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Inclusion and Separation of Lutidine Isomers by a Diol Host Compound

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Structures of the inclusion compounds formed between the host compound 1,1-bis(4-hydroxyphenyl)cyclohexane and selected lutidine isomers have been elucidated. The activation energies and kinetics of desolvation for the complexes were determined. Competition experiments were performed to investigate preferential enclathration. Lattice energy calculations explain the results of the competition experiments.

Keywords: Inclusion, separation, lutidines

INTRODUCTION

One of the important applications of Supramolecular Chemistry is the separation of close isomers by the process of enclathration. This involves the choice of a suitable host compound which, when exposed to a mixture of guest molecules, combines selectively with a particular guest forming a crystalline inclusion compound. The latter is filtered and the guest is released by gentle warming, enabling the host to be recycled. The selectivity of the process depends on the efficiency of the molecular recognition between host and guest, and is seldom totally achieved after one cycle. However, by proper selection of the host compound, a selectivity >99% can often be achieved after a few cycles. We have used the host 1,1-bis(4-hydroxyphenyl)cyclohexane to separate the isomers of the phenylenediamines [1], the benzenediols [2] and the picolines [3]. This host also forms inclusion compounds with phenol and the cresols and their structures have been elucidated [4]. We now present the results of competition experiments between this host and three lutidine isomers.

EXPERIMENTAL

Suitable crystals of inclusion compounds **1** and **2**, refer to Scheme I, were obtained by slow evaporation over a period of 4 days. Numerous attempts to obtain suitable crystals of the inclusion compound of the host with 2,6-lutidine were unsuccessful, and therefore the structure of this complex cannot be reported. Preliminary cell dimensions and space group symmetry

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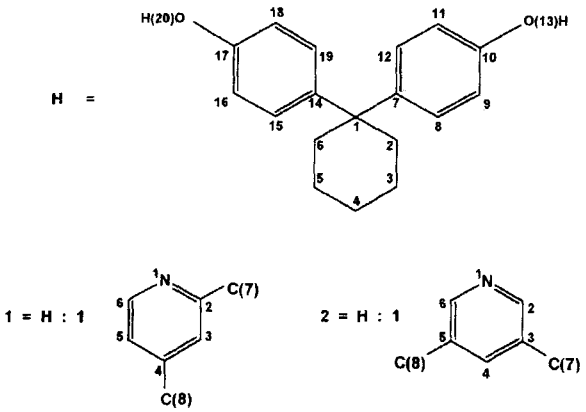
were determined photographically and the cell data were subsequently refined by standard procedures on a CAD4 diffractometer. The intensities were collected in the $\omega-2\theta$ scan mode and crystal stabilities were monitored by periodic reference reflections. The important crystal and experimental data are given in Table I. Both structures were solved by direct methods using SHELX-86[5] and refined employing full-matrix least-squares using the program SHELX-93 [6], refining on F^2. The numbering scheme is shown in Scheme I. In the final refinement for both structures all non-hydrogen atoms were treated anisotropically. The aromatic, methylenic and methyl hydrogens were geometrically constrained and refined with common isotropic temperature factors. The hydroxy hydrogens were all located in difference electron density maps and refined with independent temperature factors, and with simple bond length constraints.



X-ray powder diffraction (XRD) patterns were recorded in a Philips PW1050/80 vertical goniometer with a PW1394 motor control unit. The patterns were collected over a 2θ range of 6–40°.

Competition Experiments

Competition experiments were conducted between the 3,5-lutidine and 2,4-lutidine guests as

