N,N'-Ditritylurea, a Versatile Host for Crystalline Host–Guest Complexes

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N,N'-Ditritylurea forms stoicheiometric crystalline complexes with guests containing varied functionality; its large rigid end-groups prevent host–host close packing and leave substantial voids for guests, many of which hydrogen bond to the urea moiety.

Recently[1] we proposed that compounds with a long molecular axis holding large rigid groups at each end might function as hosts in crystalline host–guest complexes. Nineteen hosts and thirty-seven new complexes of this type were described, as well as possible examples from the literature.[2] However, most of these complexes involved nonpolar hosts and guests, and relatively weak binding forces.

To broaden the scope of this host design, we decided to incorporate in the long axis functionality which would be rigid yet capable of hydrogen bonding to guests. To prevent host–host hydrogen bonding and to create voids, large rigid groups would still be required at each end of the host molecule. These requirements led us to consider *N,N'*-ditritylurea (DTU). There was already a hint in the literature that DTU might form complexes, since it was reported to crystallize from ethanol with two molecules of solvent.[3] We report here on the exceptional host properties of DTU.

DTU was prepared from trityl isocyanate and tritylamine.[4] It crystallizes without complex formation from anhydrous ethyl acetate or tetrahydrofuran (THF) (however, *vide infra*); the former was used as the solvent to test for complexation. DTU was dissolved in hot ethyl acetate, five equivalents of guest were added and the solution was allowed to cool gradually. The host/guest ratio in the resulting crystals was determined by solution n.m.r. integration and by elemental analysis.

DTU formed 1:1 complexes with the following guests: diethyl ether, methyl n-propyl ether, diethylamine, methyl n-propylamine, acetone, allyl alcohol, dimethylformamide, propanamide, 2-methylpropanamide, 2,2-dimethylpropanamide, benzamide, dichloromethane, and toluene. It also formed 1:1 complexes with the *N*-acetyl derivatives of the following amino acid ethyl esters: glycine, alanine, methionine, and aspartic acid. It formed 1:2 complexes with methanol, ethanol,[3] propan-1-ol, and butan-1-ol and a 2:1 complex with *N,N,N',N'*-tetramethylsuccinamide. Curiously, although DTU did not complex ethyl acetate directly, it formed a 1:1 complex with this guest during an unsuccessful attempt to prepare a complex with ethyl 4-aminobenzoate. Also, although DTU did not form a complex from anhydrous THF, it did form a 1:1 complex (that does not contain water), when crystallized from THF containing 30% water.

Of 33 guests tried to date, 25 have formed complexes with DTU. Simple guests which did not form a complex were cyclohexanone, camphor, triethylamine, and butan-2-ol, and the *N*-acetyl derivatives of the following amino acid ethyl esters: proline, serine, phenylalanine, and glutamic acid.

These complexes are stable and can be heated under vacuum well above the boiling points of low-boiling guests without decomposition. However, guests with similar functionality are not equally bound; hence the complexes can be used for separations. For example, the following ratios of guests were incorporated in the complex after one crystallization of DTU from ethyl acetate containing a 1:1 guest mixture: $Et_2O:Pr^nOMe$, 3.5:1.0; $Et_2NH:Pr^nNHMe$, 4.6:1.0; 2-PrOH:1-PrOH, 4.0:1.0; $Et_2O:Et_2NH$, >25:1.0.

X-Ray studies should help define the necessary requirements for complexation. Figures 1 and 2 show stereoviews of the *X*-ray structure of the diethyl ether complex; an *X*-ray structure of the diethylamine complex shows it to be isostruc-

