Molecular Compounds and Complexes. XVI.* 9,10-Dihydroanthracene (I) (C₁₄H₁₂) (a Redetermination) and 9,10-Dihydroanthracene:bis(1,3,5-trinitrobenzene) (II) (C₁₄H₁₂·2C₆H₃N₃O₆)

By F. H. Herbstein, M. Kapon and G. M. Reisner

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel 32000

Abstract

(I) $M_r = 180.2$, monoclinic, $P2_1$, $a = 7.733$ (3), $b = 6.245$ (3), $c = 10.815$ (4) Å, $\beta = 108.34$ (5)°, $V = 495.8$ Å³, $Z = 2$, $D_x = 1.207$ g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.34$ cm⁻¹, $F(000) = 192$, room temperature, $R_F = 0.045$ ($wR = 0.038$) for 637 unique reflections. The molecule has a folded shape, with a dihedral angle (defined as the angle between the planes of the two benzene rings) of 144.7°. These results confirm and extend the earlier work of Ferrier & Iball [*Chem. Ind. (London)* (1954), pp. 1296–1297]. (II) $M_r = 606.6$, monoclinic, $P2_1/a$, $a = 25.259$ (8), $b = 7.246$ (3), $c = 7.390$ (3) Å, $\beta = 92.10$ (5)°, $V = 1351.7$ Å³, $Z = 2$, $D_m = 1.50$ g cm⁻³, $D_x = 1.490$ g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.78$ cm⁻¹, $F(000) = 624$, room temperature, $R_F = 0.101$ ($wR = 0.087$) for 1176 unique reflections. The DHA molecule was found to be virtually planar. The structure consists of stacks of alternating donor (DHA) and acceptor (TNB) molecules with the stacking axis parallel to **b**. The two benzene rings of DHA each participate independently in donor–acceptor stacks.

Introduction

Formation of π-molecular compounds by donors and acceptors (for review see Herbstein, 1971) should lead to perturbation of the participant molecules. The effects on bond lengths and angles appear, however, to be too small to be detected by crystallographic techniques although it has been reported that there are small changes in the degree of planarity of anthracene in anthracene:picric acid (Herbstein & Kaftory, 1976) and of benzo[c]phenanthrene in benzo[c]phenanthrene:2,3-dichloro-5,6-dicyanobenzoquinone (Bernstein, Herbstein & Regev, 1977). We have now encountered a system in which there is a marked conformational change; the 9,10-dihydroanthracene (DHA) molecule, which has been reported to have a dihedral angle of ~145° in its neat crystals (Ferrier & Iball, 1954), is found to be planar (or almost so) in its 1:2 molecular compound with 1,3,5-trinitrobenzene (TNB).

As the available results for DHA are based only on two projections [$R(0kl) = 0.19$, $R(h0l) = 0.21$; atomic coordinates not reported], we have redetermined the crystal structure of this compound.

Experimental

For experimental and refinement details see Table 1.

(*a*) DHA

Transparent elongated prisms were obtained by reduction of anthraquinone (Clemmensen, 1914). Since the compound was found to be volatile (*cf. Dictionary of Organic Compounds*, 1965), a crystal (0.2 × 0.2 × 0.45 mm) was sealed in a 0.3 mm capillary.† Intensities were collected on a Philips PW 1100/20 four-circle diffractometer.

Approximate coordinates measured from the [100] and [010] projections given by Ferrier & Iball (1954) were used as starting point in the refinement. Anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the H atoms. Atomic parameters are listed in Table 2.‡ All calculations reported here were performed using the *SHELX*77 system of programms (Sheldrick, 1977) including the atomic scattering factors provided (*International Tables for X-ray Crystallography*, 1974).

(*b*) DHA.2TNB

DHA.2TNB was first prepared by Sudborough (1916). A preliminary photographic study by Herbstein, Kaftory & Regev (1976) showed that DHA has site symmetry C_i ($\bar{1}$) in the molecular compound,

---

† The density is reported as 0.8976 g cm⁻³ in the literature (*Dictionary of Organic Compounds*, 1965). Two separate measurements in solutions of Cd(NO₃)₂ and MgCl₂ gave a density of 1.110 g cm⁻³ which is still about 10% less than the calculated density of 1.207 g cm⁻³. These discrepancies are perhaps due to the volatility of DHA.

‡ Lists of structure factors, anisotropic thermal parameters and details of least-squares planes for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42452 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

* Part XV: Herbstein & Reisner (1984).

