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Benzocyclobutadienes.
4.* 1,2-Di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene

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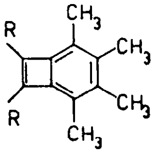
Abstract

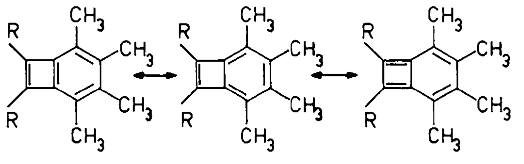
$C_{20}H_{30}$ is orthorhombic, space group $P2_12_12_1$, with a = 10·056 (1), b = 10·905 (2), c = 16·218 (2) Å, Z = 4. Final R = 0·051 for 3147 independent reflections. The central benzocyclobutadiene skeleton is planar and shows bond-length alternations in accordance with the Kekulé structure:



Whereas electronic interactions between the alkyl substituents and the benzocyclobutadiene moiety are minimized, the steric interactions between these substituents cause a considerable strain in the molecule. In comparison with the calculated geometry of the parent compound, C(1)—C(4) and C(2)—C(3) within the four-membered ring are stretched by 0·04 Å on account of these repulsions.

Introduction

Although the parent cyclobutadiene molecule was isolated in 1965 (Emerson, Watts & Pettit, 1965), progress in benzocyclobutadiene chemistry was much slower and the first well characterized benzocyclobutadiene (1) (R = Ph) was reported by Straub (1974).



(1*A*) (1*B*) (1*C*)

The compound (1) with R = *tert*-butyl is remarkably stable at room temperature in the crystalline state (Straub, 1976) and in a preliminary communication (Winter & Straub, 1978) we have reported our X-ray results on this derivative. The observed bond lengths in (1) rule out any noticeable participation of the resonance structure (1*C*) and the benzocyclobutadiene ground state is accordingly best described in terms of the two resonance structures (1*A*) and (1*B*). The distribution of bond lengths in the six-membered ring suggests a predominance of resonance structure (1*B*).

Despite the good quality of the crystals, R in our first communication was rather high by current standards (0·092), probably because of the use of Mo radiation for data collection. Therefore, we decided to recollect the intensities with Cu radiation and we give here an account of our final results.

Experimental

Large, slightly yellow crystals were formed from ethanol under nitrogen (m.p. 398–400 K). Precession photographs revealed orthorhombic symmetry and systematically extinct reflections which correspond to the space group $P2_12_12_1$. For the determination of the cell constants (least-squares refinement of 25 strong high-angle reflections) and for data collection we used three different crystals. Two of them were measured with Mo $K\alpha$ radiation and the third with Cu $K\alpha$ radiation. The crystal data and data collection parameters are summarized in Table 1. All data collection was performed on the same Nonius CAD-4 instrument.

The phase problem was solved with the first data set (Mo $K\alpha$) and the *TANG* program for non-centrosymmetric structures, which is part of *SHELX* 76 (Sheldrick, 1976). A suitable starting set could be developed for 282 phases by multisolution tangent refinement. The best set of phases afforded an E map which showed all non-H atoms. After full-matrix least-squares refinement with isotropic and later anisotropic temperature factors, a difference synthesis revealed the coordinates of the H atoms. They were

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* Part 1: Winter & Straub (1978); part 2: Straub, Döring & Winter (1979); part 3: Butters, Toda & Winter (1980).

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refined with a common isotropic temperature factor. The final refinement results are summarized in Table 1. The refinements were considered complete when shifts/e.s.d.'s were <0·3, the difference map showed no significant peaks and when the weighting scheme afforded the most flat analysis of variance.

After completion of the structure determination with the first data set (Mo $K\alpha$), R seemed relatively high, because the structure was of medium size and there was no disorder in the crystal. With a second crystal of comparable size we obtained a similar R after data collection with Mo $K\alpha$ radiation and, within the limits of errors, identical atomic parameters.

