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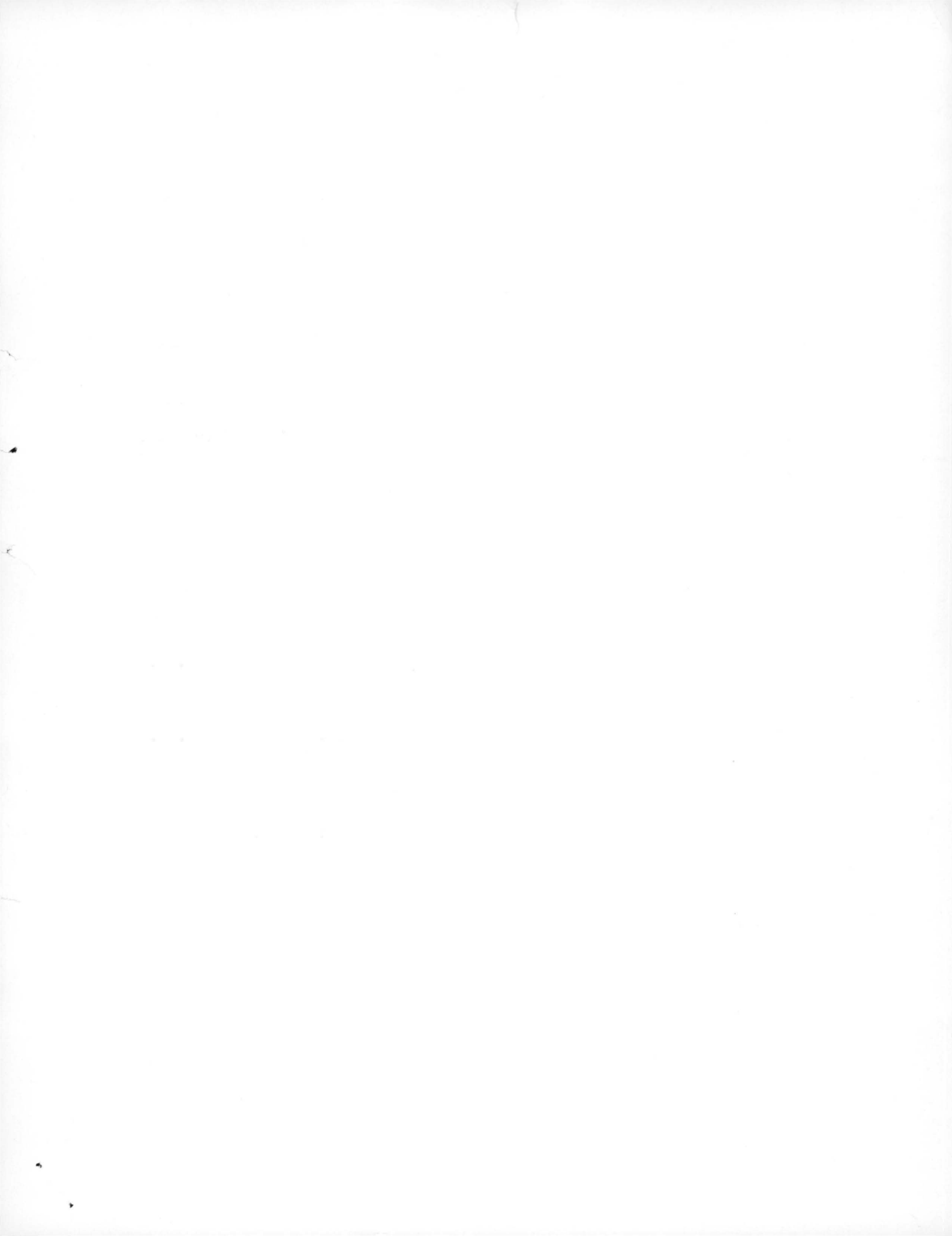National Research Council of Canada

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ABSTRACT

The aromaticity of a number of whole and quinoline solvent-fractionated pitches was determined by means of CP/MAS ^{13}C NMR spectroscopy. Several factors which had to be taken into account include spinning sideband intensity, and the variation of aliphatic and aromatic band intensities with cross-polarization time. ^{1}H NMR lineshapes and spin-lattice relaxation times are presented as well.

