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An X-ray diffraction study of partially ordered electron density in clathrates of Dianin's compound that include simple carboxylic acids

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The nature of the inclusions in ten clathrate complexes of Dianin's compound have been investigated by the use of electron-density difference maps. The guest species are the first eight straight-chain carboxylic acids, formic to octanoic, a branched-chain acid (dimethylacetic acid) and trifluoroacetic acid. The point-group symmetry of the clathrate cavity, $\bar{3}$, is satisfied by partial occupation of symmetry-related sites by two included molecules in the case of formic, acetic and trifluoroacetic acids and by a single molecule in the remainder. Hydrogen-bonding requirements in the case of formic and acetic acids are satisfied by dimer formation; in the trifluoroacetic acid complex the two acid molecules form hydrogen bonds to framework O atoms at either end of the cavity. The adoption of *gauche* conformations in heptanoic and octanoic acid chains shortens them sufficiently that they fit the cavity with only slight distortion.

1. Introduction

Dianin's compound (DIN) is a well established cage-forming host that gives clathrate compounds with a wide range of guest molecules. The structural characteristics of the series were first established by Flippen *et al.* (1970) and Flippen & Karle (1971). Their crystallographic investigations indicated a β-quinol type cage system in space group $R\bar{3}$ with cavities that are bounded by six host molecules, where each host molecule is shared by two cavities. These cavities were described as hour-glass shaped with the axis aligned along the trigonal c axis. The length of the cavity is 11.0 Å, with a waist diameter of 4.2 Å at $z = 0.5$ and a greatest diameter of 6.2 Å at $z = 0.3$ and 0.7. The ends of the cavity are closed by a ring of six $\mathrm{O{-}H}\cdots\mathrm{O}^{\mathrm{i}}$ (i: $x - y, x, z$) hydrogen bonds. The cage so formed is larger than the more familiar β-quinol structure, which differs by having molecules hydrogen bonded at both ends. In Dianin's compound (DIN) the six larger molecules are hydrogen bonded (three up and three down) at only one end, the lower ends being simply enmeshed. In the structures reported by the earlier workers the host network was able to enclose such diverse guests as heptanol (one molecule per cavity), ethanol (two molecules per cavity) or chloroform (two molecules per cavity). The trigonal spacegroup $R\bar{3}$ requires that the cavity has $\bar{3}$ symmetry, which implies that a single unsymmetrical guest molecule be statistically sixfold disordered.

An extensive spectroscopic investigation of the clathrates formed by Dianin's compound and a series of carboxylic acids (formic to octanoic) has already been reported (Davies &

Tabner, 1997). The investigation described here is concerned with the crystallographic aspects of this series of clathrates.

2. The scope of the investigation

The preparation of Dianin's compound was described by Davies & Tabner (1997). The complexes were readily obtained by simple recrystallization from the appropriate guest acids, all of which were liquids at or near 293 K.

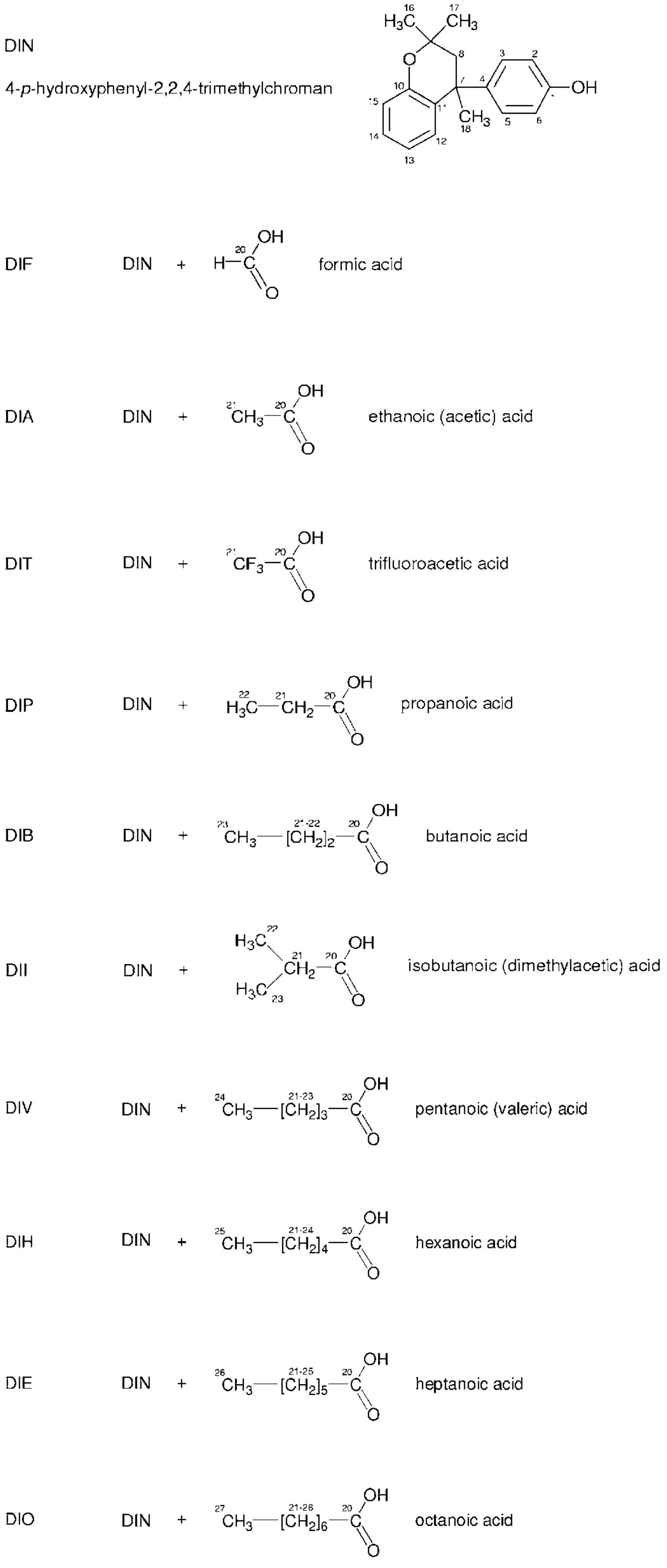
In addition to crystals containing the straight-chain acids (formic to octanoic), it was possible to prepare crystals containing the branched-chain isobutyric acid (dimethylacetic acid). Attempts were then made, unsuccessfully, to prepare the complex with pivalic (trimethylacetic) acid, which is a solid at room temperature (melting point 308.3 K), by using a solution of Dianin's compound in the molten acid. A further attempt, which used stoichiometric amounts of the host and guest in carbon tetrachloride solution, yielded only the carbon tetrachloride clathrate. It was concluded that the breadth of the pivalic acid molecule was incompatible with the shape of the Dianin cavity.

