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Studies in Werner Clathrates.
Part 3. Structures of Bis(isothiocyanato)tetra(4-vinylpyridine)nickel(II) and its Clathrates with *ortho-*, *meta-* and *para*-Xylenes

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Abstract

The crystal structures of the α-phase $Ni(NCS)_2(4ViPy)_4$ (I) Werner complex and of its β-phase clathrates with *p*-xylene (II), *m*-xylene (III), and *o*-xylene (IV) have been elucidated. The $Ni(NCS)_2(4ViPy)_4$ molecules in all four structures have octahedral coordination and 'propeller' conformation. The shape of a typical channel in a β-phase structure is portrayed by potential energy calculations. The potential energy of each xylene in its respective cavity is calculated. A comparison of packing efficiencies in all four structures is discussed. Results of packing modes and energy calculations both imply that matching the symmetry of the cavity in the β-phase with a prospective guest is favoured.

Introduction

Interest in Werner clathrates was stimulated by Schaeffer and coworkers who announced a new method of separating various aromatic mixtures from petroleum fractions [1]. These compounds are made up of 'host' molecules, of general formula MX_2L_4 (M = Ni, Co, Fe, Mn, Zn, Cu; X = SCN, CNO, NO_2; L = substituted pyridine or α-alkylarylamine), which entrap a variety of organic compounds as 'guest' molecules forming inclusion compounds of the 'channel' or 'cavity' type. The compound $Ni(NCS)_2(4\text{-}MePy)_4$ is the most versatile 'host' and has been the most widely studied so far. Its crystal structures with several aromatic molecules as 'guests' have been reviewed recently by Lipkowski [2] and the thermodynamics of the clathration process have been studied [3].

We are studying the selectivity of these clathrates towards various 'guest' molecules, and we have synthesised and characterised the structures of $Ni(NCS)_2(4\text{-}MePy)_4\cdot$*p*-cymene, $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2\cdot$methyl cellosolve [4], $Ni(NCS)_2(4\text{-}PhPy)_4\cdot4DMSO$ and $Ni(NCS)_2(3\text{-}MePy)_4\cdot CHCl_3$ [5].

We now report the structure of the 4-vinyl derivative $Ni(NCS)_2(4\text{-}ViPy)_4$ in the α-phase and as the 'host' in the β-phase structures of its clathrates, with *p*-, *m*- and *o*-xylenes as 'guests'. During the course of this investigation Lipkowski published the structure of the non-clathrating α-phase of $Ni(NCS)_2(4\text{-}ViPy)_4$ and reported the unit cell parameters of its three xylene clathrates [6]. However, our data of the three β-phase clathrating structures yield considerably different results, both as regards unit cell dimensions and the stoicheiometry of the host:guest ratio. The discrepancy may be due to the different ways in which the compounds were prepared.

Experimental Procedure and Structure Solutions

The host complex, compound **I**, was prepared by reacting an aqueous solution of nickel isothiocyanate with a stoicheiometric quantity of 4-vinylpyridine. The compound was dissolved in tetrahydrofuran and layered with diethylether. Blue needle-shaped crystals grew within twenty-four hours.

The clathrate compounds with *p*-xylene (compound **II**), *m*-xylene (compound **III**), and *o*-xylene (compound **IV**) were prepared by dissolving the host (compound **I**) in the respective xylene and layering with diethylether, to yield dark blue octahedral crystals.

