steric requirements of the ligands. Inasmuch as comparisons and correlations have been reported to exist in the iron(II) and copper(II) metal–amine coördination compounds,[14] it was of interest to observe whether similar correlations could be made in the present situation.

In the matter of wave lengths of maximum absorption, the copper(I) system of complexes shows a much smaller variation than does the iron(II) system. This is reasonable in light of the apparent influence of the solvent system on the copper complexes. Only the copper(I)–2,2′-biquinoline complex shows a large deviation. This is not surprising in view of the unique character of this reagent. (2,2′-Biquinoline gives a specific reaction with the copper(I) ion under most conditions.)

The magnitude of the molar absorptivities do not follow the same pattern in the compounds of the two metallic ions. The value of the copper(I)–2,2′,2″-terpyridine complex appears to be abnormally small. This may be related to the different number of coördination positions filled in the two metal ions, and possibly to the inherent differences in steric requirements of the reagents. Thus, there is a danger in predicting color intensity and sensitivity on the basis of the nature of the reagent alone when comparing dissimilar ions such as iron(II) and copper(I).

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The Electric Moments of Mono- and Diacetylferrocene

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Much interest has centered about the structure of the recently discovered dicyclopentadienyliron, or ferrocene, and similar compounds. The "molecular sandwich" structure proposed by Wilkinson, *et al.*,[1] to explain the unique stability of ferrocene has received support by X-ray diffraction studies[2] and is generally accepted as correct.

Considerable attention has been devoted to the electronic structure of ferrocene. Jaffe[3] concluded from his molecular orbital calculations that in ferrocene there are eight bonding and one nonbonding orbitals. All the orbitals are filled resulting in a diamagnetic ferrocene having the rare gas configuration. The eight bonding molecular orbitals indicate that the iron atom is bound to each of the cyclopentadienyl radicals by four covalent bonds.

Jaffe concluded that there was no barrier to the free rotation of the cyclopentadienyl groups.

More recently, Moffitt[4] described the ferrocene structure in terms of one covalent bond between the iron atom and each of the two cyclopentadienyl groups. This description helps explain the "aromatic" properties of ferrocene. Moffitt, like Jaffe, predicted the free rotation of the two organic rings.

The study of the dipole moments of mono- and diacetylferrocene was undertaken as a means of obtaining experimental evidence for free rotation of the organic rings in ferrocene.

Experimental

Purification of Benzene.—Nitration grade benzene, supplied by the Pittsburgh Coke and Chemical Co., was fractionally crystallized twice by partial freezing in an ice–water bath and decanting the unfrozen benzene. The remaining frozen benzene after melting was stirred at 40–50° with an equal volume of 96%, reagent grade sulfuric acid for several hours and the process repeated until the sulfuric acid layer was colorless. After the acid layer was removed, the benzene was washed with water and then with sodium bicarbonate solution. The benzene was then dried, first, by azeotropic distillation followed by refluxing over sodium and finally fractionally distilled, a central fraction boiling within 0.1° being collected, whose freezing point was 5.5°. The benzene was stored over sodium in the absence of air.

Preparation of Materials.—The monoacetylferrocene, m.p. 89–90°, and the diacetylferrocene, m.p. 130–131°, both of which were well-defined crystalline red solids, were supplied by Drs. R. B. Woodward and M. Rosenblum of Harvard University.

Measurements and Calculations.—The equipment used for the measurement of dielectric constant was based on the heterodyne beat method.[5,6] It consisted of a Clough–Brengle Beat Frequency Audio Oscillator Model 179A modified by replacing a portion of the capacitance by a General Radio Precision Condenser 722F, and a dielectric cell in parallel. The equipment and measurement procedure have been reported in detail.[7,8] The density measurements were made in a 100-ml. flask type pycnometer equipped with calibrated capillary necks, in a manner similar to that reported.[9]

The molar refractions of the acetylferrocenes were calculated from the molar refraction of ferrocene which was determined[10] to be 46.8.

The dielectric constants, densities, weight fractions are given in Table I, along with the empirical constants, and molar polarizations were calculated from them. The molar polarizations were calculated by the Debye method as modified by Halverstadt and Kumler.[11] The empirical constants α and β were obtained graphically from the equations relating the dielectric constants, ϵ_{12}, and the specific volumes V_{12} as linear functions of the weight fraction of the solute

$$\epsilon_{12} = \epsilon_1 + \alpha w_2; \; V_{12} = V_1 + \beta w_2$$

The polarization was then calculated from the equation

$$P_{2\infty} = \frac{3\alpha V_1}{(\epsilon_1 + 2)^2} + (V_1 + \beta)\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

The electric moment was then calculated from

$$\mu = 0.01281 \times 10^{-18} \sqrt{(P_{2\infty} - MR_\mathrm{D})T}$$

Discussion of Results

There are a number of values reported for the

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electric moment of acetophenone 2.97 *D*,[12] 2.90 *D*,[13] 2.77 *D*,[14] 2.96.[15] Hassel reported the value 2.97 four separate times. It therefore appears probable that the moment in benzene is in the range 2.90–2.97 *D*. The electric moment value obtained for monoacetylferrocene, 3.02 *D*, is in good agreement with the acetophenone value, indicating once again the aromatic nature of the ferrocene molecule.[16]