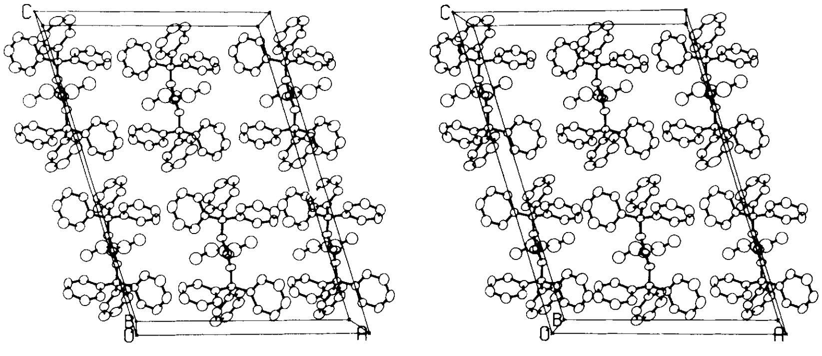

Figure 1. Stereoview of the DTU-Et_2O 1:1 complex; hydrogens are omitted for clarity. The CH_2 and CH_3 groups of the ether are present in one of two slightly shifted positions, only one of which is shown for clarity.

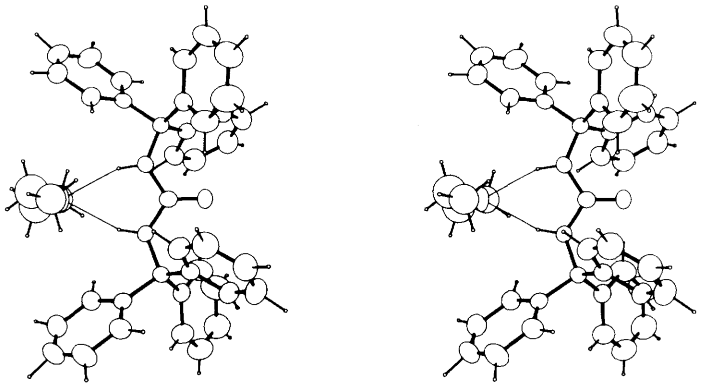

Figure 2. Stereoview of the hydrogen-bonding interaction in the DTU–Et_2O complex. The interaction is described by the following parameters: NH(host) · · · · O(guest) = 2.960 Å; H · · · · O = 2.11 Å, N–H · · · · O = 160.6°.

tural with the ether complex. Both crystals are in the same space group with nearly identical cell dimensions.† As anticipated, the urea functionality holds the six atoms of the long molecular axis nearly coplanar. Guests lie roughly perpendicular to that plane (vastly different from ordinary urea complexes[5]). The host–guest interaction in both complexes is hydrogen bonding between the heteroatom of the guest and both N–H bonds of the host. Surprisingly, the N–H of diethylamine is not bonded to the carbonyl of the host, although with amide hosts, both types of H-bonds are important.[6]

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† *Crystal data:* DTU–Et_2O: $C_{39}H_{32}N_2O$–C_4H_9O, monoclinic, space group *C2/c*, $a = 16.707(4)$, $b = 8.793(2)$, $c = 24.376(5)$ Å, $\beta = 106.94(2)°$; $Z = 4$, $M = 617.81$, $D_c = 1.198$ g cm^{-3}, $R = 0.066$, $2\theta_{max.} = 55°$ yielding 3955 total unique data and, based on $I > 2\sigma(I)$, 1917 observed data. DTU–Et_2NH: $C_{39}H_{32}N_2O$–$C_4H_{11}N$, monoclinic, space group *C2/c*, $a = 16.926(9)$, $b = 8.740(5)$, $c = 24.404(13)$ Å, $\beta = 106.99(4)°$; $Z = 4$, $M = 617.84$, $D_c = 1.189$ g cm^{-3}, $R = 0.077$, $2\theta_{max.} = 50°$ yielding 3066 total unique data and, based on $I > 2\sigma(I)$, 1699 observed data. A Picker FACS-I diffractometer and Mo-$K\alpha_1$ ($\lambda = 0.70926$ Å) radiation were used. The amine complex was solved by direct methods using MULTAN 78; the ether complex solution was accomplished by a series of structure factor calculations followed by difference maps with the initial co-ordinates being those of the isostructural amine complex; refinement in both cases was by full-matrix least squares techniques. Computer-generated figures were drawn by the ORTEP program. The atomic co-ordinates are obtainable on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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