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Tetrabenzotricyclo[5.5.0.$0^{2,8}$]dodeca-3,5,9,11-tetraene,* $C_{28}H_{20}$

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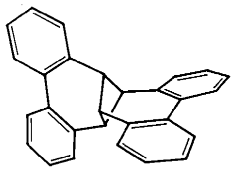
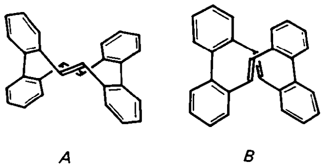
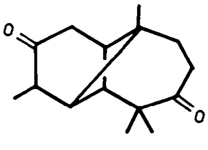
Abstract. $M_r = 356\cdot47$, orthorhombic, *Pbca*, $a = 12\cdot765\,(4)$, $b = 12\cdot905\,(3)$, $c = 22\cdot139\,(7)$ Å, $V = 3647\,(3)$ Å^3, $Z = 8$, $D_x = 1\cdot30$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0\cdot068$ mm^{-1}, $F(000) = 1504$, $T = 295$ K, $R = 0\cdot042$ for 2821 observed reflections. The central four-membered ring is puckered [30·3 (1)°]. The transannular C···C distances are 2·155 (2) Å. The seven-membered rings are strained with bond angles of 124·1 (1) and 125·7 (2)°. The biphenyl groups are twisted. The molecule shows only small deviations from $\bar{4}$ symmetry.



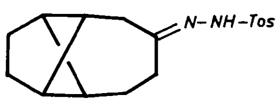
(1)



(2)



(3)



(4)

Introduction. Intramolecular thermal and photochemical [2+2]cycloadditions in 5-*trans*-15-*trans*-tetrabenzo-[*a,c,g,i*]cyclododecene (2) and its *cis–cis*- and *cis–trans*-isomers result in 1,2- and 1,3-substituted cyclobutane derivatives (Wittig & Skipka, 1975). The crystal structures of these olefins have been determined (Irngartinger, 1972, 1973*a,b*; Roberts & Kennard, 1973). Conformation *A* has been found in the crystal of (2). Photochemical intramolecular cycloaddition of (2) results in 1,2-substituted cyclobutane but thermal reaction by melting (2) at 583 K leads to a 1,3-substituted one, tetrabenzotricyclo[5.5.0.$0^{2,8}$]dodeca-3,5,9,11-tetraene (1) (Wittig & Skipka, 1975). This reaction starts probably from conformation *B* of (2). We now describe the crystal structure of (1) which is strained. Because of electronic 'through-bond' interactions *via* the cyclobutane ring (Gleiter, Haider, Spanget-Larsen & Bischof, 1983; Spanget-Larsen, Gleiter & Haider, 1983), the crystal structure of (1) is of additional interest.

Experimental. Crystal $0\cdot4 \times 0\cdot4 \times 0\cdot3$ mm, grown from ethyl acetate; CAD-4 diffractometer (Enraf–Nonius), cell dimensions from 2θ angles of 25 reflections ($16 < 2\theta < 33°$); 4387 data up to $2\theta = 56°$ (excluding systematic absences), $0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 29$, standard reflections $\bar{3}\bar{4}2$, $\bar{4}\bar{3}\bar{2}$ and 624 (variation of intensities less than 3%), 4387 unique reflections; Lorentz and polarization corrections applied; absorption and extinction effects neglected; 2821 intensities, $I > 3\sigma(I)$; structure solution by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); structure refined by full-matrix least squares on F^2 with anisotropic thermal parameters for C atoms. Positions of H atoms calculated according to geometrical requirements. H atoms refined isotropically. 333 variables, $R = 0\cdot042$, $wR = 0\cdot047$ for 2821 reflections, $w = 4F^2/\sigma^2(F^2) + (0\cdot03F^2)^2$; $S = 1\cdot89$; $\Delta/\sigma < 0\cdot05$, largest peak = 0·18 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974);

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* IUPAC name: heptacyclo[13.13.$0^{2,7}$.$0^{8,13}$.$0^{14,28}$.$0^{16,21}$.$0^{22,27}$]-octacosa-2(7),3,5,8(13),9,11,16(21),17,19,22(27),23,25-dodecaene.

0108-2701/85/071136-03$01.50

Enraf–Nonius *SDP* (Frenz, 1978) used on a PDP 11/44.

Discussion. Final atomic parameters are given in Table 1.* Chemically equivalent bond lengths and bond angles agree within the errors of determination. Therefore the averaged values together with their values of scatter are used in the discussion exclusively.

