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Complete ^{1}H and ^{13}C NMR Assignment of Complex Polycyclic Aromatic Hydrocarbons

Ad Bax,*† James A. Ferretti,‡ Nashaat Nashed,§ and Donald M. Jerina§

Laboratory of Chemical Physics and Laboratory of Bioorganic Chemistry, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, and Laboratory of Chemistry, National Heart, Lung and Blood Institute, National Institutes of Health, Bethesda, Maryland 20205

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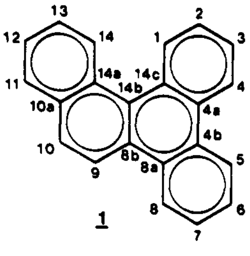
A general procedure for the complete assignment of ^{1}H and ^{13}C NMR spectra of polycyclic hydrocarbons is presented. It is shown that well-accepted two-dimensional NMR techniques (homo- and heteronuclear shift correlation) in combination with a recently developed one-dimensional NMR experiment for the determination of long-range heteronuclear connectivity provide sufficient information for complete and unambiguous ^{1}H and ^{13}C assignment of complex organic molecules. The procedure is illustrated for benzo[c]phenanthrene and its 5-bromo derivative, chrysene, and two benzochrysenes.

Polycyclic aromatic hydrocarbons are of interest both because of their chemistry[1,2] and their carcinogenic activity.[3,4] They have been studied extensively by both ^{1}H and ^{13}C NMR. Assignment of the ^{1}H spectrum of such compounds has mainly relied on double-resonance experiments, interpretation of ring current shifts, and on deuterium substitution. ^{13}C assignments most commonly were based on coherent proton decoupling experiments and on observation of ^{2}H isotope shift effects.[5] Complete spectral assignment of more complicated polycyclic aromatic hydrocarbons, using these methods, is difficult since ^{1}H resonances often overlap, even at the highest magnetic fields available, and also because of the similarity in coupling networks at different parts of the molecule. Consider, for example, benzo[*g*]chrysene (1). Protons H1–H4, H5–H8, and H11–H14 form very similar proton subsystems, showing strong overlap and non-first-order effects in spectra recorded at 500 MHz (top trace in Figure 1). Very small four- or five-bond couplings could, at least in principle, be used for linking these subsystems together, but such an approach is often ambiguous. Proton NOE effects are difficult to observe because of the spectral complexity and are therefore of limited use for spectral assignment. We propose the use of a new one-dimensional NMR technique[6] that relies on the three-bond heteronuclear coupling, $^3J_{CH}$. Additionally, standard experiments are used for obtaining ^{1}H–^{1}H and ^{1}H–^{13}C two-dimensional (2D) chemical shift correlation spectra.[7-12] A number of aromatic hydrocarbons have been studied with these methods, but for illustrative purposes the procedure will first be outlined in detail for benzo[*g*]chrysene.



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Results and Discussion

NMR Analysis of Benzo[*g*]chrysene. The first steps in the NMR analysis consist of recording the ^{1}H–^{1}H COSY

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† Laboratory of Chemical Physics.

‡ Laboratory of Chemistry.

§ Laboratory of Bioorganic Chemistry.

(1) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964; Vol. 1, 2.

(2) Boyd, D. R.; Jerina, D. M. In "Small Ring Heterocycles"; Hassner, A., Ed.; Wiley: New York, 1985; Vol. 42, part 3, pp 197–282.

(3) Dipple, A. In "Chemical Carcinogens"; Searle, C. E., Ed.; American Chemical Society: Washington, DC, 1976; ACS Monogr. No. 173, p 245.

(4) Nordqvist, M.; Thakker, D. R.; Yagi, H.; Lehr, R. E.; Wood, A. W.; Levin, W.; Conney, A. H.; and Jerina, D. M. In "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 329–357.

(5) Hansen, P. E. *Org. Magn. Reson.* **1979**, *12*, 109.

(6) Bax, A., *J. Magn. Reson.* **1984**, *57*, 314.

(7) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(8) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.

(9) Nagayama, K.; Kumar, A.; Wuthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.

(10) Bax, A. "Two-Dimensional Magnetic Resonance in Liquids"; Reidel: Boston, 1982; Chapter 2.

(11) Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.

(12) Bax, A.; Morris, G. A.; *J. Magn. Reson.* **1981**, *42*, 501.

