SHORT PAPER

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Novel bisurea host compounds†

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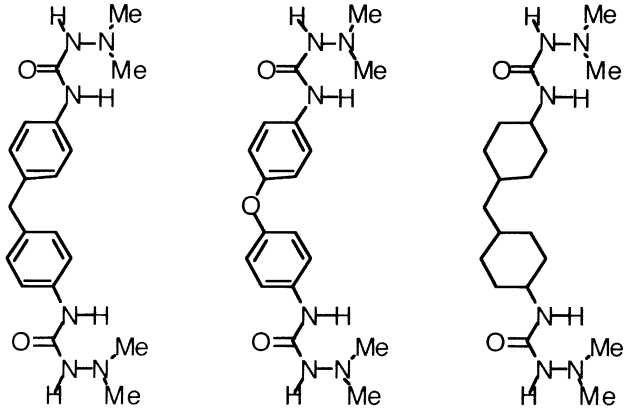
New host molecules, 4,4′-bis(dimethylamino-urea)diphenylmethane (**1**) and its derivatives (**2** and **3**), are reported. These hosts are shown to give inclusion complex crystals with a wide variety of organic guest molecules with high selectivity. The crystal structure of 1:2 inclusion complex of **1** with THF has been determined from X-ray crystal structure analysis. The cyclic N–H...O intermolecular hydrogen bonds between host molecules were found to form columns for accommodation of the guest molecules.

Keywords: 4,4′-bis(dimethylamino-urea) diphenylmethane, bisurea host compounds

The design of host–guest inclusion systems has been of interest in recent years due to their potential applications for chemical separation, selective reactions and porous materials having optical, magnetic and catalytic properties.[1] We now report the synthesis, inclusion properties of novel host compounds, 4,4′-bis(dimethylamino-urea)diphenylmethane (**1**), 4,4'-bis(dimethylamino-urea)diphenylether (**2**) and 4,4′-bis(dimethylamino-urea)dicyclohexylmethane (**3**). The X-ray crystal structure of a 1:2 inclusion complex of **1** with THF is also reported.



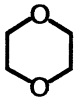
1 **2** **3**

Results and discussion

When a solution of 4,4′-bis(diisocyanato)diphenylmethane (1.25 g, 5.00 mmol) and *N*,*N*-dimethylhydrazine (0.73 g, 12.1 mmol) in toluene (20 ml) was stirred at room temperature for 30 min, 1:1 inclusion complex crystals of 4,4′-Bis(dimethylamino-urea)diphenylmethane (**1**) with toluene were obtained as colourless needles (2.22 g) in 96% yield. Upon heating the inclusion complex under vacuum, free host compound (**1**) was obtained as a white powder (1.78 g). A similar treatment of 4,4′-bis(diisocyanato)diphenylether and 4,4′-bis(diisocyanato)dicyclohexylmethane with *N*,*N*-dimethylhydrazine in toluene gave 4,4′-bis(dimethylamino-urea)diphenylether (**2**) and 4,4′-bis(dimethylamino-urea)dicyclohexylmethane (**3**) in 95 and 49% yield, respectively.

When the host compounds (**1**–**3**) were recrystallised from the usual organic guest solvents, inclusion crystals were formed, containing the guest molecules in host–guest ratios as indicated in Table 1. The most efficient host was **1** followed by **2**, while host (**3**) with dicyclohexylmethane flamework was less effective at inclusion formation. Host (**1**) includes wide range of protic and aprotic, cyclic and acyclic, aliphatic and aromatic guest molecules. (Table 1) Host (**2**) mostly forms inclusion complexes with polar aprotic solvents such as cyclopentanone, THF and DMF. In contrast, host (**3**) includes only THF and DMSO in 1:1 and 2:1 ratios, respectively. The scissors topology of rigid host framework of **1** and **2** plays an important role in these excellent inclusion abilities.

Table 1 Host–guest ratios of inclusion complexes of **1–3**[a]

Guest	**1**	**2**	**3**
MeOH	1:1	–[b]	–
EtOH	1:1	–	–
acetone	2:1	–	–
	1:1	1:1	–
AcOEt	2:1	–	–
	1:2	1:1	1:1
	1:2	1:1	–
CH_3CN	1:1	–	–
DMSO	1:2	1:2	2:1
DMF	1:1	4:1	–
toluene	1:1	1:1	–
	1:1	–	–

[a]The ratios were determined by ^{1}H NMR spectroscopy.
[b]No complexation occurred.

