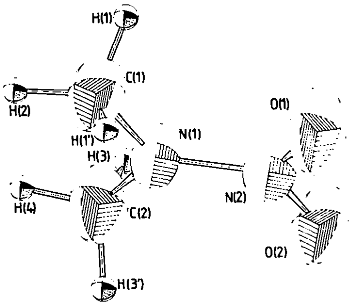

Fig. 1. Vibration ellipsoids (at 293 K) for *N*,*N*-dimethylnitramine scaled to 50% probability for non-H atoms. For clarity H atoms are scaled to $B = 0{\cdot}7$ Å^2.

orientation of the CH_3 groups in DMN is excluded by H···O repulsion. The present compound may be compared with *N*-nitrosodimethylamine (Krebs & Mandt, 1975) which also has a symmetry plane passing through the C, N, O and two H atoms. It differs from DMN by having one O less, thus enabling the CH_3 furthest from the N—O bond to rotate through 60° since there is no H···O contact on this side of the molecule. The H···H distance with this arrangement is 2·57 Å in spite of a decrease of the C—N—C angle to 120°.

Although there is no simple explanation of the planarity of the molecule, *ab initio* MO calculations by Duke (1978) have shown that over a limited range of models with varying degrees of planarity, the one found in the present work has the lowest energy. The bond distances and angles within the molecule, apart from the C—N—C angle already mentioned, are similar to those in other nitramine structures. Two types of intermolecular interaction in nitramines have been proposed, C—H···O hydrogen bonding (Choi & Boutin, 1970) and an interaction between a nitro N and an O (Cobbledick & Small, 1973). The closest intermolecular contacts found here are 2·64 Å for H···O, a value too large to be considered as an interaction. N···O contacts of 3·32 Å (for the 293 K results) of screw-axis-related N—O bonds are possible interactions in view of the expected thickness of a π-bonded system of 3·50 Å, and the highly polar nature of the N—O bonds; this N···O distance falls to 3·19 Å at 143 K.

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X-ray Diffraction Studies of 9-Methylanthracene and 5-Methylnaphthacene

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Abstract

The crystal structures of 9-methylanthracene (I) and 5-methylnaphthacene (II) have been elucidated by direct methods, with adjustment of pseudohomometric variants on *E* maps. Both compounds crystallize in the monoclinic space group $P2_1/c$, with $a = 8{\cdot}920$ (3), $b = 14{\cdot}641$ (4), $c = 8{\cdot}078$ (4) Å, $\beta = 96{\cdot}47$ (3)°, $Z = 4$ for (I), and $a = 10{\cdot}794$ (2), $b = 14{\cdot}697$ (4), $c = 7{\cdot}980$ (2) Å, $\beta = 93{\cdot}95$ (3)°, $Z = 4$ for (II). Least-squares adjustment of the atomic parameters resulted in $R = 0{\cdot}079$ over 1166 reflexions for (I) and $R = 0{\cdot}066$ over 1088

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reflexions for (II). Both molecules are distorted from planarity.

Introduction

The ^{1}H NMR spectra of 9-methylanthracene (I) and 5-methylnaphthacene (II) show the methyl signals split into doublets by direct coupling with the proton at the *para* position C(10) (Clar & Mackay, 1972). We undertook X-ray determinations of the geometries of these molecules to compare the C(9)···C(10) distance with the other ring diagonals.

Experimental

Yellow lath-like crystals of (I) and similar red crystals of (II) were supplied by Professor E. Clar. The intensities were collected on a Hilger & Watts Y290 automatic diffractometer with monochromated Mo $K\alpha$ radiation. For (I) 2292 independent reflexions were surveyed, of which 1166 had $I > 3\sigma(I)$; for (II) the numbers were 2756 and 1088.

Crystal data

9-Methylanthracene (I), $C_{15}H_{12}$, $M_r = 192{\cdot}2$, monoclinic, $a = 8{\cdot}920\ (3)$, $b = 14{\cdot}641\ (4)$, $c = 8{\cdot}078\ (4)$ Å, $\beta = 96{\cdot}47\ (3)°$, $U = 1048{\cdot}3$ Å^3, $D_m = 1{\cdot}24$, $Z = 4$, $D_c = 1{\cdot}22$ Mg m^{-3}, $F(000) = 408$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) = 0·074 mm^{-1}, space group $P2_1/c$.

5-Methylnaphthacene (II), $C_{19}H_{14}$, $M_r = 242{\cdot}3$, monoclinic, $a = 10{\cdot}794\ (2)$, $b = 14{\cdot}697\ (4)$, $c = 7{\cdot}980\ (2)$ Å, $\beta = 93{\cdot}95\ (3)°$, $U = 1262{\cdot}8$ Å^3, $D_m = 1{\cdot}25$, $Z = 4$, $D_c = 1{\cdot}27$ Mg m^{-3}, $F(000) = 512$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) = 0·078 mm^{-1}, space group $P2_1/c$.