TABLE I

DIELECTRIC CONSTANTS, SPECIFIC VOLUMES, POLARIZATIONS AND MOLECULAR REFRACTIONS OF COMPOUNDS STUDIED, DETERMINED IN BENZENE SOLUTION AT 30.0°

w^a	ϵ	V	$P_{2\infty}$	μ
Monoacetylferrocene, $MR_D = 56.0$, $\alpha = 4.593$, $\beta = -0.4070$				
0.00000	2.2700	1.1508	248.8	3.02
.00619	2.2986	1.1490		
.00705	2.3030	1.1485		
.00729	2.3023	1.1485		
.00768		1.1483		
.00770	2.3051	1.1483		
.00865	2.3094	1.1480		
.00955		1.1478		
.01154	2.3234	1.1466		
.01932	2.3585	1.1433		
Diacetylferrocene, $MR_D = 65.2$, $\alpha = 7.7207$, $\beta = -0.4571$				
0.00000	2.2635	1.1519	424.4	4.23
.00802	2.3216			
.01141	2.3485	1.1465		
.01554	2.3748	1.1449		
.01913	2.3992	1.1432		

[a] The symbols used are; *w*, weight fraction of solute; ϵ, dielectric constant; *V*, specific volume; P_2, solute molar polarization at infinite dilution; MR_D, solute molar refraction for the sodium-D line.

Table I summarizes the dipole moment values of ferrocene and the acetylferrocenes. The zero moment for ferrocene is in accord with the sandwich structure. The equation of Fuchs[17] was developed for the calculation of the resultant moment of compounds with freely rotating angular groups

$$\mu_r = \sqrt{a^2 + b^2 + 2ab \cos \alpha \cos \beta \cos \theta}$$

where α and β are the angles which the resultant of the angular groups make with the axes about which they rotate and θ is the angle between these axes; *a* and *b* are electric moment vectors. Applying this equation

$$\mu = (3.02^2 + 3.02^2 + 2 \times 3.02 \times \cos 90° \cos 90° \cos 180°)^{1/2}$$

The close agreement between the experimental value of diacetylferrocene and that calculated for free rotation is indicative of the probability of free rotation in ferrocene.

If the alternative assumption were made that there was no rotation of the cyclopentadiene groups then the angle between the moment vectors can be calculated from the equation

$$4.23^2 = (3.02^2 + 3.02^2 + 2 \times 3.02 \times \cos \theta)$$

From this it follows that $\theta = 91°$. This result would indicate that the structure of the diacetylferrocene is half-way between the prismatic and the antiprismatic form. A structure intermediate between the prismatic and antiprismatic form would not be centrosymmetrical and hence not in agreement with X-ray data of ferrocene.[18]

Thus the dipole moment data would seem to confirm the free rotation of the cyclopentadiene rings predicted by molecular orbital theory.

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Investigation of Hydrogen Solubility in Molten Alkali Metal Hydroxides

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Under certain conditions, molten alkali metal hydroxides have been observed to absorb appreciable quantities of hydrogen gas. Thus, if sodium hydroxide or potassium hydroxide contained in a nickel vessel is heated to 500° under vacuum and an hydrogen atmosphere admitted, hydrogen is rapidly absorbed into the melt. This investigation was made, therefore, to determine the solubility of hydrogen in molten sodium hydroxide and potassium hydroxide at 500° and pressures up to 800 p.s.i.a. Since the hydrogen solubility would be expected to be greatest just above the melting point of the hydroxide in question, the solubility in potassium hydroxide was determined also at 410°.

In every case the hydrogen solubility was found to be so small that it was within the experimental error of the measurements involved. The absorption of hydrogen into the melt was found not to depend upon the temperature and pressure, as would be expected if the phenomenon were due to dissolution of hydrogen gas into the molten hydroxide but, rather, was found to be related to the previous treatment of the hydroxide. In the absence of conditions which would cause interaction between the hydroxide and its container, no hydrogen absorption was observed. Conversely, when the hydroxide had been subjected to conditions which caused attack on its container, hydrogen absorption was observed. Thus the observed absorption of hydrogen must be due to its interaction with a corrosion product or products, and not to dissolution of hydrogen gas as such in the molten hydroxide.

In the particular case where nickel containers were used, it has been found that heating the hydroxide to 400° under vacuum does not cause detectable corrosion, while heating to 500° under vacuum introduces a nickel corrosion product into the melt. The exact nature of the corrosion is not entirely certain, but it probably may be represented adequately by the equilibrium[1]

$$2NaOH + Ni \rightleftarrows Na_2NiO_2 + H_2$$

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[1] D. D. Williams, private communication; to be published by Wright Air Development Center, as Report WADC Tr 54-185, Part 2.