

annulene<sup>11</sup> shows that in its crystalline state the compound is solely present as conformer **5a** (Figure 1). The fact that **5a** is found to be centrosymmetric allows one to rule out bond alternation immediately. In accord with predictions based on molecular models, **5a** avoids the severe crowding of the inner hydrogen atoms that would exist in the planar molecule. As demonstrated by the side view of **5a** (Figure 2), the carbon skeleton adopts the shape of a puckered loop with the inner hydrogen atoms H3/H6 and H10/H13 located above and below, respectively, the median ring plane. Most significantly, the carbon-carbon bond lengths ranging from 1.364 to 1.407 Å are typical of benzenoid aromatic bonds although torsional angles in the carbon skeleton of up to 20° are encountered.<sup>12</sup> These structural findings on 1,8-dimethyl[14]-annulene attest to our previous conclusions, derived from a study of bent bridged [14]annulenes, that a cyclically conjugated ( $4n + 2$ ) $\pi$ -electron system is capable of tolerating rather striking deviations from planarity without suffering a substantial loss in  $\pi$ -electron delocalization.<sup>13</sup>

From the preparative point of view the conversion of octalene to 1,8-dimethyl[14]annulene harmoniously complements the previous synthesis of the parent [14]annulene since treatment of the latter with electrophilic reagents leads to polymerization rather than to substitution products.<sup>14</sup> Further work on this new approach to the [14]annulene system is currently in progress.

**Registry No.** 1, 257-55-6; 3, 69502-53-0; **5a**, 81770-67-4; dihydrodithiooctalene, 69517-01-7.

**Supplementary Material Available:** Crystallographic data of 1,8-dimethyl[14]annulene and a structure indicating the numbering of the atoms of 1,8-dimethyl[14]annulene according to the crystallographic data given (2 pages). Ordering information is given on any current masthead page.

(11) The compound crystallizes in the monoclinic system, space group  $C2/c$ , with  $a = 19.010$  (7) Å,  $b = 4.178$  (1) Å,  $c = 15.926$  (4) Å,  $\beta = 98.70$  (3)°,  $d_{\text{obsd}} = 1.10$ ,  $d_{\text{calcd}} = 1.117$  g cm<sup>-3</sup>,  $Z = 4$ . Three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares calculations to  $R = 0.069$  for 497 observed reflections with  $I \geq 2\sigma(I)$ .

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## Exploring Nuclear Spin Systems by Relayed Magnetization Transfer

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We should like to address one of the basic problems of NMR spectroscopy: the task of identifying families of signals belonging to the same network of coupled spins. For large molecules such as biopolymers, this is by no means straightforward. Consider for example a scalar-coupled AMX system with a vanishing long-range coupling  $J_{AX} = 0$  Hz. There are situations where none of the methods available to date can provide unequivocal proof that A and X belong to the same spin system. Selective double resonance or two-dimensional (2-D) correlation spectroscopy<sup>1,2</sup> can certainly be employed to identify the couplings  $J_{AM}$  and  $J_{MX}$ . Very similar responses could, however, be obtained from two distinct pairs AM and M'X with accidental overlap in the M region. Experimental evidence of two couplings does not constitute

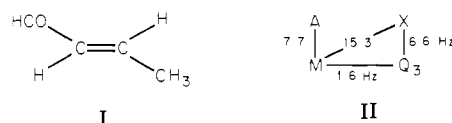
sufficient proof that one is dealing with a three-spin system, unless the multiplet structure of all lines can be fully analyzed, which is usually impossible for biomolecules.

We propose a novel approach that exploits the existence of a coupling network to prove the connectivity between two remote nuclei A and X. The method employs two or more consecutive steps where transverse magnetization is relayed from nucleus to nucleus along a path defined by a sequence of resolved couplings.

Conventional 2-D correlation spectroscopy<sup>1-4</sup> uses a  $90^\circ-t_1-\beta-t_2$  sequence, where the second "mixing" pulse with flip angle  $\beta$  induces transfer of transverse magnetization between coupled spins. After 2-D Fourier transformation, such coherence transfer processes lead to cross-peaks, the frequency coordinates being characteristic of the chemical shifts of directly coupled pairs of nuclei.

In relayed correlation spectroscopy, the second pulse of the two-dimensional experiment is replaced by a  $90^\circ-\tau-180^\circ-\tau-90^\circ$  sequence, which may induce two consecutive coherence transfer processes. More sophisticated sequences can be designed to relay the information over a greater number of couplings. It can be shown for the AMX system with  $J_{AX} = 0$  Hz that the transfer efficiency from A to X is proportional to the product  $\sin(2\pi J_{AM}\tau) \cdot \sin(2\pi J_{MX}\tau)$  if all three pulses have the same phase.

