

Ritter Reactions. VIII. Inclusion Compounds Formed between *N*-(5*H*-Dibenzo[*a*, *d*]cycloheptyl)acetamides and Dioxane

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Abstract. 5*H*-Dibenzo[*a*, *d*]cyclohepten-5-ol **2** and its saturated analogue **4** undergo Ritter reactions with acetonitrile and sulfuric acid to afford the acetamide derivatives **3** or **5** respectively. Both products form unstable inclusion compounds when crystallised from dioxane. The crystal structure of the dioxane compound of **3** is reported. This material [(C₁₇H₁₅NO)·(C₄H₈O₂)₂], *Prma*, *a* = 9.616(1), *b* = 23.280(2), *c* = 10.298(1) Å, *Z* = 4, *R* = 0.054] has the amide molecules arranged in parallel chains by means of intermolecular –N–H···O=C hydrogen bonds. The inclusion compound is stabilised by means of –C–H···O– hydrogen bonds. Each dioxane molecule is involved in five such interactions to neighbouring molecules of **3** and dioxane.

Key words: Amide hosts, dioxane, hydrogen bonding, Ritter reaction, –C–H···O– hydrogen bonds.

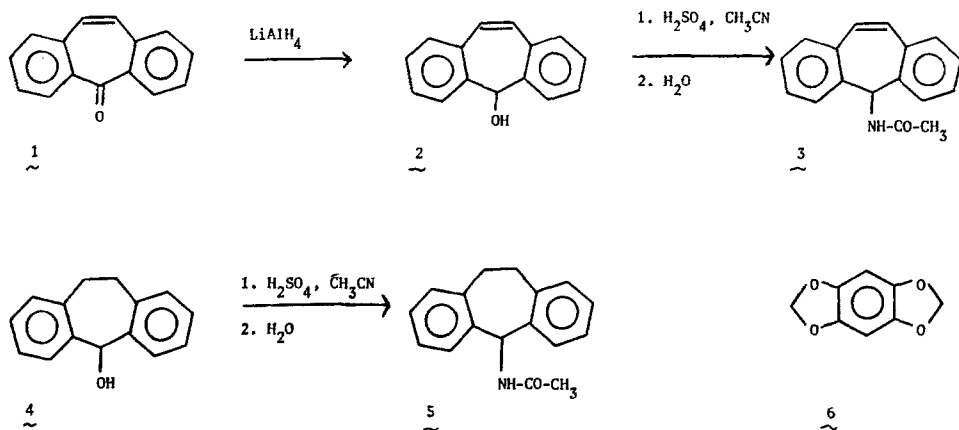
Supplementary Data relating to this article are deposited with the British Library as supplementary publication No. SUP 82173 (5 pages).

1. Introduction

A common feature of many classes of lattice inclusion compounds is the presence of a strong hydrogen bonding network which holds the host molecules in appropriate geometries for guest inclusion. Although Toda [1], Weber [2], Hiratani [3] and other workers have successfully used the amide functional group in the design and synthesis of new lattice inclusion compounds, this excellent hydrogen bonding group has so far enjoyed much less favour for this purpose than use of the well-tried hydroxy or carboxylic acid functionalities [4].

As part of our recent work [5] on synthetic applications of the Ritter reaction [6,7] we have reported previously that certain multicyclic systems bearing both hydroxy and amide groups form hydrogen bonded lattices trapping guest molecules as clathrate structures [8]. In an extension of these studies we have now found other

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multicyclic Ritter products which yield inclusion compounds as a consequence of their amide-amide hydrogen bonding network.

Reduction of ketone **1** affords *5H*-dibenzo[*a, d*]cyclohepten-5-ol **2**. Both alcohol **2** and its saturated analogue **4** undergo efficient Ritter reaction with acetonitrile in the presence of sulfuric acid to yield the acetamide derivatives **3** or **5**, respectively. These two amides have both been prepared previously by a different procedure (acetylation of the corresponding amine) but no indication of co-crystallisation behaviour was reported [9,10]. However, we observed that both acetamides formed crystalline inclusion compounds when recrystallised from dioxane.

