methyldisilane (6.36 g, 0.030 mol) and 2-butyne (2.9 g, 0.054 mol) were placed neat into a 25-mL thick-walled sealed tube (3-mm glass) and after several freeze–thaw degassing cycles the tube was sealed under a high vacuum (5×10^{-5} torr). The reaction vessel was placed in a Lindberg Type furance and pyrolyzed for 18 h at 250–60 °C. **CAUTION**: During two of the experiments the tube exploded violently; appropriate high-pressure safety procedures should be employed. The tube was removed and cooled to −196 °C before opening. The volatile reaction products, mostly $(MeO)_2SiMe_2$, were removed in vacuo leaving 3.5 g (90%) of crude 1,4-dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene as an oily solid. This material was generally used without further purification, but was recrystallized from CCl_4 if higher purity was required. NMR analysis showed it to be a mixture of cis and trans isomers but absolute assignment was not possible even with the use of Eu(fod)$_3$ shift reagent. NMR (major isomer) ($CDCl_3$) δ 3.20 (s, 6 H), 1.80 (s, 12 H), 0.0 (s, 6 H); (minor isomer) δ 3.17 (s, 6 H), 1.80 (s, 12 H), 0.02 (s, 6 H).

Synthesis of 1,2,3,4,5,6-Hexamethyl-1,4-disilacyclohexa-2,5-diene (2). To a solution of 1.4 g (3.7×10^{-2} mol) of lithium aluminum hydride in 25 mL of THF was added slowly at room temperature 1.5 g (5.8×10^{-3} mol) of a mixture of isomers of 1,4-dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (**1**) over a period of 30 min. The resulting mixture was stirred at room temperature for 24 h and then poured *slowly* onto a mixture of 10% aqueous HCl and crushed ice. The product was extracted with ether, removed, and washed several times with water. The organic layer was dried over sodium sulfate and filtered and removal of the solvent gave 0.80 g (71%) of **2** as a clear liquid. Careful purification by preparative GC (6 ft × $^3/_8$ in. 20% SE30 on Chromosorb W 60/80, 170°) yielded the product as a solid with a melting point slightly above room temperature. NMR (CCl_4, $CHCl_3$) δ 4.1 (m, 2 H, Si-H), 1.8 (s, 12 H, allylic Me), 0.2 (2 d of d, 6 H, Si-CH_3). The Si-CH_3 resonance for each isomer is split into a doublet of doublets by unequal coupling to both Si-H protons. IR 2950, 2900, 2845 (s, C-H stretch), 2085 (vs, Si-H), 1565 (w, C=C), 1360–1450 (w, C-H bending), 1245 cm^{-1} (s, Si-C stretch); MS calcd $C_{10}H_{20}Si_2$ m/e 196.11035, obsd 196.1104, dev 0.25 ppm.

Synthesis of 1,4-Dideuterio-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (3). The procedure was identical with that used in the synthesis of the 1,4-dihydro derivative **2** except that lithium aluminum deuteride was used as the reducing agent. Proton NMR showed collapse of the two doublets of doublets at δ 0.2 for **2** to a broad singlet. NMR (CCl_4, ref $CHCl_3$) δ 1.85 (s, 12 H, allylic methyl), δ 0.2 (bs, 6 H, D-Si-CH_3); MS calcd $C_{10}H_{18}Si_2D_2$ m/e 198.1229, obsd 198.1228, dev 0.5 ppm.

Synthesis of 1,4-Dideuterio-2-butyne. 1,4-Dichloro-2-butyne (6.1 g, 0.05 mol) was slowly added at room temperature to 100 mL of a 1.0 M solution of lithium triethylboron deuteride in THF. The resulting mixture was stirred at 25 °C for 10 h after which an excess of water was slowly added to react with the triethylborane formed. Fractional distillation gave 0.95 g (34%) of 1,4-dideuterio-2-butyne, bp collected 28–32 °C.

Synthesis of Hexadeuterio Derivative 4. The synthesis employed was the same as described for **1** and **2** except that 1,4-dideuterio-2-butyne was used in place of 2-butyne in the synthesis of the 1,4-dimethoxy derivative and lithium aluminum deuteride was used as a reducing agent. NMR δ 0.20 (s, 6 H), 1.75 (t, J = 2 Hz, 8 H); MS calcd 202.1476, obsd 202.1481, dev −4.6 ppm.

Synthesis of 1,4-Dichloro-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-5-diene (5). A solution of 8.5 g (0.033 mol) of a mixture of isomers of **1** in 30 mL of acetyl chloride was heated to reflux for 3 days. The excess acetyl chloride and the methyl acetate formed were distilled under nitrogen with the final amounts being removed under high vacuum. Sublimation (70 °C, 1 torr) from the distillation residue yielded 5.2 g (60%) of 1,4-dichloro-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene. GC analysis showed the product to be a nearly 1:1 mixture of isomers. NMR (CCl_4, $CHCl_3$ ref) (isomer **a**) δ 1.85 (s, 12 H), 0.42 (s, 6 H); (isomer **b**) δ 1.85 (s, 12 H), 0.39 (s, 6 H); MS calcd 264.0324, obsd 264.0325, dev 0.4 ppm.

