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The utilization of the long range optimized proton-carbon chemical shift correlation experiment in the total assignment of the proton and carbon nmr spectra of 9-methylphenanthro[4,3-*a*]dibenzothiophene is described. The experiment was employed in concert with conventional proton-carbon chemical shift correlation, heteronuclear relayed coherence transfer and broad band homonuclear decoupled proton-carbon chemical shift correlation experiments. The experiments in combination offer a useful alternative to the ^{13}C - ^{13}C double quantum coherence experiments, providing significantly better sensitivity and nearly the same capabilities.

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Introduction.

New two-dimensional nmr experiments are now appearing in the literature with increasing frequency, and provide the investigator with experimental access to a diverse assortment of spectral information. Unfortunately, as the numbers of new experiments continue to proliferate, there is, quite probably, a widening gap developing between the initial demonstration of an experiment and a full appreciation of all of its capabilities.

Perhaps among the most, if not the most powerful of the new experiments available are the double quantum coherence experiments which make it possible to exploit natural abundance ^{13}C - ^{13}C spin couplings to derive carbon-carbon connectivity networks [3-13]. Importantly, the ^{13}C - ^{13}C double quantum coherence experiment, regardless of the form in which it is employed, provides the means of making unequivocal assignments of congested carbon nmr spectra including the quaternary carbon resonances. These capabilities are useful since there are many instances in which it would be otherwise impossible to arrive at unequivocal quaternary carbon resonance assignments. Indeed, we have utilized the autocorrelated variant of the ^{13}C - ^{13}C double quantum coherence experiment with a modified read pulse [6,10-13] to establish unequivocal assignments for the homologous series including: phenanthro[3,4-*b*]thiophene [10], benzo[*b*]phenanthro[4,3-*a*]thiophene [13] and phenanthro[4,3-*a*]dibenzothiophene (**1**) [12]. Because of the relative insensitivity of the experiment, a consequence of the limited sample pool of only about 1 molecule in 10,000, most of the work just describ-

ed was performed on a 500 MHz spectrometer and required accumulation times ranging from 24-48 hours. Thus, it would clearly be desirable to have an alternative means of approaching these assignments which affords better sensitivity and the possibility of performing the experiments at somewhat lower and more generally available field strengths. As an alternative, Reynolds and co-workers [14] and more recently other groups [15,16] have begun to explore the optimization of the heteronuclear proton-carbon chemical shift correlation experiment for transfer of magnetization *via* long range two and three bond couplings rather than through the customary direct or one bond coupling. The potential advantages which accrue are obvious: the accessible sample pool is larger with consequently higher relative sensitivity and the means is now available for transferring magnetization to quaternary carbon resonances which are inaccessible in the conventional heteronuclear chemical shift correlation experiment.

To demonstrate the potential utility of this experiment in the assignment of the spectra of polynuclear aromatics, we wish to describe its application to the total assignment of the proton and carbon nmr spectra of 9-methylphenanthro[4,3-*a*]dibenzothiophene (**2**). The selection of this compound is based on the availability of established ^{13}C -nmr chemical shifts of the parent system **1** which were obtained using ^{13}C - ^{13}C double quantum coherence techniques, and upon the fact that the proton spectrum is severely congested simultaneously allowing a further demonstration of the abilities of the heteronuclear relayed coherence transfer experiment in establishing spin system component identi-

