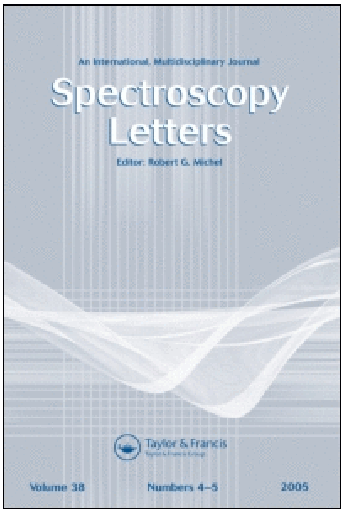

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A Reinvestigatton of the ^{13}C-NMR Chemical Shift Assignments of Fluoranthene

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A REINVESTIGATION OF THE ^{13}C-NMR CHEMICAL SHIFT ASSIGNMENTS OF FLUORANTHENE

Key Words: two-dimensional nmr; carbon-carbon double quantum coherence; fluoranthene

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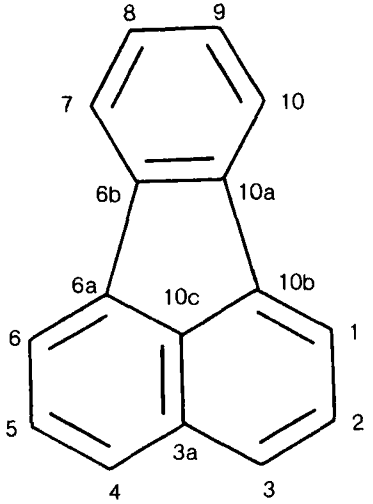
ABSTRACT: Disparities in the protonated carbon NMR chemical shift assignments of the polynuclear aromatic molecule, fluoranthene, have been noted. Using two-dimensional ^{13}C-^{13}C double quantum coherence, the ^{13}C-NMR chemical shift assignments were reinvestigated and a set of unequivocal assignments obtained.

INTRODUCTION

While carrying out investigations of various nitrofluoranthenes,[2] we noted descrepancies in the ^{13}C-NMR chemical shift assignments which have been reported for the parent fluoranthene(**1**) system.[3,4] Before directing our attention to the assignment of any of the mononitrofluoranthene analogs, which was to be undertaken using long range heteronuclear chemical shift



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correlation, we felt it necessary to resolve the disparity in the assignments for the parent fluoranthene ring system. An unequivocal set of assignments derived using $^{13}C-^{13}C$ double quantum coherence are presented and discussed in this paper.

RESULTS AND DISCUSSION

Since fluoranthene is readily available and reasonably soluble in common deuterated solvents, the simplest way to establish unequivocal ^{13}C resonance assignments is through the two-dimensional $^{13}C-^{13}C$ double quantum INADEQUATE experiment.[5] In previous studies we have used the autocorrelated pulse sequence of Turner[6,7] coupled with a 135° read pulse as suggested by Mareci and Freeman[8] to assign the ^{13}C-NMR spectra of a series of complex helical polynuclear heteroaromatics.[9-12] Improved sensitivity can, however, be had by returning to a single evolution period.[13] This was done to compensate for the slight losses incurred by employing the double selection pulse sequence proposed by

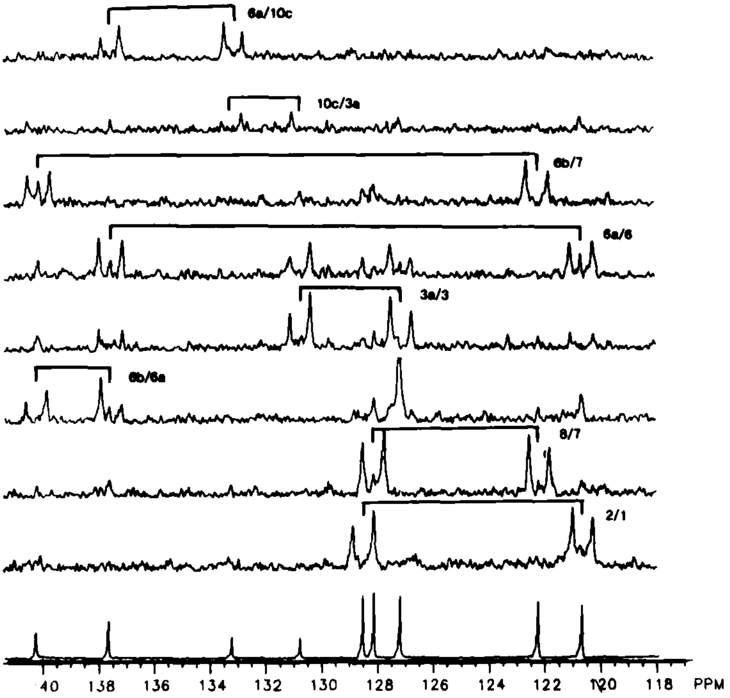

FIG. 1. Traces obtained from a $^{13}C-^{13}C$ double quantum INADEQUATE experimental study of fluoranthene (**1**). Of all possible connectivities, only those between C2 and C3 and between C8 and C9 could not be observed. The broadening in the peaks is caused by the presence of $Cr(acac)_3$.

Lallemand and co-workers[14] to obtain better discrimination between the coherence transfer echo and the antiecho. Thus, the pulse sequence used contained a 135° pulse as the final pulse of the excitation interval and a 135° read pulse following the evolution period.

Individual slices showing eight of the ten possible $^{13}C-^{13}C$ connectivities of fluoranthene (**1**) are shown in FIG. 1. From these data, it was possible to ascertain that the assignments for **1** reported by Ernst[4] were indeed correct as shown on the structure. Only the connectivities between C2 and C3 and C8 and C9 were not observed. The former could not be seen probably because this pair of resonances is more AB and AX in character and the latter, of course, because of the equivalence of C8 and C9.

EXPERIMENTAL

The two-dimensional $^{13}C-^{13}C$ double quantum INADEQUATE spectrum was acquired overnight on a ca. 2M solution of fluoranthene in deuterochloroform at 333°K as 40 x 2K complex points with 1K acquisitions/t_1 increment using a Nicolet NT-300 spectrometer operating at 75.459 MHz for ^{13}C observation. The sample was doped with $Cr(acac)_3$ to afford quaternary carbon relaxation times in the range of 700 msec allowing a 1.5 sec recycle time. The fixed delays in the excitation interval, t, were set to 5.0 msec, corresponding to an assumed 50 Hz $^{13}C-^{13}C$ coupling constant. The evolution period, t_1, was incremented as a function of the dwell time in F_2. The parameter selection causes intentional folding of the double quantum frequency domain but provides correspondingly better digital resolution. The data were processed with a 5 Hz exponential multiplication prior to the first Fourier transformation and a 1 Hz exponential multiplication after zero-filling to 128 points prior to the second transformation.

Values of the chemical shifts obtained are as follows and, except for solvent effects deriving from both the high concentration of fluoranthene and the presence of $Cr(acac)_3$, agree quite closely with those obtained by Ernst:[4] C1(C6) = 120.71; C2(C5) = 128.55; C3(C4) = 127.232; C6a(C10b) = 137.83; C6b(C10a) = 140.44; C7(C10) = 122.31; C8(C9) = 128.17; C3a = 130.91; C10c = 133.40 ppm. Shifts are defined relative to the ^{13}C shift of deuterochlorform defined as 77.00 ppm.

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