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Registry No. *cis*-**1a**, 85977-35-1; *trans*-**1a**, 85977-36-2; **1b**, 85995-12-6; **2**, 85977-37-3; **3**, 85977-38-4; **4**, 85995-11-5; *cis*-**5**, 83447-54-5; *trans*-**5**, 83447-55-6; **8a**, 85977-39-5; **8b**, 85977-40-8; **9**, 4363-45-5; **11a**, 85977-41-9; **11b**, 85977-42-0; *tert*-butyl hypochlorite, 507-40-4; *tert*-butyl peroxide, 110-05-4; *sym*-tetramethoxydimethyldisilane, 18107-32-9; 2-butyne, 503-17-3; 1,4-dideuterio-2-butyne, 85977-43-1; 1,4-dichloro-2-butyne, 821-10-3.

Molecular Quadrupole Moments, Magnetic Anisotropies, and Charge Distributions of Ferrocene and Ruthenocene

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Abstract: Measurements of the infinite-dilution molar Kerr constants, field-gradient birefringence constants, and Cotton–Mouton constants of ferrocene and ruthenocene as solutes in cyclohexane at 25 °C are reported. The observations yield the effective polarizability anisotropy, the electric quadrupole moment, and the magnetic anisotropy of each molecule. Analysis of these properties shows that ferrocene and ruthenocene are more polarizable in directions parallel, rather than perpendicular, to the ligand–metal–ligand axes; it suggests that the bonding results in transfer of electronic charge from the metal atom toward the cyclopentadienyl rings; and it enables the observed magnetic anisotropies to be separated into oppositely signed diamagnetic and temperature-independent paramagnetic contributions. A useful new synthesis of ruthenocene is described.

Introduction

Although the basic qualitative features of the bonding in ferrocene and related metallocenes are considered to be well understood,[1] it is nevertheless true, as noted by Haaland,[2] that little is known with certainty concerning the charge distributions in such molecules. In the case of ferrocene, much controversy has surrounded the question of whether the bonding results in transfer of electronic charge *to* or *from* the cyclopentadienyl rings.[3] Early molecular-orbital studies[4,5] generated conflicting views, but subsequent theoretical work,[6] with a wide range of computational

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models, has predicted that the iron atom carries a net *positive* charge, albeit of uncertain magnitude. In fact, it was recently shown[7,8] that large-scale ab initio LCAO–SCF calculations, using basis sets of better than triple-ζ quality, are unable to account for the observed metal-to-ring distance in ferrocene, and that the Mulliken population analysis is of little value in relation to the effective charge on the iron atom. Likewise, available experimental evidence is insufficient to define the charge distributions in ferrocene and other metallocenes.

The electric quadrupole moment[9] and the magnetic anisotropy[10] are observable manifestations of the molecular charge distribution and its interaction with electric and magnetic fields. Procedures developed in this laboratory, involving the measurement of field-induced birefringence in dilute solutions, are well established[11] as a particularly useful route to electric and magnetic properties of involatile nondipolar molecules, which cannot easily be examined by other methods. We have now determined the quadrupole moments and magnetic anisotropies of ferrocene and ruthenocene as solutes in cyclohexane at 25 °C, and we show here that these fundamental properties provide considerable insight into the molecular charge distributions. There are, in addition, close relationships between these and other electric and magnetic quantities: the anisotropy in the second moment of the electronic charge distribution, the diamagnetic and temperature-independent paramagnetic contributions to the magnetizability, and the molecular *g* value. The quadrupole moments reported here are the first determinations for organometallic molecules. Estimates of the magnetic anisotropies of ferrocene[12] and ruthenocene[13] have previously been obtained from direct measurements on single crystals, but interpretations[14] of the results in terms of π-electron theories are incorrect and seriously misleading, as others have noted.[15]