2. Experimental

2.1. PREPARATIVE WORK

^1H (300 MHz; Bruker AC300F) and ^{13}C (126 MHz; Bruker AM500) NMR spectra are reported as chemical shifts (δ) relative to SiMe_4 . The substitution of carbon atoms was determined by the DEPT procedure. Melting points were determined with a Kofler instrument and are uncorrected. Mass spectra were recorded on an AEI MS-12 instrument. 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.

5H-Dibenzo[*a, d*]cyclohepten-5-ol **2**

A solution of ketone **1** (2.06 g, 10 mmol) in dry tetrahydrofuran (THF, 50 mL) was added slowly to a stirred solution of lithium aluminium hydride (0.65 g, 17 mmol) in dry THF (100 mL) under nitrogen. The resulting mixture was refluxed overnight. Excess reducing agent was destroyed by careful addition of wet ether. THF was evaporated under reduced pressure, the residue dissolved in dil. HCl, and

organic material extracted using chloroform. The combined extracts were washed, dried (Na_2SO_4), and solvent evaporated from the filtrate to give the *alcohol 2*, yield (1.75 g, 85%), m.p. 121–123°C (from hexane/chloroform); lit. [11] 120°C. (Found: C, 86.86; H, 5.89. $\text{C}_{15}\text{H}_{12}\text{O}$ requires C, 86.51; H, 5.81%). ν_{max} . (paraffin mull) 3380s, 1185w, 1020m, 785m, 760w, 720m cm^{-1} . m/z ($> 10\%$) 208 (M^+ , 32%), 207 (14), 192 (14), 191 (50), 189 (19), 180 (17), 179 (100), 178 (47), 176 (10), 165 (14), 152 (10). $^1\text{H NMR } \delta$ (d_6 -DMSO) 7.75, d, 2H, J 7.76 Hz; 7.46–7.35, m, 4H; 7.27–7.22, m, 2H; 7.15, s, 2H; 6.12, br d, 1H, J ca. 4 Hz, –OH; 5.06, d, 1H, J 4.0 Hz. $^{13}\text{C NMR } \delta$ (d_6 -DMSO) 142.0 (C), 132.4 (C), 131.2 (CH), 128.5 (CH), 127.7 (CH), 126.2 (CH), 123.1 (CH), 70.0 (CH).

N-(5*H*-Dibenzo[*a,d*]cyclohepten-5-yl)acetamide **3**

Sulfuric acid (98%; 0.57 mL) was placed in a round-bottomed flask fitted with a reflux condenser/drying tube and was cooled to 0°C. Acetonitrile (5.7 mL) was then added with stirring. A solution of alcohol **1** (0.42 g, 2 mmol) in benzene (5 mL) was added dropwise but rapidly via the condenser. After addition of the alcohol was complete, the reaction was stirred for 30 min. at 0°C and then for 4 h at room temperature. Water (20 mL) was added, and after 0.5 h the material was transferred to a separating funnel containing sodium hydroxide solution (1M; 50 ml). Organic material was extracted using dichloromethane, then the combined extracts washed with water (2×50 mL), and dried (Na_2SO_4). Evaporation of dichloromethane from the filtrate gave the *amide 3*, yield (0.39 g, 78%), m.p. 289–290°C (from dioxane); lit. [9] m.p. 289–290°C). (Found: C, 81.75; H, 6.40; N, 5.68. $\text{C}_{17}\text{H}_{15}\text{NO}$ requires C, 81.89; H, 6.06; N, 5.62%). ν_{max} . (paraffin mull) 3280s, 1630s, 1535m, 785m, 765w, 730m cm^{-1} . m/z ($> 10\%$) 250 (20%), 249 (M^+ , 100%), 232 (12), 207 (33), 206 (M–CH₃–CO, 51), 192 (14), 191 (M–CH₃–CO–NH, 46), 190 (19), 189 (31), 179 (26), 178 (25). $^1\text{H NMR } \delta$ (d_6 -DMSO) 9.1, v br s, 1H (exchanged with D₂O); 7.59, d, 2H, J 7.9 Hz; 7.43–7.38, m, 4H; 7.30–7.25, m, 2H; 7.17, s, 2H; 5.68, br d, 1H, J ca. 4.25 Hz, (collapsed to br s on D₂O exchange); 1.98, s, 3H. $^{13}\text{C NMR } \delta$ (d_6 -DMSO) 169.0 (C), 139.0 (C), 133.7 (CH), 131.4 (CH), 128.6 (CH), 128.5 (C), 126.7 (CH), 124.7 (CH, weak & broad), 53.3 (CH, weak & broad), 22.4 (CH₃).

