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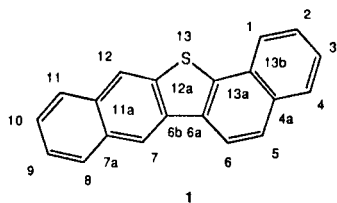
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Recently, there has been some question regarding the ^1H -nmr spectrum of dinaphtho[1,2-*b*:2',3'-*d*]thiophene. A recent study has reported differences in some of the proton resonance positions from results of earlier work. We report the total assignment of the ^1H -nmr spectrum of the title compound using a combination of ^1H -COSY and one dimensional NOE-difference spectroscopy (NOEDS).

J. Heterocyclic Chem., **25**, 1593 (1988).

Unequivocal synthetic routes to a number of dinaphthothiophenes, including the title compound, dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**1**), have been reported [1]. A recent study by Klemm and co-workers [2] led to the preparation of the title compound and related isomers by the insertion of sulfur into the corresponding binaphthyls. In that study, a discrepancy in the proton nmr chemical shift data relative to the original study was noted. It is on this basis that we wish to report the re-examination of the proton nmr spectrum of **1** at high field and its total assignment.



The high resolution proton nmr spectrum of **1** is shown beneath the COSY contour plot presented in Figure 1. (The unconventional appearance of this plot will be explained later.) It will be immediately noted that the two singlets furthest downfield are consistent with the structure, arising from H7 and H12. Intuitively, we may assign H7 as the singlet further downfield resonating at 8.68 ppm; H12 is assigned as the singlet at 8.42 ppm. These assignments and resonance positions are consistent with the previous report of Castle and co-workers [1]. We also note that the COSY spectrum shown in Figure 1 contains responses which correlate H7 and H12 with one another and that, further, each is correlated upfield to other protons. Usefully, only two probable long range coupling responses exist for each of the protons. Each may be coupled *peri* to H8 and H11 for H7 and H12, respectively. Alternately, H7 and H12 may be coupled *via* a five bond epi-zig-zag pathway to H11 and H8, respectively. In our experience,

while the latter long range responses of polynuclear aromatics are quite common, the former, which are generally smaller in size [3], are much less commonly observed. Thus, given the observed long range responses, we initially attributed H8 to the resonance at 8.09 ppm and H11 to the proton resonating at 7.96 ppm. From these assignments, which locate the two terminal spins of the four spin system, we may next use the COSY spectrum to locate H9 and H10 which both resonate in the highly overlapped multiplet centered at about 7.53 ppm. Hence, the H9-H12 four spin system is best classified as an ABXY system.

At this point, before continuing to finish the assignment, we must recall that all of the assignments made thus far are predicated on the intuitive assignment of H7 as the proton resonating furthest downfield in the spectrum. Clearly, if the assignments of H7 and H12 are reversed, the assignments made within the four spin system must also be reversed. To confirm the assignment of H7, a one dimensional nuclear Overhauser difference experiment (NOEDS) was performed using a 6 sec irradiation of the singlet furthest downfield which we have attributed to H7. The difference spectrum showed a 12.7% NOE to the doublet centered at 8.31 ppm. The existence of a large NOE between H6 and H7 is to be expected when the structure is considered since these two protons will be in close proximity to one another. Furthermore, the doublet assigned as H6 at this point is unequivocally assignable when all other factors are taken into consideration.

Continuing from the H6 resonance at 8.31 ppm, the COSY spectrum clearly shows it to be coupled to a doublet resonating at 7.92 ppm which is H5. Further, H5 also shows a long range coupling response to the proton resonating at 8.13 ppm which is assignable as H1. Once again, H1 and H5 are correlated *via* a five bond epi-zig-zag coupling pathway (see **2**).