Theory

Our objective is to obtain experimental values of the quadrupole moments and magnetic anisotropies of ferrocene and ruthenocene from the measured infinite-dilution molar Kerr, field-gradient birefringence and Cotton–Mouton constants of these molecules. For a nondipolar molecule possessing a threefold or higher-order rotation axis (labeled with subscript *z*) the theoretical expressions for these properties are, in SI units[11]

$$ {}_{\mathrm{m}}K = (N_{\mathrm{A}}/405\epsilon_0 kT)(\Delta\alpha^0/\Delta\alpha)(\Delta\alpha)^2 \tag{1}$$

$$ {}_{\mathrm{m}}Q = (2N_{\mathrm{A}}/45\epsilon_0 kT)\ \Delta\alpha f\Theta \tag{2}$$

$$ {}_{\mathrm{m}}C = (N_{\mathrm{A}}\mu_0{}^2/405\epsilon_0 kT)\Delta\alpha\Delta\chi \tag{3}$$

in which $\Delta\alpha^0(=\alpha^0{}_{zz}-\alpha^0{}_{xx})$ and $\Delta\alpha(=\alpha_{zz}-\alpha_{xx})$ are the effective anisotropies in the static and optical frequency molecular polarizabilities; f arises from a consideration of the quadrupole moment induced in a molecule by its own reaction-field gradient;[16] $\Theta(=\Theta_{zz}=-2\Theta_{xx})$ is the unique molecular quadrupole moment; $\Delta\chi(=\chi_{zz}-\chi_{xx})$ is the anisotropy in the molecular magnetizability; and other symbols have their usual meanings. Note that hyperpolarizabilities,[17] considered to be negligibly small, have been omitted from eq 1–3. The Kerr constant therefore defines, through eq 1, the polarizability anisotropy, knowledge of which enables the field-gradient birefringence and Cotton–Mouton constants to be analyzed, using eq 2 and 3, to yield the quadrupole moment and magnetic anisotropy, respectively.

The molecular quadrupole moment is defined by the equation[9]

$$\Theta_{\alpha\beta} = \left\langle 0\left|\frac{1}{2}\sum_j e_j(3r_{j\alpha}r_{j\beta} - r_j{}^2\delta_{\alpha\beta})\right|0\right\rangle \tag{4}$$

in which the summation is over all nuclear and electronic charges, e_j, and $r_{j\alpha}$ is the position vector locating the *j*th charge. It is of interest to separate the nuclear (subscript *n*) and electronic (subscript *i*) contributions to $\Theta_{\alpha\beta}$, and for an axially symmetric molecule eq 4 can be written as

$$\Theta = e\sum_n Z_n(z_n{}^2 - x_n{}^2) - e(0|\sum_i(z_i{}^2 - x_i{}^2)|0\rangle = e\sum_n Z_n(z_n{}^2 - x_n{}^2) - e\{(z^2) - (x^2\rangle\} \tag{5}$$

where e is the protonic charge, Z_n is the atomic number of the *n*th nucleus, and $e\{(z^2) - (x^2\rangle\}$ is the anisotropy in the second moment of the electronic charge distribution. From perturbation theory the magnetizability of a diamagnetic molecule is[10,18]

$$\chi_{\alpha\beta} = -\frac{e^2}{4m_e}(0|\sum_i(r_i{}^2\delta_{\alpha\beta} - r_{i\alpha}r_{i\beta})|0\rangle + \frac{e^2\hbar^2}{4m_e{}^2}\sum_k{}' \frac{(0|L_\alpha|k\rangle(k|L_\beta|0\rangle + (0|L_\beta|k\rangle(k|L_\alpha|0\rangle}{E_{\mathrm{k}} - E_0} = \chi_{\alpha\beta}{}^d + \chi_{\alpha\beta}{}^p \tag{6}$$

and since $\Delta\chi^d$ can be written in terms of the electronic contribution to the molecular quadrupole moment as

$$\Delta\chi^d = \frac{e^2}{4m_e}\{(z^2\rangle - (x^2\rangle\} = \frac{e^2}{4m_e}\left\{\sum_n Z_n(z_n{}^2 - x_n{}^2) - \frac{\Theta}{e}\right\} \tag{7}$$

the separation of $\Delta\chi$ into diamagnetic and temperature-independent paramagnetic terms is readily effected. It is clear from the foregoing that if the arrangement in space of the nuclei is known, the electric quadrupole moment and the magnetic anisotropy can provide useful information concerning the electronic charge distribution.

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Table I. Infinite-Dilution Molar Kerr Constants, ${}_{\infty}({}_{\mathrm{m}}K_2)$, Field-Gradient Birefringence Constants, ${}_{\infty}({}_{\mathrm{m}}Q_2)$, and Cotton-Mouton Constants, ${}_{\infty}({}_{\mathrm{m}}C_2)$, from Observations of Incremental Birefringences of Solutions of Metallocenes MCp_2 (M = Fe,Ru) in Cyclohexane at 298 K and 632.8 nm[a]

