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The Crystal and Molecular Structure of 1,2,4,5-Tetra-t-butylbenzene

BY C. H. STAM

Laboratorium voor Kristallografie, Nieuwe Prinsengracht 126, *Amsterdam, The Netherlands*

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The crystal structure of a monoclinic modification of 1,2,4,5-tetra-t-butylbenzene has been determined using three-dimensional Cu $K\alpha$ counter data. The final R index is 7·5%. The benzene ring with the adjacent quaternary carbon atoms is planar within the limits of accuracy. The benzene ring has angular deviations up to 10° from a regular hexagon. The exocyclic C–C bonds have lengths of 1·57 Å. There are indications of disorder involving the t-butyl groups.

Introduction

Because of the strong steric interaction of the bulky t-butyl groups in *o*-t-butylbenzenes considerable distortion of the benzene ring is to be expected. Dale (1961) on the evidence of infrared and ultraviolet spectra for 1,2,4 tri-t-butylbenzene was led to conclude that *ortho*-positioned t-butyl groups cause a (probably small) out of plane distortion of the benzene ring. A similar conclusion was drawn by Hoogzand & Hübel (1961) from the IR and UV spectra of 1,2,4,5-tetra-t-butylbenzene (TTBB). As the IR spectrum indicated the loss of centrosymmetry a chair-like distortion was considered impossible and a boat-like deformation was assumed. Arnett, Sanda, Bollinger & Barber (1967) have determined the strain energy resulting from a pair of *ortho*-positioned t-butyl groups as 22·3 ± 0·5 kcal/mole. They see no conclusive evidence from n.m.r., IR or UV spectra or from the reactivity of these compounds for a warping of the ring. The only indication for an appreciable influence on the aromatic π-electron system according to these authors is a noticeable decrease of the diamagnetic suspectibility exaltation relative to benzene.

It is borne out by the structure determination of monoclinic TTBB (preliminary communication: van Bruynsvoort, Eilermann, van der Meer & Stam, (1968) that there is indeed a strong deformation of the benzene ring, without, however, affecting the planarity of the ring.

Two other *o*-t-butyl aromatics have recently been investigated: 4,5-di-t-butylimidazole (DTBI, Visser & Vos, 1971*a*) and 2,3-di-t-butylquinoxaline (DTBQ, Visser & Vos, 1971*b*). Here also the planarity of the aromatic ring is not or little affected.

Experimental

Recrystallization of TTBB from alcohol yielded two modifications, an orthorhombic and a monoclinic one. At about 80° the orthorhombic crystals transform irreversibly into the monoclinic form. The monoclinic modification was chosen for a crystal structure determination.

The monoclinic crystals were usually rhombohedral blocks with the forms {011} and {10$\bar{1}$} predominant and smaller faces {110}. The cell constants were determined from zero-layer Weissenberg diagrams about [010], [001] and [101], calibrated with Al powder lines. A least-squares procedure applied to 45 reflexions of high θ yielded:

$$\begin{aligned} a &= 10\cdot910\ (3)\ \text{Å} \\ b &= 9\cdot988\ (3) \\ c &= 10\cdot051\ (3) \\ \beta &= 112\cdot29\ (2)^\circ . \end{aligned}$$

The numbers in parentheses are standard deviations. The space group is $P2_1/n$. Because of the scarcity of the material no experimental density was determined.

With $Z=2$ the calculated density is 0·988 g.cm^{-3} and the molecular volume 506·7 Å^3, which are quite acceptable values.

The structure was solved from photographic data obtained from integrated Weissenberg diagrams about [010] (0–8th layer) and [111] (0–2nd layer) made with Cu $K\alpha$ radiation. 1256 non-zero reflexions were collected in this way. Later, counter data were collected on a NONIUS automatic three-circle diffractometer equipped with a scintillation counter and a frequency discriminator. The θ–2θ scan technique was employed using Ni-filtered Cu $K\alpha$ radiation. The crystal had dimensions 0·20 × 0·25 × 0·50 mm and was mounted with [111] (the direction of largest dimension) along the φ axis of the instrument. Because of its volatility the crystal was covered with a layer of lacquer. In all, 1453 independent non-zero reflexions with $4·5° < \theta < 68·5°$ were obtained. Reflexions for which the net count was less than three times the statistical standard deviation were considered unobserved. No absorption correction was applied.

