Ritter Reactions. VI. Crystal Structure of a New Multicyclic Hydroxy Amide Clathrate

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Abstract. The compound 9-benzamido-6,7,8,9,10,11-hexahydro-5,9 : 7,11-dimethano-5*H*-benzocyclononen-7-ol, **3**, has been prepared, and found to crystallise as inclusion complexes (**3**)$_2$·G where the guest G is ethyl acetate or carbon tetrachloride. The host molecule contains a benzo group as part of a rigid polycyclic framework, on which there are hydroxy and benzamido substituents. The crystal structure of the complex with CCl$_4$ contains the host molecules hydrogen-bonded in layers, with the CCl$_4$ molecules trapped between the layers. Two types of host–host hydrogen bonds, OH to amide carbonyl O, and amide NH to hydroxyl O, maintain the host layers. The benzo groups protrude normal to these host layers, and six such groups provide the closest surroundings of the CCl$_4$, which is constrained to two disordered orientations at the one location. This is a layer clathrate structure.

1. Introduction

As part of our recent work [1] on synthetic applications of the Ritter reaction [2] we have described the interesting behaviour of 11-methylene-5,6,8,9-tetrahydro-5,9-propano-7*H*-benzocyclohepten-7-one **1** [3]. This keto olefin undergoes efficient intramolecular cyclization and Ritter reaction in a one-flask procedure providing good yields of multicyclic hydroxy amides such as **2** and **3** or, under more vigorous conditions, bis(amide) products like **4** (see Figure 1). Alternatively, mixed bis(amide) products can be produced from the hydroxy amides if a separate, second Ritter reaction is employed [4].

A notable characteristic of some of these multicyclic amides is their tendency to participate in co-crystallization phenomena. For example the bis(acetamide) compound **4** is normally isolated as its monohydrate, which crystallizes in the centrosymmetric space group $P2_1/c$. This structure is built up from hydrogen bonded dimeric units of the bis(amide) surrounded by six water molecules which participate in three different hydrogen bonded arrangements [4]. The present study describes the entirely different inclusion behaviour shown by the hydroxy amide **3** when crystallized from ethyl acetate or carbon tetrachloride.
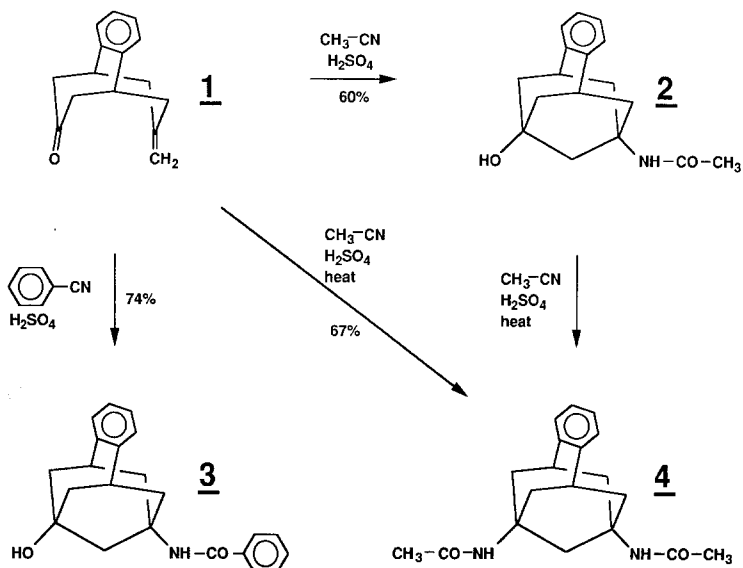
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Fig. 1. Synthetic scheme.

2. Experimental

2.1. PREPARATIVE WORK

Melting points were determined on a Kofler instrument and are uncorrected. NMR data were recorded with a Bruker AM-500 instrument (125.8 MHz for ^{13}C) and are reported as chemical shifts (δ) relative to tetramethylsilane. Substitution of carbon atoms was determined by the DEPT procedure. The IR spectra were recorded on a Hitachi 260-10 spectrophotometer. Elemental analyses were carried out at The University of New South Wales by Dr H. P. Pham.

