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The Crystal Structure of 2,7-Di-t-butylpyrene

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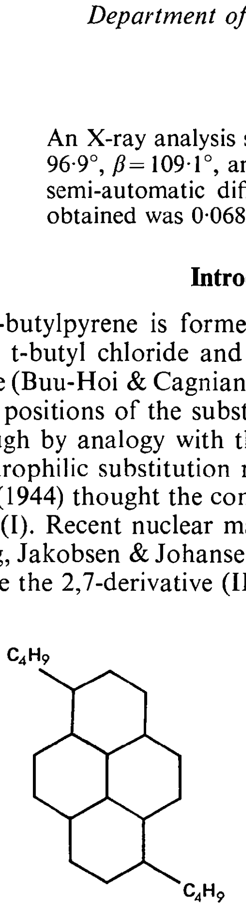
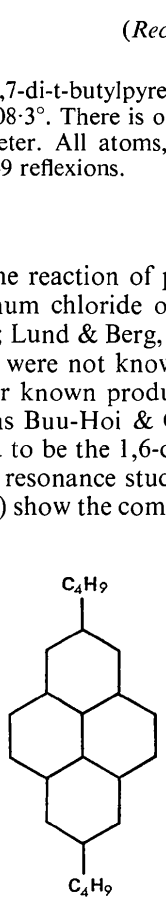
An X-ray analysis shows 2,7-di-t-butylpyrene to be triclinic with $a=9\cdot004$, $b=6\cdot138$, $c=9\cdot153$ Å, $\alpha=96\cdot9°$, $\beta=109\cdot1°$, and $\gamma=108\cdot3°$. There is one molecule in the cell. Intensity data were collected with a semi-automatic diffractometer. All atoms, including hydrogen, were located and the final R value obtained was 0·068 for 1369 reflexions.

Introduction

Di-t-butylpyrene is formed by the reaction of pyrene with t-butyl chloride and aluminum chloride or bromide (Buu-Hoi & Cagniant, 1944; Lund & Berg, 1946). The positions of the substituents were not known, although by analogy with the other known products of electrophilic substitution reactions Buu-Hoi & Cagniant (1944) thought the compound to be the 1,6-derivative (I). Recent nuclear magnetic resonance studies by Berg, Jakobsen & Johansen (1969) show the compound to be the 2,7-derivative (II).



(I)



(II)

Doubt, however, was cast on these results by Thulstrup, Michl & Eggers (1970) who inferred, from their studies of the molecular geometry and dichroism of compounds dissolved in stretched films, that the 1,6-configuration was the correct one.

A three-dimensional X-ray analysis was carried out to resolve the ambiguity, and showed the substituents to be in the 2,7-positions. The anomalous results from the dichroism in stretched films are attributed (Thulstrup, Michl & Eggers, 1970) to the fact that the bulky t-butyl groups prevent the molecules from orienting as well as the other 2,7 pyrene derivatives with non-bulky substituents which they had studied.

Crystal data

$C_{24}H_{26}$, M.W. 314·5. Triclinic, $a=9\cdot004\pm0\cdot005$, $b=6\cdot138\pm0\cdot005$, $c=9\cdot153\pm0\cdot005$ Å, $\alpha=96\cdot9\pm0\cdot3$, $\beta=109\cdot1\pm0\cdot3$, $\gamma=108\cdot3\pm0\cdot3°$, $U=439\cdot8$ Å^3, $D_m=1\cdot18$ (by flotation in aqueous $ZnCl_2$ solution), $Z=1$, $D_c=1\cdot19$, $F(000)=170$.

Possible space-groups are $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2). Single-crystal oscillation, Weissenberg, and precession photographs were taken using Cu $K\alpha$ and Mo $K\alpha$ radiations. No piezoelectricity could be observed. The implied molecular symmetry is $\bar{1}$ in $P\bar{1}$; no conditions are imposed on the molecular symmetry in $P1$. The space group was assumed to be $P\bar{1}$.

The crystals, which are colourless, crystallize as needles from an ethyl acetate solution. The needles are elongated in the [010] direction.

The linear absorption coefficient is $\mu=0\cdot72$ cm^{-1} for Mo $K\alpha$ radiation and $\mu=5\cdot04$ cm^{-1} for Cu $K\alpha$ radiation.