Structure determination and refinement

Since there are two molecules in the unit cell the centres of the molecules have to occupy centres of symmetry in the space group $P2_1/n$. In a sharpened three-dimensional Patterson synthesis calculated from the photographic data, the orientation of the benzene ring was clearly indicated. The indications for the methyl groups were less certain. The structure derived from the Patterson function proved essentially correct during the subsequent refinement.

The least-squares refinement, using a block-diagonal procedure with a weighting scheme according to Cruickshank (1961), was started isotropically with the photographic data. After a few cycles of anisotropic refinement the counter data were substituted. In a difference Fourier synthesis eleven out of the nineteen independent hydrogen atoms were represented by well resolved peaks of heights 0·3–0·55 e.Å^{-3}. The remaining hydrogen atoms were in non-resolved positive regions and their positions were deduced from the known parts of the methyl groups to which they belonged. Refinement was continued with the hydrogen atoms fixed with isotropic temperature parameters equal to the equivalent isotropic B's of the carbon atoms to which they are attached (Hamilton, 1959). Another difference Fourier synthesis, based on the calculated structure factors for carbon and hydrogen, revealed a pattern of positive areas of heights 0·25–0·45 e.Å^{-3} which roughly exhibited twofold symmetry about the twofold axis of the molecule (see Discussion). It proved possible to interpret this as being due to disorder in which a small fraction of the molecules have one pair, or perhaps both pairs of t-butyl groups in mirrored position with respect to the plane of the benzene ring. It was estimated that about 5 % of the pairs of t-butyl groups have this alternative conformation. This disorder was introduced into the refinement in the form of 6 additional atoms with 5 % of the carbon scattering power, while the original 6 methyl carbon atoms had their scattering factor reduced to 95 % (our least-squares program could not handle occupancy refinement). In the final refinement cycles all atoms were allowed to move, the hydrogen atoms and the 6 disordered atoms with isotropic temperature parameters. 7 strong reflexions apparently suffering from extinction were omitted, whilst a number of very weak reflexions which obtained an unduly large weight in the Cruickshank scheme were allotted zero weight. The final R index for 1446 observed reflexions was 7·5 %. The scattering factors were taken from Moore (1963).

In view of the relatively high R value another difference Fourier synthesis based on the final structure factors was calculated. It showed a number of peaks of heights up to 0·3 e.Å^{-3}, which had no obvious relation to the structure. It is evident that some minor feature of the crystal structure has not been accounted for.

The final parameters of the main conformation and their estimated standard deviations are given in Table 1.*

Table 1. *Final positional and thermal parameters*

The fractional positional parameters of carbon have been multiplied by 10^4, those of hydrogen by 10^3. The U_{ij} (in Å^2) have been multiplied by 10^4. Standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1)	945 (2)	840 (2)	−303 (3)	40 (1)	39 (1)	46 (1)	−3 (2)	7 (2)	36 (2)
C(2)	675 (2)	1085 (2)	947 (3)	43 (1)	37 (1)	44 (1)	−1 (2)	−11 (2)	30 (2)
C(3)	−259 (3)	231 (3)	1138 (3)	48 (1)	46 (1)	42 (1)	−0 (2)	−9 (2)	43 (2)
C(4)	1904 (3)	1570 (3)	−886 (4)	60 (2)	64 (2)	67 (2)	−23 (3)	19 (3)	66 (3)
C(5)	1216 (3)	2185 (3)	2138 (3)	60 (2)	51 (2)	58 (2)	−15 (3)	−34 (3)	32 (3)
C(6)	1796 (6)	3118 (5)	−837 (6)	138 (4)	66 (2)	134 (5)	−39 (5)	41 (5)	154 (7)
C(7)	3298 (4)	1067 (6)	−105 (6)	54 (2)	151 (5)	142 (5)	18 (5)	136 (8)	103 (5)
C(8)	1530 (5)	1321 (6)	−2510 (6)	120 (4)	128 (4)	83 (3)	−76 (7)	12 (6)	128 (6)
C(9)	2702 (4)	2419 (5)	2676 (5)	73 (3)	125 (4)	88 (3)	−45 (5)	−78 (6)	9 (5)
C(10)	416 (6)	3455 (4)	1661 (6)	134 (4)	58 (2)	106 (4)	44 (5)	−67 (5)	15 (6)
C(11)	1061 (6)	1748 (6)	3568 (5)	138 (4)	112 (4)	60 (2)	−61 (7)	−71 (5)	84 (5)

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* A list of structure factors can be obtained from the authors on request.

