

CP/MAS ^{13}C NMR Study of Dianin's Compound [4-(*p*-Hydroxyphenyl)-2,2,4-trimethylchroman]Clathrates

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Abstract. Solid-state ^{13}C NMR spectra are reported for Dianin's compound [4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman] and its clathrates with acetic acid, ethanol, acetonitrile and octanoic acid. Some of the methyl carbon chemical shifts depend on the presence of guest molecules and are also sensitive to guest size. Methyl ^{13}C spin-lattice relaxation times, reflecting the methyl reorientational barrier heights, are also extremely sensitive to guest size.

Key words: Dianin's compound, ^{13}C NMR magic angle spectra, clathrate, carbon chemical shift

1. Introduction

Solid state NMR techniques such as cross-polarization [1] and magic angle spinning [2] are of special importance in the study of clathrates and other solid complexes, as traditional solution techniques cannot be employed. ^{13}C NMR spectroscopy is especially significant, as the nuclear shielding reflects not only chemical distinctions, but also crystallographic inequivalence in the unit cell. The importance of such effects was illustrated recently [3,4] in the case of quinol clathrates, where the empty α -quinol could easily be distinguished from the β -quinol clathrate structures.

In this contribution applications of ^{13}C NMR to the study of Dianin's compound [5] [4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman] clathrates are reported. For this clathrate [6,7,8], six molecules make up each hourglass-shaped cage. The ends of each cage are formed by six hydrogen-bonded hydroxyl groups, with alternate chroman molecules pointing up and down with respect to the plane of the hexagonal OH ring. The cages may hold two small molecules in the wide parts of the cage, or one larger guest.

As distinct from quinols, in which clathrates and the guest-free compound have different structures [9,10], full and empty Dianin's compound clathrate structures are the same [8], each belonging to space group $R\bar{3}$, with 18 molecules per unit cell.

2. Experimental Section

4-(*p*-Hydroxyphenyl)-2,2,4-trimethylchroman was prepared according to the method of Baker *et al.* [5]. The crude product was recrystallized from ethanol, the guest-free material resulting on vacuum sublimation. Clathrates were prepared by recrystallization of the chroman from the appropriate guest material.

^{13}C NMR spectra were obtained on Bruker CXP spectrometers operating at 45.3 or 50 MHz. A single, matched cross-polarization contact of 3 msec was used [1], the rf field amplitudes being 50 kHz. Up to 400 transients were added with spin-temperature alternation

on successive scans. Before Fourier transformation, 1600 pt-free induction decays obtained at a sweep width of 20 kHz were zero-filled to give 8 k datum points.

Sample spinning rates of 3.4 kHz were achieved by means of Kel-F rotors of the Andrew type. Spinning side bands in Figures 1 and 2 are starred.

Spin-lattice relaxation times were measured according to the technique proposed by Torchia [11], T_1 values being obtained from the slope of a log-amplitude vs time plot for the different spectral lines.

Dipolar dephasing [12] ($\tau = 40 \mu\text{sec}$) was used to obtain ^{13}C spectra of carbons coupled weakly to protons.

3. Results and Discussion

^{13}C NMR spectra obtained for Dianin's compound clathrates with several different guests, as well as that of the empty host lattice are shown in Figures 1 and 2. The asymmetric unit in the unit cell is one complete molecule [6] so that no more than 18 lines are expected and, indeed, for the ethanol and acetic acid (Figure 1,a,b,) clathrates all 18 lines are more or less resolved. The spectra for all of the clathrates and also the empty host lattice are very similar, as expected for identical structures with nearly the same lattice parameters [8].