It is also remarkable that host (**1**) exhibits selective inclusion behaviour toward some guest compounds. For example, **1** forms a 1:2 inclusion complex with 1,4-cyclohexanediol, but 1,2- and 1,3-isomers do not. Host (**1**) includes *o*-cresol and *p*-cresol as a 1:1 complex, but not *m*-cresol. The IR spectrum of free host (**1**) showed νNH absorption at 3314 and 3210 cm^{-1},

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

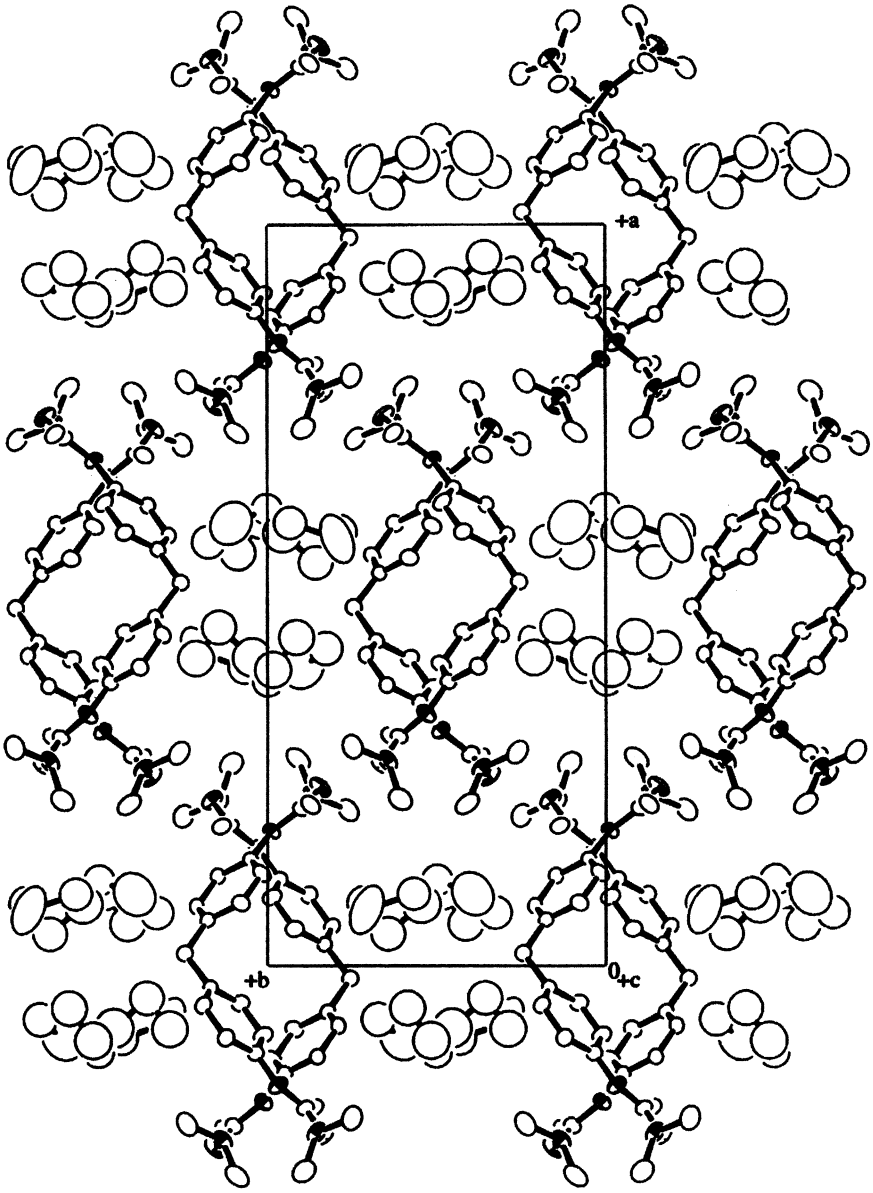

Fig. 1 Ellipsoid representation (50%) of 1.2 THF.

respectively, and the former was found to shift to lower frequencies (3294 cm^{-1}) by forming hydrogen bonds between host molecules when complexed with guest compounds.