Table 1. *Experimental conditions (Philips PW 1100/20 four-circle diffractometer, graphite-monochromated Mo Kα, no corrections for absorption or extinction)*

	DHA	DHA.2TNB
Measurement mode	$\omega/2\theta$	$\omega/2\theta$
θ limits (°)	$2\cdot5 \le \theta \le 22\cdot5$	$2\cdot5 \le \theta \le 22\cdot5$
Scan speed [°(ω) min^{-1}]	1·5	1·5
Scan width [°(ω)]	1·10	1·10
Standard reflections	110, 112, 200 (<5% variation)	201, $\bar{3}$10, 510 (<5% variation)
No. of independent reflections measured	712	1668
Limits on indices	$-7 \le h \le 7, 0 \le k \le 6,$ $0 \le l \le 11$	$-26 \le h \le 26, 0 \le k \le 7,$ $0 \le l \le 7$
Restrictions on reflections	$F_o \le 1\cdot5\sigma(F_o)$	$F_o \le 1\cdot5\sigma(F_o)$
No. of reflections in the final refinement cycle	637	1176
No. of parameters refined	174	206
R_{int}	0·037 (by merging $hk0$ and $\bar{h}k0$ reflections)	0·033 (by merging $hk0$ and $\bar{h}k0$ reflections)
R_F	0·045	0·101
wR	0·038	0·087
Weighting scheme $w(F) = a/[\sigma^2(F_o) + bF_o]^2$	$a = 1\cdot0832$ $b = 0\cdot0$	$a = 1\cdot6944$ $b = 0\cdot0$
Max. final $\Delta\rho$ values (e Å^{-3})	+0·13 to −0·15	+0·33 to −0·27
Final $(\Delta/\sigma)_{max}$	0·2	3·1

indicating either a conformational change from that in the parent crystals, or disorder.

Yellow, prismatic crystals were obtained by slow cooling of a saturated ethanol solution of 9,10-dihydroanthracene and 1,3,5-trinitrobenzene in 1:2 ratio. The crystals were found to be air sensitive. $D_m = 1\cdot50$ g cm^{-3} (measured by flotation in *sym*-tetrabromoethane/toluene mixture). A prismatic crystal ($0\cdot4 \times 0\cdot3 \times 0\cdot3$ mm) was sealed in a 0·3 mm capillary and mounted on the diffractometer. The structure was solved by *MULTAN*77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977) after some effort. Final refinement using anisotropic temperature factors for all the non-hydrogen atoms and isotropic temperature factors for the H atoms treated as 'riding' atoms (except for those attached to the sp^3 C atom of DHA which could not be located). A final difference synthesis showed $\Delta\rho$ excursions within −0·27 to +0·33 e Å^{-3} mainly in the vicinity of the sp^3 C atom of DHA. The value of R_F is somewhat higher than usual; this is presumably to be ascribed to inadequacies in the model proposed for the disorder of DHA and the large thermal vibrations of the NO$_2$ groups in TNB. Atomic parameters are listed in Table 3.*

Results

(a) Molecular geometry of DHA

The atomic numbering system and molecular geometry of DHA in the parent compound and in DHA.2TNB are given in Figs. 1 and 2, respectively; packing diagrams are shown in Figs. 3 and 4. The

* See deposition footnote.

Table 2. *Atomic positional parameters of DHA in the neat compound ($\times 10^4$ for the nonhydrogen atoms, $\times 10^3$ for the H atoms), equivalent isotropic temperature factors of the nonhydrogen atoms ($\times 10^3$) and isotropic temperature factors of the H atoms ($\times 10^2$)*

$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$; $\sigma(U_{eq})$ calculated according to Schomaker & Marsh (1983).

	x	y	z	U_{eq}/U_{iso} (Å^2)
C(1)	2007 (6)	1509	5402 (5)	52 (1)
C(2)	3088 (7)	2519 (15)	6517 (5)	63 (2)
C(3)	3875 (7)	4466 (15)	6405 (4)	61 (2)
C(4)	3573 (6)	5407 (13)	5202 (5)	50 (1)
C(5)	−680 (6)	6304 (13)	886 (4)	45 (1)
C(6)	−2384 (7)	5805 (13)	59 (5)	55 (1)
C(7)	−3180 (7)	3864 (12)	173 (5)	59 (2)
C(8)	−2247 (6)	2405 (14)	1113 (5)	50 (1)
C(9)	571 (8)	1320 (13)	2956 (5)	52 (1)
C(10)	2165 (6)	5340 (12)	2736 (5)	47 (1)
C(11)	1710 (5)	2427 (12)	4184 (4)	43 (1)
C(12)	2485 (5)	4398 (12)	4085 (4)	40 (1)
C(13)	−507 (5)	2884 (12)	1949 (4)	42 (1)
C(14)	270 (5)	4870 (12)	1828 (4)	39 (1)
H(1)	138 (5)	14 (7)	547 (3)	5 (1)
H(2)	333 (7)	185 (9)	736 (5)	11 (2)
H(3)	470 (6)	521 (9)	730 (5)	10 (2)
H(4)	406 (6)	682 (9)	510 (5)	9 (2)
H(5)	−10 (5)	764 (8)	85 (4)	5 (1)
H(6)	−310 (5)	676 (6)	−63 (4)	5 (1)
H(7)	−439 (6)	339 (8)	−40 (4)	7 (2)
H(8)	−276 (5)	99 (8)	120 (4)	6 (1)
H(9)A	142 (7)	64 (8)	260 (5)	9 (2)
H(9)B	−28 (5)	29 (7)	314 (3)	6 (1)
H(10)A	308 (5)	467 (9)	241 (4)	7 (1)
H(10)B	238 (5)	699 (8)	277 (4)	7 (2)

geometry of DHA in the parent compound confirms the results reported earlier by Ferrier & Iball (1954), the molecule assuming a boat conformation with a dihedral angle of 144·7 °.* Atoms C(9) and C(10) were found to be 0·43 and 0·44 Å, respectively, from the plane of the four sp^2 C atoms of the central ring.