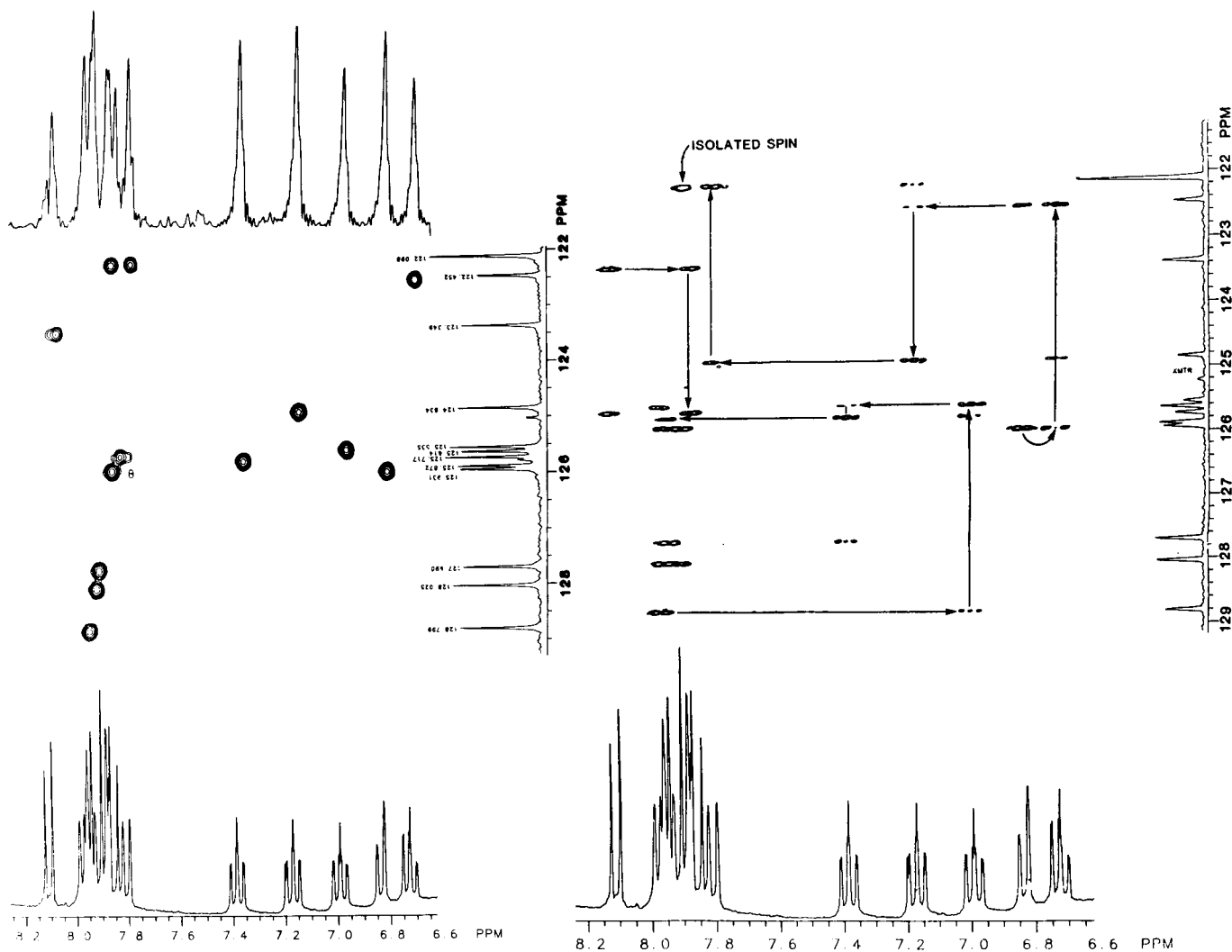


Figure 1. A) Heteronuclear chemical shift correlation spectrum of 9-methylphenanthro[4,3-*a*]dibenzothiophene (**2**) with broad band homonuclear proton decoupling recorded in deuteriochloroform at observation frequencies of 300.068/75.457 MHz at 30°. The conventional high resolution proton spectrum is shown below the contour plot while the projected proton spectrum is shown above the contour plot showing the protons as broad band decoupled singlets. The projected carbon spectrum is shown vertically flanking the contour plot; B) Heteronuclear relayed coherence transfer (RELAY) spectrum of **2** recorded in deuteriochloroform at 30°. The conventional high resolution proton spectrum is plotted below the contour plot while the projected carbon spectrum is plotted vertically flanking the contour plot.

ties when the autocorrelated proton (COSY) experiment would be of relatively little utility. This latter consideration also provides an excellent opportunity to demonstrate the ability of the heteronuclear chemical shift correlation experiment with broad band homonuclear proton decoupling to provide exact proton chemical shifts even in highly congested spectral regions.

Assignment Strategy.