9-Benzamido-6,7,8,9,10,11-hexahydro-5,9 : 7,11-dimethano-
5H-benzocyclonen-7-ol **3**

The keto olefin **1** [3] and benzonitrile were reacted in the presence of concentrated sulfuric acid as previously described [4], and the crude product chromatographed on activated type H alumina to remove unreacted benzonitrile and small amounts of bis(amide) material. Elution with ethyl acetate gave fractions containing the hydroxy amide **3**. Removal of solvent using a rotary evaporator and warm water bath afforded pure **3**, m.p. 171–172°C; lit. [4] m.p. 169–170°C. (Found: C, 79.04; H, 6.77; N, 4.27. $C_{22}H_{23}NO_2$ requires C, 79.25; H, 6.95; N, 4.20%). ν_{max} (paraffin mull) 3375s, 3320s, 3070w, 3020w, 1655s, 1630s, 1600w, 1575m, 1540s, 1510m, 1490m, 1300m, 1270m, 1100m, 1035m, 905w, 865w, 760s cm^{-1}, ^{13}C NMR δ [$(CD_3)_2SO$] 166.5 (C), 146.2 (C) 136.2 (C), 131.1 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 126.6 (CH), 69.4 (C), 56.8 (C), 48.7 (CH$_2$), 43.0 (CH$_2$), 39.8 (CH), 38.3 (CH$_2$).

Inclusion compound $(3)_2 \cdot C_4H_8O_2$

Crystallization of **3** from ethyl acetate gave an inclusion compound which partly melted over 120–125°C (approximately) with loss of guest, then resolidified, and finally melted as 171–172°C. [Found: C, 76.36; H, 7.19; N, 4.13. $(C_{22}H_{23}NO_2)_2 \cdot C_4H_8O_2$ requires C, 76.36; H, 7.21; N, 3.71%]. ν_{max} (paraffin mull) 3480s, 3440s, 3275s, 3060w, 1710s, 1640s, 1545s, 1490m, 1265s, 1150m, 1100m, 1045m, 1030s, 935w, 910w, 870w, 805w, 770s cm^{-1}. The inclusion compound was stable at room temperature. On heating in a drying pistol at *ca.* 100°C for 5 days the guest ethyl acetate had been lost and the IR spectrum had reverted to that of pure **3**.

Inclusion compound $(3)_2 \cdot CCl_4$

Crystallization of **3** from carbon tetrachloride gave an inclusion compound which partly melted over 110–125°C with loss of guest, resolidified, and finally melted at 169–170°C. [Found: C, 65.36, H, 6.23, N, 3.38. $(C_{22}H_{23}NO_2)_2 \cdot CCl_4$ requires C, 65.86; H, 5.65; N, 3.41%]. ν_{max} (paraffin mull) 3450s, 3370m, 3320s, 3065w, 1645s, 1605w, 1585m, 1535s, 1490m, 1310m, 1265m, 1100m, 1085w, 1040m, 990w, 905w, 865w, 785s, 765s, 750s, 710m, 685m cm^{-1}. The inclusion compound was stable at room temperature.

2.2. X-RAY DATA COLLECTION, PROCESSING, AND REFINEMENT FOR THE STRUCTURE $(3)_2 \cdot CCl_4$

Crystallization of the pure hydroxy amide **3** from ethyl acetate or carbon tetrachloride (but not benzene) resulted in formation of inclusion compounds with the formula $(3)_2 \cdot G$ (G ≡ guest) indicated by combustion analysis data.

Intensity data were recorded for a single crystal of $(3)_2 \cdot CCl_4$ using a Nonius CAD4 X-ray diffractometer. The crystal structure was solved by a combination of direct methods (program MULTAN) and Fourier syntheses. The asymmetric unit contained two molecules (labelled A and B) of the hydroxy amide and a single carbon tetrachloride molecule. Block diagonal least squares refinement (program BLOCKLS) included anomalous dispersion corrections for Cl. Hydrogen atoms were included in calculated positions (except those on the hydroxyl groups, which were omitted), with isotropic temperature factors equal to those of the atoms to which they were bound. All non-hydrogen atoms were assigned anisotropic temperature factors. Refinement converged with $R = 0.12$. It was clear that there was disorder associated with the CCl_4 molecule. Rigid body least squares (program RAELS) was used to complete the refinement of the structure. Two independent CCl_4 molecules were included with occupancies whose sum was constrained to be 1 (final values of the occupancies were 0.688(2) and 0.312). Each CCl_4 molecule was constrained to perfect T_d symmetry, with refinable size, orientation and location. A TLX model was used to describe the thermal motion of each CCl_4 with the centre of libration fixed at the position of its C atom. The refined C—Cl distance was 1.734(1) Å. Hydroxyl H atoms were located in a difference Fourier synthesis and were included in the final refinement. The final residual R was 0.066. A summary of data collection parameters is given in Table I.