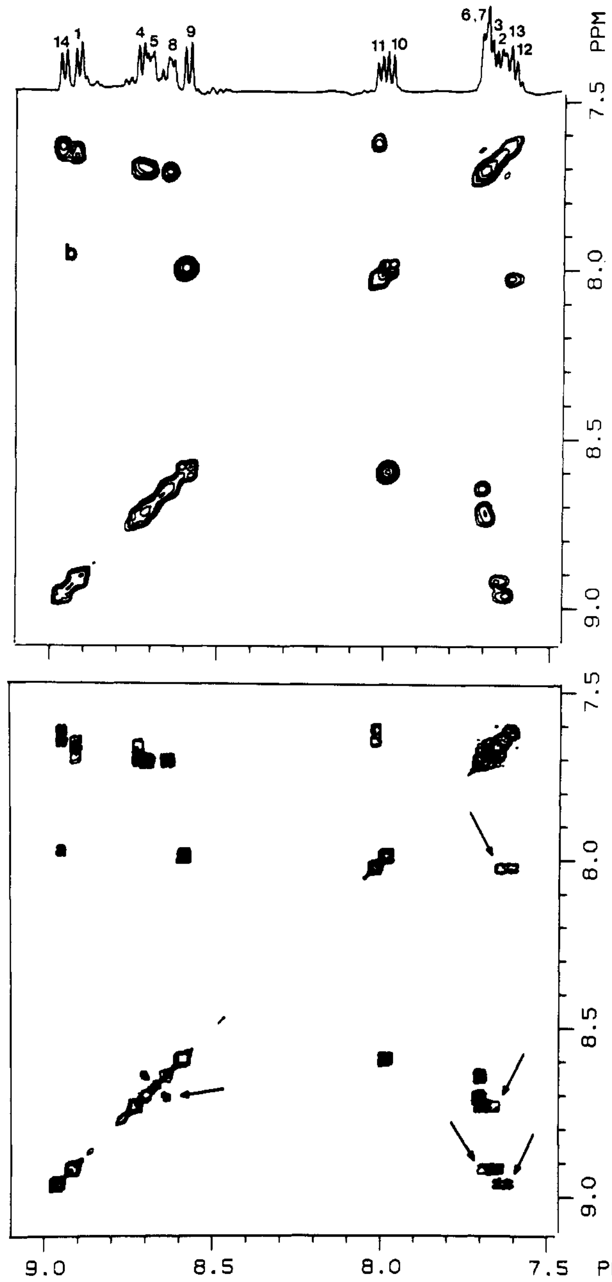

Figure 1. Homonuclear correlated (COSY) spectra of benzo[*g*]chrysene. The bottom spectrum (a) is a regular COSY spectrum obtained by using a sine bell filtering function. Cross peaks due to four-bond couplings are indicated by arrows. The top spectrum (b) is a COSY spectrum for which the long-range cross peaks have been removed by using a sine bell and additionally a 10-Hz Gaussian line broadening function in both dimensions. Both spectra are obtained from the same set of acquired data.

spectrum[7-10] (Figure 1) and a ^{1}H-^{13}C chemical shift correlation spectrum[10-13] (Figure 2). The data obtained with the COSY experiment are processed in two different ways; first, to show cross peaks for both large and small homonuclear couplings (Figure 1a) and then with a strong filtering function (see Experimental Section) to eliminate all cross peaks due to four- and five-bond couplings. Protons of H1 and H14 (8.91 and 8.95 ppm) are easily identified on the basis of their low-field chemical shift due to edge-deshielding of these so-called "bay-region" and "fjord-region" hydrogens[14] and relatively short T_1 value (due to steric interaction). However, which doublet corresponds

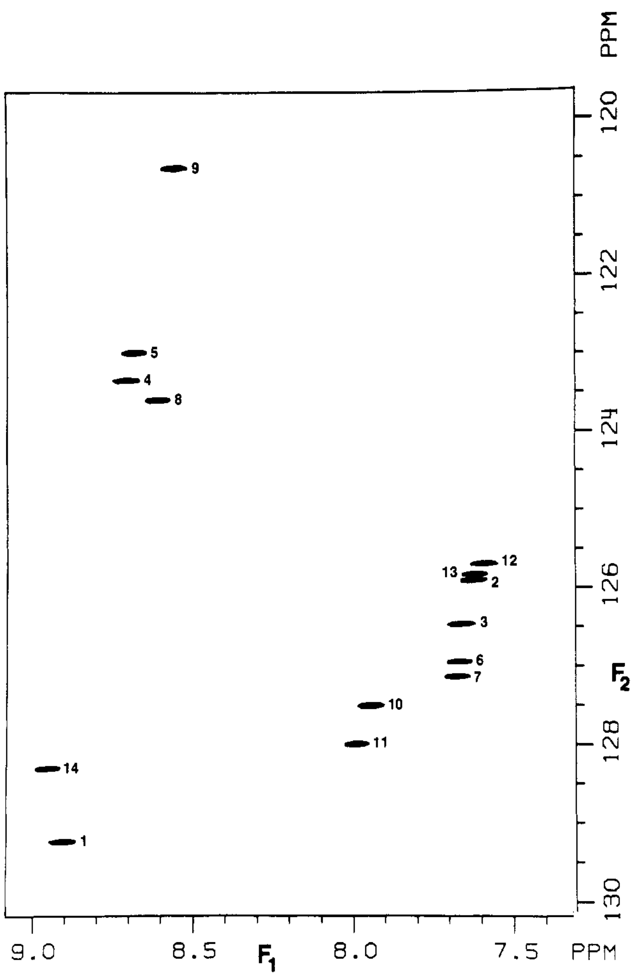

Figure 2. ^{1}H-^{13}C chemical shift correlation spectrum of benzo[*g*]chrysene, presented in the absolute value mode. The F_1 coordinate of a resonance in the 2D spectrum represents a ^{1}H frequency, and the corresponding F_2 coordinate is the resonance frequency of its directly bonded ^{13}C nucleus.