The host molecule has a non-crystallographic twofold axis as shown in Fig. 1, and the dihedral angle between the phenyl rings is 77.4(2)°. The planes of the urea moieties, N3–C9(=O1)–N4 and N6–C12(=O2)–N7, rotate to the bonded phenyl ring by 19.6(2)° and 14.1(2)°, respectively. The dihedral angle between the two urea moieties is 92.3(2)°. The dimethylamino-urea group has an N–H...N intramolecular hydrogen bond. Host molecules related by the *a* glide symmetry are connected by the cyclic N–H...O intermolecular hydrogen bonds to form zigzag chains along *a*. The guest THF molecules are accomodated in the columns running parallel to *c*. The THF molecules were easily lost from the crystals in the air. The abnormally large atom displacement parameters of THF correspond to their rough packing (Fig. 2)

Experimental

General methods and materials: Melting points were recorded on a Yanaco MP-3 melting apparatus and are not corrected. IR spectra were recorded on a JASCO FTIR-200 spectrometer in Nujol mulls. ^{1}H NMR spectra were recorded on JEOL Lambda-300 spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The host–guest inclusion compouds were prepared by recrystallisation of host compounds (**1**–**3**) from the neat guest solution and the host–guest ratios were determined by TG and ^{1}H NMR. The data are summarised in Table 1.

Preparation of 4,4′-bis(dimethylamino-urea)diphenylmethane (**1**): When a solution of 4,4′-bis(diisocyanato)diphenylmethane (1.25 g, 5.00 mmol) and *N,N*-dimethylhydrazine (0.73 g, 12.1 mmol) in toluene (20 ml) was stirred at room temperature for 30 min, 1:1 inclusion complex crystals of 4,4′-bis(dimethylamino-urea)diphenylmethane (**1**) with toluene were obtained as colourless needles (2.22 g) in 96% yield. Upon heating the inclusion complex under vacuum, the free host compound (**1**) was obtained as a white powder (1.78 g). M.p.: 171–173°C; IR (Nujol) 3313, 3204, 1685 cm^{-1}; δH (300 MHz, $CDCl_3$) 8.05 (s, 2 H), 7.39 (d, J = 8.4 Hz, 4 H), 7.10 (d, J = 8.4 Hz, 4 H), 5.15 (s, 2 H), 3.88 (s, 2 H), 2.58 (s, 12 H). Anal. Calc. For $C_{19}H_{26}N_6O_2$: C, 61.60; H, 7.07; N, 22.69. Found: C, 61.58; H, 7.13; N, 22.90.

Preparation of 4,4′-bis(dimethylamino-urea)diphenylether (**2**): When a solution of 4,4′-bis(diisocyanato)diphenylether (0.5 g, 1.98 mmol) and *N,N*-dimethylhydrazine (0.24 g, 3.99 mmol) in toluene (20 ml) was stirred at room temperature for 1 h, 1:1 inclusion complex crystals of 4,4′-bis(dimethylamino-urea)diphenylether (**2**) with

