

CONTRIBUTION FROM THE R. G. WRIGHT LABORATORY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, NEW JERSEY, THE MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA, AND THE BELL TELEPHONE LABORATORIES, MURRAY HILL, NEW JERSEY

Systematics of Mössbauer Isomer Shifts of Iron-Organic Compounds

By R. H. HERBER, R. B. KING, AND G. K. WERTHEIM

Received May 17, 1963

The resonant γ -ray absorption spectra of 51 iron-organic compounds (in which iron has an effective atomic number of 36) have been obtained at 78°K., and quadrupole splittings and isomer shifts (referred to a source of Co^{57} diffused into metallic chromium) have been determined. The latter parameter, which is sensitive to the chemical environment of the iron atom, can be treated as the sum of the partial isomer shifts, ζ_i , of the individual ligands. For ligands without appreciable electron delocalization, a single ζ_i value satisfies the additivity properties of the partial isomer shift. For π -cyclopentadienyl derivatives, the appropriate $\zeta_{\text{C}_5\text{H}_5}$ value can be correlated with proton n.m.r. chemical shifts. Inequality of the intensity of the two components of quadrupole split resonance lines has been observed in a number of polycrystalline metal-organic compounds. This asymmetry is related to the anisotropy of the recoil-free fraction relative to the crystallographic axes of the individual crystallites.

1. Introduction

Of the several parameters related to molecular structure which can be extracted from Mössbauer (resonant γ -ray absorption) spectra, the isomer shift (I.S.), the quadrupole splitting (Q.S.), and the temperature dependence of the recoil-free fraction (d^2f/dT) have been of greatest interest to chemists. Since the initial study of ferrocene and related compounds,¹⁻⁴ a number of other iron-organic compounds have been studied with respect to their Mössbauer spectra.^{5,6} The wealth of the resultant data has made evident a simple correlation between I.S. and the chemical nature of the ligand bonded to the Fe^{57} atom.

2. Origin of the Isomer Shift

The isomer shift is the dominant contribution to the displacement from zero velocity of the centroid of the Mössbauer resonance spectrum and was first identified by Kistner and Sunyar.⁷ This effect arises from the interaction between the nuclear charge distribution and the extranuclear electrons, principally those in s states.

The change in the energy of a γ -ray resulting from a nucleus undergoing a transition from an excited state with a nuclear potential $V_e(r)$ to a ground state with a nuclear potential $V_g(r)$ is given by

$$\Delta E = \int P(r)[V_e(r) - V_g(r)]4\pi r^2 dr$$

where $P(r)$ is the probability distribution of an s-electron in the neighborhood of the center of the nuclear charge distribution. Using an expression developed by Bodmer⁸ for a charge distribution characterized only by the mean square radius value, the energy difference

can be written as

$$\Delta E = F(z)|\Psi_s(o)|^2\delta R_u/R_u$$

in which $\Psi_s(o)$ is the s-electron wave function at the iron nucleus and R_u is the radius of equivalent charge distribution. Although ΔE is by itself not measurable, the difference in ΔE between a source iron atom (ΔE_s) and absorber iron atom (ΔE_a) can be extracted from the Mössbauer data. The displacement of the center of the resonance spectrum from zero velocity gives the Doppler velocity, v , required to effect γ -ray resonance between the source and the absorber. From this velocity the Doppler energy is

$$\begin{aligned} \delta E &= \frac{v}{c} E_0 = \Delta E_a - \Delta E_s \\ &= F(z) \frac{\delta R_u}{R_u} [|\Psi(o)|_a^2 - |\Psi(o)|_s^2] \end{aligned}$$

in which E_0 is the (14.4 kev.) nuclear level transition energy, and the s-electron wave functions refer to the absorber and source, respectively. An appropriate value for the radius of equivalent uniform charge separation, R_u , is⁹ $\sim 1.2A^{1/3} \times 10^{-13}$ cm. = 4.6×10^{-13} cm. A value of 1.8×10^{-3} has been calculated for the fractional change in the charge radius, $\delta R_u/R_u$, for the isomeric and ground state configurations of Fe^{57} ,¹⁰ with the effective radius of the ground state larger than that of the excited state.

3. Experimental

With the exception of $\text{Fe}(\text{CO})_5$ and $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_5$ all of the compounds used as absorbers in the present study are solids at room temperature. The samples—usually in the form of microcrystalline powders—were compressed into layers approximately 10 mils thick, sandwiched between layers of aluminum foil, and clamped into a copper holder. This in turn was affixed to the bottom of the cooling block of a dewar provided with thin windows in the same arrangement employed in previously reported studies.^{11,12} The treatment of liquid $\text{Fe}(\text{CO})_5$ has also been discussed earlier.¹³

(1) R. H. Herber and G. K. Wertheim, "The Mössbauer Effect," Proc. of the 2nd Intern. Conf. on the Mössbauer Effect, Saclay, Sept., 1961, John Wiley and Sons, New York, N. Y., 1962, p. 105; 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961; see also U. Zahn, P. Kienle, and H. Eicher, *Z. Physik*, **166**, 200 (1962).

(2) L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

(3) A. D. Harris, R. H. Herber, H. B. Jonassen, and G. K. Wertheim, *J. Am. Chem. Soc.*, **85**, 2927 (1963).

(4) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **38**, 2106 (1963).

(5) M. Kalvius, et al., *Z. Naturforsch.*, **17a**, 494 (1962); R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(6) G. K. Wertheim and R. H. Herber, *J. Am. Chem. Soc.*, **84**, 2274 (1962).

(7) O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960).

(8) A. R. Bodmer, *Nucl. Phys.*, **21**, 347 (1961).

