little from that in pure water. The main peak is not shifted, but there is a general broadening of the spectrum at the long-wavelength side and a blurring of the distinction between the peak and the shoulder. The spectrum could be interpreted as the superposition of the spectrum in water and of a weaker spectrum corresponding to that found in methanol or ethylene glycol (*cf.* Figure 1). It does not correspond to that in a uniform mixed aqueous solvent medium (*cf.* Figure 4 or 6). Thus it appears that the phenol molecules incorporated in the micelle are hydrogen bonded in the manner found in water or alcohols, and that their environment is polar, *i.e.*, they do not penetrate into the alkyl interior of the micelle. However, the lack of definite features in the spectrum of Figure 7 precludes the drawing of more detailed or specific conclusions.

Acknowledgment. We thank Mr. Gerald Rosenberg and Miss Hilda Malodeczky for their competent technical assistance.

Carbon-13 Magnetic Resonance in Diamonds, Coals, and Graphite

H. L. Retcofsky* and R. A. Friedel

Pittsburgh Energy Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pennsylvania 15213

(Received June 30, 1972)

Publication costs assisted by the U. S. Bureau of Mines

Carbon-13 magnetic resonance (^{13}C nmr) spectra of gem-quality diamonds, powdered natural graphite, and four coals were obtained as part of a comprehensive spectral investigation of the structure of coal and other carbonaceous materials. The chemical shift in diamond was found to agree well with empirical predictions based on prior studies of pure aliphatic and alicyclic hydrocarbons. The spectrum of graphite reflects both a chemical shift anisotropy and the semiconductivity of the material. The results for the coals were compared with those for diamond and graphite and found to be best rationalized in terms of increasing carbon aromaticity with increasing coal rank leading finally to the formation of graphite-like structures.

Introduction

Despite recent advances in experimental techniques,[1-5] applications of carbon-13 magnetic resonance (^{13}C nmr) spectrometry to materials in the solid state are relatively few. Of the studies that have appeared in the literature, most have been concerned with the determination of chemical shift anisotropies,[5-8] although some have been devoted to semiconductors,[9,10] intercalation compounds,[10] and simple paramagnetic systems.[11] It is of interest that one of the earliest observations of dynamic nuclear polarization in a nonmetallic solid was the result of a ^{13}C nmr experiment.[12]

Practically nonexistent in the literature are actual examples of the use of ^{13}C nmr in problems typical of those encountered by the practicing chemist engaged in structure elucidation of solids of complex chemical makeup. The present authors have applied ^{13}C nmr to studies of the chemical structure of coal. After detecting the ^{13}C resonance in an anthracitic coal,[13] the high aromaticity of anthracites was confirmed by comparing a later, more highly resolved spectrum with that of solid adamantane.[14] It should be noted that Pines, Gibby, and Waugh[2] have recently shown that spin-decoupled, *high-resolution* spectra of solids can be obtained by use of a specialized series of pulse sequences followed by a Fourier transformation. These experiments, though quite exciting, are generally beyond the scope of most laboratories; the work described in the present paper was all accomplished using conventional broadline techniques with accompanying signal averaging of spectra. The primary purpose of this investigation is to deduce information about the chemical structure of coal and the changes that occur in chemical structure during the coalification process. Because of the long periods of signal averaging required, the coals studied were limited to four: two bituminous coals, an anthracite, and a meta-anthracite. In addition, spectra of the two allotropes of carbon, diamond and graphite, were also ob-

(1) J. S. Waugh and L. M. Huber, *J. Chem. Phys.*, **47**, 1862 (1967).
(2) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **56**, 1776 (1972).
(3) M. Schwab and E. L. Hahn, *J. Chem. Phys.*, **52**, 3152 (1970).
(4) H. E. Bleich and A. G. Redfield, *J. Chem. Phys.*, **55**, 5405 (1971).
(5) C. S. Yannoni and H. E. Bleich, *J. Chem. Phys.*, **55**, 5406 (1971).
(6) P. C. Lauterbur, *Phys. Rev. Lett.*, **1**, 343 (1958).
(7) A. Pines, W-K. Rhim, and J. S. Waugh, *J. Chem. Phys.*, **54**, 5438 (1971).
(8) A. Pines, W-K. Rhim, and J. S. Waugh, *J. Magn. Resonance*, **6**, 457 (1972).
(9) M. N. Alexander, *Phys. Rev.*, **172**, 331 (1968).
(10) G. P. Carver, *Phys. Rev. B*, **2**, 2284 (1970).
(11) D. G. Davis, *J. Chem. Phys.*, **46**, 388 (1967).
(12) A. Abragam, A. Landesman, and J. M. Winter, *C. R. Acad. Sci.*, **247**, 1852 (1958).
(13) H. L. Retcofsky and R. A. Friedel, "Spectrometry of Fuels," R. A. Friedel, Ed., Plenum Press, New York, N. Y., 1970, p 99.
(14) H. L. Retcofsky and R. A. Friedel, *Anal. Chem.*, **43**, 485 (1971).