A different conformation of the DHA molecule was found in DHA.2TNB, the molecule being virtually planar. The temperature factors of the C atoms are normal except for U_{22} [0·164 (9) Å^2] of the central sp^3 C atom C(9). This high temperature factor may be explained either as being the result of genuine thermal motion of C(9) perpendicular to the plane of the molecule or in terms of disorder. Since the molecule is virtually planar and the temperature factors of the peripheral benzene C atoms are normal, disorder in terms of folded boat-shaped molecules (in analogy to the conformation found in the parent compound) taking up two centrosymmetrically related positions with equal probabilities is excluded [see Fig. 4; compare the pattern of temperature factors of the DHA with that of phenothiazine in phenothiazine:TNB (see below) where such disorder is present]. However, disorder of molecules with almost flattened chair-like central rings is possible.

The value of U_{22} for C(9) corresponds to a r.m.s. displacement of about 0·4 Å along the **b** direction, which is appreciably larger than would be expected

* E.s.d.'s for interplanar angles are ~ 0·5° and for distances from planes ~0·01 Å.

Table 3. *Atomic positional parameters of DHA and TNB in DHA.2TNB* ($\times 10^4$), *equivalent isotropic temperature factors of the nonhydrogen atoms* ($\times 10^3$) *and isotropic temperature factors of the* H *atoms* ($\times 10^2$)

	x	y	z	$U_{eq}/$ U_{iso} (Å^2)
TNB				
C(1)	5895 (3)	764 (10)	7700 (12)	64 (2)
C(2)	6053 (3)	51 (10)	6092 (11)	61 (2)
C(3)	6577 (3)	−217 (11)	5894 (12)	73 (2)
C(4)	6960 (3)	244 (11)	7253 (14)	77 (3)
C(5)	6775 (4)	957 (11)	8811 (12)	77 (3)
C(6)	6242 (4)	1252 (11)	9107 (12)	75 (3)
N(1)	5336 (3)	1050 (10)	8016 (11)	77 (2)
N(2)	6761 (3)	−986 (12)	4189 (12)	102 (3)
N(3)	7197 (5)	1465 (15)	10222 (14)	126 (4)
O(1)	5213 (2)	1740 (9)	9440 (9)	116 (2)
O(2)	5025 (2)	608 (10)	6860 (9)	118 (2)
O(3)	6425 (3)	−1179 (10)	2921 (8)	115 (2)
O(4)	7227 (3)	−1428 (11)	4094 (11)	153 (3)
O(5)	7630 (3)	1165 (16)	10062 (14)	208 (4)
O(6)	6999 (3)	2272 (12)	11572 (11)	143 (3)
H(2)	5782 (3)	−325 (10)	4984 (11)	7 (3)
H(4)	7379 (3)	246 (11)	6995 (14)	9 (3)
H(6)	6120 (4)	1943 (11)	10320 (12)	20 (3)
DHA				
C(1)	6134 (3)	4772 (10)	5046 (11)	70 (2)
C(2)	6428 (3)	5237 (11)	6584 (14)	82 (3)
C(3)	6185 (3)	5769 (11)	8115 (13)	81 (3)
C(4)	5673 (3)	5872 (10)	8137 (12)	76 (2)
C(9)	5273 (3)	4358 (13)	3259 (11)	93 (3)
C(11)	5574 (3)	4884 (10)	5006 (10)	63 (2)
C(12)	5326 (3)	5454 (11)	6583 (11)	73 (2)
H(1)	6340 (3)	4500 (10)	3814 (11)	10 (3)
H(2)	6852 (3)	5034 (11)	6615 (14)	11 (2)
H(3)	6424 (3)	6097 (10)	9316 (12)	11 (3)
H(4)	5435 (3)	6368 (10)	9307 (13)	11 (3)

for intramolecular thermal motion. However, a difference synthesis computed using all atoms except C(9) showed no evidence for disorder. Thus the explanation for the large value of U_{22} at C(9) remains moot and will probably only be resolved by low-temperature measurements.