(9) A. J. F. Boyle and H. E. Hall, *Rept. Progr. Phys.*, **25**, 441 (1962).

(10) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters*, **6**, 98 (1961).

(11) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **36**, 2497 (1962); **37**, 687 (1962).

(12) G. K. Wertheim, *J. Appl. Phys.*, **S32**, 110 (1961).

(13) H. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17**, 494 (1962).

TABLE I
 ISOMER SHIFTS^a AND QUADRUPOLE SPLITTINGS^b

Compound	I.S.		Q.S.
	Measured	Calcd.	
A. Compounds without π -bonding ligands			
(i) This Work			
1. $\{[(\text{CH}_3)_2\text{N}]_3\text{P}\}_2\text{Fe}(\text{CO})_3^{16}$	0.004	^c	0.227
2. $[(\text{CH}_3)_2\text{N}]_3\text{PFe}(\text{CO})_4^{16}$	0.004	0.006	0.222
3. $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4^{17}$	0.006	0.008	0.242
4. $\text{C}_5\text{F}_7\text{Fe}(\text{CO})_4\text{I}^{18}$	0.015		0.056
5. $\text{Hg}[\text{Fe}(\text{CO})_2\text{NOP}(\text{C}_6\text{H}_5)_3]_2^{19}$	0.016	0.017	0.142
6. $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2^{19}$	0.016	0.019	0.126
7. $[(\text{C}_4\text{H}_9)_2\text{SnFe}(\text{CO})_4]_2$	0.016		0.02
8. $(\text{C}_6\text{H}_5)_3\text{PFeCO}(\text{NO})_2^{20}$	0.018	^c	0.050
9. $[\text{Fe}(\text{CO})_3\text{SCH}_3]_2^{21}$	0.020	0.022	0.089
10. $\{[(\text{CH}_3)_2\text{N}]_3\text{P}\}_2\text{Fe}(\text{NO})_2^{19}$	0.021	0.017	0.087
11. $[\text{Fe}(\text{CO})_3\text{SC}(\text{CH}_3)_3]_2^{21}$	0.021	0.022	0.093
12. $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6^{21}$	0.022	0.022	0.105
13. $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6^{21}$	0.022	0.022	0.134
14. $[\text{C}_4\text{F}_6\text{S}_2\text{FeNO}]_2^1$	0.044	0.043	0.120
(ii) Previous work ⁵			
1. $\text{Fe}(\text{CO})_5$	0.009	^c	0.257
2. $\text{Fe}_3(\text{CO})_{12}$	0.021 (central Fe)	^d	0
	0.028 (terminal Fe)	0.028	0.112
3. $\text{Fe}_2(\text{CO})_9$	0.028	^c	0.054
4. $\text{Fe}(\text{CO})_4\text{I}_2$	0.055	^c	0.085
B. Compounds with five-electron π -bonding ligands			
(i) This work			
1. $(\text{CF}_2)_3(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2^{22}$	0.019	0.017	0.185
2. $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_6\text{H}_5^{22}$	0.019	0.019	0.168
3. $\{\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{P}[\text{N}(\text{CH}_3)_2]_3\}^+\text{I}^{-16}$	0.020		0.178
4. $(\text{C}_2\text{H}_5)_2\text{NCOFe}(\text{CO})_2\text{C}_6\text{H}_5^{22}$	0.021	0.019	0.173
5. $\text{C}_6\text{H}_5\text{Fe}^{\text{A}}(\text{CO})_2(\text{CH}_2)_3\text{COFe}^{\text{B}}(\text{CO})_2\text{C}_6\text{H}_5^{22}$	0.021	0.022 (A) 0.020 (B)	0.166
6. $(\text{CH}_2)_4(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2^{22}$	0.022	0.020	0.170
7. $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_3]^+\text{PF}_6^{-23}$	0.023		0.188
8. $(\text{CH}_2)_4[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2^{22}$	0.023	0.024	0.167
9. $[\text{C}_7\text{H}_9\text{Fe}(\text{CO})_3]^+\text{BF}_4^{-24}$	0.025		0.154
10. $[\text{C}_6\text{H}_7\text{Fe}(\text{CO})_3]^+\text{BF}_4^{-25}$	0.026		0.156
11. $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}^{26}$	0.028	^c	0.160
12. $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{SCOC}_6\text{H}_5^{22}$	0.032	^c	0.179
13. $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5^{27}$	0.036	^c	0.168
14. $\text{C}_7\text{H}_9\text{Fe}(\text{CO})_2\text{I}^{24}$	0.037	0.038	0.152
15. $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2^{28}$	0.038	^e	0.189
16. $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{I}^{29}$	0.038	^e	0.183
17. $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}^{30}$	0.039	^e	0.188
18. $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Br}^{30}$	0.040	^e	0.187
19. $[\text{C}_9\text{H}_7\text{Fe}(\text{CO})_2]_2^{31}$	0.041	0.040	0.172
20. $[\text{C}_6\text{H}_5\text{FeCOSCH}_3]_2^{32}$	0.045	0.048	0.166
21. $[\text{C}_5\text{H}_5\text{FeCOS}(\text{CH}_3)_3]_2^{32}$	0.046	^c	0.170
22. $(\text{C}_9\text{H}_7)_2\text{Fe}^{33}$	0.077	0.077	0.254
(ii) Previous work ⁴			
1. $(\text{C}_6\text{H}_5)_2\text{Fe}$	0.069	^e	0.237
C. Compounds with other π -bonding ligands			
(i) This work			
1. $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6^{34}$	0.014		0.123
2. $\text{C}_8\text{H}_8\text{SFe}_2(\text{CO})_6^{32}$	0.016		0.111
3. $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3^{35}$	0.016		0.143
4. $\text{C}_6\text{H}_{10}\text{COFe}(\text{CO})_3^{36}$	0.020		0.149
5. $\text{C}_6\text{H}_7\text{CO}_2\text{H}_5\text{Fe}(\text{CO})_3^{37}$	0.021		0.173
6. $\text{C}_7\text{H}_6\text{OFe}(\text{CO})_3^{38}$	0.021		0.149
7. $\text{C}_6\text{H}_7\text{CONH}_2\text{Fe}(\text{CO})_3^{37}$	0.022		0.154
8. $\text{C}_8\text{H}_{10}\text{Fe}_2(\text{CO})_6^{38}$	0.022		0.088
9. $\text{C}_8\text{H}_8\text{OFe}(\text{CO})_3^{38}$	0.022		0.141
10. $\text{C}_8\text{H}_8\text{OF}_2\text{Fe}_2(\text{CO})_6^{38}$	0.025		0.084

