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BRIDGED FERROCENES—IX[1]
ELECTRIC DIPOLE MOMENTS AND PREFERRED CONFORMATIONS OF [m]FERROCENOPHANES AND RELATED COMPOUNDS

H. LUMBROSO and C. PIGENET
Laboratoire de Chimie Générale, Sorbonne, Paris, France

and

H. L. LENTZNER* and W. E. WATTS
School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland

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Abstract—The electric dipole moments of a series of bridged and non-bridged ferrocene derivatives have been measured and the results interpreted in terms of the preferred conformations of these molecules.

INTRODUCTION

THE DETERMINATION of the dipole moments of organic molecules has proved to be a most useful experimental probe for the elucidation of the electronic distribution and preferred conformation of a large variety of molecules.[2] Surprisingly this technique has been used only infrequently in the investigation of organo-transition metal complexes in general and metallocene derivatives in particular although the zero dipole moments exhibited by the iron group metallocenes themselves provided early indication of the sandwich structure of these complexes. For those metallocene derivatives which have been examined, the measured dipole moments have been interpreted in favour of a model in which there is essentially free rotation of the cyclopentadienyl rings, except in special cases where dispersion forces between heteroannular substituents favour a partially eclipsed rotameric conformation.[3]

In a recent study,[4] Sorriso and Lumbroso concluded that certain 1,1′-diacylferrocenes may exist in three conformations *viz.* a *meso* structure and two equally abundant *d* and *l* forms of lower energy. The potential energy barrier to ring rotation was calculated to be highest for the *meso* structure. Since the dipole moments of these compounds are compatible with the moment of *dl* bis(1,2)(1′,2′)-(α-ketotetramethylene)-ferrocene and not with the moment of the corresponding *meso* isomer, it was also inferred that 1,1′-diacylferrocenes exist mainly in *d* and *l* conformations.

In an extension of this work, we have measured the dipole moments of a series of [m]ferrocenophanes[5] in which the geometry and rotational freedom of the ferrocene molecule are modified to varying extents by the interannular bridging chains. The unique conformational properties of compounds of this type have previously been studied by spectroscopic means[6,7] and the results of the present investigation provide complementary information.

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* Present address: Collège Scientifique Universitaire, Rue des Frères Lumière, Mulhouse, France.

DISCUSSION

The dipole moments were measured at 25° for benzene solutions. In Table 1, the values for several monosubstituted ferrocenes and the corresponding heteroannularly disubstituted derivates are listed. Literature values for analogous benzenoid compounds are included for comparison. The results obtained for a series of bridged ferrocenes are collected in Table 2.

TABLE 1. DIPOLE MOMENTS OF BENZENE AND FERROCENE DERIVATIVES[a]

Substituent R	μ (PhR) D	μ (FcR) D	μ[$(C_5H_4R)_2Fe$] D
Me	0·35[13]	—	0·54 (0·03)[b]
Et	0·35[13]	0·57 (0·03)[b]	0·88 (0·03)[b]
Pr, Bu	0·37[13]	—	—
Cl	1·59[13]	1·55[10,c]	2·07[4,d]
CHO	2·99[13]	3·46[4]	4·04[4]
COMe	2·92[19]	3·09[4,e]	4·23[4,e]
COPh	3·00[20]	3·01[4]	3·75[4,e]

[a] In benzene solution at 25° unless indicated otherwise, taking $({}_{E}P + {}_{A}P) = R_D$. References to previous measurements are indicated by superscript.

[b] This work. Estimated limits of error are given in brackets.

[c] 1·59D in decane at 20°.[11]

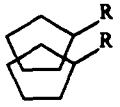
[d] 2·04–2·07D in decane between 4·92° and 60·47°.[11]

[e] In benzene solution at 30°.