For all structural determinations which were carried out at 293 K, small crystals were mounted in Lindemann tubes with mother liquor to prevent deterioration in air. Preliminary cell dimensions and space group symmetry were determined photographically. Accurate cell parameters were then obtained by least-squares analysis of twenty-five reflections measured in the range $16° < \theta < 17°$ on a Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). During the intensity data collection of each structure three reference reflections were periodically monitored

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TABLE I. Crystal Data and Experimental and Refinement Parameters for the Structures

Crystal data				
Compound	I	II	III	IV
Molecular formula	$C_{30}H_{28}N_6NiS_2$	$C_{38}H_{38}N_6NiS_2$	$C_{38}H_{38}N_6NiS_2$	$C_{38}H_{38}N_6NiS_2$
M_r (g mol^{-1})	595.42	701.60	701.60	701.60
Space group	*Pbca*	$I4_1/a$	$I4_1/a$	$I4_1/a$
a (Å)	11.351(6)	17.039(5)	16.950(3)	16.941(9)
b (Å)	16.924(3)	17.039(5)	16.950(3)	16.941(9)
c (Å)	32.247(6)	25.508(6)	26.325(6)	26.629(9)
V (Å^3)	6194.8	7405.7	7563.2	7642.4
Z	8	8	8	8
Host:guest ratio	–	1:1	1:1	1:1
D_m (g cm^{-3})	1.22	1.26	1.24	1.24
D_c (g cm^{-3})	1.27	1.26	1.23	1.22
μ (Mo Kα) (cm^{-1})	65.53	54.86	53.72	53.16
$F(000)$	2464	2928	2928	2928
Data collection				
Crystal dimensions (mm)	0.19 ×0.19 ×0.47	0.50 ×0.43 ×0.58	0.31 ×0.31 ×0.25	0.31 ×0.38 × 0.44
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan width, $\Delta\omega$ (°)	$(0.79 + 0.35 \tan\theta)$	$(0.59 + 0.35 \tan\theta)$	$(0.54 + 0.35 \tan\theta)$	$(0.64 + 0.35 \tan\theta)$
Vertical aperture length (mm)	4	4	4	4
Aperture width (mm)	$(1.66 + 1.05 \tan\theta)$	$(1.13 + 1.05 \tan\theta)$	$(1.12 + 1.05 \tan\theta)$	$(1.11 + 1.05 \tan\theta)$
Final acceptance limit	20σ at 20° min^{-1} in ω	20σ at 20° min^{-1} in ω	20σ at 20° min^{-1} in ω	20σ at 20° min^{-1} in ω
Max recording time (s)	40	40	40	40
Total number of reflections	6081	3582	3654	8280
Total number of observed reflections with $I_{rel} > 2\sigma I_{rel}$	3530	2650	2671	3076
Crystal stability (%)	2.3	1.63	1.65	1.7
2θ range (°)	2–50	2–50	2–50	2–50
Final refinement				
Number of variables	203	104	107	112
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.0710	0.0763	0.09	0.1106
$R_w = \Sigma w^{1/2} \lVert F_o \rvert - \lvert F_c \rVert / \Sigma w^{1/2} \lvert F_o \rvert$	0.0625	0.0763	0.09	0.0921
Weighting scheme w	$(\sigma^2 F)^{-1}$	unity	unity	$(\sigma^2 F)^{-1}$

to check crystal stability. Crystal data and experimental details of the data collections are listed in Table I. All data were corrected by a Lorentz polarisation factor and also for absorption [7].

The structures were solved by the heavy-atom method and refined by full-matrix least-squares using the SHELX76 [8] program system.

For compound **I** the final refinement was carried out with the Ni and S atoms treated anisotropically, and with the H atoms constrained to 1.08 Å from their parent C atoms, with a common temperature factor.

The β-phase structures **II**, **III** and **IV** were refined in a similar manner, with special care being taken over the location of the guest molecules. These three compounds all crystallise in the space group $I4_1/a$ and their structures are reported with respect to the second origin choice at $\bar{1}$ [9].

In all four structures, several of the bond lengths involving the vinyl carbon atoms are outside the usually quoted limits. The isotropic temperature factors of these vinyl carbons are consistently higher than those in the phenyl rings. Thus there is some disorder in these moieties.

