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The Crystal and Molecular Structure of the Heterohelicene 1-*tert*-Butylbenzo[*d*]naphtho[1,2-*d′*]benzo[1,2-*b*:4,3-*b′*]dithiophene at 110 K

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$C_{26}H_{20}S_2$, orthorhombic, *Pbca*, $a = 12{\cdot}970\ (5)$, $b = 25{\cdot}875\ (10)$, $c = 11{\cdot}660\ (5)$ Å. The weighted index *R* is 0·094 for 4538 reflections with $\sin\theta/\lambda \le 0{\cdot}81$ Å^{-1}. The molecule has a helical structure and exhibits considerable strain. In comparison with the non-substituted compound the introduction of the *tert*-butyl group clearly changes the geometry of the molecule. The presence of the *tert*-butyl group increases the shortest non-bonded C···C distance between the outer ends of the molecule from 2·91 to 3·095 Å.

Introduction

In the organic chemistry laboratory of this University, CD and ORD measurements are being performed on a series of 1-substituted heterohelicenes: the 1-*R*-benzo[*d*]naphtho[1,2-*d′*]benzo[1,2-*b*;4,3-*b′*]dithiophenes with $R = \mathrm{H}$, CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$. The aim of this research is to correlate changes in chiroptical properties of these compounds with changes in their helical geometry due to the varying size of the substituents *R*. The structure of the unsubstituted heterohelicene has already been determined (Stulen & Visser, 1969). The present paper describes the X-ray diffraction study of the heterohelicene with the largest substituent, $R = C(CH_3)_3$.

Compound abbreviations used in the paper are X = hexahelicene, DMX = 1,16-dimethylhexahelicene, Y = the heterohelicene mentioned above with $R = \mathrm{H}$, tBuY = the *tert*-butyl substituent of Y. The structural formula of the tBuY molecule is given in Fig. 1.

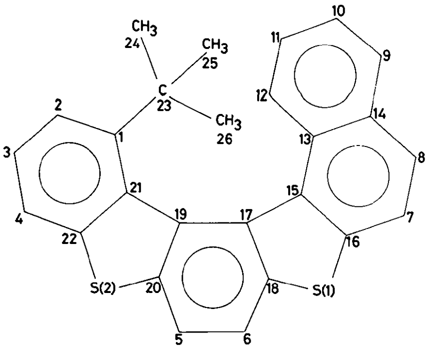

Fig. 1. Structural formula of 1-*tert*-butylbenzo[*d*]naphtho[1,2-*d′*]-benzo[1,2-*b*:4,3-*b′*]dithiophene (tBu*Y*) and numbering scheme.

Experimental

The compound tBuY was synthesized according to the method described for the unsubstituted heterohelicene (Groen, Schadenberg & Wijnberg, 1971). Good crystals were obtained by recrystallization from methylcyclohexane. Weissenberg photographs of the zero and first layer lines about the three axes showed the symmetry relations $I(hkl) = I(\bar{h}kl) = I(h\bar{k}l) = I(hk\bar{l}) = I(\bar{h}\bar{k}\bar{l})$ and the systematic absences $0kl$ for $k \ne 2n$, $h0l$ for $l \ne 2n$ and $hk0$ for $h \ne 2n$. For the measurement of the cell dimensions and the intensities an automated Enraf–Nonius CAD-4 diffractometer was used. All measurements were made at 110 K by cooling the crystal by a stream of cold nitrogen gas (van Bolhuis, 1971). The cell dimensions were found by minimizing the function $D = \Sigma_j\,[\theta_j(\mathrm{calc.}) - \theta_j(\mathrm{obs.})]^2$ for 15 independent reflections. The crystallographic data are given in Table 1. Intensities were collected by the $\theta/2\theta$ scan technique with Zr-filtered Mo radiation. The intensities of the three reference reflections measured at regular intervals did not show systematic variation with time. Two crystals were used; the two sets of intensities were put on the same scale with 70 reflections measured for both crystals. Owing to the use of an incorrect code the reflections $0kl$ for $l \ne 2n$ were not collected, whereas the reflections $h0l$ with $l \ne 2n$ were measured in the usual way. The intensities of 4680 independent reflections with $|F| \ge 3\sigma_c(|F|)$ and up to $\sin\theta/\lambda = 0{\cdot}81$ Å^{-1} were obtained. Among these