Solution and refinement

Both structures were determined by centrosymmetric direct phasing (Stewart, Kundell & Baldwin, 1970). All reflexions, including unobserved, were used to calculate normalized structure amplitudes. E maps were generated with 142 phases for (I) and 177 for (II). Table 1 lists the values of the starting phases and the E statistics. In both cases it was necessary to adjust pseudohomometric variants (Bürgi & Dunitz, 1971) to locate the molecules correctly in the unit cell. The molecules appeared on the maps as two overlapping images so that, for example, in (I) the methyl C atom images appeared at the positions 0·87, 0·45, 0·33 and 0·65, 0·45, 0·13 which when averaged gave the correct position as 0·76, 0·45, 0·23.

Table 1. *Direct-methods data*

Starting phases
(*a*) 9-Methylanthracene

h k l	*E*	φ	
$\bar{7}$ $\bar{2}$ 3	5·68	0	Origin-defining
$\bar{2}$ $\bar{1}$ 7	5·02	0	
6 $\bar{2}$ 3	4·05	0	
$\bar{6}$ $\bar{6}$ 2	4·36	0/π	Enantiomorph-defining

(*b*) 5-Methylnaphthacene

h k l	*E*	φ	
1 1 7	6·47	0	Origin-defining
2 7 8	5·26	0	
8 2 3	5·24	0	
3 4 9	5·02	0/π	Enantiomorph-defining

Statistics

	$\langle \lvert E \rvert \rangle$	$\langle \lvert E^2 - 1 \rvert \rangle$
Acentric distribution (theory)	0·886	0·736
Centric distribution (theory)	0·798	0·968
9-Methylanthracene	0·670	1·180
5-Methylnaphthacene	0·654	1·253

Table 2. 9-*Methylanthracene: fractional atomic coordinates with e.s.d.'s*

	x	*y*	*z*
C(1)	1·1008 (6)	0·4204 (4)	0·3033 (7)
C(2)	1·2498 (7)	0·4021 (4)	0·3416 (8)
C(3)	1·3308 (7)	0·3590 (4)	0·2212 (8)
C(4)	1·2619 (5)	0·3354 (4)	0·0736 (7)
C(5)	0·8051 (6)	0·3188 (3)	−0·3276 (7)
C(6)	0·6540 (6)	0·3299 (4)	−0·3690 (7)
C(7)	0·5684 (7)	0·3690 (4)	−0·2492 (8)
C(8)	0·6334 (5)	0·3977 (4)	−0·1029 (8)
C(9)	0·8640 (5)	0·4136 (3)	0·1063 (6)
C(10)	1·0331 (5)	0·3296 (3)	−0·1285 (6)
C(11)	1·0206 (5)	0·3972 (3)	0·1479 (6)
C(12)	1·1045 (5)	0·3542 (3)	0·0248 (6)
C(13)	0·8784 (5)	0·3463 (3)	−0·1720 (6)
C(14)	0·7935 (5)	0·3875 (3)	−0·0507 (6)
C(15)	0·7753 (7)	0·4564 (5)	0·2332 (8)
H(1)	1·046 (5)	0·452 (3)	0·390 (6)
H(2)	1·301 (6)	0·419 (3)	0·435 (7)
H(3)	1·416 (9)	0·345 (5)	0·250 (9)
H(4)	1·311 (5)	0·303 (4)	−0·030 (6)
H(5)	0·864 (5)	0·300 (3)	0·409 (6)
H(6)	0·604 (6)	0·314 (4)	−0·490 (7)
H(7)	0·475 (8)	0·378 (5)	−0·259 (9)
H(8)	0·584 (5)	0·418 (3)	−0·017 (6)
H(10)	1·093 (4)	0·299 (3)	−0·214 (5)
H(15*A*)	0·683 (8)	0·475 (5)	0·165 (9)
H(15*B*)	0·810 (10)	0·511 (7)	0·257 (11)
H(15*C*)	0·780 (12)	0·435 (8)	0·350 (12)

Full-matrix least-squares refinement with isotropic thermal parameters for the C atoms lowered R to 15·0% for (I) and to 13·0% for (II). The H atoms were then located from difference syntheses. The C atoms were given anisotropic and the H atoms isotropic thermal parameters and refinement converged at R = 7·9% for (I) and 6·6% for (II). The weighting scheme was $w = 1/[1 + (F_O - F_B)/F_A]^2$. For (I) the final values assigned to F_A and F_B were 9·7 and 2·8, and for (II) 10·6 and 4·6. No extinction correction was applied. Scattering factors for C were taken from *International Tables for X-ray Crystallography* (1962), those for H from Stewart, Davidson & Simpson (1965).*

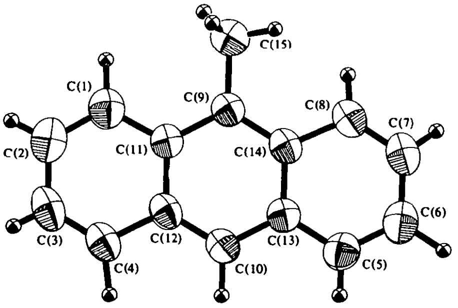

Fig. 1. The atomic arrangement in 9-methylanthracene.

