PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

^{13}C n.m.r. Studies of Coal and Coal Extracts [and Discussion]

D. E. Wemmer, A. Pines, D. D. Whitehurst and W. R. Ladner

Phil. Trans. R. Soc. Lond. A 1981 **300**, doi: 10.1098/rsta.1981.0045, published 20 March 1981

Phil. Trans. R. Soc. Lond. A **300**, 15–41 (1981) [15]
Printed in Great Britain

^{13}C n.m.r. studies of coal and coal extracts

By D. E. Wemmer[†], A. Pines[†] and D. D. Whitehurst[‡]
[†] *Department of Chemistry, University of California, Berkeley, California* 94720, *U.S.A.*
[‡] *Mobil Research and Development Corporation, Princeton, New Jersey* 08540, *U.S.A.*

The technique of proton-enhanced ^{13}C n.m.r. has turned out to be a useful tool for the study of composition and structure of whole coals. In particular, four functional types of carbons can be resolved and recognized in studies on model compounds and a series of coals: polycondensed aromatic, simple aromatic, oxygen-bonded aliphatic and simple aliphatic. The principles of the techniques are described and examples given of application to model compounds, aromaticity of coals and coal processing by-products, and time-resolved changes in carbon distribution during coal processing.

1. INTRODUCTION

The importance of coal as a source of energy has prompted its investigation with virtually every known analytical technique. However, still relatively little has been learned about the composition and microscopic structure of solid coals. In this work we discuss the application of solid state n.m.r. to quantitative analysis of coal and other similar materials of natural origin. N.m.r. has gained an important role in modern analytical chemistry because of its almost unique ability to look at the microscopic environment of a spin and count the relative number of spins in different environments rather accurately. Until recently, however, most analytical applications of n.m.r. had been in liquid samples, since strong anisotropic couplings in solid samples are not removed by the rapid isotropic motions of molecules in the liquid state. With the application of new methods, however, it is possible to analyse solids in a fashion rather similar to that used in liquids. This is a particularly important development for coals, since many coal samples can be neither dissolved nor melted, and it therefore provides a new approach to following the changes in composition of all fractions of coal and coal extracts during processing. We shall discuss the principles of these new techniques, the relevant experimental parameters, the line shapes obtained, the methods used for quantitative analysis, and finally present some illustrative applications to model compounds and coal samples.

2. PRINCIPLES OF THE N.M.R. METHOD

(*a*) ^{13}C *n.m.r.*

In solid state n.m.r. studies of organic materials, ^{13}C is often the most favourable nucleus to observe since its spectra provide the most direct structural information (relative numbers of carbons in various functional groups), and are experimentally easiest to obtain with good signal:noise ratio and resolution. Some attempts have been made to study protons in coal (Gerstein *et al.* 1976, 1977; Ryan *et al.* 1980) by using multiple-pulse techniques (Haeberlen 1976). The experimental difficulty, limited resolution obtained and more difficult interpretation have restricted application of this approach. However, tracer applications of ^{2}H for following processing may be quite promising. Possibilities for other nuclei, ^{14}N or ^{17}O, have not yet been investigated.

In solid state n.m.r., we must consider several interactions that do not directly affect solution spectra. These include dipolar couplings, anisotropic chemical shielding, and quadrupole coupling. In the liquid state the anisotropic part of all of these interactions is averaged away and it contributes to line broadening only through relaxation. In the solid state, however, the full interaction must be considered. Each of these is briefly described along with its effect on a spectrum, and possible ways to eliminate each are outlined.

(*b*) *Dipolar coupling*

One can write the coupling Hamiltonian *for two spins* I and S fixed in space, separated by a distance r_{IS}, with their internuclear vector making an angle θ with the applied magnetic field as

$$H_{IS} = B_{IS}\frac{(3\cos^2\theta - 1)}{r_{IS}^3}(3I_zS_z - \delta_{IS}\boldsymbol{I}\cdot\boldsymbol{S}).$$

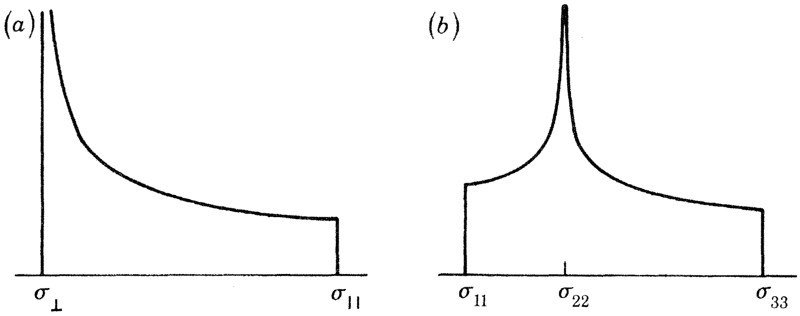


FIGURE 1. Line shapes for ^{13}C powder distributions due to chemical shielding anisotropy: (*a*) axial symmetry; (*b*) the general case.

For a single pair of spins this gives rise to a simple splitting in the spectrum. However, for a real system the full Hamiltonian is a sum of terms such as this over *all* spins in the sample. This generally gives rise then to a very broad spectrum with no structure and hence no information. If the spins are alike (i.e. protons coupled to protons, $\delta_{IS} = 1$ above), one can apply multiple-pulse methods (Haeberlen 1976) to obtain better resolution. If the spins are unlike (i.e. protons coupled to carbon, $\delta_{IS} = 0$ above), the dipolar coupling may be removed by strong irradiation at the frequency of the offending spin species. Such methods are well known (Sinning *et al.* 1976; Mehring 1976), but it is to be noted that the decoupling was not used in obtaining the first ^{13}C spectra in solid coals (Retcofsky & Friedel 1971, 1973), and hence no chemical interpretation could be made. Additionally, we note that for species at low abundance (i.e. ^{13}C at 1.1% natural abundance) the average distance between spins, $_{I\ S}$, is large and hence dipolar couplings among them become negligbly small.

(*c*) *Anisotropic chemical shielding*

The chemical shift of a spin in the solid state is not determined only by the chemical species, but also by the orientation of the molecule containing the spin, relative to the applied field. To give a complete description of this interaction one must specify the complete shielding tensor $\boldsymbol{\sigma}$ and its orientation in a molecular frame. The tensor may be characterized by its three principal values σ_{11}, σ_{22} and σ_{33}. The transformation of such tensors under rotations is well known (Mehring 1976), and gives rise to spectra referred to as powder patterns, examples of which are shown in figure 1. We have assumed, of course, that chemical shielding is the only interaction the spin experiences, others being absent or removed. For any real sample the spectrum will consist of overlapping tensors, one for each chemically distinct site for the spin, as will be discussed further below. Also, from the transformations of such tensors it is easily shown (Mehring 1976) that there exists a 'magic angle' about which the sample may be macroscopically rotated (relative to the external field, 54° 44′) to average the anisotropic chemical shielding to its isotropic value, as would be observed in solution. Unfortunately, this rotation must reach several kilohertz (some 250000 rev/min) to become effective, introducing some challenging but surmountable technical problems.

(*d*) *Quadrupole coupling*

This interaction must be considered only for nuclei with spin $\geqslant 1$, in particular for studies of coal ^{2}H, ^{14}N and ^{17}O. For a spin $\geqslant 1$, the quadrupole moment of the non-spherically symmetric nucleus may couple to electric field gradients in surrounding bonds. Such couplings may be described by a tensor $\boldsymbol{q}$, as for chemical shielding, but are quite strong, exceeding by orders of magnitude both the dipolar and chemical shielding interactions. The quadrupolar powder patterns are very broad, often bordering on indetectably weak, and do not simply reflect the chemical composition of the sample. Since the transformation properties are the same as for chemical shielding, rotation at the magic angle may also be used to reomve the quadrupole coupling, revealing the isotropic chemical shifts. This is however, even more difficult than for chemical shielding, requiring much more precise angle adjustment. Line widths may still be limited by second-order terms in the quadrupole coupling.

(*e*) *Proton-enhanced n.m.r. double resonance*

While in principle proper decoupling is all that is required to obtain high-resolution ^{13}C spectra in solids, in practice we have applied the technique of proton-enhanced nuclear induction spectroscopy (Pines *et al.* 1972*a*; Pines & Wemmer 1976) to overcome the problem of long ^{13}C relaxation times and to provide an enhancement of the ^{13}C signal. Since this technique has been discussed in greater detail elsewhere (Pines *et al.* 1972*a*; Pines & Wemmer 1976; Mehring 1976), only a brief description of it in application to coals will be presented here. This technique is based upon transfer of energy from an abundant spin system, prepared in some way to have a very low spin temperature, to another that we wish to observe and that is usually dilute. In the case at hand, of course, we shall prepare the protons at low temperature and observe ^{13}C. Though there are many experimental approaches for this technique, we shall apply the simplest, spin locking the protons and irradiating the ^{13}C such that $^{\mathrm{H}}\gamma^{\mathrm{H}}H_1 = {}^{\mathrm{C}}\gamma^{\mathrm{C}}H_1$. Under these conditions it has been shown (Pines *et al.* 1972*a*; Pines & Wemmer 1976) that a rapid equilibration of energy occurs in the two spin systems and at equilibrium the ^{13}C polarization is four times that which would be obtained by equilibration with H_0. Clearly, this signal enhancement is desirable, but in addition, since the protons are the 'source' of magnetization, a time of *ca.* T_1 for protons must elapse before the experiment (Sinning *et al.* 1976) may be repeated instead of the longer T_1 of ^{13}C in a usual f.i.d. experiment. In this sense the experimental approach seems very good, but it gives rise to some complications if a quantitative analysis is desired.

These complications arise from a competition between the transfer of energy between the two spin systems and transfer of energy from the lattice to the cold spin system. In almost all cases these two processes can be considered to be incoherent and describable with single time constants T_{CH} and $T_{1\rho}$ respectively. The dynamics of the cross-relaxation process for ^{1}H and ^{13}C has been studied in a number of cases both theoretically and experimentally (Arthur *et al.* 1969; Demco *et al.* 1975). The transfer of magnetization is quite fast for ^{13}C with directly bonded protons ($T_{\mathrm{CH}} \approx 50$ μs) but increases rapidly (*ca.* R^{-6}) as the distance from ^{13}C to the nearest proton increases. The competing process, $T_{1\rho}$, is determined by the spectral density of magnetic fluctuations at the spin-locking frequency (γH_1), coming from molecular motion and relaxation of paramagnetic species in the sample. The experimenter can only adjust the temperature and spin-lock field strength in the hope of changing the strength of fluctuations at ω_1. Of course it is desirable to have $T_{1\rho} \gg T_{\mathrm{CH}}$ so that all carbons are equally and fully polarized, to give a signal truly representative of the carbons in the sample. VanderHart & Retcofsky (1976*a*, *b*) have given considerable discussion to the possible effects on the accuracy of quantitative analysis arising from incomplete polarization of some carbons. Problems arise when there exist reasonably large or frequently occurring regions of very high carbon density with very few protons (small regions similar in structure to diamond or graphite). These carbons will not be cross-polarized fully and will not contribute to the carbon line shape with the proper weight, causing errors in the estimation of parameters such as the fraction of aromatic carbon. These problems become severe when $T_{1\rho}$ is quite short, so that even carbons near but not directly bound to protons do not have time to equilibrate fully. Since the structure of coal is not known, it is impossible to say *a priori* how large the errors due to such regions might be. $T_{1\rho}$ has been measured to be in the 5–10 ms range for several coals in the temperature range -100 to 20 °C (VanderHart & Retcofsky 1976*a*); we must therefore bear this problem in mind when evaluating the accuracy of our experiments.

