

126. High-Resolution Solid-State MAS ^{13}C - and ^1H -NMR Spectra of Benzenoid Aromatics Adsorbed on Alumina and Silica: Successful Applications of 1D and 2D Pulse Experiments from Liquid-State NMR

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Dedicated to Prof. Edgar Heilbronner on the occasion of his 70th birthday

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Strong line-narrowing effects in solid-state, magic-angle-spinning (MAS) ^{13}C - as well as ^1H -NMR spectra of benzenoid aromatics adsorbed at alumina or silica surfaces indicate high mobility of the organic adsorbates. Even under modest spinning rates (1 kHz), dipolar couplings are sufficiently reduced to allow scalar ^{13}C , ^1H couplings to be measured. Hetero- and homonuclear pulse sequences known from high-resolution NMR in liquids, like SEFT, *J*-RESOLVED, DEPT, COSY, and ^{13}C , ^1H shift-correlation experiments are successfully applicable. ^{13}C spin-lattice relaxation times are as short as 0.5 s (CH) and 1.1 s (C_q), and $T_1(^1\text{H})$ values are in the order of 0.3 s.

Introduction. – Solid-state NMR is a valuable tool in the field of surface phenomena, both with respect to the study of adsorbents with catalytic activity as well as to the investigation of the chemical and physical behaviour of adsorbed molecules (for reviews, see [1]). Many liquids and gases are highly mobile when physisorbed on silica [1a], zeolites [1a, c], graphite [1b], or boron nitride [1b] [2]. As a consequence of this mobility, line-narrowing effects have been observed in solid-state NMR spectra of adsorbed molecules like olefins, methylated and other substituted benzenes, or pyridine [1].

We now report for the first time drastic line-narrowing effects in the solid-state ^{13}C - as well as ^1H -NMR spectra, if larger benzenoid aromatics (M.W. > 120), many of them fused ring systems, are adsorbed on alumina or silica, materials widely used for column and thin-layer chromatography. For many systems, we ultimately obtain conditions that are similar to those that prevail in solution, and the spectral resolution achieved surpasses the resolution observed so far for the majority of the smaller molecules. As a consequence, a number of one- and two-dimensional pulse experiments can be performed with physisorbed materials, an aspect important for structure elucidations in connection with surface reactions or catalytic transformations.

Results and Discussion. – A) ^{13}C -NMR Spectra. While the combination of cross polarization (CP) with magic angle spinning (MAS) [3] has paved the way for the observation of highly resolved solid-state NMR spectra, in particular for rare spin- $\frac{1}{2}$ nuclei like ^{13}C [4], it still proves difficult for a number of compounds, among them condensed benzenoid aromatics, to obtain enough sensitivity and line-narrowing effects to allow the complete resolution of all ^{13}C signals. Typical results are exemplified in Fig. 1a, b with the ^{13}C -CP/MAS spectra of 1,4-dibromonaphthalene and benzophenone.

