Determination of Nonprotonated Aromatic Carbon Concentrations in Coals by Single-pulse Excitation 13C NMR

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Determination of Nonprotonated Aromatic Carbon Concentrations in Coals by Single Pulse Excitation ^{13}C NMR

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It is now generally accepted that single pulse excitation (SPE) or Bloch decay measurements are essential for obtaining reliable aromaticity values for coals by solid-state ^{13}C NMR although such measurements are considerably more time consuming than cross-polarization (CP). Just as with normal CP, SPE can be combined with dipolar dephasing (DD) to derive nonprotonated aromatic carbon concentrations. This approach has been applied to four of the Argonne premium coal samples (APCS, N. Dakota lignite, Wyodak, Illinois no. 6, and Pocahontas), two vitrinite concentrates from UK bituminous coals, and an anthracite. The results have been compared with those obtained from CP and, for the APCS, nonprotonated aromatic carbon concentrations derived indirectly from FTIR and ^{1}H CRAMPS. As with the overall aromaticity, SPE invariably gives higher values than CP for nonprotonated aromatic carbon concentrations with differences of up to 10 mol % carbon being found, the greatest being found for the two low-rank coals. However, in some instances, reasonable agreement has been obtained with CP data when long contact times are employed to minimize the discrimination against aromatic carbons. The aliphatic H/C ratios in the range 2.0–2.5 derived from the SPE-DD measurements are much more consistent with other available structural information on coals than the much lower values generally derived from CP, FTIR, and ^{1}H CRAMPS.

Introduction

In view of the well-documented inherent problems with cross-polarization (CP) ^{13}C NMR concerning quantification for coals,[1-5] it is now generally accepted that the more time-consuming single pulse excitation (SPE) or Bloch decay measurements are essential for obtaining reliable aromaticities for coals. Although the rate of magnetization transfer from abundant ^{1}H to dilute ^{13}C spins during CP is slower for nonprotonated aromatic carbons than for protonated carbons, the major problem for coals is undoubtedly the presence of paramagnetic species which cause ^{1}H spins to relax too quickly in the rotating frame during CP, i.e., before polarization transfer to ^{13}C spins has been achieved. In addition, carbons in the vicinity of paramagnetic centers are not observed due to a combination of shielding effects and rapid rotating frame relaxation. However, aromaticity and other structural parameters obtained by CP continue to be reported.[6,7,8] In a recent study,[9] SPE ^{13}C NMR was carried out on the Argonne premium coal samples (APCS) at both a low-

and a high-field strength (25 and 75 MHz, respectively), high speed magic angle spinning (13 kHz) being used to suppress spinning sidebands at the higher field. The aromaticity values measured at low and high field were generally in excellent agreement and were consistently higher than those from CP, the greatest differences being found for the two low-rank coals in the Argonne suite (N. Dakota and Wyodak). These results and other recent measurements by the authors[10,11] on other bituminous coals and oil shales confirm that there is often a clear discrimination against aromatic carbon by CP. The use of tetrakis(trimethylsilyl)silane as an internal standard in the low-field measurements indicated that over 80% of the carbon in coals is typically observed by SPE and this proportion generally increases after acid washing to remove inorganic paramagnetic species.

If CP can strongly discriminate against aromatic carbon in coals, then it is more than likely that nonprotonated aromatic carbon concentrations are also going to be underestimated when dipolar dephasing (DD) is used with CP. SPE can readily be combined with dipolar dephasing (DD) in the same way as CP to derive nonprotonated aromatic carbon concentrations. Probably due to the long accumulation times required for this experiment with normal size rotors, there has only been one other brief report of this approach to date.[12] In this study, the SPE-DD technique has been applied to four of the APCS, namely N. Dakota lignite, Wyodak, Illinois no. 6, and

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(3) Botto, R. E.; Axelson, D. E. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1988, *33* (3), 50–57.

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(8) Cagniant, D.; Gruber, R.; Lacordaire, C.; Legrand, A. P.; Sderi, D.; Sfihi, H.; Tougne, P.; Quinton, M. F.; Bunte, G.; Jasienko, S.; Machinkowdska *Fuel* 1991, *70*, 675–682.

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Table I. Analyses of the UK Coal Samples[a]

| | Cynheidre anthracite | vitrinite concentrates | |
		Oakdale	Snibson
% moisture (as determined)	1.6	1.5	8.9
% ash (dry basis)	1.8	7.8	2.7
		(9.2)	(5.2)
% VM (dry ash free basis)	4.8	22.0	40.8
		(21.0)	(39.5)
% dmmf C	95.2	85.8	79.0
% dmmf H	2.9	4.3	5.0
% dmmf N	1.0	1.5	1.6
% total S (dry basis)	0.63	0.46	<0.3
H/C ratio	0.36	0.61	0.76
		(0.62)	(0.77)
vitrinite reflectance, R_0 % av	3.92	1.32	0.47
		(1.46)	(0.46)
maceral composition			
liptinite		2.0	7.6
vitrinite, % v/v		93.6	87.8
inertinite		4.4	4.6

[a] Numbers in parentheses indicate values for whole coals.