3. ^{13}C N.M.R. LINE SHAPES

In the following discussion we shall consider ^{13}C line shapes for coals and related materials under conditions of high-power proton decoupling, *without* magic angle spinning. It will be shown that such spectra may be analysed with reasonable accuracy to obtain relative amounts of aromatic, aliphatic and alkoxy carbons. The simplicity and speed of this approach makes it feasible for application in a wide variety of systems.

As already mentioned, ^{13}C spectra will consist of overlapping powder patterns for chemically distinct species. If the breadth of such patterns much exceeded the spread in isotropic values, useful information could be obtained only for simple compounds in which the features from individual tensor elements could be recognized. For ^{13}C the spread of isotropic shifts is of the same order as the pattern width so that different carbon types give rise to recognizable features in the spectrum even for very complex systems such as coal. By studying model compounds of known composition, we may identify and characterize the features in the spectrum and learn to make a quantitative separation for the various carbon types.

The ^{13}C chemical shielding parameters for many different types of carbon have been measured in powder and single crystal samples. Quite a number of these have been tabulated (Mehring 1976), mainly for simple compounds. Tensor elements for more complex compounds have been estimated from powder pattern data obtained in this laboratory (A. Höhener, unpublished). For our work we have tried to characterize three different carbon types that we felt were of interest in coal analysis and which might be distinguishable in the coal line shapes. These are aromatic (simple and condensed), aliphatic and alkoxy. Each of these are defined and the line shape characteristics discussed below.

(*a*) *Aromatic carbon*

The primary component of this group is carbon in aromatic systems, the type or number of substituents in the aromatic system having little influence. Also included, however, are all sp, and sp^2 carbons, in non-aromatic systems, including ethylene, acetylene and carbonyl (aldehydes, ketones, carboxylic acids and esters) carbons. The tensors for aromatic carbons are characterized by large width, often 200×10^{-6}, and high asymmetry with isotropic values near zero (relative to isotropic benzene). All tensors and shifts reported in this work are referred to liquid benzene. Ethylene- and acetylene-type carbons have not yet been extensively characterized, but in the few cases that have been studied, they appear to be like aromatics.

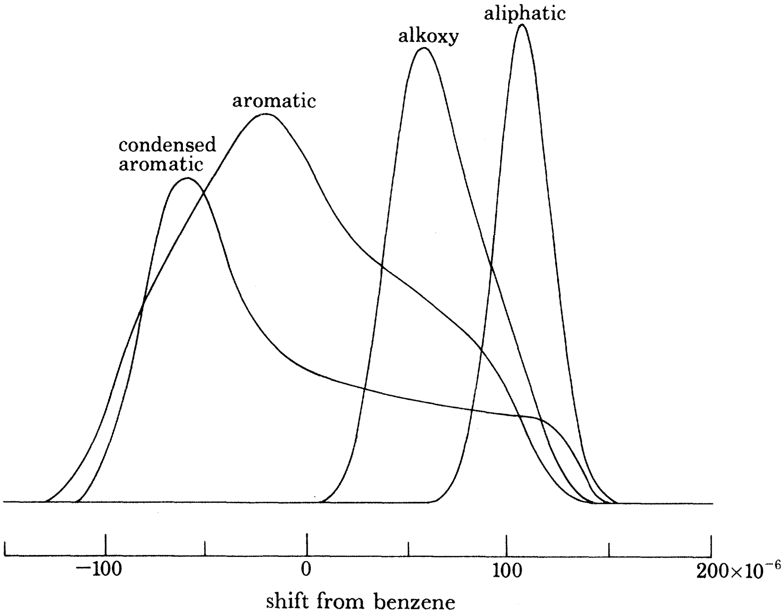


FIGURE 2. Model compound 'universal' line shapes for four types of carbon.

Carboxyl carbons have been studied in considerable numbers. The isotropic resonance is usually shifted downfield of benzene, but depends strongly on the type of compound, from acids and esters *ca.* -40×10^{-6} to ketones *ca.* -70×10^{-6}. The anisotropies are not quite as large as aromatics, and asymmetries range from -1 to 0. Thus the anisotropic line shapes from these carbons will not allow us to distinguish them from aromatics, though the isotropic shifts are often quite different. To simulate the line shape that would be obtained from a sample containing a large mixture of various sorts of aromatic carbon, as is expected for coal, we summed the powder line shapes for a large number of aromatic carbons (table 1) then convoluted this with a Gaussian function of width *ca.* 20×10^{-6} to remove all sharp features (figure 2). The result is one of the curves in figure 2 which we use as the aromatic line shape.

Condensed aromatic, such as *bridge* carbons (e.g. 9,10 in naphthalene) in polycyclic aromatic compounds are somewhat different from simple aromatics above in two ways that make these resonances characteristic. First, they have a local symmetry approximating C_{3v}, and

TABLE 1 (*a*)

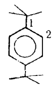
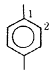
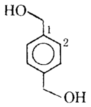
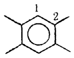
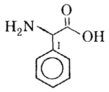
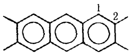
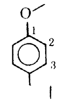
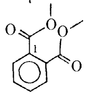
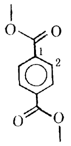
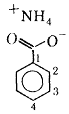
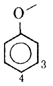
		σ_{11}	σ_{22}	σ_{33}	reference
	(1)	−103,	−66,	111	A. Höhener, unpublished
	(2)	−81,	−12,	104	
	(1)	−90,	−35,	107	
	(2)	−109,	−10,	119	
	(1)	−104,	−42,	116	
	(2)	−95,	−16,	105	
	(1)	−94,	6,	83	Pausak *et al.* (1973)
	(2)	−100,	−24,	111	
	(1)	−103,	−25,	113	D. Wemmer, unpublished
	(1)	−100,	−20,	109	
	(2)	−82,	−92,	114	
	(1)	−109,	−38,	61	A. Höhener, unpublished
	(2, 6)	−56,	−3,	110	
	(3, 5)	−98,	−13,	113	
	(1)	−97,	−24,	114	
	(1)	−102,	−25,	107	
	(2)	−88,	−17,	104	
	(1)	−99,	−27,	120	
	(2)	−94,	−18,	112	
	(3)	−102,	−23,	123	
	(4)	−107,	−20,	99	
	(C)	−110,	−43,	19	
	(3)	−81,	−6,	108	
	(4)	−88,	−18,	100	

TABLE 1 (*b*)

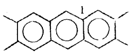
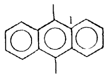
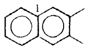
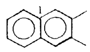
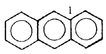
	σ_{11}	σ_{22}	σ_{33}	reference
	−77,	−59,	135	D. Wemmer, unpublished
	−72,	−53,	134	
	−81,	−69,	132	
	−88,	−70,	135	
	−89,	−59,	138	

TABLE 1 (*c*)

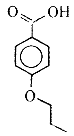
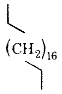
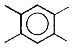
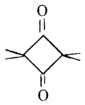
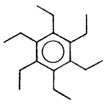
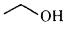
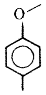
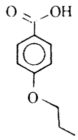
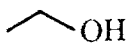
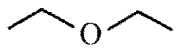
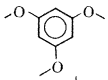
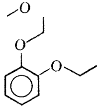
		σ_{11}	σ_{22}	σ_{33}	reference
	CH_2	98,	108,	114	A. Höhener, unpublished
	CH_3	107,	119,	125	
	CH_3	102,	106,	125	VanderHart (1976)
	γCH_2	91,	98,	113	
	CH_2	78,	90,	111	
	CH_3	98,	105,	127	Pausak *et al.* (1973)
	CH_3	102,	104,	127	Kaplan (1976)
	CH_2	101,	104,	121	Pausak *et al.* (1976)
	CH_3	105,	112,	130	
	CH_3	104,	113,	128	Pines *et al.* (1972*b*)
	CH_3	90,	103,	129	A. Höhener, unpublished

TABLE 1 (*d*)

		σ_{11}	σ_{22}	σ_{33}	reference
	OCH_2	38,	49,	91	A. Höhener, unpublished
	OCH_2	56,	56,	113	Pines *et al.* (1972*b*)
	OCH_2	31,	43,	110	
	OCH_3	47,	58,	116	A. Höhener, unpublished
	OCH_2	43,	49,	103	
	OCH_3	49,	58,	124	

hence will have rather small asymmetry parameters. Secondly, these carbons lie in the interior of aromatic ring systems and hence suffer ring current shifts in the direction perpendicular to the aromatic plane (σ_{33}). These effects have been confirmed in a number of model compounds. In general, the σ_{11} and σ_{22} tensor elements fall in the range -60 to -80×10^{-6} separated by *ca.* 20×10^{-6}. The σ_{33} element fall in the range $+130$ to 145×10^{-6}. Because of the small asymmetry parameter in these compounds, most of the intensity is in the σ_{11}–σ_{22} range, with a relatively weak signal near σ_{33}. Since the region of peak intensity is shifted downfield of the peak for most other aromatics, these carbons will be distinguishable if present in large amounts. As was done for simple aromatics, we may approximate the line shape for these carbons by summing a number of them and convoluting. The tensors used are in table 1, and the line shape is shown as one of the curves in figure 2.

(*b*) *Aliphatic carbon*

In this category fall sp^3 carbons bonded to other carbons of any type. These then may occur bonded to aromatic systems as side chains, or as independent chains or groups. The most common carbons in this group are methyl and methylene, having three or two directly bonded protons respectively, and we have taken these as representative of the aliphatic carbon. The tensor values for these carbons are very different from aromatics, having large upfield isotropic shifts $+100$ to 120×10^{-6}, and much smaller anistropies, *ca.* 30×10^{-6}. In addition, the methyls are generally to higher field with smaller anisotropies than the methylenes. The average of a number of tensors (table 1) are shown in one of the broadened line shapes of figure 2. The position and width of this line are sensitive to the relative amounts of methyl and methylene carbons induced, but it is probably not possible to do any quantitative analysis based upon this, since amounts of benzyl compared with chain methylene, and concentrations of oxygen and other heteroatoms in the chains, may produce competing effects.