to H1 and which one to H14 cannot be seen from the spectrum. Resonances from the K-region, H9 and H10 (7.98 and 8.58 ppm), can easily be identified from Figure 1 because they form an isolated AX spin pair, but again, it is not immediately clear which one is which. Other connectivity information present in the COSY spectrum in Figure 1 will be used later to assign the remaining resonances. The 2D heteronuclear shift correlation spectrum of benzo[*g*]chrysene (Figure 2) provides a direct way of correlating proton and ^{13}C chemical shifts. However, this spectrum alone does not give any crucial assignment information. As will be illustrated, it is the use of a third method, the so-called "INAPT" experiment (insensitive nuclei assigned by polarization transfer), that provides the crucial assignment information. This technique, described in more detail in the Experimental Section, provides long-range heteronuclear connectivity information. In this experiment, a set of low-intensity radiofrequency pulses are applied to a preselected proton multiplet. This pulse sequence can transfer proton magnetization to any ^{13}C nucleus that has a significant long-range scalar interaction with this proton. The major advantage of this technique over other methods is that this long-range connectivity is obtained with high sensitivity, on the order of the regular ^{1}H decoupled ^{13}C spectrum. The INAPT experiment is relatively easy to set up. For non-proton-bearing carbons, the technique often gives superior sensitivity compared to a regular spectrum. The selectivity in the ^{1}H spectrum that is obtainable with this experiment is better than 10

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(13) Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* **1977**, *28*, 471.
(14) Bartle, K. D.; Jones, D. W. *Adv. Org. Chem.* **1972**, *8*, 317.

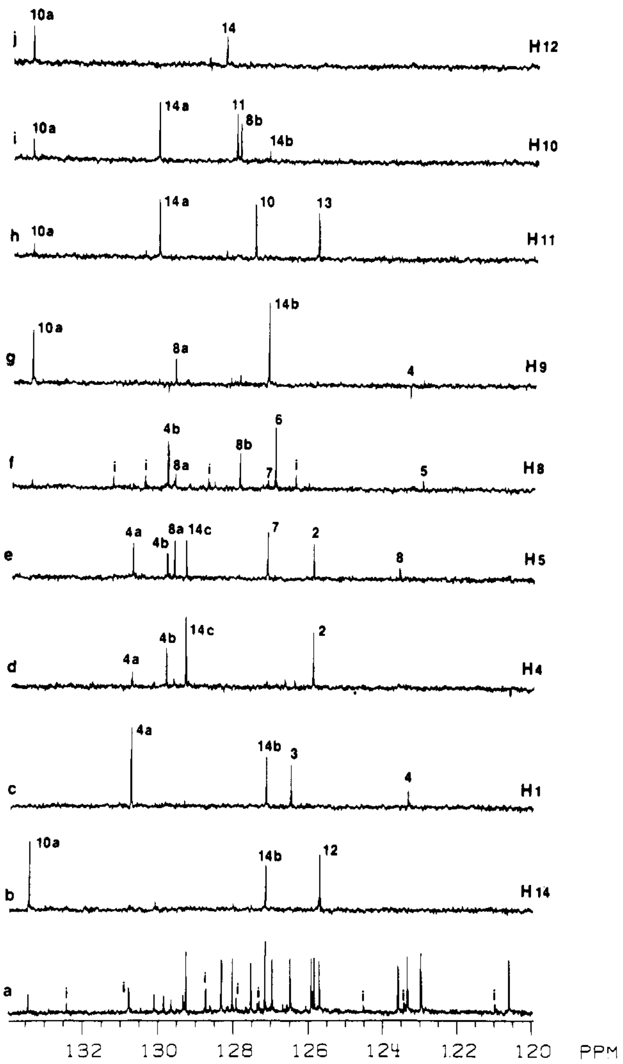

Figure 3. Spectra of benzo[*g*]chrysene. (a) Regular proton-decoupled ^{13}C spectrum obtained from 100 scans. (b–j) INAPT spectra obtained by transfer from H14, H1, H4, H5, H8, H9, H11, H10, and H12. Each spectrum results from 200 scans (15 min). Resonances due to impurities in the sample are indicated by "i".

Hz. Figure 3a shows the regular ^{1}H decoupled ^{13}C spectrum obtained from 100 scans. Figure 3b–j shows the spectra obtained with the INAPT transfers (200 scans each) from the various resolvable proton multiplets. A brief discussion of the experimental results follows to outline the assignment procedure. Advantage is taken of the fact that in polycyclic aromatic hydrocarbons $^{3}J_{CH}$ is always on the order of 5 Hz, whereas both $^{2}J_{CH}$ and $^{4}J_{CH}$ are significantly smaller.[5] The experiment is optimized for transfer through 7-Hz couplings. Since the transfer efficiency then depends on $\sin^2 (\pi J/14)$, low-intensity ^{13}C resonances can be expected if transfer occurs via a small coupling constant ($J < 3$ Hz).