Crotonaldehyde (I) provides an interesting test case. In the



AMQ<sub>3</sub>X proton coupling network (II), the aldehyde proton A does not exhibit a resolved coupling to either Q or X nuclei. As a result, the normal 2-D correlation spectrum fails to reveal connectivities between A and either Q or X (empty circles in Figure 1a). The complexity of the M region makes it difficult to obtain clear-cut information from the multiplet structure: the spectrum in Figure 1a could also be explained by invoking a superposition of an AM system with an M'Q<sub>3</sub>X system.

The new two-dimensional method, as can be appreciated in Figure 1b, provides unequivocal proof that all six spins belong to one and the same coupling network. In this spectrum, the interval  $\tau$  has been adjusted intentionally to favor the transfer from A to Q. Nonetheless sufficient magnetization is transferred from A to X to allow immediate identification.

Variations of the basic relay experiment discussed here can be designed to obtain responses for arbitrary scalar couplings in unknown coupling networks. Besides inclusion of more coherence transfer steps, it is possible to increment the interval  $\tau$  in concert with  $t_1$  in the manner of accordion spectroscopy.<sup>5-7</sup> In principle, the transfer processes can be made virtually independent of the magnitude and the number of couplings if a spin-locking period is inserted between evolution and detection periods of the two-dimensional experiment.<sup>8</sup>

Relayed coherence transfer need not be combined with two-dimensional spectroscopy. It is also possible to replace the initial excitation by a selective  $90^\circ$  pulse in order to monitor the propagation of magnetization throughout the coupling network in a one-dimensional experiment.<sup>9</sup>

A number of promising applications are feasible in heteronuclear systems. In particular, the chemical shift of carbon-13 can be correlated not only with the chemical shift of directly bound protons (as is customary in conventional correlation spectroscopy<sup>10</sup>) but also with the shifts of protons attached to neighboring carbons.<sup>11</sup> This information makes it possible to trace out the entire

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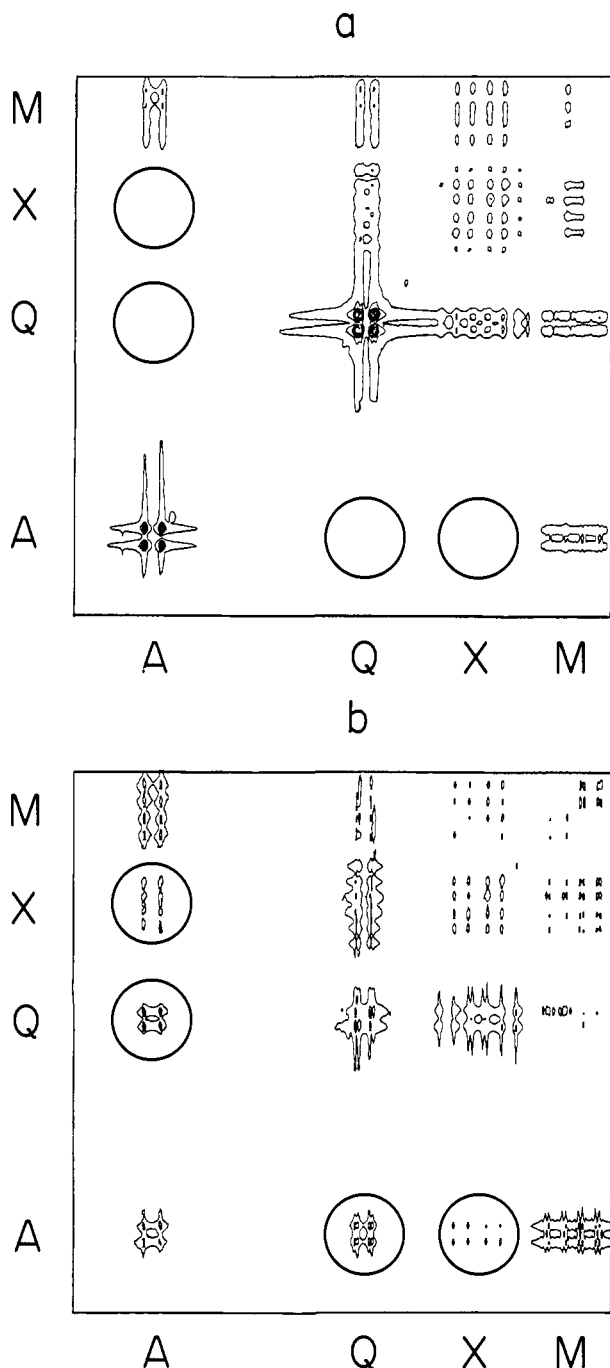
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**Figure 1.** Two-dimensional proton spectra of crotonaldehyde (I) in the isotropic phase (50% acetone- $d_6$ ), obtained with a home-built 90-MHz spectrometer: (a) conventional 2-D correlation map, showing the absence of connectivity between the aldehyde proton, the methyl group, and the trans proton (empty circles); (b) relayed correlation map obtained with two consecutive magnetization transfer steps, showing that all resonances belong to the same coupling network. Resonances A and Q appear folded, as the spectral width has been set to 250 Hz in both dimensions. The delay  $\tau$  equals 32 ms; free-induction decays were recorded for 256  $\tau_1$  values.