The bond lengths in folded and planar DHA molecules do not differ significantly; indeed this conclusion extends to the substituted DHA's as well, as is shown in Table 4(b) where C_{2v} ($mm2$) symmetry has been assumed for the DHA skeleton. The sum of the bond angles in the central ring depends on the dihedral angle; this sum is 720° for a planar ring and less when the ring is non-planar. The peripheral bond lengths in the benzene rings are significantly shorter than the inner bonds. However, it is not clear to what extent this difference is an artifact because the results have not been corrected for thermal libration. Any in-plane orientational disorder of DHA will be appreciably less than that found in classic examples such as naphthalene:tetracyanoethylene [see *e.g.* Herbstein (1971) for review].
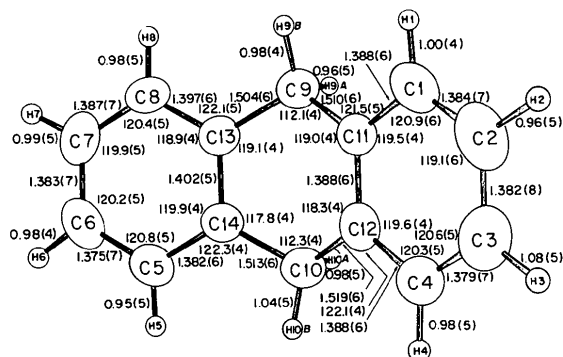

Fig. 1. Molecular dimensions and numbering scheme of 9,10-dihydroanthracene in the parent compound (distances in Å, angles in deg).
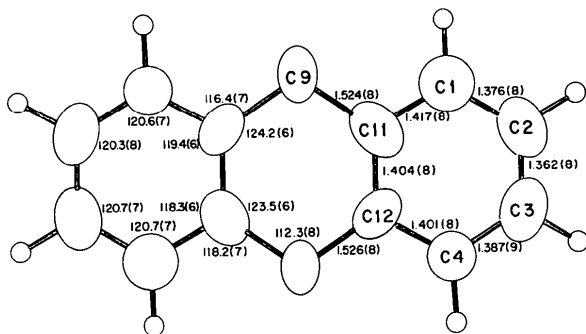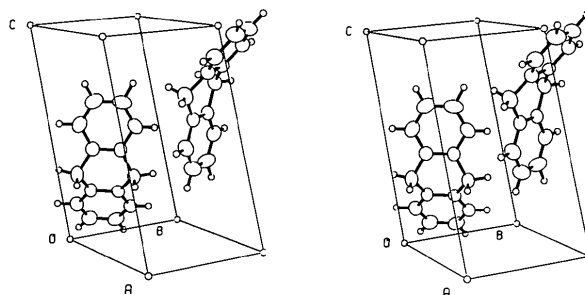

Fig. 2. Molecular dimensions of 9,10-dihydroanthracene in DHA.2TNB.

Fig. 3. *ORTEP* (Johnson, 1965) stereodiagram of the unit cell of DHA. The ellipsoids are of 50% probability.
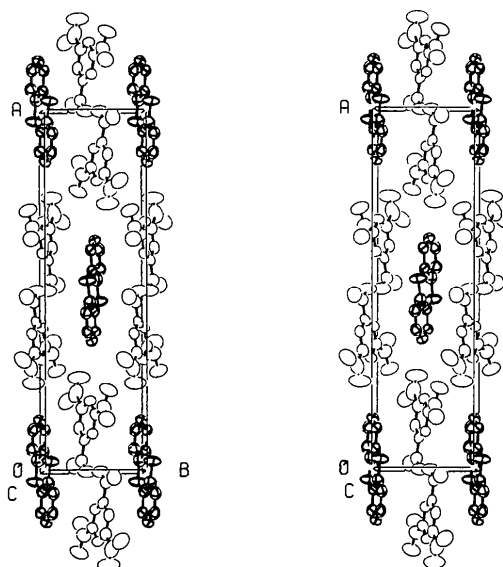

Fig. 4. *ORTEP* stereodiagram of the unit cell of DHA.2TNB.

(*b*) *Molecular geometry of TNB*

The atomic numbering system and molecular dimensions of TNB (*cf.* Choi & Abel, 1972) are given in Fig. 5.

The distortion of the benzene ring from hexagonal symmetry as evidenced by the deviation of its internal angles from 120° is consistent in magnitude and direction with that expected for nitro substitution (Domenicano, Vaciago & Coulson, 1975). The three planes of the nitro groups make angles of 2·3, 2·7 and 2·3 ° with the best plane of the benzene ring. This is consistent with the fact that in all TNB molecules studied so far (Bar & Bernstein, 1981) the nitro groups
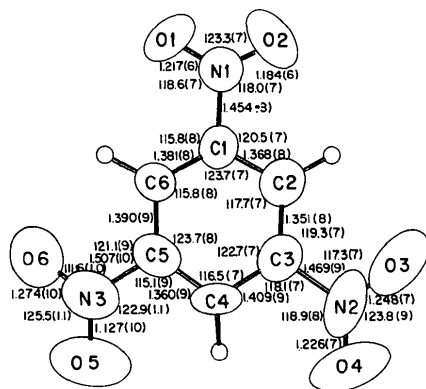

Fig. 5. Molecular   dimensions   of   1,3,5-trinitrobenzene   in DHA.2TNB.

make angles less than 15° with the benzene ring. The bond lengths clearly suffer from appreciable systematic errors presumably caused by inadequate allowance for thermal motion.

