conditions, ^{3}DPC and ^{3}DPC* might both contribute to the formation of **6** through reactions with either cyclobutanol **8** or photoenol **3** followed by cyclization.

These simple experiments clearly demonstrate the viability of targeting one transient species with another under high-intensity, laser-jet conditions. In many cases, this transient–transient reaction strategy promises to provide access to fascinating novel reactions, as well as new insights into the chemistry of transient intermediates.

Acknowledgment. We thank the National Science Foundation for support of this work (CHE-8914889).

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High-Resolution Two-Dimensional In-Phase Multiplets in Nuclear Magnetic Resonance Correlation Spectroscopy

Sébastien J. F. Vincent, Catherine Zwahlen, and
Geoffrey Bodenhausen*

Section de Chimie, Université de Lausanne
Rue de la Barre 2, CH-1005 Lausanne, Switzerland

Received September 17, 1992

In multidimensional nuclear magnetic resonance,[1] selective methods such as "soft COSY"[2-5] allow one to boost the resolution in comparison with conventional, nonselective correlation spectroscopy ("hard COSY"). Improved resolution, obtained by "zooming in" on multiplets of interest, allows one to measure the magnitudes and signs of scalar coupling constants with very high accuracy. In various forms of COSY, however, the proximity of peaks with opposite signs (antiphase multiplets) may lead to distortions and partial peak cancellation. In nonselective experiments, this problem may be overcome by switching to "total correlation spectroscopy" (TOCSY),[6] which yields in-phase multiplets. However, these multiplets usually suffer from limited resolution, their fine structure is difficult to interpret, and unlike the situation prevailing in COSY, the mere presence of a TOCSY cross-peak at frequency coordinates (Ω_A, Ω_X) does not imply that $J_{AX} \neq 0$. So far, no techniques are available which can deliver high-resolution in-phase multiplets that are easy to interpret. This communication describes a new selective method which fills this gap.

In the pulse sequence shown in the upper right part of Figure 1, the initial 270° Gaussian pulse[7] excites in-phase coherence I_x^A of a selected spin A. Evolution during t_1 leads to four terms, I_x^A, I_y^A, $2I_x^AI_z^X$, and $2I_y^AI_z^X$, modulated as usual by scalar coupling constants and chemical shifts.[8,9] In the mixing period of duration τ_{DSI}, a doubly selective irradiation is applied by placing the carrier frequency half-way between two chosen chemical shifts at $\omega_0 = {}^1/_2(\Omega_A + \Omega_X)$ and by modulating the amplitude with cos ($\omega_a t$), where $\omega_a = {}^1/_2(\Omega_A - \Omega_X)$. This generates two sidebands at $\omega_0 \pm \omega_a$, which coincide with the chemical shifts of the two selected spins.[10,11] During the doubly selective irradiation, I_x^A is converted into in-phase magnetization I_x^X, which gives rise to a pure absorptive in-phase multiplet. An ideal transfer is obtained for $\tau_{DSI} = 1/J_{AX}$.[11] The terms I_y^A and $2I_x^AI_z^X$ do not lead to any observable coherence on spin X. The terms I_x^A and $2I_y^AI_z^X$ can only be converted into $2I_z^AI_y^X$ and I_x^X, respectively, if $\tau_{DSI} \neq 1/J_{AX}$. The term $2I_y^AI_z^X$, however, can be converted into an undesirable term $2I_z^AI_y^X$, which leads to a contamination of the multiplet by dispersive antiphase signals. This transfer is negligible if the amplitude of the radio frequency (rf) field of each sideband accidentally or deliberately fulfills the condition $\omega_1 = \pi J[n(n+1)]^{1/2}$, with n integer.[12] In practice, the $2I_z^AI_y^X$ term can be purged by applying another 270° Gaussian pulse to spin A while one continues to spin-lock the desirable I_x^X coherence by a phase-modulated rf field (see Figure 1).