Non-bridged ferrocenes

The dipole moments of simple monosubstituted ferrocene derivatives are similar in magnitude to those observed for benzenoid analogous (Table 1). The greater capacity for electron release by the ferrocenyl group compared to phenyl, however, is manifested in the values measured for derivatives containing electron-withdrawing substituents (*e.g.* COR). Thus, a more pronounced polarization of the carbonyl group is found for acylferrocenes (FcCOR) whose moments are correspondingly higher than those of analogous acylbenzenes (PhCOR). This divergence is particularly marked in the case of the formyl derivatives ($\Delta\mu$ = *ca.* 0·5D). The abnormal basicity of formylferrocene, which is readily soluble in aqueous mineral acids,[8] is also clearly related to an accumulation of negative charge on the carbonyl oxygen atom which is readily protonated. Predictably, electron withdrawal from the ferrocenyl system by the carbonyl groups in acetyl- and benzoyl-ferrocene is attenuated by the methyl and phenyl groups which may also supply electron density through hyperconjugative (Me) or conjugative (Ph) effects. The dipole moments of these ketones approach more closely the values for the corresponding benzene derivatives (PhCOMe and PhCOPh respectively).

The close similarity between the moments of chlorobenzene and chloroferrocene indicates that the halogen atom exerts an electron-releasing mesomeric effect of similar magnitude for each compound. Hyperconjugative electron donation by the ethyl substituent seems to be somewhat more important in ethylferrocene than in ethylbenzene even allowing for the relatively high errors associated with the measurement of low dipole moments. From these results, it may be concluded that, while the ferrocenyl and phenyl groups show a similar response to electron-releasing substituents, the former possesses a greater capacity for mesomeric (*i.e.* conjugative) electron donation in the ground state. The same conclusion may be drawn from a comparison of other physical properties of benzene and ferrocene derivatives.[3]



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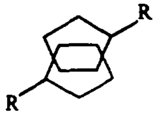

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The dipole moments of symmetrically 1,1′-disubstituted ferrocenes (Table 1) are intermediate between those calculated for an eclipsed conformation (**1**) and an anti structure (**2**) (*i.e.* with respect to the orientation of the ring substituents). Assuming that the ring planes are parallel, as with ferrocene itself, the latter conformation (**2**) of necessity would possess a zero moment. In the gas phase, ferrocene is known to adopt preferentially a prismatic conformation (**1**; R = H) with a low potential energy barrier (*ca.* 1 kcal/mole[9]) to ring rotation. In fact, the moments of 1,1′-dimethylferrocene (0·54D), 1,1′-diethylferrocene (0·88D), and 1,1′-dichloroferrocene (2·07D) are close to those calculated for an equimolecular mixture of all possible rotameric conformations (*i.e.* $0{\cdot}35\sqrt{2} = 0{\cdot}49$D, $0{\cdot}57\sqrt{2} = 0{\cdot}81$D, and $1{\cdot}55\sqrt{2} = 2{\cdot}19$D respectively). The experimental moments of these compounds could also be accounted for on the basis of conformationally "frozen" structures with dihedral angles between

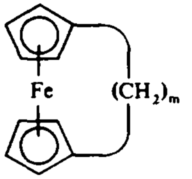
TABLE 2. DIPOLE MOMENTS OF BRIDGED FERROCENES AND RELATED COMPOUNDS[a]

