

# Assignment of the $^{13}\text{C}$ -NMR Spectrum of Phenanthro[4,3-*a*]dibenzothiophene Through the Utilization of Two-Dimensional Relayed Coherence Transfer and Double Quantum Coherence Spectroscopy

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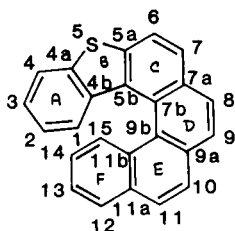
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Total assignment of the  $^{13}\text{C}$ -nmr spectrum of the helical molecule phenanthro[4,3-*a*]dibenzothiophene at 125.762 MHz is reported. Assignments were made by the combined application of  $^{13}\text{C}$ - $^{13}\text{C}$  autocorrelated double quantum coherence and heteronuclear relayed coherence transfer (RELAY) experiments.

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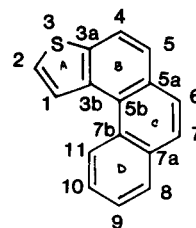
Recently, we communicated the results of our attempted assignment of the  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectra of phenanthro[4,3-*a*]dibenzothiophene (**1**) [3] through the utilization of COSY,  $^1\text{H}/^{13}\text{C}$  heteronuclear chemical shift correlation and the relatively new two-dimensional relayed coherence



transfer experiment [3-9]. Unfortunately, because of the highly congested nature of the proton spectrum of **1**, it was not possible to proceed beyond the subgrouping of the protons into their respective spin systems *via* the relayed coherence transfer (RELAY) spectrum and the assignment of a pair of carbon resonances. Thus, we would now like to report the completion of the assignment of the  $^{13}\text{C}$ -nmr spectrum through the combined application of RELAY and  $^{13}\text{C}$ - $^{13}\text{C}$  double quantum coherence [10-19] spectra. In combination, these techniques are powerfully synergistic. They have facilitated the total assignment of other highly complex molecules.

A convenient starting point for the assignment of the  $^{13}\text{C}$ -nmr spectrum of **1** is provided by the H6/C6-H7/C7

pairings which were assigned in the previous study [3]. From the RELAY spectrum shown in Figure 1, the readily identifiable C6 resonance ( $\delta = 121.47$ ), which compares favorably with the chemical shift of the C4 resonance of phenanthro[3,4-*b*]thiophene (**2**) [17], easily provides the location of the C7 resonance at  $\delta = 126.83$ . Double quantum connectivities shown in Figure 2 readily lead to the



assignment of the C5a, C7a and C7b resonances ( $\delta = 139.40, 131.51$  and  $124.69$ , respectively). The remaining downfield quaternary carbon at  $\delta = 138.43$  was thus assigned as C4a and consequently provides an unequivocal entry point into the assignment of the ring A carbon resonances.

Beginning from the C4a resonance, the identity of C4 is unequivocally established as the resonance at  $\delta = 122.13$  *via* the double quantum spectrum shown in Figure 2. Then, using the RELAY spectrum shown in Figure 1, the identities of the remaining carbons, C3, C2 and C1 are es-