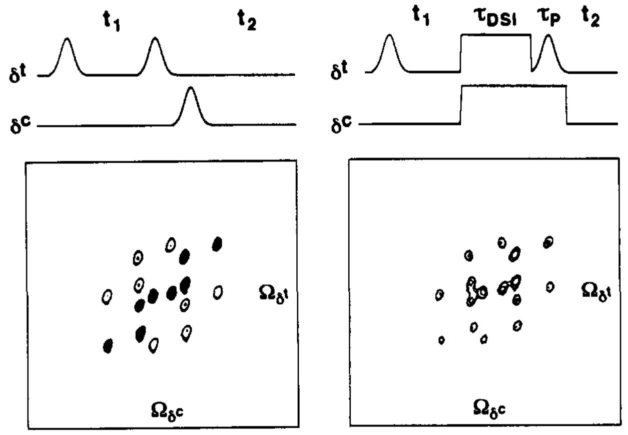

Figure 1. Top: Pulse sequences for soft COSY (left) and PICSY (right). Bottom: Corresponding multiplets of cyclo-(L-Pro-L-Pro-D-Pro),[15] correlating the proton resonances of δ^{trans} (3.23 ppm) with δ^{cis} (3.81 ppm) of the D-proline residue. The doubly selective irradiation period τ_{DSI} was set to 80.7 ms, i.e., to an integer (14-fold) multiple of the inverse of the frequency separation $(\Omega_A - \Omega_X)/2\pi = 173.5$ Hz while being close to $1/J$, and the purging pulse τ_P was set to 30 ms. The rf amplitude for each sideband was $\nu_1 = 55$ Hz. Two scans were recorded for each t_1 increment with alternation of the phase of the first pulse and of the receiver. For PICSY, the spectral widths were 75 Hz in ω_1 and 3000 Hz in ω_2; the matrix consisted of 128 × 8K data points before and 256 × 8K after zero-filling. For soft COSY, the spectral widths were 75 Hz in both dimensions and the matrix consisted of 128 × 1K data points before and 256 × 1K after zero-filling. In both cases, a Lorentz–Gauss transformation was applied (LB = −0.3, GB = 0.05) before Fourier transformation. The experiments were carried out on a Bruker MSL 300 spectrometer equipped with an Oxford Research Systems selective excitation unit.

It can be shown that the transfer of in-phase coherence occurs in much the same way in systems with more than two spins. The in-phase multiplets obtained therefore feature the same square patterns as soft COSY spectra, which are reminiscent of those in E. COSY[13] or z-COSY.[14] The soft COSY multiplet of cyclo-(L-Pro-L-Pro-D-Pro),[15] shown for comparison on the left of Figure 1, is composed of four antiphase square patterns, each with an active splitting $J(\delta^{cis}, \delta^{trans})$, which are displaced with respect to each other by passive splittings to the protons γ^{trans} and γ^{cis} of D-proline. In the multiplet shown on the right, one recognizes

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the same square patterns, so that the multiplet structure is preserved, but all peaks are positive. This multiplet is less prone to distortions and signal cancellation, and the comparison of in-phase and antiphase multiplets allows one to extract coupling constants with high accuracy.[16,17] Because the undesirable terms have vanished as if by a pixie's magic wand, we like to refer to this experiment as *p*ure *i*n-phase *c*orrelation *s*pectroscop*y* (PICSY).

Acknowledgment. This research was supported by the Swiss Fonds National de la Recherche Scientifique (FNRS) and by the Commission pour l'Encouragement de la Recherche Scientifique (CERS). We gratefully acknowledge a sample of cyclo-(L-Pro-L-Pro-D-Pro) from Dr. W. Bermel, Karlsruhe, and Prof. H. Kessler, Garching.

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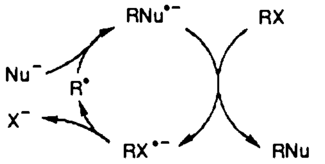
Dimerization of Aryl Radicals as a Termination Step in $S_{RN}1$ Aromatic Nucleophilic Substitution

Rofia Ettayeb,[1a] Jean-Michel Savéant,*[1b] and
André Thiébault*[1a]

Laboratoire de Chimie et Electrochimie des
Matériaux Moléculaires de l'ESPCI
Unité Associée au CNRS No. 429
10 rue Vauquelin, 75005, Paris, France
Laboratoire d'Electrochimie Moléculaire de
l'Université de Paris 7, Unité Associée au
CNRS No. 438, 2 place Jussieu
75251 Paris Cedex 05, France

