The π-Molecular Complexes *trans*-Azobenzene–(*sym*-Trinitrobenzene)₂ and N-Benzylideneaniline–(*sym*-Trinitrobenzene)₂

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## Abstract

The isomorphous crystal structures of two π-molecular complexes of the isoelectronic analogues *trans*-azobenzene (AB) and N-benzylideneaniline (BA) with trinitrobenzene (TNB) in a 1:2 ratio have been determined by X-ray analysis. Both complexes crystallize in space group $C2/c$, with $Z = 4$. For AB:TNB₂: $a = 10\cdot896\,(2)$, $b = 9\cdot993\,(2)$, $c = 24\cdot932\,(6)$ Å, $\beta = 97\cdot66\,(2)°$; for BA:TNB₂: $a = 11\cdot034\,(3)$, $b = 9\cdot973\,(1)$, $c = 24\cdot940\,(8)$ Å, $\beta = 95\cdot17\,(2)°$. The structures were refined to $R = 0\cdot062$ (1777 observed reflections) and $0\cdot070$ (2039) respectively. The donor molecule in these compounds takes on two orientations with population ratio 1:1. Comparison of the structures of the AB and BA molecules here and in their pure crystal shows that AB is more distorted from planarity in the present molecular compound, while BA is significantly less distorted.

Introduction

N-Benzylideneaniline (BA) is an excellent model compound for the investigation of the relationship between molecular conformation and electronic or structural influences. The conformation can be defined in terms of two geometric parameters: the rotations of the two phenyl rings with respect to the plane of the four atoms which form the bridge between them. Interest in this compound arose from its anomalous solution spectral properties compared with its isoelectronic analogues *trans*-azobenzene (AB) and *trans*-stilbene (S) (Jaffe, Yeh & Gardiner, 1958; Wiegand & Merkel, 1942). Through a wide variety of experimental and theoretical investigations the dissimilarity in spectral response has been shown to be due to conformational differences, AB and S being essentially planar, while BA is non-planar (Bally, Haselbach, Lanyiova, Marschner & Rossi, 1976, and references therein; Eckhardt &

Bernstein, 1972; Bernstein, Hagler & Engel, 1981; Bernstein, Anderson & Eckhardt, 1979).
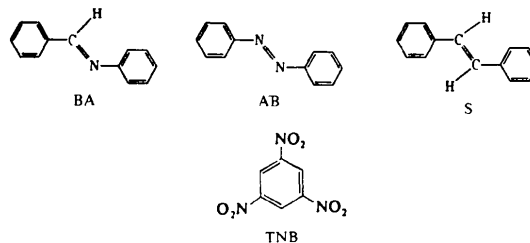
In its crystal structure BA is non-planar (Bürgi & Dunitz, 1970), while AB is essentially planar (Brown, 1966a; De Lange, Robertson & Woodward, 1939). Theoretical calculations indicate that the non-planar BA molecule is about 6·7 kJ lower in energy than the planar conformation (Bürgi & Dunitz, 1971; Bernstein, Hagler & Engel, 1981). This is the order of magnitude of the energy involved in the formation of π-charge-transfer complexes, which in most cases studied to date crystallize in infinite stacks of alternating donor and acceptor molecules with close plane-to-plane packing (Herbstein, 1971). Such a stacking arrangement suggests that the charge-transfer forces act along the stack axis which is nearly perpendicular to the molecular plane. The goal of the present study was to employ these forces to obtain a planar BA molecule. In an earlier example the formation of a π-charge-transfer complex of a fairly rigid but strained molecule, benzo[c]phenanthrene, with 2,3-dichloro-5,6-dicyano-benzoquinone led to an experimentally significant increase in planarity compared to its conformation in the pure crystal (Bernstein, Regev & Herbstein, 1977). In the present case of a significantly more flexible molecule, the compatibility of the crystal and molecular energies and a presumably favorable packing mode suggested that formation of a complex of BA with a suitable acceptor might be a means of applying crystal engineering to achieve the desired conformation in BA. The structures of the 1:2 complexes of trinitrobenzene with AB (present work) and S (Bar & Bernstein, 1978) were carried out to serve as reference structures for comparison with the BA:TNB₂ structure.

