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FUNDAMENTAL STUDIES OF SUBSTITUTED FERROCENE SYSTEMS. IV+

SOME ASPECTS OF THE CONTRIBUTION OF CONFORMER POPULATION TO THE MAGNETIC NONEQUIVALENCE OF DIASTEREOTOPIC NUCLEI

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Magnetic nonequivalence has been observed in many types of dissymmetric molecules. This nonequivalence is believed to arise from two factors, namely, (1) intrinsic diastereoisomerism and (2) relative conformer populations.[1,2] The equation $\Delta\nu_{total}=\Delta\nu_{id}+\Delta\nu_{cp}$ has been proposed to describe this relationship.[3] The term $\Delta\nu_{id}$ should be temperature independent while $\Delta\nu_{cp}$ should be temperature dependent. Aside from these initial papers, two other studies have been reported. The latter papers described the behavior of diastereotopic groups with change in temperature, a process which has been interpreted as an approach of the ratio of all conformations to unity (i.e., $\Delta\nu_{cp} \rightarrow 0$) with concomitant observation of $\Delta\nu_{total\ or\ observed} = \Delta\nu_{id}$. In one instance essentially straight lines were obtained (plain curve) from a plot of $\Delta\nu_{total}$ vs temperature,[4] but in the other an asymptotic approach of $\Delta\nu_{total}$ to a limiting value was observed at higher temperatures.[5] Implicity in at least one of these papers has been the assumption that the expected curve shape was sigmoid. Indeed in the instance where a sigmoid curve was not observed, the suggestion was advanced that a sufficient temperature range could not be examined and that a sigmoid curve would appear at some higher temperature.[4] In this communication are recorded data which demonstrate that observation of a plain or sigmoid curve may actually be exceptional and that more complex curves are in many cases to be expected.

As a continuation of our inquiries into the observation of geminal magnetic nonequivalence in 1,2-disubstituted ferrocenes,[6,7] 2-isopropyl dimethylaminomethylferrocene (1) was prepared. This compound possesses two sites of magnetic nonequivalence, the methylene protons and the two methyl groups of the isopropyl substituent. Table I contains the experimental data for this compound for $\Delta\nu_{obs}$

+ For part III, cf preceding communication at various temperatures obtained in benzene, o-xylene and toluene solvents. The two solvents, o-xylene and toluene, complement each other by allowing measurements from -60° to 180°. The fact that the data for o-xylene and toluene have nearby identical slopes in overlapping regions lends confidence to the correlation of the data over the entire temperature range. Evaluation of the effect of temperature on the nonequivalent methylene and methyl groups revealed some interesting phenomena. As can be seen from Fig. I, the methylene group exhibited what we have described as a plain curve, although some tendency to level off at the highest temperatures was noted. The methyl groups exhibited a more striking behavior; the two pairs of doublets apparently moved towards each other, coalesced, and then moved away from each other.* Fig. I contains a graphical illustration $|\Delta\nu|_{obs}$ in Hz vs temperature which demonstrates the unique behavior of the chemical shift of the methyl groups with temperature in this compound.

Quite possibly the behavior illustrated in the parabolic curve in Fig. I is in fact not unusual. A simple example involving two conformers will suffice. Assume conformer A has a $\Delta\nu_{total}$ of X while conformer B has a $\Delta\nu_{total}$ twice as large but with the proton positions reversed relative to conformer A, i.e., -2X. Assume that A > B in stability. At low temperatures A will predominate. As the temperature is raised more B will contribute and $\Delta\nu_{total}$ will decease, until at some temperature the contributions from A and B will be equal but of opposite signs, i.e., $\Delta\nu_{total}$ will drop to zero. This point for our hypothetical but general case would be at 2/3A and 1/3B. As the temperature is increased, the conformers A and B will approach equal population. If the plot involves $|\Delta\nu_{total}|$ the curve will rise with temperature. This is exactly the shape of the curve found for the methyl protons in compound **1**. Clearly a more complex shape to these curves than has previously been held is entirely possible.

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*It is possible that this could be viewed as an approach, coalescence and then shifting back in the same direction. However, the fact that coalescence was observed in both benzene and toluene (Fig. I) renders this interpretation less likely.