TABLE I (Continued)

Compound	I.S.		Q.S.
	Measured	Calcd.	
11. $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}]_2$	0.027		0.128
12. $[\text{C}_8\text{H}_9\text{Fe}_2(\text{CO})_6][\text{PF}_6]$	0.030		0.113
13. $[\text{C}_8\text{H}_9\text{Fe}_2(\text{CO})_6][\text{BF}_4]$	0.029		0.120
14. $\text{C}_{12}\text{H}_8\text{Fe}_2(\text{CO})_6$	0.060		0.088
(ii) Previous work ^g			
1. $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$	0.018		0.132
2. $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$	0.023		0.123

^a All values are positive and in cm./sec. ^b In cm./sec. ^c Used in deriving partial isomer shifts. ^d The effective atomic number of this iron atom is not 36. ^e Used in deriving the linear relationship between τ and the partial isomer shift for the cyclopentadienyl group (cf. Fig. 1).

The calibration of the Doppler motion was effected by determining the hyperfine structure of a metallic iron absorber for which the ground state splitting has been accurately measured by n.m.r. techniques.¹⁴ The value obtained by these authors on a sample of iron 99.999% pure is 45.43 Mc. (corresponding to 3.926 mm. sec.⁻¹) at 297°K., in good agreement with the Mössbauer value of 3.924 mm. sec.⁻¹ at 293.0°K. from data accumulated using an independently calibrated constant velocity drive.¹⁵ A value of 0.392 cm. sec.⁻¹ for the ground state splitting has been used in this work.

The iron-organic compounds were prepared by methods described elsewhere.¹⁶⁻³⁸ The proton n.m.r. data reported for the π -cyclopentadienyl derivatives were recorded on a Varian Associates Model A-60 spectrometer in carbon disulfide or chloroform solution with hexamethyldisiloxane ($\tau = 9.95$) as an internal standard. It was found necessary to avoid using results of n.m.r. measurements carried out in benzene solutions due to a large solvent effect.

(14) J. I. Budnick, L. J. Bruner, R. J. Blume, and E. L. Boyd, *J. Appl. Phys.*, **32**, 120S (1961).

(15) R. S. Preston, S. S. Hanna, and J. Heberle, *Phys. Rev.*, **128**, 2207 (1962).

(16) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(17) W. Reppe and W. J. Schweckendick, *Ann.*, **560**, 104 (1948); F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

(18) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 249 (1961); R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3604 (1961).

(19) R. B. King, *Inorg. Chem.*, **2**, 1275 (1963).

(20) D. W. McBride, S. L. Stafford, and F. G. A. Stone, *ibid.*, **1**, 386 (1962).

(21) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963), and references cited in this article. $\text{C}_4\text{F}_6\text{S}_2$ refers to bis(trifluoromethyl)dithietene and $\text{C}_2\text{F}_4\text{S}_2$ refers to the $\text{SCF}_2\text{CF}_2\text{S}$ bridging group.

(22) R. B. King, *ibid.*, **85**, 1918 (1963).

(23) R. B. King, *Inorg. Chem.*, **1**, 964 (1962).

(24) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961); $\text{C}_7\text{H}_8 = \pi$ -cycloheptadienyl.

(25) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).

(26) E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955).

(27) R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)*, 747 (1961).

(28) B. F. Hallam, O. S. Mills, and P. L. Pauson, *J. Inorg. Nucl. Chem.*, **1**, 313 (1955).

(29) T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956).

(30) T. S. Piper, F. A. Cotton, and G. Wilkinson, *ibid.*, **1**, 165 (1955); B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1965).

(31) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 646 (1958).

(32) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(33) E. O. Fischer and D. Seus, *Z. Naturforsch.*, **8b**, 694 (1953); P. L. Pauson and G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 2024 (1954).

(34) H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *ibid.*, **82**, 4749 (1960).

(35) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(36) R. B. King, *Inorg. Chem.*, **2**, 642 (1963). $\text{C}_8\text{H}_{10}\text{COFe}(\text{CO})_3$ refers to the product, m.p. 69°, of the reaction between triiron dodecacarbonyl and 1,3,3-trimethylcyclopropene.

(37) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

(38) R. B. King, *Inorg. Chem.*, **2**, 807 (1963). See also E. Weiss and W. Hübel, *Ber.*, **95**, 1179 (1962). The designations $\text{C}_7\text{H}_8\text{O}$, $\text{C}_8\text{H}_8\text{O}$, and C_8H_{10} correspond to tropone, cyclooctatrienone, and 1,3,5-cyclooctatriene, respectively.