Pocahontas, two vitrinite concentrates from UK bituminous coals and an anthracite to fully cover the rank range. A preliminary account of the measurements on the anthracite has been published.[11] The results are compared with those obtained from corresponding CP experiments and, for the four APCS, nonprotonated aromatic carbon concentrations derived indirectly from FTIR and ¹H CRAMPS.[7]

Experimental Section

Details on the four APCS investigated, including their elemental, proximate, and maceral analyses, have been reported by Vorres,[13] and their analyses are also in the User Handbook, together with a list of the numerous studies in which these samples have already been used. Analytical data for the UK anthracite (Cynheidre, provided by British Coal) and the two hand-picked vitrinite concentrates from UK bituminous coals (Snibson and Oakdale, sampled by British Gas) are listed in Table I.

All the ¹³C NMR measurements were carried out at 25 MHz on a Bruker MSL100 spectrometer with MAS at 4.5–5.0 kHz to give spectra in which the sideband intensities are only *ca.* 3% of the central aromatic bands. Prior to analysis, the coals were vacuum dried and the Pocahontas and Illinois no. 6 samples were partially demineralized by washing with dilute hydrochloric acid. It was possible to pack *ca.* 250 mg of sample into the zirconia rotors. For CP-DD, contact times of 1.5 and 5 ms were used with 10 dephasing periods in the range of 1–200 μs before the first rotational modulation. In order to check that the tuning had remained virtually constant throughout the duration of all the DD experiments, the delays were arranged in a random order. The ¹H decoupling and spin-lock field was *ca.* 60 kHz. ¹³C thermal relaxation times (T_1's) of the coals were determined using the CP pulse sequence devised by Torchia[14] with a contact time of 5 ms in most cases.

A relaxation delay of 20 s was used for the variable delay SPE-DD measurements. However, for the samples with ¹³C T_1's much longer than 5 s, a recycle time of either 60 or 100 s was used in the SPE-DD experiment with, due to the sensitivity limitations, only a single delay of 60 μs. The same dephasing delays in the range 0–250 μs were used as in the corresponding CP experiments, and between 1000 and 3000 scans were accumulated for each delay. A typical SPE-DD experiment using 10 delays with 1000 scans and a 20-s recycle delay takes 56 h. No background signal was evident in the SPE spectra from the Kel-F rotor caps, and for SPE, the 90° ¹³C pulse width was 4.5 μs. All the FIDs were processed using a line broadening factor of either 50 or 100 Hz. The measurement of aromatic and aliphatic peak areas manually
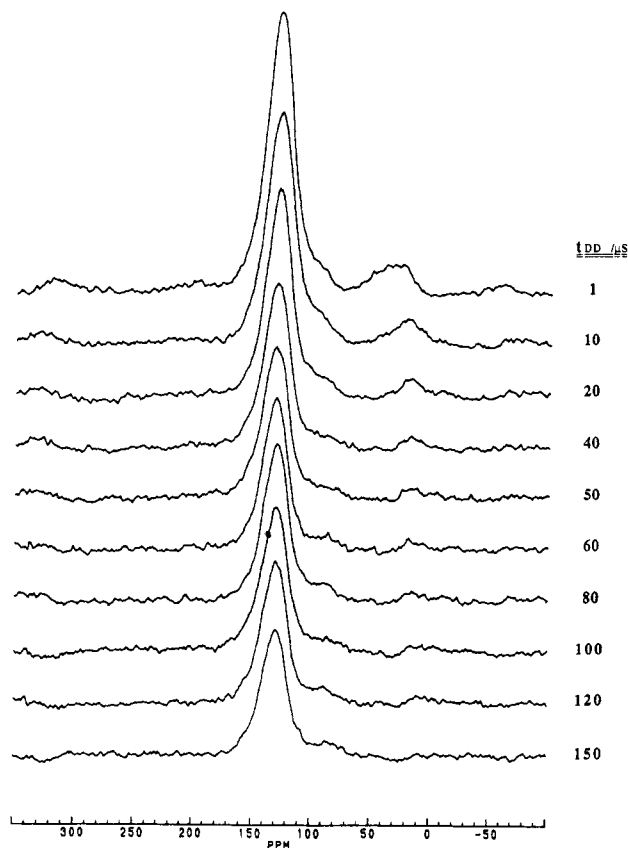
(13) Vorres, K. S. *Energy Fuels* **1990**, *4*, 420–426.
(14) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613–616.

