

Clathrate and Inclusion Compounds. Part 12. Vibrational and NMR Spectroscopic Studies of Carboxylic Acid Guests in Dianin's Compound

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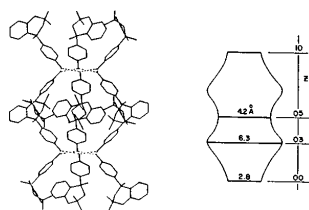
Abstract. Infrared, Raman and solid state ^{13}C -NMR spectra have been recorded for a range of clathrates of Dianin's compound containing straight chain aliphatic carboxylic acids (formic – octanoic) as guests. The IR, Raman and NMR spectra can be satisfactorily interpreted in terms of dimer (formic and acetic) and monomer (propionic – octanoic) occupation of the cavities. The clathrates containing straight chain alcohol guests (methanol – octanol) have also been prepared to aid in the interpretation of the NMR data.

Key words: IR spectroscopy, Raman spectroscopy, ^{13}C -MAS NMR spectroscopy, Dianin's compound, clathrates, carboxylic acids, alcohols.

1. Introduction

Dianin's compound (**1**) is a well known polymolecular host showing extremely versatile inclusion properties towards a wide range of guest molecules [1, 2]. The cavity is formed by hydrogen bonding between the OH groups of six molecules to give a hexameric structure with the molecules pointing alternately above and below this unit. Two of these arrangements come together to form the top and bottom of the cavity (Figure 1). The hourglass-shaped cavity is more spacious than that formed by β -quinol (**2**) and can consequently accommodate two small guest molecules [3]. The infrared (IR) spectra of the clathrates formed by formic, acetic and hexanoic acids were reported in 1965 but could not be fully explained in terms of monomeric and dimeric guest species [4]. The present paper reports a detailed study of the IR, Raman and solid state ^{13}C -NMR spectra of a series of clathrates containing the straight chain carboxylic acids formic to octanoic. An associated crystallographic study will be reported elsewhere [5]. The clathrates containing straight chain alcohol guests (methanol – octanol) have also been prepared to aid in the interpretation of the NMR data.

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Formulas

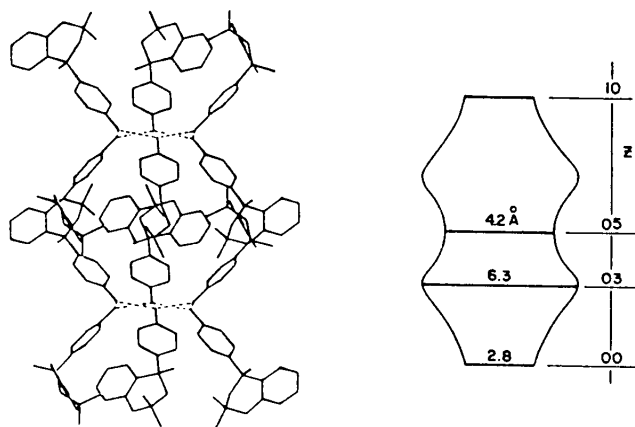


Figure 1. The structure and shape of the cavity in Dianin's compound. The cavity height is about 11 Å.

2. Experimental

2.1. CLATHRATE PREPARATION

Dianin's compound was prepared by the standard literature method [3] and characterized from its melting point and $^1\text{H-NMR}$ spectrum (solution in $\text{DMSO-}d_6$). The clathrates were prepared by recrystallising Dianin's compound from the neat liquid acid or alcohol. The solids were filtered and dried thoroughly in a desiccator before use.

2.2. CHARACTERIZATION TECHNIQUES

2.2.1. Chemical Analysis

The host-guest ratios of the samples were obtained using three methods.

Titrimetric analysis. About 0.5 g of the clathrate was dissolved in 50 mL ethanol and the liberated acid titrated with 0.02 M NaOH. Blank analysis was performed using 50 mL ethanol.

Thermal analysis. About 0.3 g of the clathrate was heated on an oil bath to 190 °C and the weight loss determined. For the high boiling point acids the sample tube was evacuated. IR spectroscopy was used to check that all the guest had been liberated on heating. Blank analysis was performed using Dianin's compound alone.

Elemental analysis. Performed using a Carlo-Erba 1106 Analyser.

