Extension of Saunders' Isotopic Perturbation Method as Probe for the Structures in Solution of 2,4,6,8-Substituted Barbaralanes − NMR-Spectroscopic Evidence for the Coexistence of Localised and Delocalised States

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Because of a typesetting error, the pages 2767−2768 of the printed version have been corrupted. Their correction is printed on the following pages. The online version has not been affected by this error.

The Editors
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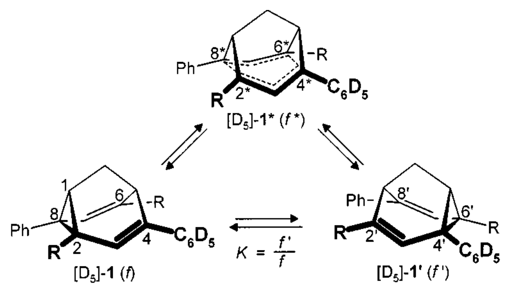

dation, we refer to the temperature-independent small isotopic splittings characteristic of single-minimum species as "*isotopic perturbation of shift equivalence in delocalised systems*".

The recent discovery of the equilibrium between localised (**1**, **1′**) and delocalised (**1***) states of thermochromic barbaralanes[10] necessitates an extension of Saunders' method, which considers only one or the other possible structure but not an equilibrium between them. In the general case of the coexistence of both, the observed isotopic splitting will be the average over those molecules that are delocalised (fraction f^*) and those that are localised (fractions f and f').

The weighted average $\bar{\delta}_i$ of the chemical shifts δ_i, $\delta_{i'}$, and δ_{i^*} of a ^{13}C atom C_i in three different environments is given by Equation 2. Because $\delta_i = \delta_{j'}$ and $\delta_j = \delta_{i'}$, provided intrinsic isotope effects are neglected, the shift difference $\Delta\delta^P_{ij}$ between two carbon atoms C_i and C_j that are equivalent in the absence of the isotopic perturbation is given by Equation 3 where $\Delta\delta_{ij}$ denotes the difference in the chemical shifts of C_i and C_j in the limit of slow exchange. The shift difference $\delta_{i^*} - \delta_{j^*} = \Delta\delta^*$ is the isotopic perturbation of shift equivalence in delocalised systems.

$$f + f' + f^* = 1 \tag{1}$$

$$\bar{\delta}_i = f\delta_i + f'\delta_{i'} + f^*\delta_{i^*} \tag{2}$$

$$\Delta\delta^P_{i,j} = \bar{\delta}_i - \bar{\delta}_j = (f - f')\,\Delta\delta_{i,j} + f^*\Delta\delta^* \tag{3}$$

The *relative* isotopic splitting (Equation 4) is obtained from Equation 3 and recognised as the difference between the fractions of the equilibrating localised molecules plus a second term which accounts for the presence of the delocalised species.

$$\frac{\Delta\delta^P}{\Delta\delta} = (f - f') + f^*\frac{\Delta\delta^*}{\Delta\delta} \tag{4}$$

$$= (1 - f^*)\frac{1-K}{1+K} + f^*\frac{\Delta\delta^*}{\Delta\delta} \tag{5}$$

Defining the equilibrium constants K such that they are less than unity ($K = f'/f$) yields Equation 5, which comprises Saunders′ relative splittings for the isotopic perturbation of degeneracy ($f^* = 0$)[7a] and shift equivalence in delocalised systems ($f^* = 1$)[7b,c] as limiting cases. The second terms in Equation 3−5 only play a role, if both the fraction f^* of the delocalised species *and* the isotopic perturbation of shift equivalence in delocalised systems, $\Delta\delta^*$, assume sizeable values. The latter is much smaller than the isotopic perturbation of degeneracy.[7−9] Therefore we neglect the last term.