(*c*) *Alkoxy carbon*

The major carbon type in this group is sp^3 carbon bonded to oxygen, although other sp^3 carbon bonded to heteroatoms (i.e. N and S) may contribute. The shielding characteristics of these carbons lie between those of aliphatic and aromatic, overlapping with both. The isotropic resonance is in general shifted downfield of other aliphatics, resonating *ca.* 75×10^{-6} with intermediate anisotropies 60–70×10^{-6}, and often small asymmetries. Thus the region of peak intensity, 45–50×10^{-6}, is separated from those for other carbons. The tensor elements used to generate a general line shape (figure 2) are given in table 1. Again the line shape is somewhat sensitive to relative amounts of OCH_3 and OCH_2X taken, but these differences cannot be quantified. There is a lack of data on nitrogen-bonded carbon shielding tensors in the literature; however, preliminary investigations in this laboratory (A. Höhener, unpublished; D. Wemmer, unpublished) indicate that they are similar to oxygen bonded with slightly smaller downfield shifts, and are broadened through dipolar coupling to the nitrogen.

(*d*) *Simulation of line shapes*

If we assume that we have included every type of carbon occurring in coal, we should be able to reproduce the spectrum of any coal sample by taking the correct linear combination of the line shapes described above. This general approach has been used successfully in simulation of powder line shapes where the sharp features at σ_{11}, σ_{22} and σ_{33} may be seen

(Höhener 1978). Examples of this are given in the next sections. In these cases it is possible to separate qualitatively and quantitatively the contributions from different carbons, since the line shapes for each are known. With coals we have applied the same approach, using the line shapes discussed above. Although the line shapes for aromatic and bridge aromatic look quite different, they overlap over so large a range that it is normally difficult to make a quantitative separation, especially at low bridge carbon concentration. Henceforth, we shall only consider a 'general' aromatic line shape – simple aromatic + 10 % bridge carbon in most cases – and speak of its separation from the other types of carbon. In experimental spectra, where there is evidence for a larger amount of bridge aromatic, this will be noted.

VanderHart & Retcofsky (1976*a*, *b*) have used an experimental, empirical approach to the determination of the aromatic and aliphatic components of the coal line shape. They have done this by taking linear combinations of two spectra from coals with different aromaticities, trying to eliminate one peak, with the restriction that there be no negative intensity. The samples that they chose contained relatively little oxygen, so that the restriction of two types of carbon seems valid. The qualitative features of the line shapes they obtained agree with ours. However, the aromatic component is significantly different at the high field end, and the use of 'nearly a linear decreasing function through the region of overlap between the components' is only a first approximation.

4. Experimental details

(*a*) *Samples*

The samples used in this work were obtained from a variety of sources. Since it is our intention here to present the principles of our approach, rather than to catalogue data, we shall not discuss the samples, their source or prior analysis in detail. Coal samples (including processed coals) were always used as finely ground powders, which had been packed in a dry, oxygen-free atmosphere. About 150 mg of such a powder was transferred to a 6 mm outside diameter glass tube, which was then sealed. Other geological materials were also examined as fine powder, but no precautions to exclude air or water were made.

(*b*) *Spectrometer*

The spectrometer used for this work was home-built, with a Bruker 42 kG (4.2 T) wide-bore magnet. The spectrometer is quite conventional for double resonance experiments and is described elsewhere (Wemmer 1978). Rotating fields of 10 G (1 mT) for protons and 40 G (4 mT) for carbon were obtained in a crossed-coil configuration. All experiments were performed at room temperature.

(*c*) *Pulse sequence*

All experiments are done with the single contact spin-locking version of the cross-polarization experiment (Pines *et al.* 1972*a*; Pines & Wemmer 1976). The contact time varied according to the material; for most coals a contact of 2 ms was found to be optimal, althought for some processed coals a shorter contact (1 ms) was necessary to obtain spectra with reasonable signal:noise ratio. The recycle delay was usually about 1 s, though 0.5 s was sometimes used, with little decrease of signal, consistent with the very short proton relaxation times reported in a number of coals (Gerstein *et al.* 1977; Ryan *et al.* 1980). In model compounds, longer relaxation times necessitated longer recycle delays, and longer contact times were sometimes employed.

5. Experimental results on model compounds and coals

The validity of some of the assumptions and of the general approach have been tested in a number of different experiments, which we shall describe. In addition, may coals and other naturally occurring organic geological materials have been examined.

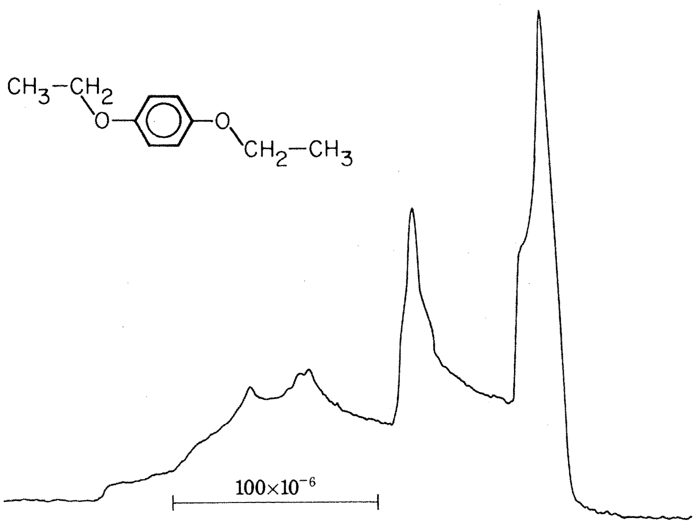


Figure 3. Superposed experimental ^{13}C n.m.r. line shapes for carbon types in a simple model compound Conditions: 46.5 MHz, room temperature, proton-enhanced, 10 ms mixing time, 15 s recycle, 2550 shots.

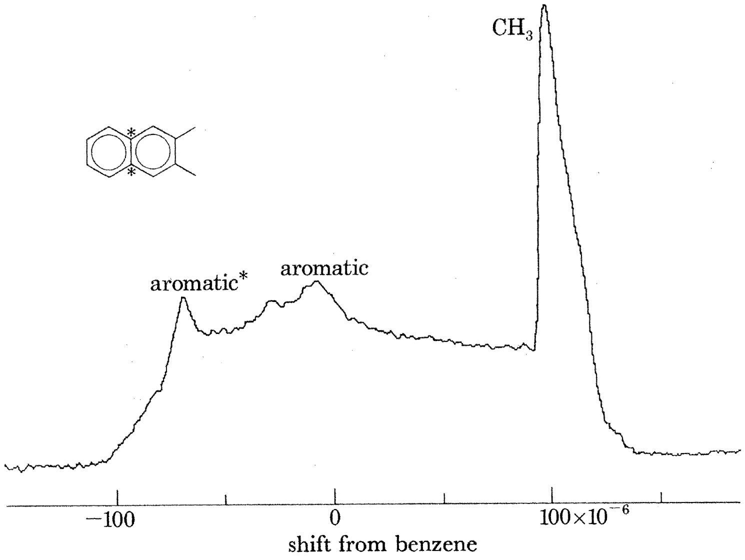


Figure 4. Experimental line shape of dimethylnaphthalene showing pronounced left peak due to condensed aromatic (asterisk indicates approximately C_{3v} symmetry) carbons.

(*a*) *Simple model compounds*

The simplest place to begin with experimental tests is in simple pure organic solid substances. Two examples of this are shown in figures 3 and 4 for the compounds *p*-diethoxybenzene and dimethylnaphthalene. In such simple compounds the powder pattern features of individual tensors are observed; particularly easy to recognize is the singularity at σ_{22}. These spectra bear out quite well some of the observations that we have made about shielding tensors. From comparison with other compounds we assign the furthest downfield σ_{22} element in figure 4 to the bridge carbons. The next σ_{22} element comes from the substituted carbons, and the last group of aromatic σ_{22} elements for the unsubstituted positions. The methyl carbons, as expected, are much sharper and upfield, in the same region as the aromatic σ_{33} elements. Because of the overlap in this region, only the furthest upfield of the aromatic σ_{33} values in dimethylnaphthalene can be distinguished. This can be assigned, through the use of known isotropic chemical shifts, to the bridge carbon. This upfield shift is probably attributable to ring currents and has been observed in other aromatic compounds as well (D. Wemmer, unpublished). The line drawn between aromatic and aliphatic regions is based upon estimates of the aromatic line shape in that region, and allows us then to qualify the amounts of the two carbon types. The results obtained are summarized in table 2. The agreement in this case is well within the estimated experimental errors, including possible line shape distortions, error in separation of peak regions and errors in area determination.

Table 2

	experimental (%)			theoretical (%)		
compound	aromatic	aliphatic	alkoxy	aromatic	aliphatic	alkoxy
p-diethoxybenzene	63	18	19	60	20	20
2,3-dimethylnaphthalene	84	16	0	83	17	0

(*b*) *Complex model compounds*

The next class of models examined were pure organic compounds with known structure, but complex enough that the tensor elements of individual carbon types could not be discerned (with magic angle sample spinning, features are indeed observed in these compounds). This is close to what we expect from coals. In such a case the general line shapes derived earlier are appropriate, but the actual values are known from the chemical structure so the analysis of carbon distribution obtained by our technique can be checked. Two examples are shown in figures 5 and 6 for rutin and quinine. The line shapes in this case still show a little more structure than coal, but individual tensors cannot be discerned. Table 3 shows the results of carbon distribution obtained with the line shape method for a variety of model compounds. Again the agreement is quite satisfactory. A number of other compounds of similar complexity but varying amounts of different carbon types, have been studied. The determination of the faction of a carbon type seems to be good to ± 5 %, including all possible sources of error, for experiments and analysis.

(*c*) *Tests of quantitative reliability*

Of course, coal may be quite different in many ways from the compounds discussed above, in that there may be regions of much larger 'inhomogeneity' of both a chemical and physical nature. For this reason it is important to test our methods against other accepted ones on coal samples. One possible method for this comparison of solution and solid state n.m.r. analysis for some coals or coal fractions that are soluble. This has been done for a CS_2-soluble fraction of coal in which solution analysis gave 58 % aromatic and solid state gave 65 %. This difference is about as large as we have observed; repeating the solid state measurement under several cross-polarization conditions gave consistent results. Similar experiments have also been performed by VanderHart & Retcofsky (1976*a*), with differences in the aromatic traction ranging from +5% to +7%. It is worth noting that in all samples measured, the aromatic content is higher in the solid state analysis. The reason for this is not completely clear, though it may stem from rates of cross-polarization comparable to $T_{1\rho}$ for some aromatic carbons far from protons (VanderHart & Retcofsky 1976*a*).