2.2.2. IR and Raman Spectroscopy

IR spectra of liquids and KBr discs (4000–200 cm^{-1}) were recorded on a Nicolet MX-10 FT spectrometer and transformed at 2 cm^{-1} resolution. Low temperature IR spectra of KBr discs were obtained using a Beckman VLT-2 variable temperature accessory. The Raman spectra were recorded using Ar^+ 514.5 nm excitation (Spectra Physics 164 laser) on a Cary 81 spectrometer modified as detailed elsewhere [6].

2.2.3. NMR Spectroscopy

The CP ^{13}C solid state NMR spectra were recorded on a Varian VXR spectrometer operating at 75.43 MHz at the University of Durham. Depending on the sample the spinning rate was 3–5 kHz and the number of acquisitions varied between 50 and 1000. Liquid and solution phase spectra were recorded on a JEOL FX-100 FT NMR spectrometer operating at 25.05 MHz.

3. Results and Discussion

3.1. HOST–GUEST RATIOS

Table I summarises the host-guest ratios obtained using the different analytical techniques. The discrepancies between the results from the different techniques confirm a previous report of the difficulty of obtaining consistent analytical results [7]. The host-guest ratios vary from 2.6 : 1 to 6.8 : 1 on going from the formic to the octanoic acid clathrate. As six molecules of Dianin's compound participate in the formation of one cavity the ratios for the formic and acetic acid clathrates are close to the value of 3 : 1 required for dimer occupation of the cavities. The values for the propionic, butyric, valeric and hexanoic acids are inconclusive as they lie in the range 3.9–5.2 and could be interpreted as being due to < 100% occupancy of cavities by dimers, although the cavity dimensions shown in Figure 1 point clearly to the fact that there is insufficient room for dimers of valeric and hexanoic acids. The value of 6.1 : 1 obtained for heptanoic acid indicates monomer occupancy, whilst the value of 6.8 : 1 obtained for octanoic acid indicates < 100% occupancy of cavities by monomer.

Table I. Host-guest ratios for the carboxylic acid clathrates.

Guest	Titrimetry	CHN analysis	Thermal analysis	Mean value
Formic acid	2.7	2.5	2.5	2.6
Acetic acid	2.7	2.5	2.6	2.6
<i>n</i> -Propionic acid	4.4	4.7	4.2	4.4
<i>n</i> -Butyric acid	3.6	3.9	4.3	3.9
<i>n</i> -Valeric acid	4.6	5.1	4.9	4.9
<i>n</i> -Hexanoic acid	4.6	5.6	5.4	5.2
<i>n</i> -Heptanoic acid	5.9	6.3	6.0	6.1
<i>n</i> -Octanoic acid	6.9	7.1	6.3	6.8

3.2. IR AND RAMAN SPECTRA

The IR and Raman spectra of Dianin's compound consist of a multitude of bands [8]. There is, however, a convenient window in which the carbonyl band of the acid guests can be observed.

3.2.1. Guest Carbonyl Bands

Figures 2 and 3 illustrate the IR spectra of the carbonyl bands of the acid guest molecules recorded at room temperature and at 93 K respectively. The centrosymmetric formic acid dimer would give symmetric and asymmetric CO₂ stretching modes having Raman and IR activity respectively. This mutual exclusion of IR and Raman bands could be destroyed when the dimer is placed in the cavity in Dianin's compound.

The IR spectrum of the formic acid clathrate at room temperature gives a peak at 1727 with a shoulder at 1742 cm⁻¹. The formic acid guest in the quinol host, where there is monomer occupation of the cavity, gives a band at 1747 cm⁻¹. The spectrum observed for the Dianin clathrate could thus be interpreted as arising from a mixture of monomer and dimer occupation of the cavities. The analytical data, however, clearly require dimer occupation of cavities and the crystallographic data [5] support this conclusion by showing dimer occupation with the two acid molecules hydrogen bonded across the waist of the cavity. The spectrum is thus interpreted as arising from a dimer species with the 1742 cm⁻¹ band arising from the symmetric stretching mode becoming IR active as a result of the distortion of the dimer in the cavity.