(*c*) *Molecular arrangement in DHA*

This is shown in Fig. 3. The space group is chiral, although the molecular symmetry is very nearly C_{2v} (*mm2*). It is unusual, but not unprecedented, that achiral molecules crystallize in chiral space groups.

(*d*) *Molecular arrangement in DHA.2 TNB*

A stereoview of the crystal packing is shown in Fig. 4. The structure of the complex is such that it consists of stacks of alternating donor and acceptor components with the stacking axis parallel to **b**. The reference DHA molecule (coordinates given in Table 3) is centred at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ whereas the TNB molecules are at general positions. The stacking is generated by the inversion-centre operation which brings one TNB molecule below one benzene ring of DHA and the other above the second benzene ring. Thus, the structure can formally be described as a complex between two TNB molecules and two benzene rings linked *via* a pair of CH_2 groups. The angle between the plane of the trinitrobenzene molecule (through the benzene ring and the three N atoms) and the plane of DHA is 5·0°. The distance between the DHA plane and the centroid of TNB is 3·77 Å; this is 0·3 Å or more larger than found in other TNB π-molecular compounds.

Table 4. *Structures of some 9,10-substituted 9,10-dihydroanthracenes* [R_1, R_3 = *substituents at* C(9); R_2, R_4 = *substituents at* C(10)]

(*a*) Conformation of the central ring (α = dihedral angle between outer aromatic rings; in present work e.s.d. ~0·5°)

R_1	R_2	R_3	R_4	Central ring	Reference
H	H	H	H	Folded, $\alpha = 145°$	Ferrier & Iball (1954)
H	H	H	H	Folded, $\alpha = 144·7°$	This work (parent compound)
H	H	H	H	Planar	This work (DHA.2TNB)
t-Bu	H	H	H	Folded, $\alpha = 146·6°$	Brennan, Putkey & Sundaralingam (1971)
Me	Et	H	H	Folded, $\alpha = 152°$	Bordner, Stanford & Ziegler (1973)
Me	H	H	*i*-Pr	Folded, $\alpha = 129°$	Stanford (1973)
SiMe₃	SiMe₃	H	H	Folded, $\alpha = 150°$ (*cis* isomer)	Leroy, Courseille, Doney & Bouas-Laurent (1976)
SiMe₃	H	H	SiMe₃	Deformed chair (*trans* isomer)	
H	CH₃	H	(CH₂)₃N(CH₃)₂	Folded, $\alpha = 155·6°*$	Chu & Chung (1976)
Cl	Cl	Cl	Cl	Planar*	Yannoni & Silverman (1966)
OH	Ph	Ph	OH	Slightly* puckered	Toda, Tanaka & Mak (1984)
OH	Ph	Ph	OH	Planar	Toda, Tanaka & Mak (1985)
OH	Ph	Ph	OH	Planar (parent compound: DDDA)	Toda, Tanaka, Nagamatsu & Mak (1985)
OH	Ph	Ph	OH	Planar (DDDA.2methanol)	

Note: Dalling, Zilm, Grant, Heeschen, Horton & Pugmire (1981, p. 4822) report that in 9,9,10,10-tetramethyldihydroanthracene the two aromatic rings lie in the same plane, the molecule being located at a crystallographic centre of symmetry. Further details were not given. There appear to be similarities to 9,9,10,10-tetrachlorodihydroanthracene.

Table 4 (cont.)

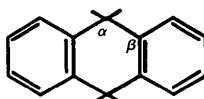(b) Geometry of DHA – averaged bond lengths (Å)
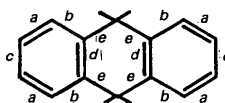
(i) Folded DHA

Bond	DHA	cis-9-Methyl-10-ethyl-DHA	trans-9-Isopropyl-10-methyl-DHA	cis-Bis-(trimethyl-silyl)-DHA	Grand average
a	1·381 (5)	1·373 (3)	1·377 (2)	1·382 (8)	1·378 (4)
b	1·389 (6)	1·394 (4)	1·387 (2)	1·396 (7)	1·392 (4)
c	1·382 (1)	1·374 (1)	1·377 (-)	1·374 (2)	1·377 (4)
d	1·395 (10)	1·390 (1)	1·398 (-)	1·393 (15)	1·394 (3)
e	1·512 (6)	1·515 (3)	1·519 (6)	1·519 (8)	1·516 (3)