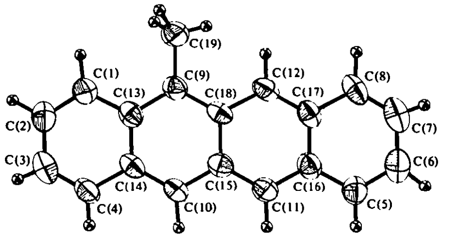

Fig. 2. The atomic arrangement in 5-methylnaphthacene.

Table 3. 5-*Methylnaphthacene: fractional atomic coordinates with e.s.d.'s*

	x	y	z
C(1)	0·8916 (4)	0·3985 (3)	−0·1337 (6)
C(2)	0·9424 (5)	0·3701 (4)	−0·2755 (6)
C(3)	0·8668 (4)	0·3299 (4)	−0·4079 (6)
C(4)	0·7445 (4)	0·3211 (3)	−0·3958 (5)
C(5)	0·1964 (4)	0·3339 (4)	0·1065 (6)
C(6)	0·1437 (4)	0·3564 (4)	0·2523 (7)
C(7)	0·2176 (5)	0·3971 (4)	0·3848 (7)
C(8)	0·3375 (5)	0·4168 (3)	0·3718 (5)
C(9)	0·7074 (4)	0·4132 (3)	0·0382 (5)
C(10)	0·5612 (4)	0·3318 (3)	−0·2312 (5)
C(11)	0·3804 (4)	0·3345 (3)	−0·0626 (5)
C(12)	0·5208 (4)	0·4140 (3)	0·2041 (5)
C(13)	0·7619 (4)	0·3873 (3)	−0·1118 (5)
C(14)	0·6849 (4)	0·3479 (3)	−0·2477 (5)
C(15)	0·5055 (4)	0·3538 (3)	−0·0815 (5)
C(16)	0·3239 (4)	0·3528 (3)	0·0852 (5)
C(17)	0·3974 (4)	0·3965 (3)	0·2210 (5)
C(18)	0·5806 (4)	0·3958 (3)	0·0551 (5)
C(19)	0·7837 (3)	0·4570 (4)	0·1806 (5)
H(1)	0·949 (4)	0·434 (3)	−0·050 (6)
H(2)	1·031 (4)	0·381 (3)	−0·290 (5)
H(3)	0·913 (5)	0·308 (3)	−0·485 (7)
H(4)	0·692 (3)	0·289 (2)	−0·480 (4)
H(5)	0·145 (3)	0·298 (3)	0·018 (5)
H(6)	0·059 (3)	0·336 (3)	0·255 (5)
H(7)	0·172 (5)	0·416 (4)	0·454 (7)
H(8)	0·387 (3)	0·454 (3)	0·467 (5)
H(10)	0·504 (3)	0·298 (3)	−0·322 (5)
H(11)	0·326 (3)	0·298 (2)	−0·153 (4)
H(12)	0·571 (3)	0·446 (2)	0·296 (4)
H(19*A*)	0·826 (4)	0·526 (3)	0·171 (6)
H(19*B*)	0·860 (5)	0·428 (3)	0·205 (6)
H(19*C*)	0·729 (4)	0·471 (3)	0·254 (6)

Discussion

The arrangement of atoms in the molecules and the thermal ellipsoids of the C atoms are shown in Figs. 1 and 2 and the crystal structures in Figs. 3 and 4. The atomic coordinates are listed in Tables 2 and 3. The bond lengths, valency angles and intermolecular separations are given in Tables 4 to 6 and 7 to 9.

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34036 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. 9-*Methylanthracene: bond distances* (Å) *and bond orders*

Intramolecular bonded atoms	Uncorrected	Corrected	Bond orders* (uncorrected)
C(1)–C(2)	1·357(8)	1·362	1·656 [1·653]
C(1)–C(11)	1·414(7)	1·419	1·213 [1·200]
C(2)–C(3)	1·424(10)	1·430	1·197 [1·237]
C(3)–C(4)	1·324(8)	1·329	1·681 [1·653]
C(4)–C(12)	1·441(6)	1·446	1·177 [1·200]
C(5)–C(6)	1·361(8)	1·366	1·650 [1·653]
C(5)–C(13)	1·409(7)	1·414	1·206 [1·200]
C(6)–C(7)	1·419(9)	1·426	1·221 [1·237]
C(7)–C(8)	1·324(8)	1·329	1·662 [1·653]
C(8)–C(14)	1·451(6)	1·456	1·179 [1·200]
C(9)–C(11)	1·420(6)	1·425	1·349 [1·387]
C(9)–C(14)	1·403(6)	1·408	1·361 [1·387]
C(10)–C(12)	1·375(7)	1·380	1·412 [1·387]
C(10)–C(13)	1·407(6)	1·412	1·355 [1·387]
C(11)–C(12)	1·454(7)	1·461	1·222 [1·223]
C(13)–C(14)	1·437(7)	1·444	1·243 [1·223]
C(9)–C(15)	1·501(8)	1·508	1·018