Assignment of the ^1H - and ^{13}C -nmr spectra of 9-methyl-

phenanthro[4,3-*a*]dibenzothiophene (**2**) requires that the direct ^1H - ^{13}C connectivities first be established using the conventional heteronuclear $^1\text{H}/^{13}\text{C}$ chemical shift correlation experiment or heteronuclear chemical shift correlation with broad band homonuclear proton decoupling, the latter shown in Figure 1A. Next, the components of the individual spin systems can be established using the heteronuclear relayed coherence transfer (RELAY) experiment [12,17-23] which is shown in Figure 1B. A conventional ^1H -decoupled ^{13}C -nmr spectrum was acquired using an inter-

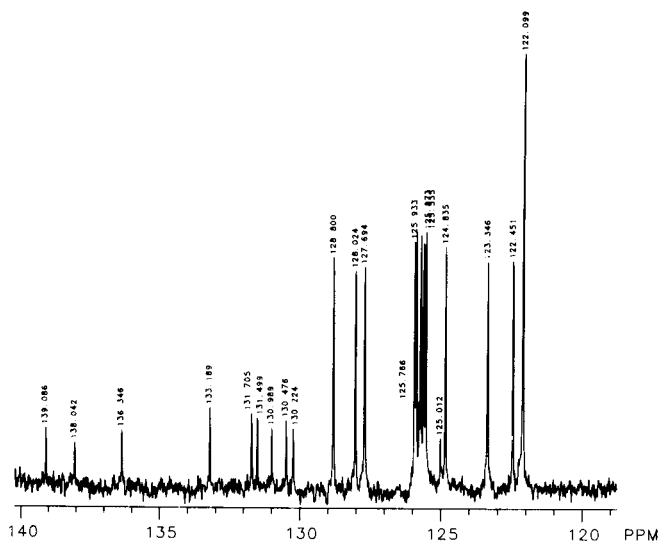


Figure 2. ¹H-Decoupled ¹³C-nmr spectrum of 9-methylphenanthro[4,3-*a*]dibenzothiophene recorded at 75.457 MHz in deuteriochloroform at 30°. The interpulse delay was set to 1 second to intentionally suppress the intensities of the quaternary carbon resonances.

pulse delay sufficiently short to allow incomplete relaxation of the quaternary carbon resonances thereby making them readily identifiable (Figure 2). Finally, with the proton spin systems and their related carbons identified through the RELAY spectrum it is possible to begin to make assignments using the long range optimized heteronuclear ¹H/¹³C chemical shift correlation spectrum. The long range optimized experiment was performed twice, once incorporating full sweep widths to include the methyl proton/carbon responses in their correct positions and once with the sweep widths set to cover only the aromatic region, the latter shown in Figure 3.

Optimization of the heteronuclear ¹H/¹³C chemical shift correlation for a 10 Hz coupling provides the means of transferring heteronuclear spin coupling information over two and/or three bonds. On this basis, it is clearly possible to link the proton spin systems to the quaternary carbon resonances and to one another, thereby circumventing the necessity of acquiring a ¹³C-¹³C double quantum coherence spectrum which still might allow for breaks in the connectivity network anyway in the event that AB rather than AX carbon-carbon pairings are encountered.

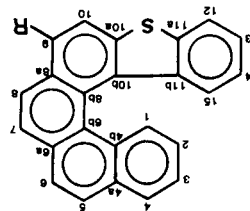
Assignments Using Long Range Coupling Constants.

The first problem to be dealt with in making the assignment of the ¹³C-nmr spectrum of **2** is the unequivocal identification of the two four spin systems and their orientations. This task, although it might initially appear to be formidable, is really quite simple. First the two sulfur

bearing quaternary carbon resonances are readily identifiable on the basis of their chemical shifts as the carbons resonating at 139.08 and 138.04 ppm. Next, by considering the long range coupling possibilities, one of these resonances should couple to one of the four spin systems. For a two bond coupling a single possibility exists; coupling between the C11a quaternary carbon and the H12 proton. In contrast, there are two potential three bond coupling pathways: coupling between C11a and H13 and between C11a

Table I

Proton and Carbon Chemical Shift Assignments of 9-Methylphenanthro[4,3-*a*]dibenzothiophene (**2**) in Deuteriochloroform at 30° with the Observation Frequencies of 300.068 and 75.457 MHz Obtained using the Long Range Heteronuclear Chemical Shift Correlation Technique. For Comparison, Chemical Shift Assignments for the Parent Phenanthro[4,3-*a*]dibenzothiophene (**1**) System [12] Obtained from a 125.762 MHz ¹³C-¹³C Double Quantum Coherence Experiment are Also Shown