Table 1 (*cont.*)

	x	y	z	B
H(1)	−49 (3)	45 (3)	196 (3)	2 (1)
H(2)	239 (6)	345 (7)	−121 (6)	9 (2)
H(3)	208 (8)	355 (9)	49 (8)	15 (2)
H(4)	82 (8)	345 (9)	−149 (9)	16 (3)
H(5)	385 (5)	144 (6)	−43 (6)	8 (1)
H(6)	323 (6)	−5 (6)	−50 (7)	11 (2)
H(7)	363 (5)	100 (5)	94 (5)	7 (1)
H(8)	211 (5)	204 (5)	−277 (6)	7 (1)
H(9)	54 (5)	140 (6)	−309 (6)	8 (1)
H(10)	172 (5)	26 (5)	−271 (6)	8 (1)
H(11)	288 (5)	321 (6)	338 (6)	8 (1)
H(12)	296 (7)	259 (7)	170 (8)	13 (2)
H(13)	320 (5)	159 (5)	300 (5)	7 (1)
H(14)	75 (6)	412 (7)	246 (7)	9 (2)
H(15)	65 (6)	381 (6)	75 (6)	8 (2)
H(16)	−60 (7)	311 (7)	158 (7)	11 (2)
H(17)	140 (6)	249 (6)	432 (7)	9 (2)
H(18)	−6 (5)	180 (5)	328 (6)	8 (1)
H(19)	162 (7)	77 (7)	394 (7)	12 (2)

Results and discussion

Accuracy

The standard deviations in Table 1 have been derived from the least-squares refinement. Those for the methyl carbon atoms C(6)–C(11) especially do not reflect the accuracy of the parameters. This is clear from the C–CH_3 distances in Table 2 which have a much larger spread than is justified by the standard deviations of Table 1 [σ(exp) = 0·027, σ(calc) = 0·007 Å]. This must be due to the disorder in the t-butyl groups having been insufficiently accounted for. The core atoms C(1)–C(5), however, seem to be much less affected, judging from the consistency of the results based on the parameters for these atoms. Their least-squares standard deviations are probably much more realistic than those of the methyl groups.

Table 2. *Bond lengths and angles*

Bond lengths corrected for thermal motion

C(1)–C(2)	1·425 (5) Å	C(2)C(1)C(3′)	115·0 (3)°
C(1)–C(3′)	1·395 (4)	C(2)C(1)C(4)	130·3 (2)
C(1)–C(4)	1·567 (5)	C(3′)C(1)C(4)	114·7 (3)
C(2)–C(3)	1·402 (4)	C(1)C(2)C(3)	115·1 (2)
C(2)–C(5)	1·572 (4)	C(1)C(2)C(5)	130·8 (3)
C(4)–C(6)	1·560 (2)	C(3)C(2)C(5)	114·0 (3)
C(4)–C(7)	1·515 (5)	C(1)C(4)C(6)	112·6 (4)
C(4)–C(8)	1·554 (6)	C(1)C(4)C(7)	109·7 (3)
C(5)–C(9)	1·525 (6)	C(1)C(4)C(8)	112·0 (3)
C(5)–C(10)	1·519 (6)	C(6)C(4)C(7)	112·9 (4)
C(5)–C(11)	1·581 (7)	C(6)C(4)C(8)	101·6 (4)
		C(7)C(4)C(8)	107·8 (4)
		C(2)C(5)C(9)	115·0 (3)
		C(2)C(5)C(10)	110·0 (3)
		C(2)C(5)C(11)	111·3 (3)
		C(9)C(5)C(10)	113·2 (4)
		C(9)C(5)C(11)	100·8 (3)
		C(10)C(5)C(11)	105·9 (4)