TABLE I Details of crystals, data collections and final refinements

	1	2
	$C_{16}H_{20}O_2 \bullet C_7H_9N$	$C_{18}H_{20}O_2 \bullet C_7H_9N$
Molecular formula		
Molecular weight/g mol^{-1}	375.49	375.49
Space group	$P2_1/n$	$P2_1$
a/Å	7.665(9)	10.509(2)
b/Å	31.361(5)	6.309(2)
c/Å	8.874(2)	16.118(6)
β/°	99.14(1)	96.99(2)
V/Å^3	2106.0(6)	1060.7(5)
Z	4	2
D_c/g cm^{-3}	1.18	1.18
D_m/g cm^{-3}	1.16(2)	1.15(4)
μ (Mo-K$_\alpha$)/cm^{-1}	0.70	0.74
F(000)	808	404
Data Collection (20°C)		
Crystal size/mm	0.34×0.34×0.30	0.4×0.5×0.35
Range scanned, θ/°	1–25	1–25
Range of indices	h: ±9; k: 0,37; l: 0,10	h: ±12; k: 0,7; l: 0,19
Crystal decay, /%	−1.9	2.4
No. reflections collected	3937	2136
No. reflections observed [$I_{rel} > 2\sigma(I_{rel})$]	3696	2059
No. parameters	271	271
R	0.045	0.037
R_W	0.125	0.089
S	1.046	1.075
$\Delta\rho$/e Å^{-3}	0.183; −0.242	0.129; −0.198

follows: A series of 11 vials was made up with mixtures of the two liquid guests, varying the mole fraction of the guests from 0 to 1 in the series, but keeping the host:guest ratio at 1:20 in each vial. Crystals were obtained by slow evaporation, were filtered from the mother liquor and dissolved in ethyl acetate. The relative composition of the included guests and of the mother liquors with which they were in equilibrium were determined by gas chromatography using a Carlo Erba Fractovap 4200 instrument equipped with a BP255 capillary column (0.25 mm diameter, 25 m length) and a Spectra-Physics SP4290 integrator.

The experiment was extended to analyse simultaneous competition by three lutidine isomers: 2,4-lutidine, 2,6-lutidine and 3,5-lutidine. Initial mixtures of the three guests were selected on a circle drawn on a triangular diagram representing the compositions of the isomers, as shown in Figure 1. The equimixture of the guests, with mole fraction 1/3 each, representing the centre of the circle, was also analysed. The relative compositions of the included guests and mother liquors were analysed as before.

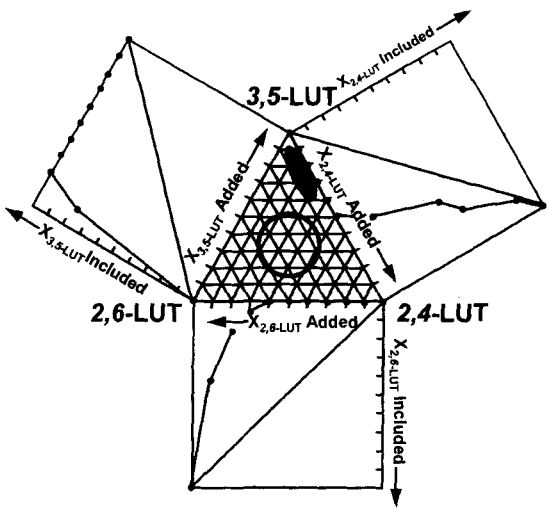


FIGURE 1 Results of the competition experiments.

Thermal Analysis and Kinetics

Differential scanning calorimetry (DSC) and thermal gravimetry (TG) were performed on a Perkin Elmer PC7 series system. Fine powdered specimens, obtained from continuously stirred solutions, were dried in air and placed in open platinum pans for TG experiments and in crimped, vented aluminium sample pans for DSC experiments. Sample masses in each case were 2–5 mg, and the samples were purged by a stream of nitrogen flowing at 40 ml min^{-1}. Kinetic data for the desolvation of guest were obtained both from isothermal TG experiments and nonisothermal experiments at variable heating rates.

RESULTS AND DISCUSSION

For **1**, the space group is $P2_1/n$ with $Z = 4$. There are thus four host molecules and four guest molecules in the unit cell, and no crystallographic symmetry is imposed on either host or guest molecule. The packing of the structure, shown as a projection viewed along [001] is given in Figure 2. The cyclohexane moiety of the host is in the chair conformation and the host molecules pack in a double ribbon motif running parallel to *a*. The host molecules are stabilised by intermolecular hydrogen bonding. The 2,4-lutidine guest molecules are hydrogen bonded to the host framework, and lie in channels, parallel to *a*, formed by the packing of the host molecules. Stabilising $\pi-\pi$ interactions occur between the guest molecules, with partial overlap of parallel adjacent molecules. C–C stack distances between a guest molecule and its

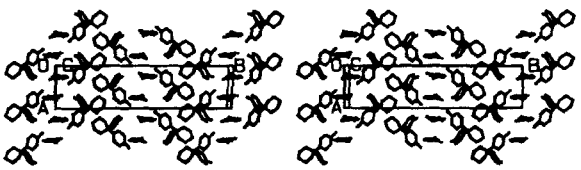


FIGURE 2 Packing diagram for **1**.

nearest neighbouring guest molecule are all in the range 3.574(2) – 4.909(1) Å.

