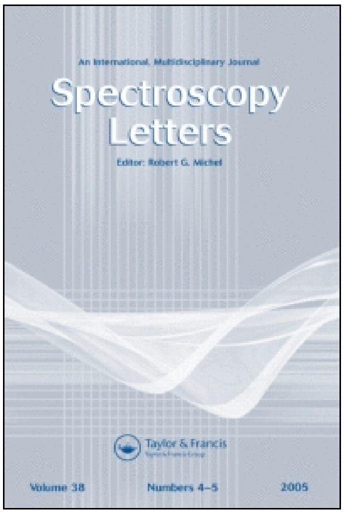

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Complete ^{13}C and ^{1}H NMR Chemical Shift Assignments of 1-Nitropyrene

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COMPLETE ^{13}C AND ^{1}H NMR CHEMICAL SHIFT ASSIGNMENTS OF 1-NITROPYRENE

KEY WORDS: 1-nitropyrene; two-dimensional NMR; long-range heteronuclear chemical shift correlation; bilinear rotational decoupling

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ABSTRACT:

Ambiguities in the ^{13}C NMR chemical shift assignments of 1-nitropyrene were resolved using direct and long-range two-dimensional heteronuclear chemical shift correlation experiments. The latter was modified with a bilinear rotational decoupling (BIRD) pulse sequence, which enabled detection of all three-bond long-range correlations.

INTRODUCTION

We noted some ambiguities in the ^{13}C NMR chemical shift assignments of 1-nitropyrene (1-NP),[1-3] while conducting NMR studies on nitrated fluoranthene compounds.[4] 1-NP is a major component of diesel exhaust and a potent environmental carcinogen.[5-6] It has been often used as a model compound for assigning the ^{13}C resonances of other nitrated-polyaromatic hydrocarbons.[1-3] The assignments of the quaternary carbons, in particular, are difficult owing to low solubility of 1-NP, which renders 2D-INADEQUATE technique impractical. Here, ^{13}C and ^{1}H NMR assignments of 1-NP were obtained by using two-dimensional NMR methods, the most important being a long-range heteronuclear chemical shift correlation experiment that has been modified by addition of a BIRD sequence.[7] This is the first application of a BIRD sequence to nitrated-polyaromatic hydrocarbons.

EXPERIMENTAL

1-NP was obtained from Aldrich (Milwaukee, WI) and used without further purification. ^{1}H NMR spectra were obtained in $CDCl_3$ at 500 MHz on a Bruker AM500 spectrometer using a 5 mm probe. Chemical shifts (δ) in ppm were determined relative to the residual $CHCl_3$ absorption and converted to the TMS scale using $\delta(^{1}H)_{CHCl3} = 7.24$ ppm.

The ^{13}C NMR experiments were recorded at 126 MHz using a 10 mm broad-band probe on the same spectrometer. Chemical shifts (ppm) are defined relative to the ^{13}C resonance of $CDCl_3$ (77.0 ppm).

In a direct one-bond ^{13}C-^{1}H shift correlation experiment, the following pulse sequence (XHCORR)[8] was used: RD-$90^o(^{1}H)$-t/2-$180^o(^{13}C)$-t/2-Δ_1-$90^o(^{1}H)$-$90^o(^{13}C)$-Δ_2-acquire (t2)(proton BB decoupling). In the modified long-range optimized ^{13}C-^{1}H chemical shift correlation experiment, a BIRD pulse sequence was inserted midway through the Δ_2 delay of the above pulse sequence (XHCORR) to provide 'modulation decoupling' as described by Zektzer and co-workers[7]: RD-$90^o(^1H)$-t/2-$180^o(^{13}C)$-t/2-Δ_1-$90^o(^1H)$-$90^o(^{13}C)$-$90^o_x(^1H)$-Δ_2-τ-$180^o_x(^1H)/180^o_x(^{13}C)$-$\tau$-$90^o_{-x}(^1H)$-$\Delta_2$-acquire (t2)(proton BB decoupling). The delay times were optimized to detect long-range couplings of 8 Hz, for both the conventional (Δ_1=63.0 ms and Δ_2=31.2 ms) and the modified long-range correlation experiments (Δ_1=63.0 ms, Δ_2=12.6 ms, and τ=3.1 ms). The spectral width was ± 262 Hz in t1 and 3145 Hz in t2. The spectrum was accumulated with 128 FIDs of 256 scans each in t1 and 1K data points in t2. The relaxation delay was 1 sec. The FID was zero filled in the t1 dimension. Unshifted sine bell functions were used in both dimensions.

