In order to see whether the trimer exists in a preferentially nonpolar solvent, the complex constant for the formation of one mol of trimer was estimated by cryoscopic methods in cyclohexane with only 30 mg compound. The observed value was 1500 (mol fractions). Thus in a solution of 0·01 mol africanol per mol cyclohexane, 11% of the molecules occur as trimers.

The author is indebted to Professor P. Kierkegaard and Professor B. Tursch (Brussels) for their kind interest. The work has been supported by Statens Naturvetenskapliga Forskningsråd. I thank Dr D. F. Koenig for his correction of the English.

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Structures of Nitrogen-Containing Aromatic Compounds.
I. The Metastable Crystalline Form of Dibenzo-1,3a,4,6a-tetraazapentalene (DBTAP-2)

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The crystalline form of dibenzo-1,3a,4,6a-tetraazapentalene that is metastable at room temperature, DBTAP-2, is monoclinic, $P2_1/c$, $a = 6.943$ (5), $b = 4.473$ (5), $c = 16.11$ (1) Å, $\beta = 101.1$ (1)°, $V = 491$ Å^3, $Z = 2$, $D_m = 1.395$ (5) g cm^{-3}. $R = 0.059$ for 688 observed data (diffractometer, monochromated Mo $K\alpha$); six C and two N anisotropic, four H's included. The N–N, C–N and C–C lengths are all within 2σ of those in the thermodynamically stable form, DBTAP-1. N(1)–N(1′) 1·368 (10), N(1)–N(2) 1·336 (5), mean C–N 1·383 (5) Å; C–C in the aromatic ring ranges from 1·362 to 1·412 Å. DBTAP-1 changes to DBTAP-2 at 127°C, which then melts at 237°C. DBTAP-2 changes to DBTAP-1 merely upon crushing and gentle grinding at room temperature.

Introduction

Dibenzo-1,3a,4,6a-tetraazapentalene (I) was reported to be an unusually stable heteroaromatic compound (Carboni & Castle, 1962); to obtain information about the bond lengths (and, therefore, bond orders), a determination of the crystal structure was undertaken (Burke, 1964). This work showed that two crystalline forms existed: one modification, DBTAP-1, was obtained from CHCl$_3$/CCl$_4$ solution, the second, DBTAP-2, from CH$_3$OH. A study was therefore made of the differences between the molecular packing in the two forms (Laing, 1965). Subsequently, a DTA study (Allais, 1966) showed that DBTAP-1 changed to DBTAP-2 at 127°C and that the melting point reported by Carboni & Castle (1962) is in fact that of DBTAP-2, the form that is metastable at room tem-

perature. The crystal structure of DBTAP-1 has now been reported (Burke Laing, Sparks, Laing & Trueblood, 1976); to obtain a comparison between the bond lengths in the two forms, the structure of DBTAP-2 has been redetermined and refined.

Experimental

Good crystals were obtained with difficulty from a carefully dried methanol solution by evaporation at room temperature. They were parallelepipeds, elongated along [010]. If the methanol was not water-free, the crystals were feathery and consisted of intractable clumps of needles.

Accurate cell dimensions were obtained by a least-squares refinement of 2θ, χ and φ angles for 25 reflexions measured on a Philips four-circle diffractom-

eter. Intensities were measured for a crystal $0.2 \times 0.4 \times 0.2$ mm with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for θ between 3 and 27°. The ω–2θ scan mode was used; the scan width was 1°, the scan time 33 s, and the background counted for 33 s for each reflexion. Three reflexions were used as standards and remeasured after every 60 reflexions; no crystal decomposition was detectable. Of the 1217 reflexions measured (including space-group extinctions), 714 were initially classed as observed, i.e. $I > 1.65\sigma(I)$. Only Lorentz–polarization corrections were applied to the intensity data.

Crystal data

$C_{12}N_4H_8$, monoclinic $P2_1/c$, $a = 6.943$ (5), $b = 4.473$ (5), $c = 16.11$ (1) Å, $\beta = 101.1$ (1)°, $V = 491$ Å³, $Z = 2$, $D_m = 1.395$ (5) g cm⁻³, $M = 208$.

