

SYNTHESIS OF 2,3,5,6-TETRAHYDRO-1H,4H,11cH-3a,6a,11b-TRIAZABENZ[de]  
ANTHRACENE (5) AND X-RAY CRYSTAL STRUCTURE DETERMINATIONS OF (5),  
HEXAHYDRO-1H,4H,7H,9bH-3a,6a,9a-TRIAZAPHENALENE (1), BENZO[b]-1,5,9-  
TRIAZADODECANE N,N',N"-TRITOSYLAMIDE, AND OF 1,5,9-TRIAZADODECANE N,N',N"-  
TRITOSYLAMIDE

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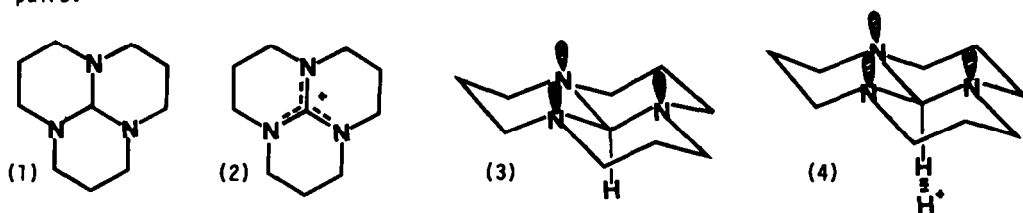
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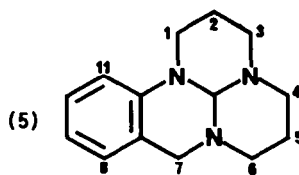
Abstract-The synthesis of 2,3,5,6-tetrahydro-1H,4H,11cH-3a,6a,11b-triaza-  
benz[de]anthracene (5) is described. X-ray crystal structure determinations  
on hexahydro-1H,4H,7H,9bH-3a,6a,9a-triazaphenalene (1) and its benzo-  
analogue (5) show them to adopt differing conformations; the reasons for  
this are discussed.

INTRODUCTION

The tricyclic orthoamide (1) was shown<sup>1</sup> to undergo a remarkably easy oxidation by a proton; when the tetrafluoroborate salt of (1) was heated, at only 110°C, the guanidinium salt (2) was formed together with a mol equivalent of hydrogen gas. Strong NMR and IR evidence was adduced<sup>1,2</sup> in support of conformation (3) for the orthoamide. This allowed an interpretation<sup>1</sup> of the reaction as involving firstly, dissociation of the N-protonic salt, followed by C-hydrogen protonation (as in (4)) aided by mixing of the  $\sigma_{CH}^*$  with the three antiperiplanar nitrogen lone pairs.



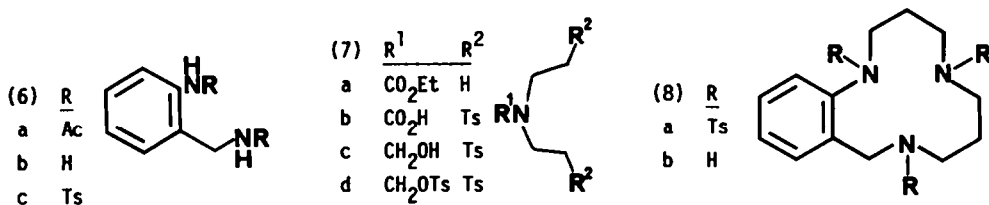
Our interest in this process led to speculation as to the generality of this thermally induced production of hydrogen and, in particular, to the effect that conjugation might have on the process, in possibly allowing it to be driven photochemically rather than thermally. Accordingly we have embarked on a programme of synthesis to produce analogues of (1) which also contain chromophores. We report here on the synthesis of the simplest such analogue (5), and on its crystal structure determination which in turn led us to carry out a comparable determination for (1). Future publications will describe the thermo- and photochemistry of (5) and other analogues.



## SYNTHESIS

A compound with the tetracyclic nucleus present in (5) has been prepared<sup>3</sup> previously, however we chose an alternative route which was based upon the strategy used for the synthesis<sup>2b,c,4</sup> of (1). Catalytic reduction of anthranilonitrile over palladium-charcoal in acetic anhydride gave di-amide (6a), acid hydrolysis to the dihydrochloride of diamine (6b) followed by tosylation in refluxing pyridine produced the desired ditosylamide (6c).

Following Wuest *et al.*<sup>2b,4</sup>, diethyl 3,3'-iminodipropionate (7a) was converted into the tosylamide-diacid (7b) by reaction with *p*-toluenesulphonyl chloride in alkaline solution. Reduction to the diol (7c) with borane-THF and *O*-tosylation gave (7d). The combination of (7d) with (6c) was effected by the slow addition of the former to a hot solution of the dipotassium salt of the latter, to give the macrocyclic tritosylamide (8a), in 63% yield.

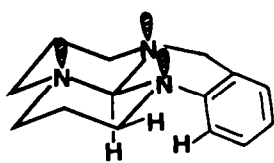


Various methods were examined for the deprotection of (8a): sodium naphthalenide did produce triamine (8b), but none of a number of variations in conditions gave it in acceptable yield. Lithium aluminium hydride in refluxing THF was without effect on (8a), but sodium bis(methoxyethoxy)-aluminium hydride in refluxing toluene did give the desired triamine, in 70% yield. However, the method of choice proved to be sodium in liquid ammonia, producing the unstable triamine in 88% yield. The synthesis of (5) was completed by the clean insertion of the required one carbon unit using formamidinium acetate in refluxing ethanol.

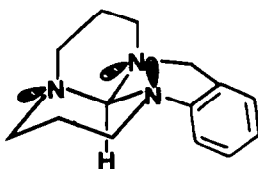
## DISCUSSION

It was of relevance to examine the UV absorption of (5) and also the effect of acid upon that absorption. The spectrum was aniline in type; in acidic solution a hypsochromic shift of the entire spectrum by 8 nm was observed. This is consistent with protonation at one or other of the aliphatic, more basic, nitrogen atoms, the positive charge thus generated preventing, by its proximity, the protonation of the aniline nitrogen and also influencing, by its proximity, the ground and/or excited state energies of the aniline chromophore, resulting in the observed shift in the absorption, a phenomenon first noted<sup>5</sup> in studies on eserine-type alkaloids, which also contain an ArN-C-N system.

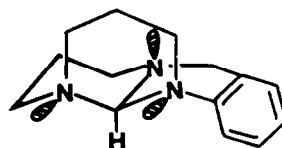
For the operation of any process involving participation of the three nitrogen lone pairs in (5) in a central C-H bond breaking, the orthoamide would have to utilise a conformation (9), comparable to (3), and since there are three other reasonable conformational possibilities, (10), (11), and (12) for (5), which also contain chair and half-chair six-membered rings, it was clearly vital to establish the preferred conformation.



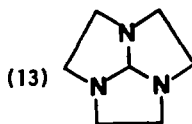
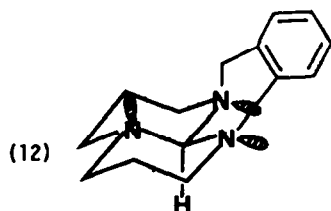
(9)



(10)



(11)



The tetracyclic orthoamide (5) showed Bohlmann bands<sup>6</sup> at 2820 and 2770  $\text{cm}^{-1}$  in its IR absorption spectrum, but in contrast to that of (1) there was no absorption at around 2450  $\text{cm}^{-1}$  attributed<sup>2</sup> in the latter case to the stretching of the central methine C-H, being trans antiperiplanar to three nitrogen lone pairs.

As well as the absence of a Bohlmann band corresponding to that observed for the central C-H stretch in (1), a considerable difference was also noted in the chemical shift of this proton in the two compounds,  $\delta$  2.31 for (1) and  $\delta$  3.81 for (5). One may further compare the methine shift in (5) with that <sup>2a,c</sup> ( $\delta$  5.03) in tripentacycle (13) where the stereochemistry demands that the C-H be syn planar to three nitrogen lone pairs. The value for (5) lies intermediate between those for (1) and (13) suggesting one of (10), (11) or (12) as the conformation for (5). Further information concerning the conformation was obtained from a more detailed study of the <sup>1</sup>H NMR spectrum of (5).

Table 1: <sup>1</sup>H NMR (400 MHz) signals of (5)

Proton	Chemical Shift, $\delta$	Multiplicity	Coupling Constants J(Hz)	Coupled* Signals
1eq	4.03	ddt	1eq, 1ax 12.8 1eq, 2ax 4.4 1eq, 2eq 4.4 1eq, 3eq 2.2	2.845 2.04 1.52 2.95
1ax	2.845	dt	1ax, 1eq 12.9 1ax, 2ax 12.8 1ax, 2eq 2.9	4.03 2.04 1.52
2eq	1.52	complex multiplet	-	-
2ax	2.04	qt	2ax, 2eq 12.8 2ax, 1ax 12.8 2ax, 3ax 4.4 2ax, 1eq 4.4 2ax, 3eq 4.4	-
3eq	2.95	complex multiplet	-	-
3ax	2.385	dt	3ax, 3eq 12.8 3ax, 2ax 12.8 3ax, 2eq 3.05	2.95 2.04 1.52
4eq	2.95	complex multiplet	-	-
4ax	2.305	dt	4ax, 4eq 11.2 4ax, 5ax 11.2 4ax, 5eq 3.3	2.95 2.13 1.52

Proton	Chemical Shift $\delta$	Multiplicity	Coupling Constants J(Hz)	Coupled* Signals
5eq	1.52	complex multiplet	-	-
5ax	2.13	ddt	5ax, 5eq 13.1 5ax, 4ax 11.2 5ax, 6ax 4.05 5ax, 4eq 4.05 5ax, 6eq 4.05	-
6eq	3.10	ddt	6eq, 6ax 12.0 6eq, 5eq 3.9 6eq, 5ax 2.13 6eq, 4eq 1.7	2.60 1.52 2.13 2.95
6ax	2.60	ddd	6ax, 6eq 12.0 6ax, 5eq 3.4 6ax, 5ax 11.2	3.10 1.52 2.13
7H <sub>2</sub>	3.66	d	14.5	-
	3.92	d	14.5	-
8	7.08	t	8	-
9	6.97	d	8	-
10	6.89	d	8	-
11	6.65	t	8	-
11a	3.81	s	-	-

\*The figures in this column refer to the chemical shifts of the proton to which the proton in question is coupled, as experimentally determined by decoupling.

The isolated methylene at C-7 is represented by an AB quartet at  $\delta$  3.66 and 3.92, the former component of which was slightly broadened by long range coupling. For the remaining two sets of  $\text{CH}_2\text{CH}_2\text{CH}_2$  signals, those to lower field than  $\delta$  2.2 represent protons on carbons adjacent to nitrogen. Of these eight signals, the four lowest, viz. those at  $\delta$  4.03, 3.10, and two

overlapping at  $\delta$  2.95, were assigned to equatorial protons. Decoupling experiments established that the pairs of signals at  $\delta$  4.03 and 2.95, and 3.10 and 2.95 represent the termini of the two  $\text{CH}_2\text{CH}_2\text{CH}_2$  systems. We assign the lowest field signal to the equatorial hydrogen at C-1, being closest to the influence of the aromatic ring current, and, less securely, the next lowest signal to the equatorial proton on C-6, though clearly there is not a great difference between values of  $\delta$  3.10 and 2.95. With these assignments it became possible to trace the couplings (see Table 1) along each system of methylene groups and thus to note the typical equatorial/axial couplings along the chain in each case, consistent with chair-shaped rings and thus with any of the conformations (9)-(12), but not with any other possibilities in which there were appreciable distortions from chair conformations.