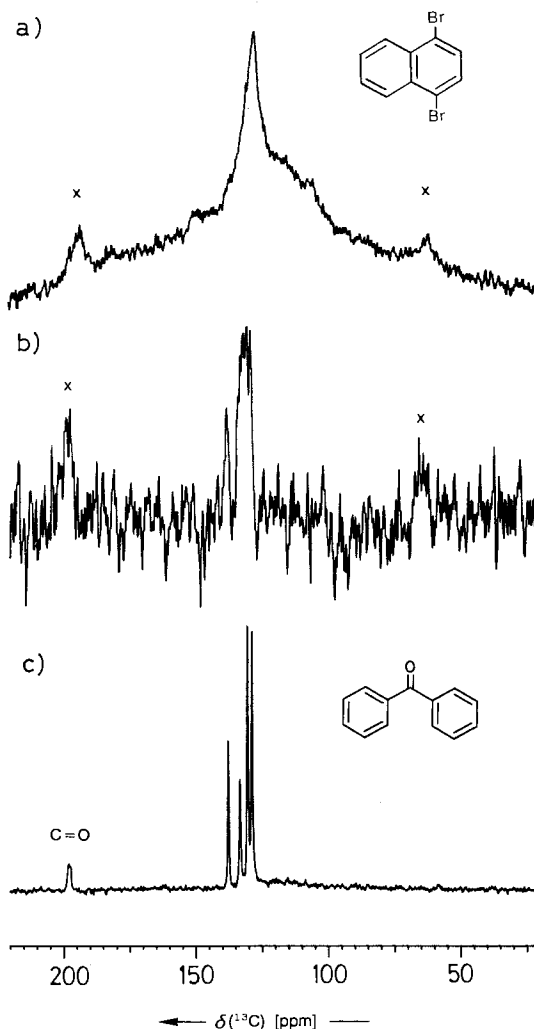


Fig. 1. 75.5-MHz Solid-state ^{13}C -NMR spectra of 1,4-dibromonaphthalene (a) and benzophenone (b). CP/MAS experiments with the pure solids, 4450 and 5700 transients, respectively, spinning rate 4 kHz, high-power ^1H decoupling; x indicates sidebands. c) MAS experiment for benzophenone adsorbed on aluminum oxide. 670 transients, other conditions as above; δ scale refers to TMS as reference.

Accordingly, high-resolution solid-state ^{13}C -NMR powder spectra of this class of compounds have not been reported.

During ^{13}C -NMR experiments with adsorbed materials, we noted that after dissolving benzophenone in CH_2Cl_2 , digesting the solution with neutral aluminum oxide (*cf. Exper. Part*) and evaporating the solvent, a highly resolved ^{13}C -MAS spectrum could be obtained (*Fig. 1c*). Subsequently, it was found that a mere grinding of the organic material with aluminum oxide or silica gel (*cf. Exper. Part*) in an achat mortar was sufficient in order to obtain spectra identical in quality to the one shown in *Fig. 1c*.

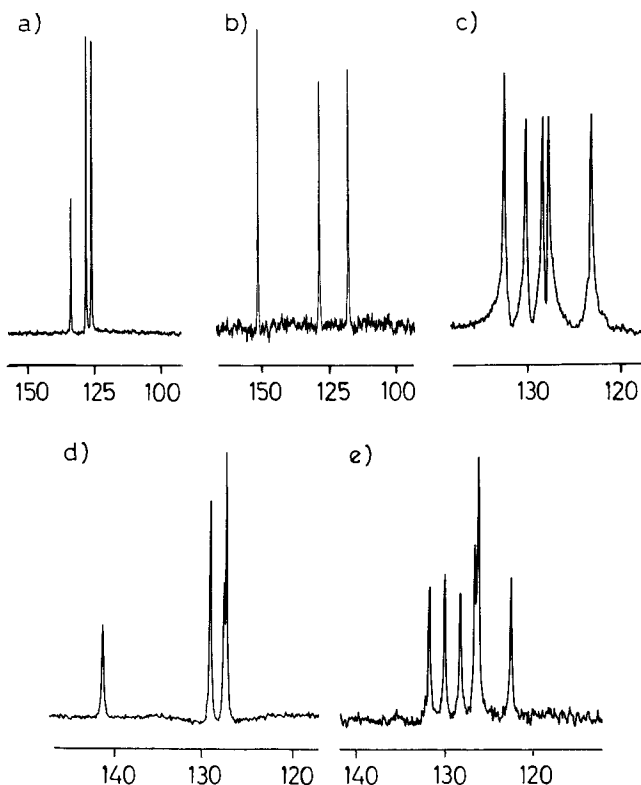


Fig. 2. 75.5-MHz High-resolution ^{13}C -MAS spectra of benzenoid aromatics adsorbed on aluminum oxide (number of transients in parenthesis): Naphthalene (215); biphenylene (437); 1,4-dibromonaphthalene (600); biphenyl (488); phenanthrene (162); $\delta(^{13}\text{C})_{\text{TMS}}$ values.

