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DIPOLE MOMENTS AND INTERNAL ROTATION IN 1,1'-DIHALOFERROCENES

S. SORRISO, G. CARDACI and S. M. MURGIA

Institute of Physical Chemistry, University of Perugia, Perugia (Italy)

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SUMMARY

The dipole moments of bromoferrocene, iodoferrocene, 1,1'-dibromoferrocene and 1,1'-diiodoferrocene have been measured in benzene. They indicate that the potential barrier between the *cis* and *trans* forms, which is very small for 1,1'-dichloroferrocene, increases for 1,1'-dibromo- and 1,1'-diiodoferrocene. The potential energy function shows minima at 36°, 108° and 180°. The differences $\Delta E_1 = E_{36°} - E_{180°}$ for the series have been calculated on the assumption that the minima at 180° and 108° are equal. The values obtained are consistent with increasing steric hindrance in the series Cl, Br, I.

INTRODUCTION

In a previous study of the molecular conformation of ferrocene derivatives, it was observed that 1,1'-diacetylferrocene and 1,1'-dibenzoylferrocene can exist in two isomeric rotational conformations, *meso* and racemic, in benzene, the racemic conformation being preferred[1]. It was also shown that there is free internal rotation in ferrocene dissolved in benzene. The mean azimuthal angle in 1,1'-dichloroferrocene suggests that there is hindrance to rotation in this case because of interaction between the chlorine atoms. This interaction is both steric and electrostatic, and it follows that increase in the size of the halogen should increase the hindrance to rotation.

In this work we propose to study steric hindrance in the Cl, Br, and I derivatives of ferrocene, in solution, by measurements of dipole moments.

EXPERIMENTAL

The monohalo and dihalo derivatives of ferrocene were prepared as described in ref. 2. The 1,1'-dibromo, 1-iodo and 1-bromo derivatives were purified by crystallization from ethanol. 1,1'-Diiodoferrocene (a liquid at room temperature) was purified by crystallization at −30° from ethanol. The purity of the compounds was checked by elemental analysis.

The dipole moment measurements were performed at 25 ± 0.1° in benzene[3]. The $P_{2\infty}$ values (total polarization at infinite dilution of the solute) were calculated by the Halverstadt and Kumler method[4]. The P_D value (deformation polarization)

TABLE 1

$FeC_5H_5H_4Br$			$Fe(C_5H_4Br)_2$		
$W_2 \times 10^{3a}$	$\varepsilon_{12}{}^b$	$V_{12}^c(cm^3/g)$	$W_2 \times 10^3$	ε_{12}	$V_{12}(cm^3/g)$
0.51	2.2733	1.1442	0.45	2.2730	1.1443
1.24	2.2742	1.1438	0.95	2.2734	1.1440
2.36	2.2754	1.1433	1.22	2.2741	1.1439
3.73	2.2769	1.1426	2.03		1.1433
5.01	2.2783	1.1419	4.65	2.2787	1.1414
ε_1^d 2.2728	V_1^e 1.1446 cm^3/g		ε_1 2.2722	V_1 1.1446 cm^3/g	
α^f 1.109	β^g 0.505		α 1.37	β −0.701	
R_D 57.9 cm^3	$P_{2\infty}$ 105.6 cm^3		R_d 65.4 cm^3	$P_{2\infty}$ 134.1 cm^3 μ 1.83 D	
	$\mu = 1.530$ D				
$FeC_5H_5C_5H_4I$			$Fe(C_5H_4I)_2$		
$W_2 \times 10^3$	ε_{12}	$V_{12}(cm^3/g)$	$W_2 \times 10^3$	ε_{12}	$V_{12}(cm^3/g)$
0.79	2.2725	1.1446	1.02	2.2737	1.1435
1.87	2.2734		2.96	2.2756	1.1422
3.92	2.2753	1.1425	4.51	2.2770	1.1411
7.99	2.2789	1.1402	6.01	2.2784	
8.75		1.1398	8.44	2.2808	1.1383
ε_1 2.2717	V_1 1.1446 cm^3/g		ε_1 2.2727	V_1 1.1442 cm^3/g	
α 0.892	β −0.555		α 0.939	β 0.702	
μ 1.46 D	R_D 63.1 cm^3 $P_{2\infty}$ 107.2 cm^3		R_D 75.9	$P_{2\infty}$ 134.7 cm^3 μ 1.68 D	