INTRODUCTION

Pitches from a variety of sources are currently used as binders in the production of metallurgical coke from poor coking coals (1) and as an essential ingredient in the formation of carbon anodes for the aluminum industry (2). The desirability of certain properties such as chemical composition, rheology, quinoline insoluble fraction, benzene soluble fraction etc. depends to a large extent on the use for which a given pitch is destined. Until recently relatively few studies of a more fundamental nature that attempt to relate chemical structure to

technological behaviour have been available (3). A
publication dealing with the formation of mesophase from
asphaltenes from different bitumens (4) and one treating the
formation of mesophase from various coal derived liquid
fractions (5) demonstrate that carbon aromaticity (f_a) is
one of the important factors in determining the carbonization
behaviour (mesophase texture, bonding ability etc.) of coal
and petroleum derivatives.

The role played by aromatcity and other factors in determining
the technological properties of pitches will become clearer as
more results become available. As a step towards a more
complete understanding of the carbonization behaviour of coal
and petroleum derivatives two pitches were selected for study:
one of these, a coal tar pitch (Aluminum Company of Canada)
and the other a pitch from a processed petroleum residue
(Kureha Chemical Co., Japan). These two pitch samples were
separated into quinoline soluble (QS) and insoluble fractions
(QI), also used in this study. In the past the amount of
quinoline insoluble material in the pitch was taken as an
indication of pitch aromaticity. This is not always
satisfactory. Since the determination of aromaticity by
chemical means is a complicated and time consuming process, we
have explored the possibility of using solid state ^{13}C NMR as
a rapid method of determining pitch aromaticity.

Experimental Methods

^{13}C spectra were obtained by means of cross-polarization and
magic angle spinning at a frequency of 45.28 MHz with a Bruker
CXP-180 NMR spectrometer. A single cross-polarization contact
(6) was used with flip-back of the proton magnetization (7).
Radio frequency field amplitudes were 45 kHz. Typically,
400-1000 free induction decays (fids) were added at ≈2 or 4
sec repetition rates. The fids, consisting of 500 points
digitized at a rate of 25 μsec/point, were zero filled to 4K
before Fourier transformation. In order to obtain spectra for
^{13}C nuclei coupled weakly to protons, a delay of 40 μsec with
the high power decoupler off was inserted before data
acquisition (8) (dipolar dephasing). Kel-F rotors of the
Andrew type were used to achieve magic angle spinning rates of
≈3.3 kHz.

Proton NMR spectra were obtained at 180 MHz by Fourier
transformation of the fids. Proton spin-lattice relaxation
times were measured at 60 MHz on a Bruker SXP pulsed NMR
spectrometer by means of 90°-τ-90° pulse sequences.

Elemental analyses (C, H, N) were performed using the Perkin
Elmer 240 Analyser and are given in Table 1.

Table 1

		N%	C%	H%	H/C	Ash(%)	QI(%)
1.	Coal Tar Pitch	0.94	93.95	4.06	0.52	0.22	16.1
2.	Processed Petroleum Pitch	1.03	85.74	6.69	0.93	0.086	8.6

Quinoline Insolubles

	N%	C%	H%	H/C
1.	0.57	94.72	2.11	0.27
2.	1.24	85.62	4.68	0.65

Quinoline Solubles

	N%	C%	H%	H/C
1.	0.68	93.05	4.44	0.57
2.	1.02	86.74	6.84	0.94

RESULTS AND DISCUSSION

Proton NMR

Proton NMR spectra of the whole pitches are shown in Figure 1
where it is seen that the lines are quite broad, $\approx$40 kHz width
at half height. There is thus relatively little motional
freedom of the protons in these samples.