Thermal motion

The principle axes of the vibration ellipsoids and their directions are listed in Table 3. Application of the rigid-body analysis according to Cruickshank (1956) suggests that the benzene ring together with the four adjacent carbon atoms behaves as a rigid body to a good approximation. The results of this analysis are reproduced in Table 4. They show a similarity to the corresponding results for durene (Stam, 1972). The axis of largest libration deviates 11° from the long axis of the molecule (durene 1½°), the axis of smallest libration is deviating 2½° from the short axis of the molecule (durene 13½°). The third libration axis is roughly in the direction of the ring normal with a deviation of 11° (durene 13½°).

Table 3. *Root-mean-square amplitudes of the vibrations along the axes of the vibration ellipsoids, and their angles q, p and r relative to* **a**, **b** *and* **c**

	$A_{\rm RMS}$	p	q	r
C(1)	0·2178	93	67	23
	0·2029	143	57	106
	0·1871	127	138	74
C(2)	0·1847	94	28	62
	0·2198	124	115	44
	0·2071	146	78	121
C(3)	0·1874	122	66	42
	0·2241	57	120	48
	0·2170	130	140	92
C(4)	0·1881	138	124	68
	0·2772	113	36	64
	0·2649	123	80	145
C(5)	0·1903	80	41	50
	0·2714	118	120	44
	0·2533	150	65	105
C(6)	0·2054	117	146	71
	0·3930	54	90	36
	0·3451	48	124	119
C(7)	0·4647	95	43	47
	0·2847	104	50	137
	0·1924	165	103	83
C(8)	0·2016	133	112	51
	0·4033	52	139	77
	0·3245	113	122	139
C(9)	0·2111	59	66	42
	0·3892	101	142	55
	0·3356	34	117	109
C(10)	0·4475	147	109	6
	0·3064	121	76	145
	0·1956	99	24	69
C(11)	0·2018	97	65	26
	0·3978	42	125	69
	0·3263	49	45	14

Table 4. *Principal axes of the libration and translation tensors*

Principal axes of the libration tensor.

	Direction cosines relative to **a**, **b** and **c***.		
29·3 (°)^2	+0·677	+0·636	+0·372
12·8	−0·459	+0·759	−0·462
3·7	−0·576	+0·142	+0·805

Principal axes of the translational tensor.

0·034 Å^2	+0·304	−0·951	+0·057
0·039	+0·689	+0·261	+0·676
0·037	+0·658	+0·167	−0·734

The corrections to the bond lengths (Busing & Levy, 1964) vary from 0·005 to 0·010 Å.

Because of their lower accuracy a further analysis of the thermal parameters of the methyl carbon atoms has not been attempted.

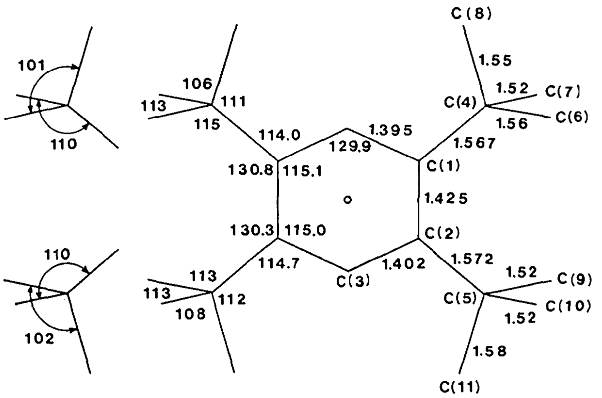
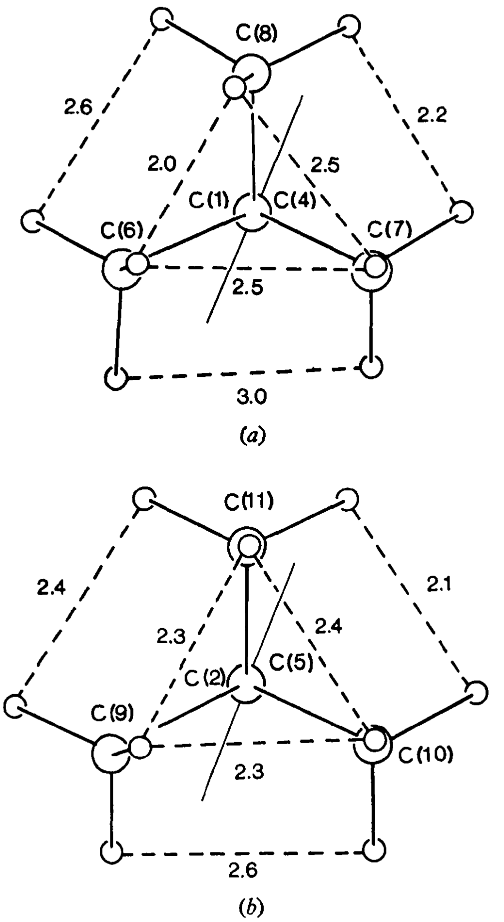