[a] g solute/g soln. [b,c] Dielectric constant and specific volume, respectively, of the solution. [d,e] Dielectric constant and specific volume, respectively, of the solvent, obtained by extrapolating the solution values to infinite dilution. [f] $\Delta\varepsilon_{12}/\Delta W_2$. [g] $\Delta V_{12}/\Delta W_2$.

was equated to R_D and calculated using $R_D = 50.4$ cm^3 for ferrocene[5] and bond refraction values taken from the literature[6].

The experimental dipole moments were reproducible to within ±0.02 D. The experimental results are shown in Table 1.

RESULTS AND DISCUSSION

1. *Internal rotation*

Taking the dipole moment of the bond C–X (X = Cl, Br, I) as being equal to those of the corresponding monosubstituted derivatives of ferrocene, it is possible to calculate the dipole moment of the 1,1′-dihalo derivatives of ferrocene for the case of free internal rotation around the ring–Fe–ring bond by using the relation $\mu = \sqrt{2} \cdot \mu_0 \cdot \sin\phi$ $(\phi = 90°)$. A comparison between the measured and theoretical values (Table 2) shows that internal rotation, which is almost free for the 1,1′-dichloroferrocene, as observed previously[1], is more hindered for the 1,1′-dibromo and 1,1′-diiodoferrocene, as expected from the Van-der-Waals atomic radii[7].

2. *Potential energy barrier*

The interaction of halogen atoms in 1,1′-dihaloferrocenes is very similar to that

TABLE 2

Compound	$\mu_{obs}(D)$	$\mu_{calcd}(D)$ *free rotation*	$\Delta E_1(cal)$ $(\Delta E_2=0)$
Chloroferrocene	1.53[a]		
1,1'-Dichloroferrocene	2.07[a]	2.16	160±80[b]
Bromoferrocene	1.53		
1,1'-Dibromoferrocene	1.83	2.16	620±80
Iodoferrocene	1.46		
1,1'-Diiodoferrocene	1.69	2.03	760±80

[a] H.Lumbroso, M. Sato, ref. 1. [b] The uncertainty in the energy determination arises from the uncertainty of ±0.02 D in the measured dipole moment.

in dihaloethanes. Thus it is initially assumed that the hindrance to free rotation is due only to the energy barrier between the halogen atoms. If the energy function is of the type $V = V_0 \cdot (1-\cos\phi)$, the energy barriers between the *cis* and *trans* conformers may be calculated from the expression[9]:

$$\mu^2 = 2\mu_0^2 \cdot \sin^2\phi \cdot \left[1 + \frac{i \cdot j_1\left(i \cdot \dfrac{V_0}{k \cdot T}\right)}{j_0\left(i \cdot \dfrac{V_0}{k \cdot T}\right)}\right]$$

where μ_0 is the dipole moment of the monohaloferrocene, μ is the experimental dipole moment for 1,1'-dihalogenoferrocene, j_1 and j_0 are the Bessel functions of 1 and 0 order, with complex argument[10]. The values of $2V_0$ are ≈200 cal for 1,1'-dichloroferrocene, ≈700 cal for 1,1'-dibromoferrocene and ≈850 cal for 1,1'-diiodoferrocene. These values are very small in comparison with the calculated energy barriers[11] (1950 cal and 2800 cal for 1,1'-dichloroferrocene and 1,1'-dibromoferrocene respectively). This indicates that the potential function shows different minima corresponding to the various conformations in the dihalogenoferrocenes. The shape of the potential energy *vs.* the rotation angle ϕ is shown in Fig. 1. From the experimental