Position	Chemical Shifts		1 (R = -H) ¹³ C (ppm)
	2 (R = -CH ₃) ¹ H (ppm) [a]	¹³ C (ppm)	
1	7.97	128.80	128.61
2	6.99	125.53	125.52
3	7.38	125.72	125.80
4	7.94	127.69	127.71
4a	—	131.50	131.42
4b	—	130.48	130.17
5	7.95	128.03	128.05
6	7.88	125.87	126.04
6a	—	131.71	132.11
6b	—	125.77	125.57
7	7.85	125.61	125.87
8	8.13	123.35	127.40
8a	—	130.99	131.51
8b	—	125.04	124.69
9	—	133.19	126.83
10	7.88	122.10	121.47
10a	—	139.08	139.40
10b	—	130.23	131.48
11	—	—	—
11a	—	138.04	138.43
11b	—	136.35	136.08
12	7.80	122.10	122.13
13	7.16	124.83	125.25
14	6.72	122.45	122.41
15	6.83	125.93	126.30
-CH ₃	2.88	19.67	—

[a] Proton chemical shifts were obtained from the heteronuclear chemical shift correlation experiment with broad band homonuclear proton decoupling [24] by taking individual interferograms which were subjected to double exponential apodization and zero filled to 2K points prior to the second Fourier transform, affording an effective digital resolution of 0.01 ppm.