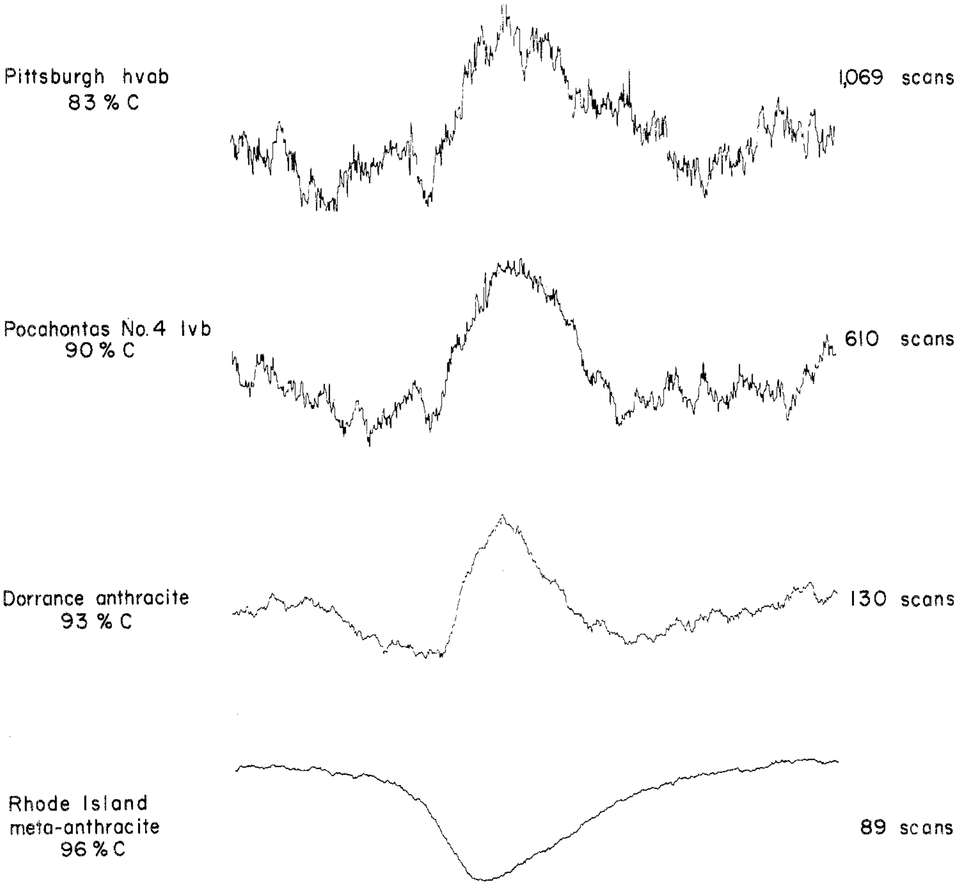

Figure 1. 15.085-MHz ^{13}C nmr spectra of selected coals.

tained since the presence of both graphite-like layers[15] and diamond-like structures[16] in coal has been considered.

Experimental Section

The four coals examined were high-quality vitrains separated petrographically from bulk samples. The graphite was a polycrystalline sample from Madagascar; the diamonds were gem-quality ones believed to be low in paramagnetic impurities. Spectra were obtained essentially as described in a previous publication[14] and are presented as first derivatives of the dispersion mode. All chemical shifts are referred to that of carbon disulfide and are designated δ_C. The semiconductivity of the graphite sample was such that the sample had to be finely ground and dispersed in silica in order to prevent electrical contact between the particles.

Results and Discussion

Representative spectra of the four coals investigated are reproduced in Figure 1; that of diamonds is shown in Figure 2. The spectrum of graphite is not shown but is qualitatively quite similar to that of the meta-anthracite (Figure 1, bottom).