Under more vigorous Ritter conditions an alternative product, m.p. 223–224°C, is obtained. Details of this material have been described separately [12].

Crystals of **3** freshly grown from dioxane turned opaque on heating to about 100°C. Considerable crystal reorganisation took place over 240–260°C, and then there was a rapid phase change at about 265–270°C as fibrous needles were produced. The sample then melted at 289–290°C. At room temperature, the crystals slowly lost dioxane on standing and turned opaque.

N-(5*H*-Dibenzo[*a,d*]cyclohept-5-yl)acetamide **5**

Ritter reaction was carried out on alcohol **4** (2.10 g, 10 mmol) in benzene (10.5 mL) as described for the preparation of **3** but using sulfuric acid (98%; 3.0 mL) and acetonitrile (30 mL). Work up of the reaction as before gave the amide **5** (1.91 g, 76%), m.p. 278–279°C (from dioxane); lit. [10] 282–283°C (from dioxane). (*Found*: C, 80.95; H, 6.86; N, 5.68. $C_{17}H_{17}NO$ requires C, 81.24; H, 6.82; N, 5.57%). ν_{\max} . (paraffin mull) 3400m, 3295s, 3050w, 1635m, 1540m, 1480m, 1290m, 1125m, 980m, 770s, 740m, 720m cm^{-1} . m/z ($> 10\%$) 251 (M^+ , 18), 208 (12), 193 (22), 192 (100), 191 (65), 189 (18), 178 (24), 165 (23), 115 (21), 91 (11), 43 (18). 1H NMR δ (d_6 -DMSO) 8.20, d, 1H, J 8.46 Hz; 6.68–6.64, m, 2H; 6.46–6.41, m, 6H; 5.67, d, 1H, J 8.46 Hz; 2.50–2.45, m, 4H; 1.26, s, 3H. ^{13}C NMR δ (d_6 -DMSO) 168.6 (C), 140.0 (C), 138.7 (C), 130.2 (CH), 127.5 (CH), 127.2 (CH), 126.2 (CH), 54.5 (CH), 32.0 (CH_2), 22.9 (CH_3).

Crystals of **5** freshly grown from dioxane turned opaque on heating up to about 90°C. At room temperature, the crystals slowly lost dioxane on standing and turned opaque.

2.2. X-RAY DATA COLLECTION, PROCESSING, AND REFINEMENT FOR THE STRUCTURE (**3**)·(DIOXANE)₂

Both acetamides **3** and **5** gave crystals which included dioxane (by IR mull and solution 1H NMR spectroscopy) when grown by evaporation from solutions in that solvent. Those of acetamide **5** and dioxane were too unstable to undertake a single crystal X-ray structural determination, but since the two compounds had the almost identical X-ray powder diffraction patterns, shown in Figure 1, they can be assumed to have the same type of crystalline arrangement. The peak positions of the pattern of **3** corresponded to those calculated from the crystal structure.

Data for a crystal of acetamide **3** grown from dioxane were recorded using an Enraf-Nonius CAD4 X-ray diffractometer. The crystal used was freshly prepared and studied at once. Despite this, significant crystal decay was observed. Data collection and processing procedures have been described [13]. Corrections were made for absorption and for decomposition. The positions of all 18 non-hydrogen atoms present in the asymmetric unit were located using direct methods (MULTAN) [14]. A mirror plane at $y = 1/4$ related the two halves of the amide molecule, with the atoms of the amide group lying on the mirror plane. Initially all six atoms of the dioxane molecule were included in the structure as carbon atoms. After refinement, the isotropic temperature factors of these six atoms were (around the ring) 4.4, 7.7, 8.0, 4.8, 7.7 and 8.6, making assignment of the two oxygen atoms unequivocal. Full matrix least squares refinement (BLOCKLS) [15], with anisotropic thermal parameters for the non-hydrogen atoms converged with $R = 0.054$. Hydrogen atoms were included in the refinement at calculated positions, and they were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound and were not refined. The largest peak in the final difference