As can be seen in Table 1, there are only about half of the reflections with $I \geq 2\sigma(I)$ in the usual 2θ range. For the second crystal, for example, 750 reflections had intensities between $2\sigma(I)$ and $3\sigma(I)$. We suggested that, for this type of compound, the ratio peak/background was too unfavourable with Mo radiation. After a Cu tube had been mounted on the diffractometer, we collected a third data set and the improvement was obvious: although the maximum scan time per reflection was only a quarter to a third in comparison to the earlier Mo data sets, the number of reflections with $I \geq 2\sigma(I)$ was twice as large and the final R was considerably lower (Table 1). Nevertheless, five strong low-angle reflections (110, 101, 011, 012 and 022)

Table 1. *Crystal data and experimental and refinement parameters*

Crystal data			
Crystal No.	1	2	3
Formula		$C_{20}H_{30}$	
M_r		270·46	
Crystal system		Orthorhombic	
Space group		$P2_12_12_1$	
a (Å)	10·042 (3)	10·047 (4)	10·056 (1)
b (Å)	10·875 (4)	10·895 (4)	10·905 (2)
c (Å)	16·155 (5)	16·212 (6)	16·218 (2)
V (Å^3)	1764·2	1774·6	1778·4
Z		4	
μ(mm^{-1})	0·03	0·03	0·35
Radiation (graphite monochromator)	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
Data collection			
Crystal size (mm)	0·43 × 0·38 × 0·35 (sealed in a Lindemann capillary)	0·42 × 0·31 × 0·26	0·52 × 0·45 × 0·31
Scan mode	ω/θ	ω/θ	ω/θ
Scan width $\Delta\omega$ (°)	0·8 + 0·35 tan θ	0·7 + 0·35 tan θ	0·9 + 0·14 tan θ
Maximum scan time (s)	150	120	40
2θ range (°)	5–62	5–64	5–140
Number of measured reflections	3201	3440	3668
Number of independent reflections with $I \geq 2\sigma(I)$	1616	1807	3152
Final refinement			
R	0·092	0·090	0·051
R_G ($R_G = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$)	0·096	0·077	0·049
Number of reflections used	1616	1807	3147
Weighting scheme	$0{\cdot}111/\sigma^2(F_o) + 0{\cdot}0141F_o^2$	Unit weights	Unit weights

Table 2. *Positional parameters* (×10^4 *for non-*H *atoms*; ×10^3 *for* H *atoms*) *and equivalent isotropic temperature factors for the non-*H *atoms* (×10^4) *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11}.U_{22}.U_{33})^{1/3}.$$