Recent studies of the thermochromism of **1a** and **b** have not only disclosed an equilibrium between localised and delocalised structures but also afforded the enthalpy differences ΔH^0 between them, from which f^* values may be calculated according to Equation 6.[10]

$$f^* \approx \left(1 + 2\cdot\exp\frac{\Delta H^0}{R\cdot T}\right)^{-1} \tag{6}$$

Considering the well-known temperature dependence of the equilibrium constant $K = \exp(\Delta S^P/R - \Delta H^P/RT)$, where ΔH^P and ΔS^P (the perturbation parameters) are the differences between the thermodynamic parameters of the two labelled localised valence tautomers, we obtain from Equation 5 and 6 an expression for the temperature dependence of the relative splitting, Equation 7. Application of Equation 7 is superior to the traditional calculation of equilibrium parameters with the linear relationship ln$K$ vs. $1/T$, because Equation 7 correctly weights the experimental data.

$$\frac{\Delta\delta^P}{\Delta\delta} = \left(1 - \frac{1}{1 + 2\exp\left(\Delta H^0/RT\right)}\right)\frac{1 - \exp\left(\Delta S^P/R - \Delta H^P/RT\right)}{1 + \exp\left(\Delta S^P/R - \Delta H^P/RT\right)} \tag{7}$$

Equation 7 may be used to calculate enlightening curves in relative splitting vs. temperature diagrams *that are characterised by a certain pair of perturbation parameters* ΔH^P *and* ΔS^P. Besides Saunders′ limiting cases $f^* = 0$ and $f^* = 1$, there exists a third interesting situation, in which the localised and the delocalised species possess the same enthalpy, i.e. $\Delta H^0 = 0$ and $f^* = 1/3$ (Equation 6). This is the borderline that cuts each of these certain ($\Delta\delta^P/\Delta\delta$)−temperature diagrams into an upper section between the limit $f^* = 0$ and the borderline $f^* = 1/3$ − the area where ΔH^0 is positive − and a lower section between borderline $f^* = 1/3$ and the limit $f^* = 1$ − the area where ΔH^0 is negative, in other words, the delocalised species more stable than the two equilibrating localised valence tautomers. Thus, a cursory inspection of the observed relative splitting vs. temperature data in these diagrams (Figures 6−9) immediately reveals the relative stability of the coexisting species.

Deuterium Isotopic Splittings in Carbon-13 Spectra of the Barbaralanes [D$_5$]-1a and b

Variable-temperature 151-MHz ^{13}C spectra were recorded for solutions of [D$_5$]-**1a** and **b** in two widely different solvents. Our recent study of thermochromic semibullvalenes and barbaralanes has shown that the localised structures **1a** and **b** are preferred in nonpolar solvents while dipolar solvents, in particular *N*,*N*′-dimethylpropylene urea, render the delocalised structure **1b*** even more stable than **1b**.[10b]

Deuterium isotopic splittings in ^{13}C spectra of [D$_5$]-**1a** in [D$_8$]toluene solutions are displayed in Figure 4. The assignment of the signals is immediately obvious. Most importantly, Figure 4 provides unequivocal evidence for the pre-

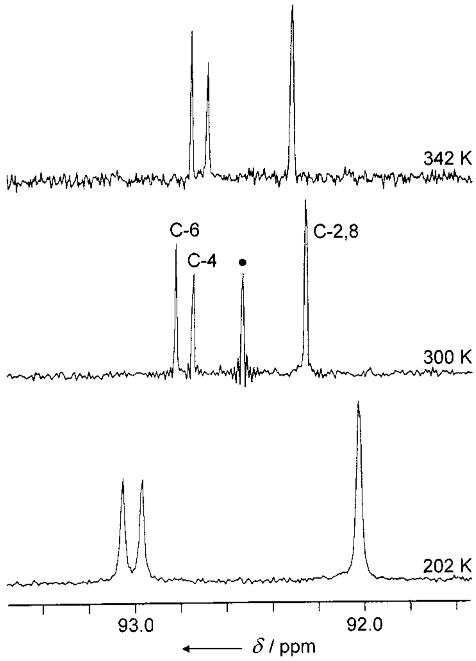

Figure 4. Deuterium isotope splittings in 151-MHz ^{13}C spectra recorded for a solution of $[D_5]$-**1a** in $[D_8]$toluene at various temperatures. The signal marked with a dot stems from added unlabelled tetraphenylbarbaralane **1a**

ferred position of the pentadeuterophenyl group, viz. the vinyl position (C-4). Thus $[D_5]$-**1a** is slightly more stable than $[D_5]$-**1a′**. It is unnecessary to consider the cumulative isotope effect on the chemical shift of C-4, because the isotopic splitting can be measured directly using the signal of C-6, which is separated by five bonds from the next deuterium atoms. That these do not influence the shift of C-2, which is also five bonds away, is seen from the single high-field signal which has double intensity and hence is assigned C-2 and C-8. The isotopic splittings observed for a solution of $[D_5]$-**1a** in *N,N′*-dimethylpropylene urea (DMPU) are of similar size (Table 2).