The IR spectrum of the acetic acid clathrate, where the two components have a greater separation, is interpreted in a similar fashion. Support for assigning the 1762 cm⁻¹ band to the normally IR inactive but Raman active mode comes from the Raman spectrum of the clathrate. Although the carbonyl bands are weak, spectral accumulation showed the presence of two Raman bands at 1720 and 1762 cm⁻¹,

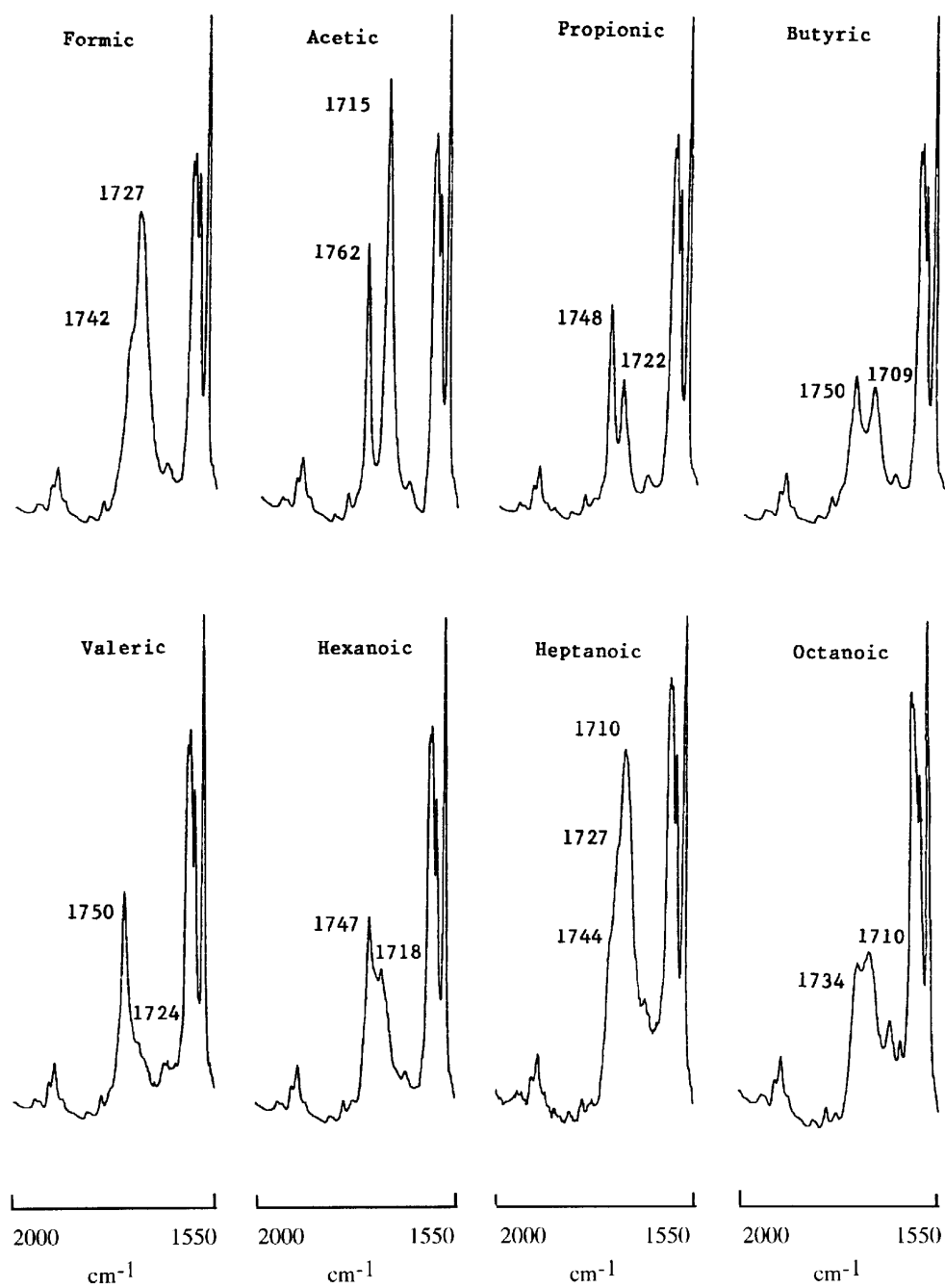


Figure 2. IR spectra (1550–2000 cm^{-1}) recorded at room temperature of the carboxylic acid clathrates formed by Dianin's compound.