property[b]	M	solutions[c]	concn dependence	birefringence param	birefringence const
(1)	Fe	1.0–2.0, 15	$10^{15}\Delta K = (3.44 \pm 0.26)w_2$	$\delta = 6.19 \pm 0.47$	${}_{\infty}({}_{\mathrm{m}}K_2) = (17.9 \pm 1.3) \times 10^{-27}$ m^5 V^{-2} mol^{-1}
	Ru	1.2–1.9, 12	$10^{15}\Delta K = (2.99 \pm 0.20)w_2$	$\delta = 5.39 \pm 0.37$	${}_{\infty}({}_{\mathrm{m}}K_2) = (19.2 \pm 1.3) \times 10^{-27}$ m^5 V^{-2} mol^{-1}
(2)	Fe	0.5–2.6, 8	$10^{15}\Delta Q = (-26.0 \pm 5.8)w_2$	$\xi = 25.0 \pm 5.6$	${}_{\infty}({}_{\mathrm{m}}Q_2) = (-169 \pm 37) \times 10^{-26}$ m^5 V^{-1} mol^{-1}
	Ru	1.9–2.1, 6	$10^{15}\Delta Q = (-19.4 \pm 3.6)w_2$	$\xi = 18.7 \pm 3.4$	${}_{\infty}({}_{\mathrm{m}}Q_2) = (-157 \pm 28) \times 10^{-26}$ m^5 V^{-1} mol^{-1}
(3)	Fe	0.8–2.0, 9	$10^{15}\Delta C = (-4.33 \pm 0.24)w_2$	$\delta' = 24.9 \pm 1.4$	${}_{\infty}({}_{\mathrm{m}}C_2) = (-39.3 \pm 2.1) \times 10^{-27}$ m^5 A^{-2} mol^{-1}
	Ru	1.1-1.9, 13	$10^{15}\Delta C = (-2.06 \pm 0.22)w_2$	$\delta' = 11.8 \pm 1.3$	${}_{\infty}({}_{\mathrm{m}}C_2) = (-23.5 \pm 2.4) \times 10^{-27}$ m^5 A^{-2} mol^{-1}

[a] Quoted precisions are 90% confidence limits derived by standard statistical treatment of experimental data; the absolute accuracies are not greater than ±5% because of calibration uncertainties and other systematic errors. [b] (1) Molar Kerr constant; (2) molar field-gradient birefringence constant; (3) molar Cotton–Mouton constant. [c] Data shown indicate the approximate weight-fraction concentration range (expressed as $10^2 w_2$) and the number of solutions from which the concentration dependences of the bulk birefringence constants (*K*, *Q*, and *C*) were determined. [d] $\delta = (\Delta K/w_2K_1)_{w_2=0}$; $\xi = (\Delta Q/w_2Q_1)w_{2=0}$; $\delta' = (\Delta C/w_2C_1)w_{2=0}$.

Experimental Section

Materials. The original synthesis of ruthenocene by Wilkinson[19] involved the reaction of ruthenium(III) acetylacetonate with an excess of cyclopentadienylmagnesium bromide and gave a yield of about 20%. A method developed by Rausch, Fischer, and Grubert[20] utilized the reaction of sodium cyclopentadienide and ruthenium trichloride and yielded 43–52% of the product. A similar procedure, but involving chlorination of ruthenium to give a mixture of ruthenium trichloride and the metal, was reported by Bublitz, McEwen, and Kleinberg[21] to yield 56–69% of ruthenocene, based on the total amount of ruthenium present. An improved synthesis is now described, in which sodium cyclopentadienide is reacted with dichlorotetrakis(dimethyl sulfoxide)ruthenium(II), $RuCl_2(Me_2SO)_4$, the latter being formed through the reduction of ruthenium trichloride by hydrogen in dry dimethyl sulfoxide. Use of this intermediate has several advantages: its preparation from ruthenium trichloride is simple and nearly quantitative; it contains coordinated Me_2SO which is a good leaving group with respect to substitution by Cp^-; and, most importantly, it contains ruthenium(II) exclusively, so that reduction is not required to form the product.

$RuCl_3{\cdot}2.4H_2O$[22] (Johnson Matthey Chemicals Ltd., 5.80 g, 0.023 mol) and Me_2SO (60 mL, dried over molecular sieves) were stirred at 76–80 °C, and hydrogen gas was bubbled through the mixture for 20 h.[23] The solution was then cooled, yellow crystals of $RuCl_2(Me_2SO)_4$ were filtered off, and the mother liquor was evaporated to dryness under vacuum (80 °C, liquid-nitrogen cooled Dewar condenser). The combined products were washed with acetone and dried under vacuum (24 °C, 0.05 mmHg). Anal.[22] ($RuCl_2C_8H_{24}S_4O_4$)Ru,Cl,C,H,S.