Table 1. *Atomic coordinates uncorrected for thermal motion, expressed as fractions of the cell edges*

The numbers in parentheses give the estimated standard deviation ×10⁴ for carbon atoms and ×10³ for hydrogen atoms. For the hydrogen atoms the isotropic temperature factor coefficients (in Å^2) and their standard deviations are listed.

	x	*y*	*z*	*B*
C(1)	−0·2266 (3)	0·1744 (5)	−0·0372 (3)	
C(2)	−0·1481 (3)	0·2546 (5)	−0·1334 (3)	
C(3)	−0·0097 (3)	0·1923 (4)	−0·1437 (3)	
C(4)	0·0750 (3)	0·2741 (5)	−0·2407 (3)	
C(5)	0·2083 (3)	0·2122 (4)	−0·2502 (3)	
C(6)	0·2565 (3)	0·0625 (4)	−0·1586 (3)	
C(7)	0·1767 (3)	−0·0236 (4)	−0·0592 (3)	
C(8)	0·0413 (3)	0·0417 (4)	−0·0508 (3)	
C(9)	0·3067 (3)	0·3144 (5)	−0·3505 (3)	
C(10)	0·4664 (4)	0·5257 (6)	−0·2380 (4)	
C(11)	0·3608 (5)	0·1308 (6)	−0·4255 (4)	
C(12)	0·2012 (5)	0·3952 (8)	−0·4838 (4)	
H(1)	−0·318 (4)	0·223 (5)	−0·030 (3)	2·0 (0·6)
H(2)	−0·180 (3)	0·366 (5)	−0·194 (3)	1·7 (0·6)
H(4)	0·042 (3)	0·379 (5)	−0·300 (3)	1·1 (0·5)
H(6)	0·346 (3)	0·019 (4)	−0·160 (3)	0·9 (0·5)
H(101)	0·533 (4)	0·589 (6)	−0·295 (4)	3·7 (0·8)
H(102)	0·547 (4)	0·477 (6)	−0·142 (4)	3·1 (0·7)
H(103)	0·425 (4)	0·640 (6)	−0·194 (4)	3·3 (0·8)
H(111)	0·417 (4)	0·192 (6)	−0·493 (4)	3·0 (0·7)
H(112)	0·267 (4)	−0·015 (6)	−0·493 (4)	3·1 (0·8)
H(113)	0·444 (4)	0·079 (6)	−0·348 (4)	3·1 (0·7)
H(121)	0·264 (4)	0·451 (6)	−0·548 (4)	2·9 (0·7)
H(122)	0·183 (4)	0·535 (6)	−0·436 (4)	3·4 (0·8)
H(123)	0·099 (5)	0·271 (7)	−0·544 (4)	3·7 (0·9)

Table 2. *Thermal parameters and their estimated standard deviations* (*in* $\text{Å}^2 \times 10^{-4}$)

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
C(1)	365 (14)	540 (15)	481 (15)	248 (13)	213 (13)	241 (13)
C(2)	445 (15)	547 (15)	474 (15)	282 (13)	231 (13)	280 (13)
C(3)	318 (13)	413 (13)	341 (13)	152 (10)	138 (10)	147 (10)
C(4)	379 (14)	455 (14)	374 (14)	165 (11)	181 (11)	196 (11)
C(5)	293 (13)	396 (13)	286 (13)	73 (10)	118 (10)	86 (10)
C(6)	328 (14)	472 (14)	390 (14)	175 (11)	181 (11)	151 (11)
C(7)	298 (13)	404 (13)	343 (13)	141 (10)	144 (10)	129 (10)
C(8)	291 (11)	344 (11)	304 (11)	87 (10)	117 (10)	100 (9)
C(9)	391 (14)	480 (14)	389 (14)	152 (11)	222 (11)	193 (11)
C(10)	464 (18)	547 (16)	610 (20)	67 (14)	275 (16)	190 (15)
C(11)	681 (22)	623 (19)	518 (19)	270 (18)	412 (18)	204 (17)
C(12)	570 (22)	875 (25)	543 (20)	313 (20)	319 (18)	438 (20)

Table 3. *Bond lengths, and their standard deviations*

The distances, l_{corr}, corrected for thermal vibration are given for that part of the molecule which vibrates as a rigid body.

	l	l_{corr}
C(1)—C(2)	1·345 (5) Å	1·346 Å
C(2)—C(3)	1·440 (5)	1·443
C(3)—C(4)	1·390 (4)	1·391
C(4)—C(5)	1·392 (4)	1·395
C(5)—C(6)	1·390 (4)	1·393
C(6)—C(7)	1·388 (4)	1·389
C(7)—C(8)	1·418 (4)	1·421
C(8)—C(3)	1·409 (4)	1·412
C(7)—C(1′)	1·426 (4)	1·430
C(8)—C(8′)	1·418 (4)	1·418
C(5)—C(9)	1·531 (4)	1·532
C(9)—C(10)	1·534 (3)	–
C(9)—C(11)	1·535 (6)	–
C(9)—C(12)	1·523 (5)	–
C(1)—H(1)	0·980 (37)	–
C(2)—H(2)	0·982 (32)	–
C(4)—H(4)	0·949 (31)	–
C(6)—H(6)	0·932 (33)	–
C(10)-H(101)	0·940 (42)	–
C(10)-H(102)	1·081 (36)	–
C(10)-H(103)	0·993 (43)	–
C(11)-H(111)	0·962 (39)	–
C(11)-H(112)	0·974 (27)	–
C(11)-H(113)	1·003 (37)	–
C(12)-H(121)	0·958 (40)	–
C(12)-H(122)	0·999 (43)	–
C(12)-H(123)	0·945 (29)	–

Table 4. *Angles and their standard deviations*

Angles within the rigid body, pyrene + C(9) + C(9′), are corrected for thermal motion.