In view of the interest in this laboratory in the trifluoroacetate group (Gleghorn & Small, 1995) small crystals of the clathrate from trifluoroacetic acid solution were grown and included in the investigation.

In all, ten such complexes were crystallized. We will refer to them by code names according to the scheme below.

3. Experimental

The colourless crystals of all of the clathrate complexes were small (0.4–0.8 mm long) and all possessed the same thin acicular hexagonal prismatic habit. The largest available crystal of each complex was selected for intensity data collection.[1] A Stoë Stadi-2 two-circle diffractometer was used with the **c** direction of each crystal aligned with the diffractometer ω axis. An identical counting procedure, which involved variable ω scans with 2θ fixed, was followed for each crystal, and the same set of layer-line standard reflections and counting times was used for each compound. A useful estimate of the relative sizes of the crystals used was provided by comparison of the intensities of the zero-layer standard reflection, (330). These values are recorded in Table 1 and show a factor of five in size between the largest and smallest crystals used (Small, 1977). Intensity data for the complex with pentanoic (valeric) acid, DIV, was collected first. The structure of the host network was confirmed with the direct-methods program *MULTAN*87 (Debaerdemaeker *et al.*, 1987), which gave DIN coordinates equivalent to those reported by the original workers (Flippen *et al.*, 1970). At the same time, using the experimental data for DIV and a theoretical structure containing only DIN, a difference map showed a distinct region of ordered electron density, presumably the result of the valeric acid solvent interacting with the host molecules or neighbouring guests.



In view of the wide range of sizes and shapes of the possible entrapped acid species, a fuller investigation that used a more extended system appeared justified. For convenience of comparison and in the interest of consistency, the atomic DIN