The structure had already been solved by a combination of Patterson and weighted reciprocal lattice techniques (Laing, 1965) and the positional parameters obtained from this study were used as the starting point for the refinement. The structure was refined by block-diagonal least squares, first isotropically then anisotropically. Initially the weights were proportional to $1/\sigma(F)$, but this scheme seemed to be overemphasizing the weakest data. The weights were then changed to be proportional to $1/F$ for $F > 5$ and to F for $F < 5$ with a proportionality constant that gave a weight $= 1$ for $F = 5$. This change produced differences in the parameters of less than 1σ. At convergence, $R = 0.059$ for 688 observed data.* Details of the steps of the refinement are given below. The scattering factors, for neutral atoms, were taken from *International Tables for X-ray Crystallography* (1962).

Refinement procedure

1. Six C, two N, four H; x, y, z, B parameters from Laing (1965), five cycles BDLS, all H parameters held fixed. $R = 0.11$ (714 F's).

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* A list of structure factors (observed and unobserved) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31777 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
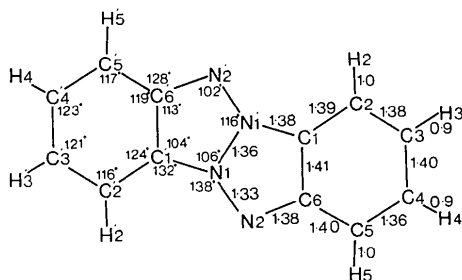

Fig. 1. Numbering system, and bond lengths (± 0.01 Å) and angles ($\pm 1°$) not corrected for thermal motion.

Table 1. *Positional coordinates, thermal parameters and least-squares plane*

Positional ($\times 10^4$ for C, N; $\times 10^3$ for H) and isotropic thermal parameters

	x	y	z	B (Å²)
N(1)	-947 (3)	(1)0156 (6)	48 (2)	$-$
N(2)	-1445 (4)	8563 (6)	672 (2)	$-$
C(1)	1814 (4)	7860 (7)	571 (2)	$-$
C(2)	3703 (5)	6729 (8)	788 (2)	$-$
C(3)	4027 (5)	4714 (9)	1451 (2)	$-$
C(4)	2519 (6)	3936 (9)	1874 (2)	$-$
C(5)	675 (5)	5079 (9)	1672 (2)	$-$
C(6)	289 (4)	7107 (7)	995 (2)	$-$
H(2)	474 (5)	727 (8)	48 (2)	2.2 (7)
H(3)	531 (6)	403 (10)	161 (3)	5.6 (11)
H(4)	279 (5)	264 (9)	232 (2)	3.2 (8)
H(5)	-43 (5)	457 (9)	197 (2)	4.3 (9)

Anisotropic thermal parameters ($\times 10^4$)
The form of the expression is
$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	207 (5)	490 (14)	47 (1)	-81 (17)	64 (4)	-25 (8)
N(2)	270 (7)	591 (16)	55 (1)	-96 (18)	85 (5)	-33 (8)
C(1)	234 (7)	410 (15)	41 (1)	-49 (19)	16 (5)	-39 (8)
C(2)	216 (7)	495 (19)	61 (2)	-54 (20)	34 (6)	-84 (10)
C(3)	267 (9)	581 (20)	67 (2)	45 (25)	-39 (6)	-70 (12)
C(4)	365 (11)	615 (23)	57 (2)	-68 (26)	-5 (7)	16 (12)
C(5)	314 (9)	596 (19)	54 (2)	-75 (26)	59 (6)	27 (12)
C(6)	232 (8)	473 (18)	49 (2)	-47 (19)	40 (5)	-58 (9)

Least-squares plane defined by the eight heavy atoms

Direction cosines referred to:	a	b	c^*
	0.143	0.756	0.638

Deviations from the plane in Å

N(1)	N(2)	C(1)	C(2)
-0.006	0.008	-0.005	0.009

C(3)	C(4)	C(5)	C(6)
-0.001	-0.006	0.003	-0.001

Table 2. *Bond lengths in Å, with and without correction for thermal motion, compared with those found in the crystalline modification that is stable at room temperature*

E.s.d.'s lie between 0.005 and 0.01 Å, increasing for the bonds furthest from the origin, except for N(1)–N(1)' whose e.s.d. is 0.01 Å (Stout & Jensen, 1968). The errors in the bond lengths derived from DBTAP-2 are larger than those from DBTAP-1 because the thermal motion of the molecule in DBTAP-2 is considerably greater. (The densities and volume/molecule reflect this difference: 1.42 g cm⁻³ and 243 Å³ in DBTAP-1, 1.40 g cm⁻³ and 246 Å³ in DBTAP-2.)