(ii) Planar (or almost planar) DHA

Bond	DHA.2TNB	trans-Bis-(trimethyl-silyl)-DHA	trans-9,10-Dihydroxy-9,10-diphenyl-DHA†	9,9,10,10-Tetrachloro DHA‡	Grand average
a	1·382 (8)	1·375 (-)	1·373 (10)	1·37 (1)	1·375 (5)
b	1·409 (11)	1·40 (-)	1·403 (8)	1·39 (3)	1·401 (8)
c	1·362 (-)	1·39 (-)	1·382 (9)	1·39 (2)	1·381 (13)
d	1·404 (-)	1·42 (-)	1·389 (6)	1·41 (-)	1·406 (13)
e	1·525 (-)	1·495 (-)	1·520 (8)	1·51 (-)	1·511 (15)

(c) Geometry of DHA – averaged bond angles (°)

(i) Folded DHA

Angle	DHA	cis-9-Methyl-10-ethyl-DHA	trans-9-Isopropyl-10-methyl-DHA	cis-Bis(trimethyl-silyl)-DHA	Grand average
α	112·2 (1)	111·9 (7)	107·9 (1)	111·9 (5)	111·0 (2·0)
β	118·6 (6)	121·0 (2)	118·6 (1)	121·7 (2)	120·0 (1·6)
(2α+4β)	698·8	707·8	690·2	709·8	701·6 (9·0)

(ii) Planar (or almost planar) DHA

Angle	DHA.2TNB	trans-Bis-(trimethyl silyl)-DHA	trans-9,10-Di-hydroxy-9,10-diphenyl-DHA	9,9,10,10-Tetrachloro-DHA	Grand average
α	112·3 (-)	116 (-)	113·3 (4)	117·9 (1·7)	114·9 (2·6)
β	123·8 (3)	120 (-)	123·3 (3)	120·9 (8)	122 (1·8)
(2α+4β)	719·8	712	719·8	719·4	717·7 (3·8)

* Two independent molecules in the asymmetric unit.
† Average of five molecules.
‡ Average of two molecules.

The tilt between the planes of the components and the large interplanar distance suggest weak charge-transfer interaction, which is also indicated by the yellow colour of the crystals. The relative disposition of the two TNB molecules with respect to DHA is shown in Fig. 6.

Thus the present molecular compound has an essentially 1:1 character, with the benzene rings behaving as π-donor groups. Similar types of arrangement are found in bis(8-hydroxyquinolinato)Cu[II]: (1,2,4,5-tetracyanobenzene)$_2$ (Murray-Rust & Wright, 1968), bis(8-hydroxyquinolinato)Cu[II]:(picryl azide)$_2$ (Bailey & Prout, 1965) and bis(N-alkyl-2-oxy-1-naphthylideneaminato)Cu[II]: (7,7,8,8-tetra-
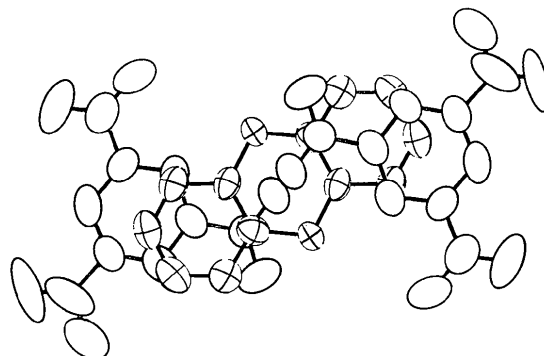

Fig. 6. Overlap diagram with the TNB molecules projected onto the mean plane of DHA.

cyano-*p*-quinodimethane)$_2$ (Matsumoto, Nonaka, Kida, Kawano & Ueda, 1979).

Discussion

In broad terms there are two preferred conformations for the DHA molecular skeleton, either folded with the dihedral angle distributed around 146·2° (sample standard deviation 9·2°), or planar (or very nearly so); the individual values (Table 4) depend on the nature of the substituents. In the folded molecules the central ring necessarily has a boat conformation; in the other examples the central ring is planar as in 9,9,10,10-tetrachloro-9,10-DHA and in all but one of the *trans*-9,10-dihydroxy-9,10-diphenyl-DHA molecules. Flattened chair conformations are found for *trans*-bis(trimethylsilyl)-DHA, once in *trans*-9,10-hydroxy-9,10-diphenyl-DHA and, perhaps, in DHA.2TNB.

Molecular-mechanics calculations (*MM*1) reported by Rabideau, Lipkowitz & Nachbar (1984) and MNDO calculations by Sygula & Holak (1983) give curves of potential energy *versus* dihedral angle φ which are qualitatively very similar but differ slightly in detail. The *MM*1 curve is flat for $-140° < \varphi < 140°$ while the MNDO curve has a minimum at $\varphi = \pm159°$ and a potential barrier of ~0.2 kJ mol^{-1} at $\varphi = 180°$. It seems probable at this juncture that neither quantum-mechanical nor molecular-mechanics calculations are sensitive enough to reveal the detailed form of the potential energy-φ curve for the DHA molecule. However, it is clear that the potential-energy curve is rather flat over the range of φ between ~140 and 180°.

