligands has been prepared. These species have structural features similar to those of certain compounds

of biological significance, notably deoxyhemoglobin and deoxymyoglobin. We report here the synthesis and characterization of nine compounds of this new class, involving three ligands of varying degrees of unsaturation. In view of these results we feel that the five-coordinate high-spin configuration for Fe(II) should no longer be considered rare and that the binding of Fe(II) in the extremely important naturally occurring hemes properly fits into the systematic chemistry of that species. It has also been found that the Mössbauer parameters of the five-coordinate Fe(II) compounds fall into a unique range with unusually large quadrupole splitting.

The ligands are (a) *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CRH, structure I); (b) 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene (1,7 CT, structure II); and (c) 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),3,7,10-tetraene (1,3,7,10 CT, structure III). Complexes of CRH¹ and 1,7 CT² with other metal ions are well known. Each ligand presents a square array of nitrogen atoms with the metal ion nominally in the center. The new iron compounds with



these ligands are given in Table I, together with some of their more pertinent physical properties. Details will appear later.

Evidence supporting a five-coordinate square-pyramidal geometry of the [Fe(1,7 CT)X]ClO₄ and [Fe(1,3,7,10 CT)X]ClO₄ series (X = Cl, Br, I) involves their stoichiometries, magnetic moments, molar conductivities, infrared spectra, and d-d electronic spectra. The infrared spectra indicated the absence of water or other hydroxylic species and showed only free perchlorate ions. Conductivity data indicate univalent electrolytes in nitromethane.³ Most helpful, the d-d electronic spectra show that the strong tetragonal distortion (C_{4v} symmetry) present in these five-coordinate complexes produces a very large splitting of the 5E spectroscopic term state (derived from O_h symmetry) into 5B_1 and 5A_1 states (corresponding to the $d_{x^2-y^2}$ and d_{z^2} orbitals of the one-electron orbital description). This is consistent with the behavior of other metal ions.⁴ Careful spectroscopic measurements on these complexes (solid state and nitromethane solution; 3.0–25-kK region) reveal two broad weak d-d transitions near 5.0 and 12.5 kK for each compound (Table I). The higher energy absorption occurs at the same energy for each complex and is assigned to the transition to the B_1 ($d_{x^2-y^2}$) state. The position of the lower energy absorption (transition to A_1 (d_{z^2})) is dependent upon the field strength of the axial ligand.

(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 174 (1967).

(2) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(3) R. D. Feltham and R. G. Hayer, *J. Chem. Soc.*, 4587 (1964).

(4) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967).