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.

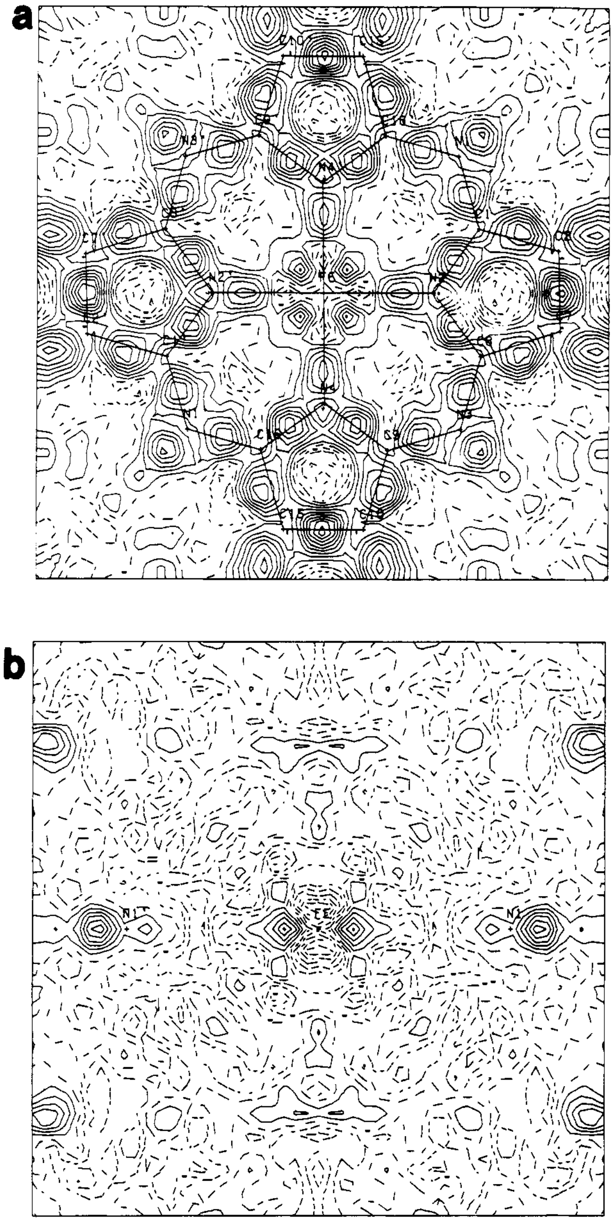

Figure 1. (a) Deformation density in the plane of the iron phthalocyanine molecule averaged over chemically equivalent sections. Contours at 0.05 e Å^{-3}. Negative contours broken. (b) Deformation density section perpendicular to the molecular plane bisecting the NFeN angles, averaged over chemically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

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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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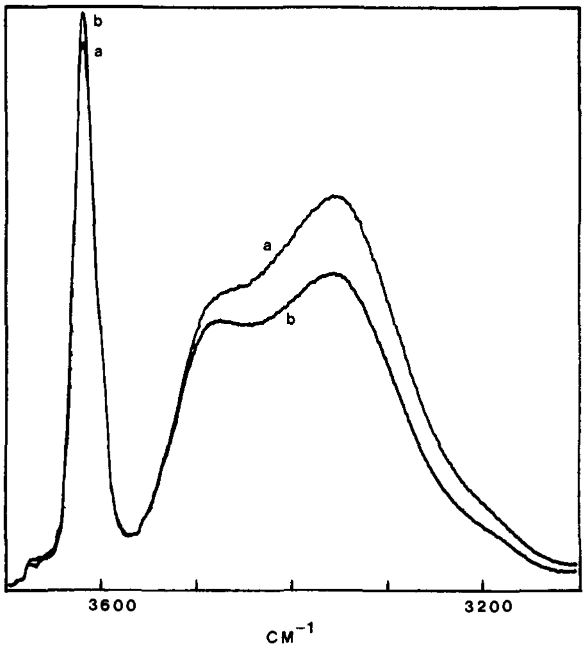

Figure 1. IR spectra of 2-butanol in carbon tetrachloride solution at 0.210 M concentration: (a) (*S*)-(+)-2-butanol or (*R*)-(−)-2-butanol; (b) racemic mixture.