The enthalpy of formation of DHA.2TNB is not known but, by analogy with other TNB π-molecular compounds, it is unlikely to be more than ~5 kJ mol^{-1} (Herbstein, 1971; see p. 234). The potential barriers found in the calculations referred to in the previous paragraph are, however, even smaller than this value and so it seems reasonable to infer that the enthalpy decrement from molecular-compound formation is enough to offset the enthalpy required to change the conformation of DHA from folded to planar (this discussion should have referred to free energies but the entropies involved are unknown).

Phenothiazine molecular compounds provide some interesting comparisons with DHA.2TNB. Phenothiazine itself has a dihedral angle of 153·3° in the polymorph with space group $P2_1$ (Bell, Blount, Briscoe & Freeman, 1968); we do not quote a value for the second polymorph (McDowell, 1976) because of problems due to disorder (van de Waal & Feil, 1977). In phenothiazine:3,5-dinitrobenzoic acid (Fritchie & Trus, 1968) the molecules pack in mixed stacks in alternate array, with each molecule overlapping one of its neighbours more extensively than the other. The phenothiazine moiety is folded about the

N–S axis, with a dihedral angle of 156±2°. Lack of atomic coordinates prevents more extensive discussion of this structure. Phenothiazine:TNB also has a mixed-stack structure (Fritchie, 1969); as the phenothiazine molecule at room temperature has a crystallographic twofold axis passing through the N, S atoms, it appears to be planar but the pattern of temperature factors suggests that the molecule is in fact folded along the N–S axis with an average dihedral angle of ~165–172°, there being dynamic or static disorder. There is a phase change, of unknown kind, at ~240 K. Thus the phenothiazine molecular compounds also provide evidence of the influence of crystal packing on molecular conformation.

Note added in proof. The crystal structures have been reported of *cis*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol [(II), room temperature], *cis*-9,10-diethyl-9,10-dihydroanthracene [(III), 200 K] and *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol [(I), room temperature] (Ahmad, Goddard, Hatton, Howard, Lewis & MacMillan, 1985). The two *cis* compounds are folded about the C(9)–C(10) axes, with dihedral angles of 149 and 147° respectively. The dimensions of (III) are most accurate and the bond lengths agree well with those found here for DHA itself. However, the value of $2\alpha + 4\beta$ is 706·2° showing that the central ring has angles similar to those in *cis*-9-methyl-10-ethyl-DHA and *cis*-bis(trimethylsilyl)-DHA [see Table 4, *b*(i) and *c*(i)]. The solid-state conformations of (II) and (III) are the same as those found in solution by NMR studies (Ahmad, Cloke, Hatton, Lewis & MacMillan, 1985). In the crystals of (I), the two crystallographically independent molecules lie on centres of symmetry and the central rings have flattened chair conformations with the bridging C atoms displaced by 0·135 and 0·168 Å respectively. The situation is thus rather similar to that of DHA in DHA.2TNB.

Molecules of various bimanes [1,5-diazabicyclo-[3.3.0]octadienediones (9,10-dioxabimanes)] show features which resemble those of the DHA system (Goldberg, Bernstein & Kosower, 1982; Goldberg, Bernstein, Kosower, Goldstein & Pazhenchevsky, 1983). The more highly substituted bimanes are folded about the central N–N bond, with ring–ring dihedral angles ranging from 172–139°. The simplest bimanes appear to be planar but the N atoms have appreciable components of thermal motion normal

to the mean molecular planes, suggesting that the planarity is an artifact due to superposition of two non-planar forms. This situation is again rather similar to that of DHA in DHA.2TNB; both systems would appear to require further study, preferably over a range of temperatures.

References

AHMAD, N., CLOKE, C., HATTON, I. K., LEWIS, N. J. & MACMILLAN, J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1849-1858.

AHMAD, N., GODDARD, R. J., HATTON, I. K., HOWARD, J. A. K., LEWIS, N. J. & MACMILLAN, J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1859-1863.

BAILEY, A. S. & PROUT, C. K. (1965). *J. Chem. Soc.* pp. 4867-4881.

BAR, I. & BERNSTEIN, J. (1981). *Acta Cryst.* B37, 569-575.

BELL, J. D., BLOUNT, J. F., BRISCOE, O. V. & FREEMAN, H. C. (1968). *Chem. Commun.* pp. 1656-1657.

BERNSTEIN, J., HERBSTEIN, F. H. & REGEV, H. (1977). *Acta Cryst.* B33, 1716-1724.

BORDNER, J., STANFORD, R. H. JR & ZIEGLER, H. E. (1973). *Acta Cryst.* B29, 313-318.

BRENNAN, T., PUTKEY, E. F. & SUNDARALINGAM, M. (1971). *Chem. Commun.* pp. 1490-1491.