A threefold excess (11.7 g, 0.13 mol) of crystalline sodium cyclopentadienide, NaCp, prepared by reacting fresh cyclopentadiene with sodium in dry 1,2-dimethoxyethane, was added to a two-necked 500-mL flask containing the $RuCl_2(Me_2SO)_4$; dry, 1,2-dimethoxyethane (200 mL) was added and the mixture was refluxed for 80 h. The solution was then cooled, distilled water (4 mL) was added, the solvent was removed by rotary evaporation, and the remaining dark solid was transferred to a Soxhlet apparatus for extraction into benzene. After reduction to about 40 mL the benzene solution was passed through a 50-cm column of freshly activated alumina; elution was continued until the first yellow-colored band had almost reached the outlet. The eluate gave pale-yellow crystalline ruthenocene, mp 199.5–200 °C cor), yield 4.68 g (87% based on $RuCl_3{\cdot}2.4H_2O$, range 72–87%).[24]

Ferrocene was purified by an initial high-vacuum sublimation onto an ice-cooled probe; it was then recrystallized from cyclohexane and resublimed several times. The solvent, Merck analytical reagent grade cyclohexane, was dried and fractionated before use.

Apparatus, Procedures, and Results. Apparatus and procedures for determining the infinite-dilution molar Kerr constants, ${}_{\infty}({}_{\mathrm{m}}K_2)$, field-gradient birefringence constants, ${}_{\infty}({}_{\mathrm{m}}Q_2)$, and Cotton–Mouton constants, ${}_{\infty}({}_{\mathrm{m}}C_2)$, of ferrocene and ruthenocene as solutes in cyclohexane were as previously described.[11,25] Unfortunately, the precision of the observations was limited by the low solubility of these compounds in cyclohexane; carbon tetrachloride, the preferred solvent for dilute-solution field-gradient birefringence studies, is thought to react, under irradiation, with ferrocene,[26] while benzene and dioxane are unsuitable for such measurements because both possess a large molecular quadrupole moment.

The definitions of ${}_{\infty}({}_{\mathrm{m}}K_2)$, ${}_{\infty}({}_{\mathrm{m}}Q_2)$ and ${}_{\infty}({}_{\mathrm{m}}C_2)$ in terms of experimental observables are, with symbols, solvent constants, etc. as in ref 11 and 25,

$${}_{\infty}({}_{\mathrm{m}}K_2) = {}_{\mathrm{s}}K_1(1 - \beta - F\gamma - J\alpha\epsilon_1 + \delta)M_2 \tag{8}$$

$${}_{\infty}({}_{\mathrm{m}}Q_2) = {}_{\mathrm{s}}Q_1(1 - \beta - F\gamma - L\alpha\epsilon_1 + \xi)M_2 \tag{9}$$

$${}_{\infty}({}_{\mathrm{m}}C_2) = {}_{\mathrm{s}}C_1(1 - \beta - F\gamma + \delta')M_2 \tag{10}$$

in which quantities obtained from incremental densities, refractive indices, and relative permittivities of solutions are, for ferrocene, $\beta = 0.435$, $\gamma = 0.085$, and $\alpha\epsilon_1 = 0.347$; and for ruthenocene, $\beta = 0.536$, $\gamma = 0.083$, and $\alpha\epsilon_1 = 0.365$. Details of the birefringence measurements are shown in Table I, which includes the concentration ranges and numbers of solutions examined for each property, the concentration dependences of the bulk birefringence constants *K*, *Q*, and *C*, derived values of δ, ξ, and δ', and the infinite-dilution molar birefringence constants. SI units are used throughout; factors for converting relevant quantities to nonrationalized cgs esu or emu have been given elsewhere.[11]

Discussion

Polarizability Anisotropies. It is apparent that analysis of the experimental Kerr constants of the metallocenes through eq 1 leads to the magnitude, but not the sign, of the anisotropy in the molecular polarizability. However, the magnetic anisotropies, $\Delta\chi$, of ferrocene and ruthenocene are known[12,13] to be negative in sign and, since the experimental Cotton–Mouton constants (Table I) are also negative, it follows from eq 3 that the polarizability anisotropies, $\Delta\alpha$, are *positive in sign*. In consequence, and notwithstanding earlier assertions to the contrary,[27] ferrocene and ruthenocene are, as expected, more polarizable in directions parallel, rather than perpendicular, to the C_5 axes.

In order to use eq 1 to determine the polarizability anisotropy it is also necessary, in the absence of appropriate experimental data, to estimate the ratio, $\Delta\alpha^0/\Delta\alpha$, of the static to the high-frequency anisotropy. The difference between $\Delta\alpha^0$ and $\Delta\alpha$ is determined by two factors: the dispersion of the anisotropy in the electronic polarizability; and the corresponding anisotropy in the atomic polarizability, which depends on the symmetry of the infrared-active vibrational modes giving rise to the atomic po-