Table I. Numerical details of the solution and refinement of structure of $(3)_2 \cdot CCl_4$.

Formula, formula mass	$(C_{22}H_{23}NO_2)_2 \cdot CCl_4$, 820.7
Crystal description	$\{001\}\{021\}(410)$
Space group	$P\bar{1}$
$a/\text{Å}$	10.723(5)
$b/\text{Å}$	13.600(5)
$c/\text{Å}$	15.171(6)
$\alpha/°$	96.78(3)
$\beta/°$	110.67(2)
$\gamma/°$	91.19(3)
$V/\text{Å}^3$	2051(2)
Temp./$°C$	21(1)
Z	2
$D_{calc.}/\text{g cm}^{-3}$	1.33
Radiation, $\lambda/\text{Å}$	Mo$K\alpha$, 0.7107
μ/cm^{-1}	3.3
Crystal dimensions/mm	$0.17 \times 0.18 \times 0.24$
Scan mode	$\theta/2\theta$
$2\theta_{max}/$deg.	46
No. of intensity measurements	5701
Criterion for observed reflection	$I/\sigma(I) > 3$
No. of independent obsd. reflections	3334
No. of reflections (m) and variables	
(n) in final refinement	3334, 495
$R = \Sigma^m \|\Delta F\|/\Sigma^m \|F_0\|$	0.066
$R_w = [\Sigma^m w \|\Delta F\|^2/\Sigma^m w \|F_0\|^2]^{1/2}$	0.084
$s = [\Sigma^m w \|\Delta F\|^2/(m - n)]^{1/2}$	2.70
Crystal decay	1 to 0.90
Max., min. transmission coefficients	0.95, 0.92

3. Results and Discussion

The contents of the triclinic unit cell are four molecules of **3** and two molecules of CCl_4. The space group is $P\bar{1}$, and therefore there are two independent molecules of **3** in the asymmetric unit. The crystallographic numbering system used to describe **3** is shown in Figure 2, with addenda A and B to distinguish the two molecules of **3**. The CCl_4 atoms are labelled C, Cl(n), $n = 1-4$, unprimed and primed for the major and minor disorder components, respectively. Positional parameters for the non-hydrogen atoms of the structure are listed in Table II. Bond lengths and bond angles involving the non-hydrogen atoms of **3** are presented in Tables III and IV.

Although the hydroxy amide molecule is not required to be chiral, the stereochemistry that it adopts in the lattice is chiral (N is an asymmetric centre), and enantiomers of molecules A and B are present. Each molecule possesses and uses three hydrogen bonding sites. The hydroxy function is an H donor and an H acceptor at O, the carbonyl oxygen atom is an H acceptor, and the amide NH function is an H donor. Details of the dimensions of these hydrogen bonds are provided in Table V. There is a two-dimensional network of hydrogen bonds in the crystal, and it is in cavities between the layers of hydrogen bonded host molecules that the CCl_4 guest molecules are located. We describe first the details of the hydrogen bonding network, then the locations and surroundings of the CCl_4 molecules.

Table II. Atomic coordinates for the non-hydrogen atoms of $(3)_2 \cdot CCl_4$.

