Journal of Organometallic Chemistry, 179 (1979) 205—213

ENERGY BARRIER TO INTERNAL ROTATION IN SOME FERROCENE DERIVATIVES FROM DIELECTRIC MEASUREMENTS

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(Received April 19th, 1979)

Summary

Dipole moments have been measured in n-decane at 5—130°C for the compounds monochloro-, 1,1′-dichloro-, monobromo-, 1,1′-dibromo-, monoiodo-, and 1,1′-diiodo-ferrocene. The energy barriers ($\Delta E_1 = E_{36^\circ} - E_{180^\circ}$ and $\Delta E_2 = E_{108^\circ} - E_{180^\circ}$) to rotation of the two cyclopentadiene rings about the bond to iron have been calculated. Conclusions are reached about the principal energy contributions giving rise to the barrier.

Introduction

The electronic structure of sandwich molecules such as ferrocene ($Fecp_2$), nickelocene ($Nicp_2$), ruthenocene ($Rucp_2$) and others [1] has long been of interest theoretically. An important question in this field regards the type of bond between the metal and the organic moiety; on this depends the possibility that the two cyclopentadiene rings may (or may not) rotate about the five-fold axis. There is hence some similarity between the 1,1′-dihalo derivatives of these sandwich molecules and the 1,2-dihaloethane derivatives. Although much information is available on the latter [2], there is very little on the organometallic compounds.

This note is a contribution to the study of such molecules, and aims to complete the series of the halo derivatives of ferrocene. The molecules investigated are: monochloroferrocene (I), 1,1′-dichloroferrocene (II), monobromoferrocene (III), 1,1′-dibromoferrocene (IV), monoiodoferrocene (V), 1,1′-diiodoferrocene (VI).

Compounds (I) to (IV) have previously been studied at various temperatures [3] with the aim of determining the energy barrier to rotation. However, they have been re-investigated so as to allow a better comparison within the series because there is some uncertainty in the earlier experimental values.

Experimental

Materials

All the compounds were prepared by published methods [4].

Physical measurements

Electric dipole moments were determined in n-decane. The dielectric constants were measured at 1.8 MHz with a heterodyne beat apparatus (WTW dipolmeter). Refractive indices were measured with a Bausch and Lomb refractometer with a reproducibility of 0.00005. The total molar polarization and molar refraction at infinite dilution of the molecules were calculated by the method of Halverstadt and Kumler [5].

Results and discussion

Table 1 lists the dipole moments, together with the parameters used to calculate them. Figure 1 shows the variation of the observed moments with temperature.

Figure 1 shows that the moments increase in a regular fashion for all the disubstituted compounds, indicating that they show restricted internal rotation about five-fold axis. For this to be possible energetically, the interaction forces between the C—X moiety (X = Cl, Br and I) of a ring and the C—H's of the other ring must be similar to the thermal energy at the temperatures investigated. Obviously, if this is the situation in these derivatives, it is reasonable to expect that virtually free rotation exists in the parent molecule, ferrocene, in

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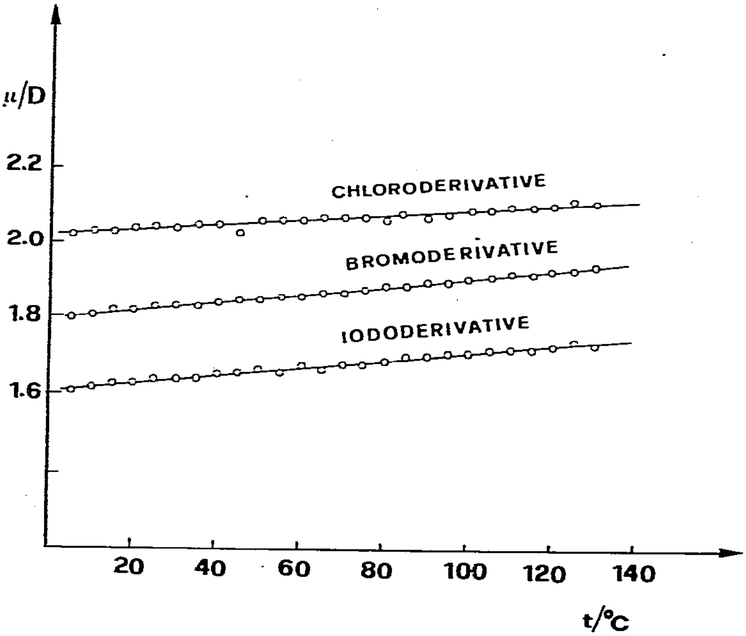

Fig. 1. The temperature dependence of the observed electric dipole moment.