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Table II. Analysis of the Infinite-Dilution Molar Kerr Constants, Field-Gradient Birefringence Constants, and Cotton–Mouton Constants of Metallocenes MCp_2 (M = Fe,Ru)

property	M = Fe	M = Ru
$10^{27}{}_{m}K/m^5\ V^{-2}\ mol^{-1}$	17.9 ± 1.3	19.2 ± 1.3
$\Delta\alpha^0/\Delta\alpha$	1.00 ± 0.05	1.00 ± 0.05
$10^{40}\Delta\alpha/C\ m^2\ V^{-1}$	6.62 ± 0.29	6.85 ± 0.28
$10^{26}{}_{m}Q/m^5\ V^{-1}\ mol^{-1}$	−169 ± 37	−157 ± 28
f^a	1.15	1.15
$10^{40}\Theta/C\ m^2$	−30 ± 7	−27 ± 5
$10^{10}r_C/m^b$	2.064	2.196
$10^{10}r_H/m^b$	2.818	2.978
$10^{10}z_C/m^b$	1.661	1.823
$10^{10}z_H/m^b$	1.590	1.823
$10^{40}e\Sigma Z_n(z_n^2 - x_n^2)/C\ m^2$	1903	2564
$-10^{40}e\{\langle z^2\rangle - \langle x^2\rangle\}/C\ m^2$	−1933	−2591
q_M	+0.9	+0.7
$10^{27}{}_{m}C/m^5\ A^{-2}\ mol^{-1}$	−39.3 ± 2.1	−23.5 ± 2.4
$10^5\Delta\chi/J\ T^{-2}\ mol^{-1}$	−55.5 ± 3.9	−32.1 ± 3.6
$10^5\chi/J\ T^{-2}\ mol^{-1}\ {}^c$	−125	−150
$10^5\chi_{xx}/J\ T^{-2}\ mol^{-1}$	−106	−139
$10^5\chi_{zz}/J\ T^{-2}\ mol^{-1}$	−162	−171
$10^5\Delta\chi^d/J\ T^{-2}\ mol^{-1}$	512	686
$10^5\Delta\chi^p/J\ T^{-2}\ mol^{-1}$	−567	−718

[a] Assumed value; see ref 11a. [b] Reference 30. [c] Reference 14b.

larization. Information concerning $\Delta\alpha^0/\Delta\alpha$ is available for only a few simple molecules. In the case of benzene, the dispersion and atomic polarization effects cooperate to make $\Delta\alpha^0/\Delta\alpha$ less than unity, and a value of 0.93 was derived from an analysis[28] of the temperature dependence of vapor-phase electric birefringence. The situation is somewhat different in the metallocenes, in that the out-of-plane C–H bending and metal-ligand vibrations, which can be expected to dominate the atomic polarization, primarily augment the larger component (α_{zz}) rather than the smaller component (α_{xx}) of the polarizability. For this reason the dispersion and atomic polarization contributions could be of opposite sign and in the present calculations, summarized in Table II, we have taken $\Delta\alpha^0/\Delta\alpha$ as 1.00 ± 0.05.

It must be emphasized that polarizability anisotropies derived by application of eq 1 to solutes at infinite dilution in a nondipolar solvent are *apparent* values which reflect the inadequacy of the spherical Lorenz–Lorentz effective field in relation to the polarizability of an anisometric molecule in a dense medium. However, it has been established experimentally[11] and theoretically[29] that reliable values of the molecular quadrupole moment and the magnetic anisotropy are obtained when the infinite-dilution field-gradient birefringence constant and Cotton–Mouton constant, respectively, are analyzed in conjunction with the apparent polarizability anisotropy deduced from the infinite-dilution Kerr constant of the solute in the same solvent.

Molecular Quadrupole Moments. Substitution of the polarizability anisotropies and the observed field-gradient birefringence constants into eq 2 leads to molecular quadrupole moments (expressed here and elsewhere as $10^{40}\Theta/C\ m^2$) of −30 ± 7 for ferrocene and −27 ± 5 for ruthenocene. For comparison, the quadrupole moments of benzene and hexafluorobenzene are −33.3 ± 2.1 and +31.7 ± 1.7, respectively.[11a] The quadrupole moment is, by definition, a measure of the extent to which the total molecular charge distribution deviates from sphericity. With the assumption that the isolated atoms have negligibly small quadrupole moments, the molecular moment can be considered a manifestation of the reorganization of the electronic charge distribution which accompanies bond formation; if the atoms had spherical charge distributions the molecular quadrupole moment would be zero. From the foregoing it is obvious that since the quadrupole moments of ferrocene and ruthenocene are indistinguishable within the errors, the electronic charge distributions in these two molecules must be very similar, as expected.