Table I

Differences in Chemical Shift of the Geminal Methyl Protons in **1** at Different Temperatures and in Various Solvents[a]

Toluene				Benzene				o-Xylene			
Temp. (C)	ν_1	ν_2	$\|\Delta\nu\|$	Temp. (C)	ν_1	ν_2	$\|\Delta\nu\|$	Temp. (C)	ν_1	ν_2	$\Delta\nu$
-60°	146.75	158.75	12.0	-11°	149.0	150.5	1.5	40°	137.75	152.25	14.5
-48°	147.25	154.25	7.0	-1°	149.0	149.0	0	50°	138.0	153.0	15.0
-45°	147.0	154.0	7.0	+9°	149.0	149.0	0	60°	137.0	153.0	16.0
-36°	147.25	152.25	5.0	19°	149.5	147.5	2.0	70°	136.0	153.0	17.0
-29°	148.75	151.75	3.0	29°	150.0	146.0	4.0	80°	137.0	155.0	18.0
-24°	150.75	150.75	0	39°	150.5	145.5	5.0	90°	136.0	154.0	18.0
-18°	150.25	150.25	0	45°	151.0	144.0	8.0	100°	136.5	155.5	19.0
-10°	149.75	149.75	0	55°	151.5	143.0	8.5	110°	136.25	155.8	19.5
-4°	150.5	148.5	2.0	65°	152.0	142.0	10.0	120°	136.0	156.0	20.0
+7°	151.5	147.75	3.3	75°	152.5	141.2	11.3	130°	135.75	156.25	20.5
+13.5°	152.0	147.0	5.0	85°	153.25	141.0	12.3	140°	136.0	157.0	21.0
+28°	152.75	144.75	8.0					150°	135.0	157.0	22.0
+52°	153.0	143.5	9.5					160°	135.0	157.0	22.0
+58°	153.25	143.5	9.8					170°	135.0	157.0	22.0
+68°	154.75	142.0	12.8								
+75°	155.0	141.5	13.5								
+85°	155.25	141.5	13.8								
+93°	156.5	141.0	15.5								
104°	156.0	140.0	16.0								

[a] Spectra run at 10% concentration on an A 56/60 nmr spectrometer vs a standard of TMS.

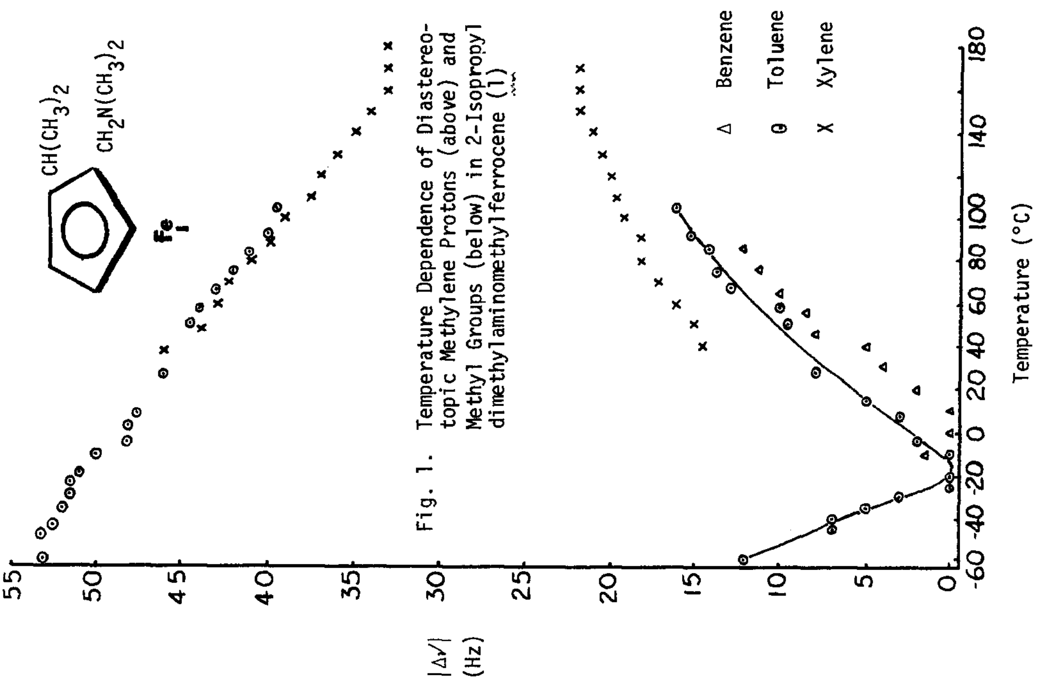

Fig. 1. Temperature Dependence of Diastereotopic Methylene Protons (above) and Methyl Groups (below) in 2-Isopropyl dimethylaminomethylferrocene (1)

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REFERENCES

1. H. S. Gutowsky, J. Chem. Phys., 37, 2196 (1962); H. S. Gutowsky, G. G. Belford and P. W. McMahon, ibid., 36, 3353 (1962).
2. G. M. Whitesides, D. Holtz and J. D. Roberts, J. Am. Chem. Soc., 86. 2628 (1964).
3. M. Raban, Tetrahedron Lett., 3105 (1966).
4. S. Seltzer and S. G. Mylonakis, J. Phys. Chem., 72, 754 (1968).
5. G. Redl and G. J. D. Peddle, J. Phys. Chem., 73, 1150 (1969).
6. P. Smith, J. J. McLeskey, III and D. W. Slocum, J. Org. Chem., 30, 4356 (1965).
7. D. W. Slocum and T. R. Engelmann, J. Org. Chem., 34, 4101 (1969).