TABLE 1

OBSERVED DIPOLE MOMENTS OF FERROCENE DERIVATIVES AND PARAMETERS USED FOR THEIR CALCULATION

Compound	T(°C)	ϵ_1 [a]	α [b]	V_1 [c] (ccg^{-1})	β [d]	n_1^2 [e]	γ [f]	R_D(cc)	$P_{2\infty}$(cc)	μ(D)
$FeC_5H_5C_5H_4Cl$	25,0	1,9799	1,224	1,3774	−0,686	1,9866	0,301	55,0	107,9	1,61
$Fe(C_5H_4Cl)_2$	5,0	2,0012	1,727	1,3501	−0,756				149,3	2,02
	10,0	1,9962	1,664	1,3570	−0,721				148,6	2,03
	15,0	1,9916	1,591	1,3637	−0,686				147,1	2,03
	20,0	1,9858	1,580	1,3700	−0,694				146,4	2,04
	25,0	1,9797	1,547	1,3776	−0,708	1,9866	0,268	60,0	145,0	2,04
	30,0	1,9737	1,502	1,3850	−0,700				143,6	2,04
	35,0	1,9677	1,469	1,3918	−0,690				143,0	2,05
	40,0	1,9616	1,434	1,3990	−0,690				141,7	2,05
	45,0	1,9556	1,380	1,4066	−0,692				138,9	2,03
	50,0	1,9494	1,373	1,4140	−0,685				139,9	2,06
	55,0	1,9432	1,334	1,4214	−0,677				138,7	2,06
	60,0	1,9372	1,313	1,4287	−0,688				137,5	2,06
	65,0	1,9308	1,302	1,4357	−0,698				137,1	2,07
	70,0	1,9248	1,284	1,4450	−0,715				136,0	2,07
	75,0	1,9182	1,266	1,4541	−0,731	1,9254	0,220	59,9	134,9	2,07
	80,0	1,9122	1,231	1,4625	−0,736				133,2	2,06
	85,0	1,9055	1,228	1,4710	−0,745				133,5	2,08
	90,0	1,8992	1,199	1,4792	−0,755				131,8	2,07
	95,0	1,8925	1,185	1,4885	−0,763				131,5	2,08
	100,0	1,8858	1,188	1,4978	−0,790				131,3	2,09
	105,0	1,8795	1,180	1,5067	−0,816				130,3	2,09
	110,0	1,8731	1,175	1,5160	−0,833				130,1	2,10
	115,0	1,8671	1,158	1,5255	−0,846				129,2	2,10
	120,0	1,8604	1,148	1,5352	−0,870				128,3	2,10
	125,0	1,8530	1,160	1,5448	−0,901				128,7	2,12
	130,0	1,8450	1,142	1,5549	−0,925				127,2	2,11
$FeC_5H_5C_5H_4Br$	25,0	1,9795	1,035	1,3770	−0,779	1,9860	0,178	58,3	110,5	1,60
$Fe(C_5H_4Br)_2$	5,0	2,0010	1,230	1,3503	−1,003				136,8	1,80
	10,0	1,9965	1,205	1,3572	−1,000				136,3	1,81
	15,0	1,9918	1,184	1,3640	−0,996				135,9	1,82
	20,0	1,9860	1,165	1,3702	−1,004				134,7	1,82
	25,0	1,9794	1,142	1,3773	−1,000	1,9869	0,378	65,9	134,3	1,83
	30,0	1,9732	1,123	1,3851	−1,011				133,1	1,83
	35,0	1,9678	1,100	1,3920	−1,013				132,1	1,83
	40,0	1,9614	1,076	1,3989	−1,005				131,7	1,84
	45,0	1,9553	1,059	1,4065	−1,006				131,4	1,85
	50,0	1,9490	1,036	1,4138	−1,008				130,4	1,85

(continued)

TABLE 1 (continued)