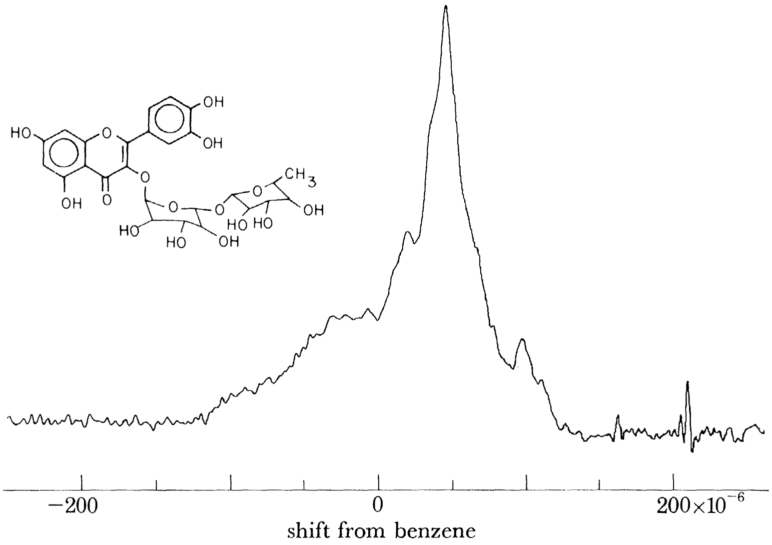


FIGURE. 5. Experimental spectrum of rutin. Analysis of this spectrum by using the line shapes of figure 2 gave the correct distribution of carbon types.

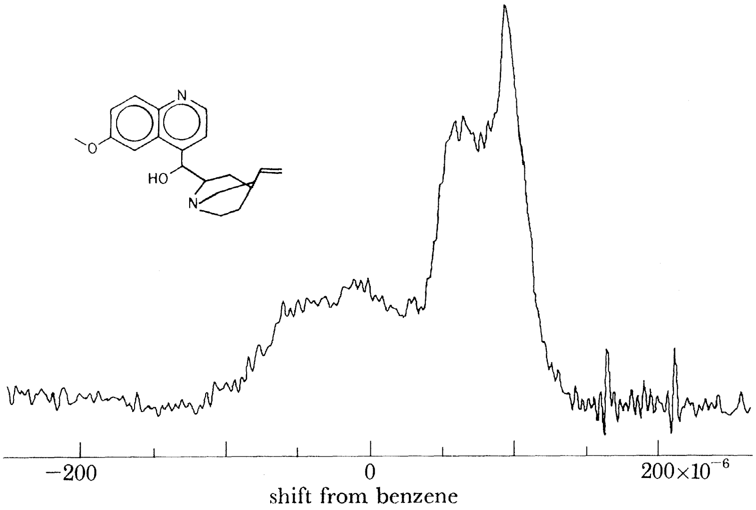
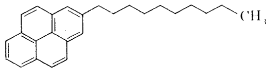
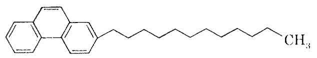
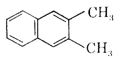
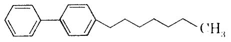
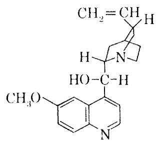
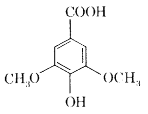
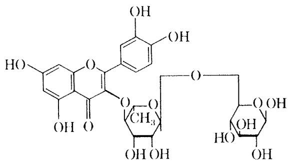
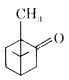


FIGURE 6. Experimental spectrum of quinine. Analysis of this spectrum by using the line shapes of figure 2 gave correct distribution of carbon types.

Another test for reliability of the line shapes and intensity is comparison of solid state f.i.d. and cross-polarization spectra. We have done this for a sample of Kentucky coal, with a 100 s recycle delay and 30° pulse for the f.i.d. and 4 ms mixing time and 2 s recycle delay for cross-polarization. No significant qualitative or quantitative differences were found between the line shapes thus obtained, consistent with the results of VanderHart & Retcofsky (1976*a*) on Pocahontas no. 4 Ivb coal.

To confirm that we are really seeing all of the carbons in coal (excluding the possibility of very large unprotonated and hence unseen regions), we may compare signal amplitudes with a compound of known structure and properties. This has been done by VanderHart by comparing the signal amplitude of a sample of known mass and structure with the signal amplitude of a coal sample. This approach has the disadvantage that slightly different spectrometer conditions (such as probe tuning) may alter the absolute amplitude from the different samples. He has found that for some coals as little as 50 % of the carbons are seen.

TABLE 3. MODEL COMPOUND ^{13}C N.M.R. COMPARISONS

	observed			theoretical		
	arom.	O–C	aliph.	arom.	O–C	aliph.
	58.6	0	41.4	61.5	0	38.5
	50.0	0	50.	53.8	0	46.2
	84.1	0	15.9	83.3	0	16.7
	60.1	0	39.9	65.0	0	35.0
	51	24	25	55	25	20
	80	20	0	78	22	0
	54	42	4	50	46	4
	9	0	91	10	0	90

We have taken a slightly different approach, studying samples that are mixtures of coal and adamantane. By studying a series of samples of increasing admantane concentration, we can predict the aromatic fraction that should be observed for each, knowing the aromatic fraction in the whole coal and the percentage of coal signal observed, without relying at all on the absolute intensity. The samples should be put in a relatively inhomogeneous part of the field so that the sharp lines from adamantane are not distinguishable from the aliphatic line of the coal. If one uses a coal that has a percentage of carbon much different from adamantane (88 % carbon), a correction for carbon content must also be included in the calculation.

A number of theoretical curves are shown in figure 7 for a coal with 80% aromatic carbon, with data taken on a sample of Kentucky coal, indicating that we do in fact see most of the coal.

From our measurements and those of VanderHart we conclude that we see most of the carbons in coal and that the carbons that we see are representative of the sample. With some confidence in our methods we now discuss its applications to other samples, which are not amenable to analysis by other means.

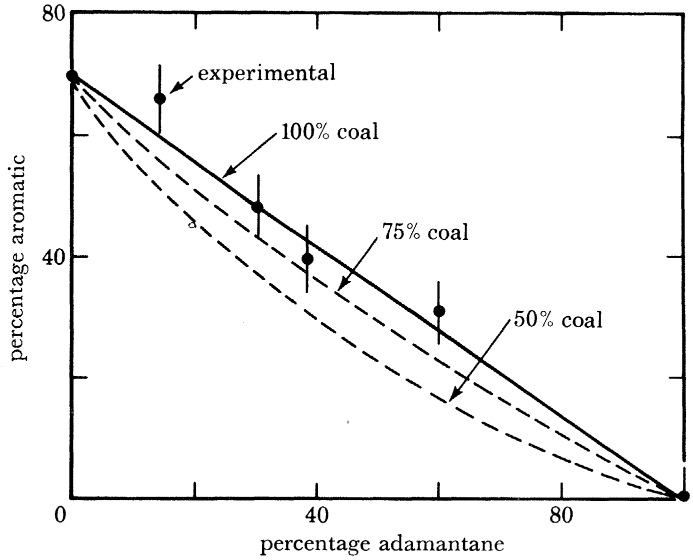


FIGURE 7. Dependence of analysed aromaticity in a coal sample on amount of added adamantane. This indicates that we are 'seeing' essentially all the carbons in the coal.

(*d*) *Coals*

We have examined quite a large number of whole and processed coal samples, varying widely in geological source, age and rank. In all of these we have been able to describe the coal line shape as a sum of the component line shapes described in the last section. Of course, the weights of the various components vary greatly from sample to sample. Figure 8 shows the spectrum of a sample of solvent-refined coal and a simulated spectrum with its decomposition into the separate components. The noise in the simulated spectrum was added artificially. The spectrum in this case is rather simple, having essentially no alkoxy (a minute amount of alkoxy gave a slightly better fit), and a relatively small amount of condensed aromatic indicated by the lack of shoulder. The simulation fits the region -60 to -70×10^{-6} quite well and yields an analysis of 76% aromatic and 25% aliphatic. Figure 9 shows another processed coal sample, in this case oxidized with sodium hypochlorite. The spectrum retains the same basic characteristics as figure 8, with the addition of a small 'peak' in the 50–70 $\times 10^{-6}$ region, which we attribute to alkoxy carbons. Again the simulated spectrum and decomposition into components are shown, yielding values of 61% aromatic, 26% aliphatic and 13% alkoxy. Again, as the amount of condensed aromatic is relatively small, we make no real attempt to quantify it, and include it just as 'aromatic' carbon. These spectra are quite typical, in line shape and signal:noise ratio, of what is obtainable for materials of 'geological' origin. Figure 10 shows spectra from our coal samples with a wide range of aromatic content. Figure 10*a* is a whole coal which has relatively large amounts of aliphatic and alkoxy carbon. The aromatic peak has very little shoulder in the -50 to -60×10^{-6} region, indicating a lack of condensed aromatic carbon. This seems to be typical of a low-rank, young coal. Our analysis gives 23% aliphatic, 10% alkoxy and 67% aromatic. Figure 10*b* is a solvent-refined coal, giving the characteristic spectrum that we have seen in figure 8. An alkoxy peak as in figure 10*a* is clearly completely missing; however, the downfield shoulder is noticeable, indicating some condensed aromatic carbon. Our analysis gives 23% aliphatic and 77% aromatic. Figure 10*c* is another solvent-refined coal, showing the consistency of line shape in these materials. All features remain the same as in figure 10*b*, but the aromatic content has gone up to 84%. Figure 10*d* shows the sptrecum of a residue from solvent refining. This is much more highly aromatic, the aliphatic peak showing only as a small bump near 100×10^{-6}. However, this bump and the extension of the high-field edge to 125×10^{-6} indicates the presence of aliphatic carbon. Our analysis gives 8% aliphatic, 2% alkoxy and 90% aromatic. The downfield put of the aromatic peak is not significantly different from the solvent-refined coals, suggesting that condensed aromatics were not preferentially left in the residue, in this instance. This is not, however, always true. Figure 11 shows the spectrum of another residue, which is also quite highly

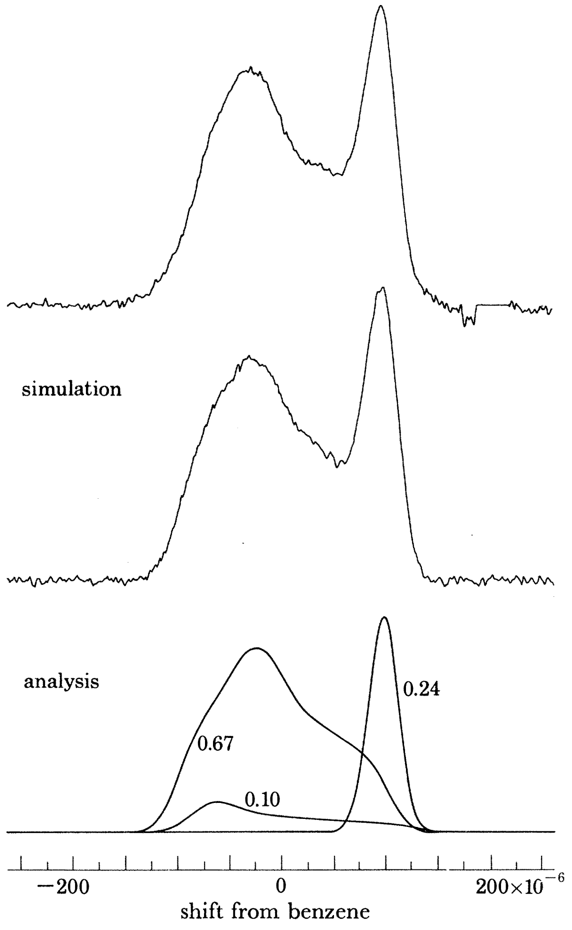


FIGURE 8. Comparison of experimental and simulated (by analysis) coal spectra in a sample with low oxygen content.