No.	Compound[b]	μ D
1	1,1,2,2-Tetramethyl[2]ferrocenophane (**4**)	1·00 (0·02)
2	[3]Ferrocenophane (**3**: m = 3)	0·85 (0·02)
3	[4]Ferrocenophane (**3**: m = 4)	0·81 (0·02)
4	[5]Ferrocenophane (**3**: m = 5)	0·76 (0·01)
5	α-Acetyl-1,1′-dimethylferrocene	3·15 (0·01)
6	α-Acetyl[4]ferrocenophane (**8**: m = 4)	3·12 (0·03)
7	α-Acetyl[5]ferrocenophane (**8**: m = 5)	2·91 (0·02)
8	β-Acetyl-1,1′-dimethylferrocene	3·61 (0·02)
9	β-Acetyl-1,1′-diethylferrocene	3·61 (0·02)
10	β-Acetyl[3]ferrocenophane (**7**: m = 3)	3·94 (0·02)
11	β-Acetyl[4]ferrocenophane (**7**: m = 4)	3·86 (0·03)
12	β-Acetyl[5]ferrocenophane (**7**: m = 5)	3·82 (0·03)
13	[3]Ferrocenophan-1-one (**9**: R = H, m = 3)	3·31 (0·03)
14	[4]Ferrocenophan-1-one (**9**: R = H, m = 4)	3·47 (0·05)
15	[5]Ferrocenophan-1-one (**9**: R = H, m = 5)	3·30 (0·01)
16	2-Methyl[5]ferrocenophan-1-one (**9**: R = Me, m = 5)	3·32 (0·02)
17	[5]Ferrocenophane-1,5-dione (**10**)	4·66 (0·01)
18	[5]Ferrocenophan-2-ene-1,5-dione (**11**)	3·96 (0·03)
19	2-Oxa[3]ferrocenophane (**12**)	1·57 (0·02)
20	1,5-Oxy[5]ferrocenophane (**13**)	1·94 (0·02)

[a] In benzene solution at 25°. Estimated limits of error are given in brackets.

[b] Formulae are given in the text.

the C—R bonds of 78° (R = Me), 78° (R = Et), and 96° (R = Cl). However, there is no reason to suppose that ring–ring torsion would be completely restricted in these molecules and we therefore favour a model in which the rings are rotating almost freely. In the case of the dichloro compound, dipole–dipole repulsion may reduce the population of eclipsed (**1**; R = Cl) or near eclipsed conformations leading to an experimental value lower than that calculated for a free-rotation model.[10] Similar conclusions were reached in a more detailed study[11] of the temperature dependence of the dipole moments of 1,1′-dichloro- and 1,1′-dibromoferrocene. The problem concerning the restriction of ring rotation for the two stereoisomeric forms of bis(α-ketotetramethylene)ferrocene and for both corresponding conformers of 1,1′-diacylferrocenes was discussed in an earlier paper.[14]



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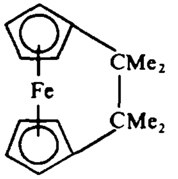

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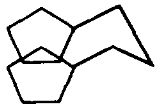

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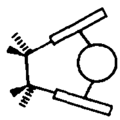

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Bridged ferrocenes

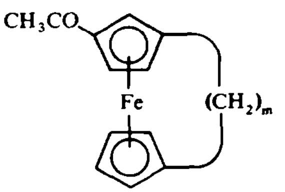
[m]Ferrocenophanes (**3** and **4**) exhibit significant differences in their dipole moments (Table 2) which follow the order

$$\mathrm{Me_4[2]} > [3] \geqslant [4] > [5].$$

For the PhR series (R = alkyl), the dipole moment does not vary with the identity of the alkyl group (Table 1). It is unlikely, therefore, that the variation in the [m]-ferrocenophane moments can be attributed to unequal [C_5H_4—$(CH_2)_m$] group moments for the compounds of the series. We therefore suggest that the variation observed is due to differences in the angle between the [C_5H_4—$(CH_2)_m$] group moments (directed from the α-methylene carbon atom to the geometrical centre of the cyclopentadienyl ring) for the preferred conformations of the molecules of the series (**3**: m = 3, 4, and 5). A special case is presented by the [2]ferrocenophane (**4**) (*vide infra*).

Dreiding molecular models show that the alkyl bridge in [3]ferrocenophane (**3**; m = 3) must adopt a "half-chair" conformation (**5**) such that the [C_5H_4—CH_2] group moments are eclipsed and almost parallel. Since the dipole moment of this compound is 0·85D, a value of *ca.* 0·42D can therefore be derived for the [C_5H_4—CH_2] group moment. The moment of [4]ferrocenophane (**3**; m = 4) is similar in magnitude but probably slightly lower than that of the [3]-homologue. The most stable conformation of the molecule will be that in which eclipsing interactions in the alkyl bridge are minimized and may be attained by a slight displacement of the α-methylene groups from an eclipsed arrangement leading to a small dihedral angle between the [C_5H_4—CH_2] group dipoles. The maximum displacement possible would permit the ferrocene system to attain an antiprismatic structure and leads to a calculated moment of 0·75D. In the case of [5]ferrocenophane (**3**; m = 5), the longer bridging chain permits a greater displacement (up to *ca.* 72°) of the α-methylene groups from an eclipsed arrangement and the dipole moment of this compound is accordingly lowest of the series.