Proton spin-lattice relaxation times (T_1) for the whole
pitches and quinoline soluble (QS) fractions are shown in
Table 2. For the processed petroleum pitch the T_1 values
increase slightly (10%-30%) whereas for the coal tar pitch T_1
decreases by a factor of almost 4 on going from the whole
pitch to the QS fraction. Since the relaxation mechanisms for
the pitches are not well understood, it is difficult to
interpret these changes in T_1 values. However, from an
empirical relationship between otpical texture of cokes and ^{1}H
T_1's of the parent materials (9) one may expect considerable
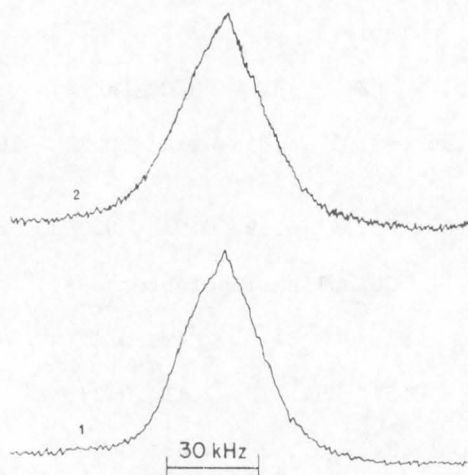differences in coking properties for the whole coal tar pitch
and its QS fraction.

Figure 1 - ^{1}H NMR spectra of solid pitches

Table 2

^{1}H Spin-Lattice Relaxation Times

	T_1/Sec	
	Whole Pitch	Quinoline Soluble Fraction
1.	0.960	0.254
2.	0.295	0.328

Quantitative Aspects of CP/MAS ^{13}C NMR

The intensity of lines in ^{13}C NMR spectra obtained by
cross-polarization techniques depends on the
cross-polarization time τ_{cp} which controls the growth of the
signal, and the ^{1}H rotating frame relaxation time $T_{1\rho}$ which
depends on the motional correlation times, the type of motion,
and perhaps free radical content and distribution.

Another aspect which must be dealt with is the significant
intensity of spinning sidebands in the ^{13}C NMR spectrum. At
the ^{13}C NMR frequency of 45.28 MHz, the usual spinning rate of
the Kel-F rotors of ≈3.3 kHz leads to spinning sidebands some
70 ppm to high and low field from spectral lines due to
aromatic and carbonyl carbons.

The importance of the above factors can be illustrated by
examining the results obtained for several pure compounds.
Figure 2 shows the spectrum of the ammonium salt of p-toluic
acid. Carbon types can be divided into four groups: methyl,
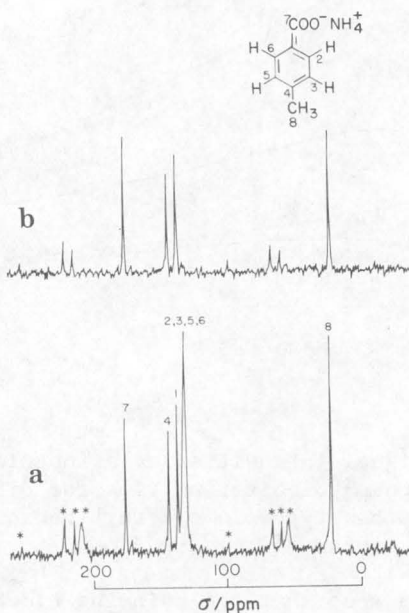quaternary aromatic, protonated aromatic and carboxyl.

Figure 2 – CP/MAS ^{13}C NMR spectra of the ammonium
            salt of p-methyl benzoic (p-toluic) acid
            without a) and with b) dipolar
            dephasing. Spinning sidebands are
            starred.