Table 1. *Crystal data*

$C_{26}H_{20}S_2$, FW 396·55, $F(000) = 208$; orthorhombic, *Pbca*, $a = 12{\cdot}970\ (5)$, $b = 25{\cdot}875\ (10)$, $c = 11{\cdot}660\ (5)$ Å, $D_m(293\ \mathrm{K}) = 1{\cdot}31$, $Z = 8$, $D_x(110\ \mathrm{K}) = 1{\cdot}35$ g cm^{-3}; $\mu(\mathrm{Mo}) = 2{\cdot}76$ cm^{-1}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å.

reflections were 18 $h0l$ with $l \neq 2n$ which on the basis of counting statistics were classified as (weakly) observed. During structure refinement 124 reflections with inaccurate intensities due to disorientation of the crystal and the 18 'observed' $h0l$ reflections with $l \neq 2n$ were not considered. The intensities were corrected for Lorentz and polarization effects in the usual way; no correction for absorption was made.

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971), using 475 reflections with $E > 1\cdot9$. The phase set with the highest combined figure of merit gave the positions of all non-hydrogen atoms on the E map. The positional and anisotropic thermal parameters of the non-hydrogen atoms and the isotropic temperature factors of the H atoms were refined with a full-matrix least-squares program. The positional parameters of the H atoms were constrained at geometrically reasonable positions with C—H = 1·08 Å. The weighting scheme $w = [\sigma_c^2(F_o) + 0\cdot0004F_o^2]^{-1}$ was applied. The residual $R_w\{= [\Sigma\, w(F_o - kF_c)^2/\Sigma\, wF_o^2]^{1/2}\}$ reduced to 0·094 for the 4538 reflections considered during refinement. The coordinates of the non-hydrogen atoms are listed in Table 2.* For the calculations the set of programs of the XRAY system (1973) was used.

Table 2. *Final coordinates (fractional, ×10⁵) with estimated standard deviations in parentheses*

For numbering see Fig. 1.

	x	y	z
S(1)	13203 (8)	44431 (5)	14194 (10)
S(2)	3769 (9)	47527 (4)	−37206 (10)
C(1)	−6315 (29)	34009 (15)	−25873 (34)
C(2)	−13546 (31)	32723 (15)	−34273 (35)
C(3)	−16253 (32)	35926 (27)	−43301 (37)
C(4)	−11009 (32)	40582 (17)	−44876 (38)
C(5)	15966 (31)	49577 (18)	−18180 (43)
C(6)	18394 (30)	48719 (17)	−6970 (45)
C(7)	−2671 (33)	38928 (16)	24686 (37)
C(8)	−12068 (35)	36548 (16)	23874 (37)
C(9)	−27671 (31)	34274 (17)	12971 (39)
C(10)	−33465 (33)	34512 (18)	3142 (42)
C(11)	−29458 (31)	36987 (16)	−6751 (40)
C(12)	−19518 (30)	38944 (15)	−6670 (36)
C(13)	−13143 (31)	38443 (14)	3063 (35)
C(14)	−17503 (30)	36345 (15)	13307 (38)
C(15)	−2692 (29)	40335 (15)	3598 (33)
C(16)	1816 (30)	40837 (16)	14386 (38)
C(17)	3864 (30)	42507 (15)	−5416 (35)
C(18)	12136 (30)	45348 (15)	−635 (40)
C(19)	3173 (29)	42411 (14)	−17665 (36)
C(20)	8279 (31)	46488 (16)	−23362 (40)
C(21)	−2633 (29)	39214 (15)	−25993 (35)
C(22)	−4164 (30)	42057 (15)	−36314 (36)
C(23)	−1810 (30)	29405 (15)	−18903 (38)
C(24)	2504 (35)	25577 (17)	−28021 (40)
C(25)	−10098 (34)	26535 (15)	−11800 (40)
C(26)	7335 (30)	30735 (15)	−11083 (39)