Compound	T(°C)	ε_1 [a]	α [b]	V_1 [c] (ccg^{-1})	β [d]	n_1^2 [e]	γ [f]	R_D(cc)	$P_{2\infty}$(cc)	μ(D)
	55,0	1,9435	1,016	1,4216	−1,004				130,1	1,86
	60,0	1,9372	1,001	1,4289	−1,014				129,1	1,86
	65,0	1,9308	0,989	1,4355	−1,016				128,9	1,87
	70,0	1,9249	0,976	1,4448	−1,031				127,9	1,87
	75,0	1,9184	0,961	1,4538	−1,034	1,9260	0,308	65,7	127,7	1,88
	80,0	1,9120	0,948	1,4624	−1,037				127,5	1,89
	85,0	1,9057	0,935	1,4708	−1,047				126,6	1,89
	90,0	1,8993	0,924	1,4790	−1,054				126,4	1,90
	95,0	1,8928	0,908	1,4884	−1,062				125,6	1,90
	100,0	1,8856	0,897	1,4980	−1,069				125,4	1,91
	105,0	1,8796	0,883	1,5065	−1,077				124,6	1,91
	110,0	1,8730	0,874	1,5155	−1,083				124,5	1,92
	115,0	1,8674	0,859	1,5250	−1,092				123,7	1,92
	120,0	1,8610	0,844	1,5352	−1,092				123,6	1,93
	125,0	1,8530	0,831	1,5446	−1,102				122,9	1,93
	130,0	1,8455	0,818	1,5548	−1,105				122,7	1,94
$FeC_5H_5C_5H_4I$	25,0	1,9790	0,813	1,3776	−0,795	1,9861	0,262	66,2	110,9	1,48
$Fe(C_5H_4I)_2$	5,0	2,0008	0,664	1,3506	−0,801				133,7	1,61
	10,0	1,9968	0,654	1,3575	−0,806				133,4	1,62
	15,0	1,9921	0,648	1,3642	−0,811				133,1	1,63
	20,0	1,9859	0,638	1,3704	−0,818				132,2	1,63
	25,0	1,9796	0,633	1,3770	−0,824	1,9872	0,150	77,0	131,9	1,64

30.0	1.9735	0.618	1.3849	−0.828				131.0	1.64
35.0	1.9675	0.608	1.3921	−0.835				130.1	1.64
40.0	1.9610	0.601	1.3991	−0.841				129.9	1.65
45.0	1.9558	0.595	1.4068	−0.845				129.7	1.66
50.0	1.9493	0.594	1.4136	−0.853				129.5	1.67
55.0	1.9433	0.575	1.4217	−0.858				128.1	1.66
60.0	1.9374	0.575	1.4291	−0.864				128.6	1.68
65.0	1.9309	0.559	1.4357	−0.867				127.2	1.67
70.0	1.9251	0.555	1.4440	−0.875				127.1	1.68
75.0	1.9183	0.543	1.4536	−0.880	1.9260	0.142	76.8	126.4	1.68
80.0	1.9119	0.534	1.4623	−0.883				126.2	1.69
85.0	1.9057	0.531	1.4705	−0.892				126.0	1.70
90.0	1.8990	0.522	1.4789	−0.897				125.5	1.70
95.0	1.8930	0.516	1.4880	−0.904				125.3	1.71
100.0	1.8850	0.505	1.4985	−0.909				124.7	1.71
105.0	1.8794	0.501	1.5064	−0.915				124.6	1.72
110.0	1.8732	0.492	1.4157	−0.921				124.0	1.72
115.0	1.8678	0.480	1.5250	−0.924				123.4	1.72
120.0	1.8615	0.475	1.5354	−0.932				123.3	1.73
125.0	1.8532	0.471	1.5449	−0.938				123.3	1.74
130.0	1.8459	0.460	1.5544	−0.945				122.2	1.73

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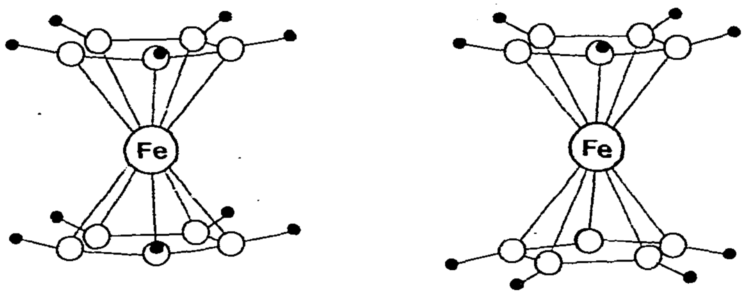
[a] Dielectric constant of the solvent, obtained by extrapolating to infinite dilution the solution values (ϵ_{12}). [b] $\Delta\epsilon_{12}/\Delta W_2$, where W_2 is the solute weight fraction (g solute/g soln.). [c] Specific volume of the solvent, obtained by extrapolating to infinite dilution the solution values (V_{12}). [d] $\Delta V_{12}/\Delta W_2$. [e] Refractive index square of the solvent, obtained by extrapolating to infinite dilution the solution values (n_{12}^2). [f] $\Delta n_{12}^2/\Delta W_2$.



eclipsed
or prismatic

(a)

staggered
or antiprismatic

(b)

Fig. 2. Rotamers suggested in the case of a fixed structure of the ferrocene.

which the electrostatic effects are reduced even further.