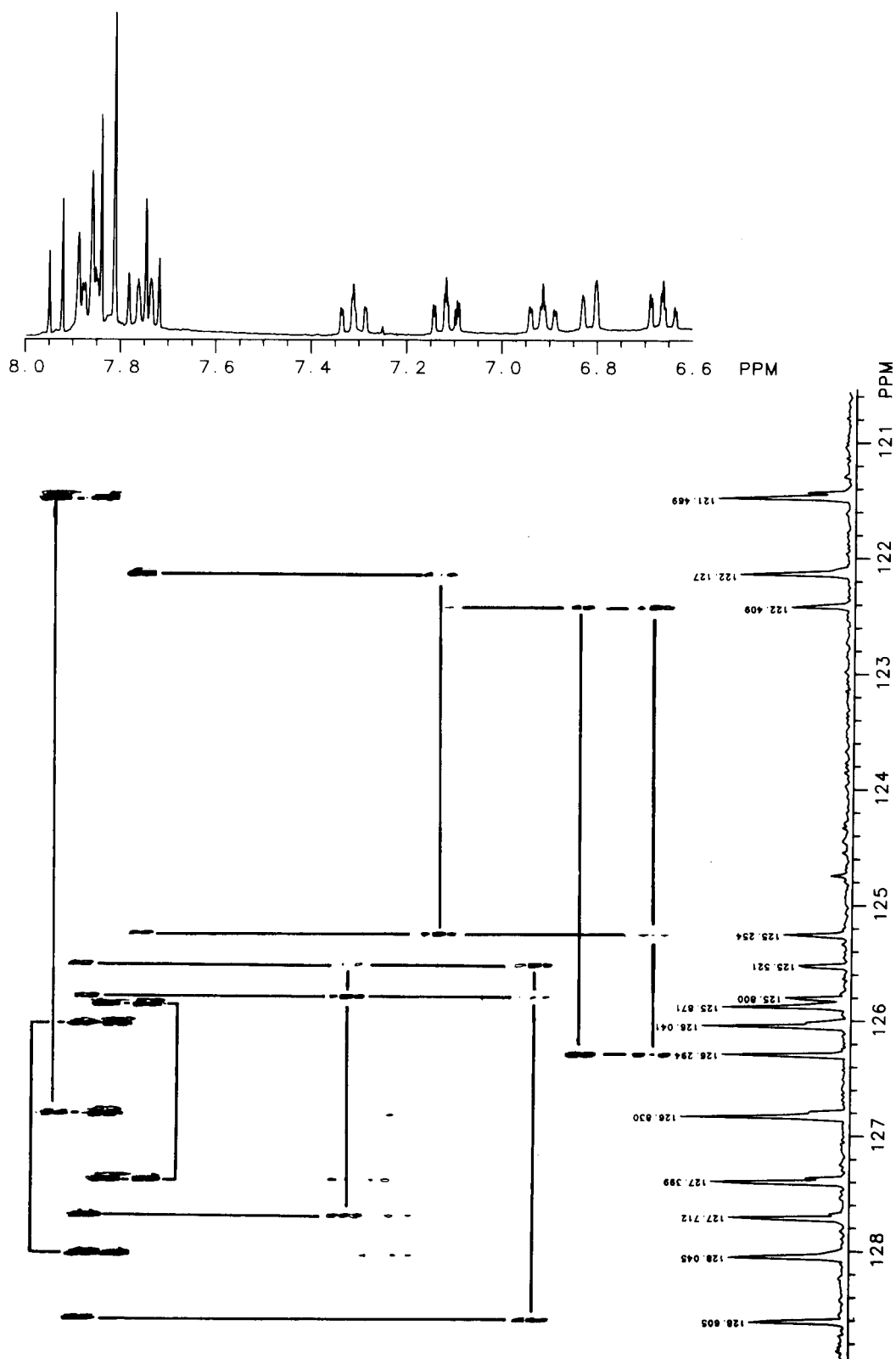


Figure 1. Contour plot of the  $^1\text{H}/^{13}\text{C}$  heteronuclear relayed coherence transfer (RELAY) two-dimensional nmr spectrum of phenanthro[4,3-*a*]dibenzothiophene in deuteriochloroform at observation frequencies of 300.068/75.457 MHz.