Some insight into the nature of the charge distributions can be gained by using the known internuclear distances, determined by gas-phase electron diffraction,[30] to calculate the nuclear contributions, $e\sum Z_n(z_n^2 - x_n^2)$, to the quadrupole moments; the corresponding electronic contributions, $e\{\langle z^2\rangle - \langle x^2\rangle\}$, then follow by difference from the measured quadrupole moments and eq 5. From the results in Table II it is clear that the quadrupole moment originates in a slight imbalance (≈ 1–2%) between the large, oppositely signed nuclear and electronic terms, a consequence of redistribution of the valence electrons relative to the nuclei. The quadrupole moment is therefore rather a subtle property, and for molecules as large as ferrocene and ruthenocene reliable prediction of even the sign, let alone the magnitude, of the moment would be difficult if not impossible by current computational procedures.[8] In both ferrocene and ruthenocene the imbalance is such that the anisotropy in the second moment of the electronic charge distribution, $e\{\langle z^2\rangle - \langle x^2\rangle\}$, is more positive than would be required for a zero molecular quadrupole moment. Of course this could be a consequence of either a *larger* value of $\langle z^2\rangle$ or a *smaller* value of $\langle x^2\rangle$, relative to the free atoms. However, bond formation in the metallocenes clearly requires some redistribution of electronic charge along the *z* direction (the ligand–metal–ligand axis) so that the former effect is likely to be by far the more important. It therefore follows that the *bonding results in transfer of electronic charge from the metal atom towards the cyclopentadienyl rings.*

A quantitative estimate of the extent of the charge transfer can be obtained by invoking a simple point-charge model. For the axially symmetric distribution of point charges q_M (M = Fe or Ru), q_H, and q_C (all in protonic charge units) comprising the metallocene, the expression for the molecular quadrupole moment is

$$\Theta = \frac{1}{2}e\sum_j q_j(3z_j^2 - r_j^2)$$

$$= \frac{1}{2}e\sum_j q_j r_j^2(3\cos^2\phi_j - 1) \qquad (11)$$

where ϕ_j is the inclination to the *z* axis of the position vector r_j which locates the charge q_j with respect to the nucleus of the metal atom as origin. Obviously q_M does not contribute to the moment relative to this origin, and, coincidentally, in both ferrocene and ruthenocene the charges q_H are positioned[30] so close to the conical surface defined by $\phi_j = \cos^{-1}(1/\sqrt{3}) = 54.7°$ (M = Fe, 55.6°; Ru, 52.2°) that their contribution to the quadrupole moment is negligibly small in comparison with that from the charges q_C. In consequence, it is possible to simplify eq 11 to

$$\Theta \approx 5eq_C(3z_C^2 - r_C^2) \qquad (12)$$

and if it is further assumed that $q_H \approx 0$, the approximate charge on the metal atom is

$$q_M \approx -2\Theta\{e(3z_C^2 - r_C^2)\}^{-1} \qquad (13)$$

The reliability of the values of q_M (Table II) derived from eq 13 ($q_{Fe} = +0.9$; $q_{Ru} = +0.7$) is, of course, limited by the validity or otherwise of the point-charge model, but it nevertheless seems clear that the charges on iron and ruthenium are very nearly the same. Several other experimental methods (e.g., NMR[31] and photoelectron[32] spectroscopy; magnetic anisotropies;[12-14] chemical

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reactivities[1]) have been applied to the problem of the charge distribution in metallocenes and related molecules. However, the only other reliable numerical result is that obtained for ferrocene ($q_{\mathrm{Fe}} = +0.7$) by Barinskii and others[33] from studies of X-ray K-absorption spectra; the concordance with our estimates is very satisfactory. It is also of interest to note that such a charge on the metal atom is in excellent agreement with the result of the original semiempirical molecular-orbital treatment of ferrocene by Shustorovich and Dyatkina ($q_{\mathrm{Fe}} = +0.7$),[4] but at variance with that of Dahl and Ballhausen ($q_{\mathrm{Fe}} = -0.7$).[5] The many subsequent theoretical investigations[6–8] have used a range of increasingly sophisticated computational models to yield a very wide span of values for q_{Fe}: -1.0 to $+1.9$. In spite of some contrary predictions, the weight of evidence indicates that the metal atom carries a net positive charge, although of uncertain magnitude. It is beyond the scope of the present report to attempt any further appraisal of these studies.[34]

Magnetic Anisotropies. Magnetic anisotropies (expressed here and elsewhere as $10^5\,\Delta\chi/\mathrm{J\,T^{-2}\,mol^{-1}}$) emerge from eq 3 as -55.5 ± 3.9 for ferrocene and -32.1 ± 3.6 for ruthenocene. Values of $\Delta\chi$ have also been obtained by Mulay and collaborators using a variant of the original Krishnan method, in which the torque acting on an anisotropic, diamagnetic single-crystal suspended in a magnetic field is measured; results were reported as -56.0 and -40.0 for ferrocene and ruthenocene, respectively. However, the molecular magnetizabilities so derived[12,13] clearly do not satisfy the symmetry requirement that $\chi_{xx} = \chi_{yy} \neq \chi_{zz}$, and it has been suggested[35] that they are in error, possibly because of difficulties concerning the relationships between the crystalline and molecular anisotropies. No such difficulties attend the derivation of free-molecule magnetic anisotropies from the infinite-dilution Kerr and Cotton–Mouton constants.