Similar experiments with naphthalene, biphenylene, 1,4-dibromonaphthalene, biphenyl, and phenanthrene were equally successful (Fig. 2a–e), while all CP/MAS as well as MAS measurements with the pure solids led to unsatisfactory results with respect to sensitivity and resolution. The same was true with CP/MAS experiments for the adsorbed materials.

With the aim to assign the spectra of the adsorbed molecules, we also applied, in analogy to the well-known NQS sequence [5], an experiment with delayed detection in order to distinguish methine and quarternary ^{13}C resonances. To our surprise, we observed unperturbed signals for both types of C-atoms. Normally, methine resonances are not detected under these conditions due to dipolar dephasing of the corresponding transverse magnetization.

Together with the failure of the cross polarization experiment this observation indicates *strong reduction of dipolar $^{13}\text{C},^1\text{H}$ interactions* for the adsorbed molecules. Apparently, a high degree of mobility exists which leads to drastic line narrowing effects. Thus, these results are in general agreement with the earlier findings for the smaller molecules [1], but show that the technique can be extended to much larger systems, eventually even to those which are difficult to measure in solution.

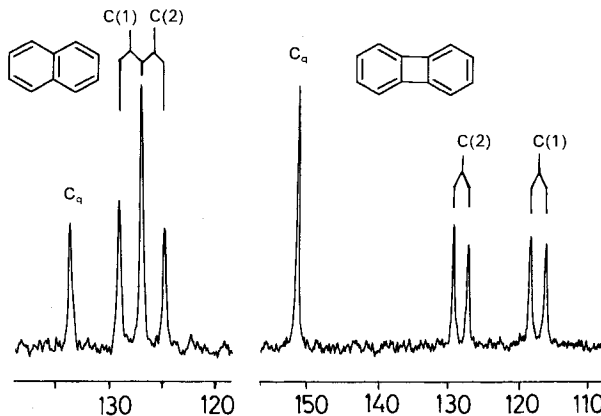


Fig. 3. 75.5-MHz ^{13}C -MAS spectra of naphthalene (a) and biphenylene (b) with scalar ^{13}C , ^1H coupling over one bond. $^1J(^{13}\text{C}, ^1\text{H})$ values are (from left to right) 161, 161, 162, and 164 Hz, resp.

