ORGANIC AND BIOLOGICAL CHEMISTRY

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The Dipole Moment of Bis-(*p*-chlorophenylcyclopentadienyl)-iron

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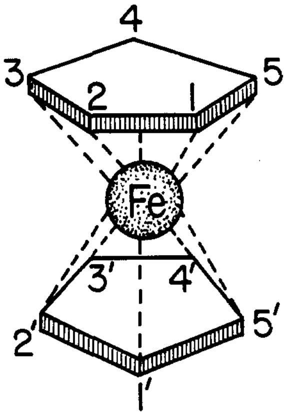
The dipole moment (3.12 *D*) found for bis-(*p*-chlorophenylcyclopentadienyl)-iron indicates a molecular configuration having the *p*-chlorophenyl groups in rather close proximity to one another.

The sandwich structure[2] for ferrocene[3] is supported by X-ray[3,4–7] and electron[3,8] diffraction, diamagnetic moment,[2] infrared absorption spectrum,[2] dipole moment[2] and chemical properties.[2] In the crystal, the rings occupy fairly fixed positions best described by the antiprismatic sandwich structure (I).[3,4–7] The apparent spreading of the carbon atoms along the circumference of the rings is regarded as being due to a fairly large amplitude of thermal vibration and hindered rotation.[3]



Free rotation is, however, suggested by electron diffraction patterns for ferrocene vapor,[3,8] as well as chemical[2,3] and dipole moment studies[9] of bis-(acetylcyclopentadienyl)-iron and molecular orbital treatments of the ferrocene molecule.[10,11] The dipole moment of a bis-(*p*-chlorophenylcyclopentadienyl)-iron measured in the present investigation provides evidence that, even though the rings may rotate freely, not all possible orientations of a bis-substituted ferrocene are equally probable.

Experimental and Results

The bis-(*p*-chlorophenylcyclopentadienyl)-iron, kindly supplied by Dr. V. Weinmayr of the Jackson Laboratory, E. I. du Pont de Nemours and Co., was prepared by treatment of the ferricinium ion $[Fe(C_5H_5)_2]^{\oplus}$ with *p*-chlorophenyldiazonium ion.[12] The purity of the compound was established by analysis.[12] Assignment of the *p*-chlorophenyl substituents to different rings is supported by the infrared spectrum (of carbon tetrachloride and carbon disulfide solutions) which showed no bands at 9.0 and 9.95 μ characteristic of unsubstituted ferrocenylcyclopentadienyl rings.[3,13,14]

The dipole moment of bis-(*p*-chlorophenylcyclopentadienyl)-iron was measured in benzene solution as described previously[15,16] and evaluated by linear extrapolation of the dielectric constant to zero concentration[17,18] (method I) to be 3.12 ± 0.03 *D*. A value of 2.96 ± 0.13 *D* was obtained by linear extrapolation of molar polarization to zero concentration[19] (method II). Method I is considered to be more reliable because the extrapolated function is linear at low concentrations whereas this is not true for method II.[17,18] The data used for method I are summarized in Table I.

TABLE I

DIPOLE MOMENT DATA FOR BIS-(*p*-CHLOROPHENYLCYCLOPENTADIENYL)-IRON IN BENZENE AT 24.90°

Wt. fract. (w_2)	Sp. vol. (V)	ϵ	$n^{24.9}D$
0.000000	1.14564	(2.26992)	1.49701
.010957	1.14073	2.30198	1.49835
.016409	1.13817	2.32112	1.49897
.022337	1.13555	2.32997	1.49960
.030856	1.13171	2.36243	1.50052

$\alpha = \Delta\epsilon/\Delta w_2 = 2.92727$ $\beta = \Delta V/\Delta w_2 = -0.45203$

$MR_D = 109.5 \pm 0.7$ $\mu = 3.12 \pm 0.03$ D.

Discussion of Results

The dipole moments expected for non-freely rotating bis-(*p*-chlorophenyl)-ferrocene structures (see I) and for a freely rotating model were calculated using the following assumptions. (1) Only the C–Cl moments make important contributions to the dipole moment of the molecule—*i.e.*, phenylferrocene would have a very low or zero dipole moment. This assumption is supported by the close agreement between the dipole moments of acetophenone (2.97 *D*)[20] and monoacetylferrocene (3.02 *D*)[9] and the near identity of the first acid ionization constant of ferrocenedicarboxylic acid with that of benzoic acid.[21] These data indicate that the ferro-

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[1] Gates and Crellin Laboratories of Chemistry, California Institute of Technology.

[2] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

[3] For a review of the literature of ferrocene and related compounds, see P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

[4] E. O. Fisher and W. Pfab, *Z. Naturforsch.*, **7b**, 377 (1952).

[5] W. Pfab and E. O. Fisher, *Z. anorg. Chem.*, **274**, 317 (1953).

[6] P. F. Eiland and R. Pepinsky, THIS JOURNAL, **74**, 4971 (1952).

[7] J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

[8] E. A. Seibold and L. E. Sutton, *J. Chem. Phys.*, **23**, 1967 (1955).

[9] H. H. Richmond and H. Freiser, THIS JOURNAL, **77**, 2022 (1955).

[10] W. Moffitt, *ibid.*, **76**, 3386 (1954).

[11] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

[12] V. Weinmayr, THIS JOURNAL, **77**, 3012 (1955).

[13] P. L. Pauson, *ibid.*, **76**, 2187 (1954).