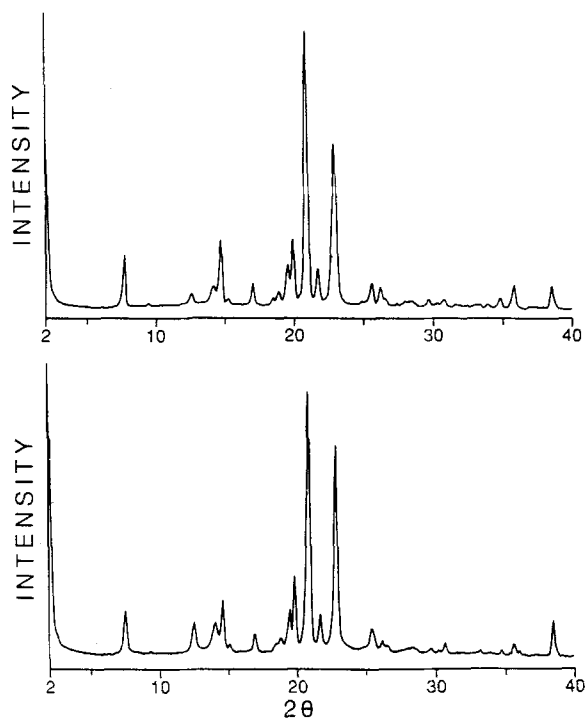


Fig. 1. X-Ray powder diffraction patterns for the inclusion compounds of **3** (top graph) and **5** (lower graph) with dioxane. The extreme similarity between the two patterns should be noted.

Fourier map was $0.18 \text{ e } \text{Å}^{-3}$. A summary of data collection parameters is given in Table I.

3. Results and Discussion

3.1. DESCRIPTION OF THE STRUCTURE

The contents of the orthorhombic unit cell are four molecules of **3** and eight molecules of dioxane in space group *Pnma*. The asymmetric unit comprises half a molecule of **3** and one molecule of dioxane, and the crystallographic numbering system used is shown in Figure 2. There is a mirror plane relating the two halves of **3**, with the overall shape of the molecule resembling that of a butterfly. The amide **3** molecules, related by a 2_1 axis parallel to *a* at $(1/4, 1/4)$, are linked in chains via $\text{-N-H} \cdots \text{O=C}$ hydrogen bonds. Dioxane molecules lie at both wingtips of the butterfly, packing between molecules of **3** in the *c* direction. An inversion centre at $(1/2, 1/2, 1/2)$ related stacks of molecules in the two halves of the unit cell. The resulting arrangement of molecules is shown in Figures 3 and 4.

Positional parameters for the non-hydrogen atoms are listed in Table II. Bond lengths and bond angles for the structure are presented in Tables III and IV, and

TABLE I. Numerical details of the solution and refinement of the structure of (3)·(dioxane)₂

Formula, formula mass	(C ₁₇ H ₁₅ NO)·(C ₄ H ₈ O ₂) ₂ , 425.6
Crystal description	{010}{011}{01-1}{101}(-100)
Space group	<i>Pnma</i>
<i>a</i> /Å	9.616(1)
<i>b</i> /Å	23.280(2)
<i>c</i> /Å	10.298(1)
<i>V</i> /Å ³	2305.5(4)
Temp./°C	21(1)
<i>Z</i>	4
<i>D</i> _{calc.} /g cm ⁻³	1.23
Radiation, λ/Å	CuK _α , 1.5418
μ/cm ⁻¹	6.51
Crystal dimensions/mm	0.30 × 0.07 × 0.20
Scan mode	θ/2θ
2θ _{max} /°	100
ω scan angle	(0.50 + 0.15 tan θ)
No. of intensity measurements	1404
Criterion for observed reflection	<i>I</i> /σ(<i>I</i>) > 3
No. of independent obsd. reflections	518
No. of reflections (<i>m</i>) and variables (<i>n</i>) in final refinement	518, 148
$R = \sum^m \Delta F / \sum^m F_o $	0.054
$R_w = [\sum^m w \Delta F ^2 / \sum^m w F_o ^2]^{1/2}$	0.062
$s = [\sum^m w \Delta F ^2 / (m - n)]^{1/2}$	2.01
Crystal decay	1 to 0.70
Max., min. transmission coefficients	0.95, 0.80
Largest peak in final diff. map/e Å ⁻³	0.18

dimensions associated with the inter-amide hydrogen bonding are given in Table V.