The crystal structure of the tetramethyl[2]ferrocenophane (4) has shown[12] that the molecule is distorted. The exocyclic C—C bonds are displaced by *ca.* 11° from the individual cyclopentadienyl ring planes, which are mutually inclined by *ca.* 23°, and the rings are staggered by *ca.* 10° (*cf.* 6). Considering only the contribution of the ring-alkyl group dipoles to the molecular moment, such a structure has a calculated dipole moment 15% lower than that of [3]ferrocenophane. In fact, the experimental moment of this compound (4) is by far the highest of the series. Clearly a finite moment must be associated with the ring-tilted ferrocene system which acts to augment the ring-alkyl group dipoles.



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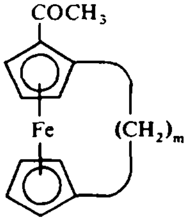

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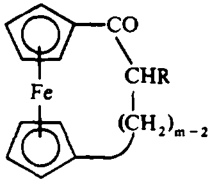
The dipole moments of the acetyl derivatives of the [m]ferrocenophanes and non-bridged analogues show some interesting trends. The values for the β-acetyl[3]-, -[4]-, and -[5]ferrocenophanes (7; m = 3, $\mu = 3{\cdot}94D$; m = 4, $\mu = 3{\cdot}86D$; m = 5, $\mu = 3{\cdot}82D$ respectively) are almost exactly the sums of the individual moments of acetylferrocene and the parent ferrocenophane (*i.e.* $3{\cdot}09 + 0{\cdot}85 = 3{\cdot}94D$; $3{\cdot}09 + 0{\cdot}81 = 3{\cdot}90D$; $3{\cdot}09 + 0{\cdot}76 = 3{\cdot}85D$ respectively). With respect to the orientation of the acetyl group, two conformations of these molecules are possible in which the carbonyl group attains coplanarity and thus maximum resonance interaction with the adjacent cyclopentadienyl ring.[4] In neither conformation, however, do the group moments associated with the acetylferrocene moiety (acting at 47° to the ring-carbonyl bond[4]) and the [m]ferrocenophane moiety become parallel and hence directly additive. The observed moments, therefore, suggest the operation of a small mesomeric (hyper-conjugative) interaction between the methylene and carbonyl groups in the β-$MeCOC_5H_3CH_2$ systems. No such effect has been found[13] for benzenoid compounds (*e.g.* between the methyl and carbonyl groups in *p*-methylbenzaldehyde or *p*-methylacetophenone).

The moments of β-acetyl-1,1′-dimethylferrocene and β-acetyl-1,1′-diethylferrocene ($\mu = 3{\cdot}61D$ for both) are lower than that of β-acetyl[3]ferrocenophane ($\mu = 3{\cdot}94D$). This is readily explained on the basis of free rotation of the cyclopentadienyl rings in these non-bridged molecules. In accord with this model, the observed moments are close to that (3·54D) calculated on the basis of an equimolecular mixture of conformers in which the alkyl groups are either eclipsed (μ taken as 3·94D = moment of 7; m = 3) or anti (μ taken as 3·09D = moment of acetylferrocene).

The dipole moments of the α-acetyl derivatives are all appreciably lower than those of the β-acetyl isomers. In the case of *o*-methylacetophenone, the low dipole moment

(2·60D,[14a] 2·65D[14b]) shows that the molecule preferentially adopts an *s–cis* conformation, presumably because the *s–trans* form incorporates greater steric hindrance between the methyl groups. The same situation is likely to obtain with the α-acetyl derivatives of 1,1′-dimethylferrocene and the ferrocenophanes (**8**; m = 4 and 5). Accurate calculation of the moments of these compounds is difficult but, at least qualitatively, it appears that an *s–cis* conformation is preferred for these molecules also.