Diamonds. The ^{13}C nmr spectrum of gem-quality diamonds (Figure 2) yields a chemical shift δ_C of 156 ppm with an estimated error of $\sim\pm3$ ppm. The chemical shift is well within the range of values reported for quaternary carbons in paraffins[17,18] and not far removed from the average chemical shift observed for solid adamantane.[2,14] It is concluded that the diamond chemical shift is little different from those of carbon atoms in similar chemical environments.

Diamond crystals, being dilute in magnetic nuclei and having a structure which should result in essentially an isotropic chemical shift, would be expected to exhibit a reasonably narrow nuclear resonance even in the tube of randomly oriented stones used in the present determination. The observed line width 0.4 G is due to instrumental broadening and does not represent the natural line width of the resonance. This is readily apparent from Figure 2; the resonance of the external carbon disulfide chemical shift standard ($\delta_C = 0$) exhibits essentially the same line width as the diamonds, although it is well known that the natural line width in liquid carbon disulfide is less than 1 mG.

Graphite. The ^{13}C resonance in graphite was first detected by Abragam, Landesman, and Winter[12] using nuclear Overhauser enhancement. By saturating the electron spin resonance absorption, a nuclear polarization of 3–12% of the maximum theoretical value was observed. Twelve years later, Carver[10] reported the ^{13}C resonance in spectroscopic-grade graphite powder as part of a study of cesium–graphite intercalation compounds. Most of Carver's measurements were made at temperatures near that of liquid helium using a pulse spectrometer. In the present work, room-temperature, broadline ^{13}C nmr spectra of

---

(15) H. Brusset, J. Devaux, and A. Guinier, *Compt. Rend.*, **216**, 152 (1943).

(16) R. A. Friedel, *Science*, **130**, 220 (1959).

(17) R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, **85**, 1300 (1963).

(18) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).

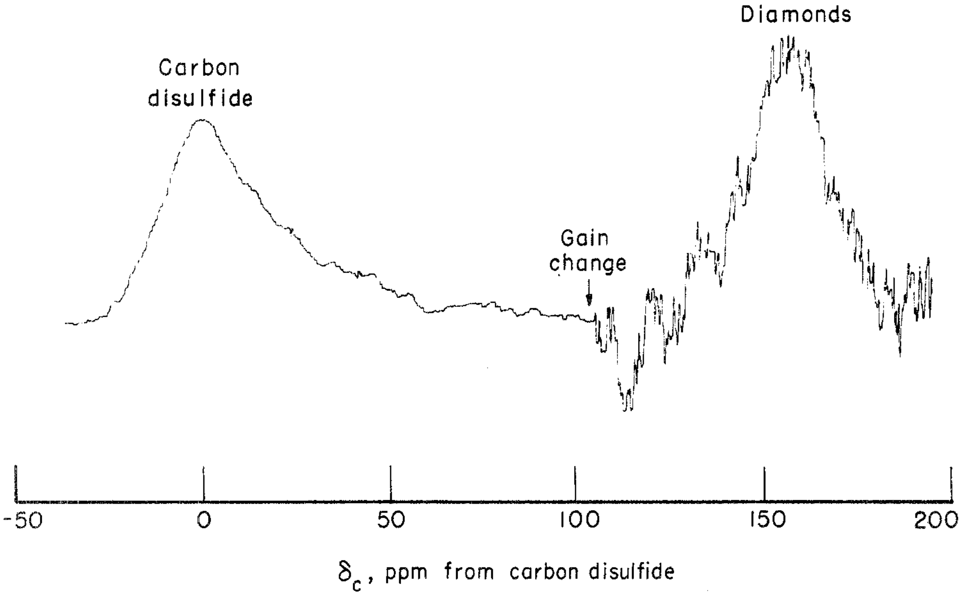

Figure 2. ^{13}C nmr spectrum of diamonds (250 scans).

natural graphite powder were acquired. It should be noted that a room-temperature spin-lattice relaxation time T_1 of 89 ± 10 sec has been reported for spectroscopic graphite.[10]

The nuclear magnetic resonance line shape exhibited by graphite suggests an anisotropic chemical shift. An axially symmetric shielding tensor would be predicted on the basis of the well-known molecular and crystal structure of graphite. Spectra obtained at higher magnetic fields or single crystal studies (in progress) should permit determination of the principal components of the tensor. Other properties of graphite, *e.g.*, the esr *g* factor,[19] also are anisotropic.