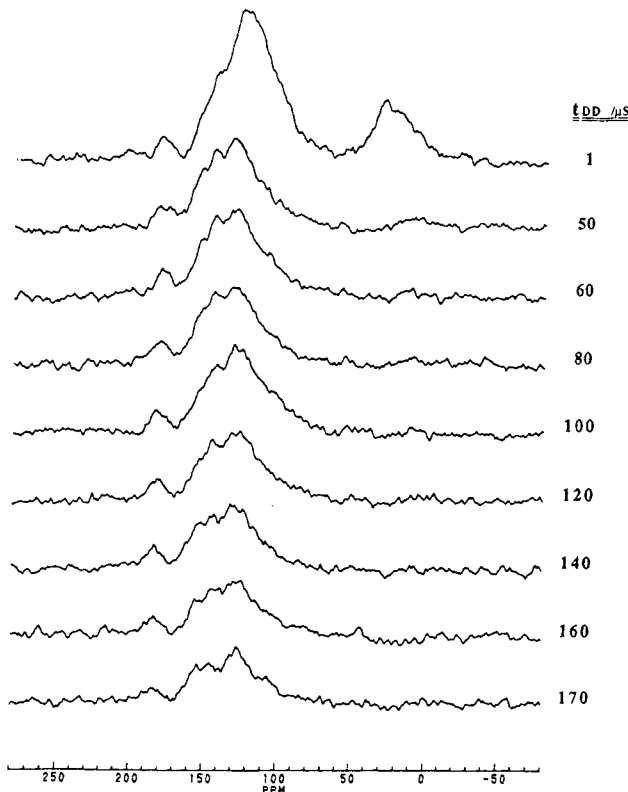**Figure 1.** SPE-DD spectra for the Pocahontas APCS.

Figure 2. SPE-DD spectra for the North Dakota APCS.

was found to be generally more precise than using the integrals generated by the spectrometer software.

Results and Discussion

General Aspects. Figures 1 and 2 show the SPE-DD ¹³C NMR spectra of the Pocahontas and N. Dakota APCS,

Ln Aromatic intensity
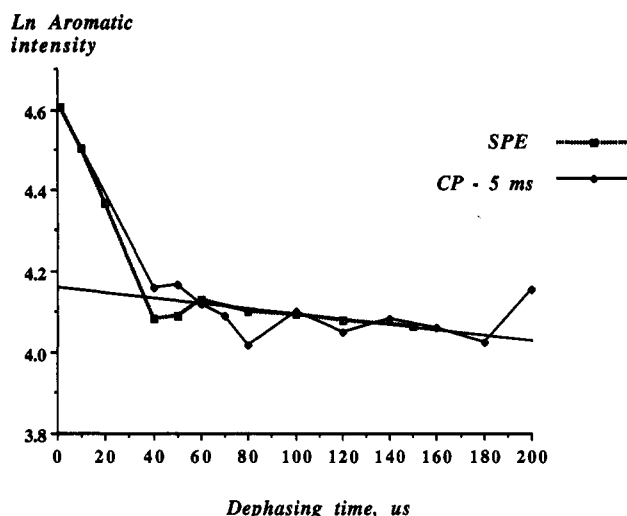

Dephasing time, us

Figure 3. Plot of ln aromatic carbon intensity vs dephasing time from the SPE and CP (5 ms contact time) DD experiments on the Pocahontas APCS, the initial intensity being assigned a value of 100.
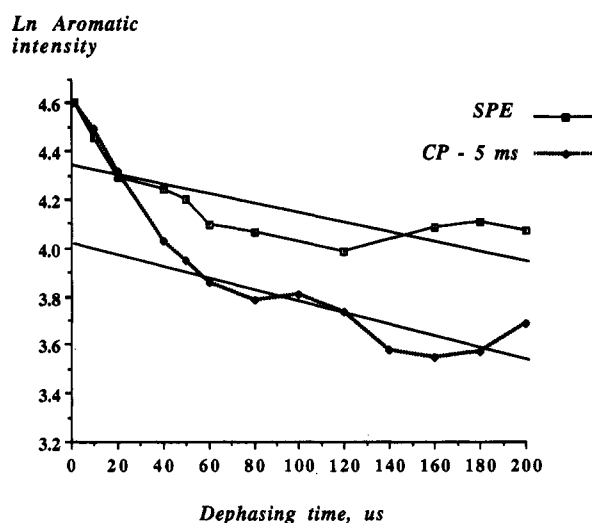
Ln Aromatic intensity