Figure 3 shows the variation of integrated line intensity as a
function of cross-polarization time. Equilibrium values of
the CP intensities are not reached because of an efficient
relaxation (T_{1_ρ}) process controlled by ammonium ion
reorientation. Cross polarization (growth) times (τ_{cp}) vary

in the order $CH < CH_3 < C_{quat.} < CO$. Correct intensity ratios for
the 4 types of carbon can be obtained at τ_{cp} values of $\approx 3-4$
msec, well away from the region where maximum signal
intensities can be obtained. In systems without an efficient
relaxation mechanism, such as the parent p-toluic acid, the
correct intensities can be simply obtained from the
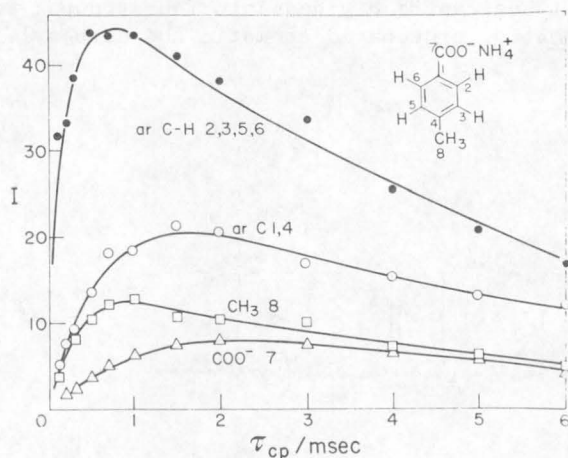equilibrium values reached at long τ_{cp}, Figure 4.

Figure 3 - Signal intensities as a function of
cross-polarization time for different
carbon types in p-methyl benzoic acid
ammonium salt.

From Figure 2 it can be seen that the spinning sidebands of
the aromatic bands have $\approx 10\%-25\%$ of the intensity of the
corresponding centre bands, and in quantitative work account
must be taken of the total integrated intensity of sidebands
plus central band. In Figure 2 it can also be seen that the
first order spinning sidebands on the high and low field sides
of the centre band are essentially equal in intensity. For
the pitches studied here, the high field sideband of the
aromatic carbons overlaps the aliphatic carbon band.

To correct the integrated aromatic and aliphatic carbon
intensities it was always assumed that the high and low field
side bands were of equal intensity. In the case of the coal
tar pitch, Figure 7, where both side bands are resolved, this
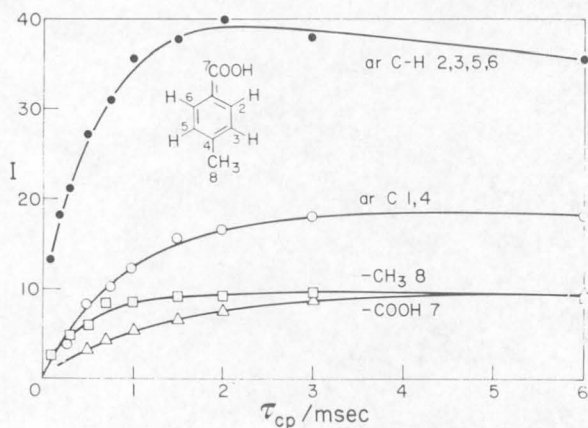can be seen to be a reasonable assumption.

Figure 4 - Signal intensities as a function of
         cross-polarization time for different
         carbon types in p-methyl benzoic acid

^{13}C NMR SPECTRA

^{13}C NMR spectra of the whole pitches are shown in Figure 5.
The pitches have some features in common, including well
separated aliphatic and aromatic carbon bands with maxima at
≈30 and 128 ppm respectively. The coal tar pitch (1) has very
little intensity in the aliphatic region, and quite a sharp
aromatic band. Dipolar dephasing can be used to obtain
spectra of carbons only weakly coupled to protons (quaternary
carbons, carbons involved in motion averaging such as methyl
groups and long chain methylenes). Then, by subtracting
spectra obtained by means of the dipolar dephasing technique
from the normal CP/MAS spectrum, a spectrum results for
carbons strongly coupled to protons. Figure 6 shows spectra
obtained in this manner for the processed petroleum pitch (2).