Fig. 1. Bond distances and angles.



(*a*)

(*b*)

Fig. 2. Projections of the t-butyl groups (*a*) along C(1)–C(4) and (*b*) along C(2)–C(5). The projection of the plane of the benzene ring is indicated by a thin line.

Bond distances and angles

The bond distances and angles involving the carbon atoms are given in Table 2 and Fig. 1. The bond lengths have been corrected for thermal motion.

From Fig. 1 it is evident that considerable strain exists in the molecule which, however, has not affected the planarity of the benzene ring but is expressed in the bond lengths and angles.

The ring angles show large deviations from 120°. These can be interpreted as resulting from the mutual repulsion of the bulky t-butyl groups in the *ortho* position. Because of this the angles C(2) C(1) C(4) and C(1) C(2) C(5) are increased by about 10°. The compensation for this increase is about equally distributed among the two other angles around C(1) and C(2). Since the ring stays planar C(2′) C(3′) C(1) has to increase to about 130°.

The strain is also manifest in part of the bond lengths. While C(1)–C(3′) and C(2)–C(3) have their

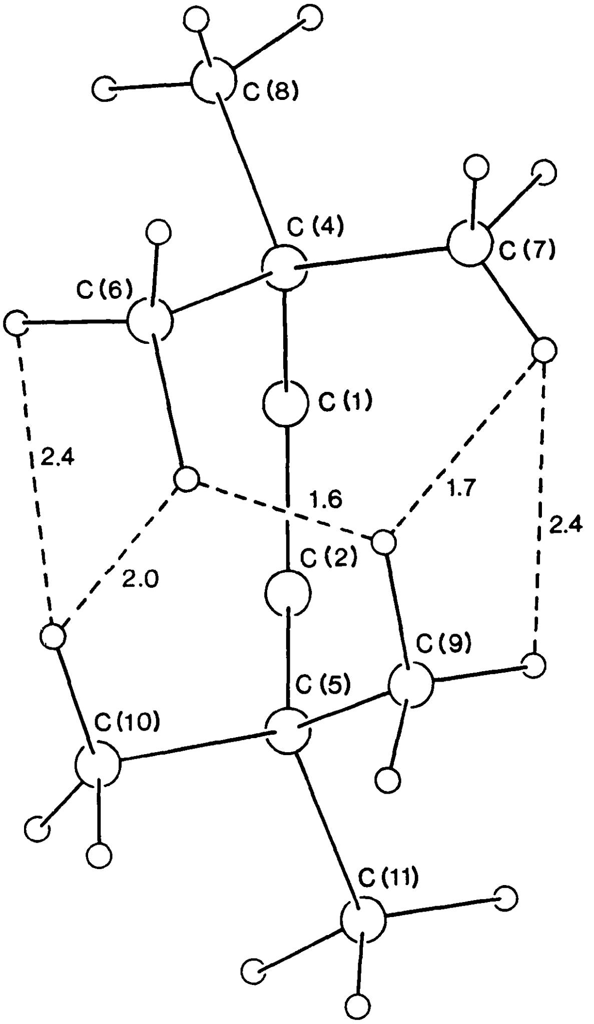


Fig. 3. Projection of the t-butyl groups onto a plane through C(3) and C(3′) perpendicular to the benzene ring.

normal benzene value, C(1)–C(2), between the two t-butyl groups carrying atoms, is significantly longer (1·425 Å). C(1)–C(4) and C(2)–C(5) (1·567 and 1·572 Å respectively) are considerably elongated with respect to the C–CH$_3$ lengths in durene (1·52 Å).