Atom	x/a	y/b	z/c	B_{iso}
NA	0.6537(4)	−0.2689(3)	0.5505(3)	3.28(6)
O(1)A	0.7245(4)	0.0917(2)	0.6041(3)	4.16(6)
O(2)A	0.4687(4)	−0.2288(3)	0.4347(3)	5.28(6)
C(1)A	0.7096(5)	0.0061(3)	0.6476(4)	2.96(5)
C(2)A	0.5912(5)	0.0151(4)	0.6807(4)	3.12(5)
C(3)A	0.5575(5)	−0.0771(4)	0.7200(4)	3.04(6)
C(4)A	0.6478(5)	−0.0804(4)	0.8221(4)	3.27(6)
C(5)A	0.7856(5)	−0.0890(4)	0.8487(4)	3.04(5)
C(6)A	0.8527(5)	−0.0937(4)	0.7758(4)	3.20(6)
C(7)A	0.8061(5)	−0.1864(4)	0.7011(4)	3.15(6)
C(8)A	0.6731(5)	−0.1784(3)	0.6203(4)	2.90(5)
C(9)A	0.6857(5)	−0.0856(4)	0.5755(4)	3.36(6)
C(10)A	0.8424(5)	0.0010(4)	0.7284(4)	3.52(7)
C(11)A	0.5533(5)	−0.1721(4)	0.6536(4)	3.26(7)
C(12)A	0.5914(6)	−0.0761(4)	0.8932(4)	4.15(10)
C(13)A	0.6680(7)	−0.0798(5)	0.9862(4)	5.12(10)
C(14)A	0.8044(7)	−0.0877(5)	1.0119(4)	5.05(8)
C(15)A	0.8622(6)	−0.0926(4)	0.9432(4)	4.25(7)
C(16)A	0.5539(5)	−0.2880(4)	0.4653(4)	3.44(6)
C(17)A	0.5495(5)	−0.3840(4)	0.4062(4)	3.22(6)
C(18)A	0.4701(5)	−0.3928(4)	0.3096(4)	3.94(11)
C(19)A	0.4595(6)	−0.4809(5)	0.2514(4)	4.56(12)
C(20)A	0.5244(6)	−0.5610(4)	0.2866(4)	4.58(13)
C(21)A	0.6018(7)	−0.5536(4)	0.3814(5)	5.30(11)
C(22)A	0.6145(6)	−0.4657(4)	0.4397(4)	4.49(12)
NB	0.0995(4)	0.7620(3)	0.4467(3)	3.45(6)
O(1)B	0.0979(4)	0.4041(3)	0.3524(3)	4.33(5)
O(2)B	0.0299(5)	0.7031(3)	0.5566(3)	5.20(6)
C(1)B	0.0434(5)	0.4955(4)	0.3216(4)	3.18(7)
C(2)B	0.0944(6)	0.5132(4)	0.2426(4)	3.94(9)
C(3)B	0.0615(5)	0.6147(4)	0.2073(4)	3.42(7)
C(4)B	−0.0795(6)	0.6155(4)	0.1373(4)	3.76(6)
C(5)B	−0.1914(6)	0.6002(4)	0.1624(4)	3.77(7)
C(6)B	−0.1765(5)	0.5820(4)	0.2621(4)	3.45(6)
C(7)B	−0.1076(5)	0.6707(4)	0.3379(4)	3.50(6)
C(8)B	0.0457(5)	0.6778(4)	0.3704(4)	2.95(7)
C(9)B	0.0996(5)	0.5794(4)	0.4037(4)	3.36(6)
C(10)B	−0.1075(5)	0.4853(4)	0.2904(4)	3.55(7)
C(11)B	0.0953(5)	0.6985(4)	0.2908(4)	3.42(6)
C(12)B	−0.1001(7)	0.6310(5)	0.0438(5)	5.68(13)
C(13)B	−0.2283(8)	0.6353(5)	−0.0219(5)	6.08(14)
C(14)B	−0.3363(7)	0.6214(5)	0.0033(5)	6.05(12)
C(15)B	−0.3185(7)	0.6041(5)	0.0956(5)	5.27(10)
C(16)B	0.0859(6)	0.7701(4)	0.5326(4)	3.60(7)
C(17)B	0.1376(5)	0.8639(4)	0.5982(4)	3.30(6)
C(18)B	0.1609(6)	0.8624(4)	0.6940(4)	4.11(10)
C(19)B	0.2030(6)	0.9470(5)	0.7587(4)	4.64(9)
C(20)B	0.2221(7)	1.0359(5)	0.7286(5)	5.11(12)
C(21)B	0.1979(7)	1.0395(4)	0.6323(5)	5.37(13)
C(22)B	0.1576(7)	0.9545(4)	0.5694(4)	4.74(13)

Table II.   (continued)

Cl(1)	0.7257(3)	0.3823(2)	0.9845(2)	7.04(6)
Cl(2)	0.8982(3)	0.2607(2)	1.1067(2)	7.36(7)
Cl(3)	0.7663(3)	0.1891(2)	0.9115(2)	10.4(1)
Cl(4)	0.6188(3)	0.2140(3)	1.0340(3)	13.4(2)
C	0.7522(2)	0.2615(2)	1.0092(2)	5.77(7)
Cl(1)′	0.7297(8)	0.3739(4)	0.9798(6)	10.42(2)
Cl(2)′	0.8134(6)	0.1801(6)	0.9532(8)	16.0(3)
Cl(3)′	0.6729(9)	0.2247(8)	1.0782(4)	17.5(3)
Cl(4)′	0.5386(5)	0.2151(5)	0.8794(4)	9.1(2)
C′	0.6886(5)	0.2484(4)	0.9726(4)	6.5(2)

Table III.   Bond lengths (Å) for $(3)_2 \cdot CCl_4$. The two independent molecules of **3** are labelled A and B.