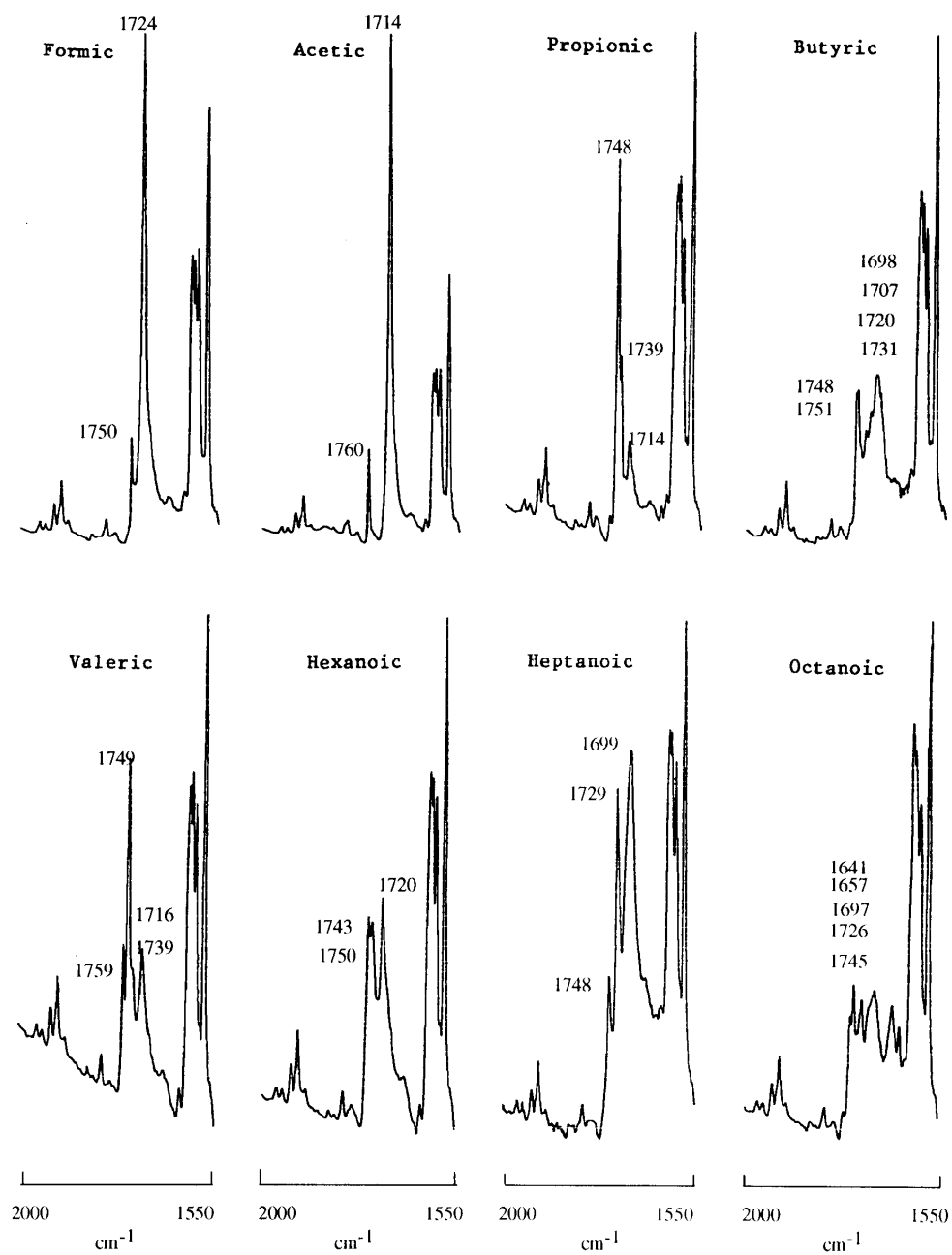


Figure 3. IR spectra ($1550\text{--}2000\text{ cm}^{-1}$) recorded at 93 K of the carboxylic acid clathrates formed by Dianin's compound.

with the 1762 cm^{-1} band being the more intense. The crystallographic study also showed hydrogen bonded dimers in the cavity [5]. The low temperature IR spectra of these two clathrates (Figure 3) support the above interpretation of the room temperature spectra. The bands sharpen up considerably with the lower cm^{-1} band increasing significantly in intensity, indicating a smaller distortion of the dimers due to the lower thermal motions of the host atoms.