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0059). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	DIF	DIA	DIP	DIB	DIV
Crystal data					
Chemical formula	$3(C_{18}H_{20}O_2)\cdot(CH_2O_2)$	$3(C_{18}H_{20}O_2)\cdot(C_2H_4O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_3H_6O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_4H_8O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_5H_{10}O_2)$
M_r	851.01	865.14	1683.1	1698.3	1712.3
Cell setting, space group	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$
a, b, c (Å)	27.19 (2), 27.19 (2), 11.02 (10)	27.19 (2), 27.19 (2), 11.06 (10)	27.24 (2), 27.24 (2), 10.96 (10)	27.26 (2), 27.26 (2), 11.00 (10)	27.21 (2), 27.21 (2), 10.930 (10)
V (Å^3)	7056 (10)	7081 (10)	7043 (10)	7079 (10)	7008 (10)
Z	6	6	3	3	3
D_x (Mg m^{-3})	1.202	1.216	1.187	1.189	1.210
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	15	15	15	15	15
θ range (°)	5–25	5–22.5	5–22.5	5–25	5–25
μ (mm^{-1})	0.08	0.08	0.08	0.08	0.08
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Acicular, hexagonal prism, colourless	Acicular, hexagonal prism, colourless	Acicular, hexagonal prism, colourless	Acicular, hexagonal prism, colourless	Acicular, hexagonal prism, colourless
Crystal size (mm)	0.6 × 0.2 × 0.2	0.5 × 0.15 × 0.15	0.5 × 0.15 × 0.15	0.6 × 0.20 × 0.20	0.6 × 0.2 × 0.2
Host:guest	3	3	6	6	6
Data collection					
Diffractometer	Stoë Stadi-2 two-circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer
Data collection method	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane.	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan$2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane.
Absorption correction	None	None	None	None	None
No. of measured, independent and observed parameters	4175, 1572, 1285	4483, 1535, 1165	4108, 1555, 1211	4683, 1659, 1376	4214, 1535, 1244
Criterion for observed reflections	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$
$R_{\rm int}$	0.080	0.047	0.056	0.018	0.084
$\theta_{\rm max}$ (°)	22.5	22.5	22.5	22.5	22.5
Range of h, k, l	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$
Standard (330) counts	112397	60284	63637	113870	96165
Refinement					
Refinement on	F	F	F	F	F
$R[F^2 > 4\sigma(F)]$ (including guest), $wR(F)$, S	0.052, 0.082, 1.15	0.064, 0.082, 1.45	0.061, 0.092, 1.23	0.053, 0.052, 1.08	0.070, 0.053, 1.55
R (host only)	0.091	0.122	0.092	0.097	0.099
No. of reflections	1285	1165	1211	1376	1244
No. of parameters	215	215	215	215	215
H-atom treatment	See text	See text	See text	See text	See text
Weighting scheme	$w = 1/(\sigma^2F + 0.00018F^2)$	$w = 1/(\sigma^2F + 0.0002F^2)$	$w = 1/(\sigma^2F + 0.00015F^2)$	$w = 1/(\sigma^2F + 0.000097)$	$w = 1/(\sigma^2F + 0.000091F^2)$
$(\Delta/\sigma)_{\rm max}$	0.01	0.002	0.001	0.001	0.001
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (including guest) (e Å^{-3})	0.27, −0.15	0.42, −0.38	0.33, −0.19	0.27, −0.15	0.40, −0.18
$\Delta\rho$ (host only) (e Å^{-3})	2.00	2.23	2.21	1.88	2.50
O1···O1 (Å)	2.820 (11)	2.905 (11)	2.852 (11)	2.826 (6)	2.838 (11)

	DII	DIH	DIE	DIO	DIT
Crystal data					
Chemical formula	$6(C_{18}H_{20}O_2)\cdot(C_4H_8O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_6H_{12}O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_7H_{14}O_2)$	$6(C_{18}H_{20}O_2)\cdot(C_8H_{16}O_2)$	$3(C_{18}H_{20}O_2)\cdot(C_2F_3O_2)$
M_r	1698.3	1726.3	1740.3	1754.4	919.02
Cell setting, space group	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$	Trigonal, $R\bar{3}$
a, b, c (Å)	27.13 (2), 27.13 (2), 10.97 (10)	27.28 (2), 27.28 (2), 10.98 (10)	27.30 (2), 27.30 (2), 11.07 (10)	27.30 (2), 27.30 (2), 11.20 (10)	27.19 (2), 27.19 (2), 11.10 (10)

Table 1 (continued)

	DII	DIH	DIE	DIO	DIT
V (Å^3)	6993 (10)	7077 (10)	7145 (10)	7229 (10)	7105 (10)
Z	3	3	3	3	6
D_x (Mg m^{-3})	1.204	1.207	1.204	1.198	1.287
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	15	15	15	15	15
θ range (°)	5–25	5–25	5–25	5–25	5–22.5
μ (mm^{-1})	0.08	0.08	0.08	0.08	0.09
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Acicular, hexagonal prism, colourless	Acicular,hexagonal prism, colourless	Acicular,hexagonal prism, colourless	Acicular, hexagonal prism, colourless	Acicular, hexagonal prism, colourless
Crystal size (mm)	0.80 × 0.25 × 0.25	0.6 × 0.2 × 0.2	0.6 × 0.2 × 0.2	0.5 × 0.15 × 0.15	0.40 × 0.12 × 0.12
Host:guest	6	6	6	6	3
Data collection					
Diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer	Stoë Stadi-2 two circle diffractometer
Data collection method	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane	Variable ω scan $2\theta'$ fixed, where θ' is the projection of θ on the equatorial plane
Absorption correction	None	None	None	None	None
No. of measured, independent and observed parameters	4376, 1594, 1353	4423, 1582, 1249	4458, 1626, 1350	4242, 1588, 1037	4176, 1521, 1013
Criterion for observed reflections	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$
$R_{\rm int}$	0.075	0.083	0.053	0.043	0.109
$\theta_{\rm max}$ (°)	22.5	22.5	22.5	22.5	22.5
Range of h, k, l	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-26 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$-26 \rightarrow h \rightarrow 26$ $-25 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$
Standard (330) counts	297166	105748	124190	41582	35495
Refinement					
Refinement on	F	F	F	F	F
$R[F^2 > 4\sigma(F)]$ (including guest), $wR(F)$, S	0.066, 0.057, 1.23	0.076, 0.055, 1.14	0.058, 0.058, 1.28	0.094, 0.085, 1.28	0.091, 0.083, 1.81
R (host only)	0.084	0.101	0.102	0.130	0.157
No. of reflections	1353	1249	1350	1037	1013
No. of parameters	215	215	215	215	215
H-atom treatment	See text	See text	See text	See text	See text
Weighting scheme	$w = 1/(\sigma^2F + 0.001F^2)$	$w = 1/(\sigma^2F + 0.000077F^2)$	$w = 1/(\sigma^2F + 0.00012F^2)$	$w = 1/(\sigma^2F + 0.00016F^2)$	$w = 1/(\sigma^2F + 0.00019F^2)$
$(\Delta/\sigma)_{\rm max}$	0.002	<0.001	0.001	<0.001	0.001
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (including guest) (e Å^{-3})	0.68, −0.28	0.30, −0.16	0.45, −0.27	0.52, −0.28	0.58, −0.32
$\Delta\rho$ (host only) (e Å^{-3})	2.76	2.08	1.58	1.23	1.53
O1···O1 (Å)	2.841 (11)	2.911 (11)	2.957 (11)	3.02 (2)	2.92 (2)