For **2**, the space group is $P2_1$ with $Z = 2$. The host and guest molecules are located at general positions in the unit cell. The strucutre, shown in Figure 3 as a projection down [010], is again made up of double ribbons of hydrogen bonded host molecules interrupted by channels of guest molecules running parallel to *a*. Each guest molecule forms one hydrogen bond to the host structure. Details of the hydrogen bonding interactions in **1** and **2** are presented in Table II.

The results of the competition experiments are illustrated in Figure 1. Each two-component result shows the mole ratio of the initial solution *versus* that included by the host. For the 2,6-lutidine/3,5-lutidine competition the latter is strongly favoured, and was the only isomer complexed by the host in those mixtures initially containing more than 10% 3,5-lutidine. 2,4-Lutidine is also convincingly favoured over 2,6-lutidine in those mixtures containing more than 10% 2,4-lutidine. In the competition between 3,5-lutidine and 2,4-lutidine, the preferential complexation of 3,5-lutidine was observed throughout the series of experiments, although 3,5-lutidine was the only isomer complexed in those solutions where it was initially present in concentrations greater than 40%. The three-component experiment is shown on the equilateral triangle. The starting mixtures were located on the circle, which migrated towards the apex of the triangle representing 3,5-lutidine. A horizontal shift of the circle, away from the 2,6-lutidine component, indicated that 2,6-lutidine was the least favoured isomer for complexation with the host.

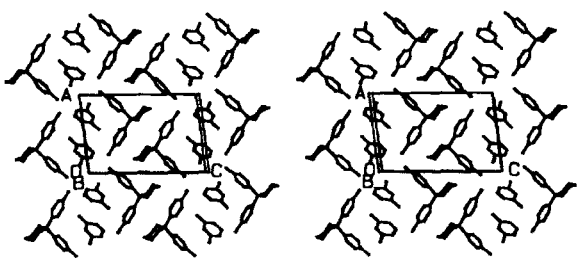


FIGURE 3 Packing diagram for **2**.

Lattice Energy Calculations

When considering the selectivity of a particular host for a given guest from a mixture of isomers, an important parameter to be evaluated is the lattice energy. There are two principal interactions that are responsible for the packing of the molecules: van der Waals forces and hydrogen bonds. The potential energy of the lattice was calculated by the method of atom – atom potentials. The program HEENY [7, 8] uses empirical atom pair potential curves to evaluate non-bonded van der Waals interactions. The coefficients of the atom – atom potentials are of the form

$$V(r) = a.\exp[(-br)/r^d - c/r^6]$$

where r is the interatomic distance and the coefficients a, b, c, d are those given by Giglio [9] and recently reviewed by Pertsin and Kitaigorodsky [10]. In addition, we have incorporated a hydrogen bonding potential into our calculations. This is a simplified version of that used by

TABLE II Hydrogen bonding data for **1** and **2**

Compound	Donor	Acceptor	D–H/Å	D···A/Å	D–H···A/°
1	O13	N1G [a]	0.96(4)	2.677(3)	172(3)
	O20	O13 [b]	0.96(3)	2.743(3)	167(3)
2	O20	N1G	0.94(4)	2.654(4)	170(4)
	O13	O20 [c]	0.95(4)	2.763(4)	167(3)

Symmetry operations: [a] $x, y, z+1$; [b] $x-1, y, z-1$; [c] $x+1, y, z$.

Vedani and Dunitz [11], using the potential

$$V_{\text{H-bond}} = (A/R^{12} - c/R^{10})\cos^2\theta$$

where R is the distance between the hydrogen and the acceptor, and θ is the donor–H-acceptor angle. Further details are given in a previous paper [12] in which the relative stabilities of a series of inclusion compounds between bulky hydroxy hosts and 1,4-dioxane were analysed.