The maximum in the graphite spectrum occurs at δ_c ~35 ppm, a much lower chemical shift than that published for any condensed polynuclear aromatic hydrocarbon.[20-23] ^{13}C spectral data for very large polynuclears such as circumanthracene, ovalene, and circumovalene, which possess two-dimensional networks of hexagonal rings similar to but much fewer in number than those in graphite, are not available for comparison. The observed width of the graphite resonance was measured to be ~1.0 G; the asymmetry of the spectrum precludes extraction of a value for the spin-spin relaxation time T_2.

Probably the most unusual feature of the graphite spectrum is that the resonance is inverted relative to that of diamond. A tentative explanation, based on passage conditions used in the experiments, is proposed for this behavior. Weger,[24] in his comprehensive study of passage effects in paramagnetic resonance experiments, has shown that the *major* effect on first derivative, dispersion mode spectra in going from rapid (adiabatic) passage to slow passage is inversion of the resonance. He further shows that the spectrum obtained in either of the two cases is independent of the direction in which the magnetic field is scanned. In the present investigation, all spectra obtained by scanning from low to high magnetic field were identical with the corresponding ones obtained while scanning from high to low field. Long periods for nuclear relaxation would be expected in the case of diamond since the material is dilute in magnetic nuclei; in the case of graphite, the presence of conduction electrons and charge carriers would probably lead to faster relaxation. Our results suggest, therefore, that the diamond spectra were obtained under conditions of fast passage, whereas essentially slow passage conditions were satisfied in the case of graphite. This argument is admittedly speculative at this time.

Coals. The ^{13}C spectra of the coals examined (Figure 1) are presented in order of increasing rank (degree of coalification); the spectrum of the most highly metamorphosed material appears at the bottom of the figure. The width of the coal resonances decreases with increasing rank for the three lower rank samples; in the case of the meta-anthracite, the signal inverts and broadens. The position of maximum signal intensity appears near δ_c = 65 ppm, the chemical shift value for liquid benzene,[25] in each case except that of the meta-anthracite which exhibits its maximum (inverted!) at considerably lower magnetic field. To account for this behavior, both chemical and physical properties of coals must be considered.

Since all coals exhibit esr signals, it is important to consider the possible effects of the presence of paramagnetic species, presumably free radicals in the case of most coals, upon the line widths of the nuclear resonances. The paramagnetic contribution to the line width can be approximated by the equation[9,26]

$$\Delta H = 3.8\gamma\hbar n$$

where γ is the magnetogyric ratio of the electron, $\hbar$ is the modified Planck constant, and n is the concentration of unpaired spins in the sample. In the case of the coals studied, the esr intensities of which have been previously

(19) G. Wagoner, *Proc. Carbon Conf., 4th,* 197 (1960).
(20) H. L. Retcofsky, J. M. Hoffman, Jr., and R. A. Friedel, *J. Chem. Phys.,* **46,** 4545 (1967).
(21) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.,* **88,** 5397 (1966).
(22) R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.,* **91,** 6381 (1969).
(23) N. Defay, D. Zimmerman, and R. H. Martin, *Tetrahedron Lett.,* **No. 21,** 1871 (1971).
(24) M. Weger, *Bell System Tech. J.,* **39,** 1013 (1960).
(25) P. C. Lauterbur, *J. Amer. Chem. Soc.,* **83,** 1838 (1961).
(26) A. Abragam, "Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 128.

reported,[27] plots of esr intensities expressed as free radicals/gram of coal and ^{13}C spectral line widths *vs.* carbon content (or other property) of the coals should show the same or quite similar functional dependence. That this is *not* the case is evident from the two lower plots of Figure 3. It should be noted that the initial exponential increase of free-radical concentration with carbon content of coals (Figure 3, middle) is based on esr measurements made on a large number of coals;[27] the ^{13}C line width data, however, are limited to the four samples of coal under discussion.

The inversion of the ^{13}C resonance in the meta-anthracite is tentatively attributed to passage effects of the type proposed above for the case of graphite. Both materials exhibit semiconductivity which probably leads to rapid rates of nuclear relaxation. A plot of the electrical resistivity of coals as a function of carbon content of the coals (Figure 3, top) illustrates the semiconductor properties of the high rank coal. The resisitivity plot is a composite one prepared from the experimental results of Schuyer and van Krevelen[28] and those of Ouchi.[29] It is interesting that each of the three plots of Figure 3 shows a pronounced inflection point near a carbon content value of 93%.