	x	y	z	U_{eq} (Å^2)		x	y	z
C(1)	−286 (2)	6216 (2)	4206 (1)	469 (12)	H(103)	470 (5)	539 (4)	229 (3)
C(2)	−68 (3)	6984 (2)	3560 (1)	531 (14)	H(111)	505 (5)	400 (4)	381 (3)
C(3)	1342 (3)	6484 (2)	3444 (1)	469 (12)	H(112)	392 (4)	313 (4)	414 (3)
C(4)	1114 (2)	5675 (2)	4112 (1)	431 (11)	H(113)	468 (4)	407 (4)	470 (3)
C(5)	2034 (2)	4855 (2)	4380 (1)	504 (13)	H(121)	82 (5)	411 (4)	547 (3)
C(6)	3274 (2)	4854 (2)	3942 (1)	586 (15)	H(122)	270 (5)	414 (4)	551 (3)
C(7)	3500 (3)	5639 (3)	3294 (2)	610 (15)	H(123)	180 (4)	313 (4)	491 (3)
C(8)	2498 (3)	6501 (2)	3025 (1)	554 (15)	H(141)	−246 (4)	426 (4)	505 (3)
C(9)	2780 (5)	7375 (4)	2311 (2)	914 (26)	H(142)	−85 (4)	395 (4)	470 (3)
C(10)	4816 (4)	5615 (4)	2830 (2)	929 (26)	H(143)	−218 (5)	440 (4)	414 (3)
C(11)	4325 (4)	3937 (4)	4203 (3)	938 (25)	H(151)	−133 (4)	582 (4)	619 (3)
C(12)	1821 (4)	3956 (3)	5084 (2)	753 (20)	H(152)	−50 (4)	712 (4)	577 (3)
C(13)	−1313 (3)	5865 (2)	4838 (2)	564 (14)	H(153)	35 (5)	575 (4)	576 (3)
C(14)	−1648 (4)	4495 (3)	4708 (2)	777 (20)	H(161)	−324 (4)	630 (4)	421 (3)
C(15)	−711 (4)	6087 (4)	5700 (2)	759 (20)	H(162)	−252 (4)	754 (5)	497 (3)
C(16)	−2643 (3)	6571 (4)	4795 (3)	852 (22)	H(163)	−335 (4)	633 (4)	521 (3)
C(17)	−740 (3)	7975 (3)	3050 (2)	758 (18)	H(181)	−22 (5)	985 (4)	270 (3)
C(18)	120 (5)	9150 (3)	3117 (3)	910 (26)	H(182)	112 (5)	898 (4)	298 (3)
C(19)	−797 (5)	7532 (4)	2153 (2)	1031 (29)	H(183)	−8 (4)	951 (4)	371 (3)
C(20)	−2166 (5)	8315 (5)	3330 (4)	1191 (35)	H(191)	−121 (4)	828 (4)	182 (3)
H(91)	353 (4)	726 (4)	205 (3)		H(192)	−147 (4)	695 (4)	212 (3)
H(92)	286 (5)	824 (4)	240 (3)		H(193)	22 (5)	728 (4)	191 (3)
H(93)	226 (4)	698 (4)	186 (3)		H(201)	−290 (4)	749 (4)	316 (3)
H(101)	559 (5)	521 (4)	312 (3)		H(202)	−238 (4)	893 (4)	287 (3)
H(102)	520 (5)	655 (4)	269 (3)		H(203)	−210 (5)	867 (4)	415 (3)

showed strong evidence of extinction and, in the final refinement cycles, we excluded these reflections.

We believe that our experiments show the superiority of Cu radiation with pure organic compounds and the subsequent tables and discussions refer to these results.

Scattering factors were taken from Cromer & Mann (1968). All calculations were performed on a Telefunken TR 440 computer at the Zentrum für Datenverarbeitung der Universität Tübingen, with *SHELX*, *XANADU* (P. Roberts & G. M. Sheldrick) and *PLUTO* (S. Motherwell).

Table 2 gives the atomic coordinates, Table 3 the bond lengths, Table 4 the bond angles and Fig. 1 illustrates the structure and atom numbering.*

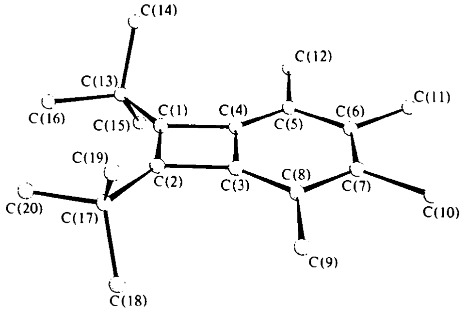

Fig. 1. Molecular structure and atom numbering.

Table 5. *Deviations* (Å) *from the least-squares plane through the central benzocyclobutadiene moiety*

Equation: $0\cdot3585x + 0\cdot6853y + 0\cdot6339z - 8\cdot8648 = 0$

C(1)*	0·002	C(11)	−0·042
C(2)*	−0·009	C(12)	−0·026
C(3)*	0·005	C(13)	0·018
C(4)*	0·005	C(14)	−1·260
C(5)*	−0·000	C(15)	1·287
C(6)*	−0·005	C(16)	0·022
C(7)*	−0·002	C(17)	−0·036
C(8)*	0·004	C(18)	1·220
C(9)	0·025	C(19)	−1·310
C(10)	−0·023	C(20)	−0·009

Asterisks denote atoms used to define the mean plane; e.s.d.'s for the distances ~0·003 Å.