	DBTAP-2 Uncorrected	Corrected*	DBTAP-1
N(1)–N(1)'	1.363	1.368	1.355
N(1)–N(2)	1.330	1.336	1.335
N(2)–C(6)	1.378	1.381	1.373
N(1)'–C(1)	1.383	1.385	1.383
C(1)–C(6)	1.407	1.412	1.422
C(1)–C(2)	1.389	1.391	1.397
C(6)–C(5)	1.404	1.406	1.409
C(2)–C(3)	1.381	1.383	1.369
C(5)–C(4)	1.360	1.362	1.371
C(3)–C(4)	1.401	1.405	1.426

* Corrected according to Cruickshank (1956) with the program *TMEGA*, a modified version of that originally written by P. Gantzel, C. Coulter & K. N. Trueblood, UCLA.

2. Six C, two N; H atoms omitted; anisotropic β_{ij}, five cycles BDLS, $R=0\cdot10$ (714 F's).

3. Six C, two N anisotropic, four H isotropic; five cycles BDLS, $R=0\cdot067$ (714 F's).

4. As 3, but weights changed from $1/\sigma$ to be a function of F; five cycles BDLS, $R=0\cdot066$ (714 F's).

5. As 4, but the 26 weakest F's with F_c close to zero removed; five cycles BDLS, $R=0\cdot059$ (688 F's).

The difference between the value of a bond length obtained after any one of steps 1 to 5 and that after any other was in all cases less than 0·005 Å. The fractional atomic coordinates and the thermal parameters are given in Table 1; the estimated standard deviations in the last figure are given in parentheses. Table 2 compares the bond lengths in DBTAP-2 with those in DBTAP-1. The numbering system and bond lengths and angles are given in Fig. 1. The differences in orientation of the molecules of the two polymorphs
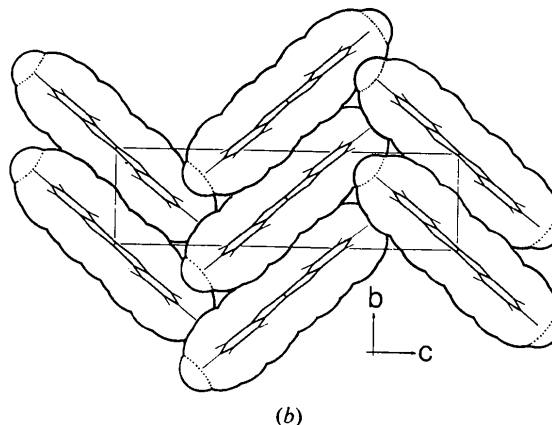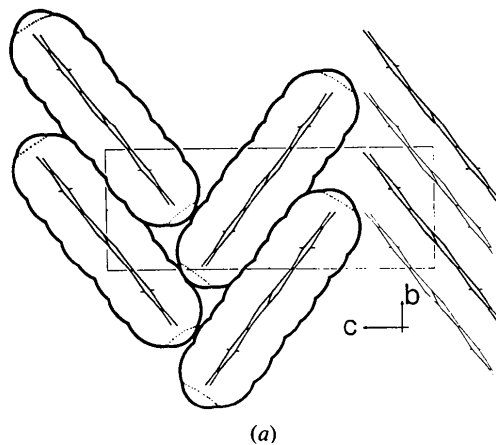

(a)

(b)

Fig. 3. Projections of the structures of the two polymorphs down a; (a) DBTAP-1, (b) DBTAP-2.

(a)

(b)

Fig. 2. Projections of the structures of the two polymorphs down b; (a) DBTAP-1, (b) DBTAP-2.
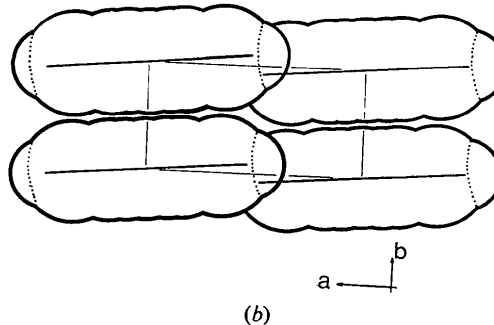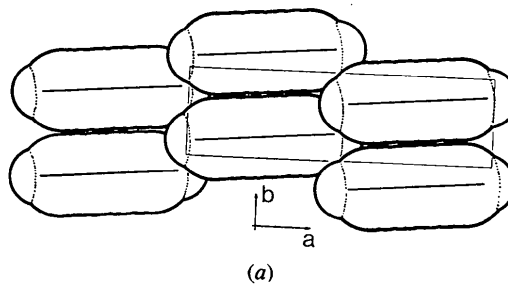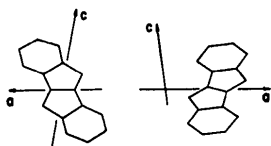

(a)

(b)

Fig. 4. Projections of the structures of the two polymorphs down c*; (a) DBTAP-1, (b) DBTAP-2.

relative to the unit-cell edges *a* and *c* are shown opposite, DBTAP-2 on the left, DBTAP-1 on the right.