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Experimental

Crystals of the 1:2 molecular compounds suitable for X-ray studies were grown from ethanolic solutions of the proper molar ratio. The AB:TNB$_2$ crystals were orange with no distinct shapes or faces (m.p. 397 K; lit. 404–405 K) (Hoffman & Kunreuther, 1910), while the BA:TNB$_2$ crystals were well formed yellow plates (m.p. 381 K; lit. 385 K) (Sudborough & Beard, 1910), with prominent {001} faces and exhibiting also {111} and {110}. Systematic absences indicated space groups $C2/c$ or Cc; the former was confirmed during the course of the study. Cell dimensions for BA:TNB$_2$ are based on a least-squares fit of fifteen reflections with $14° < 2\theta < 76°$ (Cu Kc); those for AB:TNB$_2$ were obtained from a least-squares fit of fourteen reflections with $33° < 2\theta < 66°$ (Cu $K\alpha$). Crystal data are summarized in Table 1. Intensities for both compounds were collected on a Syntex diffractometer with an ω–2θ scan and a scan rate varying from 2 to 24° min^{-1} as determined by a rapid prescan of the peak intensities. Data were corrected for Lorentz and polarization factors but not for absorption.

Structure solution and refinement

Both structures were solved in the centrosymmetric space group $C2/c$ with $SHELX$ (Sheldrick, 1976) in an automatic phase determination process. With $Z = 4$, the asymmetric unit is composed of one half of a donor moiety (either BA or AB) and one TNB molecule. Thus, the acceptor occupies a general position, while the donor may have site symmetry $\bar{1}$ or 2. For BA both of these site symmetries require orientational disorder and the two symmetries have been observed in the two

Table 1. Crystal data

	AB:TNB$_2$ $C_{12}H_{10}N_2$.- $(C_6H_3N_3O_6)_2$	BA:TNB$_2$ $C_{13}H_{11}N$.- $(C_6H_3N_3O_6)_2$
a (Å)	10·896 (2)	11·034 (3)
b (Å)	9·993 (2)	9·973 (1)
c (Å)	24·932 (6)	24·940 (8)
β (°)	97·66 (2)	95·17 (2)
V (Å^3)	2690·5	2733·3
D_x (Mg m^{-3})	1·39	1·46
D_m (Mg m^{-3})	1·39	1·45
Space group	$C2/c$	$C2/c$
Z	4	4
μ (Cu $K\alpha$) (mm^{-1})	0·96	0·94
M_r	608·4	607·5
$F(000)$	1248	1248
Total number of intensities measured	2689	3042
Total number of intensities considered observed $[I > 2·5\sigma(I)]$	1777	2039
R	0·062	0·070
R_w	0·072	0·082

polymorphs of the p-dichloro derivative of BA (Bernstein & Izak, 1976; Bernstein & Schmidt, 1972).

AB:TNB$_2$

All heavy atoms appeared in the E map based on the best set of signs with orientation and location which require molecular site symmetry 2 for the donor with two peaks corresponding to the N atom on the bridge, resembling the positional disorder in p-azotoluene (Brown, 1966b). Refinement by block-diagonal least squares proceeded smoothly, with one block containing the TNB moiety and the second block one half AB. The N atom was given a fixed occupancy of 0·5 for each of the two observed orientations. During the refinement all H atoms were located on a difference map and included (with isotropic temperature factors) in the refinement which converged for anisotropic temperature factors on all other atoms at $R = 0·062$ (0·075 including unobserveds).* A final difference map was virtually featureless and at no point exceeded 0·16 e Å^{-3}. A difference map based on the same parameters but not including the N atoms on the bridge of AB exhibited two peaks with electron densities of 4 and 3·1 e Å^{-3} at the reported positions of the N atoms, thus confirming the presence of positional disorder for the donor molecule. An attempt to refine the occupancy of these partial N atoms with fixed temperature factors was not successful.