Discussion

A stereo picture showing the helical structure of the tBuY molecule is given in Fig. 2, and the numbering scheme in Fig. 1. Geometrical data are listed in Fig. 3 and in Tables 3 and 4. In Table 5 torsional angles in tBuY are compared with those in the corresponding unsubstituted heterohelicene Y and in the hexahelicenes X and DMX. It can be seen that introduction of substituents significantly changes the geometry of the helix by steric interaction. In the unsubstituted (hetero) helicene principal twisting occurs about the central bonds C(15)—C(17) and C(17)—C(19), whereas introduction of substituents increases the twist in bonds close to the substituted C atoms. Further it is interesting to note that the mean twist increases largely by introduction of two substituents, two methyl groups, in the helicene X. A smaller increase is observed by introduction of one substituent, even as large as a *tert*-butyl group, in the heterohelicene Y. The change in

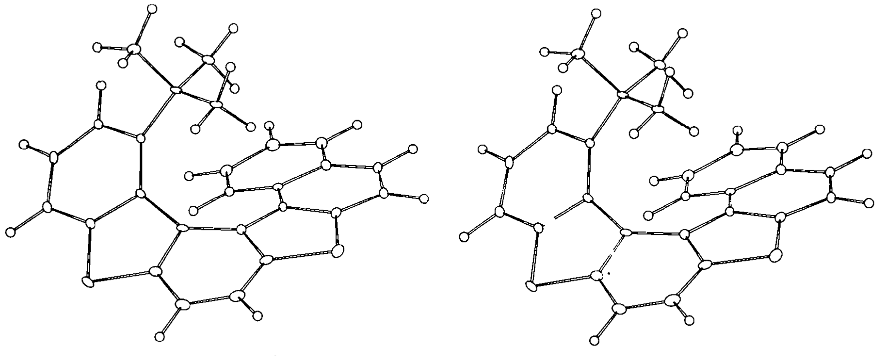

Fig. 2. Stereo picture of the tBuY molecule.

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* A list of structure factors and tables of the anisotropic thermal parameters of the heavy atoms and the final parameters of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33121 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

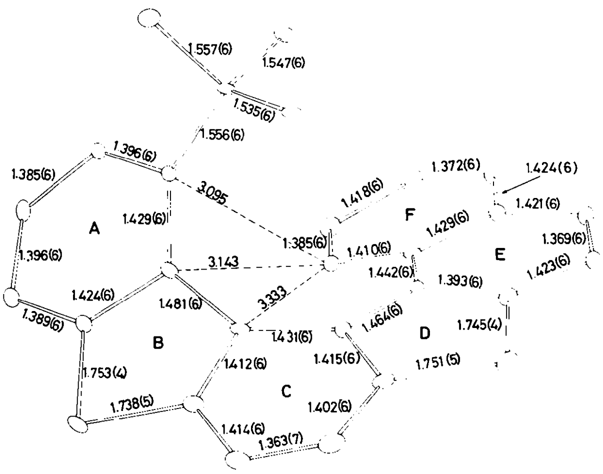

Fig. 3. Bond lengths and short non-bonded distances (Å).

Table 3. *Bond angles (°) for non-hydrogen atoms with estimated standard deviations in parentheses*