Intramolecular bonded distances involving H atoms (uncorrected)

C(1)–H(1)	1·01(5)	C(7)–H(7)	0·84(8)
C(2)–H(2)	0·87(5)	C(8)–H(8)	0·91(5)
C(3)–H(3)	0·80(8)	C(10)–H(10)	1·03(4)
C(4)–H(4)	1·09(5)	C(15)–H(15*A*)	0·98(7)
C(5)–H(5)	0·93(5)	C(15)–H(15*B*)	0·87(10)
C(6)–H(6)	1·05(6)	C(15)–H(15*C*)	0·99(13)

* Bond orders shown in square brackets refer to the unsubstituted anthracene molecule (Cruickshank, 1956).

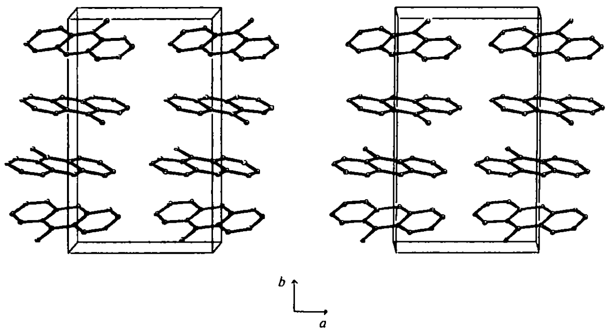

Fig. 3. The crystal structure of 9-methylanthracene.

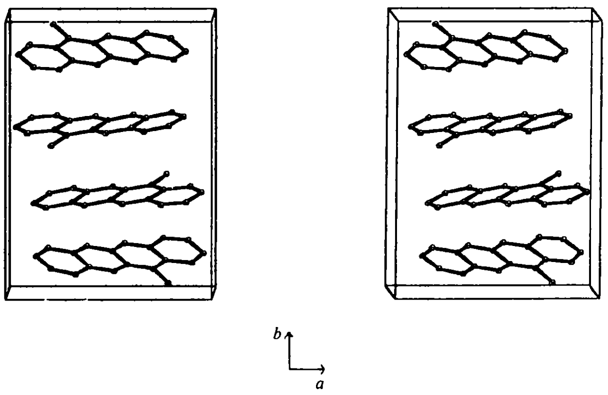

Fig. 4. The crystal structure of 5-methylnaphthacene.

Table 5. 9-*Methylanthracene: valency angles* (°) *with e.s.d.'s*

C(2)–C(1)–C(11)	122·7 (5)	C(1)–C(11)–C(9)	123·7 (4)
C(1)–C(2)–C(3)	119·4 (6)	C(1)–C(11)–C(12)	117·6 (4)
C(2)–C(3)–C(4)	120·7 (5)	C(9)–C(11)–C(12)	118·7 (4)
C(3)–C(4)–C(12)	122·4 (5)	C(4)–C(12)–C(10)	122·3 (5)
C(6)–C(5)–C(13)	122·2 (5)	C(4)–C(12)–C(11)	117·2 (4)
C(5)–C(6)–C(7)	118·3 (5)	C(10)–C(12)–C(11)	120·5 (4)
C(6)–C(7)–C(8)	121·4 (5)	C(5)–C(13)–C(10)	121·1 (5)
C(7)–C(8)–C(14)	123·0 (5)	C(5)–C(13)–C(14)	120·1 (4)
C(11)–C(9)–C(14)	119·8 (4)	C(10)–C(13)–C(14)	118·7 (4)
C(11)–C(9)–C(15)	119·3 (4)	C(8)–C(14)–C(9)	124·2 (5)
C(14)–C(9)–C(15)	120·9 (4)	C(8)–C(14)–C(13)	115·0 (4)
C(12)–C(10)–C(13)	121·4 (5)	C(9)–C(14)–C(13)	120·9 (4)

Two earlier studies of (I) based on photographic methods have been described. The packing deduced in the present study is in agreement with the results obtained by Bart & Schmidt (1971) but differs from that obtained by Verma (1969). Several molecules containing anthracene moieties have been examined as many display carcinogenic activity (*e.g.* Chomyn, Glusker, Berman & Carrell, 1972) but little crystallographic examination of naphthacene derivatives appears to have been made. The two molecules of this study crystallize in the same monoclinic space group as anthracene (Sinclair, Robertson & Mathieson, 1950) whereas naphthacene (Campbell & Robertson, 1962) adopts the space group $P\bar{1}$.