BA:TNB$_2$

20 of 22 heavy atoms appeared in the E map based on the best set of signs in positions essentially identical to the AB complex, requiring orientational disorder of the C and N bridge atoms. The remaining two atoms in the asymmetric unit were subsequently located by Fourier methods. The scattering factor of the two atoms at the bridge (denoted by X) was taken to be the average of C and N by locating one atom per block with tied positional and temperature factors (Sheldrick, 1976) and an occupancy of 0·5 for each atom. Isotropic block-diagonal least-squares refinement as above with the bridge atom ($\frac{1}{2}$C, $\frac{1}{2}$N) in a separate block led to $R = 0·205$ for sin $\theta \leq 0·7$. The difference map exhibited an additional peak of 1·5 e Å^{-3} in the vicinity of the bridge, suggesting the presence of positional disorder similar to that found in AB:TNB$_2$, in p-methyl-N-(p-methylbenzylidene)aniline (form III)

Table 2. *Atomic coordinates* $(\times 10^4$ *for non-hydrogen atoms and* $\times 10^3$ *for hydrogen atoms) and* $U_{eq} \times 10^4$ *expressed as* $(U_{11} U_{22} U_{33})^{1/3}$

	x	y	z	U_{eq} (Å²)		x	y	z	U_{eq} (Å²)
BA:(TNB)₂					AB:(TNB)₂				
C(1BA)	3908 (3)	1240 (3)	5672 (1)	686	C(1AB)	3976 (3)	1246 (3)	5678 (2)	756
C(2BA)	4517 (3)	190 (3)	5928 (1)	645	C(2AB)	4539 (3)	166 (3)	5946 (1)	683
C(3BA)	4865 (3)	251 (4)	6468 (1)	706	C(3AB)	4849 (3)	200 (4)	6494 (1)	744
C(4BA)	4618 (3)	1392 (5)	6762 (1)	805	C(4AB)	4599 (3)	1335 (5)	6778 (1)	924
C(5BA)	4009 (4)	2453 (4)	6499 (2)	873	C(5AB)	4045 (4)	2432 (5)	6498 (2)	1083
C(6BA)	3664 (4)	2370 (3)	5962 (2)	769	C(6AB)	3735 (4)	2373 (3)	5954 (2)	877
X(1BA)*	4902 (19)	971 (5)	7505 (22)	913	N(1AB)*	5077 (30)	818 (6)	7442 (15)	903
X(2BA)*	4939 (5)	1911 (4)	7291 (2)	545	N(2AB)*	4811 (5)	1848 (5)	7314 (2)	610
C(1TN)	6984 (3)	2683 (3)	5989 (1)	525	C(1TN)	7043 (2)	2679 (2)	6010 (1)	557
C(2TN)	6421 (3)	3793 (3)	5753 (1)	563	C(2TN)	6489 (3)	3783 (3)	5758 (1)	586
C(3TN)	6249 (3)	4877 (3)	6082 (1)	533	C(3TN)	6319 (2)	4866 (2)	6080 (1)	553
C(4TN)	6602 (3)	4874 (3)	6622 (1)	537	C(4TN)	6666 (2)	4879 (3)	6629 (1)	550
C(5TN)	7172 (3)	3748 (3)	6832 (1)	550	C(5TN)	7230 (3)	3745 (2)	6853 (1)	549
C(6TN)	7383 (3)	2631 (3)	6529 (1)	557	C(6TN)	7435 (3)	2630 (3)	6553 (1)	578
N(1TN)	7158 (3)	1492 (3)	5653 (1)	730	N(1TN)	7217 (3)	1488 (2)	5677 (1)	752
N(3TN)	5681 (3)	6098 (3)	5842 (2)	738	N(3TN)	5749 (3)	6089 (2)	5823 (1)	746
N(5TN)	7599 (3)	3738 (3)	7413 (1)	729	N(5TN)	7631 (3)	3743 (2)	7442 (1)	725
O(1TN)	6680 (3)	1501 (3)	5192 (1)	918	O(1TN)	6734 (3)	1483 (2)	5211 (1)	945
O(2TN)	7762 (4)	583 (3)	5853 (1)	1068	O(2TN)	7828 (3)	575 (2)	5896 (1)	1089
O(3TN)	5585 (4)	6185 (3)	5353 (1)	1022	O(3TN)	5647 (3)	6175 (2)	5336 (1)	1018
O(4TN)	5361 (4)	6936 (3)	6148 (1)	1099	O(4TN)	5428 (3)	6940 (3)	6120 (1)	1144
O(5TN)	7307 (4)	4669 (3)	7687 (1)	910	O(5TN)	7322 (3)	4666 (2)	7707 (1)	912
O(6TN)	8236 (4)	2820 (3)	7580 (1)	1071	O(6TN)	8250 (3)	2803 (2)	7625 (1)	1005
H(1BA)	382 (4)	115 (3)	530 (2)		H(1AB)	381 (4)	132 (4)	534 (2)	
H(2BA)	465 (4)	−54 (4)	575 (2)		H(2AB)	478 (3)	−60 (4)	577 (1)	
H(3BA)	526 (3)	−45 (3)	664 (1)		H(3AB)	509 (3)	−53 (4)	666 (2)	
H(5BA)	382 (4)	326 (4)	669 (2)		H(5AB)	388 (4)	331 (4)	665 (2)	
H(6BA)	321 (5)	304 (5)	581 (2)		H(6AB)	334 (3)	301 (4)	571 (2)	
H(2TN)	615 (6)	380 (6)	539 (2)		H(2TN)	625 (3)	378 (3)	539 (1)	
H(4TN)	646 (3)	544 (4)	681 (1)		H(4TN)	656 (2)	559 (3)	686 (1)	
H(6TN)	761 (7)	201 (6)	668 (3)		H(6TN)	777 (3)	188 (3)	671 (1)	