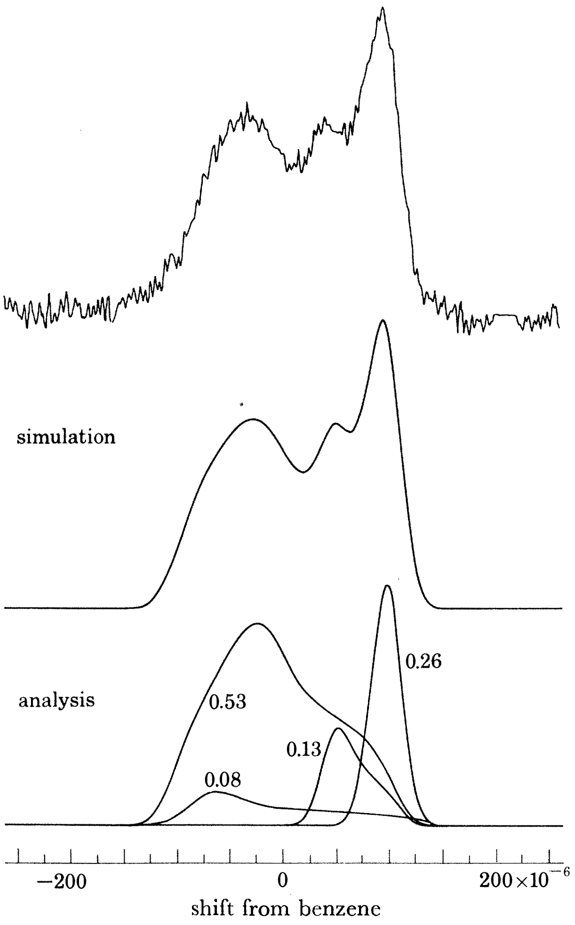


FIGURE 9. Comparison of experimental and simulated (by analysis) coal spectra in a sample with high oxygen content.

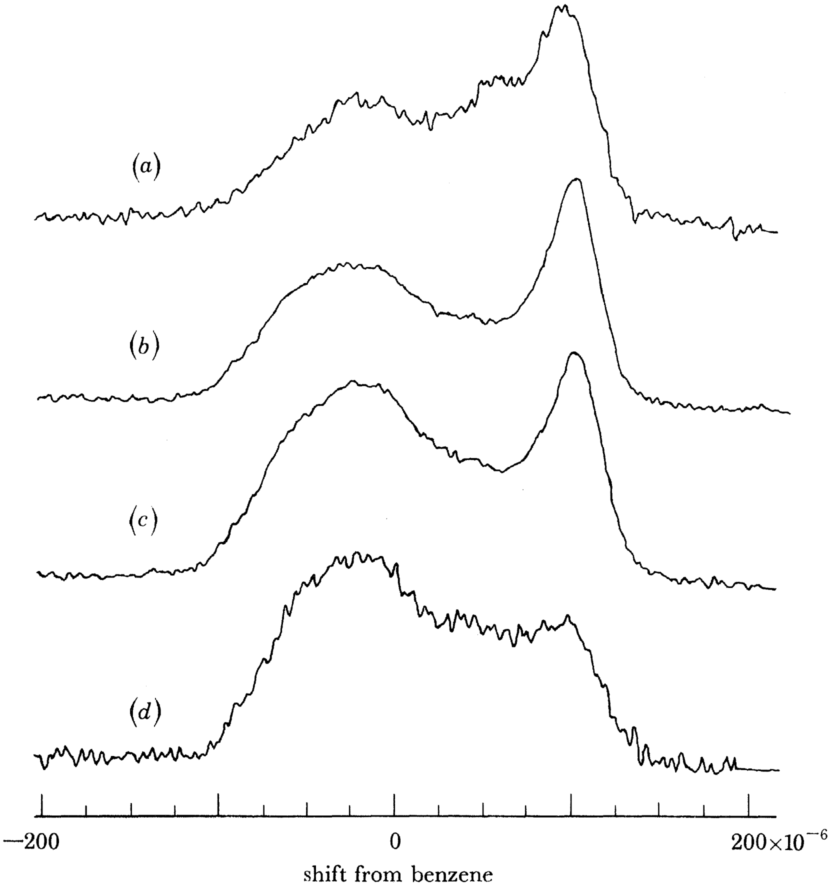


FIGURE 10. Spectra of coals with a range of aromatic carbon content.

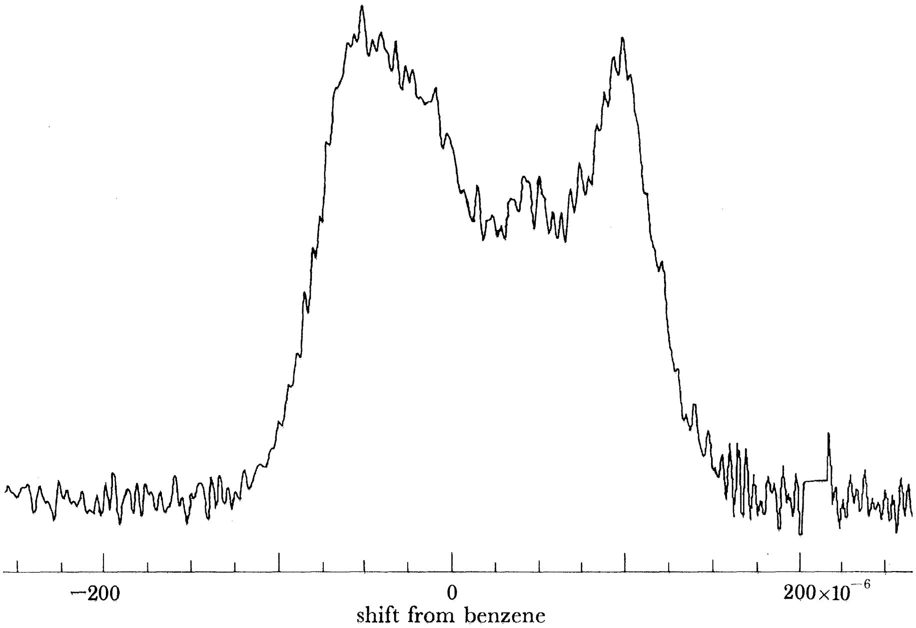


FIGURE 11. Spectrum of a residue showing high condensed aromatic carbon content. Compare with figure 4.

aromatic. In this spectrum the aromatic peak reaches its maximum in the region of -60 to -70×10^{-6}, just where we expect a condensed aromatic to peak. The usual aromatic peak now appears as a shoulder to higher field. This sort of aromatic line shape has also been observed in anthracite coals, which have very high aromatic content (VanderHart & Retcofsky 1976*b*). In some cases there is really no aliphatic carbon in the anthracite coal, and the spectra from these samples agree well with our synthetic line shapes in the usually hidden upfield region.

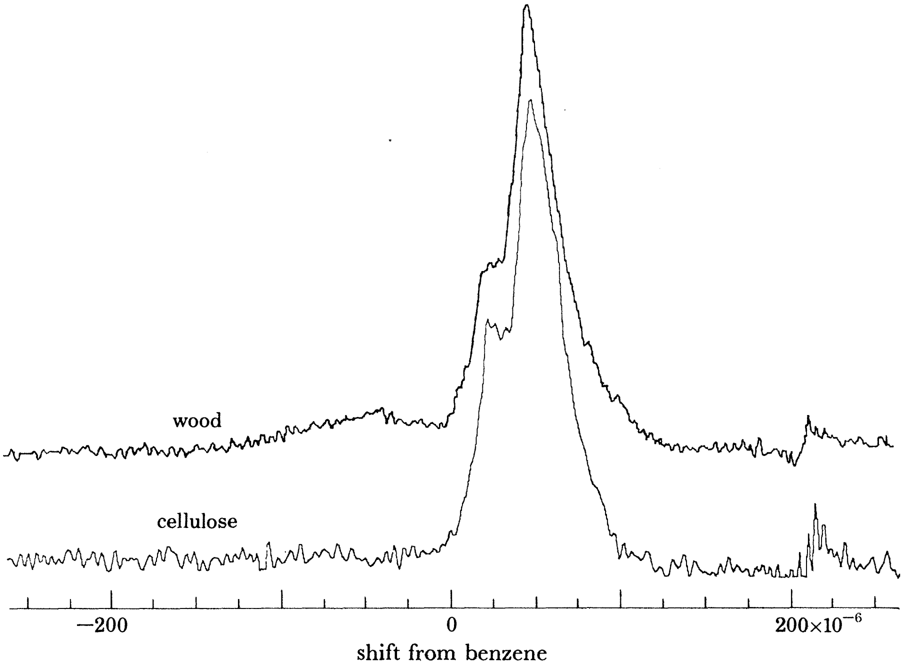


FIGURE 12. Spectra of some simple coal precursors. In these cases much higher resolution is possible with magic angle spinning as shown by several workers. The static, low resolution here, is for comparison with the coal spectra.