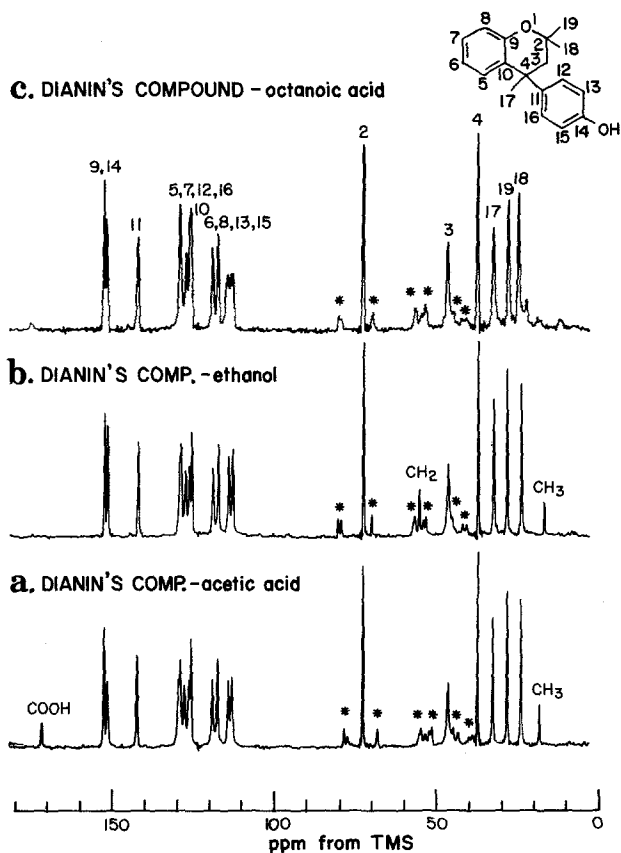


Fig. 1. CP/MAS ^{13}C NMR spectra of Dianin's compound clathrates with (a) acetic acid, (b) ethanol and (c) octanoic acid.

A complete assignment of all of the spectral lines is not possible, however with the aid of the dipolar dephasing technique, a partial assignment can be undertaken. Dipolar dephasing essentially eliminates spectral contributions from carbons strongly coupled to protons, leaving contributions from quaternary carbons and carbons coupled only weakly to protons because of averaging of dipolar interactions by molecular motions. Figure 2c shows such a spectrum obtained for the acetonitrile clathrate. The quaternary carbons appear with undiminished intensity as compared to the normal CP/MAS spectrum (Figure 2b) and may be assigned in a standard way. The methyl groups ($\text{C}_{17,18,19}$) appear with reduced intensity because of motional averaging by methyl group rotation. Guest molecule resonances also appear with undiminished intensity when the dipolar dephasing technique is used because the proton-carbon dipolar coupling is greatly reduced by extensive molecular reorientation. In the case of the acetonitrile clathrate, dipolar dephasing also reveals the cyano group carbon resonance at ~ 115 ppm (Figure 2c), hidden by host lattice lines in the normal CP/MAS spectrum (Figure 2b).

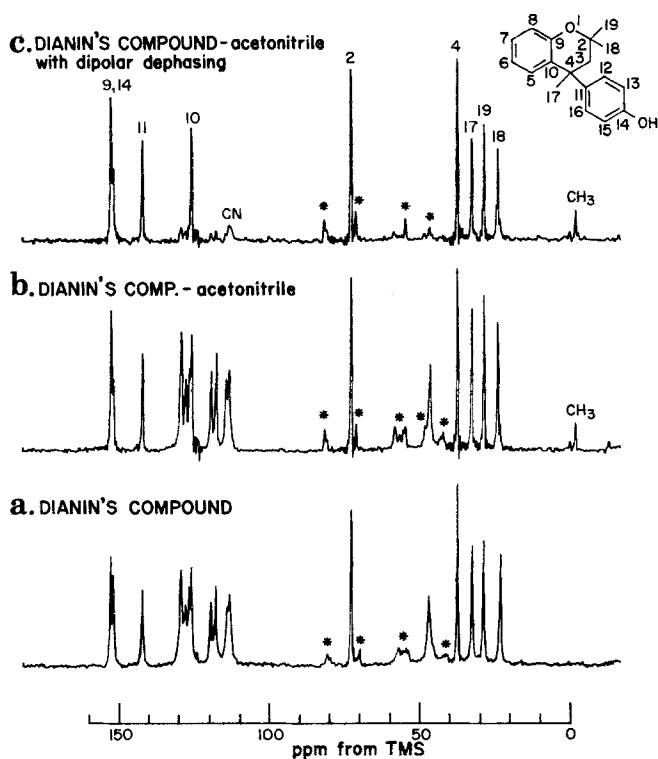


Fig. 2. CP/MAS ^{13}C NMR spectra of (a) Dianin's compound and the acetonitrile clathrate without (b) and with (c) dipolar dephasing.