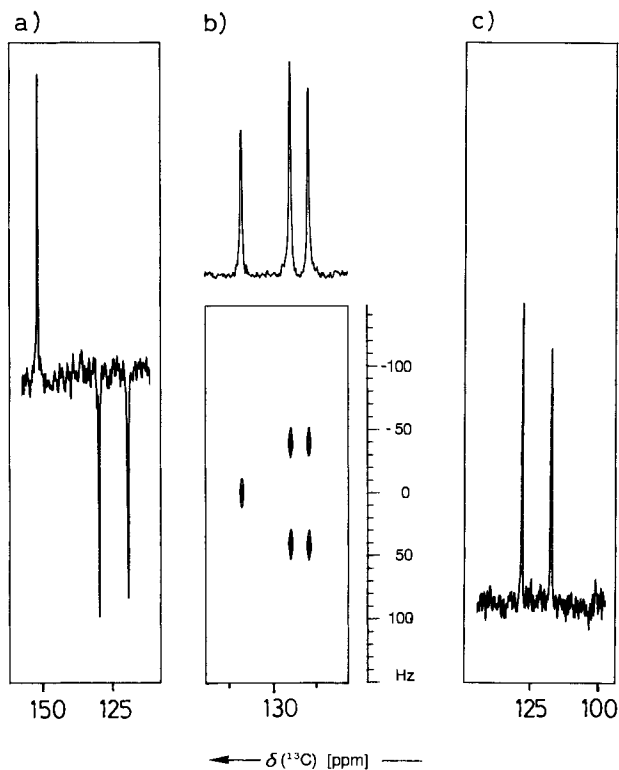


Fig. 4. Pulse experiments with adsorbed aromatics: a) SEFT experiment [6] with biphenylene. Phase selection with 0.06 ms for $1/J(^{13}\text{C}, ^1\text{H})$ as decoupler-off interval ($J = 159$ Hz). b) 2D J-resolved spectrum [7] for naphthalene. 64 t_1 experiments, 16 transients each, total exp. time 3 h. c) DEPT experiment [9] for biphenylene with selection of CH resonances. Evolution delay 0.06 ms.

If indeed dipolar interactions are strongly reduced and nearly completely eliminated even at modest spinning rates (as low as 1 kHz), scalar interactions should dominate as in high-resolution NMR spectroscopy of liquids. Indeed, ^{13}C -MAS spectra without proton decoupling yielded line splittings due to scalar ^{13}C , ^1H coupling over one bond (Fig. 3). Subsequently, successful SEFT experiments [6] as well as J -resolved 2D experiments [7] could be performed (Fig. 4a, b). The latter experiment was applied in solid-state NMR so far mainly to plastic crystals like adamantane and camphor where homonuclear dipolar interactions between protons during the evolution period could be eliminated by the MREV pulse sequence [8].

If scalar coupling dominates, on the other hand, polarization-transfer experiments should also be possible. The DEPT sequence [9], a prominent experiment in this field, yielded in the present case the expected signal selection (Fig. 4c). Thus, these experiments clearly demonstrate a solution-like behaviour of the adsorbates and the utility of 1D and 2D heteronuclear pulse sequences known from liquid-phase NMR for structure investigations.

From the ratio of organic to inorganic material used so far in our experiments (*cf. Exper. Part*) and the surface area of *ca.* 500 $\text{m}^2 \text{g}^{-1}$ for the adsorbents [10], one can estimate that the adsorbed organic molecules form a monolayer. The free enthalpy of adsorption must exceed the lattice forces and induce a kind of melting process. As a consequence, spin-lattice relaxation times should be considerably shortened. This is borne out by an inversion recovery experiment with naphthalene on silica gel which yielded T_1 values of 0.5 s for the methine and 1.1 s for the quarternary C-atoms.

B) ^1H -NMR Spectra. While line narrowing often is a routine operation in solid state NMR of dilute $I = \frac{1}{2}$ spins like ^{13}C [4], similar techniques yield less satisfying results in the case of ^1H -NMR spectra of organic solids. The high abundance of protons and their strong intra- and intermolecular dipolar interactions severely limit the application of solid-state MAS-NMR spectroscopy for this nucleus. Only recently has the combination of MAS with multipulse line-narrowing techniques (CRAMPS = combined rotation and multipulse spectroscopy) [11] revealed promising aspects that indicate future successful applications of solid-state ^1H -NMR for organic materials.

The drastic line-narrowing effects observed for the MAS ^{13}C -NMR spectra of aromatics adsorbed on alumina and silica, described above, led us to investigate the MAS ^1H -NMR spectra of these samples in the hope that high-resolution could also be observed. The results shown in Fig. 5 amply demonstrate that this is, within certain limits, indeed the case.

Since silica yields a broadened ^1H -NMR signal from protons of residual OH groups, alumina, where such a signal is missing, was used exclusively as adsorbent in the present experiments. The line widths obtained are in the order of 60–120 Hz, and scalar homonuclear ^1H couplings are not resolved. The signal separation is, however, sufficient to allow a number of individual resonances to be distinguished, notably in cases where substituent effects introduce larger chemical shifts. Thus, as in solution, H–C(4) and H–C(5) of phenanthrene (**1**) are deshielded due to ring current and *van-der-Waals* effects, and the olefinic protons of coumarin are separated as a consequence of the charge-density difference at the respective C-atoms. An inversion recovery experiment for naphthalene resulted in $T_1(^1\text{H})$ values of 0.3 s which are comparable to the data obtained in solution.

