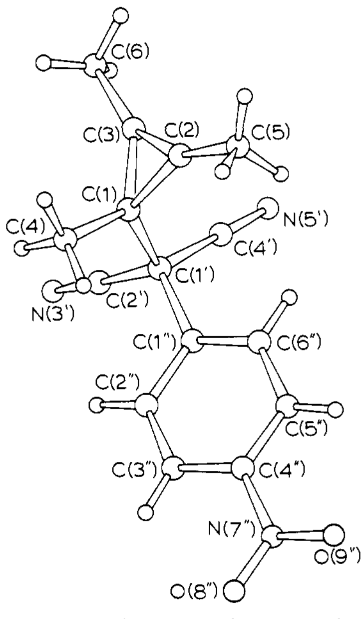

Figure 1. Structure and solid-state conformation of I.

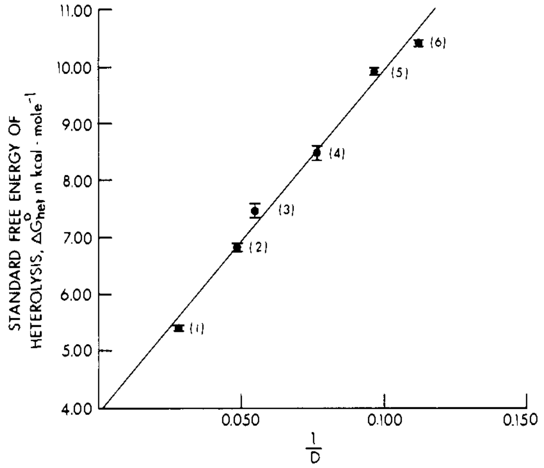

Figure 2. Born equation plot of standard free energy of heterolysis of compound II at 25 °C in six solvents of varied dielectric constant: (1) acetonitrile, (2) acetone, (3) cyclohexanone, (4) 4-methyl-2-pentanone, (5) 1,2-dichloroethane, (6) dichloromethane. Dielectric constants (D) are at 25 °C for 1, 2, 5, and 6 and at 20 °C for 3 and 4.

= -6.3 ± 0.3 kcal mol^{-1}).

We thus report unequivocal evidence for the heterolysis of a covalent compound to produce a carbocation and a carbanion under equilibrium conditions in a variety of solvents. Subsequent articles will discuss our findings regarding the effects of structural change on the thermodynamic and kinetic properties of these processes.

Acknowledgment. We gratefully acknowledge support for this work by NSF Grant CHE-8006202.

Supplementary Material Available: Tables of atomic positional parameters and interatomic distances and angles (4 pages). Ordering information is given on any current masthead page.

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(9) The observed heat of reaction was corrected for the degree of dissociation at the final concentration (2.2 mM). We believe that the small discrepancy between the van't Hoff and calorimetric enthalpies (both in CH_3CN) results from the enthalpy term for ion pairing of $K^+BF_4^-$, which would not be detected through the temperature coefficient of the equilibrium constant for heterolysis or formation of the C–C bond.

(10) **Note Added in Proof**: The study of $\Delta G_{hel}{}^\circ$ for compound I has been completed by K.E.M. in the same six solvents. In acetonitrile $\Delta G_{het}{}^\circ = 2.76$ kcal mol^{-1} for I and the slope of the Born plot is 93.8 kcal mol^{-1} with $r = 0.997$; the corresponding values for II are 5.39 kcal mol^{-1}, 60.1 kcal mol^{-1}, and 0.995.

Electronic Ground State of Iron(II) Phthalocyanine As Determined from Accurate Diffraction Data

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The electronic ground states of iron(II) phthalocyanine (FePc) and iron(II) tetraphenylporphyrin (FeTPP) have received much attention because of their relevance to the understanding of structure–function relationships in heme proteins. While the evidence indicates that the iron atom is in an intermediate spin state in both compounds, there is considerable ambiguity concerning the spatial arrangement of the electrons. Alternative configurations that have been discussed are summarized in Table I. For FePc magnetic data and Mossbauer measurements by Dale et al.[1] have been interpreted in terms of the ^3E_gA configuration, while Barraclough et al. assume the $^3B_{2g}$ state to be the ground state[2] in an interpretation of their magnetic data that is partly at variance with a later crystal structure determination.[3] The ground state for FeTPP has been discussed in several articles. Goff, La Mar, and Reed report that NMR measurements support the ^3A_g ground state,[4] while Boyd et al. on the basis of magnetic measurements and a ligand field calculation conclude that the lowest state is ^3A_g followed closely by the states ^3E_g and $^3B_{2g}$.[5] SCF calculations by Veillard et al.[6] and by Obara and Kashiwagi[7] point to the ^3A_g state as the lowest SCF state. Nevertheless on the basis of both the calculations and the Mossbauer spectra the latter group of authors assign the ground state as ^3E_gA.[7]