† Computer programs: Stoë Stadi-2; *SMALL* (Small, 1977); *MULTAN*87 (Debaerdemaeker *et al.*, 1987); *SHELX*76 (Sheldrick, 1976); *SNOOPI* (Davies, 1983); *PLATON* (Spek, 2003).

coordinates of Flippen *et al.* (1970) were adopted as the starting point for each structure refinement, thereby implying the selection of the same set of unit-cell directions; in particular, the positive direction of **c** is defined. When a crystal is being mounted on the two-circle diffractometer there are no means of identifying whether the positive or negative direction of **c** is aligned with the ω axis. The ambiguity was resolved for each crystal after it had been mounted by comparison of the relative magnitudes of the intensities of the reflections $-17\ 13\ 0$ and $-13\ 17\ 0$, which are related by symmetry in position but are quite different in intensity. The matrix transformation

$$\begin{matrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{matrix}$$

was then applied to the indices where appropriate to make the data sets consistent with the selected axial set.

4. Interpretation

*SHELX*76, which is most suited to deal with experimental data from a Weissenberg diffractometer, was used for the refinement. In order to check that no advantage would result from using the more recent routines of *SHELXL*97 (Sheldrick, 1997), three of the data sets (for DIA, DIH and DIO) were reformatted and data-reduction routines were written to make them compatible with the requirements of *SHELXL*97. The two methods gave very similar results to the rigid-body refinement of the symmetrical disorder, and the results reported here are those of *SHELX*76.

For each compound the parameters of the DIN molecule alone were refined. The refinement started with the values of Flippen *et al.* (1970) and used the collected F data. The initial R values, which at this stage were large, are included in Table 1. ΔF maps in the form of sections parallel to (100) and (001) were calculated using *SHELX*76 (Sheldrick, 1976). These sections were suitable for producing contour maps with a routine *CONTOUR* provided by Glazer (1988). A selection of the difference maps are shown in Figs. 1(*a*)–10(*a*). These contour maps vary considerably in appearance and contain definite features that are attributable to the particular guest molecules included. A discussion of the individual maps will follow later, but note that the symmetry of the difference electron density will be that implied by the space group, *i.e.* $\bar{3}$ symmetry. It follows that if the cavity holds one complete molecule it will appear in six orientations, each with one-sixth occupation. Inevitably there will be considerable overlap of the guest-atom positions, and the consequent disorder renders normal refinement of the atom coordinates impossible. When a possible interpretation of the electron density had been proposed a rigid-body model of the included guest molecule was set up by defining a sufficient number of interatomic distances using a set of *DFIX* instructions in *SHELX*76 (Sheldrick, 1976). Alternate refinement of the DIN host molecule and the rigid guest molecule then gave a significant improvement in the residual R. The DIN parameters usually converged rapidly, while the rigid guest parameters tended to drift as would be expected from the shallow nature of the residual electron-density maxima. Usually two or three refinement cycles of the rigid-body parameters gave an initial improvement of R and a perceptible reduction of the difference electron density.

This improvement in the R values was accompanied by a decrease in the level of the residual electron density; the electron-density distribution in the cavities eventually becomes low and featureless. This behaviour is illustrated by Figs. 1(*b*)–10(*b*), which are juxtaposed with the original difference maps and give an indication of the success in explaining the electron density.

Treatment of the site occupation factors of the guest atoms posed a difficult problem. Ideally, knowledge of the stoichiometric composition of the crystal actually used is required, and this composition is not necessarily identical to the overall composition of a batch measured by a method such as density determination. Furthermore, densities are difficult to determine for these compounds because of continual interchange of guest solvent and flotation liquid. On account of the large correlation of temperature and site occupation factors, refinement of both simultaneously was inadvisable. Accordingly the problem was circumvented by fixing site occupation factors at the ideal value, *i.e.* 1/3 or 1/6, and allowing the temperature factors to account for site occupation and positional disorder in addition to thermal effects. It should be stressed that the main evidence for the structures proposed lies in the general appearance of the electron-density difference maps together with the improved agreement achieved after the inclusion of the scattering that is attributed to the included guest molecule. Least-squares refinement of the atomic parameters of the included acids is not feasible because of overlap of the disordered positions.

5. Interpretation of the difference maps

It is impractical to show all the contour maps for reasons of space: some are shown as Figs. 1–10, and Table 1 includes the greatest residual electron density when the guest molecules are omitted and included. Depending on the size and shape of the guest molecules the structures can be interpreted in terms of a limited number of possibilities.