For compound **II** the *p*-xylene guest was located at Wyckoff position d, which is a centre of symmetry. The atoms were well ordered and yielded acceptable bond lengths and angles, although their isotropic temperature factors remained consistently higher than the aromatic carbon atoms in the host molecule. The guest molecules in both compounds **III** and **IV** were also located at Wyckoff position d. A difference electron density map was calculated and contoured, and since neither *m*-xylene nor *o*-xylene are centrosymmetric, the map could only be interpreted by invoking disorder. The best model for refinement was achieved by fitting a regular hexagon of carbon atoms and four methyl carbons with site occupancy of 0.5 as shown in Table IV. The isotropic temperature factors of the guest atoms were again considerably higher than those of the aromatic carbon atoms in the host molecules.

A final difference electron density map was calculated after the last full-matrix least-squares refinement. This yielded 4 small peaks all less than 1 e Å^{-3} in the vicinity of the guest molecule, which we can account for as imperfect modelling of the disorded xylene. However, there is no evidence of significant electron density at the tetrahedral site, Wyckoff position b. This shows that a maximum of one guest can be accommodated per host molecule. We confirmed the host:guest stoichiometry independently by careful measurement of the crystal densities. Because these clathrates decompose, we chose the density column technique as being the most rapid method of measurement [10]. We prepared a linear density column in the range 1.00 to 1.30 g/cm^3 using water and KI solution as the two liquids. The column was calibrated with oil droplets of predetermined densities, and a single measurement could be carried out in approximately five seconds. The ob-

TABLE II. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (×10^3) for Compound **I**[a]

Atom	x/a	y/b	z/c	U_{iso}
Ni(1)	713(1)	605(1)	1333(1)	*[b]
N(1)	33(10)	−418(6)	1087(3)	65(3)
N(2)	1385(10)	1632(7)	1552(3)	70(4)
C(1)	−485(12)	−980(8)	1015(4)	70(5)
C(2)	1666(11)	2222(8)	1694(4)	54(4)
S(1)	−1203(4)	−1784(3)	908(2)	*
S(2)	2038(4)	3053(2)	1912(1)	*
N(11)	−966(9)	905(6)	1595(3)	60(3)
C(12)	−1958(12)	730(8)	1393(4)	73(4)
C(13)	−3053(14)	1038(8)	1518(5)	84(5)
C(14)	−3109(13)	1513(9)	1850(4)	80(5)
C(15)	−2097(11)	1689(8)	2072(4)	73(5)
C(16)	−1031(11)	1361(7)	1927(4)	68(4)
C(17)	−4295(17)	1930(11)	2004(6)	132(7)
C(18)	−5192(24)	1854(15)	1853(8)	213(11)
N(21)	1140(9)	22(6)	1879(3)	57(3)
C(22)	423(11)	−519(7)	2052(4)	64(4)
C(23)	610(12)	−854(7)	2440(4)	66(4)
C(24)	1632(11)	−693(8)	2666(4)	63(4)
C(25)	2386(12)	−148(7)	2471(4)	60(4)
C(26)	2140(11)	181(7)	2093(4)	63(4)
C(27)	1883(13)	−1053(8)	3087(5)	87(5)
C(28)	1165(13)	−1451(9)	3309(5)	99(6)
N(31)	166(9)	1213(6)	794(3)	59(3)
C(32)	−494(12)	1891(8)	809(4)	75(5)
C(33)	−1131(12)	2193(8)	483(4)	74(5)
C(34)	−1105(12)	1826(8)	103(5)	75(5)
C(35)	−386(12)	1176(8)	81(5)	79(5)
C(36)	221(12)	893(7)	414(4)	67(4)
C(37)	−1832(16)	2090(10)	−286(6)	129(7)
C(38)	−2727(20)	2047(4)	−217(7)	185(10)
N(41)	2369(10)	347(7)	1066(3)	71(4)
C(42)	3045(14)	902(9)	893(4)	91(5)
C(43)	4162(14)	760(9)	732(4)	92(5)
C(44)	4618(13)	21(10)	736(5)	89(5)
C(45)	3950(12)	−560(9)	918(4)	81(5)
C(46)	2828(12)	−383(8)	1077(4)	70(5)
C(47)	5892(16)	−225(12)	564(5)	129(7)
C(48)	6456(19)	265(12)	366(6)	161(8)

[a] Estimated standard deviations are in parentheses.