* Occupancy 0·5 due to disorder.

(Bernstein, Bar & Christensen, 1976) and in salicylideneaniline (Destro, Gavezzotti & Simonetta, 1978). The refinement was continued first with isotropic temperature factors, then anisotropic, except for the atoms on the bridge, with the benzene ring of BA in one block, TNB in another and the atoms on the bridge refined one atom per block with a site-occupation factor of 0·25, with convergence at $R = 0·148$. H atoms appeared on the difference map and were included in the refinement. Further block-diagonal least-squares refinement as above with isotropic temperature factors for H atoms led to $R = 0·070$ (0·081 including unobserveds).* The final difference map exhibited no peak $>0·25$ e Å⁻³. H atoms on the bridge were not located.

Final positional parameters for both complexes are given in Table 2. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

* See deposition footnote.

Results and discussion

Molecular geometry: BA, AB

The atomic numbering for both molecules is given in Fig. 1(a); bond lengths and angles are compiled in Table 3.
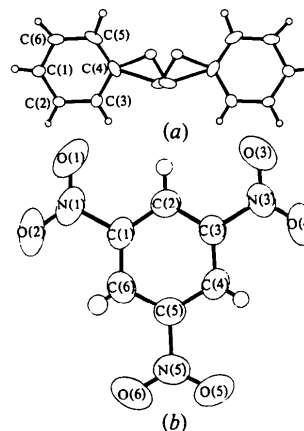

Fig. 1. Atomic numbering for (a) AB, BA and (b) TNB.

Table 3. *Interatomic distances* (Å) *and angles* (°)

(a) Bond lengths and angles for AB and BA molecules in their complexes, not including bridge atoms

	AB	BA
C(1)–C(2)	1·371 (5)	1·371 (4)
C(2)–C(3)	1·363 (4)	1·368 (4)
C(3)–C(4)	1·383 (6)	1·394 (6)
C(4)–C(5)	1·393 (7)	1·386 (6)
C(5)–C(6)	1·355 (7)	1·361 (7)
C(6)–C(1)	1·363 (5)	1·379 (5)
C(1)–C(2)–C(3)	120·3 (3)	120·5 (3)
C(2)–C(3)–C(4)	119·6 (3)	120·2 (3)
C(3)–C(4)–C(5)	119·4 (3)	118·9 (3)
C(4)–C(5)–C(6)	120·1 (4)	120·0 (4)
C(5)–C(6)–C(1)	120·1 (4)	121·0 (3)
C(6)–C(1)–C(2)	120·5 (4)	119·4 (3)

(b) Geometric features of the bridge atoms (average values)