Bond	Length	
	A	B
N—C(8)	1.486(6)	1.474(6)
N—C(16)	1.347(6)	1.353(6)
O(1)—C(1)	1.436(6)	1.442(6)
O(2)—C(16)	1.232(6)	1.239(6)
C(1)—C(2)	1.523(7)	1.523(7)
C(1)—C(9)	1.511(7)	1.524(7)
C(1)—C(10)	1.526(7)	1.514(7)
C(2)—C(3)	1.539(7)	1.542(7)
C(3)—C(4)	1.515(7)	1.511(8)
C(3)—C(11)	1.531(7)	1.534(7)
C(4)—C(5)	1.400(7)	1.400(8)
C(4)—C(12)	1.408(7)	1.398(8)
C(5)—C(6)	1.513(7)	1.514(8)
C(5)—C(15)	1.386(7)	1.389(8)
C(6)—C(7)	1.536(7)	1.536(7)
C(6)—C(10)	1.536(7)	1.554(7)
C(7)—C(8)	1.533(7)	1.538(7)
C(8)—C(9)	1.528(7)	1.538(7)
C(8)—C(11)	1.538(7)	1.532(7)
C(12)—C(13)	1.366(8)	1.392(9)
C(13)—C(14)	1.384(8)	1.358(10)
C(14)—C(15)	1.384(8)	1.394(9)
C(16)—C(17)	1.484(7)	1.486(7)
C(17)—C(18)	1.400(7)	1.389(7)
C(17)—C(22)	1.376(7)	1.392(7)
C(18)—C(19)	1.378(8)	1.374(8)
C(19)—C(20)	1.364(8)	1.379(9)
C(20)—C(21)	1.374(8)	1.398(9)
C(21)—C(22)	1.373(8)	1.365(8)

Table IV.   Bond angles (°) for the two independent molecules of **3** in $(3)_2 \cdot CCl_4$.

Atoms	Angle	
	A	B
C(8)—N—C(16)	125.7(4)	125.4(4)
O(1)—C(1)—C(2)	109.9(4)	104.8(4)
O(1)—C(1)—C(9)	108.9(4)	109.1(4)
O(1)—C(1)—C(10)	106.1(4)	109.6(4)
C(2)—C(1)—C(9)	109.4(4)	109.2(4)
C(2)—C(1)—C(10)	113.4(4)	114.1(5)
C(9)—C(1)—C(10)	108.9(4)	109.9(4)
C(1)—C(2)—C(3)	114.4(4)	113.4(4)
C(2)—C(3)—C(4)	112.2(4)	113.2(4)
C(2)—C(3)—C(11)	111.1(4)	111.3(5)
C(4)—C(3)—C(11)	113.4(4)	112.6(5)
C(3)—C(4)—C(5)	122.6(5)	122.2(5)
C(3)—C(4)—C(12)	119.2(5)	119.4(5)
C(5)—C(4)—C(12)	118.2(5)	118.3(6)
C(4)—C(5)—C(6)	121.0(5)	121.2(5)
C(4)—C(5)—C(15)	119.6(5)	119.6(6)
C(6)—C(5)—C(15)	119.4(5)	119.1(6)
C(5)—C(6)—C(7)	113.1(4)	113.3(4)
C(5)—C(6)—C(10)	113.2(4)	113.3(4)
C(7)—C(6)—C(10)	111.1(4)	110.6(4)
C(6)—C(7)—C(8)	114.4(4)	114.4(4)
N—C(8)—C(7)	106.2(4)	108.9(4)
N—C(8)—C(9)	110.4(4)	111.6(4)
N—C(8)—C(11)	109.5(4)	106.3(4)
C(7)—C(8)—C(9)	108.0(4)	109.6(4)
C(7)—C(8)—C(11)	113.3(4)	112.5(4)
C(9)—C(8)—C(11)	109.4(4)	107.9(4)
C(1)—C(9)—C(8)	110.3(4)	109.4(4)
C(1)—C(10)—C(6)	113.9(4)	114.0(4)
C(3)—C(11)—C(8)	114.0(4)	115.0(4)
C(4)—C(12)—C(13)	121.5(6)	121.1(7)
C(12)—C(13)—C(14)	119.8(6)	120.1(6)
C(13)—C(14)—C(15)	119.9(6)	119.9(6)
C(5)—C(15)—C(14)	120.9(5)	120.9(7)
N—C(16)—O(2)	122.7(5)	122.1(5)
N—C(16)—C(17)	117.8(5)	118.1(5)
O(2)—C(16)—C(17)	119.4(5)	119.8(5)
C(16)—C(17)—C(18)	117.4(5)	117.9(5)
C(16)—C(17)—C(22)	124.9(5)	124.3(5)
C(18)—C(17)—C(22)	117.7(5)	117.7(5)
C(17)—C(18)—C(19)	120.1(5)	121.5(6)
C(18)—C(19)—C(20)	121.1(6)	119.6(6)
C(19)—C(20)—C(21)	119.4(6)	119.7(6)
C(20)—C(21)—C(22)	120.0(6)	119.5(6)
C(17)—C(22)—C(21)	121.8(6)	121.7(6)