Since C14b is the only carbon that should have a significant long-range coupling with both H1 and H14, this resonance is assigned by comparison of Figure 3b,c. From the other two assigned protons, H9 and H10, H9 is also expected to have a long-range coupling with C14b. Spectrum 3g shows the transfer from H9 to C14b and therefore positively identifies H9. Carbon C10a should also be coupled to H9 and to H14. Comparison of Figure 3b,g then identifies C10a and also distinguishes H14 from H1. The only unassigned resonance left in Figure 3b then must be C12. Similarly, on the basis of transfer from H1 (Figure 3c) the ring-junction ^{13}C resonance at 130.714 ppm must be assigned to 4a, and the hydrogen-bearing carbon resonance at 126.441 ppm must be assigned to C3. The low-intensity resonance in Figure 3c at 123.294 ppm is due to the presence of a significant four-bond long-range coupling (~2 Hz) between H1 and C4. Other resonances that can immediately be identified on the basis of transfer from H9 and H10 (Figure 3g,i) are C8a, C8b, C11, and C14a. Spectrum 3e shows resonance C4a and must therefore be transferred from H5. From the same spectrum we then can identify C7 (127.12 ppm), and assignment of C8a is confirmed. Assignments of C1, C14, C9, C10, and C5 now follow directly from the chemical shift correlation spectrum (Figure 2). Also, H4 is assigned by correlation with C4 (Figure 2), and transfer from this proton (Figure 3d) shows C2 and ring-junction carbons C4b and C14c. At this point it is not clear which resonance is C14c and which is C4b. Hydrogen H8 is the only remaining low-field proton (8.63 ppm), and transfer from this proton (Figure 3f) positively identifies C4b, assigns C6, and confirms assignment of C8b. The only remaining unassigned carbon resonance is C13, whose assignment is confirmed by a combination of Figure 1 (H14–H13 connectivity) and Figure 2 (H13–C13). Finally, transfer from the highest field proton, H12 (Figure 3j) confirms the assignment of C10a and C14.

Using the procedure outlined above gives a large amount of assignment information which then can be verified from a combination of the ^{1}H–^{1}H and ^{1}H–^{13}C 2D shift correlation spectra. In cases where the proton spectrum can be assigned from the COSY spectrum alone, it will be easier to work in the reversed order, i.e., first assignment of the proton spectrum on the basis of the COSY spectrum, followed by assignment of the hydrogen-bearing carbons from the heteronuclear shift correlation spectrum and finally use of the INAPT experiment for assignment of the ring-junction carbons and verification of other possibly ambiguous assignments. Complete assignment of all resonances then becomes unequivocal and does not require any ambiguous comparison with chemical shift information of related compounds or interpretation of ring-current effects.

The high selectivity of the INAPT experiment in the ^{1}H spectrum is illustrated by the spectra obtained from protons H4, H5, H8, and H9, each of which contains little amounts of transfer from neighboring protons even though these protons all resonate within 0.16 ppm. The only significant amount of spurious transfer from a neighboring proton occurs in spectrum 3e, where resonances C4b, C14c, and C2 are due to transfer from H4, which resonates downfield by only 0.025 ppm from H5.

Care has to be taken in the interpretation of low-intensity ^{13}C resonances in INAPT spectra, since such signals can occur for hydrogen-bearing ^{13}C nuclei for which the decoupler was positioned between 5 and 10 Hz from the ^{13}C satellite of the corresponding proton. In such a case, the resonance can result from spurious selective population transfer effects via single-bond couplings, $^{1}J_{CH}$.[15,16] An example is the negative resonance in Figure 3g for C4. This signal occurs because H9 resonates at 75 Hz ($\sim J_{CH}/2$) below the frequency due to H4. When necessary for interpretation, this type of spurious resonance can be positively identified by repeating the experiment with a delay time, Δ_2, that is 6 ms longer: if the transfer is spurious, the resonance in the second spectrum will be of opposite phase.

Assignment of Benzo[*c*]chrysene. Benzo[*c*]chrysene provides a somewhat more challenging assignment problem

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(15) Pachler, K. G. R.; Wessels, P. L. *J. Magn. Reson.* **1973**, *12*, 337.

(16) Sorensen, S.; Hansen, R. S.; Jakobsen, H. J. *J. Magn. Reson.* **1974**, *14*, 243.