The C–H distances range from 0·87 to 1·32 Å (mean 1·06 Å), the H–C–H angles from 98 to 125° (mean 111°) and the C–C–H angles from 102 to 119° (mean 108°).

The t-butyl groups

The C–CH$_3$ distances vary from 1·515 to 1·581 Å. Their mean value, 1·542 Å, is in very good agreement with the corresponding averages in DTBI (1·540 Å) and DTBC (1·542 Å) (Visser, 1969). The conformations of the t-butyl groups are shown in Fig. 2, where they have been projected along C(1)–C(4) and C(2)–C(5). The methyl groups all have the usual staggered conformation. The interlocking of neighbouring t-butyl groups is indicated in Fig. 3, which is a projection onto a plane through C(3)–C(3′) perpendicular to the benzene ring.

The C–C–C bond angles within the t-butyl groups exhibit a fairly consistent pattern with the angles involving C(6) and C(9), which are most subjected to the pressure between the t-butyl groups, having the largest deviations from the normal value of 110°. In Table 5 the angles are compared with the corresponding ones in DTBI and DTBQ (Visser, 1969).

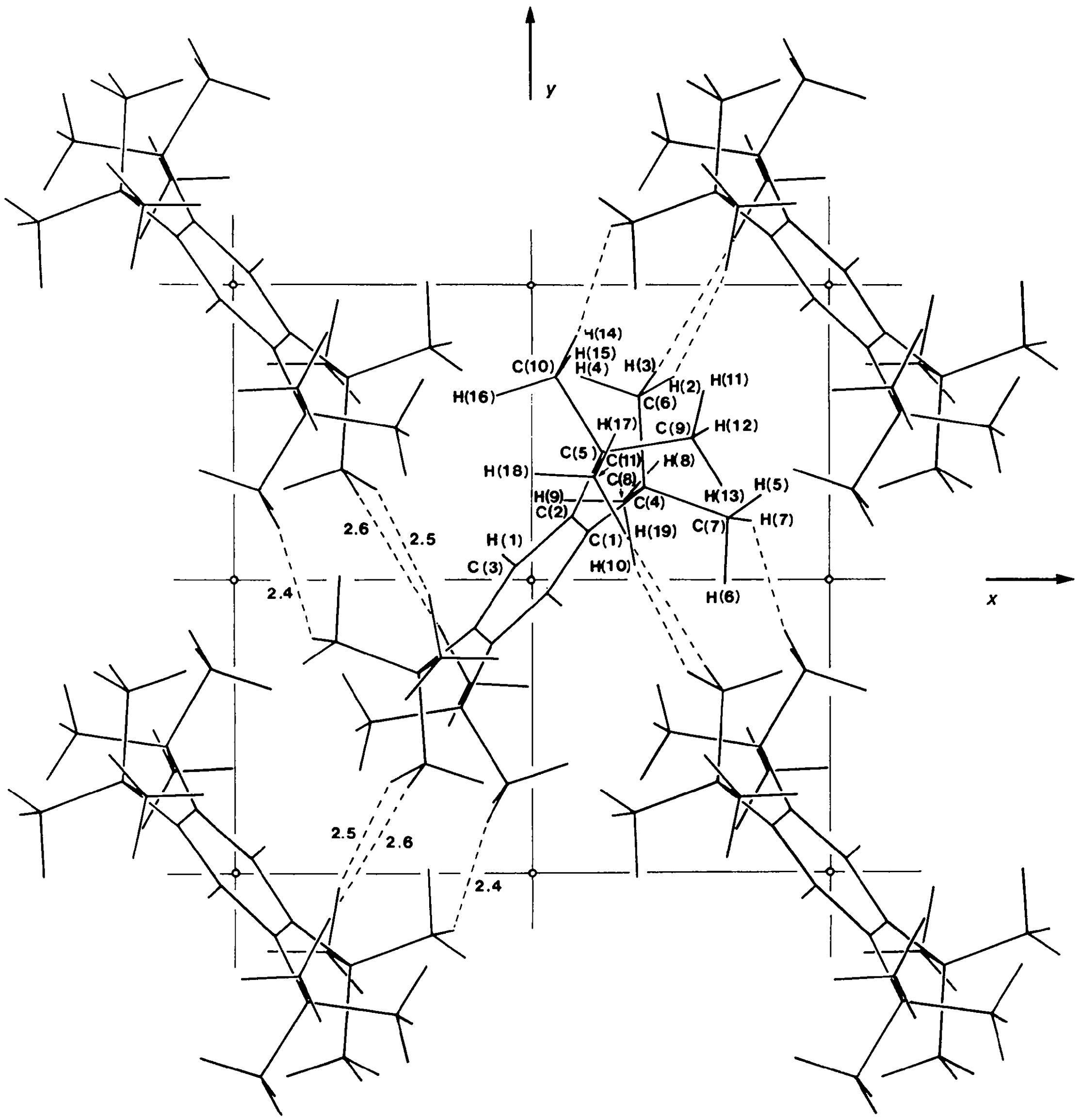


Fig. 4. Projection of the structure along [001]. Intermolecular H···H distances ≤2·6 Å have been indicated.

Table 5. *Bond angles within the t-butyl groups*

I: TTBB; II: DTBI (av.); III; DTBC (av.).

	I	II	III
C(1)—C(4)–C(6)	112·6°	113·0°	114·6°
C(2)—C(5)–C(9)	115·0		
C(1)—C(4)–C(7)	109·7	109·8	109·2
C(2)—C(5)–C(10)	110·0		
C(1)—C(4)–C(8)	112·0	109·8	109·1
C(2)—C(5)–C(11)	111·3		
C(6)—C(4)–C(7)	112·9	110·8	112·4
C(9)—C(5)–C(10)	111·3		
C(6)—C(4)–C(8)	101·6	105·6	105·0
C(9)—C(5)–C(11)	100·8		
C(7)—C(4)–C(8)	107·8	107·1	106·2
C(10)–C(5)–C(11)	105·9		

Planarity of the benzene ring