We have performed an accurate X-ray diffraction study of FePc at low temperature (110 ± 5 K) and refined the data with a multipole model aspherical atom formalism described elsewhere.[8] The 16 709 measured reflections ($\lambda = 0.71069$ Å, $(\sin\theta)/\lambda < 1.18$ Å^{-1}) were reduced to 6733 unique intensities of which 3832 have $F^2 > 3\sigma(F^2)$, by averaging over symmetry-equivalent measurements. Conventional and multipole refinements led to $R(F)$ factors of 3.6% and 2.7%, respectively. The low-temperature structure is essentially the same as the room-temperature results described by Kirner, Dow, and Scheidt.[3] The deformation density map in the plane of the molecule (Figure 1a), defined as $\rho_{obsd} - \sum\rho_{isolated\ atoms}$, shows that density in excess of the isolated atom distribution is located along the bisectrices of the Fe–N bonds. This would not be the case for either the $^3B_{2g}$ or the ^3E_gB configuration (Table I), which are electron deficient in d_{xy}. A section perpendicular to the molecular plane reproduced here (Figure 1b), shows an electron-deficient area above and below the iron atom. This indicates a less-than-spherical-atom population in the d_{z^2} orbital in support of the ^3E_gA state, but at variance with the density predicted by the other remaining configuration, ^3A_g.

A more quantitative assessment may be based on the experimental multipole populations from which the d-orbital occupancies can be derived.[9] The results given in the one but last column

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[‡] On leave from the Institute of Chemistry, Academia Sinica, Beijing, China.

(1) Dale, B. W.; Williams, R. J. P.; Johnson, C. E.; Thorp, T. L. *J. Chem. Phys.* **1968**, *49*, 3441–3444. Dale, B. W.; Williams, R. J. P.; Edwards, R. J. P.; Johnson, C. E. *Ibid.* **1968**, *49*, 3445–3449.

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Table I. Electron Occupancies in Square-Planar 3d^6 Electron Configurations and Comparison with Experimental Results[a]

term symbol[b]	^3E_gA	^3A_g	$^3B_{2g}$	$3E_gB$	X-ray exptl	spherical atom
$d_{x^2-y^2}$					0.75 (6) (13.9%)	1.2 (20%)
d_{z^2}	1 (17%)	2 (33%)	1 (17%)	2 (33%)	0.88 (6) (16.3%)	1.2 (20%)
d_{xz},d_{yz}	3 (49%)	2 (33%)	4 (67%)	3 (49%)	2.13 (6) (39.4%)	2.4 (40%)
d_{xy}	2 (33%)	2 (33%)	1 (17%)	1 (17%)	1.65 (8) (30.5%)	1.2 (20%)

[a] From refinement including 4s electrons; d-orbital occupancies from refinement excluding 4s electrons are identical within experimental errors. [b] The nomenclature ^3E_gA, ^3E_gB is as used in ref 7. [c] The z axis is the 4-fold symmetry axis perpendicular to the molecular plane. The x and y axes are in the plane along the Fe–N bonds.