Table 6. 9-*Methylanthracene: intermolecular separations* < 3·80 Å

C(1)···C(13)$^{\mathrm{I}}$	3·59 Å	C(12)···C(15)$^{\mathrm{I}}$	3·70 Å
C(1)···C(14)$^{\mathrm{I}}$	3·66	C(1)···C(10)$^{\mathrm{II}}$	3·76
C(2)···C(8)$^{\mathrm{I}}$	3·72	C(5)···C(9)$^{\mathrm{III}}$	3·49
C(3)···C(8)$^{\mathrm{I}}$	3·71	C(5)···C(11)$^{\mathrm{III}}$	3·72
C(9)···C(11)$^{\mathrm{I}}$	3·66	C(5)···C(14)$^{\mathrm{III}}$	3·51
C(9)···C(12)$^{\mathrm{I}}$	3·58	C(6)···C(14)$^{\mathrm{III}}$	3·77
C(10)···C(15)$^{\mathrm{I}}$	3·71	C(10)···C(11)$^{\mathrm{III}}$	3·78
C(11)···C(14)$^{\mathrm{I}}$	3·69		

Symmetry code

(I) $2-x,\ 1-y,\ -z$ (III) $x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$
(II) $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

Table 7. 5-*Methylnaphthacene: bond distances* (Å) *and bond orders*

Intramolecular bonded atoms	Uncorrected	Corrected	Bond orders* (uncorrected)
C(1)–C(2)	1·356 (7)	1·360	1·679 [1·678]
C(1)–C(13)	1·434 (6)	1·438	1·187 [1·185]
C(2)–C(3)	1·419 (7)	1·425	1·191 [1·204]
C(3)–C(4)	1·336 (7)	1·340	1·690 [1·678]
C(4)–C(14)	1·436 (6)	1·439	1·162 [1·185]
C(5)–C(6)	1·364 (7)	1·367	1·676 [1·678]
C(5)–C(16)	1·429 (6)	1·432	1·182 [1·185]
C(6)–C(7)	1·416 (7)	1·422	1·188 [1·204]
C(7)–C(8)	1·333 (8)	1·337	1·689 [1·678]
C(8)–C(17)	1·434 (6)	1·437	1·167 [1·185]
C(9)–C(13)	1·416 (6)	1·420	1·398 [1·435]
C(9)–C(18)	1·408 (6)	1·411	1·296 [1·321]
C(10)–C(14)	1·375 (6)	1·378	1·451 [1·435]
C(10)–C(15)	1·411 (6)	1·414	1·297 [1·321]
C(11)–C(15)	1·399 (6)	1·402	1·316 [1·321]
C(11)–C(16)	1·391 (6)	1·394	1·446 [1·435]
C(12)–C(17)	1·376 (6)	1·380	1·465 [1·435]
C(12)–C(17)	1·376 (6)	1·380	1·465 [1·435]
C(12)–C(18)	1·416 (6)	1·419	1·299 [1·321]
C(13)–C(14)	1·441 (6)	1·447	1·200 [1·192]
C(15)–C(18)	1·450 (6)	1·457	1·193 [1·169]
C(16)–C(17)	1·445 (6)	1·451	1·184 [1·192]
C(9)–C(19)	1·503 (6)	1·510	1·021

Intramolecular bonded distances (Å) involving H atoms (uncorrected)

C(1)–H(1)	1·03 (5)	C(8)–H(8)	1·05 (4)
C(2)–H(2)	0·98 (5)	C(10)–H(10)	1·04 (4)
C(3)–H(3)	0·88 (5)	C(11)–H(11)	1·04 (3)
C(4)–H(4)	0·97 (4)	C(12)–H(12)	1·00 (3)
C(5)–H(5)	1·02 (4)	C(19)–H(19*A*)	1·13 (6)
C(6)–H(6)	0·97 (4)	C(19)–H(19*B*)	0·92 (8)
C(7)–H(7)	0·81 (5)	C(19)–H(19*C*)	0·90 (8)

* Bond orders shown in square brackets refer to the unsubstituted molecule (Campbell & Robertson, 1962).

C–C lengths range from 1·324 (8)–1·454 (7) Å in the anthracene moiety and from 1·333 (8)–1·450 (6) Å

Table 8. 5-*Methylnaphthacene: valency angles* (°) *with e.s.d's*

Angle	Value	Angle	Value
C(2)–C(1)–C(13)	121·5 (4)	C(9)–C(13)–C(14)	119·6 (4)
C(1)–C(2)–C(3)	120·3 (4)	C(4)–C(14)–C(10)	121·7 (4)
C(2)–C(3)–C(4)	120·5 (4)	C(4)–C(14)–C(13)	117·8 (4)
C(3)–C(4)–C(14)	122·0 (4)	C(10)–C(14)–C(13)	120·4 (4)
C(6)–C(5)–C(16)	121·2 (4)	C(10)–C(15)–C(11)	121·0 (4)
C(5)–C(6)–C(7)	119·5 (5)	C(10)–C(15)–C(18)	119·0 (4)
C(6)–C(7)–C(8)	122·0 (5)	C(11)–C(15)–C(18)	119·9 (4)
C(7)–C(8)–C(17)	121·1 (4)	C(5)–C(16)–C(11)	123·2 (4)
C(13)–C(9)–C(18)	119·8 (4)	C(5)–C(16)–C(17)	118·4 (4)
C(13)–C(9)–C(19)	120·5 (4)	C(11)–C(16)–C(17)	118·4 (4)
C(18)–C(9)–C(19)	119·7 (4)	C(8)–C(17)–C(12)	122·7 (4)
C(14)–C(10)–C(15)	121·2 (4)	C(8)–C(17)–C(16)	117·8 (4)
C(15)–C(11)–C(16)	122·2 (4)	C(12)–C(17)–C(16)	119·5 (4)
C(17)–C(12)–C(18)	123·2 (4)	C(9)–C(18)–C(12)	123·4 (4)
C(1)–C(13)–C(9)	122·6 (4)	C(9)–C(18)–C(15)	119·9 (4)
C(1)–C(13)–C(14)	117·8 (4)	C(12)–C(18)–C(15)	116·7 (4)