Table 3. *Bond lengths* (Å) *between non*-H *atoms with e.s.d.'s in parentheses*

C(1)–C(2)	1·359 (3)	C(6)–C(11)	1·516 (4)
C(1)–C(4)	1·534 (3)	C(7)–C(8)	1·446 (4)
C(1)–C(13)	1·504 (3)	C(7)–C(10)	1·523 (4)
C(2)–C(3)	1·531 (3)	C(8)–C(9)	1·526 (4)
C(2)–C(17)	1·520 (3)	C(13)–C(14)	1·546 (4)
C(3)–C(4)	1·416 (3)	C(13)–C(15)	1·543 (4)
C(3)–C(8)	1·347 (3)	C(13)–C(16)	1·545 (4)
C(4)–C(5)	1·358 (3)	C(17)–C(18)	1·549 (5)
C(5)–C(6)	1·435 (3)	C(17)–C(19)	1·534 (5)
C(5)–C(12)	1·520 (4)	C(17)–C(20)	1·550 (5)
C(6)–C(7)	1·373 (4)		

Table 4. *Bond angles* (°) *between non*-H *atoms with e.s.d.'s in parentheses*

C(2)–C(1)–C(4)	90·7 (2)	C(6)–C(7)–C(8)	121·4 (2)
C(2)–C(1)–C(13)	142·4 (2)	C(6)–C(7)–C(10)	120·8 (3)
C(4)–C(1)–C(13)	126·9 (2)	C(8)–C(7)–C(10)	117·8 (3)
C(1)–C(2)–C(3)	91·4 (2)	C(7)–C(8)–C(3)	116·1 (2)
C(1)–C(2)–C(17)	141·8 (2)	C(7)–C(8)–C(9)	120·4 (3)
C(3)–C(2)–C(17)	126·7 (2)	C(3)–C(8)–C(9)	123·5 (3)
C(2)–C(3)–C(4)	88·7 (2)	C(1)–C(13)–C(14)	107·6 (2)
C(2)–C(3)–C(8)	148·9 (2)	C(1)–C(13)–C(15)	107·9 (2)
C(4)–C(3)–C(8)	122·4 (2)	C(1)–C(13)–C(16)	115·9 (2)
C(1)–C(4)–C(3)	89·2 (2)	C(14)–C(13)–C(15)	111·1 (3)
C(1)–C(4)–C(5)	147·8 (2)	C(14)–C(13)–C(16)	106·7 (3)
C(3)–C(4)–C(5)	123·0 (2)	C(15)–C(13)–C(16)	107·6 (3)
C(4)–C(5)–C(6)	115·7 (2)	C(2)–C(17)–C(18)	107·6 (2)
C(4)–C(5)–C(12)	124·7 (2)	C(2)–C(17)–C(19)	108·0 (2)
C(6)–C(5)–C(12)	119·6 (2)	C(2)–C(17)–C(20)	115·0 (2)
C(5)–C(6)–C(7)	121·5 (2)	C(18)–C(17)–C(19)	110·4 (3)
C(5)–C(6)–C(11)	117·9 (3)	C(18)–C(17)–C(20)	107·4 (3)
C(7)–C(6)–C(11)	120·6 (3)	C(19)–C(17)–C(20)	108·6 (3)

Discussion

The molecular structure gives a good insight into the electronic ground state of the benzocyclobutadiene molecule, because the electronic falsification by the substituents (alkyl groups here) is minimized and only steric effects have to be considered. There are two further crystal structure determinations of stable benzocyclobutadiene derivatives, which are substituted by phenyl and dicyanovinyl groups (Tsukada, Shimanouchi & Sasada, 1977, 1978). In the following discussion, they are called *S*I and *S*II respectively.