5.1. Formic and acetic acids

An obvious feature of the electron-density plots of these two acids compared with the longer-chained members of the series lies in the minimal electron density at the centre of the cavity (Figs. 1 and 2). This behaviour is consistent with the formation of conventional centrosymmetric hydrogen-bonded dimers, which requires only threefold rotational disorder to fulfil the space-group symmetry requirement. The contours at $y = 0.0$ indicate that the COOH groups lie fairly close to that plane. In the case of formic acid the electron-density features are more diffuse than in the acetic acid complex as the smaller dimer leaves more space for disorder within the cavity. This type of structure requires a host:guest ratio of 3:1 for full occupation of the cavities. In both of these acids the inclusion of H atoms in the included model further improved the R value. However, no comparable improvement in the case of the more complex acid adducts was found and H atoms are omitted from all other models.

5.2. Propionic, butyric, valeric and hexanoic acids

The residual electron density for these complexes before the guest molecules are included is in the form of a ridge along the axis of the cavity (Figs. 3–6). Dimers of these acids, even of propionic acid, would be too long to fit into the cavity. Instead the electron density from a single molecule is seen spread along the whole length of the cavity. This ridge of electron density is of about the same length irrespective of the acid chain length. This agrees with a model having one O atom of the COOH group near the axis of the cavity and hydrogen-bonded to the hexagon of DIN OH groups which link the cage together; the other O atom projects sideways, *i.e.* away from the axis into the widest part of the hour-glass-shaped cavity. This interpretation is supported by the presence of a limb of electron density in the region $z = 0.75$–0.8 for these acids (Figs. 3–7). The width of the electron-density ridge appears to indicate that these acids are present as straight chains, with the

C and O atoms in one plane. The dimensions are such that only one guest molecule can occupy each cavity, *i.e.* the ideal host:guest ratio is 6:1.

5.3. Dimethylacetic (isobutanoic) acid

Unlike the *n*-butyric acid molecule, in which the C and O atoms are coplanar, dimethylacetic acid can have a number of conformations, none of which is planar. The most satisfactory fit, which has a much broadened electron-density distribution (Fig. 7), featured a molecule with the terminal C atoms equally staggered on the same side of the plane of the carboxyl group; otherwise the structure is similar to that in DIP, DIB, DIV and DIO.

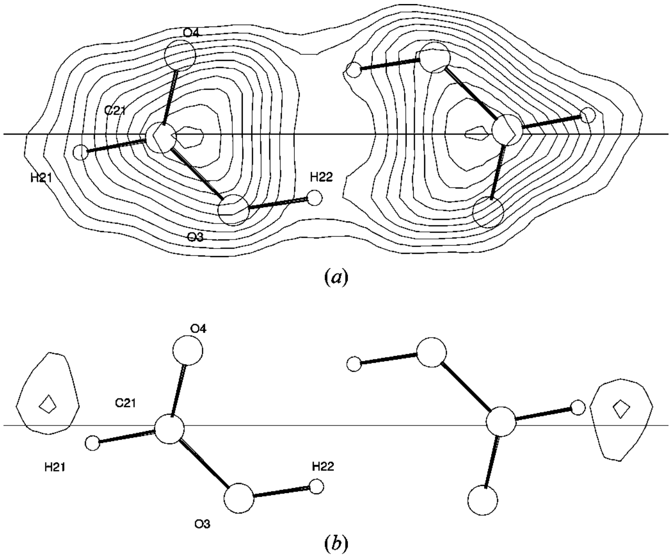

Figure 1
(*a*) DIF model including DIN atoms only. (*b*) DIF model including DIN and included acid. This figure and all other figures shown here are on the same scale and show the same region of each unit cell on (100) defined by $x = -0.10$ to 0.14 and $z = 0.0$ to 1.0 (horizontal). For all figures, the lowest residual electron density contour is at 0.2 e Å^{-3} and the increments are 0.2 e Å^{-3}. The residual electron density contours are from $F_o - F_c$ Fouriers where F_c is for the appropriate refined model. Superimposed on each contour map is a projection, using *SNOOPI* (Davies, 1983), of the included acid model. For clarity only one guest molecule (or pair of molecules in the case of DIF, DIA and DIT) is shown. The full contents of the cavity require the operation of the threefold axis.

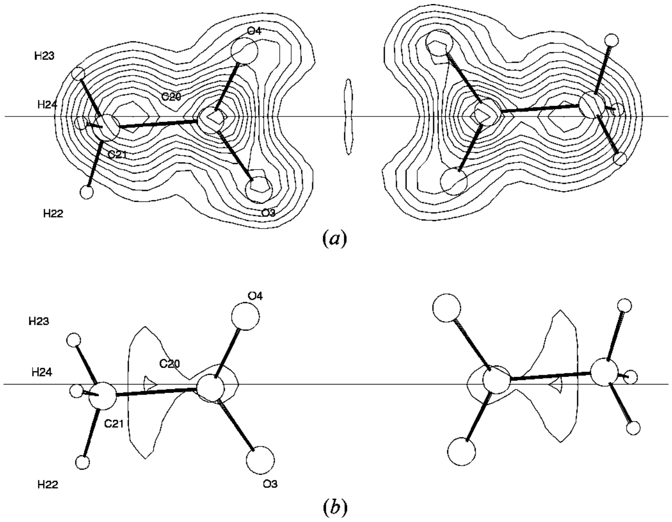

Figure 2
(*a*) DIA model including DIN atoms only. (*b*) DIA model including DIN and included acid. See Fig. 1 for details.