AB

C(4)–N	1·548	C(3)–C(4)–N	120·1
N(1)–N(2′)	1·194	C(5)–C(4)–N	120·4
		C(4)–N–N′	101·2

BA

C(4)–X	1·665	C(3)–C(4)–X	122·7
X(1)–X(2′)	1·073	C(5)–C(4)–X	117·3
		C(4)–X–X′	101·9

(c) Bond lengths and angles for TNB molecules in their complexes

	AB	BA
C(1TN)–C(2TN)	1·369 (4)	1·375 (4)
C(2TN)–C(3TN)	1·375 (4)	1·381 (4)
C(3TN)–C(4TN)	1·371 (3)	1·368 (4)
C(4TN)–C(5TN)	1·372 (4)	1·368 (4)
C(5TN)–C(6TN)	1·377 (4)	1·378 (4)
C(6TN)–C(1TN)	1·365 (4)	1·380 (4)
C(1TN)–N(1TN)	1·478 (3)	1·476 (4)
C(3TN)–N(3TN)	1·478 (3)	1·472 (5)
C(5TN)–N(5TN)	1·475 (4)	1·483 (4)
N(1TN)–O(1TN)	1·210 (4)	1·221 (4)
N(1TN)–O(2TN)	1·215 (3)	1·206 (5)
N(3TN)–O(3TN)	1·207 (3)	1·218 (6)
N(3TN)–O(4TN)	1·209 (4)	1·206 (5)
N(5TN)–O(5TN)	1·208 (3)	1·213 (4)
N(5TN)–O(6TN)	1·210 (3)	1·205 (5)
C(1TN)–C(2TN)–C(3TN)	116·9 (2)	117·2 (2)
C(2TN)–C(3TN)–C(4TN)	123·4 (2)	122·8 (3)
C(3TN)–C(4TN)–C(5TN)	116·6 (2)	117·3 (3)
C(4TN)–C(5TN)–C(6TN)	122·9 (2)	123·3 (2)
C(5TN)–C(6TN)–C(1TN)	117·2 (2)	116·8 (3)
C(6TN)–C(1TN)–C(2TN)	123·0 (2)	122·7 (3)
C(2TN)–C(1TN)–N(1TN)	118·2 (2)	118·8 (2)
C(6TN)–C(1TN)–N(1TN)	118·8 (2)	118·5 (3)
C(2TN)–C(3TN)–N(3TN)	118·6 (2)	118·8 (3)
C(4TN)–C(3TN)–N(3TN)	118·0 (2)	118·4 (3)
C(4TN)–C(5TN)–N(5TN)	117·6 (2)	118·3 (3)
C(6TN)–C(5TN)–N(5TN)	119·5 (2)	118·4 (3)
C(1TN)–N(1TN)–O(1TN)	118·1 (2)	117·5 (3)
C(1TN)–N(1TN)–O(2TN)	117·1 (2)	117·7 (3)
C(3TN)–N(3TN)–O(3TN)	118·2 (2)	117·5 (3)
C(3TN)–N(3TN)–O(4TN)	117·1 (2)	117·0 (4)
C(5TN)–N(5TN)–O(5TN)	118·4 (2)	117·9 (3)
C(5TN)–N(5TN)–O(6TN)	116·9 (2)	117·8 (3)
O(1TN)–N(1TN)–O(2TN)	124·8 (2)	124·8 (3)
O(3TN)–N(3TN)–O(4TN)	124·8 (3)	125·5 (4)
O(5TN)–N(5TN)–O(6TN)	124·6 (3)	124·2 (3)

The thermal parameters for C(4), C(5) and C(6) in both donor molecules are rather high since they absorb the disorder of the benzene rings in both structures, but the average positions yield geometric features which are essentially identical and do not differ significantly from those found in the parent molecules (Bürgi & Dunitz, 1970; Brown, 1966a). A quantitative discussion of the geometric features of the bridge atoms is ruled out by the disorder present in both structures, as shown in Scheme 1. In both cases there is positional disorder, while in the BA complex orientational disorder exists as well. Orientational disorder is possible owing to the presence of hetero-atoms in the bridge, due either to a center of symmetry or to a twofold axis perpendicular to the plane of the paper (Scheme 1a). These two types of disorder are observed in the triclinic and orthorhombic polymorphs of p-chloro-N-(p-chlorobenzylidene)aniline respectively (Bernstein & Schmidt, 1972; Bernstein & Izak, 1976). The positional disorder could be statistical or non-statistical as observed in p-methyl-N-(p-methylbenzylidene)aniline (Bernstein, Bar & Christensen, 1976). In the AB complex the presence of the twofold axis in the plane of the paper, Scheme 1(b), requires the positional disorder to be statistical. In the BA complex the positional and orientational disorder leads to a situation which is represented in Scheme 1(c), which may be considered as identical to that in the AB complex, in which the disorder is statistical.
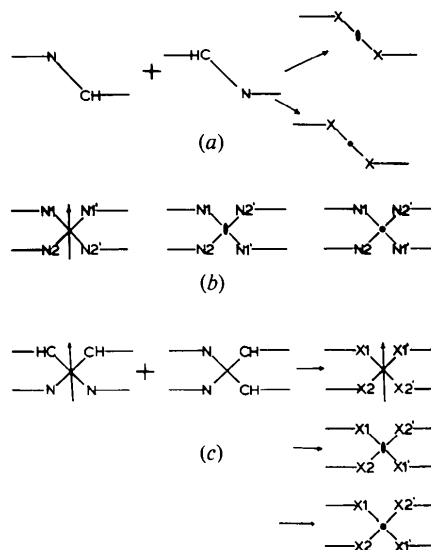
Scheme 1