Dephasing time, us

Figure 4. Plot of ln aromatic carbon intensity vs dephasing time from the SPE and CP (5 ms contact time) DD experiments on the Snibson vitrinite concentrate, the initial intensity being assigned a value of 100.

and plots of aromatic carbon intensity (ln scale with initial intensity set at 100) vs dephasing time for the Pocahontas and Snibson samples are presented in Figures 3 and 4 (both CP with a contact time of 5 ms and SPE). Table II lists the aromatic carbon ^{13}C T_1's and the characteristic time constants (T_{DD}) for the nonprotonated aromatic carbons dephasing. Table III lists the nonprotonated aromatic carbon concentrations and hydrogen aromaticities (aromatic hydrogen/total hydrogen) derived from the SPE and CP-DD experiments and, for purposes of comparison, Table IV gives values derived from other recent studies on the four APCS.[6,7]

The signal to noise levels achieved in the SPE-DD spectra (Figures 1 and 2) are considerably better than those obtained by Muntean and Stock in their single experiment on the Pocahontas APCS.[12] As anticipated, the intensities of the nonprotonated aromatic carbon bands are modulated by the MAS-induced heteronuclear dipolar oscillations after the rapid decay of the protonated aromatic carbon intensity during the first 50 μs of the DD experiments (Figures 1 and 2). The amplitudes of the modulations are typically *ca.* 10–15% of the nonprotonated aromatic carbon intensities (Figures 3 and 4). Unless

Table II. SPE-Determined Aromaticities and Relaxation Measurements

coal	aromaticity[a]	^{13}C T_1 for the aromatic carbon[b]	quaternary aromatic T_{DD}, μs
Cynheidre anthracite	0.99	2.8	>500
Pocahontas APCS[c]	0.90	6.1	>500
Oakdale	0.87	21.2	>500
	[0.88]	(11.0)[b]	
Snibson	0.77	8.4	350
Illinois no. 6 APCS[c]	0.75	10.8	340
	[0.75][c]		
Wyodak APCS	0.75 (0.09)	ND[d]	230
N. Dakota APCS	0.76 (0.08)	ND	260

[a] Total sp^2 hybridized carbon; numbers in square brackets indicate values with a 100-s recycle delay in SPE. [b] A contact time of 5 ms was used except for the Oakdale sample where a time of 1 ms was also used; numbers in parentheses indicate the mole fraction of carboxyl/carbonyl carbon. [c] Sample used was partially demineralized with HCl.[9] [d] ND = not determined.

multipoint DD experiments are carried out, this is always going to potentially be a major source of error. Indeed, Table III indicates that the values of the nonprotonated aromatic carbon concentrations obtained with a single dephasing period of 60 μs are significantly lower than those from the fits for the Illinois no. 6, Wyodak, and N. Dakota APCS, the three coals investigated here with relatively short T_{DD}'s (Table II). Good agreement has been obtained for the other coals with T_{DD}'s longer than *ca.* 500 ms.

In the time scale of 50–200 μs used to monitor the nonprotonated aromatic carbon intensities, significant dipolar relaxation occurred only for the two low-rank APCS where good agreement for the relaxation times was obtained between the SPE and CP-DD experiments (Table III). This finding is contrary to data from earlier studies where much shorter dipolar relaxation times have been observed for both anthracite[15] and bituminous coals.[6,12] Such discrepancies can easily arise from a combination of insufficient data points and the tuning of the probe deteriorating through the course of long DD experiments where strictly either the dephasing delays should be randomly arranged or the delays continuously incremented so that only a few scans are accumulated at a time for each delay. For the two low-rank APCS, it was observed that the nonprotonated aromatic carbon bound to oxygen (band at 145–165 ppm, Figure 2) relaxed faster than that bound to other carbons (120–145 ppm, Figure 2) enabling these two carbon types to be determined from the relaxation experiments. However, this was not attempted here due to the limited number of data points beyond 200 μs in the DD experiments and the fact that the time constant listed in Table II is clearly an average value for the oxygen and carbon bound quaternary aromatic carbon.

When a delay considerably shorter than that necessary of 5 times the ^{13}C T_1 to ensure complete thermal relaxation has occurred in SPE, the nonprotonated aromatic carbon concentration, like the overall aromaticity, can be underestimated considerably by SPE. Indeed, the average ^{13}C T_1 values listed in Table II for the vitrinite concentrates and the Illinois no. 6 APCS are considerably greater than 5 s meaning that the delay of 20 s used is not long enough. Examination of the spectra obtained from the ^{13}C T_1 experiments indicated that, as anticipated, the protonated carbons relaxed considerably faster than their nonprotonated counterparts and clearly, the latter have longer T_1's than the average values from the single component

(15) Murphy, P. D.; Cassidy, T. J.; Gerstein, B. C. *Fuel* **1982**, *61*, 1233–1240.