These conclusions agree with those found from electron diffraction [6], but are in conflict with results which suggest a fixed primatic-type structure [7] (Fig. 2). They have a bearing on the type of bond between the iron and the organic part of the molecule, on which point various theoretical treatments are in agreement [1].

As concerns the potential energy barrier to the rotation, the following alternative situations can be envisaged; (i) the only interaction of importance between the two of rings occurs through the two substituents X (halogen), and (ii) the barrier also includes interaction between the substituent X of one ring and the hydrogen of the other. Given the distance between the two rings and the van der Waals radii involved, there is no way of choosing between these possibilities. Both will be considered.

(i) Only C—X interaction is present

In this case, the energy function $V = V_0(1 - \cos\phi)$, ($2V_0$ is the difference in energy between the hypothetical *cis* and *trans* structures and ϕ the angle of rotation about the five-fold axis) has only one minimum (at $\phi = 180°$). The height of the barrier may be calculated from:

$$\mu^2_{\text{obsd}} = 2\mu_0^2 \sin^2\alpha \left[1 + \frac{ij_1\left(i\dfrac{V_0}{kT}\right)}{j_0\left(i\dfrac{V_0}{kT}\right)}\right] \tag{1}$$

where μ_{obsd} is the observed moment for the disubstituted compound, μ_0 is that for the mono-substituted analogue, $-V_0/kT = iz$, and j_1 and j_0 are the Bessel functions [8] of order 1 and 0, respectively, with complex argument. The values of $2V_0$ so obtained are reported in Table 2.

Before discussing these results, a few comments are necessary on their reliability. An uncertainty of 80—90 cal mol^{-1} (depending on the temperature) is estimated based on a pessimistic assessment of the uncertainty in observed

TABLE 2

ENERGY VALUES ($2V_0$) CALCULATED ASSUMING THE SIMPLE POTENTIAL FUNCTION $V = V_0(1 - \cos\phi)$ [a]

Compound	t(°C)	Energy (cal mol^{-1})	
		This work	Lit. [b]
1,1′-Dichloroferrocene	10.0	480 [c]	
	100.0	490	
	25.0		200
1,1′-Dibromoferrocene	10.0	850	
	100.0	890	
	25.0		700
1,1′-Diiodoferrocene	10.0	950	
	100.0	1040	
	25.0		850

[a] Here $2V_0$ indicates the energy difference between the hypothetic *cis* and *trans* forms. [b] From ref. 3b, in benzene. [c] The uncertainty in the energy calculation (±80—90 cal mol^{-1} at 10.0 and 100.0 °C) derives from the uncertainty of ±0.02 in the measured dipole moment. For the meaning see the text.

moment of 0.02 D (see footnote to Table 2). This uncertainty would be reasonable if the moment of the disubstituted compound had been determined at only one temperature. However, since measurements were carried out at various temperatures and the values used lay on the straight line $\mu = f(t)$, we feel secure that the uncertainty in $2V_0$ is much lower than that indicated in Table 2.

From the same Table, it is seen that the values found here are higher than those in the previous work (a different solvent was used, however). The discrepancy decreases as the atomic number of X decreases. Nevertheless, in both solvents the behaviour is as expected for an increasing steric effect of the substituent.

It is also seen that, whilst in dichloroferrocene (in which steric hindrance is negligible) the energies at two temperatures are virtually the same, for the other di-substituted derivatives this is not the case. In addition, this difference increases as the steric effect of X increases.

The uncertainty inherent in the measurements does not allow any further conclusions to be drawn, which is unfortunate given the good regularity found in the calculated values.

Given that the $2V_0$ values are not constant with change in temperature, the (not remote) possibility exists that eq. 1 may not be entirely valid. This would mean that the function $V = V_0(1 - \cos\phi)$ is not completely valid. The calculations were further developed taking into account possibility (ii).

(ii) Other interactions between the rings

In this case, the potential energy function for internal rotation should show several minima (in theory at ϕ = 36, 108, 180 (absolute minimum), 252, and 324, with $\phi = 0°$ corresponding to the hypothetical conformation in which the two C—X groups are at the minimum distance and in the same orientation) and several maxima (0 (absolute), 72, 144, 216 and 288°). The distribution of the molecules in these minima depending on the temperature would account for the change in moment with change in temperature.