The conformation of (5) in the solid state was determined by X-ray crystallography; Figures 1 show it to correspond with conformational drawing (12). Thus, in the solid state at least, (5) has only one axial nitrogen lone pair and its conformation thus contrasts with that determined for (1) by NMR measurements in solution. Notwithstanding the strength of this NMR evidence<sup>1,2</sup> for conformation (3), the contrast with (5) made it important to examine the tricyclic material in the solid state.

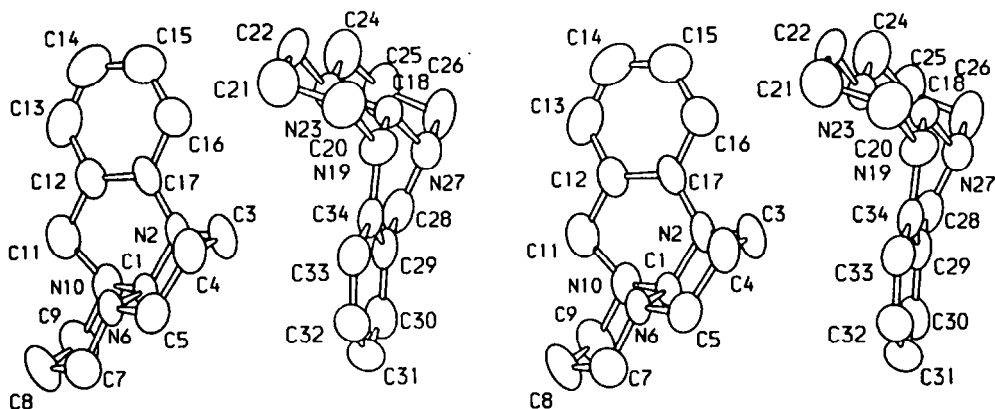


Figure 1A. Stereoscopic drawing of 2,3,5,6-tetrahydro-1H,4H,7H,11cH-3a,6a,11b-triazabenz[de]-anthracene (5), showing two molecules in the unit cell.

Despite very considerable practical difficulties in obtaining and handling suitable crystals of (1), a structure was determined from measurements made at  $-100^\circ\text{C}$  on a sample obtained by sublimation in vacuum and subsequently handled under nitrogen. Figure 2 shows that orthoamide (1) adopts in the solid state the symmetrical conformation (3), with three chairs, it being implicit that each nitrogen lone pair is oriented axially, exactly as deduced<sup>1,2</sup> from the solution spectroscopic data. It seems likely then that (5) also adopts its solid state conformation, (12), in solution.

The differing conformational preferences of (1) and (5) demand an explanation; we believe that this can be based on an interplay between steric and electronic effects. If the tricycle were to adopt a conformation (14), comparable with (12) for (5), then although there would be two favourable anomeric effects<sup>7</sup> there would also be two unfavourable 1,3-diaxial interactions (one indicated on (14)); in the conformation, (3), demonstrated for the compound, the latter are absent, although, of course, no electronic stabilisation in the form of anomeric effects is available.

The comparable conformation (9), for (5), with three axial or pseudo-axial lone pairs, would have an unfavourable interaction between an ortho aromatic proton and an adjacent N-methylene proton and, of course, no anomeric stabilisation. In the observed conformation (12), two stabilising anomeric effects are available but now only one serious unfavourable 1,3-diaxial interaction has to be set against this. The balance results in the observed conformation (12).

One may compare the situation with that found<sup>8</sup> for 1,3-dimethyl-1,3-diazacyclohexane where the same competing factors result in an 88:12 mixture of conformations with the two methyl groups both axial, and with one axial and one equatorial, respectively.

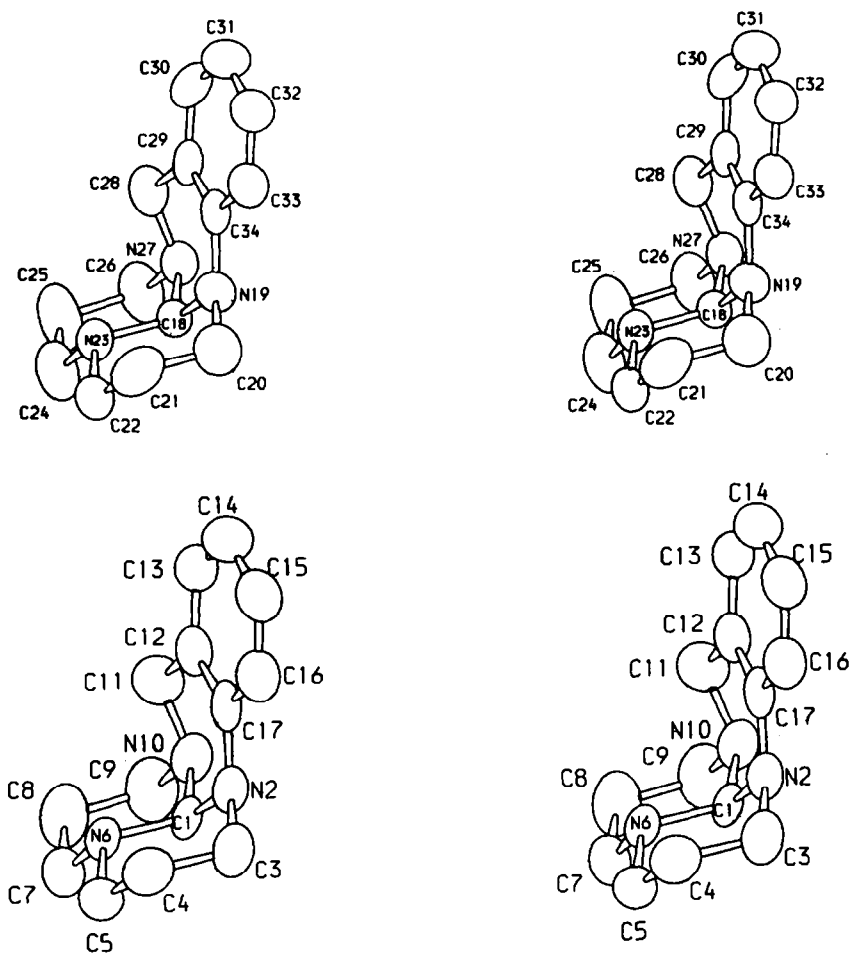


Figure 1B. Stereoscopic drawings of molecules I and II of (5), reoriented to show their stereochemical comparability.

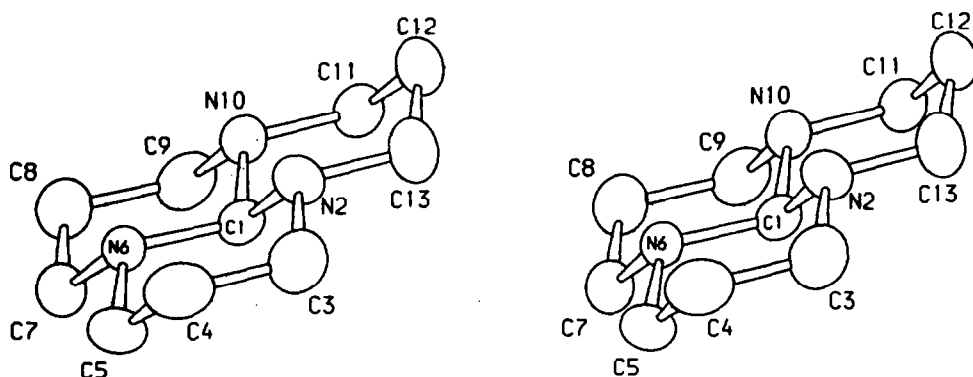
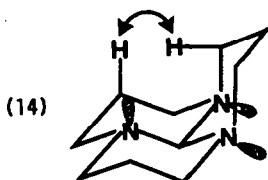
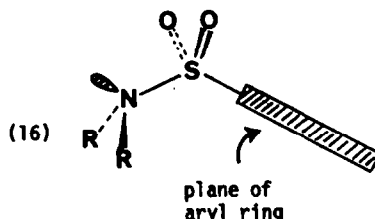
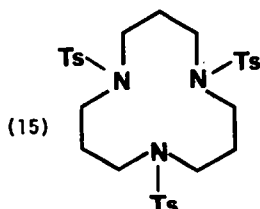


Figure 2. Stereoscopic drawing of hexahydro-1H,4H,7H,9bH-3a,6a,9a-triazaphenalene(1)



Because of the relationship, required<sup>1</sup> for hydride expulsion, between the central methine hydrogen and the nitrogen axial lone-pairs, it was important to determine the extent to which the di-axially fused ring in (12) distorts the perfect chair geometry of the other two rings, as displayed in the prototype tricyclic orthoamide (3). Reassuringly, and perhaps a little surprisingly, it could be demonstrated that there is virtually no distortion in that portion of the molecule. Thus, matching the atomic positions of the two saturated chair rings in the crystal structure of (12) with two of the chairs in that of (3) showed no atom to vary by  $>0.077$  Å from the position of its corresponding atom in (3) and the average difference was 0.048 Å. (N.B. It was necessary to compare the enantiomer of (3) with the first molecule of (5)). This bodes well for further work in which it will be the aim to tip the balance of controlling factors in favour of a conformation of type (9); for example di-methyl substitution at the benzylamine methylene carbon would disfavour conformations of the (10), (11), and (12) types in favour of the desired (9) type. It may also be possible to influence the conformation of (5) by complexation to a suitable metal centre, which could incidentally have a significant effect on the lability of the central methine hydrogen.



We<sup>9</sup> and others<sup>10-12</sup> have previously discussed the geometrical situation around the sulphur and nitrogen atoms in arylsulphonamides<sup>9-11</sup>, in N-arylsulphonyl-pyrroles and -indoles<sup>9</sup> and the related halosulphonamides<sup>12</sup>. A strong preference, for a geometry idealised in representation (16), was uncovered<sup>9</sup>. We also found<sup>9</sup> there to be considerable variation in the planarity versus pyramidality at nitrogen, though with retention of that typical geometry. An X-ray crystallographic examination (Figures 3 and 4) of the two medium ring tritosylamides (8a) and (15), intermediates for the syntheses of (5) and (1), illustrate these tendencies well. Even in the symmetrical (15), where one might have expected equivalent geometrical situations at each nitrogen atom, there is considerable variation in the planarity of the nitrogen atoms. Using the sums of the angles at nitrogen as a measure of that atom's planarity, values of 345.4, 348.7 and 355.6 were found; the last is very considerably flattened. In the benzo-analogue (8a), the benzylic nitrogen N(35), unexpectedly, is virtually planar (359.4) while the aniline nitrogen, with a sum of angles of 349.1, is pyramidal! Consistent with the absence of flattening of the aniline nitrogen is the angle of 23° between its lone pair\* and the plane which includes the benzene ring and that nitrogen N(31), which clearly makes geometrically impossible the usual p- $\pi$  overlap, which is regarded as fundamental for conjugation.