3.2. THE ROLE OF THE DIOXANE COMPONENT

Inclusion properties have been noted for other molecules with a butterfly-like shape, notably the 1 : 1 compound of [*N,N'*-bis(salicylidene-1,5-diamino-3-azapentane)]dioxouranium(VI) with ethanol where the guest molecules occupy parallel channels [16]. In the present case, samples of the acetamides **3** and **5** were tested for inclusion properties by crystallisation from a wide range of potential guests: chloroform, ethyl acetate, benzene, toluene, methanol, ethanol, tetrahydrofuran, acetonitrile, acetic acid, dimethyl sulfoxide, 1,2-dimethoxyethane, diethyl ether, pyridine and dioxane. Only dioxane was included by either acetamide on the basis of IR (mull) spectroscopic evidence. After the structure of (3)·(dioxane)₂

TABLE II. Atomic coordinates for the non-hydrogen atoms of (3)-(dioxane)₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O	0.2944(8)	0.2500	0.2383(7)	5.70(30)
N	0.5168(9)	0.2500	0.1729(9)	3.33(31)
C(1)	0.4826(11)	0.2500	0.0350(11)	3.16(38)
C(2)	0.5326(9)	0.3031(3)	-0.0349(8)	2.95(25)
C(3)	0.6332(9)	0.3397(4)	0.0154(7)	3.59(27)
C(4)	0.6697(8)	0.3897(4)	-0.0479(10)	4.56(32)
C(5)	0.6046(11)	0.4035(4)	-0.1635(10)	5.27(35)
C(6)	0.5057(9)	0.3676(4)	-0.2155(8)	4.61(29)
C(7)	0.4713(8)	0.3169(4)	-0.1544(9)	3.47(28)
C(8)	0.3710(8)	0.2780(3)	-0.2195(7)	4.36(26)
C(9)	0.4195(13)	0.2500	0.2649(14)	3.55(44)
C(10)	0.4724(12)	0.2500	0.4027(11)	4.70(43)
DO(1)	0.0520(7)	0.0998(3)	0.0339(7)	8.87(30)
DO(2)	0.2493(9)	0.0424(3)	0.1766(9)	9.82(33)
DC(1)	0.0238(12)	0.0783(6)	0.1586(11)	9.22(48)
DC(2)	0.1044(15)	0.0294(5)	0.1901(11)	9.32(48)
DC(3)	0.2763(13)	0.0635(7)	0.0488(13)	10.55(55)
DC(4)	0.1972(13)	0.1140(5)	0.0251(10)	8.18(46)

TABLE III. Bond lengths and standard deviations (Å) for (3)-(dioxane)₂

Bond, (3)	Length	Bond, (dioxane)	Length
O–C(9)	1.234(12)	DO(1)–DC(1)	1.405(11)
N–C(1)	1.458(12)	DO(1)–DC(4)	1.439(11)
N–C(9)	1.331(12)	DO(2)–DC(2)	1.432(12)
C(1)–C(2)	1.510(8)	DO(2)–DC(3)	1.429(12)
C(2)–C(3)	1.389(9)	DC(1)–DC(2)	1.416(14)
C(2)–C(7)	1.402(9)	DC(3)–DC(4)	1.422(14)
C(3)–C(4)	1.379(10)		
C(4)–C(5)	1.382(10)		
C(5)–C(6)	1.374(10)		
C(6)–C(7)	1.378(10)		
C(7)–C(8)	1.483(9)		
C(9)–C(10)	1.508(14)		
C(8)–C(8) ^a	1.304(14)		