The ^{13}C results are best rationalized in terms of existing theories of coal constitution and coal metamorphosis; for background material, the reader is referred to three excellent reviews.[30-32] Coals, in general, are considered to be highly aromatic materials and a major feature of coal metamorphosis is the progressive increase in the size and number of condensed aromatic ring structures at the expense of nonaromatic material. In coals of very high rank, these aromatic structures become increasingly graphitic as evidence by the semiconductivity[28] and the graphite-like X-ray diffraction patterns[32,33] of anthracites and meta-anthracites.

The position of spectral maxima for the two bituminous coals and the anthracite sample confirms the relatively high carbon aromaticity of these materials. The much lower absorption in the spectral region attributed to saturated carbons in the anthracite spectrum indicates that aliphatic material is present in only small amounts if at all.

In the case of the coal of 83% carbon content, the resonance is broad and exhibits considerable intensity in the region of absorption by saturated carbons. This suggests that this material has the lowest aromaticity of the coals studied, a hypothesis in accord with other spectral studies of these coals.[34] Dipolar broadening, due to the presence of hydrogen in the lower rank coals, undoubtedly accounts for some of the observed line widths, however, paramagnetic contribution to the line widths, as considered above, appears negligible. Upon close inspection, the spectrum of the 83% carbon coal appears partially resolved into two components; the low-field one could be assigned to aromatic carbons, the high-field one to nonaromatic carbons. The signal/noise ratio in the spectrum, however, is quite low; the possibility of obtaining more highly resolved spectra, perhaps at higher magnetic fields, is an attractive one and should be explored. The present results do, however, provide strong evidence for an increase in carbon aromaticity of coals as the coalification process progresses. Another point of interest concerning the spectrum of the anthracitic coal is that the presence of large quantities of diamond-like structures can be ruled out strictly on the basis of spectral comparison. The spectrum of the meta-anthracite, because of its similarity to that of graphite, indicates qualitatively the presence of graphite-like structures in agreement with X-ray and electrical conductivity data.

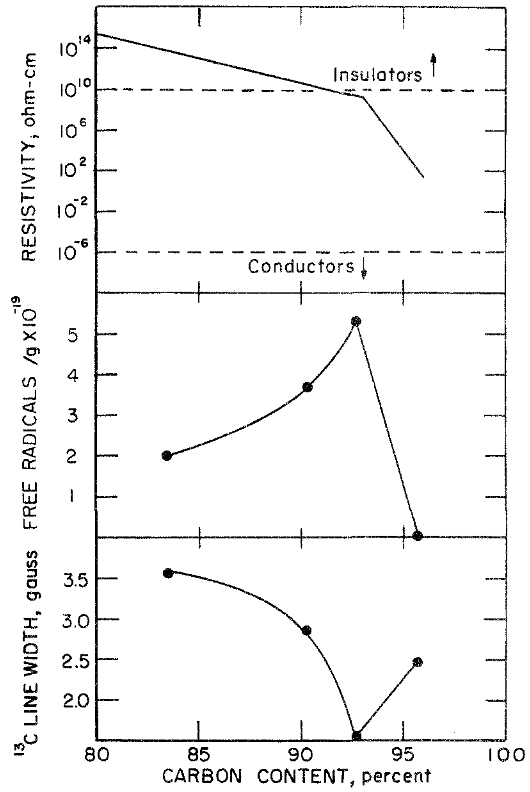

Figure 3. Some properties of coals.

(27) H. L. Retcofsky, J. M. Stark, and R. A. Friedel, *Anal. Chem.*, **40**, 1699 (1968).
(28) J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 213 (1955).
(29) K. Ouchi, *Fuel*, **46**, 71 (1967).
(30) H. Tschamler and E. DeRuiter, "Chemistry of Coal Utilization," Suppl. Vol., H. H. Lowry, Ed., Wiley, New York, N. Y., 1963, p 35.
(31) D. W. van Krevelen, "Coal," Elsevier, Amsterdam, 1961, p 431.
(32) J. G. Speight, *Appl. Spectrosc. Rev.*, **5**, 211 (1971).
(33) M. Mentser, H. J. O'Donnell, and S. Ergun, *Fuel*, 41, 153 (1962).
(34) Reference 13, p 70.