\* The direction of the lone pair was taken to be the reverse direction of the sum of the unit vectors for the three bonds from nitrogen.

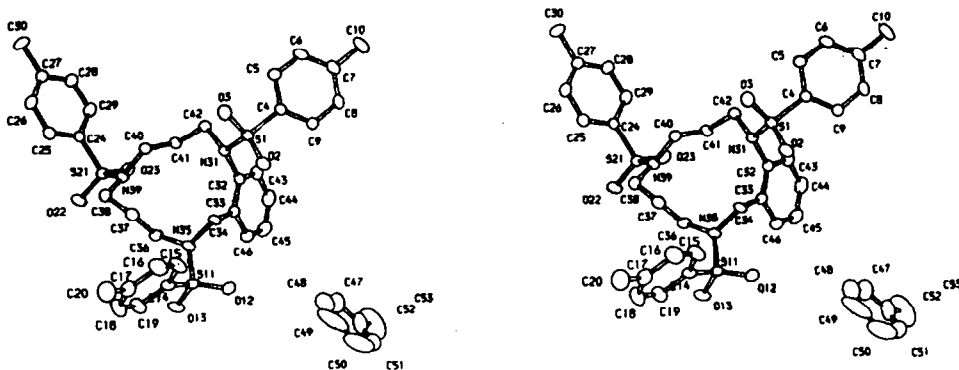


Figure 3A. Stereoscopic drawing of benzo[b]-1,5,9-triazadodecane N,N',N''-tritosylamide (8a), including solvent toluene molecule.

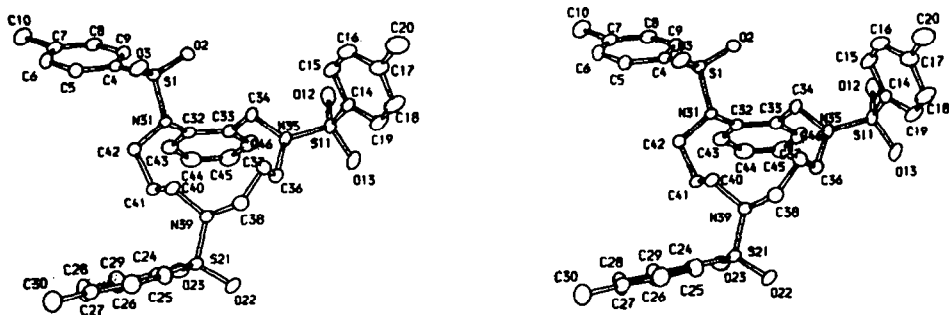


Figure 3B. Stereoscopic drawing of benzo[b]-1,5,9-triazadodecane N,N',N''-tritosylamide (8a), excluding solvent of crystallisation.

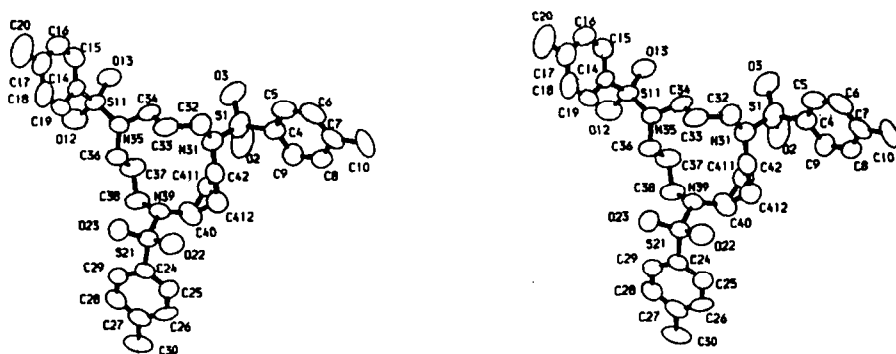


Figure 4. Stereoscopic drawing of 1,5,9-triazadodecane N,N',N''-tritosylamide (15).

With this unexpected observation, the question arose as to whether there was some over-riding conformational preference for a 1,5,9-triazadodecane tritosylamide, which requires one of the nitrogens to be flattened. Using this assumption - that the flattened nitrogens in the two molecules might correspond - an attempt to match the other atoms of the 12-membered ring was made: there was no significant correlation.

A second attempt to uncover a common conformational pattern was based on the observation that the nitrogen-nitrogen distances in the two tritosylamides are indeed quite comparable, 4.22, 4.16, and 4.10 Å for (8a) and 4.28, 4.17, and 3.94 Å for (14). However, again, attempts to match

on this basis showed there to be no significant correspondence between the medium ring atomic positions in the two molecules.

### EXPERIMENTAL

**General.**— M.ps. were determined on a Kofler hot-stage microscope and are uncorrected. Wet organic solutions/extracts were dried with anhydrous  $MgSO_4$ ,  $Na_2SO_4$ , or  $K_2CO_3$  and evaporated at ca. 20 mmHg at ca. 40–70°C using a rotary evaporator. Unless otherwise stated, u.v./vis. spectra (in nm (log  $\epsilon$ )) were measured in ethanol using a Shimadzu UV/VIS 260 instrument; i.r. spectra (in  $cm^{-1}$ ) were measured using a Pye-Unicam SP3-200 spectrometer;  $^1H$  n.m.r. spectra of deuteriochloroform solutions, with  $\delta$  values in p.p.m. with respect to internal  $SiMe_4$  (0 p.p.m.) and coupling constants, J, in Hz, were measured on Perkin-Elmer R12B (60 MHz), Perkin Elmer R34 (220 MHz), Varian SC 300 MHz or Varian XL 300 (300 MHz) spectrometers; unless otherwise stated, mass spectra were determined by the electron impact method on an AEI MS 30 instrument coupled to a DS 55 data system. Chemical ionisation (CI) mass spectra, using  $NH_3$  were obtained with a Kratos MS 25 instrument, coupled to a DS 55 data system. For i.r. and  $^1H$  n.m.r. spectra only clearly distinguished and unambiguously assignable absorptions/signals are specified, in particular those which are of greatest importance for the establishment of structure. Only ions of > 10% of base peak are given for mass spectra, except where a less intense ion is of importance for structure establishment.

**N,N'-Diacetyl-2-aminobenzylamine (6a).** — Anthranilonitrile (3.0 g, 25.4 mmol) was dissolved in  $Ac_2O$  (50 ml) and the solution was left overnight; a further portion (50 ml) of  $Ac_2O$  was added to dissolve the 2-cyanoacetanilide that had crystallised out. Pd-C (5%, 3.50 g) was added and the mixture agitated under  $H_2$  (3 atms) for 24 h, the catalyst was then filtered off with the aid of celite (10 g) and the solvent removed under reduced pressure to give a colourless oil which crystallized on standing. Recrystallization from PhMe gave the di-amide (61) (4.3 g, 82%) as a white, micro-crystalline solid m.p. 139–141°C (lit<sup>13</sup> 137–138°C),  $\lambda_{max}$  240 (3.98);  $\nu_{max}$  (Nujol) 3350, 1680, and 1640;  $\delta_H$  1.90(3H,s, $CH_3CO$ ), 2.16(3H,s, $CH_3CO$ ), 4.20(2H,bs, $ArCH_2N$ ), 6.9–7.3(4H,m,3xArH + NH), 7.93(1H,d,J 8,ArH), and 9.88(bs,1H,NH);  $m/z$  206( $M^+$ , 7%), 188(9), 163(38), 146(11), 132(6), 121(100), 106(14), and 104(8).

**2-Aminobenzylamine dihydrochloride.** — N,N'-Diacetyl-2-aminobenzylamine (6a) (3.00 g, 14.6 mmol) was heated at reflux with HCl (6M, 100 ml) for 30 min. The acid was removed under reduced pressure to give a grey-brown crystalline mass which was recrystallized from MeOH-Et<sub>2</sub>O to give the dihydrochloride (2.53 g, 89%) as a white crystalline solid, m.p. 185–190°C (dec);  $\lambda_{max}$  238 and 294 (4.05 and 3.45);  $\nu_{max}$  (Nujol) 3250–2500, 1603, and 1555;  $\delta_H$  (( $CD_3$ )<sub>2</sub>SO) 4.20(2H, s,  $ArCH_2N^+$ ), 7.3–7.7(4H,m,ArH), and 8.0–10.0 (6H, broad, removed by  $D_2O$ , 2x $NH_4^+$ ) (Found C, 43.2; H, 6.15; N, 14.15; Cl, 36.0%.  $C_7H_{12}Cl_2N_2$  requires C, 43.09; H, 6.20; N, 14.36; Cl, 36.35%).

**2-Aminobenzylamine-N,N'-ditosylamide (6c).** — The dihydrochloride of (6b) (1.00 g, 5.13 mmol), TsCl (3.3 g, 17.2 mmol) and dry pyridine (10 ml) were heated together at reflux for 30 min. The mixture was cooled, poured into water (50 ml) and crushed ice, and HCl (12M, 10 ml) was added slowly followed by further water (20 ml). The mixture was extracted with Et<sub>2</sub>O and the combined extracts washed with dilute HCl (30 ml) and brine (30 ml). The extracts were dried and the solvent removed under reduced pressure to give a light brown crystalline solid, which was recrystallised from toluene to give the ditosylamide (6c) (1.94 g, 89%), m.p. 130–132°C,  $\lambda_{max}$  227 (4.46);  $\nu_{max}$  (Nujol) 3300, 3270, 1600, and 1500;  $\delta_H$  2.35(3H,s, $ArCH_3$ ), 2.40(3H,s, $ArCH_3$ ), 3.76(2H,d,J 7 collapses to a singlet on addition of  $D_2O$ ,  $Ar-CH_2-NHTs$ ), 5.23(1H,t,J 7, removed on addition of  $D_2O$ ,  $ArCH_2NHTs$ ), and 7.05–7.68(13H, m, reduces to 12H on addition of  $D_2O$ , 12xArH + ArNHTs). (Found C, 58.7; H, 5.1; N, 6.1; S, 14.8%.  $C_{24}H_{22}N_2O_4S_2$  requires C, 58.9; H, 5.15; N, 6.51; S, 14.9%).



