When two nuclei, for example protons, are either magnetically equivalent or different but strongly coupled ($\Delta \nu / J < 10$), a first-order analysis cannot explain the NMR spectrum. In these cases, it is necessary to formulate the spin Hamiltonian and to solve the Schrödinger equation. Thus the study of an AB spectrum constitutes an interesting probe for methods of quantum chemistry when applied to spectroscopy. However, experimental verification requires compounds with appropriate values of $\Delta \nu / J$; this is particularly difficult to realize for low values of this ratio, especially at high fields (200 MHz in this report). We propose a simple and inexpensive solution to this problem.

The AB Spectrum

The quantum treatment of an AB spectrum is described in many textbooks. We shall mention only some results. The quantities $\nu_k (k = 1–4)$, $\nu_M$, $\nu_A$, $\nu_B$, $2C$, $\Delta \nu$, $\Delta \nu_e$, $\Delta \nu_i$ are defined on Figure 1. The coupling constant is given by the

$$J = \nu_1 - \nu_2 = \nu_3 - \nu_4$$

(1)

and the resonance frequencies are calculated by

$$\nu_A = \nu_M + \frac{\Delta \nu}{2} \quad \text{and} \quad \nu_B = \nu_M - \frac{\Delta \nu}{2}$$

(2)

where

$$\Delta \nu = \left(4C^2 - j^2\right)^{1/2} \quad \text{and} \quad 2C = \nu_1 - \nu_3 = \nu_2 - \nu_4$$

or

$$\Delta \nu = \sqrt{(\Delta \nu_i \Delta \nu_e)}$$

(3)

The two doublets, A and B, are dissymmetric, the outside lines (intensity $I_e$) are smaller than the inside lines ($I_i$). Their intensities can be expressed as

$$\frac{I_e}{I_i} = \frac{2C - j}{2C + j}$$

$$\frac{I_e}{I_i} = \frac{\Delta \nu_i}{\Delta \nu_e}$$

(4)

The quantity, $\nu_A$ or $\nu_B$, deviates from the median frequency of the corresponding doublet where the shift is

$$D = \left(\frac{\nu_1 + \nu_2}{2}\right) - \nu_A = \nu_B - \left(\frac{\nu_3 + \nu_4}{2}\right)$$

(5)

Note, for high values of $\Delta \nu / J$ (weak coupling), we have an AX system for which $I_e \sim I_i$ and $D \sim 0$. On the other hand, for $\Delta \nu = 0$ (A2 system), $I_e = 0$ and $\Delta \nu_i = 0$ and we observe a single line.
The Idea

To verify the properties of an AB system experimentally, it is necessary to choose adequate values of the $\Delta \nu / J$ ratio (2). That requires a set of different compounds, which depends also on the frequency $\nu_\circ$ of the spectrometer: $\Delta \nu = \nu_\circ (\Delta \delta) 10^{-6}$.

We perform the experiment with a single compound, 4-N-(2-nitrophenyl)maleamic acid, allowing the choice of any value of $\Delta \nu / J$ between 0 and 7, at 200 MHz (at $\nu_\circ$ MHz, the range would be 0 to 7 $\nu_\circ$ / 200). 4-N-(2-Nitrophenyl)maleamic acid is easy to synthesize (3) from 2-nitroaniline and maleic anhydride, both readily available and inexpensive:

$$\text{RCOO}^- + \text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{RCOOH}$$

Fast exchange is understood on the NMR scale, that is, $\tau << (\Delta \nu)^{-1}$, where $\tau$ is the mean life time of an entity and $\Delta \nu$ the difference between the frequencies of a given proton in each form.

We observe the spectrum of an hybrid compound whose characteristics ($\delta$, $J$) are the weighted average values of the two exchanging species (a) and (b) with molar fractions $(1 - x_b)$ and $x_b$, respectively. The NMR sample is a dimethyl-d$_6$ sulfoxide (d$_6$-DMSO) solution of an adequate mixture of the acid (a) and its sodium salt (b). The cis olefinic protons are investigated.

Experimental Procedures

Synthesis

The syntheses of the chemicals are reported in the Supplemental Material.

NMR Samples

In 5-mm NMR tubes, five samples of 500 µL are prepared by mixing adequate volumes of d$_6$-DMSO solutions of 0.2 mol L$^{-1}$ of maleamic acid (a) and its sodium salt (b) respectively. Molar fractions of (b) are $x_b = 0$, 0.25, 0.50, 0.75, and 1.

NMR Spectra

The spectrometer is a Bruker 200 MHz. Temperature of the NMR probe is set to 298 K. Each $^1$H spectrum is recorded between 0 and 20 ppm and peaks are integrated for intensity determination. The region of the AB system, between 5.7 and 6.6 ppm, is enlarged. Chemical shifts are calibrated with the signal of the residual protonated DMSO ($\delta = 2.50$ ppm relative to TMS).

Hazards

Strong magnetic fields are present in the NMR laboratory. Standard precautions should be used. Dimethyl-d$_6$ sulfoxide is toxic on inhalation, ingestion, and contact with skin. Maleamic acid and its derivatives should be handled with care.

Results

NMR Spectra

The spectrum of maleamic acid (a) is shown in Figure 2. Chemical shifts for (a) and (b) are collected in Table 1. Attribution of signals resulted from couplings and considerations about intramolecular electronic effects (aromatic and olefinic protons) and comparative ability to exchange for acidic (broad line) and amide (narrow line) protons, which was confirmed by 2D NMR spectra (not shown). This work is interesting in itself, but we are only concerned with olefinic protons.