	θ	θ_{corr}
C(7′)–C(1)-C(2)	121·6 (3)°	121·5°
C(1)—C(2)-C(3)	121·5 (3)	121·5
C(2)—C(3)-C(4)	122·9 (3)	122·8
C(2)—C(3)-C(8)	118·2 (3)	118·3
C(8)—C(3)-C(4)	118·9 (3)	118·9
C(3)—C(4)-C(5)	122·5 (3)	122·4
C(4)—C(5)-C(6)	117·9 (3)	118·0
C(5)—C(6)-C(7)	122·0 (3)	122·0
C(6)—C(7)-C(8)	119·3 (3)	119·3
C(6)—C(7)-C(1′)	122·6 (3)	122·5
C(8)—C(7)-C(1′)	118·1 (3)	118·2
C(3)—C(8)-C(7)	119·4 (3)	119·5
C(3)—C(8)-C(8′)	120·1 (3)	120·1
C(7)—C(8)-C(8′)	120·5 (2)	120·5
C(4)—C(5)-C(9)	121·9 (3)	121·8
C(6)—C(5)-C(9)	120·2 (3)	120·1
C(5)—C(9)-C(10)	107·3 (2)	–
C(5)—C(9)-C(11)	111·1 (3)	–
C(5)—C(9)-C(12)	111·5 (3)	–
C(10)-C(9)-C(11)	108·7 (3)	–
C(10)-C(9)-C(12)	109·9 (3)	–
C(11)-C(9)-C(12)	108·4 (3)	–

Atomic coordinates and thermal parameters, bond lengths and angles, and the observed and calculated structure factors, are listed in Tables 1, 2, 3, 4 and 5. The standard deviations quoted in these Tables have been estimated neglecting the errors in the cell dimensions.

Experimental

The crystals used in this investigation were kindly provided by Arne Berg of this institute.

X-ray intensity measurements

Data for the *h*0*l* zone were measured photometrically from integrating-Weissenberg photographs taken using Ni-filtered Cu $K\alpha$ radiation.

Intensities *hkl* ($k=0$ to 8) were recorded with a linear diffractometer of the Arndt & Phillips (1961) design. Balanced filters (SrO, ZrO_2) and a pulse height analyser were used in conjunction with a scintillation counter. The radiation used was Mo $K\alpha$ and reflexions were measured up to a Bragg angle of 27°. For the equator layer both sets of symmetry-related reflexions were measured, for the higher layer lines where there are no symmetry related reflexions each reflexion was measured twice. A total of 2321 independent reflexions were measured of which 1407 were greater than $2\sigma_c(I)$, where $\sigma_c^2(I)$ is the total number of counts in an intensity measurement.

A needle shaped crystal with mean radius 0·1 mm was used. Intensities were corrected for absorption assuming the crystal to be cylindrical and were corrected for the change in volume irradiated during measurement of the non-equatorial layer lines. Towards the end of the refinement an empirical correction was made for extinction using Larson's (1967) method.

Structure determination and refinement

Since there is only one molecule in the unit cell the molecule may be placed with its centre at the origin and

Table 5. *Observed and calculated structure factors*

The columns are h, k, l, $10\lvert F_o\rvert$, and $10F_c$. Reflexions rejected from the refinement because they were too close to the rotation axis of the crystal are marked with a cross.

