Transannular Ring Stabilisation by Hydrogen Bonding in Trianthranilide Derivatives. *X*-Ray Structures of 5,11-Dibenzyl- and 5,11-Dimethyltribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine-6(5*H*),12(11*H*),18(17*H*)-trione (*NN*′-Dibenzyl- and *NN*′-Dimethyl-trianthranilide)

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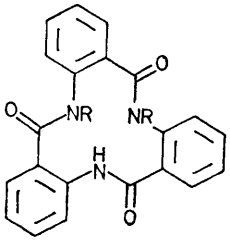
Summary Crystal structure determinations of two closely related tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine-6(5*H*),12(11*H*),18(17*H*)-trione (trianthranilide) derivatives have confirmed n.m.r. conclusions that both adopt a helical conformation in the solid state; a different transannular hydrogen bond has been found in each of these structures, in one case involving a severely distorted *trans*-amide group.

The disubstituted tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine-6(5*H*),12(11*H*),18(17*H*)-triones (trianthanilides) (**1**)[1–3] are chiral molecules that undergo conformational inversion between enantiomers *via* defined conformational itineraries[2,3] in solution. They are the subject of current studies of the dynamics of medium-ring systems.[1–4]

N.m.r. analyses of the conformational behaviour of *NN*′-dibenzyl- (**1a**) and *NN*′-dimethyl-trianthranilide (**1b**)[2,3] have indicated that both molecules adopt a helical conformation in the solid state, (*i.e.* two carbonyl oxygens lie on one side of the 12-membered ring, and one on the other). *X*-Ray analyses have been carried out to verify this conclusion.



(**1**) a; R = CH_2Ph
b; R = Me

Compound (**1a**) crystallises in the centrosymmetric monoclinic space group $P2_1/a$, $a = 14{\cdot}304(1)$, $b = 14{\cdot}090(1)$, $c = 15{\cdot}237(1)$ Å, $\beta = 96{\cdot}53(1)°$, $Z = 4$ [2 are (+) and 2 (−) *i.e.* a racemate]. Crystals of (**1b**) are monoclinic, space group $P2_1$, $a = 11{\cdot}422(1)$, $b = 12{\cdot}594(1)$, $c = 6{\cdot}537(1)$ Å, $\beta = 101{\cdot}32(1)°$, $Z = 2$. This space group is noncentrosymmetric and contains molecules of one chirality only; (**1b**) is thus an example of spontaneous resolution on crystallisation. Intensity data for both compounds were measured on a Siemens off-line four-circle diffractometer using filtered Cu-K_α radiation. The structures have been solved by direct methods and refined to current *R* values of 0·068 (**1a**) and 0·050 (**1b**).†

Both molecules adopt similar helical conformations (Figure 1), thus confirming the n.m.r. predictions. In both structures rings A and C are nearly parallel [3°, (**1a**) and 5°, (**1b**) between normals], with ring B inclined to rings A and C by 13 and 13° (**1a**) and by 19 and 14° respectively in (**1b**). The planes of the *trans*-amide linkages between rings A and B, and between B and C are in both structures approximately normal to their adjacent rings (Figure 1), but those

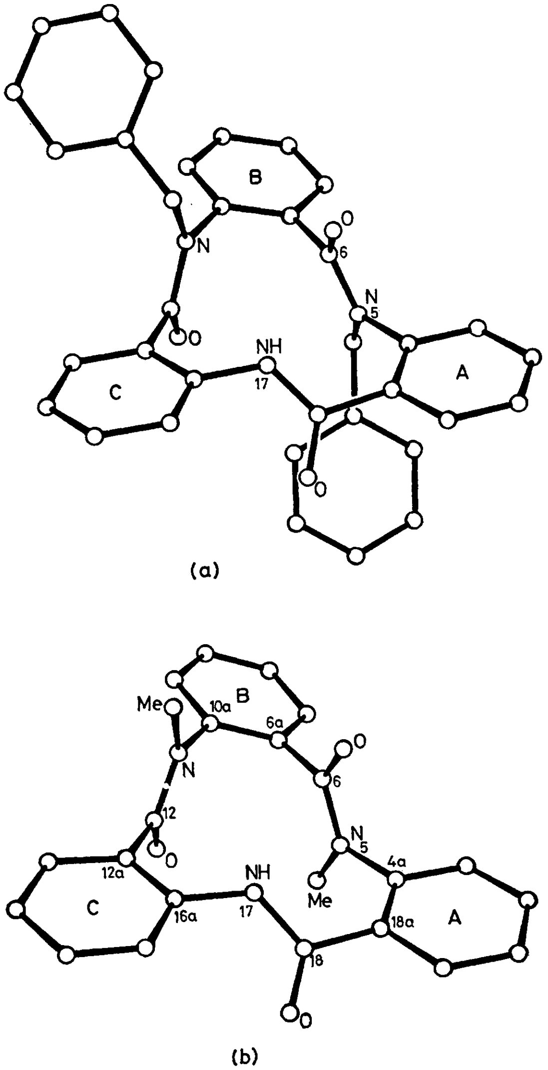


Figure 1. Comparative perspective views of (a) *NN*′-dibenzyltrianthranilide and (b) *NN*′-dimethyltrianthranilide.

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† The atomic co-ordinates for this work are available 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.

linking A and C are inclined at only *ca.* 43° in (**1a**) and *ca.* 37° in (**1b**) (*i.e.* in both cases tilted by more than 45° from the normal).

The amide hydrogen atoms were located from difference maps and their positions successfully refined to show that N(17) in (**1a**) has sp^2 geometry with the N–H bond directed toward the opposite amide carbonyl oxygen O(6), thus achieving ring stabilisation by the formation of a transannular N–H · · · · O hydrogen bond (2·94 Å). In (**1b**) however, the geometry at the nitrogen N(17) is severely distorted; instead of the trigonal planar arrangement found in (**1a**), the nitrogen is pyramidal with CNH angles of 108 and 111°, and CNC of 125° with an associated OCNH torsion angle of −138° (Figure 2). The effect of this distortion is to direct the N–H bond down into the macrocycle, the bond running nearly parallel to the planes of rings A and C; ring stabilisation is again achieved but this time by means of a transannular hydrogen bond (2·96 Å) to the opposite amide nitrogen N(5) [*cf.* O(6) in (**1a**)]. The N(17)–O(6) distance is increased to 3·26 Å.

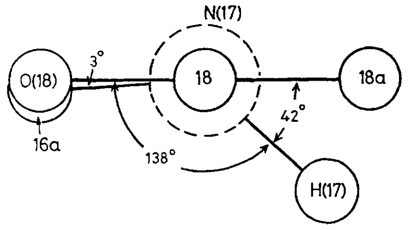

FIGURE 2. Newman projection looking down the *trans*-amide C(18)–N(17) bond in *NN*′-dimethyltrianthranilide.

Distortion of amide groups is fairly common, both as a rotation about the C–N bond and as out-of-plane bending at the nitrogen atom.[5] However, in the majority of cases, the deformations are small; they certainly do not approach the degree of distortion observed here (a notable exception is an out-of-plane rotation of *ca.* 30° of one of the substituents on each nitrogen atom in the structure of *NN*′-diethyl-*NN*′-diphenylurea[6]). This result lends further support to the deduction that the force resisting out-of-plane deformation in amides must be small.[5,7,8]

Compound (**1a**) has also demonstrated potential properties for forming inclusion compounds.

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