The presence of either kind of disorder tends to concentrate electron density towards the twofold axis. As a result, the exocyclic single bond is lengthened, the bridge double bond is shortened and the bond angle with N, CH or X as a vertex is smaller than the true value. The appropriate values obtained for these structures are given in Table 3(b). A similar type of disorder has been observed in p-methyl-N-(p-methyl-

benzylidene)aniline (form III) (Bernstein, Bar & Christensen, 1976), in *p*-azotoluene (Brown, 1966*b*) and in one of the two independent molecules in both of the isomorphous structures *trans*-AB (Brown, 1966*a*) and *trans*-S (Hoekstra, Meertens & Vos, 1975). The current examples differ from previous ones in that the positional disorder is about a twofold axis rather than about a center of symmetry. In orthorhombic *p*-chloro-*N*-(*p*-chlorobenzylidene)aniline (Bernstein & Izak, 1976) positional disorder is present only about a twofold axis which is perpendicular to the plane of the four bridge atoms, as in Scheme 1(*a*).

The donor molecules are both non-planar by slightly different amounts as measured by the angle between the best plane of the bridge atoms and that of the phenyl ring. For AB the value is 20·9°, compared to 23·9° in BA. This is equivalent to an interplanar angle between the two rings of, respectively, 41·8 and 47·8°, while in the S:TNB$_2$ structure, because the donor occupies a center of symmetry, the two phenyl rings are parallel, each making an angle of 11·9° with the bridge.

The conformation observed for AB is significantly different from that for the uncomplexed molecule wherein the comparable interplanar angles (for two independent molecules) are 17·9 and 6°, but again due to site asymmetry Ī the two rings are mutually parallel. The gas-phase electron diffraction study of AB (Trætteberg, Hilmo & Hagen, 1977) suggests the presence of angles up to 30° about the exocyclic single bond.

The conformational energetics of BA have been extensively studied by semi-empirical methods (Hofmann & Birner, 1977, and references therein); NDDO predicts a minimum for a torsion angle of *ca* 40° (apparently quite sensitive to the input geometry) with a stabilization of up to 6·3 kJ over a planar form, whereas CNDO/2, MNDO/2 and MNDO/3 treatments all favor torsion angles of 90°. A recent *ab initio* study, employing a minimal basis set (STO-4G) (Bernstein, Hagler & Engel, 1981), suggests that the potential-energy surface is broad and symmetric about a planar conformation with a shallow minimum at a torsion angle of *ca* 45° about the *N*—phenyl bond. Although a planar conformation has not been engineered in this structure, BA also adopts a conformation in the complex different from that observed in the pure crystal, for which the torsion angle about the N—phenyl bond is 55·2° and that about the CH—phenyl bond is −10·3° (Bürgi & Dunitz, 1970). The electron diffraction study of BA (Trætteberg, Hilmo, Abraham & Ljunggren, 1978) yielded a value of 52° for the former; the latter was assumed to be zero in the interpretation of the experimental scattering curve.

Photoelectron spectroscopic studies (Bailly *et al.*, 1976) indicate a nominal value of 36° for the torsion angle about the N—phenyl bond. The *ab initio* calculations (Bernstein, Hagler & Engel, 1981) suggest

that the conformation observed in the TNB complex [similar to that found in the orthorhombic form of the dichloro compound (Bernstein & Izak, 1976)] is about 5·0 kJ mol^{-1} higher in energy than the predicted low-energy conformation wherein the N—phenyl torsion angle is 45° and the CH—phenyl torsion angle is 0°.