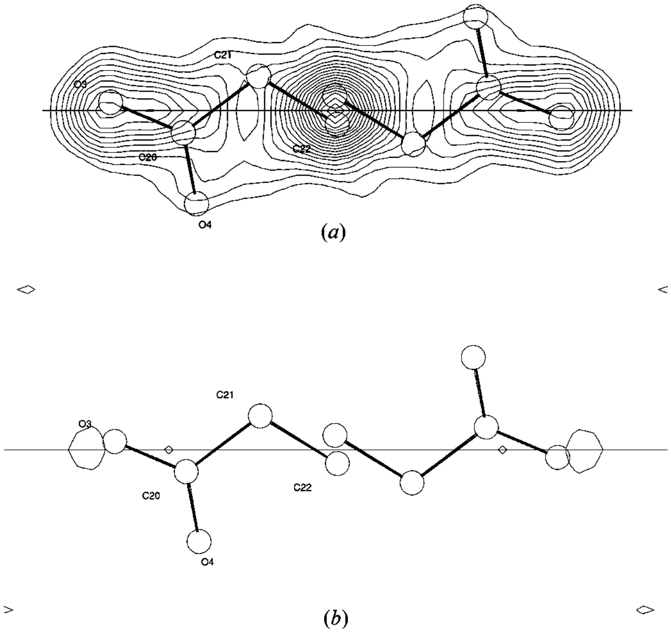

Figure 3
(*a*) DIP model including DIN atoms only. (*b*) DIP model including DIN and included acid. See Fig. 1 for details.

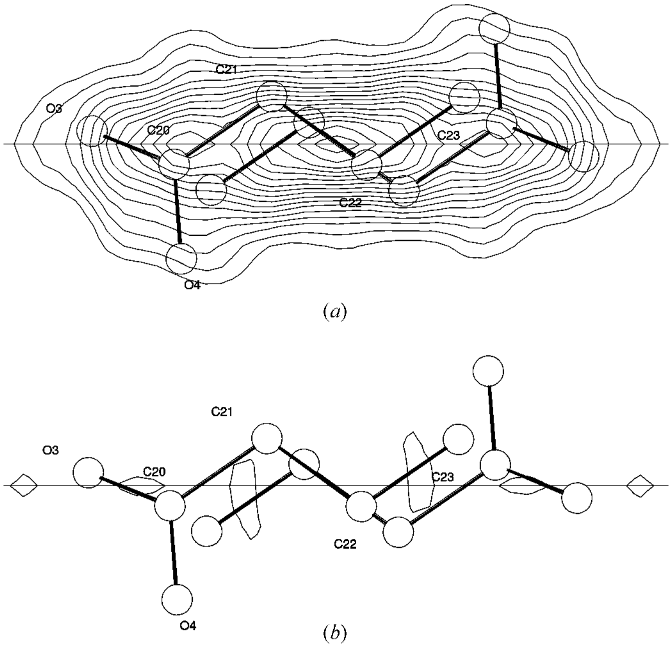

Figure 4
(*a*) DIB model including DIN atoms only. (*b*) DIB model including DIN and included acid. See Fig. 1 for details.

5.4. Heptanoic and octanoic acids

The size of the cavity formed by the hydrogen-bonded dianin molecules was estimated by Flippen *et al.* (1970) to be 11 Å long with a greatest width of 6.2 Å. The validity of this estimate was verified with the routine *VOIDS* within *PLATON* (Speck, 2003). There is clearly a limit to the length of the molecule that can be accommodated in this cavity. For the fully extended straight-chain acids the limiting chain length is six, *i.e.* hexanoic acid. However, Flippen & Karle (1971) reported the structure of the adduct with *n*-heptanol, which they deduced must contain two *gauche* conformation linkages, one at each end of the molecule. This type of conformation has the effect of folding the molecule so that it becomes shorter and wider. For a fully extended straight chain the most stable conformation is that with all C atoms in a plane. It has been estimated (*e.g.* Morawetz, 1965) that the *gauche* conformation involves an energy of only 4 kJ greater than that of the planar conformation; the increase in intramolecular conformational energy may be offset during clathrate formation by favourable hydrogen bonding. The electron-density difference maps (Figs. 8 and 9) for the present heptanoic and octanoic acid adducts both show a broadened ridge that extends along the length of the cavity, which indicates folded conformations. For heptanoic acid it was possible to construct a model that produced a satisfactory reduction of the residual electron density and the agreement index; this model includes one *gauche* conformation, between C atoms C24 and C25. For octanoic acid the preferred model has two *gauche* linkages, between C21 and C22 and between C25 and C26; this model also reduced the residual electron density and the *R* value, although the latter was still rather high. In both of these cases the carboxyl groups are positioned to interact with the OH of the DIN framework.