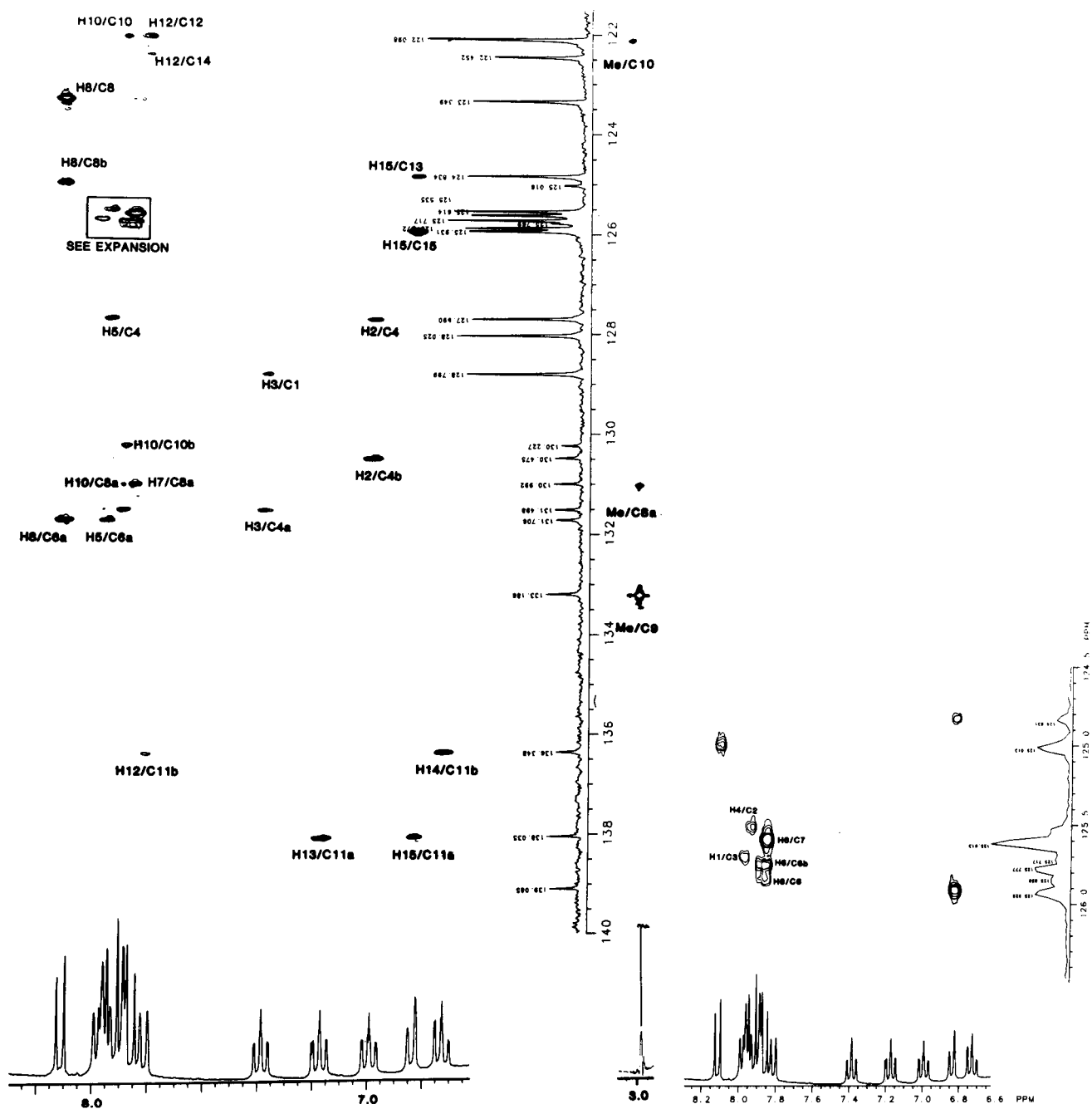


Figure 3. A) Long range optimized heteronuclear chemical shift correlation spectrum of 9-methylphenanthro[4,3-a]dibenzothiophene in deuteriochloroform recorded at observation frequencies of 300.068/75.457 MHz at 30°. The responses contained in the aromatic region are shown to the left while the slice to the right of the high resolution carbon spectrum shows the responses arising from the methyl group. The conventional high resolution proton spectrum is shown below the contour plot. B) The expansion of the congested region contained within the box in the spectrum in A) has a conventional high resolution ^1H spectrum plotted below the contour plot, and a projected ^{13}C -spectrum plotted vertically.

and H15. In the case of simpler systems, discriminating H12 from H15 would be simple since the latter would be a bay region proton and hence shifted significantly downfield. In the case at hand, the highly helical character of the molecule precludes the simple differentiation of the H12 and H15 resonances and a somewhat more sophisticated argument must instead be employed. By first mapping the proton spin system using the RELAY spectrum shown in Figure 1B, the vicinal proton-proton connectivities may be established. Then, the connectivity between H14 and/or H15 to the C11b quaternary carbon resonance, in conjunction with the connectivities discussed above to the C11a resonance will provide an unequivocal means of orienting the spin system. Finally, as an internal double check, the assignments may ultimately be compared with those made for the parent system, **1**, on the basis of the ¹³C-¹³C double quantum experiments which were recently reported [12].

Having developed the arguments on which an assignment may be based, it is appropriate to examine the spectra for responses congruent with the arguments just presented. Beginning with Figure 3, we first note that the quaternary carbon resonating at 138.04 ppm shows responses corresponding to the protons resonating at 6.83 and 7.16 ppm, the chemical shifts determined using the broad band homonuclear decoupled heteronuclear chemical shift correlation experiment described by Bax [24]. By returning to the RELAY spectrum shown in Figure 1B, we note that these two protons are noncontiguous and hence cannot be H12 and H13. Consequently, we may tentatively assign the proton resonating at 6.83 ppm as H15 and the latter as H13. Verification of these attributions was provided by the response for the proton to which both are vicinally coupled resonating at 6.72 ppm, which showed a long range coupling in Figure 3 to the quaternary carbon resonating at 136.35 ppm, the former thus assignable as H14 while the latter may be assigned as the C11b resonance. Having made these assignments, the balance of the proton and carbon resonances of the terminal ring adjacent to the thiophene may then be assigned directly from the RELAY spectrum, these assignments summarized in Table I.

Development of assignment arguments for the remaining four spin system is a much more complex undertaking and, rather than approaching it immediately, it is much more convenient to first establish the assignments of the intervening AB spin systems, linking them to one another and then finally to the four spin system. Thus, by utilizing the methyl proton long range couplings, which are the most intense in the spectrum, we may define connectivities to two quaternary carbons which resonate at 133.19 and 130.99 ppm, these assignable as C9 and C8a respectively. Similarly the proton resonating at 7.88 ppm, which cor-

responds to the isolated H10 resonance (this information is provided by both the RELAY spectrum shown in Figure 1B and through a long range coupling to the methyl protons), affords a connectivity to a quaternary carbon resonating at 130.23 ppm. Since there is no visible connectivity to the quaternary carbon resonating furthest downfield at 139.08 ppm, which must on the basis of chemical shift considerations be the C10a resonance, the connectivity between the H10 resonance and the other quaternary carbon establishes the identity of the C10b resonance.