Table V.   Dimensions associated with hydrogen bonding in $(3)_2 \cdot CCl_4$.

O(1)A—HO(1)A	0.841	NA—HNA	0.947
O(1)B—HO(1)B	0.973	NB—HNB	0.954
NA···O(1)B[a]	3.274(5)	HNA···O(1)B[a]	2.378
NB···O(1)A[b]	3.058(5)	HNB···O(1)A[b]	2.123
O(1)A···O(2)A[a]	2.770(5)	HO(1)A···O(2)A[a]	1.940
O(1)B···O(2)B[c]	2.763(5)	HO(1)B···O(2)B[c]	1.852
NA—HNA···O(1)B[a]	157.7		
C(8)A—NA···O(1)B[a]	105.5(3)	NA···O(1)B[a]—C(1)B[a]	152.7(3)
C(16)A—NA···O(1)B[a]	128.8(3)		
NB—HNB···O(1)A[b]	166.2		
C(8)B—NB···O(1)A[b]	111.1(3)	NB···O(1)A[b]—C(1)A[b]	150.4(3)
C(16)—NB···O(1)A[b]	123.2(3)		
O(1)A—HO(1)A···O(2)A[a]	168.8		
C(1)A—O(1)A···O(2)A[a]	121.0(3)	O(1)A···O(2)A[a]—C(16)A[a]	170.5(4)
O(1)B—HO(1)B···O(2)B[c]	154.7		
C(1)B—O(1)B···O(2)B[c]	117.9(3)	O(1)B···O(2)B[c]—C(16)B[c]	164.0(4)

Errors in dimensions involving hydrogen atoms have been omitted since the hydrogen atom positions were not refined.