RESULTS AND DISCUSSION

Complete assignments of the carbon resonances of 1-NP were accomplished by a combination of one-bond and modified long-range optimized ^{13}C-^1H shift correlation experiments. The inclusion of a BIRD pulse removes the effect of one-bond modulation that can diminish or eliminate the desired responses due to long-range couplings ($^3J_{C-H}$). The result of this experiment is shown as a contour plot in FIG. 1, in which the coupling correlations are indicated. The modified sequence enabled us to observe $^3J_{C1-H10}$, $^3J_{C6-H5}$, and $^3J_{C10a-H2}$ which were undetected in the conventional long-range optimized ^{13}C-^1H shift correlation spectrum recorded under identical conditions (not shown). In fact, FIG. 1 shows

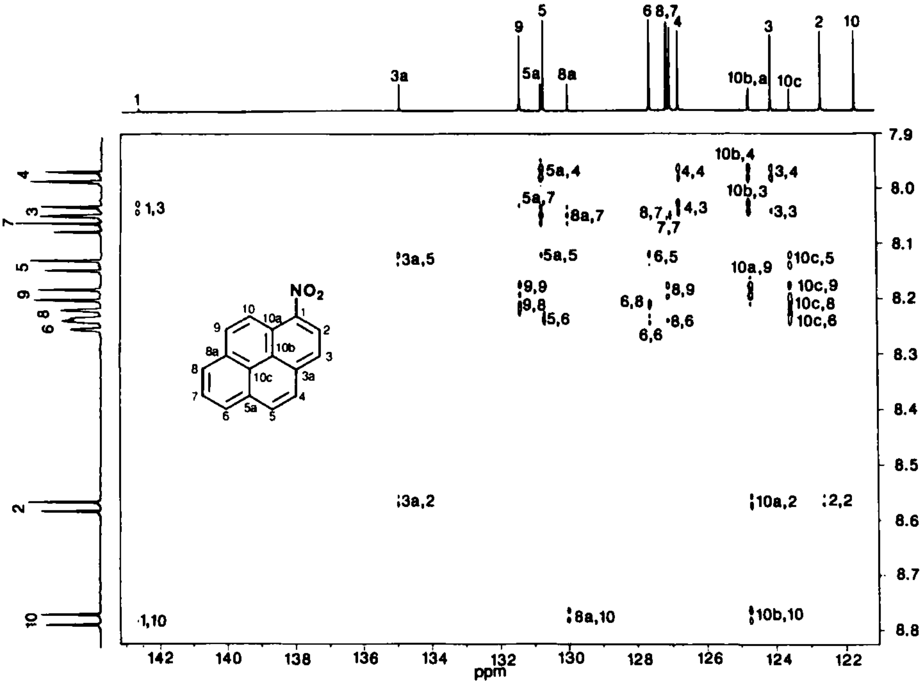

FIG. 1. Contour plot of a modified $^{13}C-^{1}H$ shift correlation spectrum of 1-NP (26 mg/mL $CDCl_3$) at 302°K, optimized for the observation of long-range couplings of 8 Hz. "Projections" were obtained from the one-dimensional spectra.

all of the expected $^{3}J_{C-H}$ couplings (optimized to 8 Hz) for 1-NP with partial suppresion of one-bond couplings, which demonstrates the utility of the modified sequence.[9] Two weak $^{2}J_{C-H}$ couplings, $^{2}J_{C8-H7}$ and $^{2}J_{C5a-H5}$, are also observed.

Since the $^{3}J_{C-H}$ values in polyaromatic hydrocarbon molecules generally lie in a narrow range of about 8 Hz, the assignment of all quaternary carbon signals is straightforward by using the procedure which has been described for several fluoranthenes.[10] For example, the C_{10c} resonance shows multiple correlations with

TABLE 1

^{1}H and ^{13}C NMR Chemical Shifts of 1-Nitropyrene.[a]

No.	^{13}C, δ	^{1}H, δ
1	142.73	
2	122.67	8.56
3	124.15	8.02
3a	135.07	
4	126.87	7.96
5	130.77	8.12
5a	130.87	
6	127.65	8.23
7	127.08	8.05
8	127.15	8.21
8a	130.12	
9	131.51	8.18
10	121.74	8.77
10a	124.79	
10b	124.88	
10c	123.68	

[a] 1-NP (26 mg) was dissolved in 1 mL of $CDCl_3$.

H_5, H_6, H_8 and H_9, while C_{10b} shows correlations with H_3, H_5 and H_{10}. All of the remaining quaternary carbons were assigned as presented (FIG. 1), which resolves the ambiguities of previous assignments.[1,2] Likewise, ambiguities in the assignments of the closely spaced C_7 and C_8 resonances are resolved. For C_7, there are no correlations, except for a weak response due to $^{1}J_{C-H}$. The C_8 slice reveals correlations with H_6, H_7 and H_9. No crossover was observed for any ^{13}C resonances in the concentration range of 2 - 26 mg/mL in $CDCl_3$.

The behavior of the ^{1}H resonances of 1-NP in $CDCl_3$ is worthy of comment. Unlike the ^{13}C NMR chemical shifts, the ^{1}H

resonances are extremely sensitive to concentration variations. For example, the ^1H signal sequence from low to high field in concentrated solution (26 mg/mL $CDCl_3$) is 10-2-6-8-9-5-7-3-4, whereas it is 10-2-9-(6,8)-5-3-7-4 in dilute solution (0.1 mg/mL $CDCl_3$). The ^1H assignments reported previously[11] (ca. 10 mg/mL $CDCl_3$) are consistent with our heteronuclear two-dimensional NMR experiments. In addition, uncertainty in the prior assignments of H_6 and H_8 resonances are now resolved. The ^1H assignments were also independently confirmed by carrying out normal, long-range and triple quantum-COSY[12] experiments (data not shown). The assigned ^1H and ^{13}C chemical shifts of 1-NP are summarized in Table 1.

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