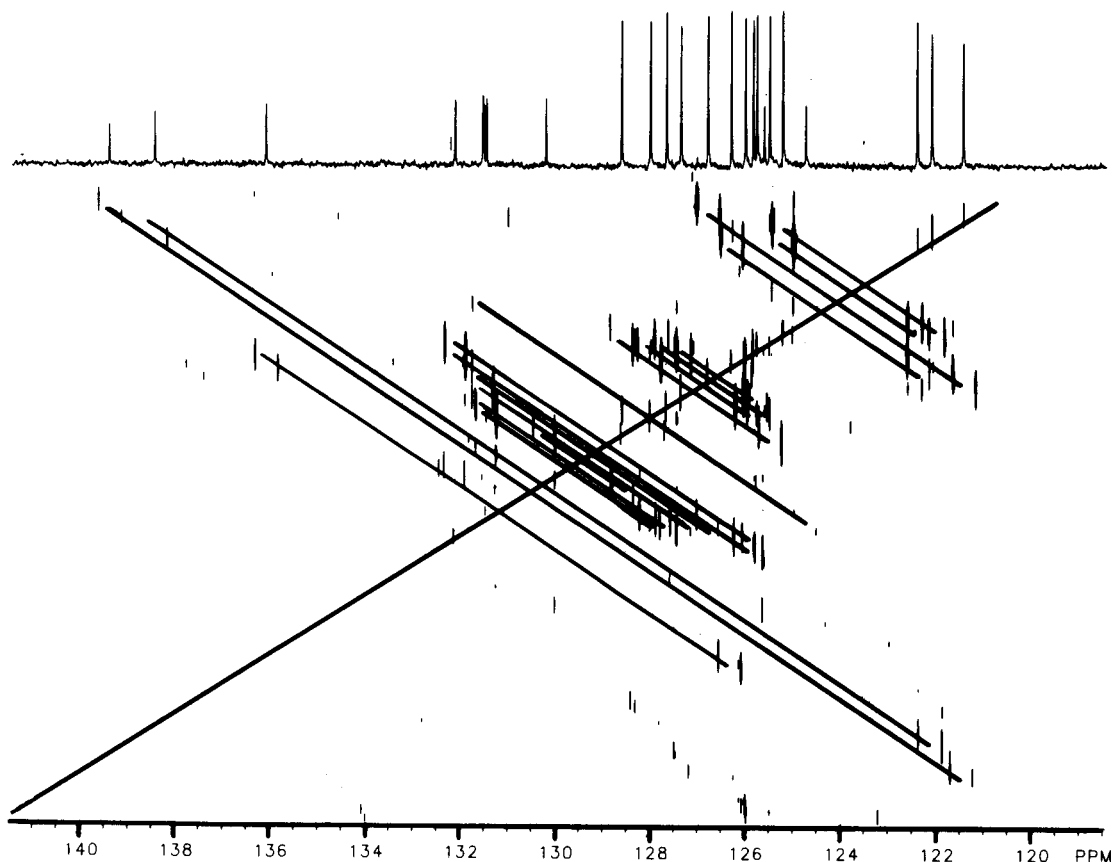


Figure 2. Contour plot of the  $^{13}\text{C}$ - $^{13}\text{C}$  autocorrelated two-dimensional double quantum coherence nmr spectrum of phenanthro[4,3-*a*]dibenzothiophene at 125.762 MHz.

tablished in turn, the double quantum spectrum providing an alternative means of making the same assignments in the absence of breaks in the connectivity pathway due to strongly AB resonance pairings. Finally, the C1 resonance provided the identity of the C4b resonance at  $\delta = 136.08$  through the double quantum spectrum. Unfortunately, the C4b-C4a and C4b-C5b connectivities were not observed in the double quantum experiment, probably due to their low intensities as quaternary carbons and/or due to incomplete relaxation as a consequence of the recycle time of the experiment.