The room temperature IR spectra of the clathrates of propionic, butyric, valeric and hexanoic acids are similar in that they display two bands of varying relative intensity but with the *higher* wavenumber band being the more intense (Figure 2). The Raman spectra of these clathrates were very weak and bands could only be observed for the propionic and valeric acid samples. In both cases the observed Raman band corresponded to the higher wavenumber value IR band. The analytical data for these clathrates were inconclusive but the crystallographic data show a monomer occupation of the cavities. These clathrates thus have a strong *host-guest* interaction involving the carboxylic acid group, replacing the hydrogen bonding *guest-guest* interaction in the formic and acetic acid clathrates. The two IR bands are thus assigned as arising from the carbonyl group of the monomer guest species either interacting with the cyclic hydrogen bonded OH hexamer at the base of the cavity, giving the lower wavenumber band, or pointing away from the base, giving the higher wavenumber band. The analytical data for the heptanoic and octanoic acid clathrates clearly indicate monomer occupancy which is confirmed by the crystallographic study. In both of these clathrates the more intense band is the lower wavenumber band, significantly so in the case of the heptanoic acid clathrate. The main effect of cooling the samples is to improve the resolution of the spectra. The intensity of the higher wavenumber band does increase in the spectra of the propionic and valeric acid clathrates suggesting that at low temperature the more stable arrangement is with the carbonyl group pointing away from the host OH groups.

3.2.2. O—H Stretching Bands

The O—H stretching mode of Dianin's compound gives a strong IR band at 3298 cm^{-1} . The effect of the guest molecule on the position of this band depends on both the size and the arrangement of the guest within the cavity.

The clathrates of formic, acetic and trifluoroacetic acid contain dimeric guest species. The band moves from 3298 to 3326 to 3348 cm^{-1} on going across this series, indicating a weakening of the hydrogen bond in the host hexameric unit. This correlates well with the O...O separation which increases from 2.831 to 2.907 to 2.958 \AA on going from the formic to the trifluoroacetic acid clathrate [5].

The remaining clathrates contain a single guest molecule per cavity with a guest-host interaction involving the carboxylic acid group and the hexameric unit. The shift in the host O—H band lies in the range $+9$ to $+30\text{ cm}^{-1}$ for the propionic

to hexanoic acid clathrates. The IR spectra in the carbonyl region were interpreted on the basis that the main host-guest interaction was via the guest O—H group. For the heptanoic and octanoic acid clathrates the spectra suggested that the main interaction involved the guest C=O group. This stronger interaction would weaken the hexameric O—H hydrogen bonds and this is reflected in the larger shifts of the host O—H band (+79 and +87 cm^{-1} respectively) together with an increased O...O separation (3.004 Å for the octanoic acid clathrate). No bands which could definitely be assigned to the guest O—H modes were observed.

3.3. SOLID STATE ^{13}C -NMR SPECTRA

Solid state NMR spectroscopy is a powerful analytical technique which, unlike X-ray crystallography, does not require single crystals. It has been applied to a wide range of host-guest systems [9]. The chemical shift values of the guest resonances, some of which have been reported previously [10], are given in Table II.

3.3.1. *Guest Carbonyl Resonances*

The value for the formic acid guest (161.1 ppm) can be compared to the corresponding values for this molecule in the quinol host (159.5 ppm) [10] and for the neat liquid (167.0 ppm). The increase in the chemical shift value on going from the quinol clathrate to Dianin's clathrate reflects the different configurations in the two clathrates (monomer in quinol, dimer in Dianin). The difference (Δ) between the liquid and guest values for acetic acid (5.3 ppm) is similar to that for formic acid (5.9 ppm), both of which exist as dimers in the Dianin cavity.