Table III. Quaternary Aromatic Carbon Concentrations and Related Parameters[a]

coal	$C_{qu\ ar}/C_{ar}$			SPE-derived values		
	SPE	CP, 5 ms	CP, 1.5 ms	$C_{qu\ ar}/C$	$(H/C)_{ar}{}^c$	H_{ar}/H^c
Cynheidre anthracite	0.67 (0.64)	0.69 (0.66)	0.50 (0.48)	0.66	0.33	0.94
Pocahontas APCS[d]	0.62 (0.62)	0.59 (0.61)	ND[b]	0.56	0.38	0.59
Oakdale	0.56 (0.50) [0.60]	0.45 (0.43)	ND	0.53[e]	0.40[e]	0.58[e]
Snibson	0.60 (0.60)	0.49 (0.47)	ND	0.46	0.40	0.41
Illinois no. 6 APCS[d]	0.75 (0.62) [0.74]	0.73 (0.60)	ND	0.55	0.26	0.25
Wyodak APCS	0.83 (0.64) [0.78]	ND	0.83[f] (0.63)	0.56	0.17	0.18
N. Dakota APCS	78 (0.57)	ND	ND	0.52	0.22	0.18

[a] Values in parentheses were obtained with a dephasing time of 60 μs; numbers in square brackets were obtained using a recycle delay of 100 s with a dephasing time of 60 μs. [b] ND = not determined. [c] Excluding phenolic and carboxylic OH. [d] Indicates a partially demineralized sample. [e] Values using a quaternary aromatic carbon concentration obtained with the 100-s recycle delay. [f] Value obtained with a contact time of 1.0 ms.

Table IV. Quaternary Aromatic Carbon Concentrations and Related Parameters for the APCS Obtained from Other Studies

APCS	$C_{qu\ ar}/C_{ar}$ (ref 6)	$C_{qu\ ar}/C$ (ref 6[b])	$(H/C)_{ar}{}^a$		H_{ar}/H^a		
			(ref 6)	(ref 7[b,c])	(ref 6[b])	(ref 7, FTIR)	(ref 7, [1]H[c])
Pocahontas	0.62	0.53	0.38	0.37	0.56	0.52	0.56
Illinois no. 6	0.64	0.48	0.36	0.47	0.34	0.36	0.42
Wyodak	0.69	0.38	0.31	0.56	0.20	0.34	0.40
N. Dakota	0.57	0.30	0.43	0.52	0.28	0.40	0.38

[a] Excluding phenolic and carboxylic OH. [b] Using CP-determined aromaticities. [c] From CRAMPS.

fits listed in Table II. Due to only one or two data points being obtained for delays greater than 10 s in the CP-based pulse sequence used,[14] two-component fits have not been attempted here. It is interesting to note that the average [13]C T_1 values derived from Torchia's experiment are a function of the CP conditions used with the nonprotonated carbons being invariably discriminated against with the relatively short contact time of 1 ms (Table II). The differences in the SPE-determined aromaticites between using a recycle time of 20 and 100 s for the Oakdale vitrinite concentrate and Illinois no. 6 APCS are relatively minor bearing in mind that the [13]C T_1's are over 10 s (Tables II and III). However, the measured aromaticity for Snibson of 0.77 may be slightly underestimated using a delay of only 20 s since, for other high-volatile UK bituminous coals with H/C ratios close to 0.75, values in the range 0.79–0.81[10,11] have been obtained.

Anthracite and Low-Volatile Bituminous Coals. Anthracites are ideal for investigating the quantitative reliability of DD as the fact that they are virtually completely aromatic (SPE-determined aromaticity of the Cynheidre sample is >0.99) means that the mole fraction of protonated aromatic carbon is simply the H/C ratio. As anticipated with a relatively short contact time (1.5 ms), the value obtained of 50 mol % nonprotonated aromatic carbon (Table III) was considerably lower than that of 0.67 derived from the H/C ratio (Table I) and the SPE-determined aromaticity. Concentrations of 69 and 67 mol % C in close agreement with this calculated value were obtained from CP with the longer contact time of 5 ms and SPE, respectively. Further, in the normal variable contact time CP experiment on the Cynheidre sample, the buildup in the intensity of the total aromatic signal could readily be fitted to two components in the approximate ratio of 70:30 (T_{CH} values of 4 and 0.02 ms, respectively, with the slower component obviously being

attributable to the bulk of the nonprotonated carbon). Although close agreement has been obtained with SPE in this particular instance using a contact time of 5 ms, the poor agreement for most of the other samples (see following) indicates that long contact time CP does not generally offer a reasonable compromise for quantitative DD measurements, especially in the absence of comprehensive information on relaxation times.