Within the two AB proton spin systems, the components are readily identifiable as being associated with the carbons resonating at 128.03 and 125.87 ppm for one pair and 123.35 and 125.61 ppm for the other pair. From Figure 3, these resonances are associated with a number of long range connectivities. First and somewhat surprisingly, the carbon resonating at 128.03 ppm does not exhibit any long range connectivity responses. Its partner, in contrast, exhibits numerous long range couplings which importantly link it to the carbon resonating at 125.61 ppm, thus orienting the two AB systems relative to one another, and to the quaternary carbon resonating at 131.50 ppm. This latter connectivity, as we shall see below is important in that it provides the means of finally orienting the remaining four spin system. The resonance at 125.61 ppm is long range coupled to the quaternary carbon resonating at 125.77 ppm, and finally, the carbon resonating at 123.35 ppm shows long range connectivities to the quaternary carbons resonating at 125.04 and 131.71 ppm.

Orienting the two AB spin systems relative to one another, as mentioned above, is based on the connectivity linking the protonated carbons resonating at 125.87 and 125.61 ppm. Orienting the resultant larger fragment relative to the balance of the molecule takes into consideration the further connectivities of the quaternary carbon resonating at 131.50 ppm which is also linked to the as yet unassigned and unoriented four spin system. Thus, the resonance at 128.03 ppm may be assigned as C5 and its neighbor resonating at 125.87 ppm as C6. The linkage from C6 to the resonance at 125.61 ppm provides the assignment for C7, leaving only the assignment of C8 as the resonance observed at 123.35 ppm.

Utilizing the resonance at 123.35 ppm as a starting point for the quaternary carbon resonance assignments, we note that it is associated with the quaternary carbons resonating at 131.71 and 125.04 ppm. Based upon the lengthening of the carbon-carbon bonds along the interior of the helical turn [25] we would expect the resonance at 125.02 ppm to be assigned as C8b while the resonance at 131.71 ppm must then be C6a. Thus, the quaternary carbon at 125.77 ppm associated with the C7 resonance at 125.61 ppm must then be C6b.

Finally, as was mentioned above, the quaternary carbon resonating at 131.50 ppm provides the means of finally orienting the remaining four spin system. Thus, the quaternary carbon exhibits long range coupling links to protons associated with the carbons resonating at 125.72 ppm and 128.80 ppm, which are once again noncontiguous. Hence, the former must be the C3 resonance while the latter must be C1. The remaining quaternary carbon at 130.48 ppm also exhibits a long range connectivity linking it with the carbon resonating at 125.53 ppm which is itself also linked with the resonance at 127.69 ppm the former assigned as C2 the latter as C4 which also completes the assignments of the carbons and protons of the four spin system (these are also in agreement with the RELAY data presented in Figure 1B).

Importantly, the assignments of 9-methylphenanthro[4,3-*a*]dibenzothiophene (**2**) which were just described compare very favorably with those made previously for the parent ring system on the basis of carbon-carbon double quantum experiments. Indeed, those of the substituted system also confirm a pair of resonance assignments made in the case of the parent system on the basis of chemical shift considerations since the connectivities to these carbons could not be observed in the double quantum experiment. For ease of comparison, chemical shift assignments for the parent system are also collected in Table I with those of the title compound.

Conclusions.

The long range optimized heteronuclear $^1\text{H}/^{13}\text{C}$ chemical shift correlation experiment provides a useful alternative to the ^{13}C - ^{13}C double quantum experiment. Importantly, the sensitivity is significantly better and, as was shown in the present case, it may provide access to assignments which cannot be made with the double quantum experiment because of the lengthy relaxation times of the quaternary carbon resonances. The long range optimized experiment is not without drawbacks: one is the lengthening of the Δ_1 and Δ_2 intervals to accommodate the long range coupling ($\frac{1}{2}J_{\text{CH}}$ and $\frac{1}{3}J_{\text{CH}}$ respectively) which results in a loss of signal due to decay of magnetization, especially when coupled with long evolution times (t_1) during the latter stages of the experiment. These problems are, however, directly dealt with in the newly reported COLOC experiment of Kessler and co-workers [26-28] which employs a fixed duration evolution period. Irrespective of which version of the long range correlation experiment which is used, this work and that by others [14-16,26-28] has served to clearly demonstrate the viability of the technique. Doubtless, additional applications to other complex assignment problems will continue to appear. Work is also under way in these laboratories which employs these techniques in structure elucidation, this to form the basis of a

forthcoming report.

EXPERIMENTAL

All of the experiments described in this work were performed using a sample prepared by dissolving 35 mg of analytically pure 9-methylphenanthro[4,3-*a*]dibenzothiophene (**2**) in 0.4 ml of deuteriochloroform. The sample of the title compound was prepared using the synthetic procedure previously described [29]. All spectra were recorded at 30°.