The central four-membered ring of (1) is puckered (Figs. 1 and 2). Since the four bond lengths and bond angles of this ring are not significantly different [1·552 (2) Å, 88·0 (1)°, Fig. 1 and Table 2], both angles of puckering are equal [30·3 (1)°, dihedral angle C(1), C(2), C(8)/C(1), C(7), C(8) and C(2), C(1), C(7)/C(2), C(8), C(7)]. The transannular C···C distances are 2·155 (2) Å. All these values are in good agreement with mean averaged values determined in other crystal structures of puckered cyclobutanes (Allen, 1984). In the structures of cyclobutanes (3) and (4) with two 1,3-bridges a stronger puckering has been found [(3): 35·0 and 35·9 (2)° (Ognyanov, Todorova, Dimitrov, Ladd, Irngartinger, Kurda & Rodewald, 1983); (4): 42·4 and 47·7 (2)° (Gleiter, Sander, Irngartinger & Lenz, 1982)] because there are shorter bridges.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C(1)	0·65016 (11)	0·06290 (10)	0·62739 (6)	317 (7)
C(2)	0·68373 (11)	0·17723 (10)	0·63799 (6)	305 (6)
C(3)	0·71865 (11)	0·20543 (10)	0·70078 (6)	326 (7)
C(4)	0·66168 (11)	0·18093 (11)	0·75375 (6)	348 (7)
C(5)	0·56834 (12)	0·11014 (11)	0·75716 (6)	346 (7)
C(6)	0·50860 (11)	0·07525 (11)	0·70733 (6)	334 (7)
C(7)	0·53648 (11)	0·09594 (11)	0·64263 (6)	329 (7)
C(8)	0·56794 (11)	0·20876 (10)	0·62687 (6)	309 (6)
C(9)	0·53774 (10)	0·23664 (10)	0·56337 (6)	309 (6)
C(10)	0·56244 (11)	0·17598 (11)	0·51215 (6)	312 (7)
C(11)	0·63281 (11)	0·08250 (11)	0·51187 (6)	323 (7)
C(12)	0·66872 (11)	0·02813 (10)	0·56350 (6)	314 (7)
C(13)	0·72912 (12)	−0·06083 (11)	0·55587 (6)	399 (8)
C(14)	0·75629 (14)	−0·09881 (12)	0·49969 (7)	492 (8)
C(15)	0·72582 (14)	−0·04439 (14)	0·44957 (7)	535 (9)
C(16)	0·66697 (13)	0·04455 (13)	0·45589 (6)	456 (8)
C(17)	0·51694 (13)	0·20709 (12)	0·45743 (6)	412 (8)
C(18)	0·45658 (13)	0·29519 (13)	0·45189 (6)	460 (8)
C(19)	0·43686 (13)	0·35615 (12)	0·50123 (7)	454 (8)
C(20)	0·47616 (12)	0·32513 (11)	0·55666 (6)	383 (7)
C(21)	0·42131 (12)	0·01303 (12)	0·71706 (7)	419 (8)
C(22)	0·38997 (13)	−0·01750 (12)	0·77409 (7)	464 (8)
C(23)	0·44848 (14)	0·01323 (13)	0·82262 (6)	489 (9)
C(24)	0·53574 (13)	0·07444 (13)	0·81403 (6)	445 (8)
C(25)	0·69678 (13)	0·22773 (14)	0·80748 (6)	490 (9)
C(26)	0·78527 (14)	0·28879 (14)	0·81034 (7)	560 (10)
C(27)	0·84333 (13)	0·30688 (13)	0·75938 (7)	501 (9)
C(28)	0·80859 (12)	0·26605 (12)	0·70535 (6)	392 (8)

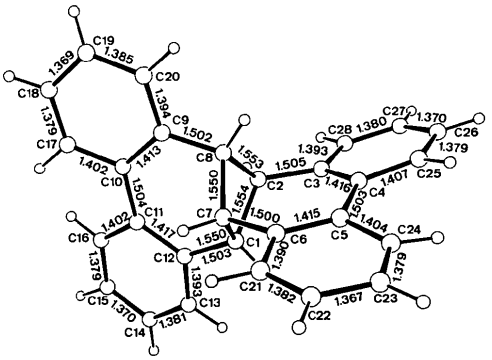

Fig. 1. Bond lengths (Å) of (1). The standard deviations are 0·001–0·002 Å.