[14] O. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[15] M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

[16] J. D. Roberts, R. Armstrong, R. F. Trimble and M. Burg, *ibid.*, **71**, 843 (1949).

[17] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[18] G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[19] C. P. Smyth, "Dielectric Constants and Molecular Structure," (The Chemical Catalog Co.) Reinhold Publ. Corp., New York, N. Y., 1931, Chap. I.

[20] O. Hassel and A. H. Uhl, *Z. physik. Chem.*, **8B**, 187 (1930).

[21] R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

cenyl and phenyl groups have comparable electronegativities. (2) The C–Cl axes lie in the planes of the cyclopentadienyl rings to which the *p*-chlorophenyl groups are attached. This orientation of the C–Cl bond is expected if the cyclopentadienyl carbon atoms form the usual aromatic-type sp^2-bonds to substituents. The calculated distance between the cyclopentadienyl rings, 3.6 Å.,[22] is probably large enough to preclude distortion by steric repulsions between substituents on different rings. The vector moment of each C–Cl bond was taken as 1.56 *D*.[23]

The dipole moment for the freely rotating model was calculated using the equation for freely rotating angular groups[9,24] where α and β are the angles (α =

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

β = 90°) which the moment vectors of the *p*-chlorophenyl groups make with the axes about which they rotate and θ (180°) is the angle between these axes; a and b ($a = b = 1.56$) are the electric moment vectors.

The dipole moments calculated for the various possible structures of the bis-(*p*-chlorophenyl)-ferrocene are summarized in Table II.

TABLE II

DIPOLE MOMENTS CALCULATED FOR DI-(*p*-CHLOROPHENYL)-FERROCENE STRUCTURES

Structure (see I)	Dipole moment, *D*
1,1′, prismatic	3.12
1,1′, antiprismatic	2.97
1,2′, antiprismatic	1.83
1,3′, antiprismatic	0
Freely rotating cyclopentadienyl rings	2.20

The experimental moment of 3.12 ± 0.03 *D* eliminates a freely rotating model (calculated μ = 2.20 *D*) and is in closest agreement with the moment expected for the 1,1′, prismatic (method I) or 1,1′-antiprismatic (method II) structure. Configurations like these with angles of only 0–36° between the two C–Cl dipole vectors would not be expected to be favored on the basis of dipole–dipole repulsions. However, the tendency for molecules to exist in "*cis*-like" configurations irrespective of such repulsions has been noted in other cases. Thus, the *cis*-configuration of disalicylide is apparently most stable and this has been attributed to resonance involving the lactone bridge.[25] An analogous preference for a *cis*-like "boat" configuration as the most stable form of 1,6-dichloro-1,5-cycloöctadiene has been explained by operation of secondary valence forces,[26] possibly dispersion forces. Such valence forces may also account for why bis-di-(*p*-chlorophenyl)-ferrocene appears to exist in a configuration with the *p*-chlorophenyl groups quite close to one another. A similar conclusion was reached by Hampson and Weissburger[27] with regard to the orientations of the *ortho*-substituents in *o,o′*-dichlorobiphenyl.

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[22] The value of 3.6 Å. is obtained using a value of 1.4 Å. for the C–C ring distance and 2.0 Å. for the C–Fe distance.[3,6,7]

[23] Reference 19, p. 203.

[24] O. Fuchs, *Z. physik. Chem.*, **14B**, 339 (1931).

[25] W. Baker, W. D. Ollis and T. S. Zeally, *J. Chem. Soc.*, 201 (1951).

[26] J. D. Roberts, THIS JOURNAL, **72**, 3300 (1950).

[27] G. C. Hampson and A. Weissberger, *ibid.*, **58**, 2113 (1936).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies in the Ferrocene Series. I. Some Reactions of Compounds Related to Monobenzoylferrocene[1]

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The ketones benzoylferrocene (I) and anisoylferrocene and several diketones have been made from ferrocene (dicyclopentadienyliron) by Friedel–Crafts acylations. Benzoylferrocene is reduced to the pinacol, 1,2-diphenyl,1,2-diferrocenylethanediol (IV), with methylmagnesium bromide in the presence of cobalt chloride; the same ketone is reduced to phenylferrocenylmethanol (II) with lithium aluminum hydride, to phenylferrocenylmethane (X) with zinc, sodium or aluminum and to still another carbinol, probably phenyldiferrocenylmethanol (IX), with sodium amalgam in benzene. The pinacol rearranges with extraordinary ease, with migration of the ferrocene moiety, and is surprisingly easily oxidized to the parent ketone by atmospheric oxygen. The secondary alcohol, phenylferrocenylmethanol, forms ethers under exceptionally mild conditions and behaves somewhat like a tertiary alcohol. These reactions suggest that a carbonium ion obtained by removal of an -OH group alpha to the ferrocene system is subject to special stabilization, possibly by dispersal of the positive charge through partial shift of *d*-electron density from the iron atom into the ring. The oxime of benzoylferrocene (VII) rearranges, through its tosylate, to the anilide of ferrocenecarboxylic acid (VIII).

The easy preparation and purification of benzoylferrocene allows the synthesis and study of a number of relatively simple compounds in which the benzene ring and the ferrocene system are attached to a common carbon atom. Chart I summarizes the transformations which we have carried out.

Acylations.—By suitable variations of reaction conditions, the Friedel–Crafts acylation of ferro-

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