All of the spectra were recorded using a Nicolet NT-300 spectrometer controlled by a Model 293-C pulse programmer and equipped with a 5 mm $^1\text{H}/^{13}\text{C}$ dual tuned probe. The 90° ^{13}C observe pulse was calibrated as 17.5 μs using the two-dimensional pulse calibration procedure described by Lawn and Jones [30]. The 90° ^1H pulse from the decoupler was calibrated as 27.5 μs by taking $\frac{1}{4}(\gamma\text{H}_2/2\pi)$. The ^{13}C reference spectrum of the aromatic region was recorded using a 12 μs pulse and a 1 second interpulse delay digitized with 8K data points. The data was processed to provide the reference spectrum shown in Figure 3 using a double exponential apodization.

Heteronuclear $^1\text{H}/^{13}\text{C}$ Chemical Shift Correlation with Broad Band Homonuclear Proton Decoupling.

Because of the inherently high congestion in the proton spectrum of the phenanthro[4,3-*a*]dibenzothiophene system, proton chemical shifts were determined using the heteronuclear chemical shift correlation experiment with broad band homonuclear proton decoupling as described by Bax [24]. The pulse sequence differs from the conventional heteronuclear chemical shift correlation sequence in that the 180° ^{13}C refocusing pulse midway through the evolution period (t_1) is replaced by a 90° $^1\text{H}-\frac{1}{2}J_{\text{CH}}-180^\circ\text{H}/180^\circ\text{C}-\frac{1}{2}J_{\text{CH}}-90^\circ\text{H}$ sequence, in which the interval $\frac{1}{2}J_{\text{CH}} = 3.0$ mseconds, based on an assumed 165 Hz heteronuclear coupling constant. Again, as in the conventional heteronuclear chemical shift correlation experiment, the coherence transfer echo was detected [31,32]. The data was collected using 192 acquisitions/block as $256 \times 1\text{K}$ points and was processed using double exponential apodization in both dimensions with zero filling to give a 512×512 matrix. Proton chemical shift locations were determined by zero filling individual interferograms corresponding to the individual carbon resonances to 2K points prior to the second Fourier transform followed by double exponential apodization. Chemical shifts of the individual protons determined in this fashion are reported in Table I and are calculated to be accurate to 0.01 ppm.

Heteronuclear Relayed Coherence Transfer (RELAY).

The heteronuclear relayed coherence transfer (RELAY) experiment was performed using the pulse sequence and phase cycling reported previously [23]. The Δ_1 and Δ_2 parameters were set as in the heteronuclear chemical shift correlation experiment with the exception that the Δ_1 delay was set to $\Delta_1/2$ because of the 180° ^{13}C refocusing pulse applied midway through the Δ_1 interval in this experiment. The mixing time was set to $1/20^3J_{\text{HH}} = 28.56$ mseconds. A 1 second interpulse delay was employed. As in the heteronuclear chemical shift correlation experiment described above, a total of 192 acquisitions/block were taken, the data collected as a $256 \times 1\text{K}$ matrix with 146 blocks of data accumulated overnight. The data was also processed as above to give a final 512×512 matrix which is presented as a four level contour plot in Figure 1B.

Long Range Optimized Heteronuclear $^1\text{H}/^{13}\text{C}$ Chemical Shift Correlation.

The pulse sequence employed for the long range optimized chemical shift correlation experiment was identical to that employed for the conventional heteronuclear chemical shift correlation experiment, the sole difference being the durations selected for the Δ_1 and Δ_2 intervals. Based upon the previous work of Reynolds and co-workers [14] a 10 Hz long range coupling was assumed to be an optimal setting which gave values for the delays of 50.0 and 33.3 mseconds respectively. The data, once again, was collected using 192 acquisitions/block as an initial $256 \times 1\text{K}$

points. The data was processed using a 2.5 Hz exponential broadening and zero filling to 2K points prior to the first Fourier transform and double exponential apodization and zero filling to give 1K points before the second Fourier transform, thus affording a final data matrix consisting of 1K × 1K points which is shown as a five level contour plot in Figure 3.

In total, two replicates of the experiment were acquired, one with sweep widths sufficient to include the methyl protons and carbon resonances and a second, which is shown in Figure 3, encompassing only the aromatic proton and carbon spectral windows. The second experiment was necessary to provide sufficient data point density to permit the interpretation of the experiment because of the numbers of long range and direct responses which were observed in the experiment.

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