3,3'-Iminodipropanoic acid tosylamide (7b).-p-Toluenesulphonyl chloride (30.0 g, 0.157 mol) was added portionwise with shaking to a suspension of diethyl 3,3'-iminodipropanoate<sup>14</sup> (25 g, 0.115 mol) in aqueous sodium hydroxide solution (30 g, 0.75 mol in 200 ml water) over 1 h. The mixture was shaken for a further 1 h and then heated at reflux for 1 h. The mixture was cooled to 10°C, acidified with concentrated HCl and the resultant white crystalline solid filtered (12.32 g, 34%). Recrystallisation from methanol gave the tosylamide (7b) as colourless needles, m.p. 167-172°C (11.17 g, 31%). An analytical pure sample was obtained upon a second recrystallisation, m.p. 169-172°C,  $\lambda_{\max}$  232 (4.09);  $\nu_{\max}$  (Nujol) 3100-2400 and 1705;  $\delta_{\text{H}}$  ((CD<sub>3</sub>)<sub>2</sub>CO) 2.47(3H,s,ArCH<sub>3</sub>), 2.67(4H,t,J 7,2xCH<sub>2</sub>CO<sub>2</sub>H), 3.52(4H,t,J 7,2xCH<sub>2</sub>N), 7.43(2H,d,J 9,ArH), and 7.76(2H,d,J 9,ArH);  $m/z$  316(MH<sup>+</sup>,2%), 256(22), 184(2), 160(78), 155(28), 142(15), 100(21), and 91(100). (Found C, 49.7; H, 5.5; N, 4.1; S, 10.27%. C<sub>13</sub>H<sub>17</sub>NSO<sub>6</sub> requires C, 49.5; H, 5.44; N, 4.44; S, 10.2%).

3,3'-Iminodipropanol tosylamide (7c).- A solution of the diacid (7b) (5.00 g, 15.9 mmol) in dry THF (100 ml) was added dropwise with stirring to a solution of borane in THF (1M, 34.0 ml, 34.0 mmol) at 0°C under N<sub>2</sub> and the solution stirred at room temperature for 8 h. Water (20 ml) was added slowly to the reaction mixture and the whole was saturated with K<sub>2</sub>CO<sub>3</sub>; two layers formed. The THF layer was removed and the aqueous layer was extracted with one 10 ml portion of THF. Removal of the THF gave a colourless oil which was separated from minor impurities by vacuum flash chromatography (EtOAc-PhMe-MeOH, 2:2:1 as eluent) to give the diol (7c) as a colourless oil (4.15 g, 91%),  $\lambda_{\max}$  231;  $\nu_{\max}$  (film) 3600-3200;  $\delta_{\text{H}}$  1.71 (4H, pent, J 6,2xCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.36(3H,s,ArCH<sub>3</sub>), 3.18(4H,t,J 6,2xCH<sub>2</sub>N), 3.63(4H,t,J 6,2xCH<sub>2</sub>O), 7.28(2H,d, J 8, ArH), 7.67(2H,d,J 8,ArH), and 2.83(2H,bs, removed by D<sub>2</sub>O, 2xOH):  $m/z$  242(22%, M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>O), 198(76), 155(37), 132(41), and 91(100);  $m/z$  (CI) 288(MH<sup>+</sup>, 63%) and 134(100) (Found M, 242.0846, and 198.0594, 132.1037. C<sub>11</sub>H<sub>16</sub>NO<sub>2</sub>S, C<sub>9</sub>H<sub>12</sub>NO<sub>2</sub>S, C<sub>6</sub>H<sub>14</sub>NO<sub>2</sub> require 242.0851, 198.0589, 132.1025).

3,3'-Iminodipropanol ditosylate tosylamide (7d).- A solution of TsCl (8.29 g, 43 mmol) in pyridine (30 ml) was cooled in ice and added slowly to a solution of the diol (7c)(4.15 g, 14.5 mmol) in pyridine (20 ml) at 0°C and the mixture left at -5°C overnight when it was poured slowly into HCl (6M, 100 ml) and then extracted with EtOAc. The extracts were washed with brine (3 x 50 ml) and then dried and evaporated to give the tosylamide-ditosylate (7d) as a white crystalline solid (8.71 g) which was recrystallised from methanol to give fine white needles (7.03 g, 82%), m.p. 76-78°C,  $\lambda_{\max}$  228, 264 and 275 (4.60, 3.25 and 2.96);  $\nu_{\max}$  (Nujol) 1600;  $\delta_{\text{H}}$  ((CD<sub>3</sub>)<sub>2</sub>O) 1.77(4H,m,J 8.5, 2xCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.44(3H,s,ArCH<sub>3</sub>), 2.47(6H,s,ArCH<sub>3</sub>), 3.05(4H,t,J 8.5, 2xCH<sub>2</sub>N), 3.86(4H,t,J 8.5, 2xCH<sub>2</sub>O), 7.53(2H,d,J 9,ArH), 7.60(4H,d,J 9,ArH), 7.79(2H,d,J 9,ArH), and 7.95(4H,d,J 9,ArH);  $m/z$  (CI) 613(MNH<sub>4</sub><sup>+</sup>,8%) and 442(4). (Found C, 54.1; H, 5.75; N, 2.4; S, 16.0%. C<sub>27</sub>H<sub>33</sub>NO<sub>8</sub>S<sub>3</sub> requires C, 54.4; H, 5.58; N, 2.35; S, 16.15%).

Benzo[b]-1,5,9-triacyclododecane N,N',N''-tritosylamide (8a).- The ditosylamide (6c) (2.15 g, 5.02 mmol) in dry DMF (50 ml) was cooled to 0°C and then added with stirring under nitrogen to KH (35% weight dispersion in oil, 1.21 g, 10.6 mmol), from which the oil had been previously removed by washing with dry THF. Evolution of hydrogen ensued. To the solution at 105°C, the ditosylate (7d) (2.98 g, 5.00 mmol) in dry DMF (25 ml) was added over 4 h. When addition was complete, the DMF was removed under reduced pressure to give a brown gum to which cold water (100 ml) was added. A precipitate (3.3 g) formed on shaking which was collected by filtration and dried to a constant weight. The crude product was purified by vacuum flash chromatography (EtOAc-PhMe solvent gradient up to 9:1) to give the trisulphonamide (8a) (2.12 g, 62%) as a white crystalline solid. A sample recrystallised from PhMe-EtOAc, 9:1 had m.p. 138°C, recrystallising and then m.p. 196-200°C. This sample was used for X-ray crystal structure analysis and was shown to contain a molecule of PhMe of crystallisation. A solvent-free analytically pure sample was obtained by recrystallisation from aqueous acetone, m.p. 193-197°C,  $\lambda_{\max}$  231(4.62);  $\nu_{\max}$  (Nujol) 1600;  $\delta_{\text{H}}$  1.50(2H,m), 2.14(1H,m), 2.35(3H,s,ArCH<sub>3</sub>), 2.39(6H,s,ArCH<sub>3</sub>), 2.45(2H,m), 2.90(3H,m), 3.20(2H,m), 3.40(1H,m), 3.62(1H,t), 4.62(2H,dd,ArCH<sub>2</sub>N), 6.39(1H,d,B,ArH), 7.14 (1H,t,J 8,ArH), and 7.24-7.80(14H,m,ArH);  $m/z$  (CI) 682(MH<sup>+</sup>,12%), 528(14), 526(5), 427(66), and 372(100);  $m/z$  526(41%,M<sup>+</sup>-C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>S), 267(22), 224(31), 196(18), 155(37), and 91(100). (Found C, 59.9; H, 5.9; N, 6.0; s, 13.6%. C<sub>34</sub>H<sub>39</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub> requires C, 59.9; H, 5.77; N, 6.16; S, 14.1%).

Benzo[b]-1,5,9-triazacyclododecane (8b).- The trisulphonamide (8a) (1.00 g, 1.47 mmol) was suspended with stirring in liquid  $\text{NH}_3$  (ca. 250 ml), freshly distilled from Na. Small pieces of Na (0.82 g, total weight) were added over 15 minutes to produce a permanent blue colour and after a further 45 min. the excess Na was destroyed with  $\text{NH}_4\text{Cl}$  and the  $\text{NH}_3$  allowed to evaporate. A solution of NaOH (10%, 10 ml) was added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 10 ml). The extracts were dried and the solvent removed under reduced pressure to give the triamine (8b) as a colourless oil (282 mg, 88%),  $\lambda_{\text{max}}$  295 and 247;  $\nu_{\text{max}}$  3400-3200 and 1583;  $\delta_{\text{H}}$  1.58(2H, pent), 1.79(2H, pent), 2.71(2H, t), 2.76(2H, t), 2.84(2H, t) 3.25(2H, t), all values of J 6, 3.78(2H, s, ArCH<sub>2</sub>N), 6.58(2H, m, ArH), 6.98(1H, d, J 8, ArH), and 7.16(1H, d, J 8, ArH);  $m/z$  219( $\text{M}^+$ , 51%), 134(58), 132(45), 120(37), 118(100), 106(37), and 91(40) (Found M, 219.1729.  $\text{C}_{13}\text{H}_{21}\text{N}_3$  requires 219.1735).

2,3,5,6-Tetrahydro-1H,4H,7H,11cH-3a,6a,11b-triazabenz[de]anthracene (5).- The triamine (8b) (282 mg, 1.29 mmol), and formamidinium acetate (300 mg, 3.41 mmol) were heated at reflux in absolute EtOH (25 ml) for 45 min., after which the solvent was removed under reduced pressure. Dilute aq.  $\text{NH}_3$  (10 ml) was added to the residue and product extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 6 ml). The extracts were dried and solvent removed under reduced pressure to give the orthoamide (5) (261 mg, 88%) as a slightly coloured oil which crystallised on standing. An analytically pure sample was obtained upon chromatography (silica, EtOAc-PhMe-MeOH, 2:2:1), m.p. 78-80°C; crystals suitable for X-ray crystallography were obtained by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution,  $\lambda_{\text{max}}$  296 and 250 (4.11 and 3.55);  $\lambda_{\text{max}}$  (EtOH + HCl) 288 and 244;  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3000, 2950, 2820, 2770, 1610, and 1500;  $\delta_{\text{H}}$  see Table 1;  $m/z$  229( $\text{M}^+$ , 30%), 228(100), 118(17), and 91(15) (Found C, 73.55, H, 8.5; N, 18.1%.  $\text{C}_{14}\text{H}_{19}\text{N}_3$  requires C, 73.3; H, 8.4; N, 18.3%).

Hexahydro-1H,4H,7H,9bH-3a,6a,9a-triazaphenalene (1) was prepared by the reported<sup>2b,4</sup> route. The material was very deliquescent, crystalline samples obtained by evaporating solvent liquified on exposure to air in ca. 1 min. In the course of attempts to recrystallise (1) from ethanol, crystals of precursor tritosylamide (15), m.p. 173-175°C were obtained and these were used for X-ray crystallography. Suitable crystals of (1) were eventually obtained by slow sublimation (sub. pt. 40°C/0.03 mm Hg) of the crude product over ca. 45 min.; the extraction of a single crystal for X-ray crystallography from the sublimate was carried out under an atmosphere of nitrogen.

#### X-ray Structure Determinations of compounds (8a), (5), (1) and (15)

In each case intensity data were collected on an Enraf Nonius CAD-4, computer-controlled, Kappa-axis, single-crystal diffractometer and the structures were solved by direct methods with the MULTAN-80 suite of programs.