h	k	l	$10\lvert F_o\rvert$	$10F_c$	
0	0	3	136	-138	
0	0	4	67	69	
0	0	6	15	-18	
0	0	8	28	29	
0	0	9	29	-31	
0	0	10	83	-86	
0	0	11	34	-41	
1	0	-10	18	-13	
1	0	-9	52	-53	
1	0	-8	33	34	
1	0	-6	19	-18	
1	0	-5	118	-117	
1	0	-4	49	54	
1	0	-3	37	-36	
1	0	-2	189	209	
1	0	1	565	589	
1	0	2	24	-29	
1	0	3	71	-67	
1	0	4	27	-30	
1	0	5	15	8	
1	0	6	13	12	
1	0	10	44	-48	
2	0	-10	37	37	
2	0	-9	19	10	
2	0	-8	18	15	
2	0	-7	12	16	
2	0	-6	108	-109	
2	0	-5	147	-141	
2	0	-4	122	-122	
2	0	-3	105	108	
2	0	-2	250	-261	
2	0	-1	142	140	
2	0	0	180	-181	
2	0	1	11	9	
2	0	2	80	-80	
2	0	3	77	-74	
2	0	4	66	64	
2	0	5	105	103	
2	0	7	14	8	
2	0	8	14	-6	
2	0	9	17	13	
3	0	-10	40	-41	
3	0	-9	26	29	
3	0	-8	40	-40	
3	0	-7	46	47	
3	0	-6	43	-44	
3	0	-5	114	-111	
3	0	-4	225	-225	
3	0	-3	80	83	
3	0	-2	48	47	
3	0	-1	67	-64	
3	0	0	73	-72	
3	0	1	61	-55	
3	0	3	26	27	
3	0	4	43	-45	
3	0	5	113	108	
3	0	6	79	80	
3	0	7	21	20	
4	0	-10	66	-69	
4	0	-9	47	-49	
4	0	-7	35	-36	
4	0	-6	25	29	
4	0	-5	72	71	
4	0	-3	72	-75	
4	0	-2	26	-28	
4	0	-1	63	61	
4	0	0	146	139	
4	0	1	110	106	
4	0	2	29	-28	
4	0	3	17	18	
4	0	4	37	37	
4	0	5	29	-30	
4	0	6	42	40	
5	0	-9	94	-99	
5	0	-7	52	56	
5	0	-5	14	-16	
5	0	-4	72	70	
5	0	-3	44	46	
5	0	-2	11	12	
5	0	-1	40	-42	
5	0	0	90	90	
5	0	1	130	125	
5	0	2	119	115	
5	0	3	67	-71	
6	0	-8	20	-23	
6	0	-7	15	16	
6	0	-6	39	38	
6	0	-5	116	-125	
6	0	-4	59	-58	
6	0	-3	37	-38	
6	0	-2	15	17	
6	0	-1	13	-10	
6	0	0	35	38	
6	0	1	33	24	
6	0	2	40	36	
6	0	4	24	-26	
6	0	5	29	26	
7	0	-11	17	18	
7	0	-9	20	-19	
7	0	-8	34	38	
7	0	-6	20	9	
7	0	-5	125	-131	
7	0	-4	208	-218	
7	0	-3	51	-54	
7	0	0	33	-32	
7	0	1	37	37	
7	0	5	29	33	
7	0	6	57	56	
8	0	-11	22	-19	
8	0	-10	37	35	
8	0	-9	23	23	
8	0	-8	30	-34	
8	0	-7	21	20	
8	0	-6	25	-27	
8	0	-5	17	18	
8	0	-4	132	-136	
8	0	-3	114	-117	
8	0	-1	54	56	
8	0	0	17	-24	
8	0	1	21	-19	
9	0	-9	64	59	
9	0	-4	38	36	
9	0	-2	21	-17	
9	0	0	15	3	
9	0	1	29	-29	
10	0	1	35	-35	
10	0	2	21	-27	
10	1	-3	35	32	
10	1	-6	21	-22	
10	1	-7	50	45	
10	1	-8	54	48	
9	1	2	28	-21	
9	1	0	18	18	
9	1	-1	26	-27	
9	1	-2	40	-44	
9	1	-3	35	-36	
9	1	-7	32	-31	
9	1	-8	55	44	
8	1	3	15	-6	
8	1	0	35	37	
8	1	-1	38	-36	
8	1	-2	110	-111	
8	1	-3	120	-120	
8	1	-4	23	-20	
8	1	-5	23	-23	
8	1	-7	15	16	
8	1	-10	20	-17	
7	1	5	17	-17	
7	1	4	18	17	
7	1	2	17	15	
7	1	1	17	-20	
7	1	-1	43	43	
7	1	-2	62	-62	