Bands at ≈13 and ≈20 ppm can be assigned to methyl groups, the
band at ≈30 ppm to methylene carbons in aliphatic chains. The
aromatic band is now resolved into two bands centered at ≈125
ppm and ≈135 ppm and correspond to protonated and quaternary
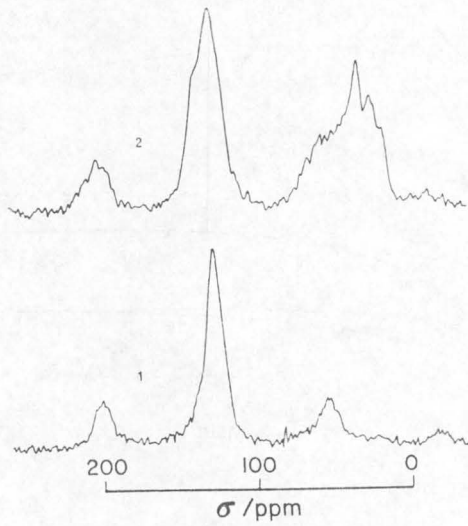aromatic carbons respectively.

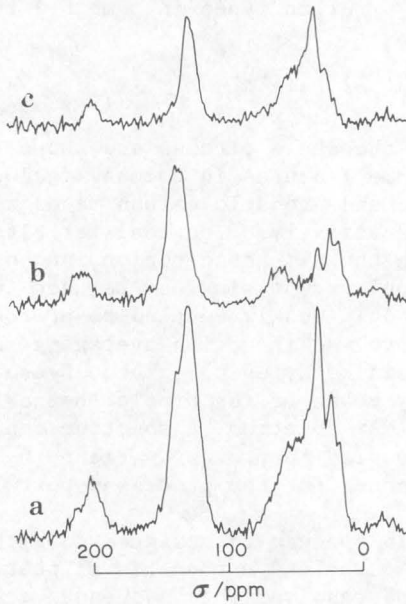Figure 5 - ^{13}C CP/MAS NMR spectra of solid pitches

Figure 6 - a) ^{13}C CP/MAS NMR spectrum of processed
petroleum pitch 2, b) with dipolar
dephasing, c) difference spectrum (a-b)

Figure 7 shows spectra obtained for the coal tar pitch (1).
In this instance the protonated and quaternary aromatic bands
occur at 125 ppm and 130 ppm. The difference in location of
the quaternary aromatic bands for the two pitches, 130 ppm and
135 ppm, indicates that 1 has more carbons in condensed
aromatic structures, whereas 2 has more peripheral carbons
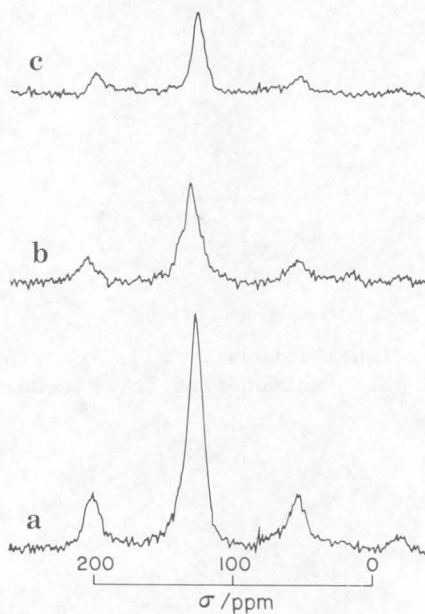bonded to aliphatic groups.

Figure 7 - ^{13}C CP/MAS NMR spectrum of coal tar pitch
          1, b) with dipolar dephasing, c)
          difference spectrum (a-b).