Discussion

Bond lengths and molecular geometry

The molecule is planar; the largest deviation of any atom from the mean plane is less than 0·01 Å. The bond lengths and angles are, for all practical purposes, identical with those found in DBTAP-1 (Burke Laing, Sparks, Laing & Trueblood, 1976). The largest differences (for two C–C bonds) are about 2σ (Table 2).

Packing

The molecules in DBTAP-2 pack in the typical 'herringbone' pattern found for planar centrosym-metric molecules in space group $P2_1/c$ (Kitaigorodsky, 1973). The differences between the mode of packing in DBTAP-1 and DBTAP-2 are illustrated in Figs. 2 to 5. The important difference is within the stacks of molecules parallel to **b**. The separation between the mean planes of the molecules is about 3·33 Å in DBTAP-1, but is distinctly greater, 3·41 Å, in DBTAP-2. The corresponding angles of tilt out of the *xz* plane are about 53 and 41° respectively (Fig. 3). The effect of the greater angle of tilt in DBTAP-1 is shown by a projection of the framework of a molecule onto that of the one below related by unit translation along **b** (Fig. 5). In DBTAP-1 there is less overlap of the frameworks of the molecules; also, two H atoms in a molecule at x,y,z lie directly above N(1) and N(2) in the molecule at $x,y-1,z$. This may be purely coincidental, but it could be related to the relatively large excess charges on these N atoms, deduced from Hückel MO calculations. These two molecular arrangements within the stacks must correspond to energy minima, with that of DBTAP-1 being the more stable.

In DBTAP-2 small channels run through the crystal parallel to **a**; but in DBTAP-1 the large gaps between the molecules in any layer parallel to the *yz* plane are covered by the next layer which is related by the twofold axis. The centring in $C2/c$ allows closer packing of the layers along **a**. The distance between layers is 6·94 Å $(=a)$ in DBTAP-2 while it is only 6·02 Å $(=a/2)$ in DBTAP-1 (Fig. 4).

Phase changes

It is evident that DBTAP-1 is the more closely packed form at room temperature: volume/molecule = 243 Å^3 compared with 246 Å^3 in DBTAP-2. The DTA results (Allais, 1966) show that DBTAP-2 is the stable form above 128 °C; however, two pieces of evidence show conclusively that DBTAP-1 is the thermodynamically stable form at room temperature.

Gentle crushing and grinding of crystals of DBTAP-2 immediately causes a change of phase to DBTAP-1. (It is impossible to obtain a powder photograph of DBTAP-2 by the usual method.) Also, when the molten compound is allowed to cool it freezes as DBTAP-2, but as the temperature drops to below about 50 °C the solid 'explodes', scattering material over a fairly wide area. (Fragments from a 0·3 g sample, left to cool on the bench-top, were found up to half a metre away. The effect was reminiscent of the popping of popcorn and the chain of 'explosions' only ceased when the sample had been totally reduced to powder. This material was shown to be DBTAP-1 by comparison of powder photographs.)

These observations support the principle that the crystal structure adopted by the molecules of an organic compound is that which is closest packed (Kitaigorodsky, 1973), and suggest that the thermodynamically stable form at any temperature will be the most dense form at that temperature (Laing, 1975).
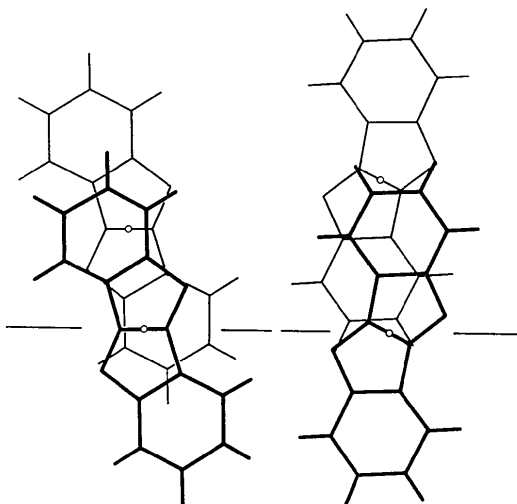