Equivalent position indicators: [a] $1-x$, $-y$, $1-z$; [b] $1-x$, $1-y$, $1-z$; [c] $-x$, $1-y$, $1-z$.
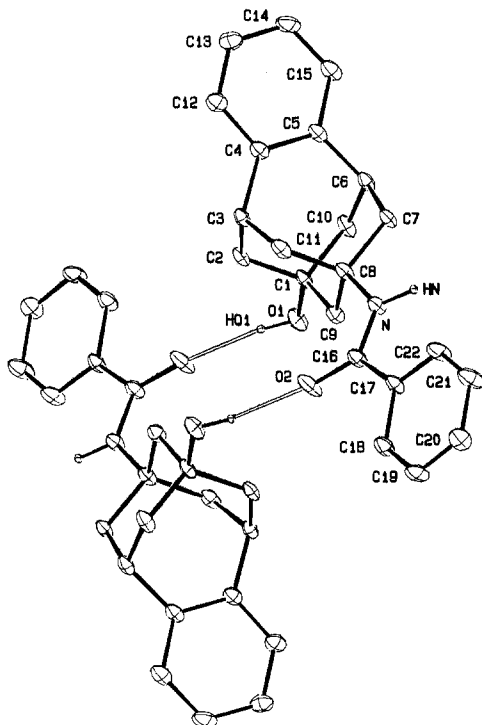
Fig. 2.   Two molecules of **3** (molecule A), hydrogen bonded hydroxyl to carbonyl across a centre of symmetry. The same atom labelling applies to both molecules per asymmetric unit, with addenda A and B.
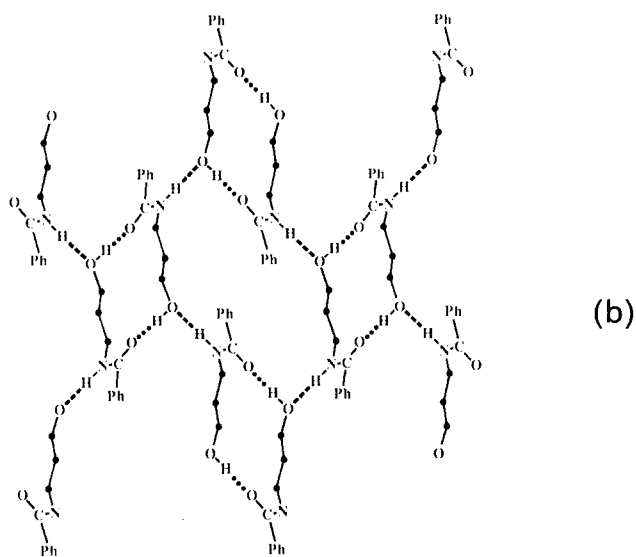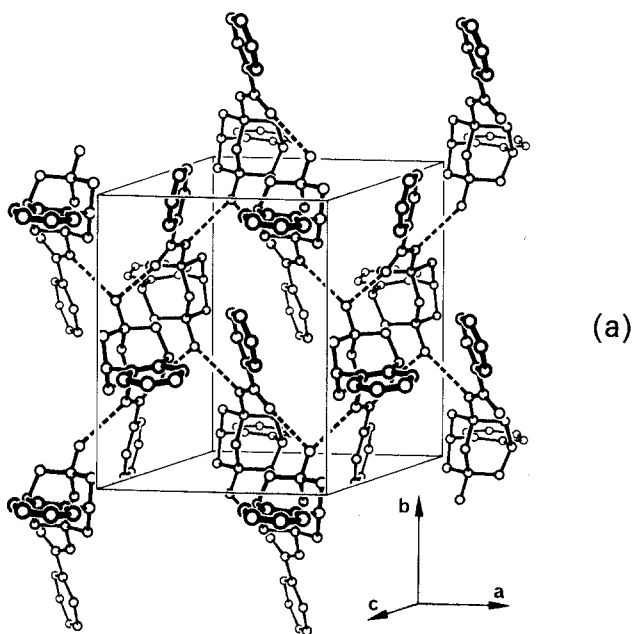
Fig. 3. Representations of the network of hydrogen bonded molecules of **3** within one layer in crystals of (**3**)$_2$·CCl$_4$. (a) Showing all non-hydrogen atoms of **3**, with hydrogen bonds marked as broken lines. (b) Schematic representation of (a), with the hydroxyl to carbonyl hydrogen bonds in the dimers marked ··· and the amide to hydroxyl hydrogen bond marked - - -.

Centrosymmetric pairs of molecules are joined by a pair of hydroxy to carbonyl hydrogen bonds, as shown in Figure 2. These pairs are inclined at a steep angle to the ab plane of the lattice, and each pair is linked by one hydrogen bond to each of four other such pairs in the ab plane (these are molecule A—molecule B linkages), such that the infinite extension of hydrogen bonds is parallel to the ab plane. This hydrogen bonding network is shown schematically and actually in Figure 3. The layer of hydrogen bonds undulates slightly about its mean position of $z = 0.5$. It can be seen from Figure 3 that both the benzo substituents and the phenyl rings of the benzamido functions are oriented approximately normal to the layer of hydrogen bonds, that is approximately normal to the ab plane.

Figure 4 shows a pair of hydrogen bonded layers and the CCl_4 molecules trapped between them, with a view direction approximately parallel to the layers, and approximately parallel to a. The benzo substituents are all approximately perpendicular to the layers and perpendicular to the b axis, while the phenyl rings are all approximately perpendicular to the layers and perpendicular to the a axis. The layer of CCl_4 molecules is centered at $z/c = 0$, the benzo groups are closest to the guest layer at $z/c = \pm(0$ to $0.1)$, the phenyl groups are more distant at $z/c = \pm(0.25$ to $0.4)$, and the host layers are located around the centers of inversion at $z/c = \pm0.5$.