Benzo[b]-1,5,9-triazacyclododecane N,N',N''-tritosylamide (8a).- Crystal data.  $\text{C}_{34}\text{H}_{39}\text{N}_3\text{O}_6\text{S}_3 + \text{C}_7\text{H}_8$ ,  $M = 773$ , monoclinic,  $a = 18.726(2)$ ,  $b = 12.717(2)$ ,  $c = 19.006(2)\text{Å}$ ;  $\beta = 118.26(1)^\circ$ ;  $U = 3986\text{Å}^3$ ,  $Z = 4$ ,  $\rho_c = 1.29$ ,  $\mu(\text{Mo-K}\alpha) = 2.49\text{ cm}^{-1}$ , space group  $P2_1/c$  (No. 14), 3 601 unique reflexions with  $F > 3\sigma(F)$ ,  $R = 5.66\%$ .

The crystals were clear, colourless and reasonably equidimensional, with six prominent faces. Intensity data were collected from a specimen of dimensions 0.23x0.34x0.38 mm out to  $\theta = 25^\circ$ , standard reflexion monitoring suggested no crystal deterioration, and as  $\mu R < 0.1$  no absorption correction was applied. Normalisation of the structure factors was assisted by supplying anticipated geometrical details for tosyl groups. The 408 highest E-values with  $E > 1.63$  were used to reveal 39 of the non-hydrogen atoms. Isotropic temperature factors and positional parameters were refined before calculating a difference Fourier synthesis which allowed the remaining atoms and an unexpected toluene molecule of crystallisation to be found. These 53 atoms were refined to  $R = 12.9\%$ , hydrogen atoms introduced at calculated positions and thermal parameters of non-hydrogen atoms then permitted anisotropy. Refinement to convergence at  $R = 5.66\%$  allowed high thermal motions in the solvent molecule to be recognised. Attempts to obtain a better model using partial solvent occupancy produced a worse residual and persistent

positive electron density on the difference Fourier distributed about the solvent atom locations and we therefore reverted to the original full-occupancy model. The 4 expected groups of 3  $sp^3$  hydrogen atoms were insufficiently resolved to warrant their inclusion. The weighting scheme  $w^{-1} = (3.0 - 0.0083 F + 0.0025 F^2)$  was used in final refinement to obtain uniform  $w\Delta F^2$  over the  $F$  range.

A stereoscopic drawing of the molecule, including the toluene of crystallisation, is shown in Figure 3A and a second view of the molecule, with solvent omitted, in Figure 3B. A list of positional co-ordinates is given in Table 2, and Tables 3-5 list bond lengths, bond angles, and selected torsion angles in (8a).

Table 2. Atomic co-ordinates for benzo[b]-1,5,9-triazacyclodecane  $N,N',N''$ -tritosylamide (8a).

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S(1)	0.1121(1)	0.1254(1)	0.3850(1)	H(5)	0.1006	0.0240	0.5130
O(2)	0.0791(2)	0.1441(3)	0.3013(2)	H(6)	0.0483	-0.1412	0.5246
O(3)	0.0935(2)	0.1953(3)	0.4327(2)	W(8)	0.0083	-0.2224	0.2998
C(4)	0.0823(3)	-0.0014(4)	0.3973(3)	H(9)	0.0580	-0.0551	0.2845
C(5)	0.0804(3)	-0.0274(5)	0.4677(3)	H(15)	0.1203	0.4506	0.2006
C(6)	0.0510(3)	-0.1238(5)	0.4746(3)	H(16)	0.0656	0.6178	0.1914
C(7)	0.0237(3)	-0.1966(4)	0.4132(4)	H(18)	0.2692	0.7515	0.2050
C(8)	0.0274(3)	-0.1701(4)	0.3445(3)	H(19)	0.3276	0.5836	0.2161
C(9)	0.0563(3)	-0.0731(4)	0.3359(3)	H(25)	0.4982	0.4973	0.6930
C(10)	-0.0115(4)	-0.3002(5)	0.4210(5)	H(26)	0.5038	0.5287	0.8184
S(11)	0.2688(1)	0.3755(1)	0.2131(1)	H(28)	0.5207	0.2150	0.8646
O(12)	0.2085(3)	0.3140(4)	0.1501(2)	H(29)	0.5140	0.1790	0.7390
O(13)	0.3473(2)	0.3905(3)	0.2171(2)	H(341)	0.2091	0.2773	0.3407
C(14)	0.2283(3)	0.5014(5)	0.2078(3)	H(342)	0.1719	0.2533	0.2457
C(15)	0.1522(4)	0.5141(6)	0.2010(4)	H(361)	0.3936	0.3874	0.3621
C(16)	0.1209(4)	0.6115(7)	0.1953(4)	H(362)	0.3747	0.2898	0.4059
C(17)	0.1609(4)	0.7009(6)	0.1949(4)	H(371)	0.2743	0.4083	0.4137
C(18)	0.2373(4)	0.6877(6)	0.2035(5)	H(372)	0.3216	0.5018	0.3944
C(19)	0.2705(4)	0.5903(6)	0.2095(4)	H(381)	0.3661	0.4798	0.5342
C(20)	0.1217(4)	0.8088(7)	0.1846(5)	H(382)	0.4393	0.4706	0.5113
S(21)	0.5021(1)	0.3091(1)	0.6130(1)	H(401)	0.2902	0.3021	0.5057
O(22)	0.5534(2)	0.3831(4)	0.6012(2)	H(402)	0.3461	0.2924	0.6017
O(23)	0.5175(2)	0.1995(3)	0.6124(2)	H(411)	0.3804	0.1272	0.5952
C(24)	0.5053(3)	0.3358(4)	0.7053(3)	H(412)	0.3662	0.1400	0.5042
C(25)	0.5027(4)	0.4367(4)	0.7288(3)	H(421)	0.2306	0.1457	0.5363
C(26)	0.5061(4)	0.4549(5)	0.8020(4)	H(422)	0.2639	0.0338	0.5214
C(27)	0.5127(3)	0.3750(5)	0.8527(3)	H(43)	0.2576	-0.0492	0.4307
C(28)	0.5153(3)	0.2753(5)	0.8284(4)	H(44)	0.3253	-0.1421	0.3563
C(29)	0.5117(5)	0.2552(5)	0.7556(4)	H(45)	0.3386	-0.0424	0.2589
C(30)	0.5156(5)	0.3965(7)	0.9330(4)	H(46)	0.2867	0.1476	0.2381
N(31)	0.2116(2)	0.1264(3)	0.4220(2)	H(47)	0.2668	-0.1113	0.1025
C(32)	0.2436(3)	0.0791(4)	0.3739(3)	H(48)	0.2006	0.0381	0.0922
C(33)	0.2517(3)	0.1397(4)	0.3172(3)	H(49)	0.1157	0.1188	-0.0170
C(34)	0.2225(3)	0.2511(4)	0.2986(3)	H(50)	0.0856	0.0421	-0.1446
N(35)	0.2830(3)	0.3217(4)	0.2953(2)	H(51)	0.1546	-0.1294	-0.1356
C(36)	0.3511(3)	0.3541(5)	0.3724(3)				
C(37)	0.3276(3)	0.4304(4)	0.4182(3)				
C(38)	0.3891(3)	0.4360(5)	0.5059(3)				
N(39)	0.4099(2)	0.3310(3)	0.5433(2)				
C(40)	0.3431(3)	0.2754(4)	0.5489(3)				
C(41)	0.3442(3)	0.1581(4)	0.5414(3)				
C(42)	0.2592(3)	0.1107(4)	0.5095(3)				
C(43)	0.2704(3)	-0.0244(5)	0.3879(3)				
C(44)	0.3056(4)	-0.0681(5)	0.3460(4)				
C(45)	0.3136(4)	-0.0107(6)	0.2902(4)				
C(46)	0.2873(4)	0.0909(5)	0.2752(4)				
C(47)	0.2270(9)	-0.0796(12)	0.0478(8)				
C(48)	0.1877(14)	0.0062(16)	0.0401(11)				
C(49)	0.1415(12)	0.0526(9)	-0.0207(17)				
C(50)	0.1239(7)	0.0080(19)	-0.0923(10)				
C(51)	0.1668(8)	-0.0909(13)	-0.0846(8)				
C(52)	0.2153(7)	-0.1267(8)	-0.0161(9)				
C(53)	0.2610(10)	-0.2234(11)	-0.0083(14)				

Numbering of atoms is given in Figure 3.

Table 3. Bond distances (Å) for (8a) with estimated standard deviations in parentheses

N(31) - C(32)	1.442(6)
C(32) - C(33)	1.391(7)
C(33) - C(34)	1.500(8)
C(34) - N(35)	1.470(6)
N(35) - C(36)	1.475(6)
C(36) - C(37)	1.503(8)
C(37) - C(38)	1.514(7)
C(38) - N(39)	1.477(7)
N(39) - C(40)	1.482(6)
C(40) - C(41)	1.500(7)
C(41) - C(42)	1.532(7)
C(42) - N(31)	1.482(6)
C(32) - C(43)	1.388(7)
C(43) - C(44)	1.370(8)
C(45) - C(46)	1.363(9)
C(46) - C(33)	1.403(7)

The bond lengths for the three tosyl groups are matched in the table below, the atomic labels for Ts(2) and Ts(3) being 10 and 20 greater than Ts(1)

	Ts(1)	Ts(2)	Ts(3)
S(1) - N(31)	1.650(4)	1.608(4)	1.627(4)
S(1) - O(2)	1.428(4)	1.429(4)	1.436(4)
S(1) - O(3)	1.425(4)	1.448(4)	1.425(4)
S(1) - C(4)	1.757(5)	1.754(6)	1.759(5)
C(4) - C(5)	1.394(7)	1.378(8)	1.367(7)
C(5) - C(6)	1.375(8)	1.353(10)	1.382(8)
O(6) - C(7)	1.384(8)	1.363(9)	1.365(8)
C(7) - C(8)	1.382(7)	1.373(8)	1.358(8)
C(8) - C(9)	1.387(7)	1.366(9)	1.378(8)
C(9) - C(4)	1.376(7)	1.371(8)	1.367(8)
C(7) - C(10)	1.511(8)	1.525(10)	1.527(7)

Table 4. Bond angles (°) for (8a) with estimated standard deviations in parentheses

C(32) - N(31) - C(42)	116.4(4)
C(32) - N(31) - S(1)	116.8(3)
C(42) - N(31) - S(1)	115.9(3)
N(31) - C(32) - C(33)	119.5(5)
N(31) - C(32) - C(43)	119.7(5)
C(33) - C(32) - C(43)	120.8(5)
C(32) - C(33) - C(34)	123.0(4)
C(32) - C(33) - C(46)	116.8(5)
C(34) - C(33) - C(46)	120.2(5)
C(33) - C(34) - N(35)	112.6(4)
C(34) - N(35) - C(36)	116.8(4)
C(34) - N(35) - S(11)	121.7(3)
C(36) - N(35) - S(11)	120.9(3)
N(35) - C(36) - C(37)	113.7(4)
C(36) - C(37) - C(38)	112.9(4)
C(37) - C(38) - N(39)	112.1(4)
C(38) - N(39) - C(40)	115.3(4)
C(38) - N(39) - S(21)	118.8(3)
C(40) - N(39) - S(21)	117.8(3)
N(39) - C(40) - C(41)	114.7(4)
C(40) - C(41) - C(42)	111.8(4)
C(41) - C(42) - N(31)	110.6(4)
C(33) - C(46) - C(45)	121.5(6)
C(45) - C(46) - C(43)	120.2(6)
C(46) - C(45) - C(44)	120.7(6)
C(44) - C(43) - C(32)	120.0(6)
N(31) - S(1) - C(4)	108.4(2)
N(35) - S(11) - C(14)	108.2(3)
N(39) - S(21) - C(24)	107.5(2)
O(2) - S(1) - O(3)	119.8(3)
O(12) - S(11) - O(13)	119.7(3)
O(22) - S(21) - O(23)	119.1(3)