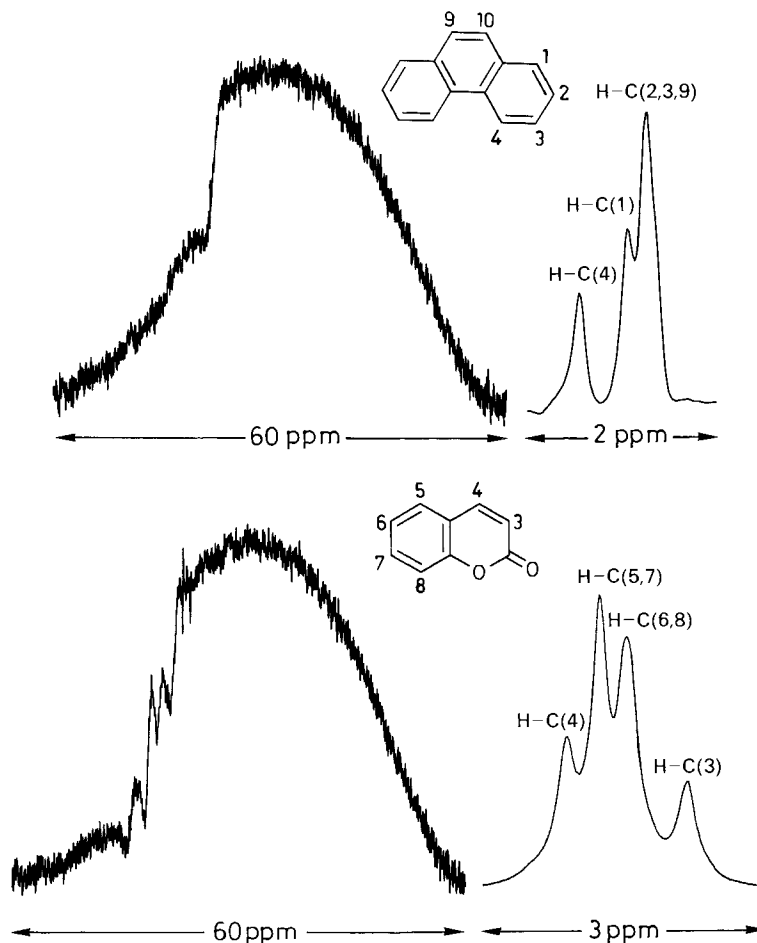


Fig. 5. 300-MHz MAS ¹H-NMR spectra of phenanthrene (above) and coumarin (below). Left side: pure solids, 32 transients; right side: adsorbed solids on Al₂O₃ (1:4 and 1:7, resp.) 8 transients; spinning rate 4 kHz. Note different ppm scales.

In some cases, improved resolution is obtained only at slightly elevated temperatures (320–350 K), as for adsorbed 7-ethoxycoumarin (**2**), where nearly all ¹H resonances are resolved in the ¹H-MAS spectrum. In contrast, for the pure solid, the ¹H-MAS spectrum remains unresolved.

Notwithstanding the broadened ¹H signals of the adsorbed materials, it is possible to perform experiments with 2D homonuclear pulse sequences known from liquid-phase NMR without modification. Thus, COSY spectra [12] were successfully recorded for **1** and **2**, in line with the observation that the COSY sequence yields cross peaks for scalar coupled protons even if the coupling is not resolved in the 1D spectrum [13] (Fig. 6).