4. Results and Discussion

The isomer shifts at 78°K. of a number of iron-organic compounds, in which the iron atom has an effective atomic number of 36, have been summarized in Table I. Unless otherwise noted, all isomer shifts reported in the present study refer to a chromium (Co^{67}) source. For reasons discussed below, the compounds are grouped in three categories: those without π -bonding ligands; those with five-electron-donating π -bonding ligands (but no other types of π -bonding ligands); and those with π -bonding ligands other than five-electron-donating ligands.

All of the compounds employed in the present study exhibit a measurable quadrupole splitting of the resonance line due to the fact that in none of these compounds is the iron atom located at a center of cubic symmetry with respect to its nearest neighbor atoms. However, the correlation of the magnitude of this splitting with features of the molecular architecture is still very poorly understood. For this reason quadrupole splitting data are not further discussed in this paper.

Upon investigation of the available data on compounds without π -bonding ligands, the relative constancy of the isomer shift for related molecules becomes apparent. From this it appears feasible to attempt to set up a table of partial isomer shift values (designated by ζ) for individual ligands in such a way that the addition of the appropriate ζ_i values leads to the observed isomer shift value for the compound; that is

$$\sum_i^N \zeta_i = \text{I.S.}$$

The ζ values which have been used in this calculation are summarized in Table II. Since a number of the ligands are involved in several molecules having significantly different isomer shift values, a reasonably good test for internal consistency can be established.

Since the isomer shift can be identified only with respect to two chemical environments (*i.e.*, in the source and in the absorber) absolute values of the isomer shift have no fundamental significance, and all absorber isomer shift values include an arbitrary constant dependent on the chemical nature of the recoil-free source. The present calculation, which is based on measurements made using a source of Co^{67} diffused into

TABLE II
PARTIAL ISOMER SHIFT PARAMETERS FOR VARIOUS LIGANDS IN
CM./SEC.

A. Ligands with $\zeta \sim 0$	
PR ₃ (R = C ₆ H ₅ , N(CH ₃) ₂)	-0.0006
CO (terminal)	+0.0017
S (electron pair donor)	0
Fe-Fe	0
-CH ₂ R	0
B. Ligands with $\zeta \neq 0$	
Hg	+0.005
CO (bridging)	+0.0076
NO	+0.009
Mn(CO) ₅	+0.014
S- (single electron donor)	+0.017
X- (Cl, Br, I)	+0.024

metallic chromium, implied a cancellation of this arbitrary constant when the total number of electrons involved in bonding remains unchanged. This cancellation obtains since the shift per electron involved in bonding remains constant as long as only iron atoms with an effective atomic number of 36 are considered.

The present data can, however, be readily converted to the appropriate values for other source host-matrices by adding to each partial isomer shift the constant Δ/N so that

$$\text{I.S.}_X = \sum_i^N \left(\zeta_{\text{icr}} + \frac{\Delta}{N} \right) = \text{I.S.}_{\text{Cr}} + \Delta$$

in which I.S._X and I.S._{Cr} are the total compound isomer shifts for Co⁵⁷ diffused into X and into chromium, respectively, ζ_{icr} is the partial isomer shift appropriate for a Cr (Co⁵⁷) source, Δ is the isomer shift of X with respect to Cr, and N is the number of electron pairs donated by the ligands.

5. Partial Isomer Shift Values

:C≡O.—The value of the partial isomer shift for a terminal (electron pair donor) carbonyl group is taken as 1/5 of the I.S. of Fe(CO)₅ since the iron atom in this compound is unambiguously in an inert gas configuration. From this $\zeta_{\text{C=O}}$ is 1/5 × 0.0085 = 0.0017 cm. sec.⁻¹.

·C=O.—The partial isomer shift for a bridging (single-electron donor) carbonyl group can be calculated from the I.S. of Fe₂(CO)₉ and the $\zeta_{\text{C=O}}$ value, above, and has a value of $\zeta_{\text{C=O}} = 1/3(0.0280 - 3 \times 0.0017) = 0.0076$ cm. sec.⁻¹. Implied in this calculation is the assumption that the partial isomer shift due to an Fe-Fe bond (which is demanded by the diamagnetism of the nonacarbonyl) is essentially equal to zero. The validity of this assumption will be examined in greater detail below.

:I.—For a covalently bonded iodine atom, ζ_{I} can be calculated from the above value for $\zeta_{\text{C=O}}$ and the I.S. for Fe(CO)₄I₂, from which $\zeta_{\text{I}} = 1/2(0.055 - 4 \times 0.0017) = 0.024$ cm. sec.⁻¹.

:PR₃.—For compounds in which R is either a phenyl or dimethylamino group, the ζ_{PR_3} value is calculated from I.S. values obtained for compounds having in

addition only terminal CO groups, *i.e.*, [(CH₃)₂N]₂Fe-(CO)₃, and is ~ -0.0006 ; that is, zero within the accuracy of the present data.

:NO.—The ζ value for the nitrosyl group may be derived either from the I.S. obtained for (C₆H₅)₃-PFeCO(NO)₂ or {[(CH₃)₂N]₃P}₂Fe(NO)₂ giving ζ_{NO} values of 0.0085 or 0.011 cm. sec.⁻¹, respectively. The intermediate value of $\zeta_{\text{NO}} = 0.009$ cm. sec.⁻¹ given in Table II is based on additional I.S. data for compounds both with and without π -cyclopentadienyl groups discussed below.

π -C₅H₅.—The most obvious datum to consider in deriving a value for $\zeta_{\text{C}_5\text{H}_5}$ is the I.S. of ferrocene. However, the value so calculated, equal to 0.069/2 = 0.0345 cm. sec.⁻¹, leads to inconsistent values for other ligands attached to iron atoms bonded to only a single π -cyclopentadienyl group.