Within the error limits, the central benzocyclobutadiene moiety is planar and the C atoms bound directly to the bicyclic unit deviate maximally by only about ±0·04 Å from this plane (Table 5). This agrees well with *S*I and *S*II, although the deviation of the direct bound substituent C atoms from the cyclobutadiene plane is somewhat higher (up to 0·22 Å) in these cases.

The observed bond lengths rule out any noticeable participation of the resonance structure (1*C*). The shortest bond in the four-membered ring lies between C(1) and C(2) [1·359 (3) Å]. In *S*I and *S*II, the corresponding bonds have lengths of 1·35 (1) and 1·336 (5) Å. These distances agree well with our value and in regard to the probable stretching of this bond by the *tert*-butyl groups (see below), this bond is to be interpreted as an isolated double bond.

A similar influence of the bulky substituents can be seen on C(1)–C(4) and C(2)–C(3). They are elongated to 1·534 (3) and 1·531 (3) Å in comparison to the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35902 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

usual single bonds of sp^2-hybridized C atoms (also observed in *S*I and *S*II).

The remaining bonds in the six-membered ring show distinct bond-length alternations in accordance with the Kekulé structure (1*B*), a phenomenon observed in *S*I which is even more pronounced in *S*II. These experimental results agree well with the calculated geometry of the benzocyclobutadiene parent compound (Dewar & Gleicher, 1965; Milun & Trinajstić, 1973). Of course, the calculated value of the corresponding C(1)–C(4) and C(2)–C(3) bonds (1·49 Å) deviates widely from the value in the present strained molecule (1·53 Å).

As depicted in Fig. 2, the central benzocyclobutadiene unit is surrounded by a girdle of alkyl substituents. The C(14), C(15) and the C(18), C(19) methyl groups show a nearly perfect staggered conformation with respect to the neighbouring C(12) and C(9) methyl groups. As a consequence, the remaining C(16) and C(20) methyl groups are forced into an eclipsed conformation. Excepting the four C(14), C(15), C(18), C(19) atoms of the *tert*-butyl groups, all other non-H atoms lie within ±0·04 Å of the aforementioned least-squares plane (Table 5). The repulsion between the C(16) and C(20) methyl groups leads to a considerable widening of the C(13)–C(1)–C(2) and C(17)–C(2)–C(1) angles (142°) at the four-membered ring, and to an additional widening of the tetrahedral angles at C(13) and C(17) (116 and 115°). The C(9) and C(12) methyl groups on the benzene ring are also affected by this repulsion, because C(3)–C(8)–C(9) and C(4)–C(5)–C(12) are widened to 123·5 (3) and 124·7 (3)°. Obviously, these two C(9) and C(12) methyl groups cause the nearly perfect C_{2v} symmetry of the non-H atoms, because they fix the positions of the *tert*-butyl groups.

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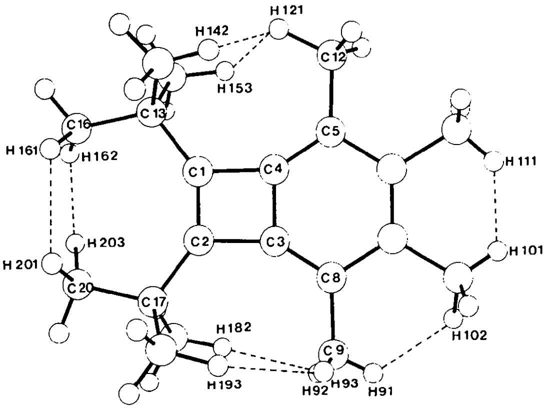

Fig. 2. Perspective view of the molecule, showing the repulsion between the alkyl groups. H atom contacts in the range of 2·0 ± 0·2 Å are marked with dashed lines.

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