(*e*) *Other materials*

In principle our analytical approach may be extended to any carbon-containing material. Figures 12 and 13 show the spectra of four naturally occurring materials which are in a sense precursors of coal. These are cellulose (wet), wood (soft), peat and humic acid. The line shapes for these materials are quite different from coals, since they contain relatively little aromatic carbon and much alkoxy carbon. The simplest material, cellulose, has a simple and known structure containing only alkoxy carbons. There are two types of alkoxy, carbons bonded to one or to two oxygens, occuring in the ratio 5:1. This is quite consistent with the spectrum observed, a peak in the 60×10^{-6} region with a shoulder on the low-field side from the OCH_2O type of carbons and no evidence of either aliphatic or aromatic carbons. In the spectrum of wood, as might well be expected, we see a peak with the same structure as the cellulose, but in addition we see small aromatic and aliphatic peaks, coming from proteins, fats, nucleic acids, etc., in the cells. Analysis of this spectrum gives less than 2 % aliphatic, 76 % alkoxy and 22 % aromatic. The spectrum of peat looks similar to wood in some respects, but with increased aromatic and aliphatic portions. The spectra of such materials, as with coals, will depend very much on the source (see, for example, VanderHart & Retcofsky 1976*a*). Our analysis in this case gives 30 % aliphatic, 30 % alkoxy and 40 % aromatic. The humic acid

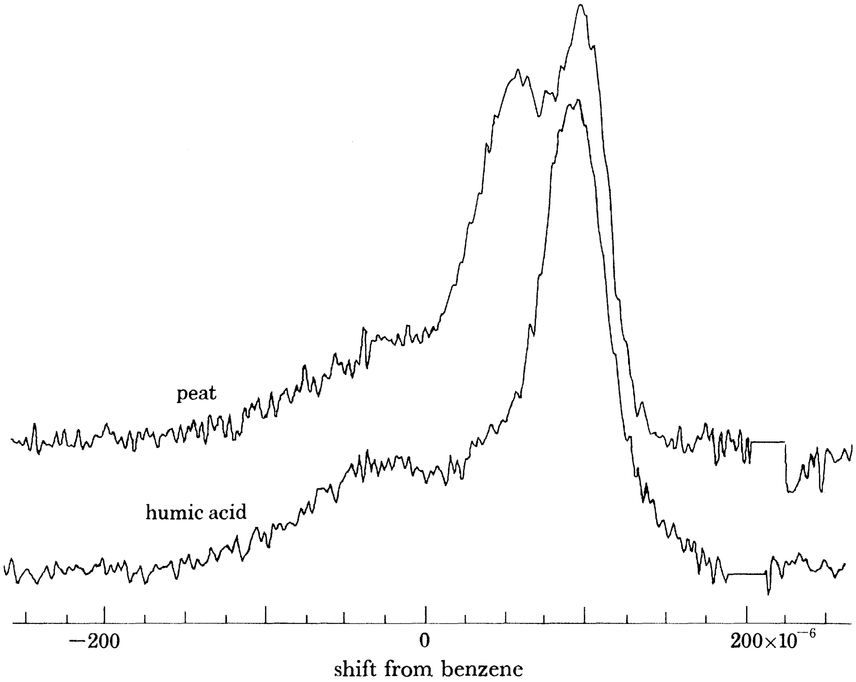


FIGURE 13. Spectra of some other simple coal precursors. The same comments as in figure 12 apply.

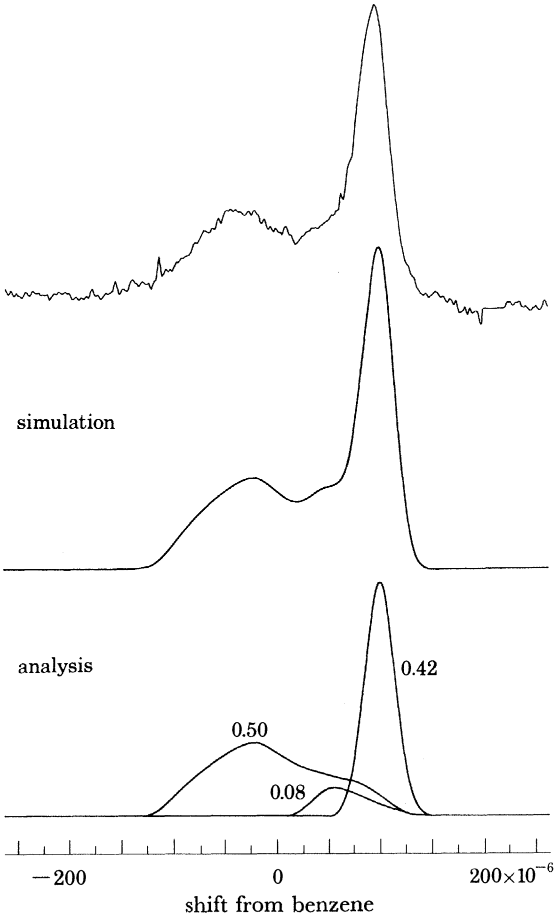


FIGURE 14. Experimental and simulated (by analysis) spectra of carbon-containing material in a kerogen sample.

spectrum begins to look more like coal, with larger aliphatic and aromatic components, though some alkoxy is still present. In such a material we must be careful to remember that carbonyl groups, such as occur in carboxylic acids, are included in our 'aromatic' component. For this spectrum our analysis gives 46 % aliphatic, 9 % alkoxy and 45 % aromatic. Note that in all these samples magic angle spinning can give many resolved peaks but our purpose here is to compare the static spectra with coals where they are valuable.

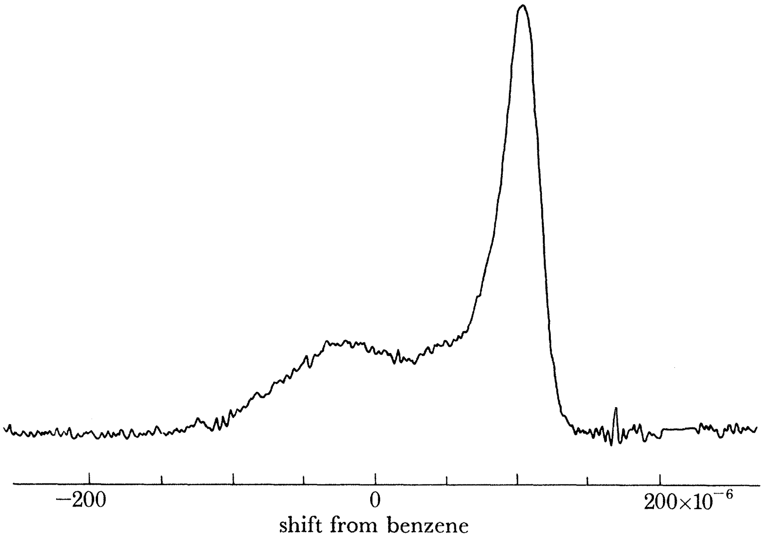


FIGURE 15. Spectrum of petroleum residue showing similarity to solvent-refined coal.

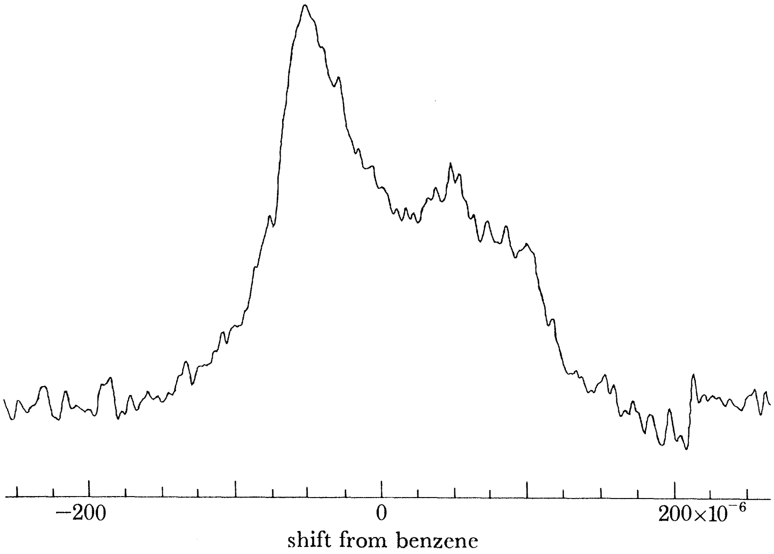


FIGURE 16. Spectrum of soot showing high graphite-like condensed aromatic carbon content.

Another type of material of interest as a fuel source is oil shale; although the concentration of carbon in these samples is rather small, reasonably good spectra can be obtained. Figure 14 shows spectra from a kerogen. The amplitude of the carbon signal has been used to estimate oil yield in such materials (Maciel *et al.* 1978). The analysis of these spectra gives 42 % aliphatic, 8% alkoxy and 50% aromatic for the kerogen. Similar results have also been obtained by Resing *et al.* (1978) on other oil shales.

In addition to fuel source materials, waste materials can also be examined. Two examples are shown in figures 15 and 16, petroleum residue and soot. The petroleum residue spectrum looks quite like refined coal with a substantial aromatic content (48%). The soot spectrum was obtained with an f.i.d. experiment rather than cross-polarization since either lack of protons or short $T_{1\rho}$ resulted in little cross-polarization signal. This sample changed the coil tuning significantly, which may be an indication of high concentration of paramagnetic impurities. The spectrum obtained shows strong peaking in the -60×10^{-6} region and very little aliphatic and alkoxy carbon. This seems to indicate a highly condensed aromatic structure, somewhat like graphite. The spectrum broadened only slightly when proton decoupling was not applied, again indicating a relatively low proton concentration.

(*f*) *Discussion and applicability of magic angle spinning*

In this section we have tried to demonstrate that solid state ^{13}C n.m.r., in particular the application of the cross-polarization techniques, is a valuable qualitative and quantitative aid for the analysis of coal and similar materials. The possible problems of quantitative inaccuracy arising from long cross-polarization times and short $T_{1\rho}$ have been investigated experimentally by us and by others and do not seem to present severe problems. In measurements on model compounds and coals that have been analysed by other means (which are considered accurate), we obtain agreement of the order of ± 5% for the percentages of aromatic, aliphatic and alkoxy carbons. Line shapes for aromatic, condensed aromatic, aliphatic and alkoxy carbons in coal have been empirically developed and can be used successfully to simulate the spectra obtained from a large variety of materials, and allow quantitative separation of overlapping lines. This approach is in principle very similar to that of high-resolution ^{13}C n.m.r. and provides the same information, though analysis is somewhat more complex. The great advantage of our approach is that it may be used on any solid sample, eliminating all solubility problems. The somewhat limited accuracy for quantitative measurements arises from a combination of errors in obtaining the spectrum and analysing it. The errors intrinsic to the cross-polarization approach have been discussed earlier. One of the problems, separation of overlapping lines, may be eliminated through the use of magic angle spinning (Bartuska *et al.* 1976; Zilm *et al.* 1979). It is well known from liquid state ^{13}C n.m.r. experiments that aliphatic and aromatic carbons fall into well separated groups of resonances, removing the problem of overlapping lines. The resonances from alkoxy carbons fall in a region slightly downfield from the aliphatic and, though not completely separated, they may be distinguishable. On the other hand, the isotropic resonances of condensed aromatics fall in the same region or simple aromatic, and they will normally be completely indistinguishable. Carboxyl carbons that were included in aromatics will generally (though not always) have isotropic shifts downfield from aromatics and hence will be distinguishable with spinning. Thus we see that the spectra obtained with sample spinning should be quite informative; the methods are most probably best considered as complementary. We have, in fact, performed a number of such complementary experiments. We stated previously that magic angle spinning reduces tensor interactions to traces if it is rapid enough; cross-polarization still works but the matching conditions are stringent, making quantitative work a problem, in particular for carbons that are relatively isolated from protons (equivalent to assuming that their dipolar coupling to protons is weak). Thus spinning may accentuate some of the quantitative problems that occur in non-spinning samples. In addition, the sensitivity of sample spinning probes is generally somewhat less than for non-spinning, making it more time-consuming to obtain spectra with good signal:noise ratios.