[b] Anisotropic atoms (marked by asterisk) have thermal parameters of the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3\}$ with parameters:

	Ni(1)	S(1)	S(2)
U_{11}	47(1)	126(4)	88(3)
U_{22}	54(1)	121(4)	60(3)
U_{33}	71(1)	140(5)	133(4)
U_{23}	−9(1)	−45(4)	−9(3)
U_{13}	3(1)	24(4)	−15(3)
U_{12}	−2(1)	−69(4)	−14(3)

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Compounds **II**, **III** and **IV**[a]

Atom	**II**				**III**				**IV**			
	x/a	y/b	z/c	U_{iso}	x/a	y/b	z/c	U_{iso}	x/a	y/b	z/c	U_{iso}
Ni(1)	5000(0)	2500(0)	5549(1)	*[b]	5000(0)	2500(0)	5452(1)	*[b]	5000(0)	2500(0)	5438(1)	*[b]
N(1)	4020(4)	3222(4)	5532(3)	61(2)	4032(5)	3245(4)	5436(3)	70(2)	4047(6)	3249(5)	5416(4)	64(3)
C(1)	3386(5)	3430(5)	5529(3)	55(2)	3388(6)	3432(5)	5439(3)	64(3)	3398(8)	3430(7)	5436(5)	57(4)
S(1)	2480(2)	3731(2)	5534(1)	*	2467(2)	3696(2)	5441(1)	*	2472(3)	3690(3)	5425(2)	*
N(11)	5486(4)	3212(4)	6149(3)	59(2)	5506(4)	3202(4)	6029(3)	64(2)	5520(6)	3201(5)	6012(3)	59(3)
C(12)	5008(6)	3537(6)	6503(4)	79(3)	5042(7)	3541(6)	6377(4)	82(3)	5062(8)	3529(7)	6348(5)	74(4)
C(13)	5303(6)	3985(6)	6941(4)	81(3)	5342(6)	3975(6)	6795(4)	81(3)	5356(8)	3960(7)	6767(5)	76(5)
C(14)	6109(6)	4088(6)	6979(4)	75(3)	6162(6)	4038(6)	6848(4)	73(3)	6159(8)	4059(8)	6830(5)	66(4)
C(15)	6580(6)	3762(5)	6611(4)	75(3)	6616(6)	3709(6)	6491(4)	76(3)	6622(8)	3689(7)	6455(5)	71(4)
C(16)	6251(5)	3320(5)	6210(3)	68(3)	6286(6)	3304(5)	6087(4)	70(3)	6300(8)	3287(7)	6061(5)	64(4)
C(17)	6485(7)	4554(6)	7437(5)	105(4)	6540(7)	4475(6)	7285(4)	96(4)	6505(9)	4475(8)	7281(5)	93(5)
C(18)	6130(8)	4700(8)	7840(5)	125(5)	6140(8)	4684(7)	7689(5)	120(5)	6160(10)	4691(10)	7679(6)	121(7)
N(21)	4447(4)	1823(4)	4956(3)	55(2)	4440(4)	1821(4)	4875(3)	62(2)	4449(5)	1829(6)	4876(4)	62(3)
C(22)	4079(5)	2186(5)	4550(3)	62(2)	4083(5)	2175(6)	4484(3)	70(3)	4084(7)	2179(8)	4479(5)	74(4)
C(23)	3740(5)	1794(5)	4131(4)	67(3)	3728(6)	1760(6)	4089(4)	71(3)	3714(7)	1768(8)	4090(5)	67(4)
C(24)	3758(5)	978(5)	4115(3)	61(2)	3742(5)	954(6)	4084(4)	65(3)	3743(7)	934(8)	4075(5)	67(4)
C(25)	4112(5)	603(5)	4529(3)	65(3)	4107(5)	578(6)	4485(4)	72(3)	4111(7)	587(8)	4480(4)	58(4)
C(26)	4456(5)	1040(5)	4934(3)	60(2)	4445(5)	1020(6)	4873(4)	71(3)	4457(7)	1022(7)	4864(5)	64(4)
C(27)	3423(6)	494(7)	3662(4)	96(4)	3380(7)	466(7)	3669(5)	102(4)	3368(8)	452(9)	3651(5)	92(5)
C(28)	3135(8)	803(8)	3252(5)	132(5)	3094(9)	749(9)	3258(6)	153(6)	3076(10)	754(10)	3263(6)	128(7)
CG(1)	−441(7)	5006(8)	5451(5)	#[c]	518(14)	4571(13)	4671(9)	#[c]	407(15)	4275(14)	4795(10)	#[c]
CG(2)	−486(7)	5643(7)	5103(5)	#	190(15)	5307(12)	4512(6)	#	440(15)	5025(13)	4544(7)	#
CG(3)	−54(8)	5639(7)	4659(5)	#	−163(15)	5779(9)	4882(8)	#	−106(17)	5677(10)	4686(8)	#
CG(21)					508(27)	5647(21)	4078(10)	#	937(23)	5060(23)	4149(12)	#
CG(31)	92(7)	3685(7)	5731(4)	#	−446(28)	6535(12)	4693(15)	#	−46(29)	6385(16)	4389(13)	#