It should be pointed out that the anthracite investigated here has a slightly higher atomic H/C ratio than that investigated by Gerstein and co-workers[15] and this is consistent with the value obtained with a contact time of 1 ms (50%) being lower than that of ca. 65% reported in Gerstein's study with a similar contact period. However, the value reported in this early study appears to be high due to the dipolar relaxation rate for the nonprotonated carbons being somewhat overestimated.

Tounge and Legrande[16] have shown that crystallinity/ordering effects in model polynuclear aromatic compounds, such as naphthalene and anthracene, can modify the dipolar interaction so that some of the nonprotonated aromatic carbon magnetization dephases quickly with time constants similar to those of protonated aromatic carbons. The close agreement between the predicted and SPE-measured nonprotonated aromatic carbon concentration for the Cynheidre sample (Table III) would suggest that such an effect is not operating on a significant scale in anthracites.

As for the anthracite, the nonprotonated aromatic carbon concentrations obtained by CP with a contact time of 5 ms and SPE for the Pocahontas APCS are in close agreement. However, spin counting experiments by both the authors[9] and Muntean and Stock[12] have indicated that only ca. 60% of the carbon is actually observed. The

(16) Tounge, P.; Legrand, A. P. *J. Chim. Phys.* **1992**, *89*, 489–494.

Table V. Aliphatic H/C Ratios Derived from ^{13}C NMR and Other Structural Data

coal	this study (SPE data)	ref 6 (CP data)	ref 7 (CP and CRAMPS)
Pocahontas APCS	2.3	1.6	1.8
Snibson	1.8 (2.0)[a]		
Illinois no. 6 APCS	2.1	1.7	1.4
Wyodak APCS	2.4	1.7	1.3
N. Dakota APCS	2.2	1.5	1.25

[a] Value assuming the aromaticity to be 0.80.

nonprotonated aromatic carbon concentrations close to 60% of the total aromatic carbon (Table III) are *ca.* 5 mol % C lower than that recently reported by Muntean and Stock[12] using SPE-DD. Although the signal to noise levels achieved here for the SPE-DD spectra are considerably better (Figure 1), this small but significant discrepancy is primarily attributed, once again, to the dipolar relaxation rate for the nonprotonated aromatic carbons being overestimated in the earlier study (Figure 3). This probably also explains the close but fortuitous agreement with the value derived from CP with a contact time of 1 ms (62% of the aromatic carbon) reported by Solum et al.[6] (Table IV).

As a check on the self-consistency of both the overall aromaticities and the nonprotonated aromatic carbon concentrations derived for the bituminous coals, their aliphatic H/C ratios have been derived using the following relationship:

$$(H/C)_{overall} = (H/C)_{ali}(1 - f_a) + (H/C)'_{ar}f_a \qquad (i)$$

where f_a is the aromaticity and $(H/C)'_{ar}$ is the aromatic H/C ratio including phenolic hydrogen = $(1 - C'_{np\ ar})/C_{ar}$, $C'_{np\ ar}/C_{ar}$ being the fraction of nonprotonated aromatic carbon corrected for phenols. For the bituminous coal samples, it has been assumed that the phenolic groups account for 60% of the total oxygen consistent with much of the information in the literature.[17,18]

The value of 2.3 obtained for Pocahontas (Table V) is highly consistent with the methyl concentration of between 45 and 50% of the aliphatic carbon (inferring that the aliphatic H/C ratio is close to 2.5) derived from the DD experiments (Figure 5). The CP-derived aromaticity of 0.86[5-7,9] gives a value of only 1.7 which is clearly inconsistent with the high methyl concentration in this high-rank bituminous coal; the estimate of *ca.* 5 mol % C derived from DD (methyl accounting for 45-50% of the aliphatic carbon, Figure 5) and the SPE-determined aromaticity of 0.90 (Table II) is somewhat lower than that of 7% for arylmethyl from RuO$_4$ oxidation.[12]

The Oakdale vitrinite concentrate is of somewhat lower rank than the Pocahontas APCS (aromaticity of 0.88 cf. 0.90, Table II; H/C of 0.61 cf. 0.58) but the concentration of nonprotonated aromatic carbon is similiar (Table III). However, the discrepancy between the values from SPE and CP with the relatively long contact time of 5 ms is large in this case strongly suggesting that a significant amount of the quaternary aromatic carbon is simply not observed by CP. Indeed, the aliphatic H/C ratio of *ca.* 1.0 derived from the CP result (taking the SPE-determined aromaticity of 0.88) is clearly erroneous in relation to that of 2.1 from the SPE data (Table V). In light of the