Table 9. 5-*Methylnaphthacene: intermolecular separations* < 3·80 Å

Contact	Distance	Contact	Distance
$C(1)\cdots C(6)^{I}$	3·74 Å	$C(16)\cdots C(19)^{I}$	3·66 Å
$C(1)\cdots C(7)^{I}$	3·74	$C(17)\cdots C(18)^{I}$	3·79
$C(8)\cdots C(13)^{I}$	3·66	$C(8)\cdots C(11)^{II}$	3·75
$C(8)\cdots C(14)^{I}$	3·61	$C(3)\cdots C(13)^{III}$	3·73
$C(9)\cdots C(16)^{I}$	3·58	$C(4)\cdots C(9)^{III}$	3·50
$C(9)\cdots C(17)^{I}$	3·61	$C(4)\cdots C(13)^{III}$	3·53
$C(11)\cdots C(19)^{I}$	3·65	$C(4)\cdots C(14)^{III}$	3·77
$C(12)\cdots C(15)^{I}$	3·55	$C(4)\cdots C(18)^{III}$	3·65
$C(12)\cdots C(18)^{I}$	3·60	$C(10)\cdots C(12)^{III}$	3·68
$C(13)\cdots C(17)^{I}$	3·68	$C(10)\cdots C(18)^{III}$	3·77

Symmetry code

(I) $1-x,\ 1-y,\ -z$

(II) $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

(III) $x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$

Table 10. *Analysis of atomic vibration tensors in terms of a rigid body*

Tensor components (e.s.d.'s × 10^4, in parentheses) and eigenvectors are referred to an orthogonal molecular coordinate system (X,Y,Z) related to the crystal system (x,y,z) by the transformation shown.

(i) 9-Methylanthracene

$$\mathbf{T}=\begin{bmatrix}0\cdot0498\,(7) & 0\cdot0067\,(7) & 0\cdot0024\,(8)\\ & 0\cdot0491\,(10) & 0\cdot0025\,(10)\\ & & 0\cdot0322\,(14)\end{bmatrix}\quad\begin{array}{llll} & l & m & n\\ 0\cdot0566\ \text{Å}^2 & 0\cdot7156 & 0\cdot6834 & 0\cdot1448\\ 0\cdot0428 & -0\cdot6922 & 0\cdot7215 & 0\cdot0159\\ 0\cdot0327 & -0\cdot0936 & -0\cdot1116 & 0\cdot9893\end{array}$$

$$\mathbf{L}=\begin{bmatrix}0\cdot0062\,(4) & -0\cdot0000\,(2) & 0\cdot0006\,(2)\\ & 0\cdot0030\,(1) & -0\cdot0003\,(1)\\ & & 0\cdot0035\,(1)\end{bmatrix}\quad\begin{array}{lllll} & l & m & n & \\ 0\cdot0063\ \text{rad}^2 & 0\cdot9763 & -0\cdot0173 & 0\cdot2158 & 20\cdot7\ \text{deg}^2\\ 0\cdot0035 & -0\cdot2004 & -0\cdot4499 & 0\cdot8703 & 11\cdot3\\ 0\cdot0028 & 0\cdot0820 & -0\cdot8929 & -0\cdot4427 & 9\cdot2\end{array}$$

$$\mathbf{S}\ (\text{rad Å})=\begin{bmatrix}-0\cdot0008\,(4) & -0\cdot0011\,(3) & -0\cdot0001\,(2)\\ & 0\cdot0009\,(3) & 0\cdot0002\,(1)\\ & & -0\cdot0001\,(5)\end{bmatrix}\quad\begin{bmatrix}X\\Y\\Z\end{bmatrix}=\begin{bmatrix}6\cdot7470 & 0\cdot8897 & 4\cdot5397\\ -5\cdot4219 & 6\cdot3421 & 5\cdot8946\\ -2\cdot1558 & -13\cdot1661 & 3\cdot1462\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

$$\langle(\Delta U_{ij})^2\rangle^{1/2}=0\cdot0027\ \text{Å}^2\qquad\langle\sigma^2(U_{ij})\rangle^{1/2}=0\cdot0028\ \text{Å}^2$$

The origin of the X,Y,Z system at (x,y,z) is (0·93825, 0·37447, 0·00348).