The difference between the liquid phase and guest values are very much higher for the remaining acids. These all have a monomer occupancy of the cavity with the *guest-guest* interaction of the formic and acetic clathrates being replaced by a *guest-host* interaction. The value decreases progressively from 10.0 ppm for propionic acid to 4.3 ppm (average) for octanoic acid. This decrease correlates well with the decreasing separation between the carboxylic acid O atom and the O atom of the hexameric unit as observed in the crystallographic study [5]. Both the crystallographic and NMR studies indicate an increasing host-guest interaction with increasing size of the guest. The observation of two components for the C=O resonances of valeric, hexanoic, heptanoic and octanoic acids reinforces the conclusion from the IR study of two possible host-guest interactions involving the host hexameric unit with either the C=O or the O—H group of the carboxylic acid.

3.3.2. *Guest Alkyl Resonances*

Most of the resonances of the guest alkyl groups were observed and are listed in Table II. The CH_3 and CH_3CH_2 resonances of valeric, hexanoic, heptanoic and octanoic acid guests consist of two components, again suggesting that there are two orientations for the guest. The Δ values for the CH_3CH_2 resonances of heptanoic

Table II. ^{13}C chemical shift values, relative to TMS, for the guest resonances.

Guest	C=O	Alkyl chain
Formic acid	161.1 (a, 167.0)	
	Δ -5.9	
Methanol		48.8 (49.3)
	Δ	-0.5
Acetic acid	173.4 (177.2, 178.7)	20.5 (20.5)
	Δ -5.3	0.0
Ethanol		18.7, 57.3 (17.9, 57.3)
	Δ	0.8, 0.0
<i>n</i> -Propionic acid	172.0 (180.4, 182.0)	7.6, b (8.6, 27.2)
	Δ -10.0	-1.0, b
1-Propanol		10.9, 24.7, 64.4 (10.3, 26.1, 63.9)
	Δ	0.6, -1.4, 0.5
<i>n</i> -Butyric acid	170.5 (179.7, 181.0)	11.7, 18.5, b (13.5, 17.9, 35.7)
	Δ -9.5	-1.8, 0.6, b
1-Butanol		10.9/11.4, 18.7, 35.4, 62.6 (13.9, 19.4, 35.3, 61.7)
	Δ	-3.0/-2.5, -0.7, 0.1, 0.9
<i>n</i> -Valeric acid	170.9/171.4 (179.8, 180.9)	13.5/13.8, 22.5, 27.8, 33.2 (13.6, 22.0, 26.5, 33.6)
	Δ -10.0, -9.5	-0.1/0.2, 0.5, 1.3, -0.4
1-Pentanol		13.4, 22.3, 28.3, b, 63.1 (14.1, 22.9, 28.5, 32.8, 62.1)
	Δ	-0.7, -0.6, -0.2, b, 1.0
<i>n</i> -Hexanoic acid	172.3/173.8 (179.8, 180.9)	14.6/15.4, 22.6/23.0, 25.2, 31.6, 33.5 (13.8, 22.1, 24.1, 31.1, 33.8)
	Δ -8.6, -7.1	0.8/1.6, 0.5/0.9, 1.1, 0.5, -0.3
1-Hexanol		15.0, 22.6, 31.7/32.0, 25.4, 32.9/33.3, 63.1 (14.5, 23.1, 32.3, 26.1, 33.1, 62.2)
	Δ	0.5, -0.5, -0.6/-0.3, -0.7, -0.2/0.2, 0.9
<i>n</i> -Heptanoic acid	173.8/176.9 (179.8, 180.8)	13.9/14.3, 20.6/21.6, 24.4/24.9, b, 32.0, 32.8 (13.9, 22.3, 24.3, 28.6, 31.3, 33.9)
	Δ -7.0, -3.9	0/0.4, -1.7/-0.7, 0.1/0.6, b, 0.7, -1.1