Somewhat larger but still small effects are the 2° difference in boiling points of racemic and active 2-octanols[8] and infrared studies giving ΔH's of 5.5 and 5.7 kJ/mol for hydrogen bonding in racemic and (*R*)-2,2,4-trimethylpentan-3-ol, respectively.[9]

An investigation of intermolecular hydrogen bonding in 2-butanol is described in this communication. The data are analyzed in terms of monomers, hydrogen-bonded dimers, and cyclic oligomers.[10] Equilibrium constants for dimer and oligomer formation are found to differ in the cases of racemic and pure enantiomeric solutions. The observed anisometric effects are much larger than those reported in the above cited works.

Optically active[11] and racemic 2-butanol samples have identical IR spectra[12] in CCl_4 solution (23 °C) at concentrations less than 0.005 M. A single OH stretching band is observed at 3621 cm^{-1}. At higher concentrations bands centered at 3490 and 3350 cm^{-1} are assignable to stretching vibrations of hydrogen-bonded OH in dimer and oligomer(s), respectively. The postulate of a three-component equilibrating system accounts for qualitative features of the spectra. Quantitative digital data handling capabilities allow obtaining separate digitalized curves for overlapping bands in the 3700–3100-cm^{-1} region. The spectrum for any concentration of alcohol is then derived as a linear combination (regression analysis) of three constituent bands. At all concentrations, spectra of the pure enantiomers remain identical with each other, but racemic mixtures shows significant decreases in intensities of lower frequency OH stretching bands as illustrated in Figure 1.

Table I. Equilibrium Constants for Hydrogen-Bonded Dimer and Cyclic Pentamer, 2-Butanol/CCl_4 System

compd	n	K^a (std dev)	K^b (std dev)
(*S*)-(+)-2-butanol	5.12	2.587 (0.087)	600.7 (27.5)
(*R*)-(−)-2-butanol	5.02	2.580 (0.137)	660.3 (32.7)
racemic mixture	4.87	1.712 (0.133)	442.3 (27.1)

^{a} Units of M^{-1}. ^{b} Units of M^{-4}.

Analysis of the IR data leads first to a determination of n, the average number of molecules in the oligomer, taken to exhibit the 3350-cm^{-1} absorption band. Values close to 5 are obtained from iterative linear regression of the log of absorbance at 3350 cm^{-1} vs. monomer concentration according to eq 1. This equation

$$n \log [\mathrm{R}_1] + \log (K_n) + \log (\epsilon_n) = \log (\mathrm{Abs}_n) \tag{1}$$

is derived from the equilibrium expression, eq 2, and makes use

$$K_n = [\mathrm{R}_n]/[\mathrm{R}_1]^n = (\mathrm{Abs}_n/\epsilon_n)/[\mathrm{R}_1]^n \tag{2}$$

of the monomer concentration expression given in eq 3. High

$$[\mathrm{R}_1] = 2\mathrm{Abs}_1/\epsilon_1 + (n/\epsilon_n)\mathrm{Abs}_n - [\mathrm{R}_0] \tag{3}$$

dilution data gives ϵ_1(3621 cm^{-1}), and an initial estimate of ϵ_n/n(3350 cm^{-1}) is obtained using the absorptivity of pure liquid alcohol. These relationships explicitly assume the existence of an open hydrogen-bonded dimer absorbing at both 3621 and 3490 cm^{-1} and also presume that oligomeric species are cyclic. The equilibrium constant for dimer formation is calculated using the measured absorptivities at 3521 and 3350 cm^{-1} according to eq 4, which is derived from eq 3 and stoichiometric expressions, eq

$$([\mathrm{R}^0] - [\mathrm{R}_1])/\mathrm{Abs}_n = 2K_2[\mathrm{R}_1]^2/\mathrm{Abs}_n + (n/\epsilon_n) \tag{4}$$

$$[\mathrm{R}^0] = [\mathrm{R}_1] + 2[\mathrm{R}_2] + n[\mathrm{R}_n] \tag{5}$$

$$[\mathrm{R}^0] = [\mathrm{R}_1] + 2K_2[\mathrm{R}_1]^2 + (n/\epsilon_n)\mathrm{Abs}_n \tag{6}$$

5 and 6. K_5 for cyclic pentamer formation is finally found using eq 2 with $n = 5$.