[a] Estimated standard deviations are in parentheses.

[b] Anisotropic atoms (marked by asterisk) have thermal parameters of the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3\}$ with parameters:

	II		**III**		**IV**	
	Ni(1)	S(1)	Ni(1)	S(1)	Ni(1)	S(1)
U_{11}	51(1)	64(2)	62(1)	76(2)	61(2)	77(3)
U_{22}	53(1)	91(2)	58(1)	111(3)	52(2)	107(4)
U_{33}	52(1)	105(2)	59(1)	161(3)	52(2)	178(5)
U_{23}	0	7(2)	0	1(3)	0	−6(4)
U_{13}	0	1(2)	0	−0(2)	0	−8(4)
U_{12}	−1(1)	18(2)	−2(1)	18(2)	−1(2)	22(3)

[c] Temperature factors of guest atoms (#) are linked and have the following values: U_{iso} **II**, 108(2); **III**, 256(6); **IV**, 317(9).

served densities and corresponding host:guest ratios are listed in Table I. Fractional atomic coordinates and thermal parameters of compound **I** are shown in Table II and of compounds **II**, **III** and **IV** in Table III.

Discussion

The structure of the complexes in all four compounds has the central nickel atom in an octahedral configuration with the isothiocyanate moieties in *trans* positions. The observed bond lengths and angles are within the accepted limits for compounds of this kind [2]; detailed Tables are available (see 'Supplementary Material'). A perspective view of a molecule of compound **I**, the α-phase, is shown in Fig. 1. The host molecules in the other compounds are essentially similar. One of the main reasons advanced to explain the versatility of Werner clathrates is the rotational freedom of the substituted pyridine ligands about their Ni–N bonds. This supposedly allows adjustment of the host molecules to accommodate a variety of guests, differing in size and shape.

The torsional configuration of the 4-vinyl pyridines is given by the torsion angles N(1)–Ni–N(x1)–C(x2) with $x = 1(\tau_1)$, $2(\tau_2)$, $3(\tau_3)$, $4(\tau_4)$. In the β-phase clathrates, compounds **II**, **III** and **IV**, the