Equivalent position indicator: ^a *x*, 1/2-*y*, *z*

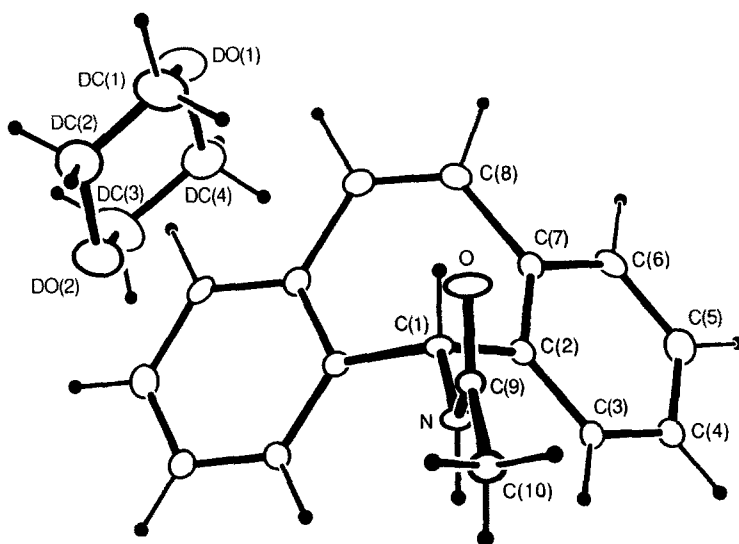


Fig. 2. The molecular structure of amide **3** and dioxane in the crystal structure of $(\mathbf{3})_2 \cdot (\text{dioxane})$, showing the crystallographic numbering system used.

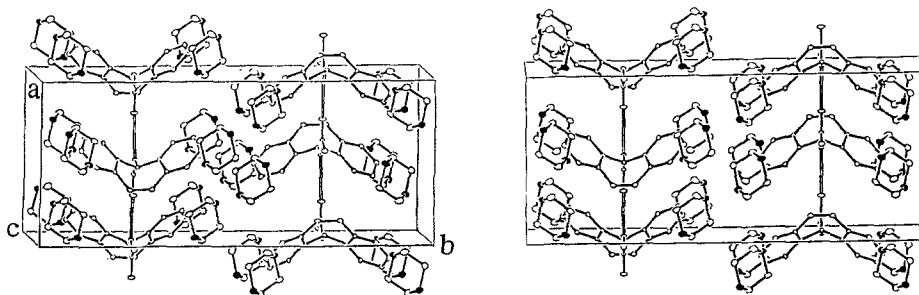


Fig. 3. A stereoscopic view of the unit cell of solid $(\mathbf{3})_2 \cdot (\text{dioxane})$ with all hydrogen atoms omitted for clarity. Inter-amide hydrogen bonding is indicated by hollow linkages, and dioxane oxygen atoms by solid ellipses.

had been determined, both acetamides were further tested with benzo[1,2-*d*:4,5-*d'*]bis[1,3]dioxol **6** which, it was hoped, might act as a bridge link between two adjacent molecules of the acetamide. This substance was prepared from sesamol using the procedure described by Dallacker *et al.* [17]. Since it is a solid at room temperature the acetamides were crystallised from a solution containing **6** in either chloroform or dioxane. However neither **3** nor **5** showed any evidence supporting inclusion of the substance **6**.

Furthermore, neither **3** nor **5** included cyclohexane on the basis of the ^1H NMR spectra of the materials produced after recrystallisation of the amides from

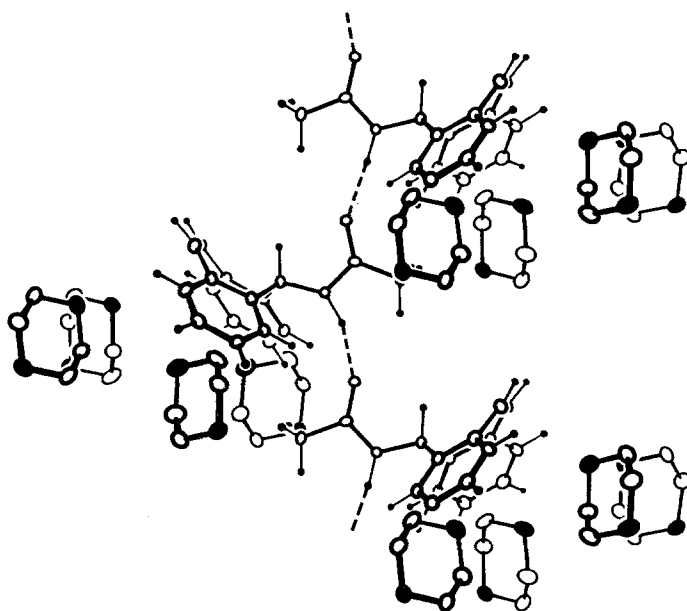


Fig. 4. Part of a hydrogen-bonded chain of amide **3** molecules viewed roughly orthogonal to the view in Figure 3. Inter-amide hydrogen bonds are represented as dashed linkages and hydrogen atoms of **3** as filled circles. The spatial arrangement of the amide and dioxane molecules is clearly seen. Dioxane hydrogen atoms are omitted for clarity and dioxane oxygen atoms are shown as filled ellipses.