Since it was demonstrated above that ¹H, ¹³C polarization-transfer experiments are possible for the adsorbed molecules, a test of the 2D ¹³C, ¹H-shift correlation [14] was of interest because of the importance of this experiment for spectral assignments. The results

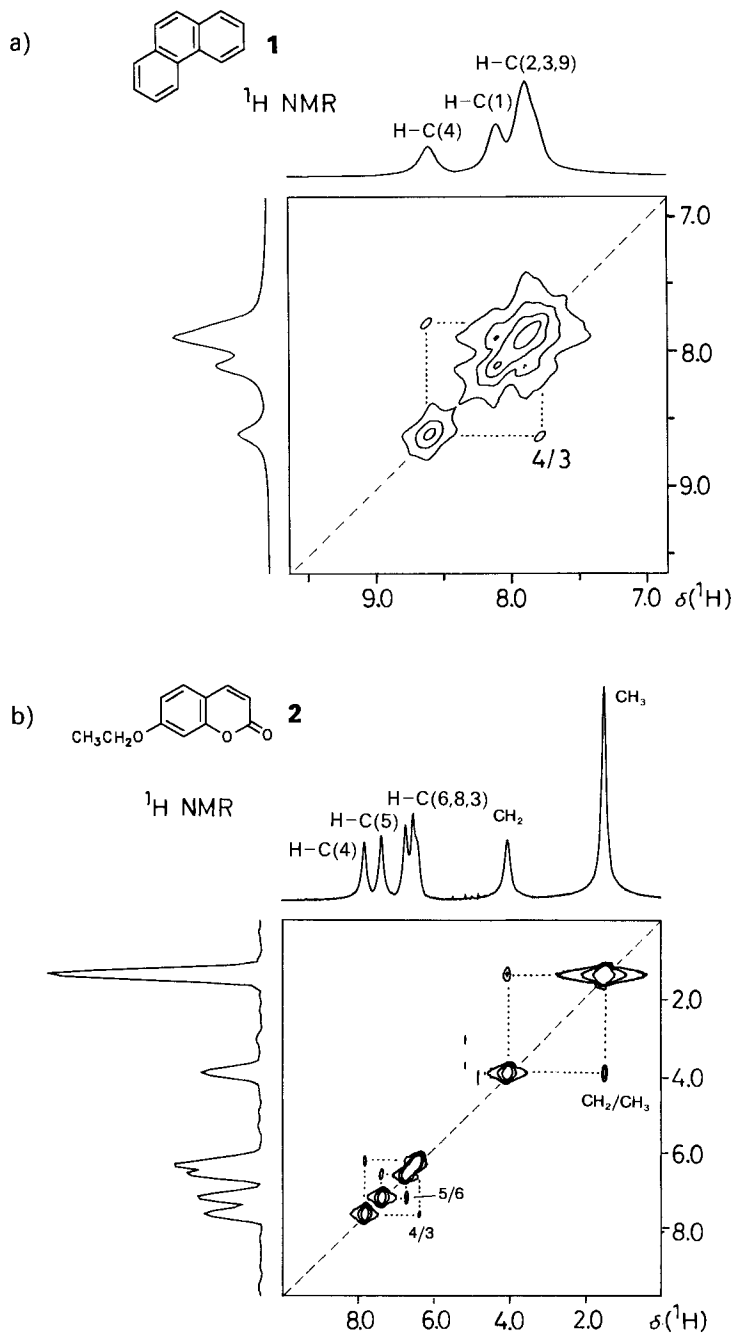


Fig. 6. 300-MHz $2D^1\text{H},^1\text{H}$ COSY spectra of phenanthrene (a) and 7-ethoxycoumarin (b) adsorbed on Al_2O_3 at 4-kHz spinning rate. Temp. 298 and 320 K, resp. Spectral parameters for (a)/(b): sweep width 2.5/2.5 kHz; 16/16 transients, 256/64 t_1 experiments, exp. time 6.3/0.8 h.