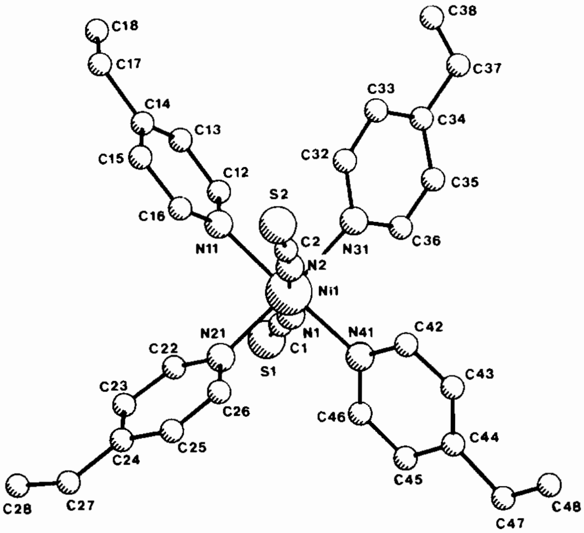
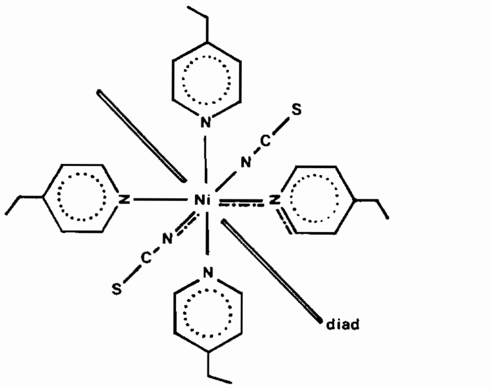


Fig. 1. Perspective view of a host molecule of compound **I** with atomic nomenclature.

Ni is located on the diad at Wyckoff position e, and thus only two 4-vinylpyridines and one isothiocyanate ligand constitute the asymmetric unit as shown in Fig. 2. The values of the four torsion angles are similar in all four compounds. In a previous potential energy study of similar compounds [5], we have shown that the conformation of the substituted pyridines is governed by the *ortho*-hydrogen atoms; therefore, we may ignore the asymmetry imposed by the 4-vinyl substituent on the pyridine. This would give two-fold axial symmetry to the pyridine and τ_3 and τ_4 would be equivalent to $(180 + \tau_3)$ and $(180 + \tau_4)$, the values reported in brackets, Fig. 2. This results in the equivalent of a ++++ conformation as reported for similar structures by Lipkowski [11]. For compound **I**, we quote the torsion angles for the molecule transposed through a centre of inversion in order to ease the comparison with the β-phase structures. We note that, there being no crystallographic diad imposed on the molecule, the four torsion angles are slightly different from each other, but do not differ significantly from the corresponding torsion angles in the other three compounds. Thus the overall conformation of the complex is insensitive to clathrate formation.

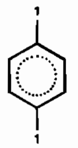
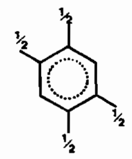


COMPOUND	I	II	III	IV
τ 1	35.6	34.8	35.1	35.9
τ 2	40.0	43.1	43.0	42.4
				diad
τ 3	-128.4(51.6)	-145.2(34.8)	-144.9(35.1)	-144.1(35.9)
τ 4	-139.9(40.0)	-136.9(43.1)	-137.0(43.0)	-137.6(42.4)

Fig. 2. Comparison of selected torsion angles in the host molecules.

It is interesting to compare the packing modes in these structures. Table IV gives the packing density, expressed as volume per non-hydrogen atom, and shows that the p-xylene clathrate is the most efficiently packed. We assumed that the volume occupied by one host molecule in the α-phase unit cell, $V_\alpha/8$ remains constant in all structures. We then evaluated the volume, $(V_\beta - V_\alpha)$, that each type of guest molecule occupies. As expected, both the disordered m- and o-xylene molecules occupy a similarly larger volume than the ordered p-xylene molecule. Taking the volume of a methyl group to be 23.5 Å^3 as evaluated by Kitaigorodsky [12], then the volume differences between the two disordered guests and the ordered guest correspond closely to one extra methyl group. This agrees with the model used in the final refinement.