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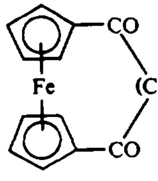

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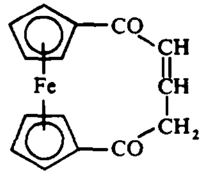

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At first sight, it is surprising that the dipole moments of the bridged ketones (**9**; R = H, m = 3, 4, and 5; R = Me, m = 5) are so similar in magnitude (3·31, 3·47, 3·30, and 3·32D respectively). The moments of compounds of this type depend mainly upon two factors *viz.* (a) the magnitude of the mesomeric interaction between the cyclopentadienyl ring and the adjacent carbonyl group, and (b) the size of the angle between the group moments of the $[C_5H_4CO(CH_2)_{m-1}]$ and $[C_5H_4(CH_2)_{m-1}]$ moieties. Earlier studies[6,7] have established that the bridge length in these compounds influences the degree of resonance interaction between the carbonyl group and the cyclopentadienyl ring and, in this light, it would have been expected that the moments of the [5]-ketones (**9**; R = H and Me, m = 5) would have been higher than those of shorter bridge length (*i.e.* **9**; R = H, m = 3 and 4). However, the rings in the [3]-ketone are known to be tilted by *ca.* 9° from parallel planes in the crystal[15] and it has been established that the torsional freedom of the rings in the [m]ferrocenophane compounds varies with the length of the interannular bridge.[6] The observed moments of these ketones may then reflect an interplay and balancing of these effects.

The interannular bridge in the [5]-diketone (**10**) is known[6] to be flexible and, in solution a mixture of various conformers will be present. Molecular models reveal that two limiting conformations of this molecule are possible in which both carbonyl groups attain coplanarity with the adjacent cyclopentadienyl rings and in which the carbonyl group dipoles are either almost exactly opposed or eclipsed. The latter conformation is disfavoured by the repulsion energy (*ca.* 1·8 kcal/mol[4]) associated with eclipsed carbonyl dipoles. Moreover, the dipole moment calculated for an eclipsed conformation (*ca.* 7·0D) is much higher than the experimental value (4·66D). Estimation of the moment of the opposed conformation is more difficult since a knowledge of the actual angles between the C=O bonds and between each vector and the $[C_5H_4—CO]$ axis is required but a value of 3·8D may be reasonably assumed. The experimental moment of the diketone (**10**) may then be accounted for on the basis of a mixture of *ca.* 80% opposed conformers and 20% eclipsed conformers.

The moment of the [5]-enedione (**11**) is lower than that of the saturated relative (**10**). The presence of a double bond in the former compound must reduce and may perhaps