Remaining to be assigned at this point are the resonances of rings D, E and F. Within these assignments, the advantages inherent to combining the RELAY and double quantum experiments are evident. As will be noted in Figure 3, the double quantum experiment fails to link the resonances which may ultimately be assigned as C13 and C14 although they are readily linked by the RELAY experiment. Conversely, the RELAY experiment does not allow

the differentiation of C12 from C15 and thus, although it does link the C13 and C14 resonances, it does not provide the means for an assignment. Beginning with the carbon resonances which could correspond to C12 and C15 which resonate at  $\delta = 127.71$  and  $128.61$ , we may follow the carbon-carbon connectivities associated with these resonances in Figure 3. From the resonance at  $\delta = 128.61$ , which is ultimately assigned as C15, we observe a connectivity to a protonated carbon resonance at  $\delta = 125.52$  and to a quaternary carbon resonating at  $\delta = 130.71$ , but no further. Examining the connectivities associated with the resonance at  $\delta = 127.71$ , we observe a connectivity to a protonated carbon at  $\delta = 125.80$  and a connectivity to a quaternary carbon resonating at  $\delta = 131.42$ . The quaternary carbon shows a further connectivity to another protonated carbon resonating at  $\delta = 128.05$ , thus establishing the identity of the starting resonance at  $\delta = 127.71$  unequivocally as C12. The identities of C13-C15a are then readily established from the combined usage of the RELAY

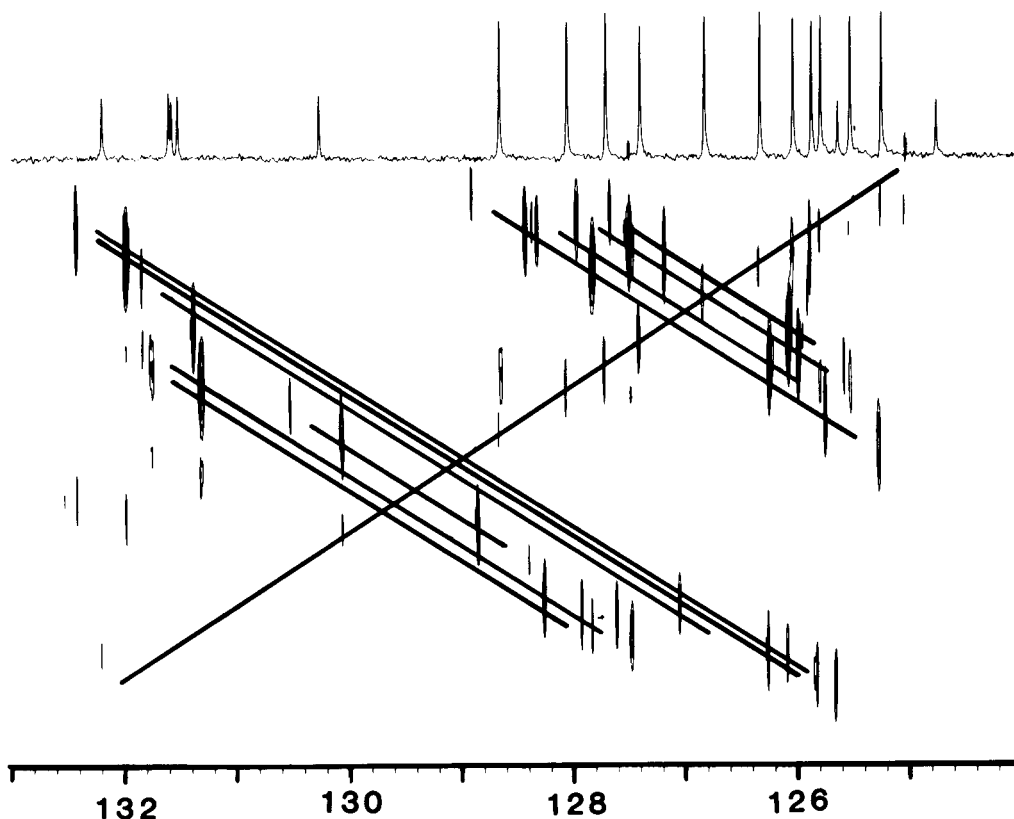


Figure 3. Expansion of the  $^{13}\text{C}$ - $^{13}\text{C}$  autocorrelated two-dimensional double quantum coherence nmr spectrum of phenanthro[4,3-*a*]dibenzothiophene to show detail in the congested region from 133-124 ppm.

and double quantum spectra. The C11a and C11 resonances are assigned as the quaternary and protonated carbon resonances linked to C12 in the double quantum spectrum which are assigned as  $\delta = 131.42$  and 128.05.