TABLE IV. Packing Densities and Volume Comparisons

	Compound			
	I	II	III	IV
V/non H atom (Å^3)	19.9	19.7	20.1	20.3
				
$V_\beta - V_\alpha/8$		151.5	171.1	181.2
$V_{m,o} - V_p$			19.6	29.6
V_{CH_3}(Å^3) = 23.5			0.8(−1)	1.3(−1)
U(kcal)		−14.47	−11.32	−9.69

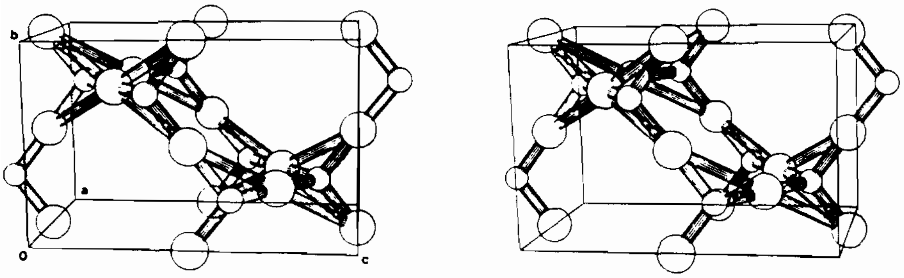


Fig. 3. A schematic view of the channels in a typical β-phase structure.

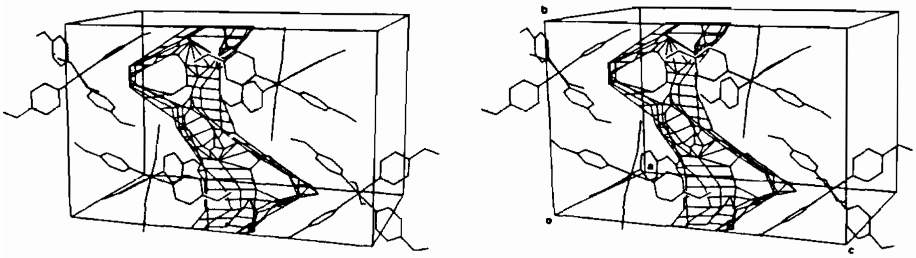


Fig. 4. The zero-energy surface of one channel and the surrounding host molecules.

We have mapped the shape of the channel by calculating the potential energy environment of a 'probe' atom, applying the technique of atom pair potentials. Using the program EENY [13] we evaluated the van der Waals energy with atom–atom potentials of the form:

$$U(r) = a \exp(-br)/r^d - cr^{-6}$$

where r is the distance between any pair of atoms, and coefficients a, b, c, d are those given by Giglio [14], Quagliata, Scarcelli and Pavel [15]. These potential energy curves were derived primarily to give good agreement for calculations of molecular position in crystal structure, and no account is taken of partial atomic charges or dipole interactions. We chose a hydrogen atom as a suitable probe and allowed this to move systematically throughout the appropriate portions of the unit cell while calculating its intermolecular interactions with the host molecules at suitable intervals. In this way we were able to map the channels of free space which may accommodate guest molecules. A schematic view of the channels which zig-zag through the entire unit cell is shown in Fig. 3, while a perspective stereo view of one such channel, as defined by its surface at zero potential, is shown in Fig. 4.

Using similar techniques we have evaluated the potential energies of the guest molecules in their cavities. The xylene molecules were given rotational freedom about the centre of inversion in their channel cavities, and the potential energy minima were evaluated. Care was taken to ensure that the disordered methyl groups in structures **III** and **IV** only contributed half of their potential to the total energy sum. This was consistent with the crystallographic disorder model used and the values are listed in Table IV. Interestingly, the energies of the guests in their cavities are in the order p-xylene $<$ m-xylene $\approx$ o-xylene, which corresponds to the finding that the p-xylene is ordered and is the most efficiently packed. This is in agreement with the view that coincidence of host cavity symmetry with guest molecular symmetry is energetically favoured [16].

Supplementary Material

Detailed Tables of observed bond lengths and angles have been deposited with the Editor-in-Chief.

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