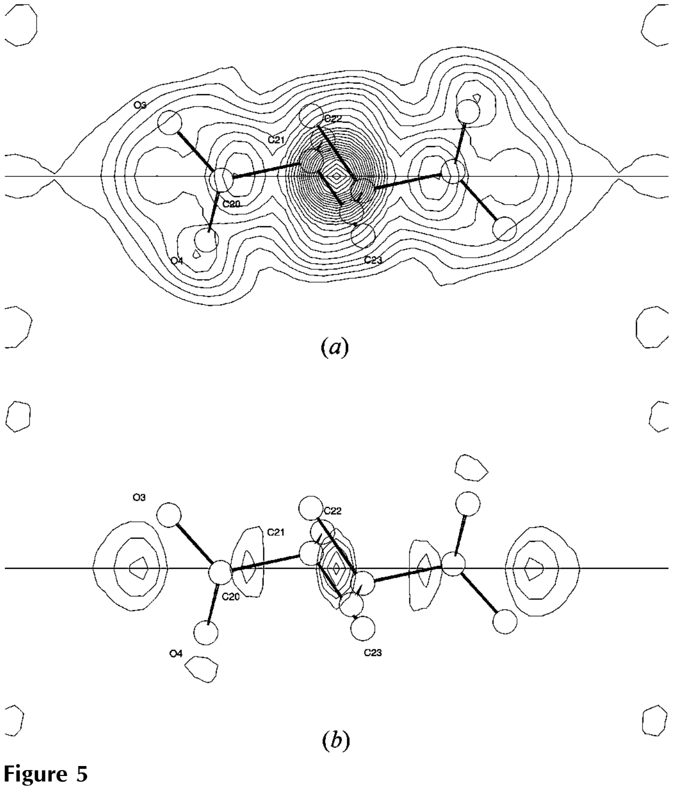

Figure 5
(*a*) DII model including DIN atoms only. (*b*) DII model including DIN and included acid. See Fig. 1 for details.

5.5. Trifluoroacetic acid

At first sight the relatively low electron density at the centre of the cavity (Fig. 10) suggested the presence of an acid dimer that is comparable to acetic acid. Fuller investigation showed that with bulkier F atoms such a model would be too large for the cavity. The alternative arrangement, which is comparable to DIP, DIB, DIV, DIO and DII, gave a more plausible structure in which the acid carboxyl groups interact with the

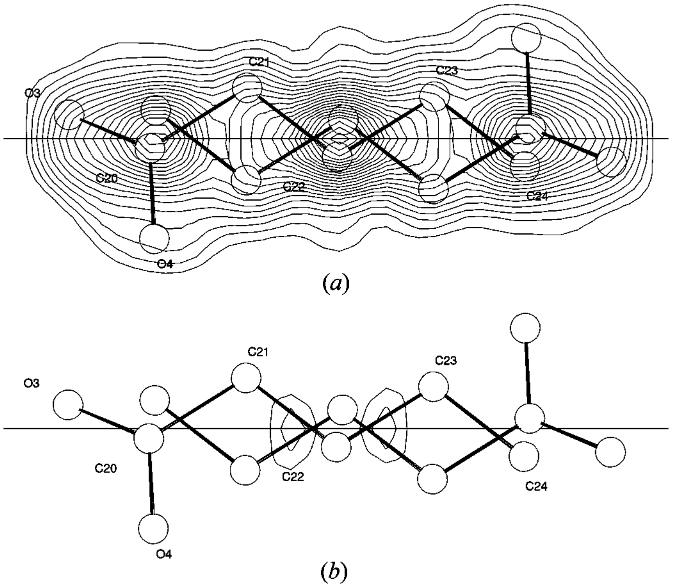

Figure 6
(*a*) DIV model including DIN atoms only. (*b*) DIV model including DIN and included acid. See Fig. 1 for details.

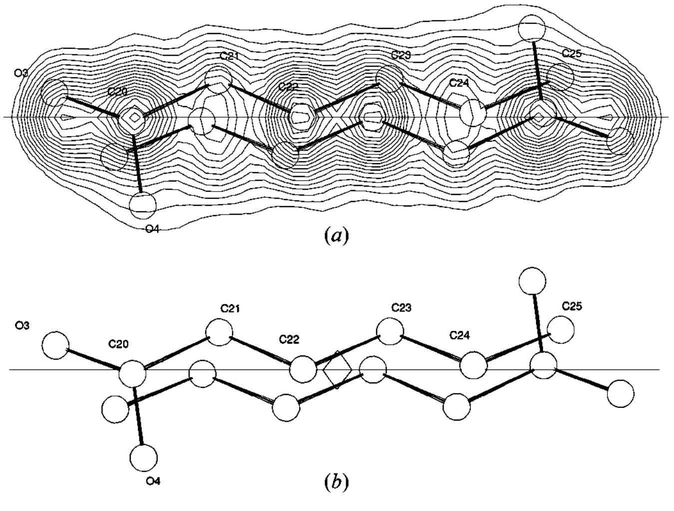

Figure 7
(*a*) DIH model including DIN atoms only. (*b*) DIH model including DIN and included acid. See Fig. 1 for details.