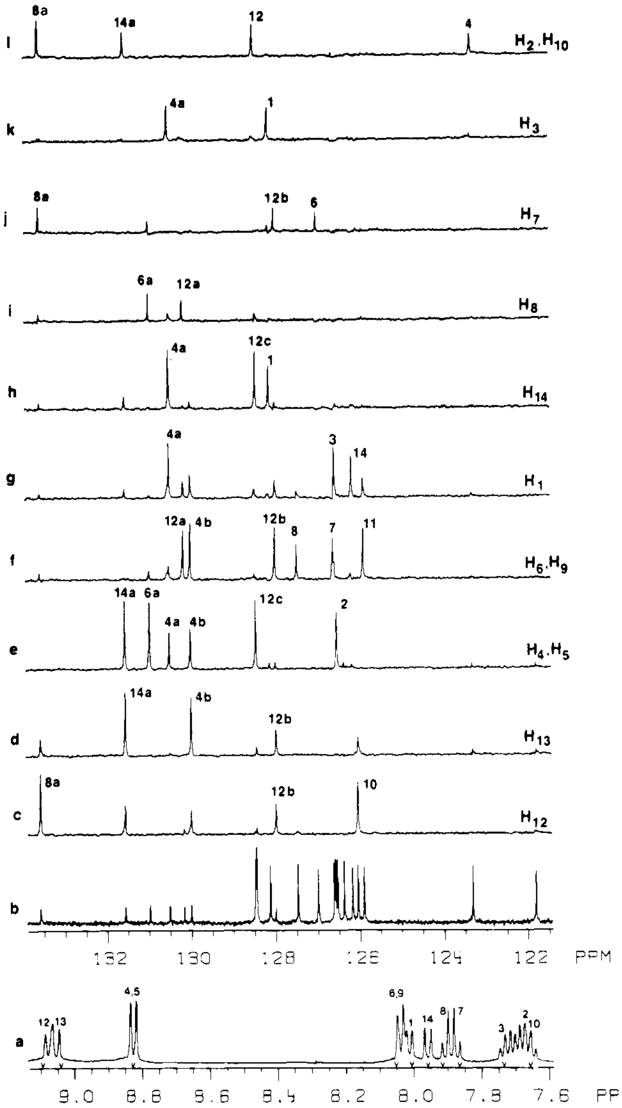


Figure 4. Spectra of benzo[c]chrysene. (a) ^{1}H spectrum, (b) ^{13}C spectrum and (c–l) INAPT spectra obtained by positioning the decoupler at positions indicated on the axis of the ^{1}H spectrum. All resonances due to three-bond transfer from the selected proton are assigned in spectra c–l.

Table I. ^{13}C and ^{1}H Chemical Shift Assignments of Benzo[*g*]chrysene

no.	^{13}C shift, ppm	^{1}H shift, ppm	no.	^{13}C shift, ppm	^{1}H shift, ppm
1	129.215	8.905	8b	127.879	
2	125.875	7.635	9	120.560	8.58
3	126.441	7.65	10	127.487	7.97
4	123.294	8.72	10a	133.397	
4a	130.712		11	127.982	8.005
4b	129.803		12	125.663	7.60
5	122.934	8.69	13	125.800	7.63
6	126.925	7.68	14	128.276	8.95
7	127.115	7.685	14a	130.054	
8	123.548	8.625	14b	127.115	
8a	129.607		14c	129.288	

Table II. ^{13}C and ^{1}H Chemical Shifts of Chrysene

no.	^{13}C shift, ppm	^{1}H shift, ppm	no.	^{13}C shift, ppm	^{1}H shift, ppm
1, 7	128.526	8.00	4b, 10b	128.184	
2, 8	126.336	7.64	5, 11	121.185	8.73
3, 9	126.642	7.72	6, 12	127.309	8.02
4, 10	123.120	8.79	6a, 12a	132.139	
4a, 10a	130.524				

Table III. ^{13}C and ^{1}H Chemical Shifts in Benzo[*c*]phenanthrene

no.	^{13}C shift, ppm	^{1}H shift, ppm	no.	^{13}C shift, ppm	^{1}H shift, ppm
1, 12	127.881	9.14	5, 8	127.427	7.90
2, 11	126.083	7.68	6, 7	126.803	7.83
3, 10	125.808	7.62	6a	130.947	
4, 9	128.502	8.02	12a, 12c	130.289	
4a, 8a	133.455		12b	127.308	

Table IV. ^{13}C and ^{1}H Chemical Shifts of 5-Bromobenzo[*c*]phenanthrene

no.	^{13}C shift, ppm	^{1}H shift, ppm	no.	^{13}C shift, ppm	^{1}H shift, ppm
1	128.220	9.08	8	128.200	7.90
2	126.800	7.72	8a	133.521	
3	126.888	7.72	9	128.618	8.005
4	127.689	8.47	10	126.163	7.63
4a	131.409		11	126.480	7.675
5	121.752		12	127.934	9.025
6	130.378	8.17	12a	129.901	
6a	131.042		12b	127.041	
7	125.689	7.72	12c	131.372	

because of severe spectral overlap in the ^{1}H NMR spectrum (Figure 4a). However, the spectral assignment proceeds along identical lines as described for benzo[*g*]chrysene and leads to unambiguous results. A brief outline is presented below.

We start again with the assumption that H12 and H13 resonate most downfield (fjord region) followed by H4 and H5 (bay region). If this assumption would be wrong, it would be rapidly detected since the INAPT spectra would give contradictory results. Ten INAPT spectra (Figure 4c–l) were recorded with the decoupler frequency positioned as indicated on the axis of the ^{1}H spectrum (Figure 4a). Figure 4c shows that the most downfield proton has three-bond connectivity to a hydrogen-bearing carbon (C10) and is therefore assigned to H12. Since the resonances of H12 and H13 partially overlap, there is also some spurious transfer from H13 in the spectrum where transfer is optimized for H12 and vice versa, but these spurious transfers are of lower intensity. One resonance shows identical intensity in the spectra in Figure 4c,d, and this resonance is therefore assigned to C12b. C8a is then also assigned on the basis of Figure 4c. Since C10 has now been identified, H10 is found to be the most upfield ^{1}H resonance by inspection of the heteronuclear shift correlation spectrum (Figure 5). From the COSY spectrum (not shown), one then identifies H9 (8.03 ppm), H14 (7.95 ppm), and H6, which overlaps with H9. INAPT transfer from H6 and H9 simultaneously (Figure 4f) shows connectivity to C4b and not to C14a and therefore identifies these two resonances by comparison of spectra 4f and 4d. Transfer from H14 shows only one hydrogen-bearing carbon, which is then assigned to C1. Inspection of Figure 5 then identifies H1, and INAPT transfer from H1 (Figure 4g) yields one ring-junction carbon (C12c) and two protonated carbons, of which one already has been assigned to C14 (from Figure 5) and therefore the other one must be C3. This assignment is confirmed by identifying H3 (Figure 5) and INAPT transfer from H3, which yields C4a and C1 (Figure 4k). All remaining resonances are straightforwardly assigned in a similar fashion.