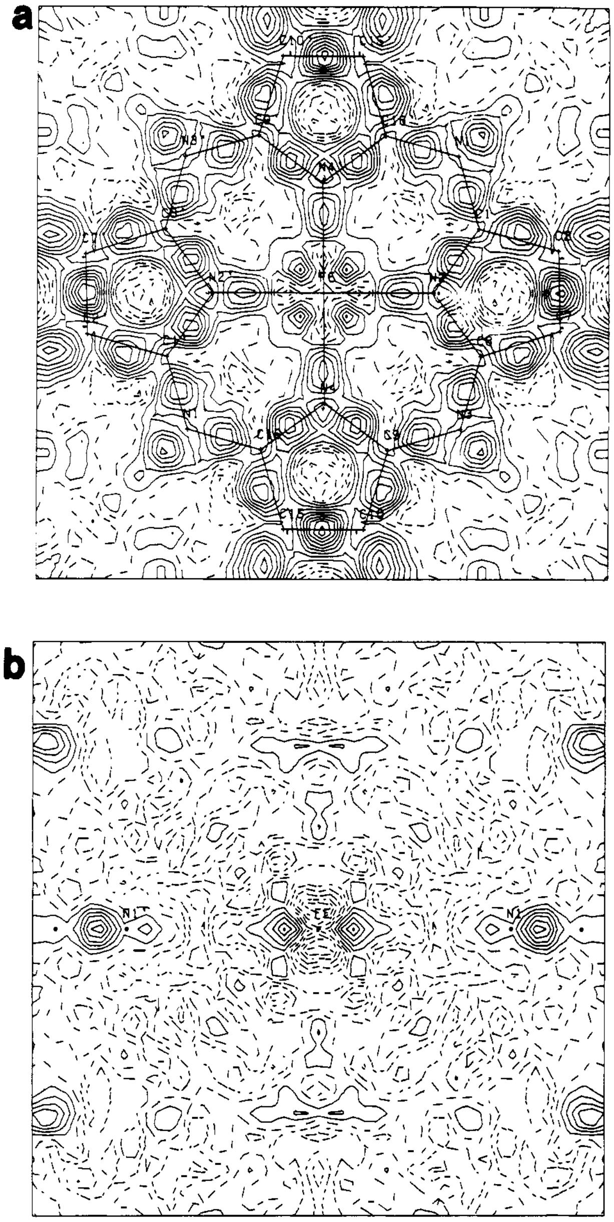

Figure 1. (a) Deformation density in the plane of the iron phthalocyanine molecule averaged over chemically equivalent sections. Contours at 0.05 e Å^{-3}. Negative contours broken. (b) Deformation density section perpendicular to the molecular plane bisecting the NFeN angles, averaged over chemically equivalent sections. Contours as in part a.

of Table I show the ratio of the d_{xy}, $d_{xz,yz}$, and d_{z^2} occupancies to be equal to 2:2.6 (2):1.1 (1). This ratio is only compatible with the ^3E_gA state, which therefore must be the major contributor to the ground state of the iron atom.

The occupancy of the $d_{x^2-y^2}$ orbital gives evidence for covalency in the Fe–N interactions, as discussed previously in the case of CoTPP.[10]

We conclude that accurate X-ray data give detailed information on the electronic ground state of FePc. To our knowledge this is the first time that experimental charge-density measurements have been used to resolve an existing controversy regarding a transition-metal-atom ground state. It is clear that the method has broad potential whenever good quality crystals are available.

Acknowledgment. Support of this work by the National Science Foundation (CHE7905897) and the National Institutes of Health (HL-23884) is gratefully acknowledged. We also thank Prasana Chandrasekhar for help with the growing of the crystals by sublimation at 400 °C.

Registry No. Iron(II) phthalocyanine, 132-16-1.

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Hydrogen Bonding in Optically Active and Racemic 2-Butanol

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Consider hydrogen-bonded dimers of chiral alcohol molecules. Homochiral dimers composed of two molecules with the same configuration are anisometric to heterochiral dimers containing enantiomeric molecules.[1-3] Therefore these ensembles must exhibit differentiation in properties due to anisometric intermolecular interactions. However, a review of the literature[4-9] reveals that anisometric effects[1] due to hydrogen bonding are either very small or nonexistent. Some examples related to the study reported herein are identical densities and dielectric constants for racemic and optically active 2-octanol,[4] a ΔH (mixing, 16 wt % solute) = +1.9 J/mol for D- and L-tartaric acids in water,[5] slightly different dielectric constants for (−)- and (±)-menthol in benzene,[6] and reported identical vapor pressures of (+)- and (±)-2-butanol.[7]

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(1) We will use classifications of pairwise relations between isomeric structures proposed by Mislow.[2] Three-dimensional structures are isomeric if their labeled graphs are identical, labeling being by atom type for vertices and internuclear distances for edges.[3] We use the term isometric because of its precise definition and because we wish to avoid use of the word diastereodifferentiation in referring to anisometric effects.

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