7	1	-3	166	-163	
7	1	-4	84	-81	
7	1	-5	47	52	
7	1	-6	13	13	
7	1	-10	24	22	
7	1	-11	22	-21	
6	1	4	16	-14	
6	1	3	52	55	
6	1	2	41	42	
6	1	1	51	55	
6	1	0	32	-32	
6	1	-1	19	-17	
6	1	-2	41	42	
6	1	-3	20	19	
6	1	-4	53	-57	
6	1	-5	25	22	
6	1	-7	13	-10	
6	1	-8	46	-53	
6	1	-10	24	-26	
6	1	-11	32	37	
5	1	6	20	-19	
5	1	5	14	8	
5	1	4	14	-10	
5	1	3	58	57	
5	1	2	74	72	
5	1	1	30	30	
5	1	0	35	31	
5	1	-1	20	18	
5	1	-2	36	-34	
5	1	-3	62	65	
5	1	-4	12	12	
5	1	-5	67	66	
5	1	-7	50	-50	
5	1	-8	98	-109	
5	1	-9	16	-25	
4	1	8	18	22	
4	1	7	33	35	
4	1	6	23	19	
4	1	5	35	-34	
4	1	2	45	46	
4	1	1	66	62	
4	1	0	64	-60	
4	1	-1	18	16	
4	1	-2	38	-36	
4	1	-3	76	-72	
4	1	-4	31	26	
4	1	-5	93	-88	
4	1	-6	44	42	
4	1	-7	27	-23	
4	1	-8	19	-17	
4	1	-9	95	-100	
4	1	-10	18	16	
3	1	7	40	45	
3	1	6	41	41	
3	1	4	18	16	
3	1	2	116	-112	
3	1	1	76	-78	
3	1	0	91	84	
3	1	-1	55	-53	
3	1	-2	58	59	
3	1	-3	366	-361	
3	1	-4	122	-102	
3	1	-5	20	-26	
3	1	-6	12	9	
3	1	-8	46	47	
3	1	-9	17	17	
2	1	8	14	-10	
2	1	6	57	58	
2	1	4	61	-65	
2	1	3	32	26	
2	1	2	252	246	
2	1	1	110	-109	
2	1	0	39	-35	
2	1	-1	45	-47	
2	1	-2	94	90	
2	1	-3	59	62	
2	1	-4	315	-298	
2	1	-5	42	-38	
2	1	-6	52	48	
2	1	-7	34	33	
2	1	-8	25	-25	
2	1	-9	25	28	
1	1	11	42	-37	
1	1	7	18	-14	
1	1	4	31	-35	
1	1	3	44	42	
1	1	2	327	328	
1	1	1	727	680	
1	1	0	16	10	
1	1	-2	264	-259	
1	1	-3	81	74	
1	1	-4	16	13	
1	1	-5	10	-8	
1	1	-6	19	19	
1	1	-7	17	18	
1	1	-8	90	-92	
1	1	-9	57	-58	
1	1	-10	21	-18	
0	1	11	35	-39	
0	1	10	19	-11	
0	1	8	35	-27	
0	1	6	19	-16	
0	1	5	29	29	
0	1	4	80	-79	
0	1	3	83	83	
0	1	2	282	276	
0	1	-2	85	86	
0	1	-3	19	-20	
0	1	-4	74	-69	
0	1	-5	18	16	
0	1	-7	38	39	
0	1	-8	86	-64	
0	1	-9	129	-133	
0	1	-10	60	-63	
-1	1	10	24	-26	
-1	1	9	34	37	
-1	1	7	82	-81	
-1	1	6	71	-68	
-1	1	4	87	88	
-1	1	3	123	-120	
-1	1	2	83	-83	
-1	1	-2	233	-233	
-1	1	-3	165	160	
-1	1	-4	76	77	
-1	1	-6	18	-18	
-1	1	-7	21	-24	
-1	1	-8	29	33	
-1	1	-9	62	-62	
-1	1	-10	57	-61	
-1	1	-11	21	-19	
-2	1	10	21	20	
-2	1	9	30	-28	
-2	1	8	27	29	
-2	1	7	70	-69	
-2	1	6	100	-100	
-2	1	5	104	-100	
-2	1	3	37	36	
-2	1	2	18	21	
-2	1	1	261	-263	
-2	1	0	202	-199	
-2	1	-1	16	-21	
-2	1	-2	75	72	
-2	1	-3	19	19	
-2	1	-4	223	214	
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the problem is reduced to that of finding the orientation of the pyrene skeleton.