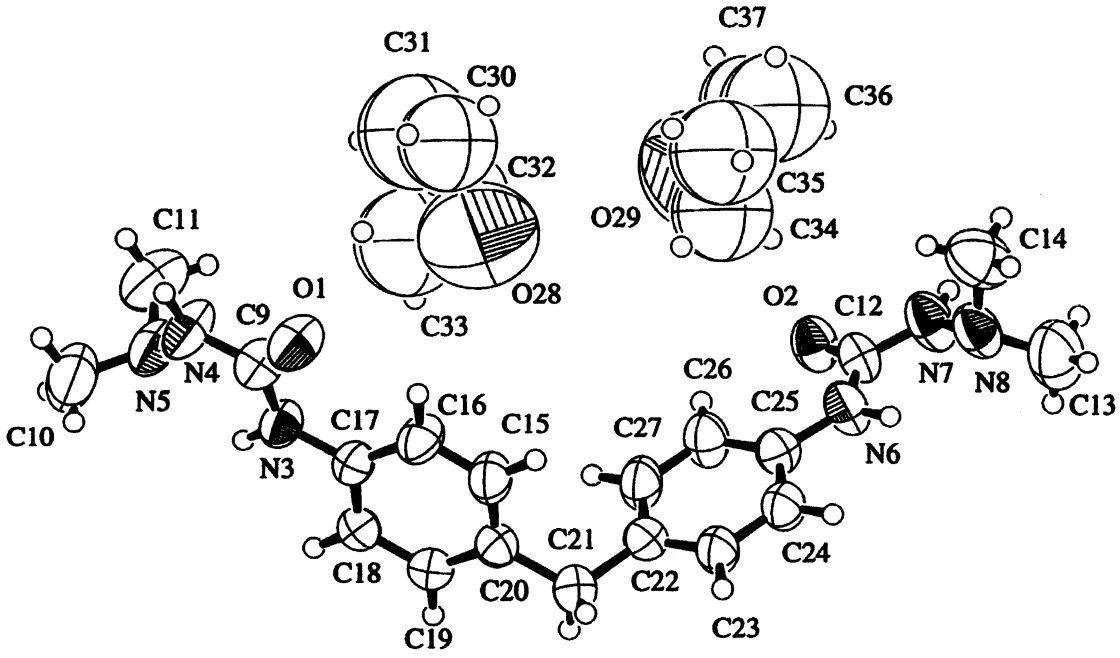

Fig. 2 Ortep drawing of the host-guest molecules (1.2 THF).

Table 2 Crystal data for 1.2THF

Formula	$C_{19}H_{26}N_6O_2.2C_4H_8O$
M	514.67
Crystal dimensions/mm	0.55 × 0.3 × 0.2
Space group	$P2_1/a$
a/Å	25.653(4)
b/Å	11.315(2)
c/Å	10.551(3)
β/°	100.31(2)
V/Å^3	3013.1(11)
Z	4
D_x/g cm^{-3}	1.134
μ(Mo Kα)/mm^{-1}	0.077
$2\theta_{max}$(Mo Kα)/°	27.5
Data collected	8019
Independent reflections	6923
Reflections with I > 2σ (I)	2152
No. variables	294
R(F) [I>2σ (I)]	0.105
$(\Delta/\sigma)_{max}$	0.37
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	0.47, –0.23
Goodness of fit	1.45

toluene were obtained as colourless needles (0.91 g). Upon heating the inclusion complex under vacuum, the free host compound (**2**) was obtained as a white powder (0.7 g) in 95% yield. M.p.: 203–205°C; IR (Nujol) 3333, 3207, 1683 cm^{-1}; δH (300 MHz, $CDCl_3$) 8.06 (s, 2 H), 7.43 (d, *J* = 9.0 Hz, 4 H), 6.95 (d, *J* = 9.0 Hz, 4 H), 5.09 (s, 2 H), 2.60 (s, 12 H). Anal. Calc. For $C_{18}H_{24}N_6O_3$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.32; H, 6.49; N, 22.51.

*Preparation of 4,4′-bis(dimethylamino-urea)dicyclohexylmethane (**3**):* When a solution of 4,4′-bis(diisocyanato)dicyclohexylmethane (0.5 g, 1.91 mmol) and *N,N*-dimethylhydrazine (0.23 g, 3.83 mmol) in toluene (20 ml) was stirred at room temperature for 48 h, 4,4′-bis(dimethylamino-urea)dicyclohexylmethane (**3**) were obtained as colourless needles (0.36 g) in 49% yield. M.p.: 165–169°C; IR (Nujol) 3398, 3373, 3199, 1677 cm^{-1}; δH (300 MHz, $CDCl_3$) 6.20 (d, *J* = 8.0 Hz, 1 H), 5.87 (d, *J* = 8.0 Hz, 1 H), 4.82 (s, 2 H), 3.89 (brs, 1 H), 3.53 (brs, 1 H), 0.88–1.70 (m, 16 H). Anal. Calc. For $C_{19}H_{38}N_6O_2$: C, 59.65; H, 10.01; N, 21.97. Found: C, 59.88; H, 9.83; N, 21.76.

X-ray analysis: The colourless crystals of 1· 2THF were grown from a THF solution. The crystal specimen was sealed in a capillary to avoid efflorescence. X-ray intensity data were collected on a Rigaku AFC-7R diffractometer with Mo Kα radiation at 298 K. Crystal data and experimental details are listed in Table 2. The C atoms of THF molecules were refined isotropically to avoid non-positive definite atomic displacement parameters. All H-atom positional parameters were calculated geometrically. The relatively large R value of 0.105 is the result of weak high order reflections, which may be due to the large displacement parameters of the THF molecules. Structure analysis was carried out using the TEXSAN program system.[2] CCDC reference number 172025.

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2 Molecular Structure Corporation, 2001. TEXSAN. Version 1.11. MSC, The Woodlands, TX, USA.