To calculate the energy difference between these minima, we use eq. 2 at two temperatures.

$$\mu^2_{\text{obsd}} = 2\mu_0^2 \frac{2(\cos 36^\circ + 1)\, e^{-\Delta E_1/(RT)} + 2(\cos 108^\circ + 1)\, e^{-\Delta E_2/(RT)}}{2\, e^{-\Delta E_1/(RT)} + 2\, e^{-\Delta E_2/(RT)} + 1} \qquad (2)$$

in which $\Delta E_1 = E_{36^\circ} - E_{180^\circ}$ and $\Delta E_2 = E_{108^\circ} - E_{180^\circ}$.

Obviously, good values of ΔE may be obtained only if a wide temperature interval is explored and many measurements need to be carried out to reduce statistical errors to a minimum. Table 3 reports the calculated values.

There is again good regularity in the energies as a function of the dimension of the substituent X. In addition, there is close similarity between the values of Table 2 and those of Table 3. As expected, in each case the $2V_0$ values (which represent the energy difference $E_{0^\circ} - E_{180^\circ}$) are greater than the ΔE_1 values (which represent the energy difference $E_{36^\circ} - E_{180^\circ}$). In the same way, ΔE_2 values (i.e. $E_{108^\circ} - E_{180^\circ}$) are always much smaller than ΔE_1 values.

The close similarity found between the two values obtained by treatments (i) and (ii), as well as their regularity, makes a choice between the two rotational situations difficult. If we follow through the evidence presented for the derivatives examined here, the effective situation is more or less intermediate between (i) and (ii).

Steric effects between the substituent X of one ring and the hydrogens of the other ring should make themselves felt on the ΔE_2 values, whilst ΔE_1 values reflect those between the X of the two rings. Now, given the similarity in ΔE_2 values, it is probable that these effects are very small. This conclusion would agree with the structural data for ferrocene and the Van der Waals atomic radii.

In conclusion, we find it of interest to compare our own results with the most recent in the literature. Not long ago, theoretical calculations using the extended Hückel method, including *s*, *p* and *d* orbitals, were carried out on ferrocene, monochloro- and 1,1′-dichloro-ferrocene molecules [9]. For the ferrocene the calculated total energy is -22946.955 kcal mol^{-1}, for the prismatic form, and -22941.466 kcal mol^{-1} for the antiprismatic (Fig. 2) indicating that the preferred form is the prismatic. In the case of monochloroferrocene the

TABLE 3

ENERGY DIFFERENCE (ΔE (cal mol^{-1})) BETWEEN THE DIFFERENT MINIMA OF 1,1′-DIHALOFERROCENES

Compound	ΔE_1	ΔE_2
1,1′-Dichloroferrocene	410	80
	280	0 [a]
	0	−670 [a]
1,1′-Dibromoferrocene	800	140
	600	−150 [a]
1,1′-Diiodoferrocene	950	150

[a] From ref. 3a.

barrier for the total energy is of the order of 4.8 kcal mol^{-1}, the prismatic form having lower energy. In the case of the 1,1′-dichloroferrocene, it was found that the function of the potential rotation energy shows minima at angles ϕ of 0, 70 and 140°. The calculated relative statistical weights are 1.5% for $\phi = 0°$, 35% for $\phi = 70°$ and 63.5% for $\phi = 140°$, while the relative energies satisfy this difference: $E_{70°} - E_{140°} = 0.36$ kcal mol^{-1} and $E_{0°} - E_{140°} = 1.82$ kcal mol^{-1}.

Apart from the problem of the preferred structures, the most important aspect which emerges from a comparison of these results and our own is the consideration of energy values. In our case these are lower and lead to the assumption, as seen above, of free rotation for the ferrocene molecule, while for the dichloro derivative there would be rapid interconversion among several rotamers. In our opinion the principal reason should be sought in the effect of the solvent, of which the theoretical calculations take no account. Such an effect has been quantified by Onsager [2] according to whom when a molecule of electric dipole moment μ is transferred from a solvent of dielectric constant 1 to another of dielectric constant ϵ its rotational energy diminishes in proportion to the square of the moment. There is, however, a good agreement between the theoretical moments calculated by the Hückel method and those observed by us for mono- and dichloroferrocene.

Acknowledgements

We are greatly indebted to Drs. M. Davies, A. Coleman, R. Haas, R. Robertson who gave us the molecules examined. Partial support of this work by CNR (Consiglio Nazionale delle Ricerche, Roma) is grateful acknowledged.

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