Examination of the weighted reciprocal lattice for the $h0l$ projection yielded the orientation of the benzene rings. This gave three possible orientations (in projection) for the pyrene skeleton. Fourier syntheses were calculated for the three different possibilities; the best model was assumed to be that which gave an electrondensity map in which the butyl groups could be distinguished and there were no other background peaks of comparable size. The coordinates and isotropic temperature factor coefficients were refined by the method of Bhuiya & Stanley (1963) to give an R value of 0·31.

The direction of the normal to the molecule was determined from the origin spikes of the transform by Stadler's (1960) method. Knowing the x- and z-coordinates from the $h0l$ projection it was then possible to calculate the y-coordinates for the atoms in the pyrene skeleton.

A Fourier synthesis calculated with signs based on these coordinates yielded the positions of the butyl groups.

Least-squares refinement of coordinates and anisotropic thermal parameters reduced the R value to 0·123.

The positions of the hydrogen atoms were calculated using *BONDLA* in the program system *X-ray* 63 (Stewart, 1966). In the calculation of the positions of the methyl hydrogen atoms a staggered configuration about bonds C(9)–C(10), C(9)–C(11), and C(9)–C(12) was assumed. The hydrogen atoms were also located on a difference Fourier synthesis. Refinement including the hydrogen atoms reduced the R value to 0·076. To test whether there was any rotation or disordering of the methyl hydrogen atoms refinement was attempted with half-hydrogen atoms in the positions already found and half-hydrogen atoms in the eclipsed positions. This model would only refine to $R=0{\cdot}093$ and gave very low temperature factor coefficients for the half-atoms in the original positions, $\langle B_{\text{staggered}}\rangle = -0{\cdot}3$ Å^2, and very high values for those in the eclipsed positions, $\langle B_{\text{eclipsed}}\rangle = 13{\cdot}3$ Å^2. The conclusion being that it is better to describe the methyl hydrogen atoms as being in the staggered conformation.

The data were corrected for extinction and 38 reflexions which were close to the φ axis were removed. Refinement was then continued and convergence was reached at an R value of 0·068 for 1369 reflexions and 162 parameters. The observed and calculated structure factors are listed in Table 5, reflexions rejected for being too close to the rotation axis are marked with a cross.

Corection of parameters for thermal motion

The thermal motion of the carbon atoms was analysed in the following three ways (a) assuming the entire carbon skeleton to be a rigid body, (b) assuming the pyrene group plus atoms C(9) and C(9′) to form a rigid body, (c) assuming that only the pyrene skeleton could be treated as a rigid body. The translation and libration tensors **T** and **L** were calculated and the goodness of fit between U_{ij} (obs) and U_{ij} (calculated from **T** and **L**) used as a criterion of the correctness of the rigid body model. The r.m.s. values of ΔU_{ij} for the three models was (a) 0·0026, (b) 0·0016, and (c) 0·0014 Å^2.

It was therefore concluded that it was incorrect to treat the entire carbon skeleton as a rigid framework, but that either the pyrene group or pyrene plus two carbon atoms could be treated as rigid bodies.

The values for **T** and **L** calculated for pyrene plus two carbon atoms are listed in Table 6. These values

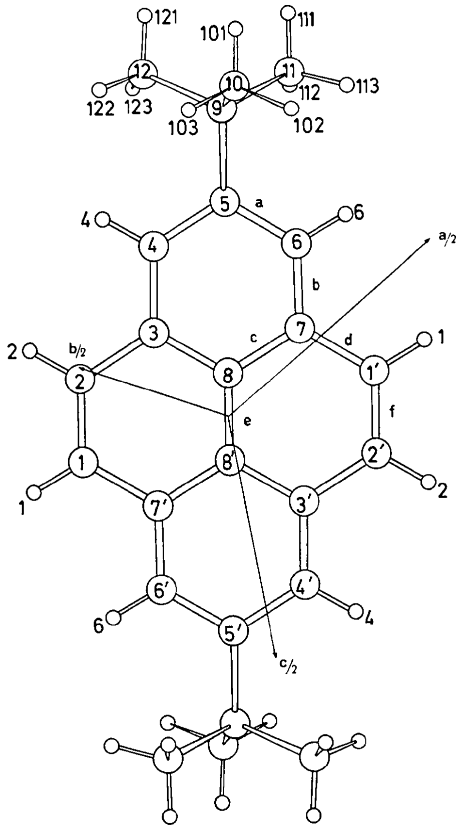

Fig. 1. The molecule drawn relative to its inertial axes. The numbering of the atoms and the lettering of the bonds are shown. The crystallographic axes are represented by lines from the origin to $a/2$, $b/2$, and to $c/2$.

Table 6. **T** *and* **L** *tensors* (*in* Å^2 *and in degrees*^{2}) *and their standard deviations*

These are all referred to an orthogonal system with the first axis parallel to a the second to $c^* \times a$ and the third to c^*. The tensors (**T**′ and **L**′) relative to the inertial axes of the pyrene group are also given, with the first axis parallel to the long axis of the molecule and the third perpendicular to the plane of the molecule.