backbone of the molecule by assigning neighboring carbon sites.<sup>12</sup>

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## Potential-Energy Surface of the $S_N2$ Reaction in Hydrated Clusters

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The  $S_N2$  nucleophilic substitution reaction is one of the most extensively studied chemical reactions in solution.<sup>1</sup> Recent studies have revealed that the reaction proceeds up to 20 orders of magnitude faster in the gas phase than in solution.<sup>2</sup> The gap between the gas phase and the solution rate has recently been filled somewhat by a study in hydrated cluster. Bohme and Mackay have found<sup>3</sup> that the rate constant of the reaction



decreases gradually from  $n = 0$  to  $n = 3$ . This change has been interpreted in terms of the qualitative potential energy profile proposed by Brauman et al.;<sup>2b,c</sup> the reaction proceeds via a three-step mechanism: the formation of a stable complex  $\text{OH}^-(\text{H}_2\text{O})_n \cdots \text{H}_3\text{CBr}$  without an activation barrier, the subsequent isomerization of the complex to  $\text{HOCH}_3 \cdots \text{Br}^-(\text{H}_2\text{O})_n$  with an activation barrier, and the final dissociation of the complex. As the nucleophile is hydrated more, the complex becomes less stable and the overall barrier higher.

In the present paper we present the results of ab initio SCF calculations of potential-energy surfaces for a similar  $S_N2$  reaction:



for  $n = 0$  (unhydrated), 1, and 2. Relevant equilibrium and transition-state geometries and energies have been determined with the energy gradient method<sup>4</sup> with the 3-21G basis set.<sup>5</sup> The potential-energy profiles and the geometries of some important species are shown in Figures 1 and 2, respectively. We find that for  $n = 1$  the  $\text{H}_2\text{O}$  migration and  $\text{CH}_3$  transfer-inversion occurs either sequentially or simultaneously. For  $n = 2$ , the initial sequential or simultaneous  $\text{H}_2\text{O}$  migration and  $\text{CH}_3$  transfer-inversion followed by the migration of the other  $\text{H}_2\text{O}$  is the most favorable path of reaction.

In the reaction of an unhydrated chloride,  $\text{Cl}^-$  at first forms the complex **1** with  $\text{CH}_3\text{Cl}$  at the  $\text{H}_3$  end and then climbs a barrier to reach the transition state **2** of the  $\text{CH}_3$  transfer-inversion,<sup>5a</sup> consistent with previous ab initio calculations for various  $S_N2$  reactions.<sup>6</sup>

In the reaction of the complex **4** of the hydrated  $\text{Cl}^-$  **3**, we find two reaction paths at a comparable energy, in one the  $\text{H}_2\text{O}$  migration and the  $\text{CH}_3$  transfer-inversion taking place sequentially and in the other simultaneously. The sequential path climbs over the transition state **5** of the  $\text{CH}_3$  transfer to form a complex **6**,

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(5) (a) A diffuse  $p$  basis function, added to better describe an anion, decreases the complex stability but does not change the general features of potential surface profiles. (b) Complexes **6** and **12** are local minima. Because the potential surfaces are rather flat near **6** and **12**, the transition states, **7** and **11**, could not be precisely determined. Therefore, the paths connecting **6** to **4** and **12** to **10** are traced by fixing the ClCO angle at various values and optimizing all the other coordinates. Geometry **11'** of Figure 2 is one of such geometries.

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