Other Aromatic Hydrocarbons. Several polycyclic aromatic hydrocarbons were studied using the procedure outlined above. The complete ^{1}H and ^{13}C assignment of benzo[*a*]pyrene was determined and was found to be in full agreement with recently published results obtained by Unkefer et al.,[17] who had used specifically ^{13}C-labeled

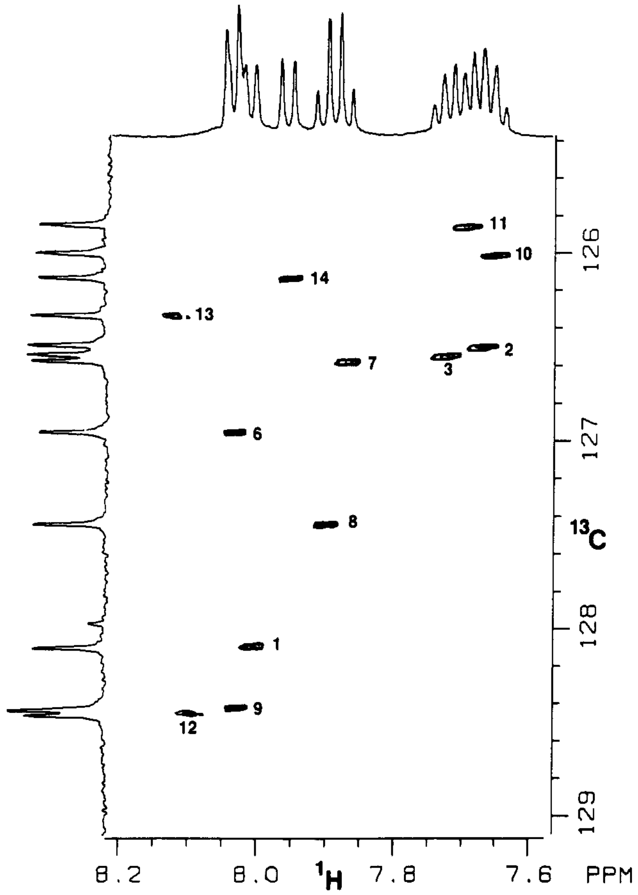
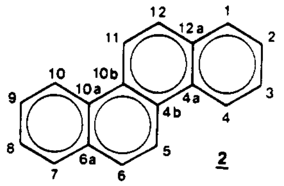


Figure 5. Most crowded region of the absorption mode heteronuclear shift correlation spectrum of benzo[c]chrysene. The corresponding one-dimensional spectra are shown along the F_1 (^{1}H) and F_2 (^{13}C) axis. In the 2D spectrum H12 and H13 have been folded to save data storage space. Since H12 has folded more than H13, H12 corresponds to the most downfield proton multiplet.

Table V. ^{13}C and ^{1}H Chemical Shifts in Benzo[c]chrysene

no.	^{13}C shift, ppm	^{1}H shift, ppm	no.	^{13}C shift, ppm	^{1}H shift, ppm
1	128.099	8.01	8a	133.556	
2	126.506	7.66	9	128.427	8.03
3	126.556	7.72	10	126.017	7.65
4	123.290	8.82	11	125.867	7.70
4a	130.473		12	125.454	9.07
4b	129.968		12a	130.137	
5	121.784	8.82	12b	127.968	
6	126.966	8.03	12c	128.421	
6a	130.945		13	126.347	9.05
7	126.588	7.87	14	126.148	7.95
8	127.450	7.89	14a	131.510	

material prepared synthetically. Complete assignments were also made for chrysene (2), benzo[c]phenanthrene [3], and 5-bromobenzo[c]phenanthrene (4). Assignment of 4 and subsequent conversion to [5-^{2}H]benzo[c]phenanthrene 5,6-oxide has proved extremely valuable in assigning absolute configuration to the 5,6-oxides of the hydrocarbon.[18] ^{1}H and ^{13}C chemical shifts for the various compounds are given in Tables I–V. 1, 4, and 5 have not been previously assigned. The recently reported ^{1}H assignment of chrysene[19] was confirmed. Assignment of the proton[18,20–22] and ^{13}C spectra[23] of 3 is also confirmed, and ambiguities in the assignments of the resonances of hydrogens H5 and H6 and carbons C6a and C12a are removed.