The benzo and phenyl groups which surround the CCl_4 guests are shown diagrammatically in Figure 5, a view perpendicular to a host—guest—host sandwich. Each CCl_4 is surrounded by six benzo groups arrayed approximately as an octahedron, and marked 1 to 6 on Figure 5. Of the six phenyl groups around each
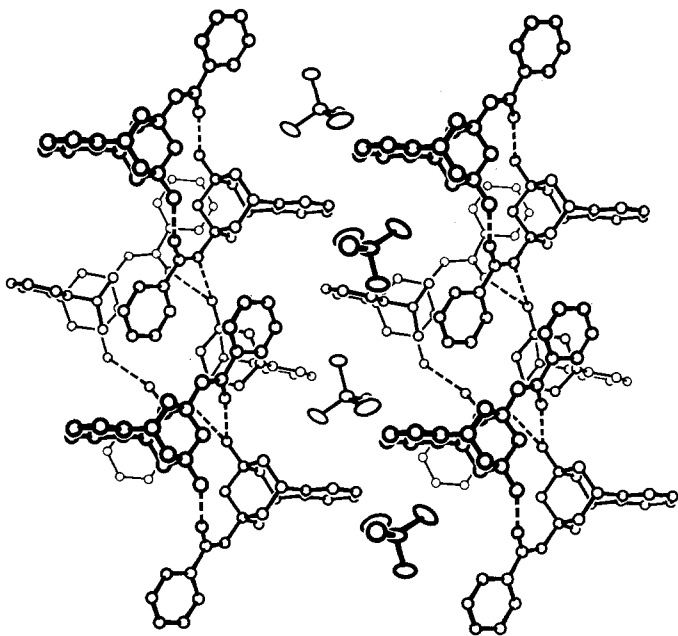

Fig. 4.   View of a pair of hydrogen bonded layers and the CCl_4 molecules sandwiched between them. The view direction is close to parallel to the layers and to the a axis, but is twisted slightly for clarity. The b axis is approximately vertical and the c axis approximately horizontal. Hydrogen bonds are drawn broken. Only the major orientation of the CCl_4 is included.
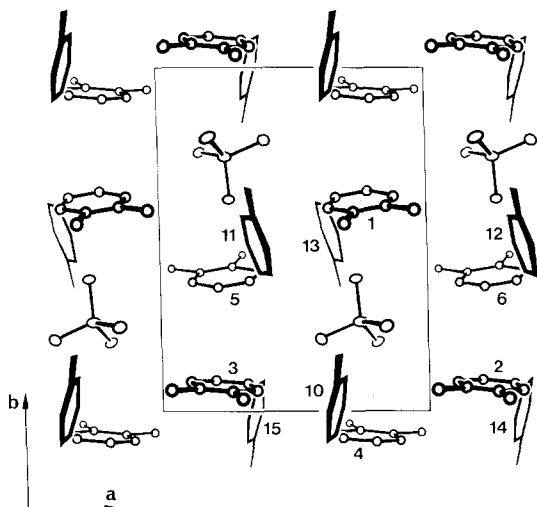
Fig. 5. Diagrammatic representation of the benzo groups (drawn with small circles) and phenyl groups (as hexagons) of one host–guest–host sandwich, as they surround the CCl_4 molecules. The view direction is normal to the sandwich, and all other parts of the host molecules are omitted. The six benzo groups of the approximate octahedron around the CCl_4 in the upper left are numbered 1 to 6, while the six phenyl groups around the same CCl_4 are numbered 10 to 15.
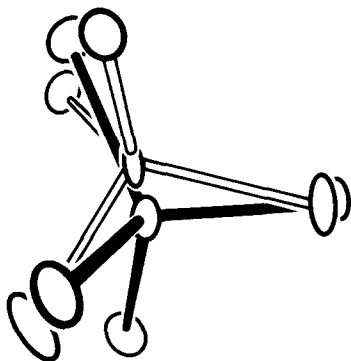

Fig. 6. The two orientations of the CCl_4 molecule disorded at the one location. The orientation drawn with the full bonds occurs in 69% of the unit cells.

CCL_4, two (marked 10 and 13 on Figure 5) are closest, two others (11 and 15) are slightly more distant, while 12 and 14 are further away. The constraint of the CCl_4 by its environment is such as to allow a small amount of orientational disorder, and the two orientations of the CCl_4 molecule that occur (disordered 69 : 31) at the same location are shown in Figure 6. Between the Cl atoms (all eight locations) of the guest and the carbon atoms of the host layers there are eleven distances that are in the range 3.3 to 3.6 Å. Ten of these are to benzo groups, one to a phenyl group.

In terms of molecular topology the structure of this hydroxy amide inclusion complex may be regarded as a layer clathrate [5], with a rather similar arrangement to that in the Hofmann type inclusion compounds such as $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ [6].

Acknowledgements

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