Moreover, it is not even possible to obtain internal consistency for the value of $\zeta_{\text{C}_5\text{H}_5}$ for mono π -cyclopentadienyl compounds by taking a single value for this partial isomer shift for the various compounds listed in Table I. In order to permit calculation of partial isomer shift values for other ligands of these mono π -cyclopentadienyl compounds, it is necessary to exploit independent physical data which are also sensitive to the nature of the metal π -cyclopentadienyl bonding.

A characteristic feature of almost all π -cyclopentadienyl derivatives is the presence of a sharp peak³⁹ in the proton n.m.r. spectrum due to the five equivalent protons of the π -cyclopentadienyl ring. The chemical shifts (τ) of these peaks are assumed to be dependent on the precise nature of the metal-cyclopentadienyl bond and thus related to the τ values for the π -cyclopentadienyl rings. The chemical shifts of the π -cyclopentadienyl derivatives considered in this paper are given in Table III.

As a first approximation it may be assumed that $\zeta_{\text{C}_5\text{H}_5}$ is a linear function of τ , at least over a limited range of values. In order to establish calibration points for this function the $\zeta_{\text{C}_5\text{H}_5}$ values for ferrocene, π -C₅H₅Fe(CO)₂X (X = Br, Cl, I) and [π -C₅H₅Fe(CO)₂]₂ were chosen since in each case the ζ values for the other ligands could be inferred without assuming a value for the partial isomer shift contribution by the π -cyclopentadienyl group. The linear function so generated is shown in Fig. 1 and obeys the relationship $\zeta_{\text{C}_5\text{H}_5} = 0.0223(\tau - 4.41)$. Hexamethyldisiloxane in CS₂ or CHCl₃ (9.95 τ) was used as an internal standard.

With the proton n.m.r. shift as a means of assigning an appropriate ζ value for the π -cyclopentadienyl group, it is then possible to calculate ζ values for other ligands. The results of this calculation for several other ligands bonded directly to the iron atom are summarized in Table II.

(39) π -Cyclopentadienyl derivatives which have a phosphorus atom attached to the same metal atom as the π -cyclopentadienyl ring may exhibit a doublet rather than a singlet in the n.m.r. due to the five cyclopentadienyl protons. Paramagnetic π -cyclopentadienyl derivatives, none of which is discussed in this paper, would not exhibit a sharp resonance due to the π -cyclopentadienyl protons.

TABLE III
C₅H₅ RING PROTON CHEMICAL SHIFTS IN
π-CYCLOPENTADIENYLIRON DERIVATIVES

Compound	Position of cyclopentadienyl resonance (τ)
[C ₅ H ₅ Fe(CO) ₃] + PF ₆ ⁻	3.92
[C ₅ H ₅ Fe(CO) ₂ P[N(CH ₃) ₂] ₃] + I ⁻	4.53
C ₅ H ₅ Fe(CO) ₂ I	4.93
C ₅ H ₅ Fe(CO) ₂ SCOC ₆ H ₅	4.95
C ₅ H ₅ Fe(CO) ₂ Cl	4.96
C ₅ H ₅ Fe(CO) ₂ Br	4.97
(CF ₂) ₃ (CO) ₂ [Fe(CO) ₂ C ₅ H ₅] ₂	5.04
CH ₃ COFe(CO) ₂ C ₅ H ₅	5.13
(C ₂ H ₅) ₂ NCOFe(CO) ₂ C ₅ H ₅	5.15
(CH ₂) ₄ (CO) ₂ [Fe(CO) ₂ C ₅ H ₅] ₂	5.16
C ₅ H ₅ Fe ^A (CO) ₂ (CH ₂) ₃ COFe ^B (CO) ₂ C ₅ H ₅	5.17 (B)
	5.27 (A)
[C ₅ H ₅ Fe(CO) ₂] ₂	5.25
C ₅ H ₅ Fe(CO) ₂ Mn(CO) ₅	5.25
[C ₅ H ₅ Fe(CO) ₂] ₂ Hg	5.29
(CH ₂) ₄ [Fe(CO) ₂ C ₅ H ₅] ₂	5.35
[C ₅ H ₅ FeCOSCH(CH ₃) ₃] ₂	5.61
[C ₅ H ₅ FeCOSCH ₃] ₂	5.68
(C ₅ H ₅) ₂ Fe	5.87

Hg.—For the mercury atom one can derive the ζ_{Hg} value from the isomer shift of [C₅H₅Fe(CO)₂]₂Hg. Since the chemical shift of the cyclopentadienyl protons in this compound is 5.29 τ (Table III), the $\zeta_{\text{C}_5\text{H}_5}$ value for the π-cyclopentadienyl group from Fig. 1 in this compound is 0.020 cm./sec. The ζ_{Hg} value for the mercury atom is therefore 0.028 - 2(0.0017) - 0.020 = 0.005 cm. sec.⁻¹. This value may be checked for consistency by calculating the isomer shifts of Hg[Fe(CO)₃NO]₂ and Hg[Fe(CO)₂NOP(C₆H₅)₃]₂ using in addition the previously determined ζ values for terminal carbonyl, nitrosyl, and triphenylphosphine groups. In each case the calculated and observed values agree to within 0.001 cm. sec.⁻¹.

S and :S.—In the case of sulfur atoms bonded directly to iron, it is necessary to distinguish between sulfur atoms which are electron pair donors and those which formally contribute only a single electron to the bond with the iron atom. In the present discussion, these will be designated as two-electron and one-electron donating sulfur atoms, respectively.