Molecular geometry: TNB

The atomic numbering for TNB is given in Fig. 1; bond lengths and angles for both complexes are given in Table 3(*c*). In all cases chemically equivalent geometric features are found to be equivalent experimentally. Aromatic C—C lengths average 1·375 Å (e.s.d. of average is 0·004 Å) in BA:TNB$_2$, while in AB:TNB$_2$ the average is 1·372 (±0·004) Å. Both values agree well with those of TNB itself (Choi & Abel, 1972) and those in S:TNB$_2$ (Bar & Bernstein, 1978). The distortion of the benzene ring from hexagonal symmetry as evidenced by the deviations of internal angles from 120° is consistent in magnitude and direction with that expected for nitro substitution (Domenicano, Vaciago & Coulson, 1975). The nitro groups all make angles of <15° with the benzene ring, consistent with all TNB molecules in complexes studied to date (Bar & Bernstein, 1978).

Packing

The packing is shown in Fig. 2 with the direction of view chosen to include the overlap diagram of the donor and acceptor on the best plane of the bridge atoms. Each donor molecule is sandwiched between two TNB's related to each other by the same crystallographic twofold axis that relates the two halves of the donor molecule. The twofold axis thus places one TNB over one phenyl ring while the second TNB is under the second phenyl ring. This arrangement differs from that found in S:TNB$_2$, wherein a center of symmetry relates the two halves of the stilbene molecule as well as the two TNB molecules. The angle between the phenyl ring of the donor and the closest TNB ring is 1·6° in both complexes, while in the S complex the angle is 4·0°. The distance between the center of a phenyl ring on TNB and one of the phenyl rings on BA is 3·71 Å while that for the AB structure is 3·72 Å; the equivalent distance in S:TNB$_2$ is 3·67 Å. The shortest interatomic distance between C(2) of a donor and N(1) of an acceptor is 3·318 (5) Å for BA and 3·351 (4) Å for AB for atoms in the asymmetric unit. Between two acceptor molecules the shortest distance is between O(1) and its equivalent related by a center of symmetry with a value of 2·911 (4) Å for BA and 2·914 (4) Å for AB. The stacking is generated by the centering operation which brings a TNB molecule below the phenyl ring of a donor to a position above the
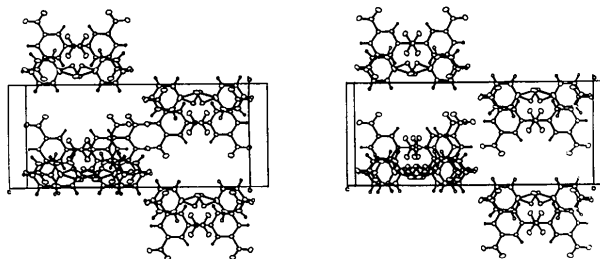
Fig. 2. View of the structure on (100) for both compounds.

Table 5. *Molecular volumes* ($Å^3$)

	Pure structures	Complex with 2TNB
BA	253	684
AB	247	672
S	256	674

Table 4. *The equations of the plane of all heavy atoms in one ring and deviations* ($Å$) *from the plane (e.s.d.'s ~0.005 $Å$)*

Atoms included in calculation

Reference phenyl ring		Second phenyl ring	
AB:TNB₂			

$-10.056x - 3.659y + 6.003z + 1.051 = 0$

C(1AB)	0.005	C(1'AB)	0.133
C(2AB)	−0.005	C(2'AB)	0.934
C(3AB)	0.000	C(3'AB)	0.904
C(4AB)	0.005	C(4'AB)	0.068
C(5AB)	−0.006	C(5'AB)	−0.724
C(6AB)	0.001	C(6'AB)	−0.687

BA:TNB₂

$-9.886x - 3.959y + 6.958z + 0.412 = 0$

C(1BA)	0.004	C(1'AB)	0.388
C(2AB)	−0.005	C(2'BA)	1.228
C(3BA)	0.003	C(3'BA)	1.172
C(4BA)	0.000	C(4'BA)	0.272
C(5AB)	−0.001	C(5'BA)	−0.568
C(6BA)	−0.001	C(6'BA)	−0.502

same phenyl ring. Within a layer two TNB molecules are mutually related by a center of symmetry. Table 4 gives details of the least-squares planes.