Proceeding from the C11 resonance at  $\delta = 128.05$ , the C10 resonance may be readily assigned *via* the RELAY spectrum as the resonance observed at  $\delta = 126.04$ , which is in turn correlated in the quaternary carbon resonating at  $\delta = 132.11$  which may thus be assigned as C9a. Finally, the C9a resonance correlates with C9 of the remaining AB spin system that was identified in the RELAY experiment, C9 resonating at  $\delta = 125.87$ . Ultimately, the C8 resonance at  $\delta = 127.40$  is linked to the quaternary carbon identified as C7a above, thus unequivocally completing the assignment of the protonated carbon resonances of **1** and leaving only C5b and C9b unassigned. These quaternary carbons resonate at  $\delta = 131.48$  and 125.57. Tentative assignments for these resonances were, however, made on the basis of the chemical shift considerations from the prior assignments of phenanthro[3,4-*b*]thiophene (**2**) [17]. Interestingly, the bay region carbons on the interior of what

should be the helical turn of the molecule in the case of both **1** and **2** resonate considerably upfield of the other quaternary carbons in the molecule, a point which could provide a useful discriminatory criterion in the assignment of related systems. In addition, the upfield shift of these resonances may be attributed to the partial single bond character that would be necessary in the helical turn for the molecule to become nonplanar.

In conclusion, we have shown that the RELAY and  $^{13}\text{C}$ - $^{13}\text{C}$  double quantum coherence nmr experiments can be efficiently utilized in a complementary fashion. In simpler systems, it is quite probable that the majority of the resonance assignments could be made without resorting to the time consuming and demanding double quantum experiment. Indeed, work nearing completion in these laboratories on other ring systems supports this contention, and will form the basis for forthcoming reports.

#### EXPERIMENTAL

The sample of phenanthro[4,3-*a*]dibenzothiophene (**1**) utilized in this study was prepared by dissolving 65 mg of analytically pure material in

Table I

<sup>13</sup>C-NMR Resonance Assignments of Phenanthro[4,3-*a*]dibenzothiophene in Deuteriochloroform at 125.762 MHz

Position	Chemical Shift (δ)
1	126.30
2	122.41
3	125.25
4	122.13
4a	138.43
4b	136.08
5a	139.40
5b	131.48 [a]
6	121.47
7	126.83
7a	131.51
7b	124.69 [b]
8	127.40
9	125.87
9a	132.11
9b	125.57 [a]
10	126.04
11	128.05
11a	131.42
11b	130.17
12	127.71
13	125.80 [c]
14	125.52 [c]
15	128.61

[a] Assigned on the basis of chemical shift considerations [17]. [b] The C7a-C7b connectivity is not shown with the contour levels plotted in Figure 2 but was visible when lower contours were plotted. [c] The C13-C14 connectivity was not established from the double quantum spectrum because of the highly AB character of this resonance pair. This connectivity was instead established from RELAY spectrum shown in Figure 1.

0.4 ml of deuteriochloroform for the RELAY experiment after which the sample volume was reduced to 0.2 ml for the acquisition of the <sup>13</sup>C-<sup>13</sup>C two-dimensional double quantum coherence spectrum. The RELAY spectrum was recorded at 75.457 MHz using an NT-300 spectrometer, the pulse sequence and parameters communicated previously [3]. The <sup>13</sup>C-<sup>13</sup>C double quantum spectrum was recorded using the autocorrelated pulse sequence of Turner [14] modified with a 135° read pulse [13,17,19]. The data were recorded at 125.762 MHz using a General Electric GN-500 spectrometer as 29 × 8K blocks of data which was zero filled during processing to give the 64 × 4K contour plot shown in Figure 2. Total accumulated time for the double quantum spectrum was 49 hours with 2048 acquisitions taken per block.

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