For both structures **1** and **2** we selected a representative host–guest pair and carried out the appropriate summations of all the host–host, host–guest and guest–guest interactions. For **1** we obtained a value of $-270.4\,\text{kJ mol}^{-1}$, while **2** yielded the value $-305.8\,\text{kJ mol}^{-1}$. These values indicate that the complex **2** is more stable than **1**. Since the structure of the complex between the host and 2,6-lutidine could not be elucidated, the lattice energy of this complex could not be calculated.

Kinetics of Desolvation

For **1** and **2**, a series of mass loss *versus* time curves were obtained for the desolvation reaction, over the temperature range 65–83°C for **1**, and 77 to 95°C for **2**. The data were reduced to fractional reaction α *versus* time curves, and were fitted to various kinetic models [13]. For **1**, the model which most closely approached linearity was deceleratory and was that for the contracting volume mechanism of a sphere, R3: $1\text{-}(1\text{-}\alpha)^{1/3} = kt$ over the complete α range. For **2**, the deceleratory contracting area kinetic model R2, where $kt = 1-(1-\alpha)^{1/2}$ was best suited to the data. Plots of $\ln k$ *versus* $1/T$ for **1** and **2** are shown in Figures 4 and 5. These yielded activation energies of 95(6) and 106(4) kJ mol^{-1}, respectively.

Thermogravimetry at various heating rates provided another method to estimate the activation energy of the guest-release reaction. We used the method developed by Flynn and Wall [14] which has previously been applied to similar compounds [15]. The decomposition

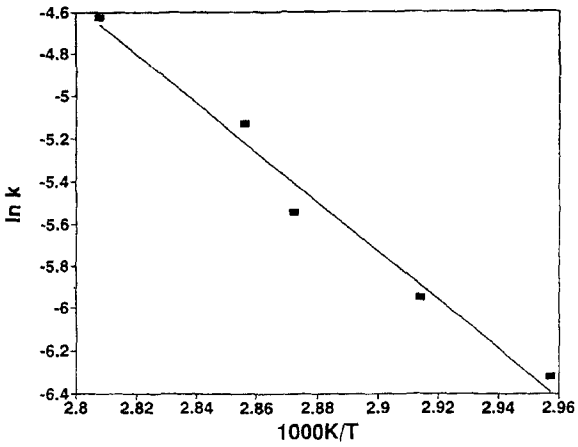


FIGURE 4 Arrhenius plot for the desolvation of **1**.

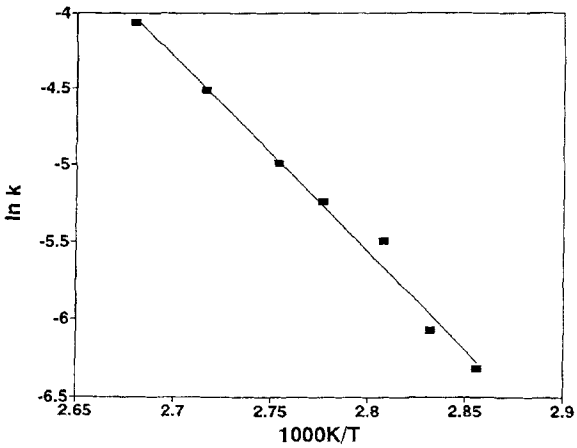


FIGURE 5 Arrhenius plot for the desolvation of **2**.

curves for both **1** and **2** were recorded at various heating rates, β, ranging from 1 to 20°C min^{-1} and the corresponding semilogarithmic plots of $\log \beta$ *versus* $1/T$ are shown in Figures 6 and 7. For **1**, the slopes of the lines correspond to activation energies varying from 81(4) to 83(5) kJ mol^{-1} while for **2** the corresponding values vary from 107(2) to 112(2) kJ mol^{-1}. The activation energy values obtained for the complexes employing the two different experimental methods are in excellent agreement.