Most of the sulfur compounds measured in this work such as [Fe(CO)₃SR]₂ and [C₅H₅FeCOSR]₂ contain two iron atoms and two sulfur bridges. In these sulfur bridges each sulfur atom donates one electron to one of the iron atoms and two electrons to the other iron atom. It is therefore impossible in these compounds to distinguish between the contributions of the one-electron-donating sulfur atoms and the two-electron-donating sulfur atoms to the total isomer shift. This distinction is also impossible in the nitrosyl derivative [C₄F₆S₂-FeNO]₂, which appears to have four sulfur bridges as in the recently described vanadium compound [C₅H₅V-(SCH₃)₂]₂.⁴⁰

However, the isomer shift value for the compound C₅H₅Fe(CO)₂SCOC₆H₅,²² which contains only a one-

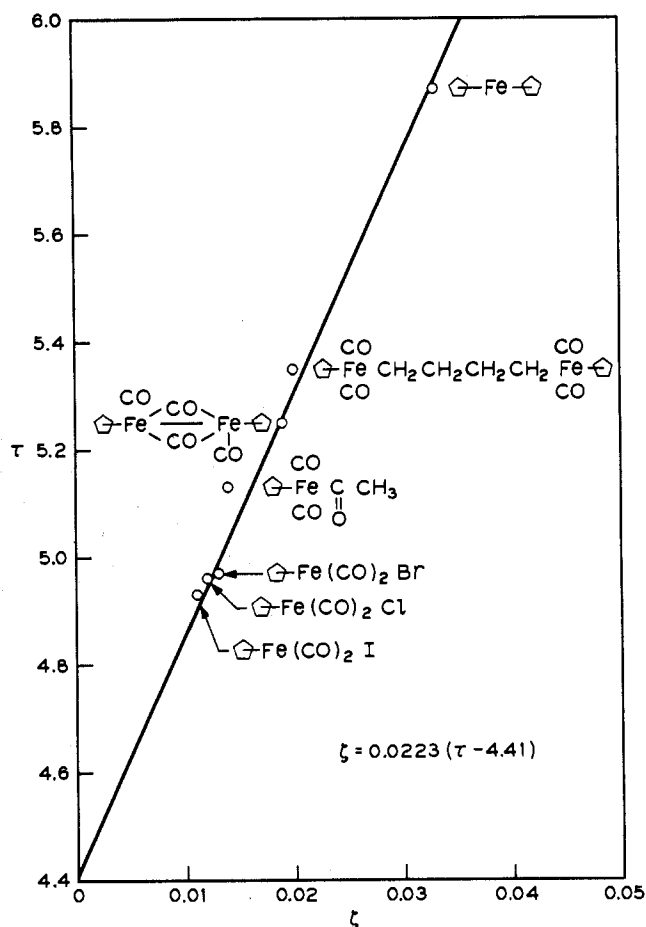


Fig. 1.—The relationship between the proton n.m.r. shift, τ (p.p.m.), and the Fe⁵⁷ isomer shifts, ζ (cm./sec.), in cyclopentadienyl-iron compounds.

electron donating sulfur atom, is available. Since the chemical shift of the cyclopentadienyl protons in this compound is 4.95 τ (Table III), the $\zeta_{\text{C}_5\text{H}_5}$ value for the π-cyclopentadienyl group is 0.0120 cm./sec. The ζ value for the one-electron-donating sulfur atom in this compound is therefore 0.032 - 2 × 0.0017 - 0.0120 = 0.017 cm./sec.

In order to obtain a ζ value for a two-electron-donating sulfur atom the isomer shift value for the compound [C₅H₅FeCOSCH(CH₃)₃]₂ can be used. Since the chemical shift of the cyclopentadienyl protons in this compound is 5.61 τ (Table III), the $\zeta_{\text{C}_5\text{H}_5}$ value for the π-cyclopentadienyl group in this compound is 0.0268 cm./sec. As indicated above, the two bridging sulfur atoms each donate one electron to one of the iron atoms and two electrons to the other iron atom. The isomer shift value for the two-electron-donating sulfur atom is therefore 0.046 - 0.0268 - 0.0017 - 0.017 = 0.000 cm./sec. Thus the partial isomer shift contribution of two-electron-donating sulfur atoms can be neglected in the calculation of the total isomer shift value.

Fe-Fe.—As already implied in the calculation of $\zeta_{\text{C=O}}$, a consideration of the isomer shift data on the compounds [Fe(CO)₃SCH₃]₂, [Fe(CO)₃SC(CH₃)₃]₂, C₂F₄S₂Fe₂(CO)₆, and C₄F₆S₂Fe₂(CO)₆ and the ζ values for sulfur atoms and terminal carbonyl groups leads to the conclusion that the ζ value for the iron-iron bond is

(40) R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

nearly zero. This conclusion is in agreement with the small shift between iron in a chromium environment and iron in an iron environment. It implies that ζ_{Fe} can be neglected in the calculation of isomer shift values relative to a chromium (Co^{57}) source, but not with respect to a copper (Co^{57}) source.

$\pi-C_4H_4$.—As in the case of the π -cyclopentadienyl group, no single value for $\zeta_{C_4H_4}$ can be fitted to the present data. The previously reported Mössbauer data for $C_8H_8Fe(CO)_3$ and $C_8H_8Fe_2(CO)_6$ lead to a value of $\zeta_{C_4H_4}$ of 0.017 cm. sec.⁻¹, since it is known from the X-ray structure data that each iron atom interacts with only four of the eight carbon atoms in the ring. This value for $\zeta_{C_4H_4}$ also gives reasonable isomer shift agreement for compounds 4 to 9 inclusive in Table I, section C, but no agreement with the observed I.S. for $C_4H_4Fe_2(CO)_6$, $C_8H_8SF_2(CO)_6$, or $C_8H_8Fe(CO)_3$. There are as yet insufficient n.m.r. data available for these compounds to permit the type of correlation between τ and $\zeta_{C_4H_4}$ which was possible in the case of the cyclopentadienyl group.