Table II. Continued

Guest	C=O	Alkyl chain
1-Heptanol		14.5/14.8, 21.5/22.1, 30.9/31.8, 27.7, 25.2, b, 62.8 (14.2, 23.1, 32.4, 29.7, 26.4, 33.2, 62.2)
	Δ	0.3/0.6, -1.6/-1.0, -1.5/-0.6, -2.0, -1.2, b, 0.6
<i>n</i> -Octanoic acid	175.9/176.9 (179.8, 180.7)	13.3/14.0, 19.7/20.7, 24.1/25.5, b, 32.5, b (13.9, 22.4, 24.4, 28.9, 31.5, 33.8)
	Δ	-4.8, -3.8
1-Octanol		-0.6/0.1, -2.7/-1.7, -0.3/1.1, b, 1.0, b 13.5/14.1, sh/21.3, b, b, b, 24.2/sh, b, 61.9 (14.2, 23.1, 32.4, 29.9, 30.0, 26.4, 33.2, 62.2)
	Δ	-0.7/-0.1, sh/-1.8, b, b, b, -1.8/sh, b, -0.3

Values in parentheses: C=O shift – 5% solution in CCl₄ and the neat liquid respectively.

^a Formic acid is insoluble at this concentration.

Alkyl chain shifts – 5% solution in CCl₄ (acids). – neat liquids (alcohols) [15].

^b Guest band obscured by host band. Δ values: C=O values: guest-liquid values

alkyl chain values: guest-solution values (acids). guest-liquid values (alcohols).

sh: shoulder present on band whose chemical shift value could not be determined.

and octanoic acid show significant upfield shifts supporting the crystallographic conclusion that the end methyl group has a gauche conformation. As these Δ values are not as large as those observed previously for the guest octane molecule [11] they were compared with the values for the straight chain alcohol guests (Table II). The Δ values for guest 1-heptanol are similar to those of guest heptanoic acid. As many of the guest 1-octanol lines are obscured by host lattice lines no definite comparison can be made. It is instructive to compare the chemical shift values for the CH₃CH₂CH₂ resonances of the C5–C8 straight chain hydrocarbons [11], acids and alcohols as guests in Dianin's compound. These will be determined by the conformation of the molecule and the location of the carbon atom in the cavity. The hydrocarbons are only subject to van der Waals interactions and will consequently adopt a minimum free energy conformation and location. The acid and alcohol guest molecules display host–guest interactions involving one end of the molecule. As there are no large differences between the chemical shift values of these three classes of guest molecules it appears that the host–guest interaction present in the acid and alcohol clathrates does not have a significant influence on the location of the carbon atoms.

3.3.3. Host Resonances

The waist in the cavity is formed by the protrusion of methyl groups 18 and 19 (**1**) and the ¹³C shifts of these two carbons have been found to be sensitive to the size of the guest [12]. The chemical shift difference between these two resonances for a range of carboxylic acid and alcohol clathrates is given in Table III. There is a sharp change in the difference value on going from the 3-carbon (4.5) to

Table III. Chemical shift difference (ppm) between the C18 and C19 ^{13}C -NMR resonances.

Guest	Value	Guest	Value
None	5.6	None	5.6
Formic acid	4.6	Methanol	5.1
Acetic acid	4.3	Ethanol	4.5
Trifluoroacetic	4.5		
<i>n</i> -Propionic acid	4.5	1-Propanol	4.4
<i>n</i> -Butyric acid	3.6	1-Butanol	3.5
Iso-butyric acid	3.9	2-Butanol	3.6
<i>n</i> -Valeric acid	3.5	1-Pentanol	3.3
<i>n</i> -Hexanoic acid	3.4	1-Hexanol	3.3
<i>n</i> -Heptanoic acid	3.2	1-Heptanol	3.3
<i>n</i> -Octanoic acid	3.2	1-Octanol	3.5

the 4-carbon (3.6) guest in both the acid and alcohol series. The only reported crystal structures for alcohol guests are those for the ethanol [13] and heptanol [14] guests. The former contains dimeric species and the latter monomeric guest species as for the corresponding acid guests. Although no crystallographic data have been reported for the propanol clathrate analytical data have been interpreted in terms of dimer occupation [3, 7]. It should be recognised that the analysis of the propionic acid clathrate also suggested dimer occupation whereas the crystallographic data showed monomer occupancy. Thus for the acid clathrates, and also possibly for the alcohol clathrates, the abrupt change in the C18,C19 chemical shift difference does not correspond with the change from dimeric to monomeric guest but simply reflects the change in size of the guest molecule. Values of both 3.4 and 4.0 have been reported for the clathrate with α -cyclohexylacetophenone (**3**), the different values indicating two non-equivalent inclusion sites [16].

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