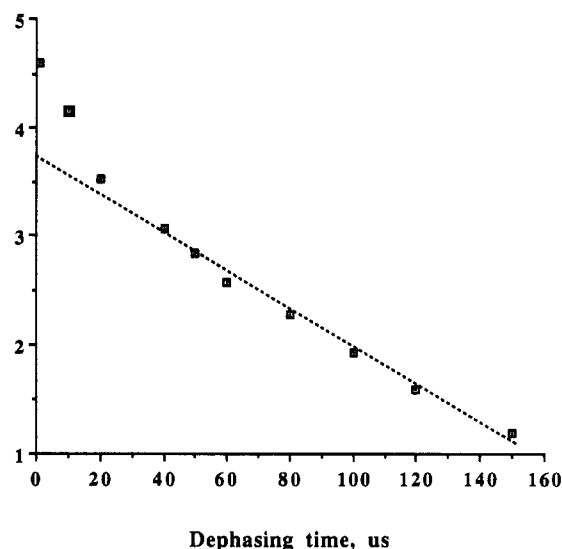**Ln intensity**

Dephasing time, us

Figure 5. Plot of ln aliphatic carbon intensity from the SPE-DD spectra of the Pocahontas APCS, the inital intensity being assigned a value of 100.

relatively high proportion of methyl groups in this low-volatile bituminous coal sample (*ca.* 35% of aliphatic carbon from DD), a value of *ca.* 2.3 would have been anticipated suggesting that the concentration of quaternary aromatic carbon may still be slightly underestimated even with a recycle delay of 100 s (Tables II and III, see above).

High-Volatile Bituminous Coals. For the Illinois no. 6 APCS and the UK vitrinite, Snibson, the SPE-determined nonprotonated aromatic carbon concentrations are higher than their CP counterparts, even when using the longer contact time of 5 ms (Table III). Not surprisingly, the SPE-determined value of 74% of the total aromatic carbon for the Illinois no. 6 APCS is also significantly higher than that of 64% from CP (1 ms contact) reported by Solum et al.[6] (Table IV). Clearly, CP can vastly underestimate nonprotonated aromatic carbon concentrations and this supposition is verified by considering the aliphatic H/C ratios. Values close to 2.0 are obtained from the SPE data for the Illinois no. 6 APCS and the Snibson vitrinite concentrate using expression i. The value for the Illinois no. 6 APCS is higher than that of 1.7 derived from the CP-DD data[6] and also that of *ca.* 1.4 obtained by dela Rosa et al.[7] using normal CP in conjunction with FTIR and ^{1}H CRAMPS (Table V). As mentioned earlier, both the aromaticity and nonprotonated aromatic carbon concentration for Snibson may have been underestimated by SPE because the delay of 20 s used is considerably less than 5 times the average [13]C T_1 for the aromatic carbons (Table II). Indeed, taking the aromaticity to be close to 0.8 as for similar UK bituminous coals with the same H/C ratio,[10,11] the calculated aliphatic H/C ratio would be close to 2.0 compared to the value of 1.8 reported here (Table V).

Low-Rank Coals. Vast differences of *ca.* 10 mol % between the SPE- and CP-determined aromaticities (total sp^2 hybridized carbon) for the N. Dakota and Wyodak APCS were reported previously.[9] Although CP strongly discriminates against sp^2 carbons in low-rank coals, Table III indicates that the fractions of the nonprotonated aromatic carbon ($C_{np\ ar}/C_{ar}$) derived from the SPE and CP DD experiments are in close agreement. However, the values of *ca.* 0.8 from these experiments are consid-

(17) Given, P. H. In *Coal Science*; Gorbaty, M. L., Larsen, J. W., Wender, I., Eds.; Academic: London, 1983; Vol. 3, and references therein.
(18) Bailey, N. T.; Ikejiani, A. O. O.; Lawson, G. J.; Monsef-Mirzai, P. *Fuel* **1992**, *71*, 45-52 and references therein.

erably higher than those close to 0.7 (Table IV) reported by Solum et al.[6] using a contact time of 1 ms in CP for the two low-rank APCS.