In considering the magnitudes of these magnetic anisotropies in comparison with those of other molecules, it is of interest to note that the corresponding values for benzene and hexafluorobenzene, in both of which there is a high degree of electron delocalization, are -63.8 ± 2.4 and -38.6 ± 1.7, respectively.[11f] The anisotropies of the metallocenes are therefore *not* specially large for molecules which contain *two* potentially delocalized ring systems: ferrocene has a slightly smaller value of $|\Delta\chi|$ than benzene, while that for ruthenocene is only half as large. In fact, the observed anisotropies of both ferrocene and ruthenocene are smaller than the value (-69.4) expected for a hypothetical structure in which two uncharged cyclopentadiene molecules, of known magnetic anisotropy (-34.7),[36] sandwich an isotropically magnetizable metal atom. It may be noted also that replacement of iron by ruthenium causes an *increase* in $|\chi|$ but a *decrease* in $|\Delta\chi|$, for the reason that $|\chi_{xx}|$ is affected to a greater extent than $|\chi_{zz}|$.

A more detailed analysis of the magnetic anisotropies is greatly complicated by the fact that the observed effect is determined by a fine balance between the large and oppositely signed diamagnetic ($\Delta\chi^{\mathrm{d}}$) and temperature-independent paramagnetic ($\Delta\chi^{\mathrm{p}}$) contributions. The diamagnetizability originates in the ability of a magnetic field to cause electron circulation within the undistorted molecular orbitals, so that a magnetic moment and a field in opposition to that applied are established. The paramagnetic contribution arises from the perturbing effect of the magnetic field, which also excites a paramagnetic current through the molecular framework by mixing in higher-energy states.[37] It is the latter which contains the correlation with electron delocalization and aromaticity,[38] so that the analysis in terms of eq 4–7 (Table II) is of interest. It is also worthy of emphasis that, as with benzene and other aromatic molecules,[39] it is likely that a significant fraction, perhaps as much as one-third to one-half, of the magnetic anisotropy of each metallocene originates in localized effects.

The foregoing discussion effectively identifies major shortcomings in earlier accounts[12–14] of the magnetic properties of the metallocenes and other molecules. First, since the observed magnetic anisotropies of ferrocene and ruthenocene cannot be considered solely as manifestations of π-electron delocalization, interpretations of this property by Mulay and collaborators in terms of Pauling's ring-current model are unacceptable and seriously misleading. Second, because of lack of information concerning either the molecular quadrupole moments or the *g* values, it has hitherto been impossible to achieve a reliable separation of the mean magnetizabilities and the magnetic anisotropies into diamagnetic and temperature-independent paramagnetic contributions. The effects of this difficulty have, in general, been greatly compounded by unsoundly based attempts to separate these terms. In particular, the procedure of Dorfman,[40] which is based on Kirkwood's approximate expression for the mean electric polarizability, has yielded mean dia- and paramagnetizabilities for benzene and other molecules which can now be seen to be in error by one or two orders of magnitude.[41] However, it is now obvious that for large, highly anisometric molecules such as ferrocene and ruthenocene $|e\sum Z_n(z_n^2 - x_n^2)| \gg |\Theta|$, in which case $\Delta\chi$ can be partitioned, using eq 7, into $\Delta\chi^{\mathrm{d}}$ and $\Delta\chi^{\mathrm{p}}$ on the basis of the molecular structure alone, without knowledge of the quadrupole moment.

Conclusions

Several important conclusions emerge from this study of electric and magnetic properties of ferrocene and ruthenocene. First, in contrast to earlier findings, an analysis of the Kerr and Cotton–Mouton constants shows unambiguously that these molecules are more polarizable in directions parallel, rather than perpendicular, to the ligand–metal–ligand axes. Second, the fact that the molecular quadrupole moments are negative in sign establishes conclusively that, relative to the free atoms, the bonding results in transfer of electronic charge from the metal atom toward and onto the cyclopentadienyl rings. A simple point-charge model indicates that the effective charges on the iron and ruthenium atoms are approximately +0.9 and +0.7 protonic charge unit, respectively; the result for ferrocene is in agreement with the only other reliable experimental value, obtained from X-ray K-absorption spectra. Finally, a knowledge of the molecular quadrupole moments makes possible the separation of the magnetic anisotropies of these molecules into diamagnetic and temperature-independent paramagnetic terms. The fact that these oppositely signed contributions are, in each case, at least an order of magnitude larger than the net effect, which is observed, is a major reason for serious shortcomings in previous interpretations of the magnetic anisotropies of the metallocenes.

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Registry No. $\mathrm{RuCl_2(Me_2SO)_4}$, 11070-19-2; $\mathrm{RuCp_2}$, 1287-13-4; $\mathrm{FeCp_2}$, 102-54-5; $\mathrm{RuCl_3}$, 10049-08-8; NaCp, 4984-82-1; $\mathrm{Me_2SO}$, 67-68-5.

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