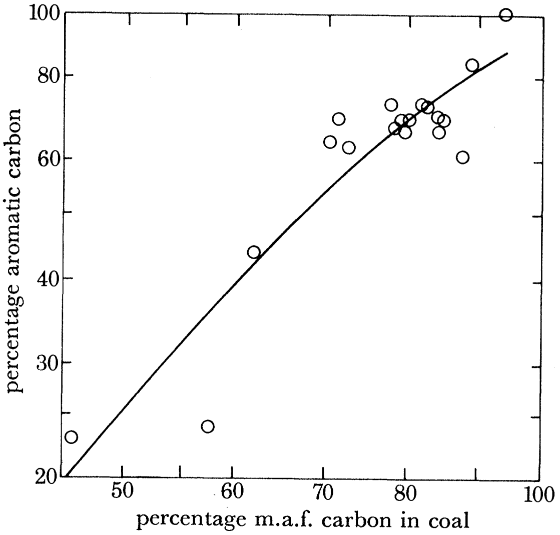


Figure 17. Correlation of aromaticity in a number of coals and coal precursors with percentage of carbon (moisture and ash free).

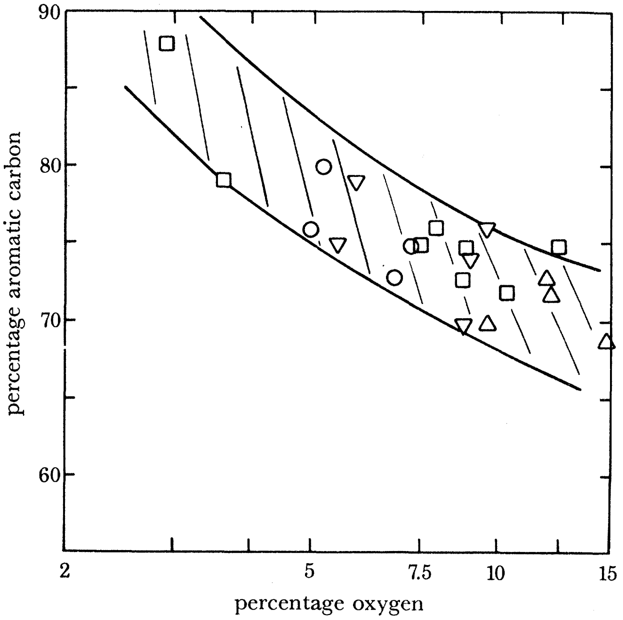


Figure 18. Correlation of aromaticity in a number of coals with oxygen content in the solvent-refined coal. ○, West Kentucky; □, Burning Star; ▽, Monterey; △, Wyodak.

6. Applications to coal processing

From the preceding discussion it is clear that n.m.r. may be used to determine the composition of coal and its precursors. It is informative to combine this with information from other sources, such as elemental analysis. Figure 17 shows the composition of a variety of coals and coal precursors as a function of percentage of carbon (moisture and ash free). Although there is considerable scatter, clear trends can be observed. As one might expect, very high carbon content is associated with high aromatic content. Another trend, shown in figure 18, is that between aromaticity and oxygen content.

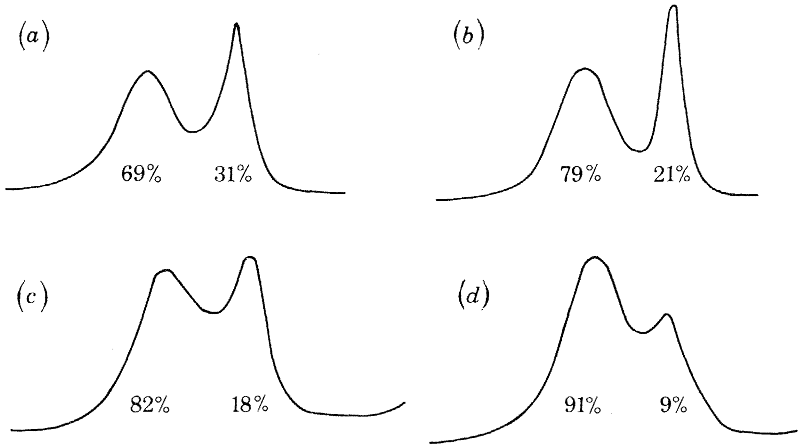


FIGURE 19. Smoothed spectra and analyses for four processed samples from the same coal (Monterey): (*a*) coal (7300); (*b*) solvent-refined coal (5000); (*c*) residue (8800); (*d*) spherical coke (9200).

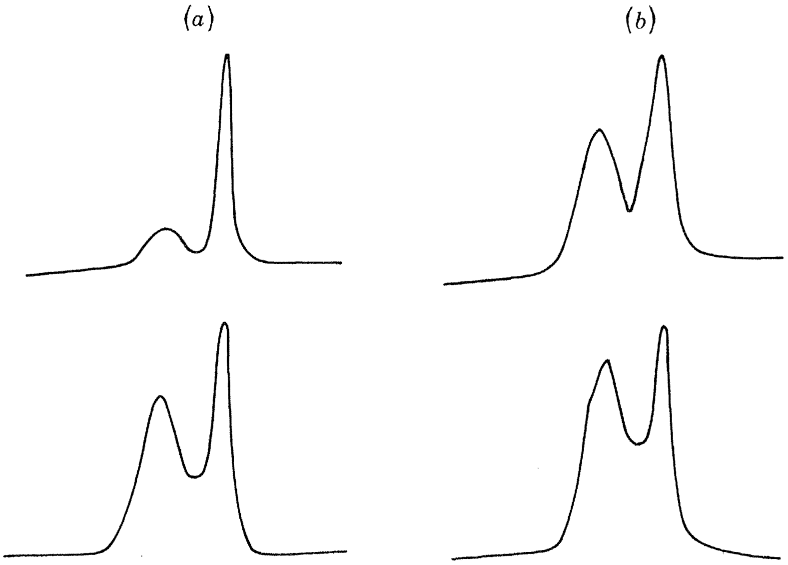


FIGURE 20. Spectra for coal (top) and solvent-refined coal (bottom) from two samples: (*a*) Wyodak; (*b*) Kentucky (one bituminous and other sub-bituminous). This shows that the solvent-refined coals have similar spectra (and carbon analyses) even though the coals are very different.

The real utility of the approach, however, is that coal may be followed by n.m.r. through various types of processing. There are no requirements on solubility, so that all fractions may be studied. Figure 19 shows a whole coal, the solvent-refined fraction, the residue from solvent refinining and a coke, all of which are from the same parent coal. Studies of many coals and their solvent refined products have shown that the fraction of aromatic carbon in the refined product is almost independent of the fraction of aromatic carbon in the parent coal. This is illustrated in figure 20, showing two coals with very different aromatic content, and their refined products, with very similar aromatic content.

Additionally, the dynamics of the refining process may be studied by extracting samples at various times. It is known that dissolving the coal is the first step in the refining process. Analysis of products after very short reaction times shows that the aromatic content was changed very little from the whole coal. However, with longer reaction times, and hence

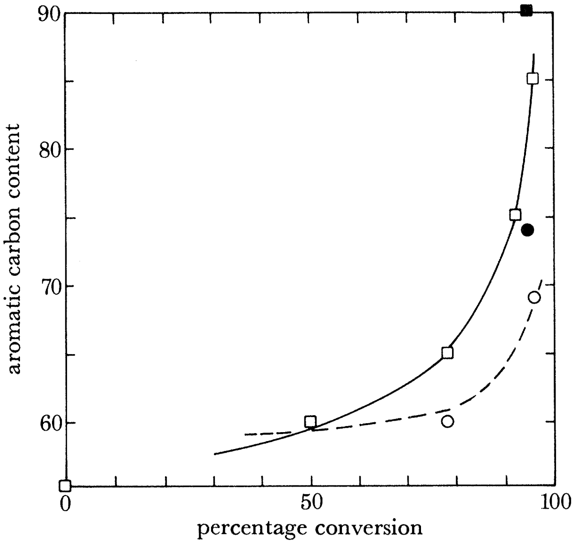


FIGURE 21. Dependence of aromaticity of solvent-refined coal (broken line) and residue (solid line) during solvent refining conversion. For short times the solvent-refined coal and residue have similar spectra but at high conversion they begin to diverge in aromatic content.

TABLE 4. COMPOSITION OF CHARS FORMED BY SRC PROCESSING

run no.	starting material	solvent	temp. °C	time min	% coke	C distribution arom.	alkoxy	aliph.
127	Battelle BS-SC-SRC	SS*40	432	5	10	82	4	12
111	solvent 6663	BP + tetr	449	156	12	83	3	14
121	solvent no. 3	BP + tetr	438	90	34	88	2	10
520	HV phenols-KY-Solv	BP + H_2	427	90	25	96	4	0
521	HV phenols-KY-Solv	BP + ar	427	90	50	89	2	9

TABLE 5. SRC CARBON DISTRIBUTION WITH DONOR VARIATION

(Cross-polarization ^{13}C n.m.r. data.)

run no.	coal	solvent	temp. °C	time min	% conv.	SRC carbons % arom.	% alkoxy	% aliph.
158	Wyodak	SS*43	427	90	88	74	1	25
135	Wyodak	SS*8.5	427	90	80	82	0	18
137	Wyodak	SS*4	427	90	64	85	0	15
159	Wyodak	SS*0	427	90	53	87	0	13
70	Monterey	SS*43	427	90	92	79	1	20
136	Monterey	SS*8.5	427	90	84	82	0	18
138	Monterey	SS*4	427	90	76	79	1	20
147	Monterey	SS*0	427	90	71	82	1	17

higher conversion, the aromatic content increases, as shown in figure 21. At very high percentage conversions this increase is quite large. Coke formed after extended reaction times at high temperatures, or in the presence of hydrogen scavengers (benzophenone) tend to have very high aromatic content, as shown in table 4.

The effects of solvent composition on reaction products can also be studied. For example, we have studied the composition of the SRC product generated by using a synthetic solvent (SS*) with varying amounts of the hydrogen donor tetralin (the figure after SS* is the percentage of tetralin). Some results are shown in table 5. For the sub-bituminous coal, Wyodak, there is a dramatic decrease in percentage conversion and increase in aromaticity as the donor is removed. However, for bituminous Monterey coal the conversion drops without significant change in aromaticity.

REFERENCES (Wemmer *et al.*)

Bartuska, J., Maciel, G. E., Schaefer, J. & Stejskal, E. O. 1976 Preprints of the 1976 Coal Chemistry Workshop, Stanford Research Institute, August.

Demco, D., Tegenfeldt, J. & Waugh, J. S. 1975 *Phys Rev.* B **11**, 4133

Gerstein, B. C., Chow C., Pembleton, R. G. & Wilson, R. C. 1976 Preprints of the 1976 Coal Chemistry Workshop, Stanford Research Institute, August.

Gerstein, B. C., Chow, C., Pembleton, R. G. & Wilson, R. C. 1977 *J. Phys. Chem.* **81**, 565.