cyclohexane solvent. Since lattice inclusion of guest molecules is partly dependent on size and shape factors, this evidence indicates that dioxane is a highly specific guest with respect to the amides **3** and **5**. We, and other investigators [18], have observed that dioxane is an especially favoured guest in many lattice inclusion materials. It is frequently included (sometimes exclusively) and often affords high quality crystals.

An examination of the crystal structure data for $(\mathbf{3}) \cdot (\text{dioxane})_2$ revealed a number of intermolecular carbon...oxygen contacts under 4.00 Å in distance (Table VI). The dioxane oxygen atoms DO(1) and DO(2) are each involved in four such close contacts, and there is also one short carbon-carbon contact present. Closer inspection of the oxygen contacts showed that five of these (see values in Table VI) were due to C-H...O-hydrogen bonds [19,20] with hydrogen...oxygen distances in the range 2.42–3.03 Å. The remaining three dioxane oxygen close contacts involved groups which were simply immediate neighbours of those involved in this hydrogen bonding.

The dioxane oxygen atom DO(2) participates in two interactions: one to an aromatic hydrogen of **3**, and the other to a hydrogen atom of another dioxane molecule. In contrast, DO(1) participates in three of these weak hydrogen bonds:

TABLE IV. Bond angles and standard deviations ($^{\circ}$) for (3)·(dioxane)₂

Atoms, (3)	Angle	Atoms, (dioxane)	Angle
C(1)–N–C(9)	122.3(9)	DC(1)–DO(1)–DC(4)	109.1(8)
N–C(1)–C(2)	113.1(6)	DC(2)–DO(2)–DC(3)	109.8(9)
C(2)–C(1)–C(2) ^a	110.0(7)	DO(1)–DC(1)–DC(2)	113.0(11)
C(1)–C(2)–C(3)	123.2(8)	DO(2)–DC(2)–DC(1)	109.9(9)
C(1)–C(2)–C(7)	118.1(8)	DO(2)–DC(3)–DC(4)	110.2(11)
C(3)–C(2)–C(7)	118.7(8)	DO(1)–DC(4)–DC(3)	108.6(9)
C(3)–C(4)–C(5)	119.2(8)		
C(2)–C(3)–C(4)	121.2(8)		
C(4)–C(5)–C(6)	120.5(9)		
C(5)–C(6)–C(7)	120.6(9)		
C(2)–C(7)–C(6)	119.7(8)		
C(2)–C(7)–C(8)	122.1(8)		
C(6)–C(7)–C(8)	118.2(9)		
O–C(9)–N	121.8(12)		
O–C(9)–C(10)	122.5(12)		
N–C(9)–C(10)	115.7(10)		
C(7)–C(8)–C(8) ^a	127.6(5)		

Equivalent position indicator: ^a $x, 1/2-y, z$

TABLE V. Dimensions associated with the inter-amide hydrogen bonding in (3)·(dioxane)₂

O...N ^b	2.822(11)
O...HN ^b	1.82(1)
C(9)–O...N ^b	148.3(8)
O...N ^b –C(1) ^b	121.9(7)
O...N ^b –C(9) ^b	115.7(7)
O...HN ^b –N ^b	175(1)

Equivalent position indicator: ^b $-1/2+x, 1/2-y, 1/2-z$

two to aromatic hydrogens of **3**, and one to a methyl group hydrogen of **3**. Hence each dioxane guest molecule is linked with five different neighbouring molecules, one dioxane and four of **3**, in the inclusion compound. The arrangement of these $-C-H \cdots O-$ hydrogen bonds is shown in Figure 5.

A statistical analysis of the directional properties of hydrogen bonds to ethers has shown a good correlation with the oxygen lone pair plane and directions [21]. It is noteworthy that the arrangement around DO(2) is of this type, but that around DO(1) is more complex. However, the above analysis also revealed that such a correlation is not perfect and that other hydrogen bonding geometries are accommodated. A possible physical interpretation of the arrangement around DO(1) is

TABLE VI. Short atomic contacts (under 4.00 Å) and relevant $-C-H \cdots O-$ angles (degrees) in the inclusion compound $(3)_2 \cdot (\text{dioxane})$. (Errors are not estimated for the figures in the second column as hydrogen atom positions were not refined.)