Received October 1, 1992

Aromatic nucleophilic substitution stimulated by light, electrodes, solvated electrons, and electrochemically generated electron donors is a well-documented reaction.[2] A large body of evidence exists to support that the reaction follows the $S_{RN}1$[3] reaction mechanism depicted by the following scheme:



in which the aryl radical, $R^{\bullet}$, derived from the cleavage of the anion radical of the substrate (RX) plays a central role in the formation of the substituted product (RNu). In this chain process, reduction of the aryl radical not only by the homogeneous or heterogeneous electron donors serving as initiators but also by the anion radicals included in the propagation loop ($RNu^{\bullet -}$ and to a lesser degree $RX^{\bullet -}$) has been recognized, on the basis of electrochemical evidence,[2b,d] as a major termination step. Another possible termination step is the coupling of two aryl radicals that would lead to the corresponding dimer:

$$2R^{\bullet} \rightarrow R\text{–}R$$

So far no such dimer has ever been found among the reaction products of $S_{RN}1$ substitution reactions. It is, however, interesting to note in this connection that a small amount of dimer has been detected in the addition of electrochemically generated cyanophenyl radicals on styrene,[4] a reaction that bears a close resemblance to the $S_{RN}1$ reaction. Although the absence of dimerization in $S_{RN}1$ reactions may be related to the likely smallness of the concentration of the $R^{\bullet}$ radical in the chain reaction, it remains surprising that it has never been detected under the largely varied experimental conditions employed heretofore.[5]

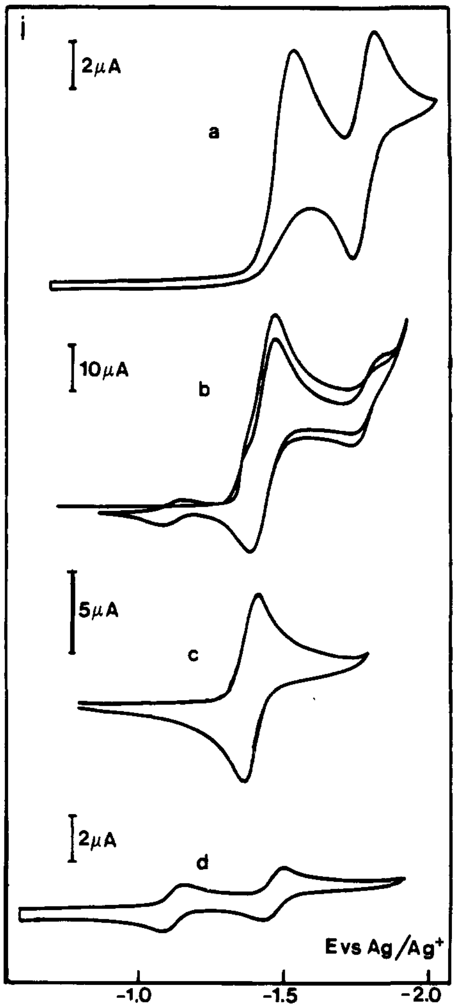


Figure 1. Cyclic voltammetry of 4-chlorobenzonitrile and reaction products in liquid NH_3 (+0.25 M KBr) at -38 °C at a 0.5 mm diameter gold disk electrode: (a) 4-chlorobenzonitrile alone in a 4.3 mM concentration; (b) 4-chlorobenzonitrile (35 mM) in the presence of 2-pyridinethiolate ions (47 mM); (c) 2-pyridyl 4-cyanophenyl sulfide (5.4 mM); (d) 4,4'-dicyanobiphenyl (0.5 mM). Scan rate: 0.2 V/s.

We have found that dimerization of aryl radicals may be, under appropriate experimental conditions, a quite efficient termination step yielding substantial quantities of the R–R dimer.

Figure 1 shows the cyclic voltammetry of 4-chlorobenzonitrile in liquid ammonia alone (a) and in the presence of 2-pyridinethiolate ions as the nucleophile (b). By comparison with the voltammogram of the substitution product (c), it appears that extensive substitution occurs in the diffusion layer. Some hydrogenolysis product (benzonitrile) also appears as demonstrated by the most negative wave in b. More important, a new reversible wave appears positive to the RX and RNu waves and located at the same potential as the first wave of 4,4'-dicyanobiphenyl (d). The second wave of the dimer is merged with the first wave of RNu. It should be noted that the concentration of RX that allows the formation of the dimer to be observed is high (35 mM), much higher than the concentrations used in past studies, and that the excess of nucleophile is small. The formation of the dimer was

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