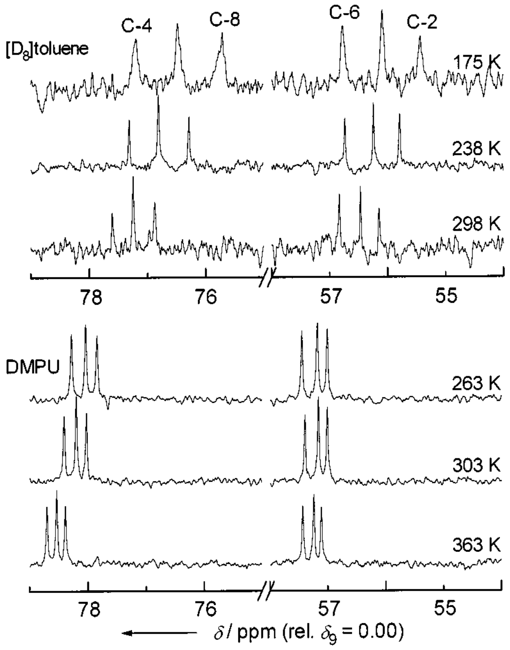

Figure 5. Deuterium isotope splittings in 151-MHz ^{13}C spectra recorded for solutions of a mixture of **1b** (middle signals) and $[D_5]$-**1b** in $[D_8]$toluene and *N,N′*-dimethylpropylene urea at various temperatures

Table 2. Deuterium isotopic splittings $\Delta\delta_{i,j}^{P}$ [ppm] in 151-MHz ^{13}C spectra taken from solutions of the barbaralanes $[D_5]$-**1a** and **b** in $[D_8]$toluene and *N,N′*-dimethylpropylene urea at various temperatures

Cpd.	T [K]	$\Delta\delta_{6,2}^{P}$	$\Delta\delta_{4,8}^{P}$
$[D_5]$-**1a** in $[D_8]$toluene	202.3	1.008	
	224.2	0.88	
	247.2	0.782	
	269.1	0.656	
	297.3	0.551	
	321.2	0.485	
	342.2	0.439	
in DMPU	265.3	0.738	
	300.4	0.591	
	330.1	0.491	
	344.9	0.449	
	359.8	0.411	
	370.1	0.387	
$[D_5]$-**1b** in $[D_8]$toluene	174.9	1.339	1.559
	195.4	1.166	1.378
	216.6	1.057	1.229
	237.9	0.943	1.097
	268.7	0.806	0.940
	298.4	0.684	0.803
in DMPU	263.0	0.440	0.508
	283.0	0.411	0.478
	303.0	0.387	0.451
	323.0	0.363	0.428
	343.0	0.340	0.405
	363.0	0.322	0.385

The deuterium isotopic splittings in ^{13}C spectra of $[D_5]$-**1b** are shown in Figure 5. The assignment of the signals is based on the assumption that the pentadeuterophenyl group prefers the same position as in $[D_5]$-**1a** and, therefore, $[D_5]$-**1b** is more stable than $[D_5]$-**1b′**. Inspection of Figure 5 reveals a dramatic difference between the two solvents, not only in the absolute size of the splittings $\Delta\delta^{P}$ but also in their temperature dependence which is much larger in $[D_8]$toluene (−0.53 ppm/100 K for $\Delta\delta_{6,2}^{P}$ and −0.61 ppm/100 K for $\Delta\delta_{4,8}^{P}$) than in *N,N′*-dimethylpropylene urea (−0.12 ppm/100 K for $\Delta\delta_{6,2}^{P}$ and $\Delta\delta_{4,8}^{P}$).

The isotopic splitting is not perfectly symmetric relative to the time-averaged signal of **1b** between the components of each pair of signals that result from isotopic splitting. Instead, the average shift of each pair is slightly changed towards lower field. Scrutiny of Figure 4 uncovers the same effect for $[D_5]$-**1a**.

On the basis of the generally accepted vibrational explanation of equilibrium isotope effects,[8] it is difficult to rationalise the position of the equilibria **1** $\rightleftharpoons$ **1′** which are skewed by the presence of deuterium atoms that are three, four and five bonds away from the carbon atom involved in the Cope rearrangement. We restrain ourselves from any attempts because they are beyond the scope of the present paper.