Table 5 gives the volume per molecule (or per complex) for the donors and their complexes with TNB. Although the complex of TNB with S is not isomorphous with the complexes with AB and BA its molecular volume falls between the two latter structures. Similarly, although BA itself is not isomorphous with S or AB, its molecular volume is intermediate between the two. However, the small differences in these numbers suggest that packing efficiencies are very nearly equal, and that only small energy differences differentiate between the single structure and the pair of isomorphs in each case. In fact, melting-point equilibrium curves of BA with AB and S (Brandstätter, 1943, 1947) indicate a rather extensive degree of mutual solubility of these materials. BA in the S or AB structure would most likely adopt a planar conformation. On the other hand, at least two additional polymorphic modifications of BA have been reported

[m.p. 321 K (Hantzsch & Schwab, 1901) and m.p. 299 K (Pascal & Normand, 1913)] and Brandstätter has shown that AB and S both prefer to form a complete series of solid solutions with the latter form. It is not unreasonable to assume that the higher-energy (m.p. 299 K) form of BA is due in part, at least, to increased planarity of the molecule and it is this feature which permits cocrystallization with S and AB.

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4,4,7,7-Tetramethylazacyclononan-2-one

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Abstract

$C_{12}H_{23}NO$ is monoclinic, $C2/c$, with $a = 26\cdot244$ (19), $b = 11\cdot957$ (5), $c = 26\cdot645$ (15) Å, $\beta = 118\cdot90$ (6)°, $V = 7319\cdot9$ Å^3 at 138 ± 2 K, $Z = 24$. The intensities of 6205 unique reflections were measured at 138 ± 2 K using Cu $K\alpha$ radiation. The structure was solved by direct methods and refined by least-squares methods to final R factors of $0\cdot065$ for 3986 observed reflections and $0\cdot114$ for all data. The three molecules in the asymmetric unit are almost identical. The molecules adopt a conformation in which the amide group is *transoid* and markedly non-planar with a torsion angle of 147°. The molecules are packed through N—H···O hydrogen bonds in a double helix along the *b* axis, leading to a pseudo-hexagonal symmetry for the crystal structure.

Introduction

Characteristic features of medium-ring lactams in the crystalline state have been studied in detail by Dunitz & Winkler (1975). One important feature of these compounds is the non-planarity of the amide group, which has also been observed in a number of polycyclic lactams (Ealick & van der Helm, 1977; Ealick, Washecheck & van der Helm, 1976). Smolikova,

Havel, Vasickova, Vitek, Svoboda & Bláha (1974) have studied the effect of geminal methyl substitution in ten- and nine-membered lactams. According to them, the introduction of the substituents manifests itself by a decreased number of conformers, that is by a greater rigidity of the molecule. Substitution of the methyl groups at positions 4,4,7,7 favors a conformation with a *trans* amide group, while substitutions at 5,5,8,8 lead exclusively to a conformer with a *cis* amide group. The crystal structure of 5,5,8,8-tetramethylazacyclononan-2-one has been reported earlier (van der Helm & Ealick, 1979). We now report the structure of 4,4,7,7-tetramethylazacyclononan-2-one in the crystalline state.

Long, thin, needle-shaped crystals of the compound were obtained from an ethanol–water solution by slow evaporation at room temperature. Cell parameters and intensity data were obtained at 138 ± 2 K with a CAD-4 counter diffractometer controlled by a PDP8/e computer and fitted with a low-temperature set-up. Cell parameters were determined by least-squares fit to $+2\theta$ and -2θ values of 24 reflections measured with Cu $K\alpha_1$ ($\lambda = 1\cdot54051$ Å) radiation.

Intensities of all independent reflections with $2\theta \leq 130°$ were measured using Cu $K\bar{\alpha}$ radiation and applying θ–2θ scan techniques. The scan width for each reflection was calculated as $(0\cdot90 + 0\cdot14 \tan \theta)°$. A receiving aperture of variable width of $(3\cdot5 + 0\cdot86 \times$