DO(1) \cdots C(6) ⁱ	3.40(1)	DO(1) \cdots HC(6) ⁱ	2.64	132.7
DO(1) \cdots C(10) ⁱⁱ	3.64(1)	DO(1) \cdots H2C(10) ⁱⁱ	2.90	131.2
DO(1) \cdots C(4) ⁱⁱⁱ	3.78(1)	DO(1) \cdots HC(4) ⁱⁱⁱ	3.03	132.2
DO(1) \cdots C(5) ⁱ	3.85(1)	DO(1) \cdots HC(5) ⁱ	3.54	100.2
DO(2) \cdots DC(1) ^{iv}	3.25(1)	DO(2) \cdots H1DC(1) ^{iv}	2.42	139.8
DO(2) \cdots C(5) ^v	3.53(1)	DO(2) \cdots HC(5) ^v	2.68	143.1
DO(2) \cdots DC(2) ^{iv}	3.69(1)	DO(2) \cdots H2DC(2) ^{iv}	3.31	105.1
DO(2) \cdots C(4) ^v	3.87(1)	DO(2) \cdots HC(4) ^v	3.41	110.3
DC(4) \cdots C(7) ^{vi}	3.60(1)			

ⁱ $-1/2+x, 1/2-y, -1/2-z$

ⁱⁱ $-1/2+x, 1/2-y, 1/2-z$

ⁱⁱⁱ $-1+x, 1/2-y, z$

^{iv} $1/2+x, y, 1/2-z$

^v $1-x, -1/2+y, -z$

^{vi} $x, 1/2-y, z.$

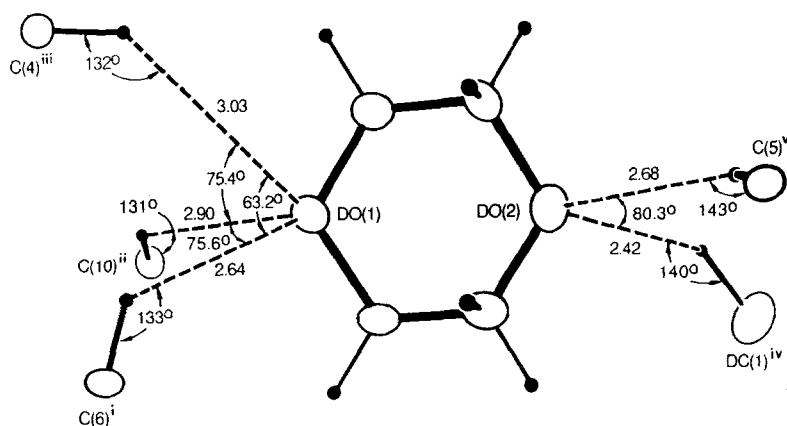


Fig. 5. The dioxane molecule present in the inclusion compound $(3)_2 \cdot (\text{dioxane})$ showing the five $-C-H \cdots O-$ hydrogen bonds (represented as dashed lines) which stabilise the structure. Bond lengths (Å) and angles (degrees) are indicated, together with details of the neighbouring carbon atoms involved. Superscripts indicate symmetry operators as listed in Table VI.

that DO(1) \cdots HC(10) involves another conventional lone pair interaction, whereas DO(1) \cdots HC(6) and DO(1) \cdots HC(4) represent two hydrogen atoms interacting with the second lone pair of DO(1) in a bifurcated manner, rather than in the manner formally represented in Figure 5.

Dioxane is an excellent guest for production of inclusion compounds because of its versatility. It has a compact and well-defined shape, the ability to participate

in $-O-H \cdots O-$ hydrogen bonds where appropriate [18], and is highly efficient in producing a variety of $-C-H \cdots O-$ hydrogen bonds with host molecules. Such interactions have an energy of only *ca.* 4–8 kJ mol⁻¹ [20], but the sum of these effects is significant on the scale of intermolecular packing energies particularly if the resultant structure (as in this case) has several interlinked molecules.

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