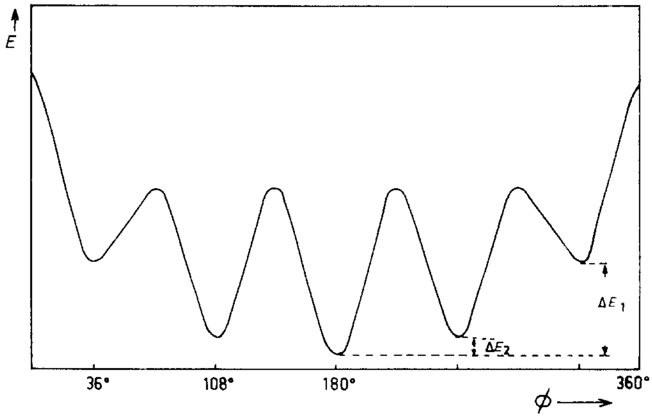

Fig. 1. Variation of dipolar potential energy with azimuthal angle in dihaloferrocenes.

dipole moments it is possible to calculate the energy differences between the different minima ($\Delta E_1 = E_{36^\circ} - E_{180^\circ}$; $\Delta E_2 = E_{108^\circ} - E_{180^\circ}$) using the following eqn.:

$$\mu^2 = 2\,\mu_0^2 \cdot \frac{2(\cos 36^\circ + 1)\cdot e^{-\Delta E_1/(R\cdot T)} + 2(\cos 108^\circ + 1)\cdot e^{-\Delta E_2/(R\cdot T)}}{2\,e^{-\Delta E_1/(R\cdot T)} + 2\,e^{-\Delta E_2/(R\cdot T)} + 1} \qquad (1)$$

In order to solve this equation it is necessary to know the dipole moments at different temperatures. Benzene solutions do not allow measurement of dipole moments over a large temperature range (m.p. 5.5° ; b.p. 80.1°), and eqn. (1) is strongly influenced by the variation of dipole moments with temperature[*], $\Delta\mu/\Delta T$. Therefore, taking $\Delta E_2 = 0$ in solution, the uncertainty in ΔE_1 is less than the experimental error[**].

Owing to the sensitivity of the method of calculation to uncertainty in the value of dipole moment, ΔE_1 values (Table 2) calculated using this approximation (± 0.02 D) are not suitable for quantitative comparison, but the trend is in keeping with increasing steric hindrance by the halogen atoms.

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[*] In ref. 11 $\Delta E_1 = 600$ cal and $\Delta E_2 = -150$ cal values are reported for 1,1′-dibromoferrocene in n-decane, using $\Delta\mu/\Delta T = 66 \times 10^{-5}$. We obtained $\Delta E_1 = 530$ cal and $\Delta E_2 = -600$ cal, using $\Delta\mu/\Delta T = 57 \times 10^{-5}$. This value is the arithmetic mean of 66×10^{-5} and 49×10^{-5}, obtained by least squares.

[**] It has been shown[12] that when a dipole of moment μ is transferred from a vacuum ($\varepsilon = 1$) into a medium of dielectric constant ε, it loses potential energy by an amount: $E_r = (\varepsilon - 1)/(2\varepsilon + 1)\cdot \mu/a^3$ where a is the molecular radius. Therefore, if $\Delta E_2 = 0$ for 1,1′-dichloroferrocene, then ΔE_2 must be either equal to zero or positive for the 1,1′-dibromo and 1,1′-diiodoferrocene, because the dipole moments of the monosubstituted complexes are equal and the molecular radii increase in the order Cl < Br < I. For this reason, and for reasons given in the preceding footnote, the ΔE_2 value of -150 cal for 1,1′-dibromoferrocene must be considered tentative.