Other π -Bonding Ligands.—The isomer shift values for $C_5H_5Fe(CO)_2I$ and $C_7H_9Fe(CO)_2I$ suggest that in the latter compound only five carbon atoms of the ring are involved in the bonding to the iron atom, in agreement with an effective atomic number of 36. Thus, while this formally indicates $\zeta_{C_7H_9} = 0.010$ cm. sec.⁻¹, this value is in fact appropriate only for the C_5H_5 fragment of the cycloheptadiene ring which participates in d-orbital overlap with the iron atom.

The data for bisindenyl iron can be exploited to designate a value of $0.077/2 = 0.0385$ cm. sec.⁻¹ for the indenyl group. Again, this value is appropriate for only the C_5H_5 fragment of the indene structure since an effective atomic number of 36 demands that each indenyl ligand contributes effectively five electrons to the iron d-orbitals. From this value, the calculated I.S. of the only other compound in the present series which involves an indenyl ligand, $[C_9H_7Fe(CO)_2]_2$, is 0.0554 cm. sec.⁻¹, compared to the experimental value of 0.041 cm. sec.⁻¹. From this discrepancy it is clear that the presently available data are too limited to permit an unambiguous determination of ζ values for a π -indenyl ligand. Again it appears necessary to exploit other molecular properties in order to determine the partial isomer shift value appropriate for a particular indenyl-iron compound.

Another class of compounds for which a satisfactory method of calculating isomer shifts has not yet been found are the carbonyl cations such as $C_5H_5Fe(CO)_2P[N(CH_3)_2]_3^+$ (B-3), $[C_5H_5Fe(CO)_3]^+$ (B-7), $[C_6H_7Fe(CO)_3]^+$ (B-10), and $[C_7H_9Fe(CO)_3]^+$ (B-9) reported in Table I. As would be expected from effective atomic number considerations described above, the values for the analogous π -cyclopentadienyl-, π -cyclohexadienyl-, and π -cycloheptadienyliron tricarbonyl cation are reasonably similar. Correlation of ζ values with proton n.m.r. shifts does not appear fruitful in these cases, in contrast to the treatment of the neutral π -cyclopentadienyl compounds. For example, the proton shift in

$C_5H_5Fe(CO)_3^+$ (which was determined in dimethylformamide solution in order to obtain high enough concentrations for a manageable signal-to-noise ratio) was found to be 3.92 p.p.m., which is much lower than any other chemical shift of the π -cyclopentadienyl derivatives discussed in this paper although it is almost identical with the chemical shift of 3.87 τ for the cyclopentadienyl protons of the isoelectronic cation $[C_5H_5Mn(CO)_2NO]^+$ measured in acetone solution. Using this proton n.m.r. shift in conjunction with the relationship between $\zeta_{C_5H_5}$ and τ of Fig. 1 leads to inconsistent values for the calculated I.S. of the cyclopentadienyl-iron cations listed in Table I. It is possible to eliminate this difficulty by assuming that in all cationic π -cyclopentadienyl derivatives the ζ value for the cyclopentadienyl ring is 0.018 cm./sec. regardless of the chemical shift of the protons. If this assumption is made, the calculated values for the cations $C_5H_5Fe(CO)_2P[N(CH_3)_2]_3^+$ and $[C_5H_5Fe(CO)_3]^+$ are 0.021 and 0.023 cm./sec., respectively, in good agreement with the observed values of 0.020 and 0.023 cm./sec., respectively. However, there is no clear reason why the ζ values for π -cyclopentadienyl groups in these cations are not dependent on the chemical shift of the π -cyclopentadienyl protons in a manner at least similar to that for the uncharged π -cyclopentadienyl compounds. This difficulty may be merely a reflection of the possibility that the straight line relationship of Fig. 1 which gives reasonable values for π -cyclopentadienyl groups with chemical shifts in the range of 4.9 to 5.9 τ cannot be successfully extrapolated to the τ values for a π -cyclopentadienyl group such as that in $[C_5H_5Fe(CO)_3]^+$. Clearly, more data on cationic species including preferably some without π -bonding groups are needed to clarify this problem; unfortunately few such compounds are now known.

The single perfluorocarbon compound included in the present study is $C_3F_7Fe(CO)_4I$. From the previously calculated values of ζ_{CO} and ζ_I , the requisite partial isomer shift value for the C_3F_7 group is -0.016 cm. sec.⁻¹. Mössbauer data for other perfluorocarbon iron-organic compounds (not here reported) indicate similar negative values as appropriate for these ligands. Any speculation regarding the significance of this large negative ζ value, and its relationship to the presence of C-F bonds, would be premature. Additional measurements on other compounds having both σ - and π -bonded perfluorocarbon group ligands is needed before such correlations can be attempted.