It is well known that different methods of preparation of inclusion compounds can lead to a variety of structures with incosistent host:guest ratios. The microcrystalline samples used

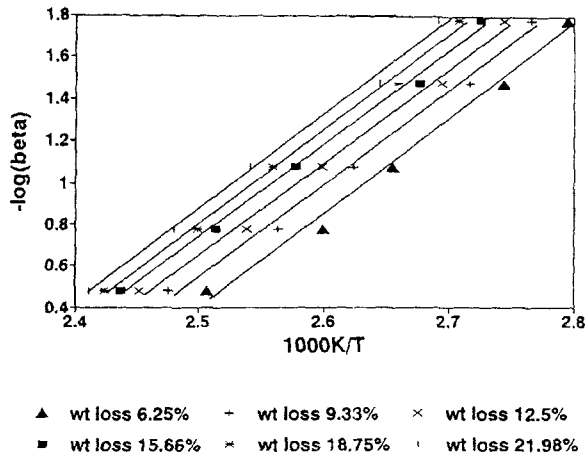


FIGURE 6 Plot of $-\log \beta$ *versus* $1/T$ for several percentages of decomposition of **1**.

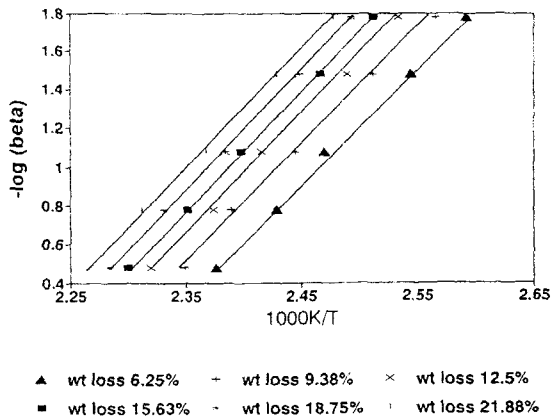


FIGURE 7 Plot of $-\log \beta$ *versus* $1/T$ for several percentages of decomposition of **2**.

for the kinetic experiments were therefore examined by XRD to ensure that they had the same crystal structure as those of the single crystals. This was achieved by recording the powder diffraction pattern of the inclusion compounds grown as microcrystalline powders by fast stirring, and comparing these to the patterns calculated from the atomic co-ordinates derived from the structure solutions using the program LAZY PULVERIX [16]. These patterns match very well both in peak position and relative intensity. The powder diffraction results for **1** are shown in Figure 8. Similar results were obtained for **2**.

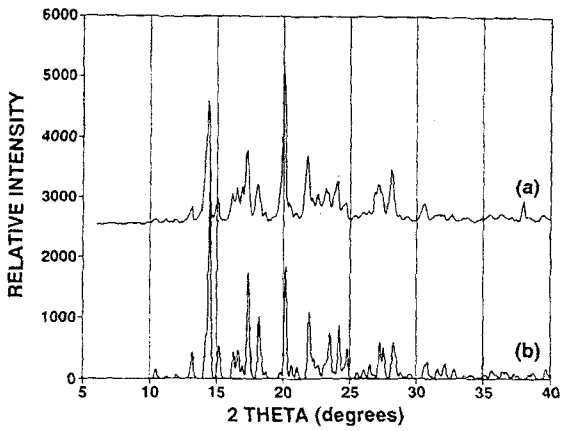


FIGURE 8 a) Experimental powder pattern of sample obtained by fast stirring of host in 2,4-lutidine. b) Calculated powder pattern for compound **1**.

The calculated lattice energy values are in good agreement with both the kinetic parameters obtained for the desolvation of the complexes, as well as the results of the competition experiments. The higher stability of the complex **2** was indicated by the activation energy of desorption, since $\sim 20\,kJ\,mol^{-1}$ more energy was required to bring about desorption of the guest molecules in **1** than in **2**. Also, the lattice energy of **2** was found to be $\sim 30\,kJ\,mol^{-1}$ lower than that of **1**. During the competition experiments, **2** was always formed preferentially. The difficulty experienced in obtaining crystals of the complex between the host and 2,6-lutidine is possibly due to the steric hindrance of the methyl substituents, which would prevent the formation of stabilising hydrogen bonds between the host framework and the nitrogen atoms of the guest molecules. Therefore complexation with 2,6-lutidine is possibly highly disfavoured, and this is indicated by the results of the competition experiments.

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