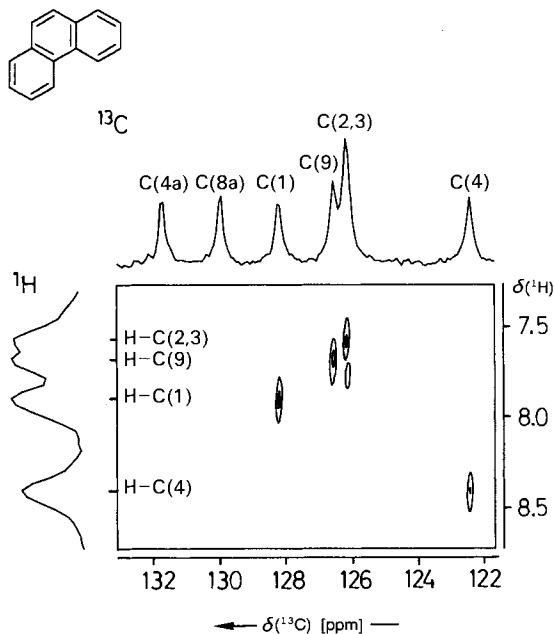


Fig. 7. 2D ^{13}C , ^1H -shift correlation for phenanthrene adsorbed on Al_2O_3 with homonuclear ^1H decoupling during t_1 ; [14d] cross peaks for CH groups; spinning rate 4 kHz. Spectral parameters: SW (F_1) = 4 kHz, SW (F_2) = 1360 Hz, 64 t_1 experiments, 32 scans each, mixing time 3.1 ms optimized for $^1J(^{13}\text{C}, ^1\text{H}) = 160$ Hz, exp. time 3.3 h.

for **1** shown in Fig. 7 demonstrate that this technique can indeed be used to correlate ^1H and ^{13}C spectra of adsorbed benzenoid solids. Similar results were obtained for **2** and other systems.

The experiments described show that the mobility of adsorbed organic materials can be high enough to allow, in addition to the ^{13}C experiments described above, even the application of solution ^1H -NMR techniques. This is of interest for structural investigations of products formed during catalytic processes on inorganic surfaces (see, e.g. [15]), but also for our understanding of adsorption phenomena.

While no detailed comparison of the ^1H and ^{13}C chemical shift data of the organic systems in the adsorbed state and in solution was attempted, the δ values obtained with the help of two reference compounds (*cf. Exper. Part*) showed, except for some ^1H lines, no significant differences when compared with the data of solution measurements.

The solids studied so far have melting points below 120° . For higher melting solids, like anthracene (m.p. 212°), only modest line narrowing effects have been observed until now, even at elevated temperatures (90°). Further work on these systems is in progress.

Experimental. – *Compounds.* The benzenoid compounds used were synthesized using standard procedures or purchased from Aldrich and purified, if necessary, by recrystallization. Purity was checked by soln. ^1H -NMR spectroscopy. The adsorbents alumina and silica (Merck, Darmstadt) were Al_2O_3 90 for column chromatography, 70–230 mesh ASTM, product No. 1077, and silica gel 60 for chromatography, 35–70 mesh ASTM, product No. 7733. For the NMR measurements, a ratio of 4:1 to 16:1 (w/w) for inorg. and org. solids was used.

Spectra. All spectra were recorded with a Bruker MSL 300 spectrometer, operating at a ^1H frequency of 300.13 MHz and a ^{13}C frequency of 75.5 MHz, using 4-kHz spinning speed, and 4-mm o.d. ZrO_2 rotors. Chemical shifts

were measured with respect to the spectrometer reference frequency which was calibrated for the ^1H spectra by the high-field signal of adsorbed naphthalene which was set to 7.3 ppm, for the ^{13}C spectra by the 38.4 ppm signal ($^{13}\text{CH}_2$ resonance) of adamantane as standard. The ^1H line widths were in the order of 60–120 Hz, ^{13}C line widths in the order of 5 to 10 Hz.

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