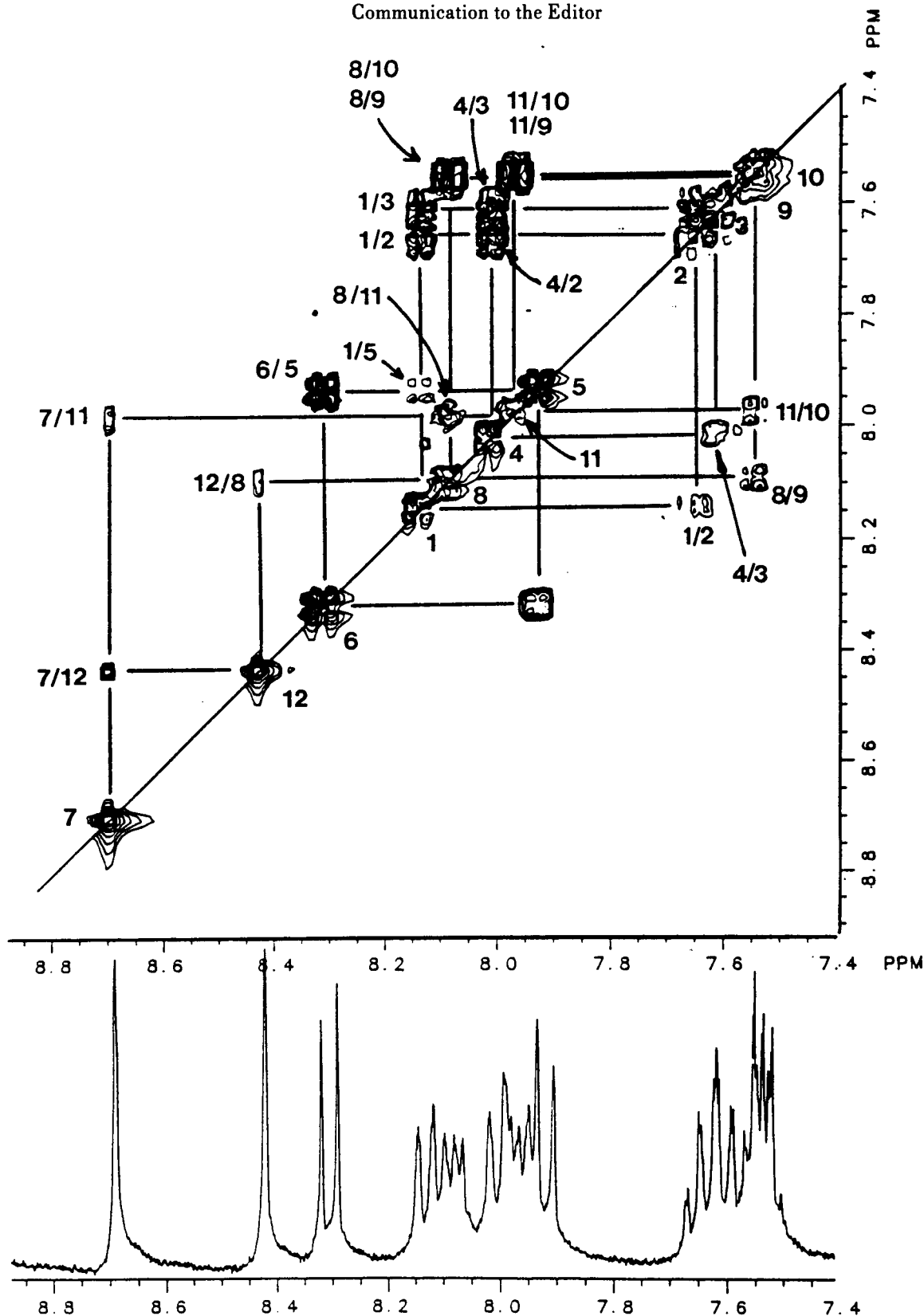


Figure 1. COSY spectrum of **1** recorded in deuteriochloroform at an observation frequency of 30.042 MHz, 30°. The data were taken as 233 × 512 points. The data matrix was zero filled to 256 × 512 points and processed first using sinusoidal multiplication prior to both Fourier transformations (shown above diagonal) and subsequently using a 2.5 Hz Gaussian multiplication prior to both Fourier transformations to eliminate all but the large vicinal couplings from the data matrix (shown below diagonal). Responses in the data matrix are labeled using the format downfield/upfield. The advantages of this type presentation, namely allowing an immediate comparison between the two types of data processing, should be obvious.

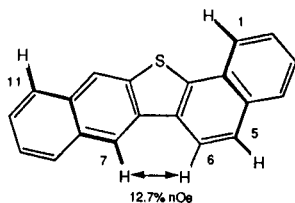


Figure 2. Two of the five bond epi-zig-zag couplings pathways are shown as is the location of the 12.7% NOE observed between H6 and H7. The remaining epi-zig-zag pathway correlating H8 and H12 is omitted for clarity.

Given the identity of H1, we next must differentiate H2 from H3. Quite simply, this was done using the suggestion of Bax and co-workers [4]. Reprocessing the COSY data matrix using a 2.5 Hz Gaussian multiplication prior to both Fourier transformations eliminated the much weaker meta and long range coupling responses, leaving only the response correlating H1 with the upfield resonance of the pair centered at 7.63 ppm. Hence, H2 resonates at 7.59 ppm, H3 at 7.65 ppm. Finally, H4 is assigned as the proton resonating at 8.04 ppm. To emphasize the usefulness of this particular approach, we have shown the COSY spectrum in Figure 1 in a somewhat unorthodox fashion. What we did was to display the ordinary spectrum below the main diagonal axis and the Gaussian-broadened presentation above the diagonal. This particular presentation serves to accentuate the differences between the two types

of data processing.

Returning, finally, to the original proton nmr chemical shift data reported by Castle and co-workers [1], all of the chemical shift information reported was correct and consistent with this study with the sole exception of the multiplet reportedly resonating in the range 7.08-7.48 ppm. Rather than the range of chemical shifts originally reported, it is quite clear that this multiplet should have been reported to resonate at 7.48-7.68 ppm. Regardless of the source of the original error, the proton nmr spectrum of **1** has now been totally and unequivocally assigned.

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