Figure 8 shows the variation of integrated band intensities as
a function of cross-polarization time for pitches 1 and 2.
The intensity ratio of the aliphatic and aromatic bands
becomes constant at τ_{cp} values of ≈1.5-3 msec, Figure 9, and
aromaticities for the pitches derived from τ_{cp} values in
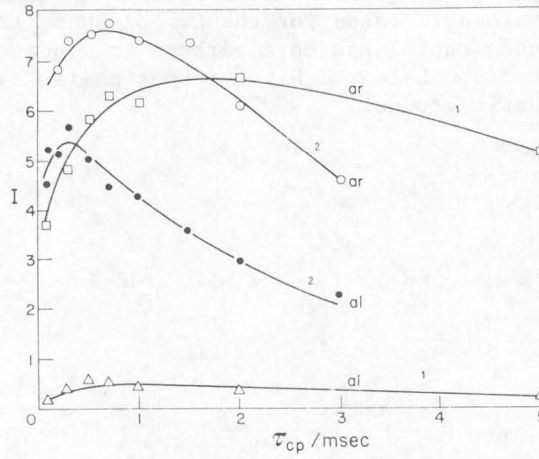this range are given in Table 3.

Figure 8 – Signal intensity as a function of cross-
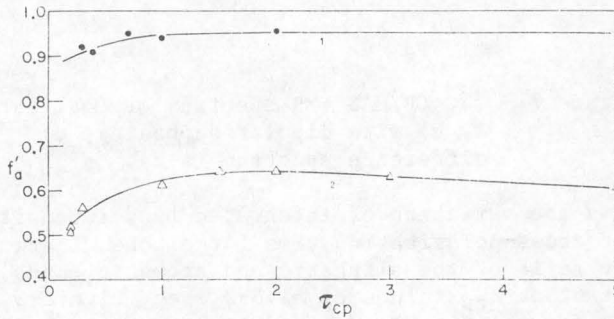polarization time for Pitches 1 and 2.

Figure 9 – Apparent aromaticity as a function of H/C
ratio for pitches and pitch fractions

Table 3

Apparent aromaticities[a]

Whole Pitch	QS	QI
1. 0.94 (0.96)	0.82	0.94
2. 0.61 (0.65)	0.62	0.68

[a]values obtained at τ_{cp} value of 1 msec;
values in brackets are from Figure 9.

For the fractionated pitches, aromaticities were estimated
from spectra obtained at a single τ_{cp} value, 1 msec, Table
3. Compared to aromaticities derived at slightly higher τ_{cp}
values, the 1 msec aromaticities are slightly underestimated.
In general, quinoline insoluble pitch fractions are slightly
more aromatic than whole pitches, and quinoline soluble
fractions are slightly less aromatic, although in some
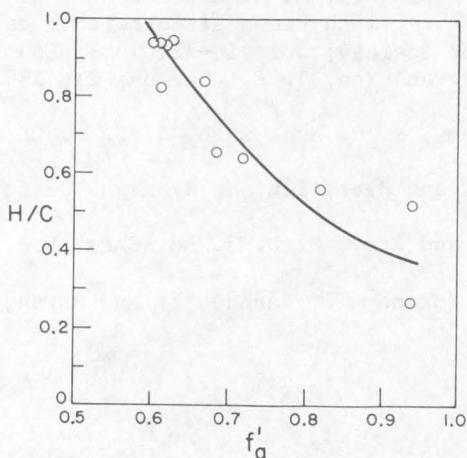instances the difference is quite small and within
experimental error.

Figure 10 - Apparent aromaticity (f'$_a$) as a
function of H/C ratio for pitches and
pitch fractions

One parameter which can be expected to correlate roughly with
pitch aromaticity is the H/C ratio, obtainable from Table 1.
Figure 10 shows a plot of this ratio as a function of apparent
aromaticity, and indeed a reasonable correlation exists. Some
scatter must be expected, especially at high aromaticity, as
the H/C ratio depends greatly on the degree of condensation of
the aromatic ring structures.

CONCLUSION

The rapid and reproducible determination of pitch
aromaticities is possible by means of ^{13}C CP/MAS NMR
spectroscopy. This provides a convenient parameter which,
along with more conventional techniques, should provide
information relating to carbonization behaviour.

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