By virtue of its nearness to two phenyl rings, the resonance line for the C_{17} methyl carbon can be assigned to the lowest field methyl carbon line. The resonances for the remaining two methyl groups are the lines in the spectrum most sensitive to the presence or absence of guest molecules, or guest molecule size (Table I). As it has been shown [8] that removal of the C_{18} methyl group markedly affects the van der Waals surface at the neck of the cage, the high-field methyl line, which is the single line most sensitive to guest size, is assigned to the C_{18} methyl group.

Table I. Chemical shift difference between the C_{18} and C_{19} ^{13}C NMR resonances

Guest	Chemical shift difference/ppm
None	5.6
Acetonitrile	4.7
Ethanol	4.5
Acetic acid	4.3
Octanoic acid	3.3

Spin-lattice relaxation time (T_1) measurements can be used to obtain information on dynamics in molecular systems. T_1 values, measured for selected carbons in the ethanol clathrate are given in Table II, and since the methyl group T_1 's proved to be the most interesting, the values are also reported for the guest-free material and the octanoic acid clathrate.

Table II. Spin-lattice relaxation times for selected ^{13}C resonance lines

Guest	T_1 /sec		
	Ethanol	Octanoic acid	None
<i>Carbon</i>			
C_{17} (Me)	0.17	0.13	0.14
C_{19} (Me)	0.91	0.52	0.78
C_{18} (Me)	0.50	0.33	0.42
C_4 (quat.)	20		
C_2 (quat.)	24		
C (arom.)	56		
C (arom., O subst.)	44		
CH_3 (guest)	14.5		
CH_2 (guest)	22		

The T_1 values obtained for two aromatic carbons of the ethanol clathrate (Table II) were quite long, 56 and 44 sec, and were typical of the chroman lattice carbon T_1 's in general. The absence of an efficient relaxation mechanism is in agreement with a relatively rigid structure where none of the ring carbons are engaged in large amplitude motions. Magnetization decays for the methyl-bearing quaternary carbons were distinctly non-exponential, the T_1 values reported being the apparent decay constant for delay times between ~ 10 and 50 sec. These two carbons are probably relaxed by dipolar interactions with the directly attached rapidly rotating methyl groups.

The T_1 values obtained for the ethanol guest carbons are also quite long. This, together with the insensitivity of the ethanol ^{13}C resonance lines to application of the dipolar dephasing technique, suggests that guest motions must be quite rapid ($\omega_0 \tau_c \ll 1$), as previously indicated by dielectric measurements [13]. The methyl group carbon T_1 's show considerable guest dependence and are relatively short and, hence, reflect an efficient dipolar relaxation mechanism due to rapid methyl group rotation. For the three materials in Table II, the motional correlation times vary in the order $\tau_c(C_{18}) < \tau_c(C_{19}) \ll \tau_c(C_{17})$. On assuming that

the fast motion limit obtains, the activation energies for methyl group rotation will vary in the same order $E_a(\text{C}_{18}) < E_a(\text{C}_{19}) \ll E_a(\text{C}_{17})$. C_{17} methyl motional parameters are little different for the three materials listed in Table II, the relatively high barrier to rotation probably arising from steric interactions with neighbouring phenyl rings. In case of the other two methyl groups, motional parameters are different by almost a factor of two for the ethanol and octanoic acid clathrates. C_{18} and C_{19} methyl group activation energies appear to be smallest for the ethanol clathrate. One possible explanation is that the most efficient packing (with minimum repulsive interactions for the methyl groups) results for the case of small guest molecules which do not occupy the neck of the hourglass-shaped cage. Less efficient packing for the methyl groups must then result either for an empty cage or for a cage where the neck is occupied, e.g., by a long molecule such as octanoic acid. It is relevant to point out that on going from the ethanol to the heptanol clathrate, the position of the C_{18} methyl was shifted 0.11 Å so as to enlarge the cavity [7].

If more structural data become available it may be possible to establish further correlations between the methyl carbon chemical shifts, T_1 's and structural differences.

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