(ii) 5-Methylnaphthacene

$$\mathbf{T}=\begin{bmatrix}0\cdot0483\,(7) & 0\cdot0094\,(7) & 0\cdot0047\,(7)\\ & 0\cdot0421\,(10) & -0\cdot0041\,(10)\\ & & 0\cdot0365\,(14)\end{bmatrix}\quad\begin{array}{llll} & l & m & n\\ 0\cdot0552\ \text{Å}^2 & 0\cdot8236 & 0\cdot5610 & 0\cdot0834\\ 0\cdot0419 & 0\cdot3307 & -0\cdot5944 & 0\cdot7330\\ 0\cdot0298 & 0\cdot4608 & -0\cdot5761 & -0\cdot6751\end{array}$$

$$\mathbf{L}=\begin{bmatrix}0\cdot0068\,(4) & -0\cdot0001\,(1) & -0\cdot0008\,(2)\\ & 0\cdot0017\,(1) & -0\cdot0001\,(1)\\ & & 0\cdot0019\,(1)\end{bmatrix}\quad\begin{array}{lllll} & l & m & n & \\ 0\cdot0069\ \text{rad}^2 & 0\cdot9872 & -0\cdot0084 & -0\cdot1591 & 22\cdot72\ \text{deg}^2\\ 0\cdot0019 & 0\cdot1196 & -0\cdot6207 & 0\cdot7748 & 6\cdot25\\ 0\cdot0016 & -0\cdot1053 & -0\cdot7840 & -0\cdot6118 & 5\cdot29\end{array}$$

$$\mathbf{S}\ (\text{rad Å})=\begin{bmatrix}0\cdot0008\,(4) & -0\cdot0009\,(2) & -0\cdot0001\,(2)\\ & -0\cdot0006\,(3) & -0\cdot0001\,(1)\\ & & -0\cdot0002\,(5)\end{bmatrix}\quad\begin{bmatrix}X\\Y\\Z\end{bmatrix}=\begin{bmatrix}9\cdot1821 & -0\cdot3491 & -4\cdot6011\\ 5\cdot2165 & 6\cdot2980 & 5\cdot8430\\ 2\cdot2334 & -13\cdot2746 & 2\cdot8931\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

$$\langle(\Delta U_{ij})^2\rangle^{1/2}=0\cdot0031\ \text{Å}^2\qquad\langle\sigma^2(U_{ij})\rangle^{1/2}=0\cdot0028\ \text{Å}^2$$

The origin of the X,Y,Z system at (x,y,z) is (0·55524, 0·37410, −0·00257).

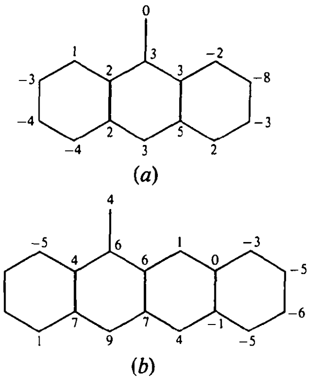

Fig. 5. Deviations (Å × 10^2) of atoms from the molecular planes: (*a*) 9-methylanthracene, (*b*) 5-methylnaphthacene.

in the naphthacene moiety, values similar to those found for anthracene and naphthacene. Bond orders based on atom positions (Armstrong, Perkins & Stewart, 1973) for the two molecules in this study are compared with those of the unsubstituted molecules (shown in square brackets) in Tables 4 and 7. Here the bond order is 1·000 for a purely single, and 2·000 for a purely double, covalent bond. As expected, small differences in bond character for the unsubstituted and substituted derivatives are found around C(9). For example, in (I) the average bond order for C(9)—C(11) and C(9)—C(14) is 1·355 compared with 1·387 in anthracene, whereas C(10)—C(12) and C(10)—C(13) average 1·384. Similarly, C(9)—C(13) and C(9)—C(18) have more single-bond character in (II) than in naphthacene. The charge on the methyl C atom is −0·26 e in (I) and −0·23 e in (II).

The valency angles range from 115·0 (4) to 124·2 (5)° for (I) and from 116·7 (4) to 123·4 (4)° for (II). In these molecules the shortest contacts between the *peri* substituents and the methyl H atoms are of the order of 2·0 Å. The in-plane bending here is evident for (I) in the valency angles C(1)—C(11)—C(9), 123·7 (4)°, and C(9)—C(14)—C(8), 124·2 (5)°; these angles are somewhat larger than the corresponding valency angles C(5)—C(13)—C(10) [121·1 (5)°] and C(4)—C(12)—C(10) [122·3 (5)°]. A similar situation occurs in (II).