Table 5. Selected torsion angles (°) for (8)

N(31) - C(32) - C(33) - C(34)	-5
C(32) - C(33) - C(34) - N(35)	133
C(33) - C(34) - N(35) - C(36)	-77
C(34) - N(35) - C(36) - C(37)	-72
N(35) - C(36) - C(37) - C(38)	162
C(36) - C(37) - C(38) - N(39)	-51
C(37) - C(38) - N(39) - C(40)	-67
C(38) - N(39) - C(40) - C(41)	147
N(39) - C(40) - C(41) - C(42)	-154
C(40) - C(41) - C(42) - N(31)	78
C(41) - C(42) - N(31) - C(32)	61
C(42) - N(31) - C(32) - C(33)	-130
S(1) - N(31) - C(32) - C(33)	88
S(11) - N(35) - C(36) - C(37)	99
S(21) - N(39) - C(40) - C(41)	-65
C(4) - S(1) - N(31) - C(32)	77
C(14) - S(11) - N(35) - C(36)	-75
C(24) - S(21) - N(39) - C(40)	-55
N(31) - S(1) - C(4) - C(5)	88
N(35) - S(11) - C(14) - C(15)	-66
N(39) - S(21) - C(24) - C(25)	-73
N(31) - C(32) - C(33) - C(46)	177

Numbering of atoms in Tables 3-5 is given in Figure 3.

## 2,3,5,6-Tetrahydro-1H,4H,7H,11cH-3a,6a,11b-triazabenz[de]anthracene (5).- Crystal Data.

$C_{14}H_{19}N_3$ ,  $M = 229$ , monoclinic,  $a = 15.608(6)$ ,  $b = 8.983(4)$ ,  $c = 17.660(8)$  Å;  $\beta = 94.28(5)^\circ$ ;  $V = 2469.1$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_c = 1.23$ ,  $\mu(\text{Mo-K}\alpha) = 0.88$  cm<sup>-1</sup>, space group  $P2_1/c$  (No. 14), 1680 unique reflexions with  $F > 3\sigma(F)$ ,  $R = 8.99\%$ .

Samples cut from irregular, semi-transparent plates showed unusually large reflexion width but without any apparent splitting. A specimen of dimensions  $0.48 \times 0.29 \times 0.10$  mm was used for collection of intensity data up to  $\theta = 25^\circ$ . No crystal deterioration was detected by standard reflection intensity monitoring and no absorption correction was applied as  $\mu R < 0.04$ . After location of two molecules in the asymmetric unit, hydrogen atoms were added at calculated positions and confirmed by difference Fourier synthesis after initial least-squares refinement. Further cycles were performed using anisotropic temperature factors for the non-hydrogen atoms until convergence at  $R = 8.99\%$ . The final weighting scheme used was  $w^{-1} = (5.9 - 0.34 F + 0.009F^2)$ .

A stereoscopic drawing showing the relative positions of the two closest molecules in the unit cell is shown in Figure 1A; stereoscopic drawings of the two distinct molecules, reoriented to show their comparability are shown in Figure 1B. A list of positional co-ordinates is given in Table 6, and Tables 7-9 list bond lengths, bond angles, and selected torsion angles for (5). In the Tables, in each case the two molecules in the cell are labelled I and II. The atom numbers of II are 17 larger than the corresponding atom numbers for I. These data illustrate the very close similarity of the two crystallographically independent molecules.

Table 6. Atomic co-ordinates for  
2,3,5,6-tetrahydro-1H,4H,7H,11cH-  
3a,6a,11b-triazabenz[de]anthracene (5).

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C(1)	0.1080(4)	0.0967(7)	0.1799(4)	H(1)	0.0968	0.1694	0.1374
N(2)	0.1477(4)	0.1768(6)	0.2443(4)	H(31)	0.2503	0.3064	0.2708
C(3)	0.2255(3)	0.2498(9)	0.2256(5)	H(32)	0.2121	0.3204	0.1826
C(4)	0.2906(5)	0.1361(10)	0.2026(5)	H(41)	0.3062	0.0674	0.2460
C(5)	0.2485(5)	0.0486(9)	0.1360(5)	H(42)	0.3430	0.1878	0.1869
N(6)	0.1665(3)	-0.0176(6)	0.1544(3)	H(51)	0.2883	-0.0328	0.1223
C(7)	0.1267(5)	-0.0865(10)	0.0861(5)	H(52)	0.2379	0.1168	0.0916
C(8)	0.0404(6)	-0.1539(10)	0.0979(6)	H(71)	0.1656	-0.1665	0.0693
C(9)	-0.0157(5)	-0.0360(11)	0.1313(6)	H(72)	0.1194	-0.0095	0.0453
N(10)	0.0265(4)	0.0371(7)	0.1986(4)	H(81)	0.0477	-0.2400	0.1336
C(11)	0.0328(5)	-0.0632(10)	0.2628(5)	H(82)	0.0127	-0.1886	0.0480
C(12)	0.0792(4)	0.0053(9)	0.3284(5)	H(91)	-0.0699	-0.0838	0.1458
C(13)	0.0662(5)	-0.0412(10)	0.4025(6)	H(92)	-0.0304	0.0415	0.0917
C(14)	0.1120(6)	0.0187(12)	0.4653(5)	H(111)	0.0639	-0.1555	0.2487
C(15)	0.1707(5)	0.1317(11)	0.4532(5)	H(112)	-0.0263	-0.0906	0.2761
C(16)	0.1847(5)	0.1810(10)	0.3826(5)	H(13)	0.0224	-0.1202	0.4101
C(17)	0.1398(4)	0.1202(8)	0.3186(5)	H(14)	0.1034	-0.0176	0.5175
C(18)	0.3934(4)	0.5998(7)	0.3391(4)	H(15)	0.2036	0.1776	0.4979
N(19)	0.4503(3)	0.5315(7)	0.2893(3)	H(16)	0.2276	0.2620	0.3764
C(20)	0.5091(5)	0.4286(10)	0.3308(5)	H(18)	0.4300	0.6527	0.3794
C(21)	0.4598(5)	0.3099(10)	0.3688(6)	H(201)	0.5453	0.4848	0.3702
C(22)	0.3984(5)	0.3865(9)	0.4204(5)	H(202)	0.5470	0.3808	0.2946
N(23)	0.3422(3)	0.4905(6)	0.3775(3)	H(211)	0.5006	0.2445	0.3999
C(24)	0.2906(6)	0.5662(10)	0.4313(6)	H(212)	0.4263	0.2492	0.3295
C(25)	0.2342(6)	0.6853(10)	0.3941(6)	H(221)	0.4326	0.4416	0.4615
C(26)	0.2870(6)	0.7897(9)	0.3503(6)	H(222)	0.3626	0.3091	0.4438
N(27)	0.3416(4)	0.7116(7)	0.2985(4)	H(241)	0.3299	0.6127	0.4719
C(28)	0.2902(5)	0.6545(9)	0.2345(5)	H(242)	0.2536	0.4912	0.4551
C(29)	0.3466(4)	0.5770(8)	0.1828(5)	H(251)	0.2059	0.7422	0.4340
C(30)	0.3212(5)	0.5612(9)	0.1045(5)	H(252)	0.1893	0.6378	0.3587
C(31)	0.3725(6)	0.4846(10)	0.0568(4)	H(261)	0.3245	0.8499	0.3871
C(32)	0.4459(5)	0.4202(9)	0.0882(5)	H(262)	0.2475	0.8584	0.3199
C(33)	0.4717(5)	0.4298(8)	0.1626(4)	H(281)	0.2597	0.7386	0.2067
C(34)	0.4216(4)	0.5090(7)	0.2109(4)	H(282)	0.2469	0.5827	0.2522
				H(30)	0.2657	0.6054	0.0834
				H(31)	0.3562	0.4773	0.0011
				H(32)	0.4824	0.3628	0.0543
				H(33)	0.5262	0.3809	0.1828

Numbering of atoms is given in Figure 1.

Table 7. Bond distances (Å) for (5) with estimated standard deviations in parentheses

	I	II
C(1) - N(2)	1.446(9)	1.434(8)
C(1) - N(6)	1.465(8)	1.464(8)
C(1) - N(10)	1.442(9)	1.445(9)
N(2) - C(3)	1.439(9)	1.462(10)
N(2) - C(17)	1.421(9)	1.437(9)
C(3) - C(4)	1.517(11)	1.501(12)
C(4) - C(5)	1.523(12)	1.535(12)
C(5) - N(6)	1.469(8)	1.455(9)
N(6) - C(7)	1.453(10)	1.459(10)
C(7) - C(8)	1.505(12)	1.504(13)
C(8) - C(9)	1.522(12)	1.501(12)
C(9) - N(10)	1.469(11)	1.474(10)
N(10) - C(11)	1.445(10)	1.431(10)
C(11) - C(12)	1.456(11)	1.488(11)
C(12) - C(13)	1.402(11)	1.418(11)
C(12) - C(17)	1.420(10)	1.378(11)
C(13) - C(14)	1.384(13)	1.387(12)
C(14) - C(15)	1.395(13)	1.363(11)
C(15) - C(16)	1.355(11)	1.348(10)
C(16) - C(17)	1.397(11)	1.395(10)

Table 8. Bond angles (°) for (5) with estimated standard deviations in parentheses

	I	II
N(2) - C(1) - N(10)	109.7(6)	110.1(6)
N(2) - C(1) - N(6)	110.5(5)	112.4(6)
N(6) - C(1) - N(10)	113.0(5)	113.0(5)
C(1) - N(2) - C(3)	111.4(6)	110.9(6)
C(1) - N(2) - C(17)	119.1(6)	119.2(5)
C(3) - N(2) - C(17)	120.5(6)	122.3(6)
N(2) - C(3) - C(4)	110.4(6)	110.5(7)
C(3) - C(4) - C(5)	107.2(7)	108.1(7)
C(4) - C(5) - N(6)	111.8(6)	110.9(7)
C(1) - N(6) - C(5)	110.9(5)	110.1(6)
C(1) - N(6) - C(7)	108.4(5)	109.6(6)
C(5) - N(6) - C(7)	108.3(6)	107.5(7)
N(6) - C(7) - C(8)	112.8(7)	112.4(8)
C(7) - C(8) - C(9)	108.7(7)	110.1(7)
C(8) - C(9) - N(10)	112.9(7)	112.8(7)
C(1) - N(10) - C(9)	109.2(6)	110.6(6)
C(1) - N(10) - C(11)	113.7(6)	113.7(6)
C(9) - N(10) - C(11)	110.9(7)	110.2(7)
N(10) - C(11) - C(12)	111.2(7)	109.3(7)
C(11) - C(12) - C(17)	120.4(7)	120.8(7)
C(11) - C(12) - C(13)	121.2(8)	120.7(7)
C(13) - C(12) - C(17)	118.4(8)	118.3(7)
C(12) - C(13) - C(14)	122.0(8)	120.7(7)
C(13) - C(14) - C(15)	117.8(8)	118.0(7)
C(14) - C(15) - C(16)	122.2(9)	123.3(8)
C(15) - C(16) - C(17)	120.7(9)	119.3(7)
C(16) - C(17) - C(12)	118.9(8)	120.4(7)
C(16) - C(17) - N(2)	122.3(7)	120.8(6)
C(12) - C(17) - N(2)	118.6(7)	118.7(6)