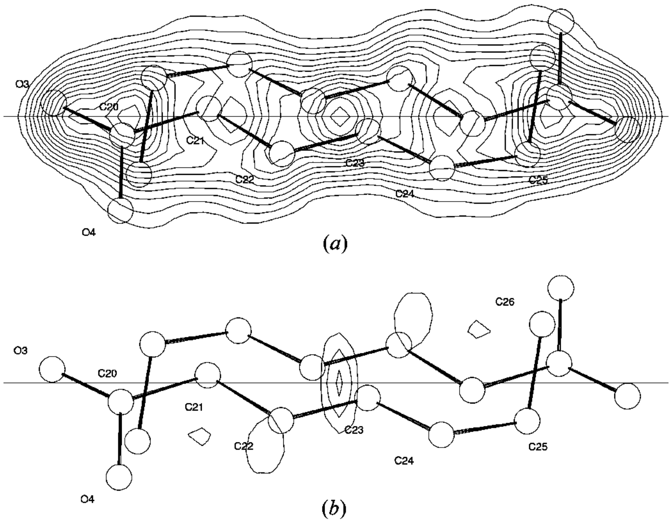

Figure 8
(*a*) DIE model including DIN atoms only. (*b*) DIE model including DIN and included acid. See Fig. 1 for details.

terminal ring of O—H···O hydrogen-bonded host groups. At the same time the shortness of the acid molecules allowed two of them to occupy opposite ends of the cavity simultaneously, thus giving a host:guest ratio of 3:1.

6. General effects on the Dianin framework

Intramolecular distances within the Dianin moiety are not significantly affected by the nature or size of the included guest molecules: the mean values of the interatomic distances over the series conform with the expected values. A significant increase in the intermolecular O1···O1^{i} (i: y, $-x+y$, $-z$) hydrogen-bond distances can be noted as strain develops from the inclusion of larger included species. The unstrained O1···O1^{i} distance appears to be 2.82–2.85 Å; increasingly larger values can be explained in terms of greater stress from larger guest molecules (Table 1). It is clear that hydrogen-bonding effects, which arise from the carboxyl groups, combined with the elongated shape of the clathrate cavity can produce partial ordering of guest molecules within these compounds.

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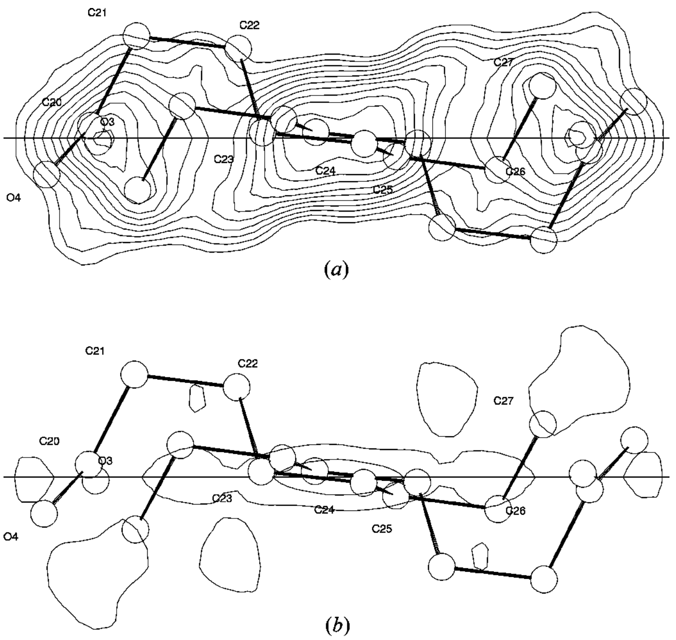

Figure 9
(*a*) DIO model including DIN atoms only. (*b*) DIO model including DIN and included acid. See Fig. 1 for details.

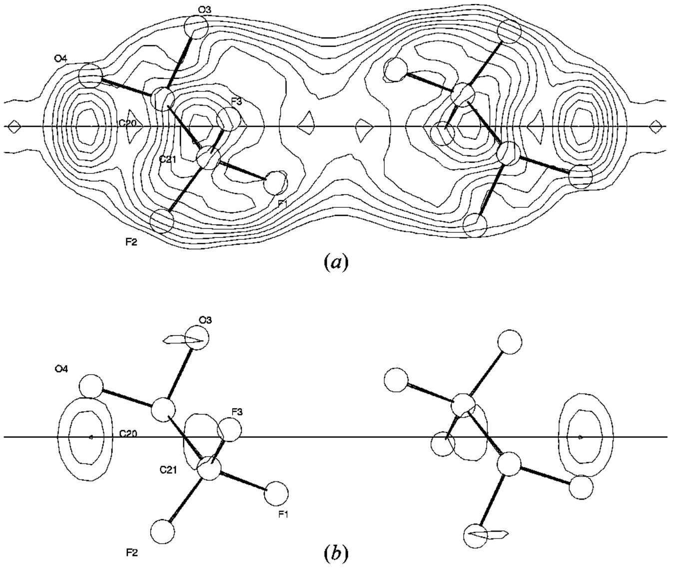

Figure 10
(*a*) DIT model including DIN atoms only. (*b*) DIT model including DIN and included acid. See Fig. 1 for details.

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