CHOI, C. S. & ABEL, J. E. (1972). *Acta Cryst.* B28, 193-201.

CHU, S. S. C. & CHUNG, B. (1976). *Acta Cryst.* B32, 836-842.

CLEMMENSEN, E. (1914). *Chem. Ber.* 47, 681-687.

DALLING, D. K., ZILM, K. W., GRANT, D. M., HEESCHEN, W. A., HORTON, W. J. & PUGMIRE, R. J. (1981). *J. Am. Chem. Soc.* 103, 4817-4824.

Dictionary of Organic Compounds (1965). 4th ed., p. 1033. London: Eyre & Spottiswoode.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B31, 221-234.

FERRIER, W. G. & IBALL, J. (1954). *Chem. Ind. (London)*, pp. 1296-1297.

FRITCHIE, C. J. JR (1969). *J. Chem. Soc. A*, pp. 1328-1334.

FRITCHIE, C. J. JR & TRUS, B. L. (1968). *Chem. Commun.* pp. 833-834.

GOLDBERG, I., BERNSTEIN, J. & KOSOWER, E. M. (1982). *Acta Cryst.* B38, 1990-2000.

GOLDBERG, I., BERNSTEIN, J., KOSOWER, E. M., GOLDSTEIN, E. & PAZHENCHEVSKY, B. (1983). *J. Heterocycl. Chem.* 20, 903-912.

HERBSTEIN, F. H. (1971). *Perspect. Struct. Chem.* 4, 166-395.

HERBSTEIN, F. H. & KAFTORY, M. (1976). *Acta Cryst.* B32, 387-396.

HERBSTEIN, F. H., KAFTORY, M. & REGEV, H. (1976). *J. Appl. Cryst.* 9, 361-364.

HERBSTEIN, F. H. & REISNER, G. M. (1984). *Acta Cryst.* C40, 202-204.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham. Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LEORY, F., COURSEILLE, C., DONEY, M. & BOUAS-LAURENT, H. (1976). *Acta Cryst.* B32, 2792-2796.

MCDOWELL, J. J. H. (1976). *Acta Cryst.* B32, 5-10.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MATSUMOTO, N., NONAKA, Y., KIDA, S., KAWANO, S. & UEDA, I. (1979). *Inorg. Chim. Acta*, 37, 27-36.

MURRAY-RUST, P. & WRIGHT, J. D. (1968). *J. Chem. Soc. A*, pp. 247-253.

RABIDEAU, P. W., LIPKOWITZ, K. B. & NACHBAR, R. B. JR (1984). *J. Am. Chem. Soc.* 106, 3119-3123.

SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* A39, 819-820.

SHELDRICK, G. M. (1977). *SHELX77.* Program for crystal structure determination. Univ. of Cambridge, England.

STANFORD, R. H. JR (1973). *Acta Cryst.* B29, 2849-2855.

SUDBOROUGH, J. J. (1916). *J. Chem. Soc.* 109, 1339-1348.

SYGULA, A. & HOLAK, T. A. (1983). *Tetrahedron Lett.* 24, 2893-2896.

TODA, F., TANAKA, K. & MAK, T. C. W. (1984). *Tetrahedron Lett.* 25, 1359-1362.

TODA, F., TANAKA, K. & MAK, T. C. W. (1985). *J. Inclusion Phenom.* 3, 225-233.

TODA, F., TANAKA, K., NAGAMATSU, S. & MAK, T. C. W. (1985). *Isr. J. Chem.* In the press.

WAAL, B. W. VAN DE & FEIL, D. (1977). *Acta Cryst.* B33, 314-315.

YANNONI, N. F. & SILVERMAN, J. (1966). *Acta Cryst.* 21, 390-396.

Structural Studies of the Phase Transition in *N*-Isopropylcarbazole

BY F. BAERT

Laboratoire de Dynamique des Cristaux Moléculaires, Associé au CNRS n° 465, Université des Sciences at Techniques de Lille, 59655 Villeneuve d'Ascq CEDEX, France

AND A. MIERZEJEWSKI, B. KUCHTA AND R. NOWAK

Institute of Organic and Physical Chemistry, Technical University of Wrocław, Wybrzeze Wyspianskiego 27, 50370 Wrocław, Poland

Abstract

The crystal structures of *N*-isopropylcarbazole ($C_{15}H_{15}N$, $M_r = 209 \cdot 27$) stable above and below 139·5 K were solved by direct methods using three-dimensional X-ray diffraction data. The structure at 294 K is orthorhombic, space group *Iba*2, with $a = 16 \cdot 808$ (5), $b = 17 \cdot 984$ (8), $c = 7 \cdot 983$ Å, $V = 2413 \cdot 1$ Å^3, $Z = 8$, $D_x = 1 \cdot 15$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0 \cdot 7107$ Å, $\mu = 0 \cdot 036$ mm^{-1}, $F(000) = 896$; the structure at 118 K is also orthorhombic, space group *Pbc*2$_1$,