In order to derive the aliphatic H/C ratios for the two low-rank APCS, expression i was modified to take account of the carboxyl/carbonyl carbon as follows.

$$(H/C)_{overall} = (H/C)_{ali}(1 - f'_a - f_c) + 0.7f_c + (H/C)'_{ar}f'_a$$

$$(ii)$$

where f'_a is the aromaticity excluding the fraction of carboxyl/carbonyl carbon (f_c). The H/C ratio for the carboxyl/carbonyl carbon was taken to be 0.7 based upon both existing information on the concentrations of carboxyl groups in low-rank coals and the split at *ca.* 185 ppm between these carbon types in the ^{13}C NMR spectra (Figure 2). $C'_{np\,ar}/C_{ar}$, the fraction of nonprotonated aromatic carbon corrected for phenols, was derived by assuming that the phenolic groups account for *ca.* 40% of the total oxygen to be consistent with the available information in the literature.[17,18]

The aliphatic H/C ratios determined from the SPE data are again much higher than those from the corresponding CP data[6] and from combining the normal CP with FTIR and ^1H CRAMPS data[7] (Table V). Indeed, as discussed later, these CP-based values well below 2 are clearly unrealistic. The only apparent discrepancy in the SPE results is the value of 2.4 obtained for Wyodak. A value of *ca.* 2.1–2.2, as deduced for the N. Dakota lignite (Table V), would have been anticipated from the wide body of other structural information.[19,20,21] Indeed, the SPE-determined aromaticities (total sp^2 hybridized carbon) and nonprotonated aromatic carbon concentrations for these two low-rank APCS are, within experimental error, virtually identical (Table III) apart from the anticipated slightly lower concentration of carboxyl/carbonyl carbon in the Wyodak sample. Given the similarity in the carbon distributions, the difference in the calculated aliphatic H/C ratios is thus a consequence of the difference of 0.05 in the total H/C ratios (0.85 for Wyodak and 0.80 for N. Dakota[13]). Such a bias also appears to be evident in the unrealistically low CP-based values derived from the earlier studies[6,7] (Table V).

General Discussion. The SPE-derived structural parameters reported here (Table III) confirm, once again, that CP has consistently discriminated against aromatic carbons in ^{13}C NMR studies on coals.[2,9–11] Although CP data has indicated some obvious trends, such as increasing hydrogen aromaticity with increasing rank (Table IV), the quantitative reliability clearly remains in doubt.

The aliphatic H/C ratio has been used here as the parameter most sensitive to the concentrations of aliphatic carbon being overestimated in the normal ^{13}C spectra of coals and the proportions of quaternary aromatic carbon being underestimated by DD. As shown earlier, errors of only *ca.* 5 mol % in aromaticity values and nonprotonated aromatic carbon concentrations markedly affect aliphatic H/C ratios giving rise to significant distortions in structural models for coals. Although it is recognized that high-

yield extracts (such as supercritical gas extracts) and pyrolysis tars are not necessarily going to be entirely representative of their parent coals due to thermal transformations that occur, the direct determination of CH, CH$_2$, and CH$_3$ concentrations by solution-state ^{13}C NMR spectral editing has indicated that aliphatic H/C ratios occur in the range 2.1–2.3 for a wide range of products with CH$_3$ accounting for between 20 and 35% of the aliphatic carbon.[19–21] Indeed, for high-volatile bituminous coal extracts obtained under relatively mild thermal regimes, arylmethyl accounts for *ca.* 50% of the total methyl corresponding to *ca.* 4 mol % carbon.[19] Further, these values are in reasonably close agreement with those determined by RuO$_4$ oxidation on coals.[19,22]

On the basis of these arguments, aliphatic H/C ratios below 2 are taken as being unrealistic for coals because large proportions of condensed naphthenic groups have to be incorporated into any resultant structural model. Although hopanes and steranes are ubiquitous constituents in coal extracts and liquefaction products, their concentrations are extremely small in relation to the acyclic alkanes.[23,24] Aliphatic H/C ratios for low-volatile bituminous coals which contain higher proportions of methyl (CH$_3$/aliphatic carbon) are clearly going to be higher than their lower rank counterparts as found here where reliable SPE data were obtained with the possible exception of the Wyodak APCS (Table V). Indeed, this study is the first time that a consistent set of aliphatic H/C ratios has been derived from ^{13}C NMR for coals of differing rank. As well as CP measurements, the results cast doubt on the ability of both FTIR and ^1H CRAMPS to determine hydrogen aromaticities accurately. A discussion of these techniques is beyond the scope of this paper, but the great care needed in calibrating FTIR measurements has been addressed in considerable detail by Painter.[25] Further, although Wilson[26] has recently reported a correlation between hydrogen aromaticites determined by CP-DD ^{13}C NMR and ^1H CRAMPS for a number of Australian coals, there is considerable scatter in the data reflecting the uncertainties concerning quantification for both techniques.

The time-consuming nature of the SPE-DD experiments has obviously limited the number of samples that could be included in this investigation. However, the emergence of large volume probes[27] will clearly increase the attractiveness of this rigorous approach for determining quaternary aromatic carbon concentrations in coals and related materials, particularly for those samples where the aromatic carbons have exceedingly long ^{13}C T_1's.

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