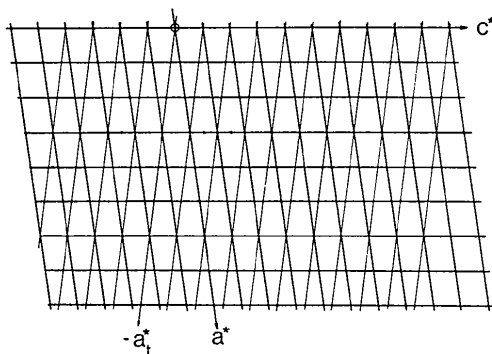Fig. 5. Projections onto the planes of the molecule in the two polymorphs; DBTAP-1 (right), DBTAP-2 (left).

Fig. 6. The *h0l* net of a twinned crystal of DBTAP-1. Every intersection between the lines corresponds to a reflexion.

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APPENDIX
Twinned crystals of DBTAP-1

DBTAP-1 readily forms twinned crystals (Burke, 1964). These crystals have the same b as the untwinned crystals but are identifiable by the appearance of their $h0l$ net. The twins share a common c^* and hence have their a axes parallel, one twin growing along [100] while the other grows along $-$[100]. The twinning seems to be caused by a 'mistake' in the stacking when molecules oriented as at $z=\frac{1}{2}$ in the untwinned crystals begin to grow at $z=0$. This is possible because of the geometrical relationship between a, c and β in DBTAP-1: $(a/2) \div 3c = 0.136$; $\sin(\beta - 90°) = 0.134$. This small difference is equivalent to about 10' of arc or 0.1 Å in cell edge. The length of c in the twinned structure is thus $3 \times c$ of the untwinned crystal, and the $h0l$ net of the twin has twice as many reflexions on the lines $h \neq 3n$ as does the $h0l$ net of an untwinned crystal (Fig. 6). A similar phenomenon has been observed in 10-methyl-1,2-benzanthracene (Herbstein, 1964). The skeletal structure of the twinned crystals is shown in Fig. 7.

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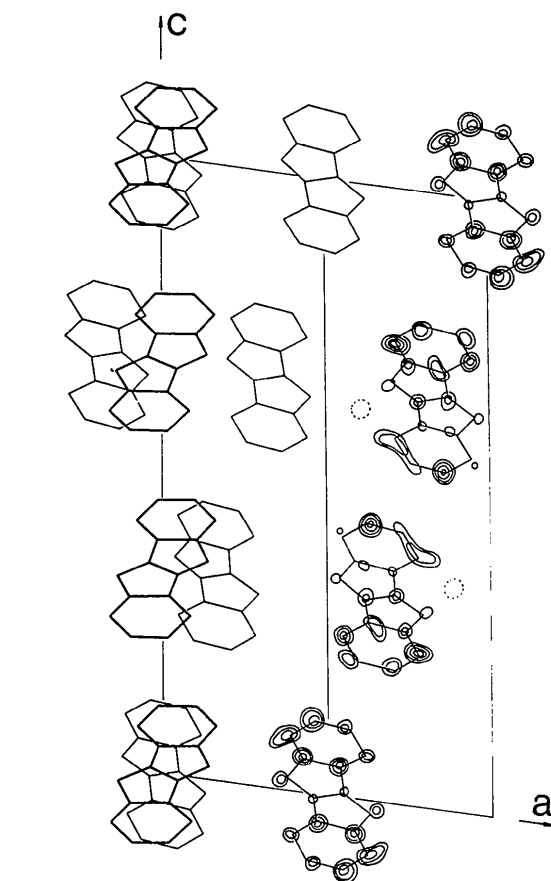International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 203. Birmingham: Kynoch Press.

Fig. 7. Left: skeletal structure of the twinned crystals; a view down b. The molecules outlined more heavily correspond to the arrangement in the untwinned structure. This pseudo unit cell has its a and $c = \frac{1}{2}a$ and $\frac{1}{3}c$ of the untwinned cell. Right: the electron density of the individual whose weight w was 0.2. The contributions of the molecules shown in heavier outline ($w = 0.8$) have been subtracted. The solid contours are at 0.75, 1.0, 1.25 and 1.50 e Å^{-3}. The dashed contour is a hole of -0.15 e Å^{-3}.

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