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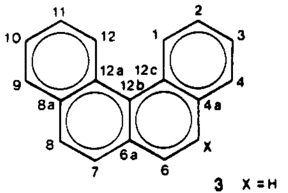
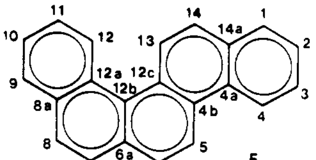


3 X = H

4 X = Br



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Summary

The combination of the new techniques described in this paper provides a direct and unambiguous means for the complete ^{1}H and ^{13}C assignment of complex polycyclic aromatic hydrocarbons and their derivatives. The approach is suitable for structure determination of a wide variety of molecules. The INAPT experiment provides crucial information by identifying long-range ^{13}C–^{1}H connectivity. Both heteroatoms and non-hydrogen-bearing ^{13}C nuclei may be bridged, thereby providing connectivity information not readily accessible by other techniques. As mentioned before, care has to be taken in the interpretation of low-intensity INAPT resonances since they may be due to four-bond transfer or residual SPT effects.[15,16] Use of the INAPT experiment is not limited to aromatic hydrocarbons. It has been used successfully to determine structures and assignment of a number of oligosaccharides and polysaccharides[24] and peptides[25] and is applicable to any type of organic compound. Recently, other approaches based on two-dimensional methods have been proposed for determining the same type of long-range connectivity.[26,27] However, it turns out that the difficulty associated with transfer by means of nonselective ^{1}H pulses through long-range couplings causes the sensitivity of these methods to be much lower than of the INAPT experiment.

Experimental Section

The samples of chrysene (2) and benzo[a]pyrene used in these experiments were obtained commercially. Benzo[c]phenanthrene (3) was prepared from 1,2-dihydrobenzo[c]phenanthrene,[18] and 5-bromobenzo[c]phenanthrene was prepared by direct bromination.[18] Benzo[g]chrysene (1) was the generous gift of D. R. Boyd at the Queens University of Belfast and R. E. Lehr at the University of Oklahoma. Benzo[c]chrysene (5), prepared by a photocyclization route,[28] was the gift of N. Miyata in these laboratories.

All compounds were dissolved in 2.5 mL of ^{2}HCCl$_3$, and spectra were recorded at 25 °C. Sample quantities used are 15 mg of 1, 15 mg of 2, 25 mg of 3, and 30 mg of 4 and 5. All spectra are recorded on a Nicolet 500-MHz NMR spectrometer using 10-mm sample tubes. Chemical shifts are reported in ppm from tetramethylsilane with the center ^{13}C resonance of ^{2}HCCl$_3$ as an internal

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[17] Unkefer, C. J.; London, R. E.; Whaley, T. W.; Daub, G. H. *J. Am. Chem. Soc.* **1983**, *105*, 733.

[18] (a) Sayer, J. M.; van Bladeren, P. J.; Yeh, H. J. C.; Jerina, D. M., manuscript in preparation. (b) Ittah, Y.; Thakker, D. R.; Croisey-Delcey, M.; Ryan, D. E.; Thomas, P. E.; Conney, A. H.; Jerina, D. M. *Chem.-Biol. Interact.* **1983**, *45*, 15.

[19] Jones, A. J.; Teity, T. *Aust. J. Chem.* **1984**, *37*, 561.

[20] Bartle, K. D.; Jones, D. W.; Matthews, R. S. *Tetrahedron* **1969**, *25*, 2704.

[21] Haigh, C. W.; Mallion, R. B. *Mol. Phys.* 1971, *22*, 945.

[22] Copper, M. A.; Manatt, S. L. *J. Am. Chem. Soc.* **1970**, *92*, 4646.

[23] Martin, R. H.; Moriau, J.; Defay, N. *Tetrahedron* **1974**, *30*, 179.

[24] Bax, A.; Egan, W.; Kovacs, P. *J. Carbohydr. Chem.* **1985**, *3*, 593.

[25] Bax, A., unpublished results.

[26] Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

[27] Bauer, C.; Freeman, R.; Wimperis, S. *J. Magn. Reson.* **1984**, *58*, 526.

[28] Dietz, F.; Scholz, M. *Tetrahedron* **1968**, *24*, 6845.

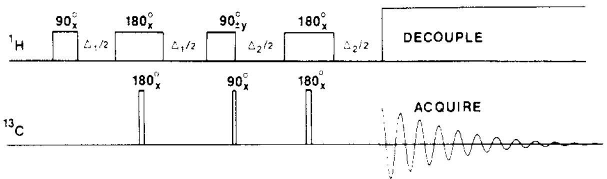

Figure 6. Pulse sequence of the INAPT experiment. The proton pulses in this scheme are soft pulses ($\gamma H_2/2\pi \sim 15$ Hz). The efficiency of polarization transfer via a long-range coupling, J, is proportional to $\sin [\pi J(\Delta_1 + 2\tau_{90})] \sin [\pi J(\Delta_2 + \tau_{90})]$, where τ_{90} is the pulse duration of the soft 90° ^1H pulse.