6. Unequal Line Intensities

As noted above, all of the compounds for which data are reported in Table I show the presence of quadrupole splitting due to the nonzero electric field gradient at the iron atom lattice site. Although the expectation is that the two components of a quadrupole split line will have the same intensity in a polycrystalline sample, unequal resonance effects have been observed for many of these compounds. This unequal line intensity has in certain cases been correctly ascribed¹³ to the accidental

preferred orientation of crystals in the absorber. In the case of $\text{Fe}(\text{CO})_5$ these workers were able to show that when the crystals are randomly oriented with respect to the source-absorber axis by rapid freezing, the inherent averaging over all possible crystal orientations restores the equality of the intensities of the two quadrupolar components. Preferentially oriented samples can also be obtained when materials with needle- or plate-like habit are packed into an absorber holder.

In the present experiments, unequal line intensities have been most pronounced in compounds in which the iron atom is bound to a single π -electron system with σ -bonded, nondelocalized ligands filling the other bonding sites, e.g., $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, $\pi\text{-C}_5\text{H}_5\text{-Fe}(\text{CO})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COFe}(\text{CO})_2\pi\text{-C}_5\text{H}_5$, etc. An initial determination of the resonance spectrum for $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2(\text{CH}_2)_4$ showed an intensity ratio of about 1.3 at 20°K. The solid material was then pulverized and remounted in the absorber holder. The replicate spectrum showed *no significant change in the line asymmetry* from the initial determination, indicating that random microcrystallite orientations *per se* do not necessarily lead to isotropic resonance conditions. This behavior has also been noted by Soviet investigators,⁴¹ who point out that such an effect can arise even in randomly oriented polycrystalline material provided only that the recoil-free fraction is a function of the crystallographic direction within each crystallite. This effect is expected to be particularly pronounced where large molecular asymmetries such as those associated with the masses of the ligands bonded to the absorbing atom exist. In the case of iron pentacarbonyl, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, etc., the molecular asymmetries are very small and thus, even though quadrupole splitting is noted due to noncubic surroundings, equal line intensities are observed when random crystal orientations are obtained.

In the case of absorbers in which the atoms or groups directly involved in the bonding to one side of the iron atom are massive compared to those on the other side, unequal line intensities of a quadrupole split pair are observed, and this effect should have applications in the elucidation of molecular structure.

7. Conclusions

In examining the ζ values obtained for a variety of ligands the following correlations between the nature of the ligand and its ζ value become apparent.

(1) Ligands which donate a lone pair to the iron atom make only a very minor contribution to the isomer shift and thus have ζ values of ~ 0 when measured with respect to Co^{57} in chromium. Examples of such ligands are two-electron-donating sulfur atoms, tris(dimethylamino)phosphine, and triphenylphosphine.

The terminal carbonyl group has a ζ value of only $+0.0017$ cm./sec.

(2) An iron-iron bond has a ζ value of ~ 0 , thus making a negligible contribution to the isomer shift. It is to be noted, however, that in all of the compounds studied the iron-iron bond links two symmetrical halves. It is entirely possible that an iron-iron bond linking two different halves of a molecule such as that in the unknown compound $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Fe}(\text{CO})_3\text{NO}$ [possibly preparable from $\text{Fe}(\text{CO})_3\text{NO}^-$ and $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{X}$] might make a positive contribution to the isomer shift of one iron atom and a correspondingly negative contribution to the isomer shift of the other iron atom. No such compounds are as yet available to test this possibility. It is of interest, however, that the $\text{Mn}(\text{CO})_5$ group as calculated from the single observation on $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$ possesses a ζ value of $+0.014$ cm./sec.

(3) An iron-carbon σ -bond in either an alkyl derivative involving an sp^3 hybridized carbon atom or an acyl derivative involving an sp^2 hybridized carbon atom makes a negligible contribution to the isomer shift and is thus assigned a ζ value of ~ 0 . However, a bridging carbonyl group which is σ -bonded to the iron atom makes an appreciable positive contribution to the isomer shift ($\zeta = +0.0085$ cm. sec.⁻¹).

(4) Ligands other than carbon which donate a single electron to the iron atom in most cases make a significant positive contribution to the isomer shift. The magnitude of this positive contribution depends on the ability of the ligand to remove electron density from the iron atom either by σ -bonding or by partial $d\pi\text{-}p\pi$ or $d\pi\text{-}d\pi$ double bonding. In the case of the halogen atoms the decrease in electronegativity in going from chlorine to iodine and the resulting increasing ability to remove electron density from the iron atom by σ -bonding is exactly compensated by the increased ability to remove electron density from the iron atom by $d\pi\text{-}d\pi$ partial double bonding so that the ζ values for chlorine, bromine, and iodine are essentially equal ($+0.024$ cm. sec.⁻¹).

(5) Hydrocarbon ligands which form π -bonds with the iron atom make significant positive contributions to the isomer shift. The magnitude of this positive contribution is dependent on the nature of the metal-ligand bond and a single ζ value cannot be assigned to ligands of this type to give reasonable agreement with all of the measured values. In the case of the π -cyclopentadienyl derivatives $\zeta_{\text{C}_5\text{H}_5}$ values ranging from 0.011 to $+0.0345$ cm. sec.⁻¹ may be derived from consideration of the chemical shifts of the π -cyclopentadienyl protons in individual compounds (Fig. 1).

Acknowledgments.—The authors are indebted to D. N. E. Buchanan for assistance with the measurements and to M. Bisnette for assistance with the preparations of some of the compounds. This research was supported in part by the Research Council, Rutgers, The State University, and by the United States Atomic Energy Commission.

(41) V. A. Bryukhanov, V. I. Goldanskii, N. N. Delyagin, L. A. Konytko, E. F. Makarov, I. P. Suzdalev, and V. S. Shpinel, *Zh. Eksperim. Teor. Phys.*, **43**, 448 (1963); V. I. Goldanskii, E. F. Makarov, and V. V. Khrapov, *Phys. Letters*, **3**, 344 (1963).