Haeberlen, U. 1976 *High resolution NMR in solids* (*Adv. magn. Reson., suppl.* 1). New York: Academic Press.

Höhener, A. 1978 *Chem. Phys. Lett.* **53**, 97.

Kaplan, S. 1976 Ph.D. thesis, Massachusetts Institute of Technology.

McArthur, D. A., Hahn, E. & Walstedt, R. E. 1969 *Phys. Rev.* **188**, 609.

Maciel, G. E., Bartuska, V. J. & Miknis F. D. 1978 *Fuel, Lond.* **57**, 505.

Mehring, M. 1976 *High resolution NMR spectroscopy in solids.* Heidelberg: Springer-Verlag.

Pausak, S., Pines, A. & Waugh, J. S. 1973 *J. chem. Phys.* **59**, 591.

Pausak, S., Tegenfeldt, J. & Waugh, J. 1976 *J. chem. Phys.* **61**, 1338.

Pines, A. & Wemmer, D. E. 1976 In *Proceedings of the E.P.R.I. and S.R.I. Workshop on Coal*, Stanford.

Pines, A., Gibby, M. G. & Waugh, J. S. 1972*a* *J. chem. Phys.* **56**, 1776.

Pines, A., Gibby, M. G. & Waugh, J. S. 1972*b* *Chem. Phys. Lett.* **15**, 373.

Resing, H. A., Garroway, A. N. & Hazlett, R. N. 1978 *Fuel, Lond.* **57**, 450.

Retcofsky, H. L. & Friedel, R. A. 1971 *Analyt. Chem.* **43**, 485.

Retcofsky, H. L. & Friedel, R. A. 1973 *J. Phys. Chem.* **77**, 68.

Ryan, L. M., Taylor, R. E., Paff, A. J. & Gerstein, B. C. 1980 *J. chem. Phys.* **72**, 508.

Sinning, G., Mehring, M. & Pines, A. 1976 *Chem. Phys. Lett.* **43**, 382.

VanderHart, D. L. 1976 *J. Chem. Phys.* **64**, 830.

VanderHart, D. L. & Retcofsky, H. L. 1976*a* Preprints of the 1976 Coal Chemistry Workshop, Stanford Research Institute, August.

VanderHart, D. L. & Retcofsky, H. L. 1976*b* *Fuel, Lond.* **55**, 202.

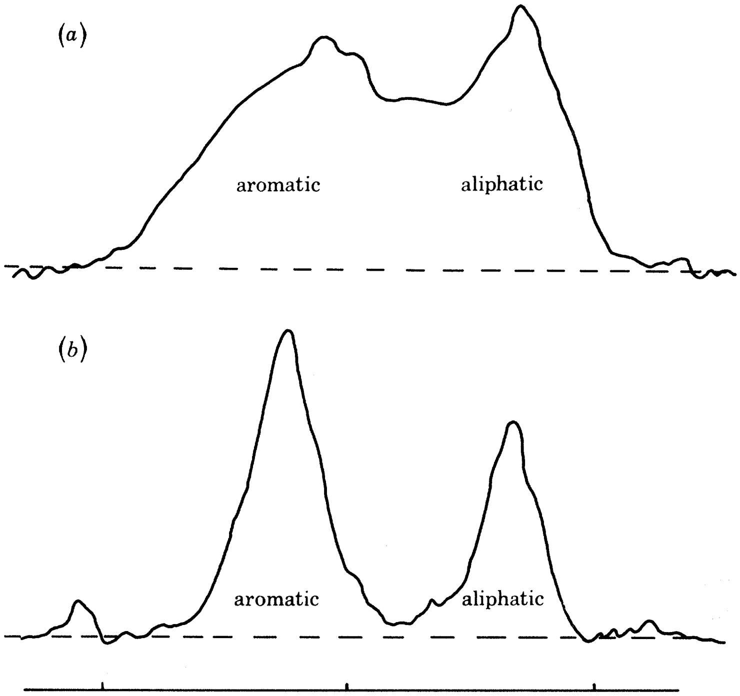
Wemmer, D. 1978 Ph.D. thesis, University of California, Berkeley.

Zilm, K. W., Pugmire, R. M., Grant, D. M., Wood, R. E. & Wiser, W. H. 1979 *Fuel, Lond.* **58**, 11.

Discussion

W. R. LADNER (*Coal Research Establishment, Cheltenham, U.K.*). The work of Professor Pines on the application of solid state ^{13}C n.m.r. to coal and coal-derived materials is an interesting and important development in the structural analysis of these complex materials. This technique should enable the much discussed aromaticity or fraction of aromatic carbon to be measured directly.

I should like to show some examples of the solid state ^{13}C n.m.r. spectra of coal and coal extract that have been obtained when a sample is rotated rapidly (2–3 kHz) at the so-called magic angle (54° 44′ to the direction of the static magnetic field). The use of this technique



22. Solid state ^{13}C n.m.r. spectra of coal at 20 MHz: (*a*) without magic angle spinning; (*b*) with magic angle spinning.

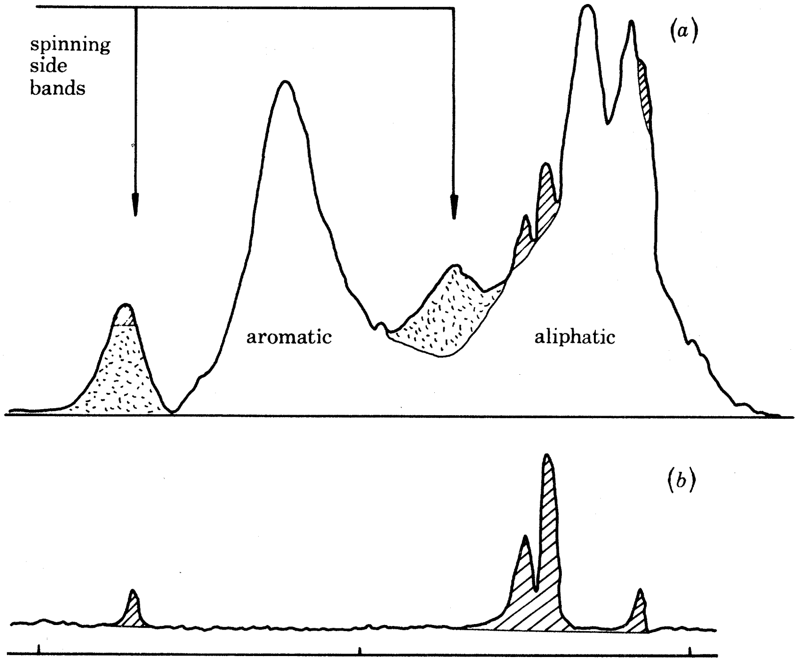


FIGURE 23. Solid state ^{13}C n.m.r. spectra at 50 MHz with magic angle spinning: (*a*) coal extract; (*b*) Perspex rotor.

removes line broadening due to chemical shift anisotropies encountered in solids, and therefore enables greater detail to be revealed in the spectra. The spectrum of coal shown in figure 22*a* was obtained at a frequency of 22.6 MHz without magic angle spinning and that in figure 22*b* with magic angle spinning. There is clearly a considerable improvement in the separation of the aromatic and aliphatic bands on spinning the sample. These spectra were obtained by Professor Harris and Dr Packer of the University of East Anglia.

An example of a ^{13}C n.m.r. spectrum of coal extract at the higher frequency of 50 MHz with the use of a Bruker spectrometer is shown in figure 23*a*. In this spectrum there is some evidence for the partial resolution of the aliphatic band, even though the spectrum is complicated to some extent by (i) bands arising from the Perspex rotor (see figure 23*b*) used to spin the sample and (ii) aromatic spinning side bands.

These examples serve, I hope, to show the advantages of magic angle spinning and the use of high magnetic fields in solid state ^{13}C n.m.r. spectroscopy, and I am sure that this technique, which is already being applied in a number of n.m.r. laboratories, will find increasing use in the future.

A. Pines. Dr Ladner's interesting examples substantiate my comments about magic angle spinning, namely that in some cases of even complex materials it can increase the resolution. This is strikingly demonstrated in simple model compounds and in coal precursors as shown by work from several laboratories, including our own, and that of Harris and Packer mentioned in the comment. The effect is particularly striking in cases of some nuclei other than ^{13}C, for example deuterium (see Pines *et al.* (1979) *Chem. Phys.* **42**, 423; and LBL-10245 (1980) *Chem. Phys. Lett.* **74**, 376), which I expect will be an excellent probe for following hydrogen evolution and distribution during coal processing.

Let me reiterate, however, some words of caution that I alluded to only briefly in the lecture.

1. Quantitative analysis with spinning may be difficult owing to the presence of unresolved sidebands and the difficulty of matching the cross-polarization condition. The figures provided by Dr Ladner do indeed show some of these complications.

2. The separation between alkyl and alkoxy as well as aromatic and condensed aromatic may be reduced (see, for example, figure 11, where a clear alkoxy peak is observed). This is because the relative symmetry difference is reduced by spinning.

3. The signal:noise ratio may be smaller owing to the lower filling factor for a spinning probe. Again, figure 11 illustrates the available signal:noise in a static wideband probe.

In conclusion, there is no question that sample spinning is extremely valuable, and I believe that a combination of spectra from both static as well as magic angle experiments will be the most efficient use of these novel n.m.r. techniques.

J. M. Thomas, F.R.S. (*Department of Physical Chemistry, University of Cambridge, U.K.*). It is encouraging that Professor Pines can, on the basis of accumulated experience, justifiably talk about 'universal line shapes.' It would indeed be a happy state of affairs if it did transpire that one could quantify the contributions from aromatic, alkoxy and aliphatic components. Recognizing some of the difficulties that spectroscopists (even in Mössbauer spectroscopy where line shapes and half-widths are rather well defined) have encountered in their deconvolution procedures, one wonders how reliably the percentage aromatic character may be recovered from the total line profile for a given coal specimen.

Take, for example, coronene and hexabenzocoronene. It would be interesting, in the light of Professor Pines's remarks about aromatic carbon atoms possessing C_3 symmetry, to ascertain what differences there are in the line profiles of standard samples rich in one or other of these two materials.

A. Pines. I believe that we have been quite conservative in our deconvolution procedure, employing only three main carbon type line shapes. Figures 3 and 9 indicate that the separation works quite well. The reliability of our procedure for extracting condensed aromatics is further confirmed by the work on complex model compounds (table 3) and by the comparison with other n.m.r. spectra in soluble materials.

The case of simple aromatic compared with condensed aromatic is more tentative. As I said in the lecture, the cases of C_3 symmetry should be distinguishable by a singularity at the edge of the spectra as shown in figure 1. The spectra of figure 4 illustrate the manifestation of this conjecture for materials containing a substantial fraction of condensed aromatic carbons. Thus it appears that the two extremes that Professor Thomas mentioned, namely simple aromatic or condensed aromatic, can certainly be distinguished. For small amounts of condensed aromatic I would indeed hesitate to perform this final step of deconvolution.