The benzene ring is planar within the limits of accuracy and the same applies to the benzene ring plus the 4 adjacent carbon atoms (Table 6). Although it is conceivable that in solution non-planar molecules occur which upon crystallization assume a planar conformation, an explanation for the occurrence of the non-centrosymmetric vibration in the IR spectrum of TTBB can be found in the possible coexistence in solution of centrosymmetric and non-centrosymmetric-molecules, both with a planar benzene ring (see next section).

Table 6. *Deviations from the best planes through* C(1), C(2), C(3), C(1′), C(2′), C(3′), (I) *and through* C(1), C(2), C(3), C(4), C(5), C(1′), C(2′), C(3′), C(4′), C(5′), (II)

	I	II
C(1)	−0·005 Å	−0·001 Å
C(2)	+0·005	+0·012
C(3)	−0·005	−0·001
C(4)	−0·006	−0·001
C(5)	−0·020	−0·005

Equations relative to **a**, **b** and **c***

I: $+0·58068x-0·62280y+0·52434z=0$

II: $+0·58173x-0·61904y+0·52761z=0$

Molecular symmetry

The molecules as found in the crystal structure have twofold symmetry to a very good approximation, the twofold axis connecting the centre of a molecule with the point midway between C(1) and C(2). This is apparent from Fig. 3 which is a projection along this axis. Thus a normal molecule in the crystal has the approximate symmetry $2/m$. If the conformation of one of the pairs of adjacent t-butyl groups is switched to the mirrored one with respect to the plane of the ring, the centrosymmetry is lost and a molecule with symmetry 222 is formed. The energy difference between the two molecular species will be small and in solution a mixture will probably be present. When the monoclinic crystals are formed from solution the molecules ought to assume a centrosymmetric form, but occasionally a molecule of the wrong symmetry may be built in, giving rise to disorder.

Packing

The packing is illustrated in Fig. 4. The shorter intermolecular distances have been indicated.

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