C(24)–C(23)–C(25)	108·1 (3)	C(7)–C(16)–S(1)	122·8 (3)
C(24)–C(23)–C(1)	105·4 (3)	C(7)–C(16)–C(15)	123·9 (4)
C(25)–C(23)–C(1)	112·7 (3)	C(8)–C(7)–C(16)	117·5 (4)
C(26)–C(23)–C(25)	109·1 (4)	C(14)–C(8)–C(7)	121·2 (4)
C(26)–C(23)–C(24)	105·7 (3)	C(13)–C(14)–C(8)	121·0 (4)
C(26)–C(23)–C(1)	115·4 (3)	C(9)–C(14)–C(8)	119·8 (4)
C(2)–C(1)–C(23)	115·9 (3)	C(9)–C(14)–C(13)	119·1 (4)
C(21)–C(1)–C(23)	127·0 (3)	C(10)–C(9)–C(14)	120·9 (4)
C(21)–C(1)–C(2)	116·2 (4)	C(11)–C(10)–C(9)	119·9 (4)
C(3)–C(2)–C(1)	124·1 (4)	C(12)–C(11)–C(10)	120·0 (4)
C(4)–C(3)–C(2)	119·5 (4)	C(13)–C(12)–C(11)	121·2 (4)
C(22)–C(4)–C(3)	117·0 (4)	C(14)–C(13)–C(12)	118·4 (4)
S(2)–C(22)–C(4)	123·7 (3)	C(15)–C(13)–C(12)	123·7 (4)
C(21)–C(22)–C(4)	123·7 (4)	C(15)–C(13)–C(14)	117·7 (4)
S(2)–C(22)–C(21)	112·7 (3)	C(16)–C(15)–C(13)	117·7 (4)
C(20)–S(2)–C(22)	91·0 (2)	C(17)–C(15)–C(13)	130·2 (4)
C(19)–C(20)–S(2)	113·3 (3)	C(17)–C(15)–C(16)	111·6 (3)
C(5)–C(20)–S(2)	123·2 (3)	C(18)–C(17)–C(15)	110·9 (4)
C(5)–C(20)–C(19)	123·5 (4)	C(19)–C(17)–C(15)	132·3 (4)
C(6)–C(5)–C(20)	118·7 (4)	C(19)–C(17)–C(18)	116·7 (4)
C(18)–C(6)–C(5)	118·2 (4)	C(20)–C(19)–C(17)	115·3 (4)
C(17)–C(18)–C(6)	123·7 (4)	C(21)–C(19)–C(17)	134·1 (4)
S(1)–C(18)–C(6)	124·0 (3)	C(21)–C(19)–C(20)	110·3 (4)
S(1)–C(18)–C(17)	112·2 (3)	C(22)–C(21)–C(19)	109·7 (3)
C(16)–S(1)–C(18)	91·0 (2)	C(1)–C(21)–C(19)	133·6 (4)
C(15)–C(16)–S(1)	113·1 (3)	C(1)–C(21)–C(22)	116·6 (4)

molecular geometry on substitution is also clearly shown in Table 6 where the angles between the plane normals for the heterohelicenes *Y* and tBu*Y* are listed. Owing to the presence of the *tert*-butyl group the short intramolecular distance between the outer ends C(1) and C(12) of the molecule increases from 2·91 Å in *Y* to 3·095 Å in tBu*Y*.

The present molecule tBu*Y* shows considerable strain. For the naphthalene part (rings *E* and *F* in Fig. 3) the strain is relatively small, as can be inferred from the relatively small deviations of the atoms forming the rings from their respective planes (Table 4) and from the relatively small torsional angles at bonds C(12)–C(13) and C(13)–C(15). The feature that bonds of the type C(11)–C(12) and angles of the type C(12)–C(13)–C(14) tend to be relatively small is also observed in naphthalene (Cruickshank, 1957).

Because of the presence of short 'inner-core' non-bonded distances (see Fig. 3) the inner part of the tBu*Y* molecule is stretched out and the outer part is compressed. This causes large C–C bond lengths and valence angles at the 'inner core' and small C–C bond lengths and angles at the periphery. For instance, the angles C(22)–S(2)–C(20) and C(18)–S(1)–C(16) (Table 3) are smaller than the C–S–C angles in thiophene (92·2°; Bak, Christensen, Hansen-Nygaard

Table 5. *Torsional angles (°) in some (hetero) helicenes*

X = hexahelicene; S in Fig. 1 replaced by C=C (de Rango, Tsoucaris, Declercq, Germain & Putzeys, 1973).
DM*X* = 1,16-dimethylhexahelicene; C(1) and C(12) each bear a methyl substituent (van den Hark & Noordik, 1973).
Y = benzo[*d*]naphtho[1,2-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (Stulen & Visser, 1969).
tBu*Y* = 1-*tert*-butylbenzo[*d*]naphtho[1,2-*d*′]benzo[1,2-*b*:4,3-*b*′]-dithiophene.