reference for ^{13}C (77.0 ppm) and with the small amount of residual $^1HCCl_3$ as an internal reference for the proton spectrum (7.24 ppm). Proton spectra were obtained by using the decoupling coil of the broad-band probe for observation. For **2** and **3**, simple selective decoupling experiments were sufficient to establish proton connectivity, and a proton-decoupled version of the selective population transfer experiment[29] was used for assignment of the protonated ^{13}C resonances. For compounds **1**, **4**, and **5** COSY spectra were recorded by using a 256 × 512 data matrix size, and four scans were acquired for each t_1 duration. Total measuring time for a COSY spectrum was approximately 50 min. Two COSY spectra were calculated for each acquired data set; one to show the presence of all couplings, for which a sine bell filtering function was used in both dimensions, and a second spectrum to emphasize cross peaks that are due to large homonuclear couplings only. This latter spectrum is obtained by using a Gaussian line broadening function of 10 Hz, superimposed on the sine bell filtering function. Heteronuclear chemical shift correlation spectra were recorded by using a 64 × 1024 data matrix size and 16 scans for each t_1 value; a measurement time of 1.2 h was required per spectrum. Gaussian line broadening was used in the t_2 dimension to avoid truncation and overenhanced Lorentzian to Gaussian transformation was used in the t_1 dimension to improve spectral resolution in the F_1 dimension[30] before an absolute value calculation was made. The heteronuclear shift correlation spectrum of **5** (Figure 5) was recorded in the absorption mode. This latter presentation is preferable because of higher resolution and sensitivity[31] but does require some operator interaction to phase the 2D spectrum. Both the two-dimensional and the INAPT spectra were recorded on nonspinning samples.

The INAPT sequence[6] is sketched in Figure 6 and is basically a modified version of the well-known refocused INEPT experiment.[32-34] The delays $\Delta_1/2$ and $\Delta_2/2$ were set to 20 and 25 ms, respectively, and the pulse width of the soft 90° ^1H pulse was set to 18 ms. Calibration of this 90° pulse was done by optimizing the INAPT experiment for a sample of 50% v/v 1,2-dihydronaphthalene in deuterochloroform. High-power (2 W) decoupling was used during data acquisition. Each of the INAPT spectra shown in Figures 3 and 4 results from 200 scans, which required approximately 15 min each. Occasionally a shorter value for Δ_2 has to be selected in symmetric molecules. This applies, for example, for transfer from H5 to C6a in benzo[*c*]phenanthrene. Experimentally very little transfer was observed under the conditions described above ($\Delta_2/2 = 25$ ms). This is due to the fact that H5 and H8 have identical chemical shifts and an identical coupling to C6a. In this case the system behaves like a $^{13}CH_2$ group in the regular INEPT experiment, and consequently, $\Delta_2/2$ has to be set to a shorter duration (10 ms) to optimize this transfer of magnetization.

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Registry No. **1**, 196-78-1; **2**, 218-01-9; **3**, 195-19-7; **4**, 89523-51-3; **5**, 194-69-4.

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(29) Sarkar, S. K.; Bax, A. *J. Magn. Reson.* **1985**, *62*, 109.

(30) Bax, A. In "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1984; Vol. 4, Chapter 8.

(31) Bax, A.; Sarkar, S. K. *J. Magn. Reson.* **1984**, *60*, 170.

(32) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

(33) Burrum, D. P.; Ernst, R. R. *J. Magn. Reson.* **1980**, *39*, 163.

(34) Bolton, P. H. *J. Magn. Reson.* **1980**, *41*, 287.

Generation and Trapping of Cyclopropene-3-carboxaldehyde and 2,3-Butadienal in Liquid Furan Photolysis

W. Alan Rendall, Manuel Torres, and Otto P. Strausz*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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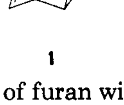
The photolysis of liquid furan at room temperature generated cyclopropene-3-carboxaldehyde and 2,3-butadienal, which were trapped as their Diels–Alder adducts with furan. In each case, both the exo and endo stereoisomers were obtained. The identity of these adducts, and also their stereochemistry, has been determined by MS, IR, and ^1H and ^{13}C NMR.

Until the pioneering work of Srinivasan in 1967, the photochemistry of furan had attracted little attention. In his first study, Srinivasan[1] reported the gas-phase triplet mercury photosensitized decarbonylation of furan. The C_3H_4 fraction formed contained cyclopropene, propyne, and allene.[1] Polymer formation also occurred.[2] A significant pressure dependence was revealed, and a maximum decarbonylation quantum yield of about 0.4 was attained at the lowest furan pressures employed (~5 torr). Under these conditions propyne was the main C_3H_4 isomer. With increasing furan pressure the CO yield decreased and the cyclopropene/propyne ratio increased.[2] At furan pressures of 0.2–1.0 atm two compounds of molecular formula C_7H_8O and a third having molecular formula $C_8H_8O_2$ were isolated. The former were assigned the structures of the exo (**1**) and endo (**2**) Diels–Alder adducts (DAa) of furan with cyclopropene, while the latter was its



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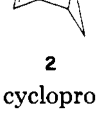

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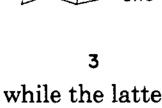

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(1) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 1758.

(2) Srinivasan, R. *Pure Appl. Chem.* **1968**, *16*, 65–74.

0022-3263/85/1950-3034$01.50/0