The results of the foregoing treatment of our data are summarized in Table I. Correlation coefficients of fits to the various working equations are consistently 0.998 or higher. Of course dimers and oligomers in the racemic mixture consist of both homochiral and heterochiral species, viz., R → R, S → S, R → S, and S → R in the case of dimers. The measured equilibrium constant for dimer formation in the racemic mixture can be shown to be

$$K_2(\text{racemic mixture}) = \tfrac{1}{2}[K_2(\text{homo}) + K_2(\text{hetero})] \tag{7}$$

which allows determination of K_2(hetero) = 0.841 M^{-1}, corresponding to a standard free energy difference at 23 °C of 2.76 kJ/mol between homodimers and heterodimers. A discussion of cyclic oligomer formation requires additional structural and symmetry assumptions, which will be deferred to a full paper. Sources of intermolecular interactions responsible for the large observed anisometric effects are being sought through experimental investigations of other chiral alcohols and through quantum mechanical and molecular mechanics calculations.

Acknowledgment. We acknowledge support for this work through a grant from the Robert A. Welch Foundation of Houston, Texas. The National Science Foundation provided funds for the purchase of the IR spectrophotometer under the aegis of the Two and Four Year College Instrumentation Program.

Registry No. (*S*)-(+)-2-Butanol, 4221-99-2; (*R*)-(−)-2-butanol, 14898-79-4; (±)-2-butanol, 15892-23-6.

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(10) Extensive reviews of hydrogen-bonding models can be found in: Schuster, P., Zundel, G., Sandorfy, C., Eds. "The Hydrogen Bond"; North Holland Publishing Co.: Amsterdam, 1976; Vol. I–III. Also see: Stokes, R. H. *Chem. Soc. Rev.* **1982**, *11*, 257–282. Egorochkin, A. N.; Skobeleva, S. E. *Russ. Chem. Rev. (Engl. Transl.)* **1979**, *48*, 1198–1211. Smith, F. *Aust. J. Chem.* **1977**, *30*, 23–42, 43–69. Stokes, R. H. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1140–1148. Renner, T. A.; Kucera, G. H.; Blander, M. *J. Chem. Phys.* **1977**, *66*, 177–184. Francis, P. G.; Phutela, R. C. *J. Chem. Thermodn.* **1979**, *11*, 747–756. Bartczak, W. M. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 987–992. Verrall, R. E.; Jacobson, D. K.; Hershberger, M. V.; Lumry, R. W. *J. Chem. Eng. Data* **1979**, *24*, 289–292. Symons, M .C. R.; Thomas, V. K. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1883–1890. Martinez, S.; Edwards, J. *Monatsh. Chem.* **1981**, *112*, 563–579, 683–695. Older works of which we were previously cognizant are: Coburn, W. C., Jr.; Grunwald, E. *J. Am. Chem. Soc.* **1958**, *80*, 1318–1322. Saunders, M.; Hyne, J. B. *J. Chem. Phys.* **1958**, *29*, 1319–1323. Joris, L.; Schleyer, P. v. R.; Osawa, E. *Tetrahedron* **1918**, *24*, 4759–4777.

(11) (*R*)-2-Butanol, $[\alpha]^{24} = -13.74°$ (neat); (*S*)-2-Butanol, $[\alpha]^{24} + 13.80°$ (neat).

(12) Perkin-Elmer 580B Infrared Spectrophotometer with Model 3600 Data Station; mode 4 of the integrated scan modes; spectra digitalized at 1.0-cm^{-1} intervals; NaCl 1.0-mm cells; concentrations range, 0.005–0.200 M.