Spectra of the olefinic protons that give an AB system are shown in Figure 3. We assume that $\delta_a$ and $\delta_b$ are the
high and low chemical shifts respectively, $\delta_\alpha$ and $\delta_\beta$ the chemical shifts of the protons at the $\alpha$ and $\beta$ positions from the carboxylic acid function. For $x_b = 1$, $\delta_\alpha = \delta_\alpha$ and $\delta_\beta = \delta_\beta$. As $x_b$ decreases, $(\delta_\alpha - \delta_\beta)$ decreases at the same time and for $x_b \sim 0.25$ the two chemical shifts are identical. At lower values of $x_b$, $\delta_\alpha = \delta_\beta$ and $\delta_\beta = \delta_\alpha$.

**Fast Chemical Exchange**

The parameters calculated from the experimental data for each molar fraction, $x_b$, are collected in Table 2: experimental values of $\delta_\alpha$ and $\delta_\beta$ (ppm) relative to TMS and $J$ (Hz) as the average of $(\nu_1 - \nu_2)$ and $(\nu_3 - \nu_4)$; $\delta_\alpha$ and $\delta_\beta$ were calculated according to eqs 2 and 3; chemical shifts are related to frequencies by $\delta = 10^6(\nu - \nu_{\text{TMS}})/\nu_0 = (\nu - \nu_{\text{TMS}})/(200.133)$. It is easy to verify that, as attempted, $\nu_\alpha$, $\nu_\beta$ (Figure 4), and $J$ are linearly related to $x_b$. A least-squares fit of the data shows that chemical shifts and coupling constant are defined by the equations:

$$\delta_\alpha = 6.38 - 0.13 x_b$$

$$\delta_\beta = 6.51 - 0.73 x_b$$

$$J = 11.9 + 1.5 x_b$$

Thus, it is possible to choose any mixture affording an AB system spectrum with a required value of $\Delta \nu/J$ between 0 and 7.1 ppm at 200 MHz.

**Table 2. Parameters Calculated for Each Value of the Molar Fraction of the Basic Form**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Molar Fraction of the Basic Form, $x_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$/Hz</td>
<td>0</td>
</tr>
<tr>
<td>$\delta_\alpha$ (ppm)</td>
<td>6.49</td>
</tr>
<tr>
<td>$\delta_\beta$ (ppm)</td>
<td>6.37</td>
</tr>
<tr>
<td>$I_e/I_i$</td>
<td>0.377</td>
</tr>
<tr>
<td>$\Delta \nu/\Delta \nu_e$</td>
<td>0.367</td>
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<tr>
<td>$\Delta \nu/J$</td>
<td>1.91</td>
</tr>
<tr>
<td>$D$/Hz</td>
<td>1.46</td>
</tr>
</tbody>
</table>

**Figure 4.** Evolution of chemical shift $\delta_\alpha$ and $\delta_\beta$ as a function of the molar fraction of the basic form $x_b$.

**Figure 5.** (A) Correlation between $\Delta \nu/J$ and $I_e/I_i$ (experimental points, theoretical curves) and (B) correlation between $\Delta \nu/J$ and $D$ (experimental points, theoretical curves).

**Figure 6.** Characteristic linear relationship for an AB system (experimental points, theoretical curves).
The dissymmetry of each doublet (A and B) decreases as $\Delta v/J$ increases (Figure 5A) and $I_e/I_i$ correlates well with $\Delta v_e/\Delta v_i$, according to eq 4 (Figure 6). On the other hand, with reference to the median of a doublet, the frequency shift $D$ of the corresponding proton increases as $\Delta v/J$ decreases (Figure 5B). It is interesting to note that this deviation is negligible as long as $\Delta v/J$ remains above 1.4, if we accept a margin of 2 Hz (0.01 ppm at 200 MHz) on the resonance frequencies. $D$ maximum value reaches $J/2$ in the case where $v_A = v_B$; here $D_{\text{max}} = 6.13$ Hz.

**Conclusion**

$N$-(2-nitrophenyl) maleamic acid is an interesting molecule for the experimental verification of the properties of an A2 system. Fast chemical exchange between acidic and basic forms allows the choice of a definite value for the ratio $\Delta v/J$ in the range 0–7.1$v_0$(MHz)/200; these limits may be modulated with an appropriate selection of the aromatic ring substitution.

**Notes**

1. $J$ is the coupling constant and $\Delta v$ the difference between resonance frequencies of the two nuclei.
2. We use the current terminology for systems of two identical nuclei (A2) or different nuclei and either weakly (AX) or strongly (AB) coupled.

3. It is crucial to mention that the solution of (b) in DMSO contains about 3 equivalents of water, whereas solution of (a) is dry. It is not necessary to further dry the sodium salt (b); results are reasonably good. Furthermore too small a proportion of water in (b) must be avoided because it leads to slow exchange and widens the lines of the AB system, dissymmetrically.

4. If $y = \Delta v/J$, then $I_e/I_i = [(1 + y^2)^{1/2} - 1]/[(1 + y^2)^{1/2} + 1]$ and $D = (J/2)[(1 + y^2)^{1/2} - y] = 6.3 [(1 + y^2)^{1/2} - y]$ assuming $J = 12.6$ Hz.

**Supplemental Material**

Notes for the instructor are available in this issue of *JCE Online*. Moreover, a set of spectra for the AB system where $x_b = 0, 0.25, 0.5, 0.75$, and 1 is provided. For each spectrum, peaks are picked and integrated. Raw data (five FIDs) are furnished as five zipped files.

**Literature Cited**