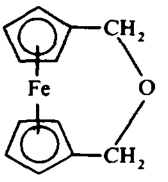
TABLE 3. PHYSICAL DATA FROM DIPOLE MOMENT DETERMINATIONS

Compound[a]	w_{max}	α_0	$-\beta$	$P_{2\infty}$	$R_D{}^b$	μ
Ethylferrocene	0·070	0·28	0·276	66·7	60·0	0·57
1,1'-Dimethylferrocene	0·038	0·37	0·340	66·2	60·3	0·54
1,1'-Diethylferrocene	0·016	0·48	0·266	85·3	69·6	0·88
(1)	0·012	0·66	0·343	97·4	76·8	1·00
(2)	0·029	0·66	0·407	77·7	62·9	0·85
(3)	0·014	0·58	0·385	80·6	67·1	0·81
(4)	0·033	0·46	0·329	84·0	72·2	0·76
(5)	0·020	4·50	0·396	273·8	70·3	3·15
(6)	0·005	3·96	0·358	276·2	77·6	3·12
(7)	0·019	3·40	0·400	255·0	82·2	2·91
(8)	0·008	5·80	0·400	336·0	70·3	3·61
(9)	0·006	5·19	0·335	345·8	79·6	3·61
(10)	0·011	6·58	0·417	389·7	72·9	3·94
(11)	0·010	5·97	0·374	381·4	77·6	3·86
(12)	0·017	5·63	0·393	379·7	82·2	3·82
(13)	0·010	5·30	0·480	286·7	63·2	3·31
(14)	0·013	5·60	0·469	318·6	67·9	3·47
(15)	0·011	4·76	0·459	294·7	72·5	3·30
(16)	0·011	4·47	0·366	302·5	77·2	3·32
(17)	0·010	8·65	0·456	516·3	72·9	4·66
(18)	0·010	6·50	0·525	393·6	72·4	3·96
(19)	0·009	1·38	0·384	110·9	60·2	1·57
(20)	0·009	1·80	0·414	149·1	71·9	1·94

[a] Bracketed numbers refer to the compound listing given in Table 2.

[b] Calculated by additivity using experimental refractions of ferrocene[21] (50·4 cm^3), toluene (31·10 cm^3), and acetophenone (36·27 cm^3), and pertinent bond refraction increments.[22] Within the estimated error ($\pm$0·5 cm^3), experimental values are in agreement with given figures.

even remove the conformation flexibility of the 5-carbon bridge. A preferred conformation may then be adopted in which the angle between the carbonyl group dipoles is increased compared with the *mean* angle described for the saturated compound (**10**). The operation of such an effect would result in a lower moment for the unsaturated diketone (**11**).



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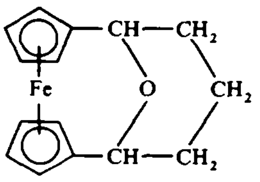

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Finally, the dipole moments of the bridged ethers (**12** and **13**) have been measured. In the former compound, the bridge most probably adopts a half-chair conformation by analogy with the structure of [3]ferrocenophane (**5**). The observed moment (1·57D) is close to the vectorial sum of the moments of tetrahydrofuran (1·75D[13]) and [3]-ferrocenophane (0·85D) which, assuming an angle of 125° between these vectors, is calculated to be 1·5D. Similarly, the observed moment of the bridged tetrahydropyranyl ether (**13**) is in accord with that calculated for a model in which the tetrahydropyran ring adopts a chair conformation with the cyclopentadienyl rings attached by axial bonds. From the known values[13] of the moments of tetrahydrofuran (1·75D), tetrahydropyran (1·55D) and dimethyl ether (1·25D), the moment calculated for this stereochemistry (1·9D) is close to the experimental value (1·94D).

EXPERIMENTAL

The methods of preparation and characterization of the compounds used in this study have been described previously.[3,5,16]

The dipole moment measurements were obtained for benzene solutions at 25·00°. The value of the polarization of the solute, extrapolated to $w = 0$, was calculated from the experimental ratios:[17]

$$\alpha_0 = \lim._{(w=0)}\left(\frac{\varepsilon - \varepsilon_1}{w}\right) \text{ and } \beta = \frac{\Sigma(v - v_1)}{\Sigma w}$$

where w is the weight fraction of the solute and ε and v are respectively the dielectric constant and the specific volume of the solutions (subscript 1 refers to the pure solvent as used). The α_0 value was obtained by a mathematical analysis of the $\varepsilon(w)$ cubic polynomial function.

All weighings were carried out using a Sartorius microbalance and precautions were taken in the preparation of solutions and reference solvent to avoid contamination by air humidity. For each compound, at least eight solutions were examined. In each case, the $({}_EP + {}_AP)$ term was assumed equal to the molar refraction of the solute. The technique for the determination of dielectric constants and specific volumes has been described elsewhere.[18] For the solutions examined, w_{max} (indicated to three decimals only) α_0, $-\beta$, $P_{2\infty}$, R_D, and μ values are given in Table 3.

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