Table 9. Selected torsion angles (°) for (5)

	I	II
N(6) - C(1) - N(2) - C(3)	60	-59
C(1) - N(2) - C(3) - C(4)	-61	59
N(2) - C(3) - C(4) - C(5)	57	-57
C(3) - C(4) - C(5) - N(6)	-55	56
C(4) - C(5) - N(6) - C(1)	56	-56
C(5) - N(6) - C(1) - N(2)	-57	58
N(10) - C(1) - N(6) - C(7)	61	-59
C(1) - N(6) - C(7) - C(8)	-58	56
N(6) - C(7) - C(8) - C(9)	53	-53
C(7) - C(8) - C(9) - N(10)	-51	51
C(8) - C(9) - N(10) - C(1)	55	-53
C(9) - N(10) - C(1) - N(6)	-60	57
N(10) - C(1) - N(2) - C(17)	38	-35
C(1) - N(2) - C(17) - C(12)	-13	11
N(2) - C(17) - C(12) - C(11)	6	-8
C(17) - C(12) - C(11) - N(10)	-26	30
C(12) - C(11) - N(10) - C(1)	53	-56
C(11) - N(10) - C(1) - N(2)	-59	59
N(10) - C(1) - N(6) - C(5)	180	-177
N(6) - C(1) - N(2) - C(17)	-87	92
N(6) - C(1) - N(10) - C(11)	65	-67
C(11) - C(12) - C(17) - C(16)	-179	177

Numbering of atoms in Tables 7-9 is given in Figure 1.

Hexahydro-1H,4H,7H,9bH-3a,6a,9a-triazaphenalene (1). Crystal data.  $C_{10}H_{19}N_3$ ,  $M = 181$ , monoclinic,  $a = 7.477(3)$ ,  $b = 8.978(4)$ ,  $c = 16.599(11)$  Å;  $\beta = 111.26(4)^\circ$ ;  $U = 1038$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.16$ ,  $\mu(Mo-K_\alpha) = 0.82$  cm<sup>-1</sup>, space group  $P2_1/c$  (No. 14), 675 unique reflexions with  $F > 3\sigma(F)$ ,  $R = 4.55\%$ .

The crystals were very hygroscopic. A sample of dimensions 0.15x0.15x0.08 mm of the air-sensitive sublimate was transferred under a stream of dry nitrogen into a thin-walled capillary tube which was then sealed and mounted for intensity data collection at  $-100^\circ\text{C}$  out to  $\theta = 25^\circ$ . A structural solution was obtained using the MULTAN direct-methods program and further refined and checked by difference Fourier synthesis. The non-hydrogen atoms were permitted anisotropic thermal parameters, but with the hydrogen atoms maintained at 0.95 Å from their bonded carbons. Convergence was reached at  $R = 4.55\%$  using the weighting scheme  $w^{-1} = (0.48 - 0.34F + 0.00104F^2)$  in the final cycles.

A stereoscopic drawing of the molecule is shown in Figure 2, a list of positional co-ordinates is given in Table 10, and Tables 11-13 list bond lengths, bond angles and selected torsion angles in (1).

Table 10. Atomic co-ordinates for hexahydro-1H,4H,7H,9bH-3a,6a,9a-triazaphenalene (1).

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C(1)	0.0365(3)	0.1861(5)	0.1206(3)	H(1)	0.068	0.095	0.100
N(2)	0.1850(4)	0.2219(4)	0.2035(2)	H(31)	0.404	0.147	0.175
C(3)	0.3709(6)	0.2380(5)	0.1946(3)	H(32)	0.465	0.262	0.249
C(4)	0.3653(6)	0.3591(6)	0.1315(3)	H(41)	0.485	0.363	0.124
C(5)	0.2081(6)	0.3256(5)	0.0467(3)	H(42)	0.341	0.452	0.153
N(6)	0.0249(4)	0.3047(4)	0.0587(2)	H(51)	0.239	0.237	0.023
C(7)	-0.1242(7)	0.2735(5)	-0.0254(3)	H(52)	0.197	0.406	0.008
C(8)	-0.3153(6)	0.2526(5)	-0.0171(3)	H(71)	-0.092	0.185	-0.049
C(9)	-0.2975(6)	0.1336(5)	0.0486(3)	H(72)	-0.132	0.354	-0.063
N(10)	-0.1473(4)	0.1702(4)	0.1310(2)	H(81)	-0.407	0.223	-0.071
C(11)	-0.1408(6)	0.0525(5)	0.1931(3)	H(82)	-0.354	0.343	0.001
C(12)	0.0118(7)	0.0868(5)	0.2798(3)	H(91)	-0.267	0.042	0.028
C(13)	0.1980(7)	0.1072(5)	0.2673(3)	H(92)	-0.416	0.124	0.057
				H(111)	-0.112	-0.040	0.172
				H(112)	-0.262	0.046	0.199
				H(121)	0.022	0.007	0.318
				H(122)	-0.021	0.176	0.303
				H(131)	0.234	0.016	0.248
				H(132)	0.294	0.135	0.321

Numbering of atoms is given in Figure 2.

1,5,9-Triazadodecane N,N',N''-tritosylamide (15).- Crystal data.  $C_{30}H_{39}N_3O_6S_3$ ,  $M = 633$ , monoclinic,  $a = 33.335(11)$ ,  $b = 14.475(3)$ ,  $c = 13.187(10)$  Å;  $\beta = 101.07(6)^\circ$ ;  $U = 6245$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_c = 1.35$ ,  $\mu(Mo-K_\alpha) = 3.0$  cm<sup>-1</sup>, space group  $C 2/c$  (No. 15), 2103 unique reflexions with  $F > 3\sigma(F)$ ,  $R = 7.98\%$ .

The crystals were clear, colourless and prismatic. Intensity data were collected from a specimen of dimensions 0.13x0.13x0.35 mm out to  $\theta = 25^\circ$ . Standard reflexion monitoring suggested no crystal deterioration, and as  $\mu R < 0.1$  no absorption correction was applied. Normalisation was aided by supplying geometrical details anticipated for tosyl groups, thus with 368 E-values greater than 1.51 all but one of the 42 non-hydrogen atoms were found; the solution was completed by difference Fourier synthesis. Isotropic refinement showed disorder at one atom of the 12-membered ring, and an investigation of occupancy and thermal motion suggested the assignment of two alternative sites with an occupancy ratio of ca. 2:1. Hydrogen atoms were added at calculated positions, constrained with  $\beta$ -values of 7.0 and anisotropic refinement of 41 atoms converged at  $R = 7.98\%$ . The hydrogen atoms of the tosyl methyl groups were not resolved. The weighting scheme  $w^{-1} = (37 - 0.88F + 0.009F^2)$  was used in a final refinement to give uniform  $w\Delta F^2$  over the  $F$  range.

A stereoscopic drawing of the molecule is shown in Figure 4, a list of positional co-ordinates is given in Table 14 and Tables 15-17 list bond lengths, bond angles, and selected torsion angles in (15).

Table 11. Bond distances (Å) for (1) with estimated standard deviations in parentheses

C(1) - N(2)	1.457(5)
C(1) - N(6)	1.461(5)
C(1) - N(10)	1.453(5)
N(2) - C(3)	1.458(6)
N(2) - C(13)	1.454(5)
C(3) - C(4)	1.499(7)
C(4) - C(5)	1.502(6)
C(5) - N(6)	1.466(5)
N(6) - C(7)	1.464(5)
C(7) - C(8)	1.496(7)
C(8) - C(9)	1.498(6)
C(9) - N(10)	1.459(5)
N(10) - C(11)	1.464(5)
C(11) - C(12)	1.509(6)
C(12) - C(13)	1.492(6)

Table 12. Bond angles (°) for (1) with estimated standard deviations in parentheses

N(2) - C(1) - N(10)	109.8(3)
N(2) - C(1) - N(6)	109.6(3)
N(6) - C(1) - N(10)	109.8(3)
C(1) - N(2) - C(3)	110.7(3)
C(1) - N(2) - C(13)	111.0(3)
C(3) - N(2) - C(13)	109.3(4)
N(2) - C(3) - C(4)	110.9(4)
C(3) - C(4) - C(5)	108.9(4)
C(4) - C(5) - N(6)	110.5(4)
C(1) - N(6) - C(5)	111.6(3)
C(1) - N(6) - C(7)	111.2(3)
C(5) - N(6) - C(7)	108.7(3)
N(6) - C(7) - C(8)	111.0(4)
C(7) - C(8) - C(9)	108.7(4)
C(8) - C(9) - N(10)	110.9(4)
C(1) - N(10) - C(9)	110.5(3)
C(1) - N(10) - C(11)	111.3(3)
C(9) - N(10) - C(11)	108.4(3)
N(10) - C(11) - C(12)	110.1(3)
C(11) - C(12) - C(13)	108.2(4)
C(12) - C(13) - N(2)	111.6(4)

Table 13. Selected torsion angles (°) for (1)

N(6) - C(1) - N(2) - C(3)	-60
C(1) - N(2) - C(3) - C(4)	59
N(2) - C(3) - C(4) - C(5)	-56
C(3) - C(4) - C(5) - N(6)	55
C(4) - C(5) - N(6) - C(7)	-57
C(5) - N(6) - C(7) - C(8)	59
N(10) - C(1) - N(6) - C(7)	-59
C(1) - N(6) - C(7) - C(8)	57
N(6) - C(7) - C(8) - C(9)	-55
C(7) - C(8) - C(9) - N(10)	56
C(8) - C(9) - N(10) - C(1)	-60
C(9) - N(10) - C(1) - N(6)	60
N(10) - C(1) - N(2) - C(3)	58
C(1) - N(2) - C(3) - C(4)	-58
N(2) - C(3) - C(4) - C(5)	56
C(3) - C(4) - C(5) - N(6)	-56
C(12) - C(11) - N(10) - C(1)	59
C(11) - N(10) - C(1) - N(6)	-59
N(10) - C(1) - N(2) - C(3)	180
N(2) - C(1) - N(6) - C(7)	-179
N(6) - C(1) - N(10) - C(9)	180

Numbering of atoms in Tables 11-13 is given in Figure 2.