Both methyl derivatives are distorted from planarity and the atom deviations from the molecular planes are shown in Fig. 5. In anthracene and 9,10-dimethylanthracene (Iball & Low, 1974) the largest displacements from the molecular plane are of the order of 0·01 Å, considerably less than the corresponding values for (I). In both the former cases the molecules are centrosymmetric with crystallographic half-molecule asymmetric units. The bent conformation of the type exhibited by the monomethyl derivative would not be possible in these molecules. In 9,10-dihydroanthracene (Ferrier & Iball, 1954) the molecule is bent about C(9)···C(10) with the planar halves of the molecule inclined to each other by 145°. In naphthacene the displacements from the molecular plane range from −0·02 to 0·04 Å, somewhat less than the displacements found for (II). Slight deformation of other polyaromatic ring systems, *e.g.* phenanthracene (Trotter, 1963), is also known. The equations of the mean planes (Schomaker, Waser, Marsh & Bergman, 1959) through (I) and (II) (C atoms only) are $0{\cdot}2417X + 0{\cdot}8993Y - 0{\cdot}3645Z - 6{\cdot}9421 = 0$ and $-0{\cdot}2068X + 0{\cdot}9026Y - 0{\cdot}3775Z - 3{\cdot}7309 = 0$.

The intramolecular separations of the *meso* C atoms in (I) are: C(1)···C(4) 2·77, C(9)···C(10) 2·83 and C(5)···C(8) 2·76 Å. For (II) these separations are: C(1)···C(4) 2·78, C(9)···C(10) 2·84, C(11)···C(12) 2·78 and C(5)···C(8) 2·79 Å. The shortest intermolecular contacts between C atoms are 3·49 Å for (I) and 3·50 Å for (II).

Analysis of thermal motion

The anisotropic thermal parameters were analysed in terms of rigid-body libration and translation (Schomaker & Trueblood, 1968). The results of the analyses are shown in Table 10. For both molecules the rigid-body approximation holds reasonably well, as the calculated tensor components, U_{ij}'s, are in close agreement with the observed values.

The C—C lengths show a small increase (0·003–0·007 Å) when corrected for the effect of libration.

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Optical Induction in Chiral Crystals. III.* The Crystal and Molecular Structures of the Mixed Crystal of 1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene and 1-(2,6-Dichlorophenyl)-4-(2-thienyl)-*trans,trans*-1,3-butadiene

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Abstract

The mixed melt of the title compounds ($C_{16}H_{12}Cl_2.C_{14}H_{10}Cl_2S$, 2·5:1) crystallizes in space group $P2_12_12_1$ with $a = 9{\cdot}3303$ (4), $b = 4{\cdot}0360$ (2), $c = 35{\cdot}2286$ (6) Å, $Z = 4$. The structure is isomorphous with the pure crystal of the host, $C_{16}H_{12}Cl_2$, and was refined to $R = 0{\cdot}04$. The absolute configuration of the molecule was determined by anomalous scattering. The thienyl group of the guest shows conformational disorder between the *syn* and *anti* orientations. The correlation between the conformation of the monomer molecules and their mixed dimer formed *via* photoreaction is discussed on the basis of experimental evidence and theoretical calculations.

Introduction

The solid-state photoreactivity of substituted 1,4-diphenylbutadiene molecules stacked along a short (*ca* 4 Å) axis has been discussed in terms of the ground- and excited-state conformations (Rabinovich & Shakked, 1975). The molecular conformation is believed to control the exclusive photodimerization at the double bond adjacent to the unsubstituted phenyl ring and the formation of an optically active heterodimer in a mixed crystal of 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (I) with its thiophene analogue (II). Warshel & Shakked (1975) have simulated the process of excimer formation in the photodimerization of these flexible conjugated molecules in the crystal by means of theoretical methods showing that the crystal forces induce asymmetry in the process of relaxation of an excited monomer into the excimer state thus leading to a preferred direction of excimer formation and subsequent dimerization. The verification of the predicted favorable path of photoreaction may be achieved experimentally by determining the absolute configuration of the starting monomers in the mixed crystal and that of the enantiomorphic heterodimer obtained in excess.

The present work deals with the determination of the absolute configuration of the monomer molecules in the mixed crystal of (I) and (II).

Experimental

A crystal (0·2 × 0·2 × 0·3 mm) was cut from a large crystal grown from the mixed melt of (I) and (II) in approximate molar ratio of 85:15. The crystal was mounted with [010] along the φ axis of an Enraf–Nonius CAD-3 three-circle diffractometer controlled by an IBM 1800 computer. Cell dimensions were determined from high-order reflections measured with Cu $K\alpha$ radiation. Crystal data are listed in Table 1.

Intensities ($\theta < 65°$, one octant of the reciprocal sphere, 1420 reflections measured twice) were collected at room temperature with graphite-monochromated Cu $K\alpha$ radiation. They were measured by an $\omega/2\theta$ scan followed by a background 2θ scan with an ω offset of 0·8° from the reflecting position. The range scanned for each reflection was 1·4° in 2θ plus the calculated α_1–α_2 separation, in steps of 0·01° with counting time of 0·5 and 0·2 s per step for intensity and background respectively. The intensities of four standard reflections

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* Part II: Rabinovich & Shakked (1975).

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