$$\mathbf{T} = \begin{pmatrix} 0{\cdot}0271 & -0{\cdot}0282 & -0{\cdot}0018 \\ & 0{\cdot}0324 & 0{\cdot}0029 \\ & & 0{\cdot}0282 \end{pmatrix} \quad \sigma(\mathbf{T}) = \begin{pmatrix} 0{\cdot}0007 & 0{\cdot}0007 & 0{\cdot}0007 \\ & 0{\cdot}0009 & 0{\cdot}0009 \\ & & 0{\cdot}0010 \end{pmatrix} \quad \mathbf{T}' = \begin{pmatrix} 0{\cdot}0271 & 0{\cdot}0002 & -0{\cdot}0007 \\ & 0{\cdot}0303 & -0{\cdot}0047 \\ & & 0{\cdot}0302 \end{pmatrix}$$

$$\mathbf{L} = \begin{pmatrix} 17{\cdot}03 & -5{\cdot}31 & 2{\cdot}00 \\ & 17{\cdot}52 & 1{\cdot}82 \\ & & 16{\cdot}82 \end{pmatrix} \quad \sigma(\mathbf{L}) = \begin{pmatrix} 1{\cdot}40 & 1{\cdot}05 & 1{\cdot}09 \\ & 1{\cdot}08 & 1{\cdot}02 \\ & & 2{\cdot}22 \end{pmatrix} \quad \mathbf{L}' = \begin{pmatrix} 15{\cdot}44 & 0{\cdot}33 & 0{\cdot}00 \\ & 0{\cdot}99 & 0{\cdot}33 \\ & & 2{\cdot}96 \end{pmatrix}$$

were used for the correction of bond lengths and angles for thermal motion.

Computational details

Initial refinement was performed by the method of Bhuiya & Stanley (1963) using Danielsen's (1966) program.

Least-squares refinement was carried out using Grønbæk Hazell's (1966) block-diagonal least-squares program G403. Reflexions for which $F_0^2 < 2\sigma_c(F^2)$ were omitted and a weighting factor of

$$w = 1/\{[\sigma_c(F^2) + (1+A)F^2]^{1/2} - |F|\}^2$$

was used. The parameter A was varied so that $\langle w|F_{\rm obs}^2 - F_{\rm calc}^2|\rangle$ was independent of the magnitude of $F_{\rm obs}$.

These calculations were performed on the Aarhus University GIER computer.

Final refinement was carried out at NEUCC, Lundtofte, using the *ORFLS* program of Busing & Levy (1966) in the X-ray 63 system (Stewart, 1966). The weights used were those from the block-diagonal refinement. Hartree–Fock scattering factors (*International Tables for X-ray Crystallography*, 1962) were used for carbon and hydrogen.

The analysis of the thermal vibration and the correction of atomic coordinates was made using the programs of Gantzel, Coulter & Trueblood (1966).

Discussion

The bond lengths and angles are given in Tables 3 and 4, the numbering of the atoms is shown in Fig. 1.

The pyrene skeleton is planar to within experimental error; C(9) is however displaced 0·09Å out of the ring. The butyl group is arranged as is shown in Fig. 2 which shows the molecule drawn with respect to the inertial axes of the pyrene skeleton. The butyl group is seen to be rotated some degrees from the idealized configuration which is shown by full lines. If the butyl group were in the idealized position there would be two very short interatomic distances: H(4) to H(122), 2·00 Å and H(6) to H(113), 1·98 Å. The distances for the twisted configuration are H(4) to H(112), 2·15 Å and H(6) to H(113), 2·19 Å. The shortest intermolecular contacts are listed in Table 7.

Table 7. *Close approaches between molecules*; H–H *distances less than* 2·85 Å, C–H *less than* 3·1 Å, *and* C–C *less than* 3·75 Å

The final column shows how the second atom of a pair is related to the equivalent atom in the asymmetric unit. Distances are calculated from coordinates which have not been corrected for rigid-body motion.

	l			
H(1)---H(6)	2·654 (38) Å	$-1+x$	y	z
H(1)---H(102)	2·391 (53)	$-1+x$	y	z
H(1)---H(103)	2·688 (55)	$-x$	$1-y$	$-z$
H(1)---H(113)	2·821 (38)	$-1+x$	y	z
H(2)---H(121)	2·723 (48)	$-x$	$1-y$	$-1-z$
H(4)---H(112)	2·820 (32)	$-x$	$-y$	$-1-z$
H(4)---H(122)	2·828 (44)	$-x$	$1-y$	$-1-z$
H(6)---H(103)	2·650 (50)	x	$-1-y$	z
H(101)–H(111)	2·568 (55)	$1-x$	$1-y$	$-1-z$
H(101)–H(121)	2·717 (60)	$1-x$	$1-y$	$-1-z$
H(112)–H(122)	2·787 (53)	x	$-1+y$	z
C(4)---H(112)	3·006 (27)	$-x$	$-y$	$-1-z$
C(1)---C(2)	3·730 (3)	$-x$	$1-y$	$-z$
C(1)---C(3)	3·651 (3)	$-x$	$1-y$	$-z$
C(1)---C(4)	3·543 (4)	$-x$	$1-y$	$-z$
C(2)---C(2)	3·328 (4)	$-x$	$1-y$	$-z$
C(2)---C(3)	3·538 (3)	$-x$	$1-y$	$-z$
C(6)---C(10)	3·701 (4)	$1-x$	$1-y$	$-z$
C(7)---C(10)	3·631 (3)	$1-x$	$1-y$	$-z$