Table 16. Bond angles (°) for (15) with estimated standard deviations in parentheses

C(32) - N(31) - C(42)	115.5(9)
C(32) - N(31) - S(1)	116.3(7)
C(42) - N(31) - S(1)	116.9(7)
N(31) - C(32) - C(33)	110.8(8)
C(32) - C(33) - C(34)	114.7(9)
C(33) - C(34) - N(35)	115.4(9)
C(34) - N(35) - C(36)	117.1(8)
C(34) - N(35) - S(1)	117.8(7)
C(36) - N(35) - S(1)	120.7(8)
N(35) - C(36) - C(37)	115.5(9)
C(36) - C(37) - C(38)	112.9(8)
C(37) - C(38) - N(39)	112.1(9)
C(38) - N(39) - C(40)	114.5(8)
C(38) - N(39) - S(21)	115.3(6)
C(40) - N(39) - S(21)	115.6(7)
N(39) - C(40) - C(41)	118.0(11)
N(39) - C(40) - C(42)	120.3(16)
C(40) - C(41) - C(42)	106.7(12)
C(40) - C(41) - C(42)	117.2(24)
N(39) - C(40) - N(31)	105.3(12)
C(41) - C(42) - N(31)	150.8(19)
N(31) - S(1) - C(4)	106.5(5)
N(35) - S(1) - C(14)	105.2(5)
N(39) - S(21) - C(24)	107.2(4)
O(2) - S(1) - O(3)	120.1(6)
O(12) - S(11) - O(13)	119.2(5)
O(22) - S(21) - O(23)	119.3(4)

Table 17. Selected torsion angles (°) for (15)

N(31) - C(32) - C(33) - C(34)	-65
C(32) - C(33) - C(34) - N(35)	156
C(33) - C(34) - N(35) - C(36)	-56
C(34) - N(35) - C(36) - C(37)	-65
N(35) - C(36) - C(37) - C(38)	163
C(36) - C(37) - C(38) - N(39)	-69
C(37) - C(38) - N(39) - C(40)	-95
C(38) - N(39) - C(40) - C(41)	79
C(38) - N(39) - C(40) - C(42)	137
N(39) - C(40) - C(41) - C(42)	66
N(39) - C(40) - C(41) - C(42)	-46
C(40) - C(41) - C(42) - N(31)	-142
C(40) - C(41) - C(42) - N(31)	-68
C(41) - C(42) - N(31) - C(32)	148
C(41) - C(42) - N(31) - C(32)	162
C(42) - N(31) - C(32) - C(33)	-79
S(1) - N(31) - C(32) - C(33)	139
S(1) - N(35) - C(36) - C(37)	91
S(21) - N(39) - C(40) - C(41)	-143
S(21) - N(39) - C(40) - C(42)	-86
C(4) - S(1) - N(31) - C(32)	78
C(14) - S(1) - N(35) - C(36)	112
C(24) - S(21) - N(39) - C(40)	-69
N(31) - S(1) - C(4) - C(5)	-87
N(35) - S(1) - C(14) - C(15)	124
N(39) - S(21) - C(24) - C(25)	88

Numbering of atoms in Tables 16 and 17 is given in Figure 4.



Table 14. Atomic co-ordinates for  
1,5,9-triazadodecane  
N,N',N''-tritosylamide (15).

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S(1)	0.4980(1)	0.2915(3)	-0.0382(2)	H(5)	0.539	0.447	0.061
O(2)	0.5005(2)	0.2086(7)	-0.0943(6)	H(6)	0.604	0.470	0.163
O(3)	0.4856(3)	0.3760(7)	-0.0923(5)	H(8)	0.628	0.194	0.146
C(4)	0.5463(3)	0.3083(7)	0.0405(7)	H(9)	0.563	0.173	0.040
C(5)	0.5580(4)	0.3946(8)	0.0775(9)	H(15)	0.286	0.540	-0.127
C(6)	0.5960(5)	0.4079(8)	0.1376(9)	H(16)	0.255	0.652	-0.035
C(7)	0.6233(4)	0.3347(9)	0.1637(7)	H(18)	0.236	0.459	0.168
C(8)	0.6103(3)	0.2478(8)	0.1278(8)	H(19)	0.268	0.346	0.082
C(9)	0.5718(4)	0.2347(7)	0.0656(9)	H(25)	0.447	-0.129	0.246
C(10)	0.6649(3)	0.3488(10)	0.2315(9)	H(26)	0.441	-0.293	0.222
S(11)	0.3017(1)	0.3514(2)	-0.1013(2)	H(28)	0.319	-0.261	0.120
O(12)	0.2723(3)	0.2797(5)	-0.1295(6)	H(29)	0.324	-0.101	0.141
O(13)	0.3164(2)	0.4008(5)	-0.1805(5)	H(321)	0.458	0.411	0.050
C(14)	0.2801(3)	0.4336(7)	-0.0310(8)	H(322)	0.468	0.360	0.160
C(15)	0.2758(4)	0.5222(9)	-0.0646(9)	H(331)	0.400	0.402	0.130
C(16)	0.2573(4)	0.5875(8)	-0.0110(12)	H(332)	0.402	0.293	0.126
C(17)	0.2414(3)	0.5653(11)	0.0743(10)	H(341)	0.394	0.318	-0.064
C(18)	0.2460(3)	0.4773(12)	0.1062(8)	H(342)	0.376	0.415	-0.038
C(19)	0.2650(3)	0.4096(8)	0.0558(9)	H(361)	0.310	0.196	0.014
C(20)	0.2201(4)	0.6351(12)	0.1310(11)	H(362)	0.354	0.210	0.086
S(21)	0.3913(1)	0.0202(2)	0.2060(2)	H(371)	0.382	0.168	-0.066
O(22)	0.4262(2)	0.0407(5)	0.2826(5)	H(372)	0.337	0.132	-0.113
O(23)	0.3523(2)	0.0575(5)	0.2158(5)	H(381)	0.373	0.006	-0.041
C(24)	0.3866(4)	-0.1018(6)	0.1941(7)	H(382)	0.342	0.030	0.032
C(25)	0.4207(3)	-0.1564(8)	0.2183(7)	H(401)	0.437	-0.020	0.030
C(26)	0.4167(4)	-0.2525(8)	0.2030(8)	H(402)	0.459	0.021	0.138
C(27)	0.3786(5)	-0.2899(8)	0.1616(8)	H(411)	0.443	0.124	-0.043
C(28)	0.3456(4)	-0.2335(9)	0.1435(9)	H(412)	0.486	0.077	0.004
C(29)	0.3487(3)	-0.1405(8)	0.1572(8)	H(421)	0.501	0.190	0.138
C(30)	0.3759(5)	-0.3950(7)	0.1433(10)	H(422)	0.455	0.194	0.153
N(31)	0.4662(3)	0.2735(6)	0.0396(6)				
C(32)	0.4525(3)	0.3557(7)	0.0889(7)				
C(33)	0.4072(4)	0.3499(7)	0.0903(8)				
C(34)	0.3796(4)	0.3508(7)	-0.0155(9)				
N(35)	0.3395(3)	0.3087(6)	-0.0207(7)				
C(36)	0.3386(3)	0.2128(7)	0.0142(8)				
C(37)	0.3563(4)	0.1430(8)	-0.0487(7)				
C(38)	0.3661(4)	0.0513(7)	0.0074(8)				
N(39)	0.4004(3)	0.0595(5)	0.0960(6)				
C(40)	0.4406(4)	0.0356(8)	0.0728(10)				
C(411)	0.4611(5)	0.1040(12)	0.0203(13)				
C(412)	0.4776(11)	0.0953(25)	0.1134(27)				
C(42)	0.4727(3)	0.1931(8)	0.1024(12)				

Numbering of atoms is given in Figure 4.

The bond lengths for the three Ts groups are

matched in the table which follows, the atomic labels for Ts(2) and Ts(3) being 10 and 20 greater than those for Ts(1)

Table 15. Bond distances (Å) for (15) with estimated standard deviations in parentheses

		Ts(1)	Ts(2)	Ts(3)
N(31) - C(32)	1.469(12)	S(1) - N(31)	1.631(9)	1.639(7)
C(32) - C(33)	1.516(15)	S(1) - O(2)	1.421(8)	1.417(7)
C(33) - C(34)	1.516(15)	S(1) - O(3)	1.435(8)	1.438(7)
C(34) - N(35)	1.459(14)	S(1) - C(4)	1.759(11)	1.776(10)
N(35) - C(36)	1.465(12)	C(4) - C(5)	1.371(14)	1.356(14)
C(36) - C(37)	1.499(14)	C(5) - C(6)	1.372(16)	1.393(16)
C(37) - C(38)	1.525(14)	C(6) - C(7)	1.396(16)	1.372(16)
C(38) - N(39)	1.473(12)	C(7) - C(8)	1.384(14)	1.340(17)
N(39) - C(40)	1.472(13)	C(8) - C(9)	1.397(14)	1.402(16)
C(40) - C(411)	1.452(19)	C(9) - C(4)	1.363(14)	1.381(13)
C(40) - C(412)	1.517(36)	C(7) - C(10)	1.514(15)	1.512(17)
C(411) - C(42)	1.680(21)			
C(412) - C(42)	1.429(36)			
C(42) - N(31)	1.421(14)			

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REFERENCES

1. J.M. Erhardt and J.D. Wuest, J. Amer. Chem. Soc., 1980, 102, 6363.
2. (a) T.J. Atkins, J. Amer. Chem. Soc., 1980, 102, 6364;  
(b) J.M. Erhardt, E.R. Grover, and J.D. Wuest, ibid., 6365;  
(c) G.R. Weisman, V. Johnson, and R.E. Fiala, Tetrahedron Lett., 1980, 3635. 3635.
3. F. Ishikawa, Chem. Pharm. Bull., 1980, 28, 2587.
4. J.M. Erhardt, Ph.D. Thesis, Univ. Microfilms Int., Ann Arbor, Order No. DA 8222 618.
5. H.F. Hodson and G.F. Smith, J. Chem. Soc., 1957, 1877.
6. F. Bohlmann, Chem. Ber., 1958, 91, 2157.
7. "Stereo-electronic effects in organic chemistry", P. Deslongchamps, Pergamon Press, Oxford, 1983.
8. A.R. Katritzky, V.J. Baker, I.J. Ferguson, and R.C. Patel, J. Chem. Soc., Perkin Trans. 2, 1979, 143; R. St-Amour and M. St-Jacques, Tetrahedron Lett., 1985, 26, 13.
9. R.L. Beddoes, L. Dalton, J.A. Joule, O.S. Mills, J.D. Street, and C.I.F. Watt, J. Chem. Soc., Perkin Trans. 2, 1986, 787.
10. P.J. Cox, P.H. McCabe, N.J. Milne and G.A. Sim, J. Chem. Soc. Chem. Commun., 1985, 626; P.H. McCabe, N.J. Milne and G.A. Sim, ibid., 625.
11. I.I. Schuster, S.H. Doss, and J.D. Roberts, J. Org. Chem., 1978, 43, 4693.
12. W.B. Jennings and R. Spratt, Chem. Commun., 1970, 1418; W.R. Jackson, J.G. Kee, R. Spratt, and W.B. Jennings, Tetrahedron Lett., 1973, 3581.
13. N. Kornblum and D.C. Iffland, J. Amer. Chem. Soc., 1949, 71, 2137.
14. G. Kuhn and E. Hoyer, Makromol. Chem., 1967, 108, 84.