	X	DM*X*	*Y*	tBu*Y*
C(23)–C(1)–C(21)–C(19)	1·5	14·2	–	25·9
C(1)–C(21)–C(19)–C(17)	11·2	31·4	6·5	29·6
C(21)–C(19)–C(17)–C(15)	30·0	23·0	19·1	17·2
C(19)–C(17)–C(15)–C(13)	30·3	23·0	21·6	16·4
C(17)–C(15)–C(13)–C(12)	15·2	31·4	11·9	7·7
C(15)–C(13)–C(12)–H(C12)	3·5	14·2	–	0·7
Mean	15·3	22·9	14·8	16·2

Table 4. *Least-squares planes*

Columns: (1) lettering of planes; (2) atoms constituting the plane; (3) and (4) r.m.s. and maximum deviations (Å) of these atoms from the plane, with, in parentheses, the number of the atom for which $|\Delta|$ is maximal; (5)–(8) coefficients of the equation $pX + qY + rZ = d$ (Å), where *X*, *Y* and *Z* are orthonormal axes along **a**, **b** and **c**.

Plane	Atoms	Δ(r.m.s.)	$|\Delta$(max.)$|$	*p*	*q*	*r*	*d*
A	C(1), C(2), C(3), C(4), C(22), C(21)	0·073	0·107 (21)	−0·7563	0·4135	0·5069	2·8103
B	S(2), C(20), C(19), C(21), C(22)	0·080	0·098 (19)	−0·7697	0·5447	0·3330	4·8767
C	C(5), C(6), C(18), C(17), C(19), C(20)	0·085	0·123 (19)	−0·6799	0·7090	0·1872	7·2383
D	C(18), S(1), C(16), C(15), C(17)	0·046	0·061 (17)	−0·5320	0·8385	0·1174	8·9433
E	C(15), C(16), C(7), C(8), C(14), C(13)	0·042	0·062 (15)	−0·4130	0·8950	0·1686	9·6171
F	C(13), C(14), C(9), C(10), C(11), C(12)	0·028	0·042 (13)	−0·3476	0·8881	0·3007	9·5759

Table 6. *Acute angles φ (°) between plane normals for compounds Y and* tBu*Y*

For definition of planes see Fig. 3 and Table 4.

Angle	*Y*	tBu*Y*
$A \wedge B$	5·0	12·5
$B \wedge C$	19·9	13·6
$C \wedge D$	9·3	12·0
$D \wedge E$	18·4	8·1
$E \wedge F$	11·1	8·5
$\langle\varphi\rangle$	12·7	10·9

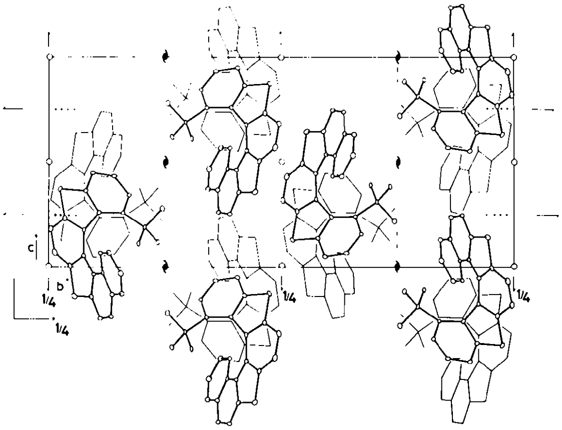

Fig. 4. The structure of tBu*Y* seen along **a**.

& Rastrup-Andersen, 1961) and in dibenzothiophene (91·5°; Schaffrin & Trotter, 1970). Bond C(17)—C(19) is longer than C(5)—C(6), whereas the lengths of these bonds are larger and smaller respectively than the value of 1·393 Å observed for the C—C bonds in solid benzene at −135 °C (Bacon, Curry & Wilson, 1964). The C—S bonds are considerably longer than in thiophene (1·714 Å), slightly longer than in dibenzothiophene (1·740 Å) and shorter than in *N*-(*p*-bromophenyl)phenothiazine (1·762 Å; Chu & Yang, 1977). In the *tert*-butyl group, which forms a crowded part of the molecule, all bonds are longer than in aliphatic hydrocarbons, such as cyclohexane (1·523 Å; Kahn, Fourme, André & Renaud, 1973), whereas C(1)—C(23) which connects the group with ring *A* is considerably longer than the value of 1·508 Å calculated by Visser (1969) and Visser & Vos (1971) for the weighted average length of C(aromatic C_6 ring)—CH_3 bonds found in different compounds.

The packing of the molecules is shown in Fig. 4. There are no intermolecular distances shorter than the sum of the relevant van der Waals radii.

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