The mean bond lengths for the pyrene skeleton are given in Table 8. For comparison the following values are also included: pyrene (Camerman & Trotter, 1965); pyrene (Allmann, 1969); the low-temperature form of pyrene–pyromellitic acid dianhydride (Herbstein & Snymann, 1969); pyrene–TCNE (Krebs Larsen, Little & Coppens, 1972). All these structures were determined by X-ray diffraction. The structure of pyrene was also determined by neutron diffraction (Hazell, Krebs Larsen & Lehmann, 1972) and the π-SCFMO calculations of Warren & Yandle (1968).

Leaving aside the values of Camerman & Trotter (1965) which are superseded by the more accurate determination of Allmann (1969) the data fall into two

Table 8. *Mean bond lengths in* 2,7-*di-t-butylpyrene and in some related compounds*

The letters *X*, *N*, or *C* indicate that the structure was determined by X-ray diffraction, neutron diffraction, or that the values are calculated.

	Pyrene (*X*) Camerman & Trotter (1965)	Pyrene (*X*) Allmann (1969)	2,7-Di-t-butylpyrene (*X*)	Pyrene–PMDA, 110° (*X*) Herbstein & Snyman (1969)	Pyrene–TCNE (*X*) Krebs Larsen, Little & Coppens (1972)	Pyrene (*N*) Hazell, Krebs Larsen & Lehmann (1972)	Pyrene (*C*) Warren & Yandle (1968)
a	1·380 (11)*	1·379 (4)	1·394 (3)	1·403 (6)†	1·390 (3)	1·395 (2)	1·396
b	1·420 (9)	1·404 (3)	1·390 (3)	1·394 (5)	1·402 (3)	1·406 (2)	1·407
c	1·417 (7)	1·425 (3)	1·417 (3)	1·430 (2)	1·422 (2)	1·425 (1)	1·419
d	1·442 (9)	1·434 (3)	1·437 (3)	1·445 (3)	1·440 (2)	1·438 (2)	1·437
e	1·417 (14)	1·429 (5)	1·418 (4)	1·426 (1)	1·426 (3)	1·430 (2)	1·427
f	1·320 (14)	1·342 (4)	1·346 (5)	1·352 (2)	1·351 (2)	1·367 (2)	1·369

* Standard deviations as published *i.e.* twice the values estimated from refinement.

† Standard deviations from comparison of two independent molecules.

groups, first the values from X-ray determinations and secondly the neutron-diffraction results and the calculated values. The differences between the X-ray and the neutron results are discussed further in the paper on the neutron study of pyrene.

The X-ray results are seen to be reasonably similar. There is no reason why the bond lengths in the four compounds should be identical since the substitution of butyl groups, or the formation of a charge-transfer complex as in pyrene–PMDA, could be expected to perturb the electron configuration of pyrene. The effects are not expected to be great. For substitution of amino groups (which are much more strongly electron donating than the t-butyl groups) in positions 2 and 7 the maximum effect is calculated to be a lengthening of about 0·01 Å for bond *a* (Table 8) and no other change greater than 0·002 Å. The changes due to substitution of t-butyl groups would be expected to be considerably smaller. These calculations were kindly performed by J. Michl who calculated the π-bond orders using the Pariser & Parr (1953) and Pople (1953) methods.

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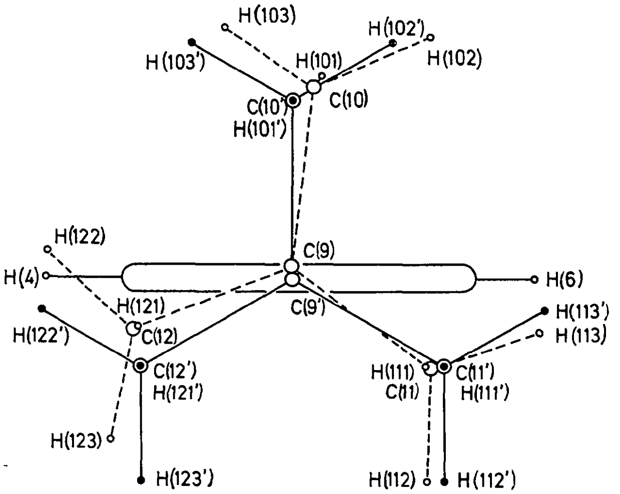

Fig. 2. The molecule drawn relative to the inertial axes of the carbon skeleton showing the deviation of the butyl group from the idealized positions.

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