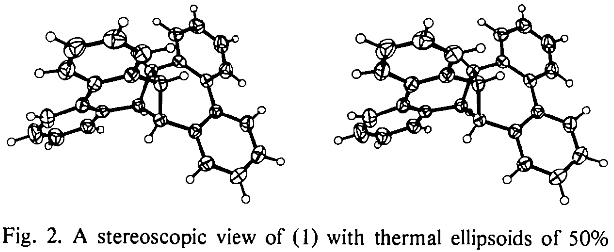

Fig. 2. A stereoscopic view of (1) with thermal ellipsoids of 50% probability (*ORTEP* plot; Johnson, 1970).

Table 2. *Bond angles of* (1) *and some torsion angles* (°)

C(2)–C(1)–C(7)	87·9 (1)	C(10)–C(9)–C(20)	119·6 (1)
C(2)–C(1)–C(12)	112·5 (1)	C(9)–C(10)–C(11)	125·5 (1)
C(7)–C(1)–C(12)	115·8 (1)	C(9)–C(10)–C(17)	116·2 (1)
C(1)–C(2)–C(3)	116·8 (1)	C(11)–C(10)–C(17)	118·3 (1)
C(1)–C(2)–C(8)	87·8 (1)	C(10)–C(11)–C(12)	125·9 (1)
C(3)–C(2)–C(8)	111·4 (1)	C(10)–C(11)–C(16)	118·0 (1)
C(2)–C(3)–C(4)	124·0 (1)	C(12)–C(11)–C(16)	116·1 (1)
C(2)–C(3)–C(28)	116·6 (1)	C(1)–C(12)–C(11)	124·1 (1)
C(4)–C(3)–C(28)	119·3 (1)	C(1)–C(12)–C(13)	116·6 (1)
C(3)–C(4)–C(5)	125·8 (1)	C(11)–C(12)–C(13)	119·3 (1)
C(3)–C(4)–C(25)	116·1 (1)	C(12)–C(13)–C(14)	122·7 (1)
C(5)–C(4)–C(25)	118·1 (1)	C(13)–C(14)–C(15)	118·4 (1)
C(4)–C(5)–C(6)	125·6 (1)	C(14)–C(15)–C(16)	120·0 (1)
C(4)–C(5)–C(24)	118·6 (1)	C(11)–C(16)–C(15)	123·4 (1)
C(6)–C(5)–C(24)	115·8 (1)	C(10)–C(17)–C(18)	123·0 (1)
C(5)–C(6)–C(7)	124·1 (1)	C(17)–C(18)–C(19)	120·4 (1)
C(5)–C(6)–C(21)	119·7 (1)	C(18)–C(19)–C(20)	118·3 (1)
C(7)–C(6)–C(21)	116·2 (1)	C(9)–C(20)–C(19)	122·4 (1)
C(1)–C(7)–C(6)	112·4 (1)	C(6)–C(21)–C(22)	122·6 (1)
C(1)–C(7)–C(8)	88·1 (1)	C(21)–C(22)–C(23)	118·5 (1)
C(6)–C(7)–C(8)	116·3 (1)	C(22)–C(23)–C(24)	119·9 (1)
C(2)–C(8)–C(7)	88·0 (1)	C(5)–C(24)–C(23)	123·5 (1)
C(2)–C(8)–C(9)	117·1 (1)	C(4)–C(25)–C(26)	123·0 (1)
C(7)–C(8)–C(9)	111·7 (1)	C(25)–C(26)–C(27)	120·2 (1)
C(8)–C(9)–C(10)	124·1 (1)	C(26)–C(27)–C(28)	118·4 (2)
C(8)–C(9)–C(20)	116·1 (1)	C(3)–C(28)–C(27)	122·8 (1)

C(1)–C(2)–C(8)–C(7)	21·3 (1)	C(3)–C(2)–C(8)–C(9)	149·9 (1)
C(1)–C(2)–C(3)–C(4)	−49·5 (2)	C(3)–C(4)–C(5)–C(6)	−14·9 (2)
C(1)–C(2)–C(8)–C(9)	−92·1 (1)	C(4)–C(3)–C(2)–C(8)	49·3 (2)
C(1)–C(7)–C(8)–C(2)	−21·4 (1)	C(4)–C(5)–C(6)–C(7)	6·3 (2)
C(1)–C(7)–C(8)–C(9)	97·1 (1)	C(5)–C(6)–C(7)–C(8)	−46·5 (2)
C(1)–C(7)–C(6)–C(5)	53·0 (2)	C(6)–C(7)–C(1)–C(12)	149·5 (1)
C(1)–C(12)–C(11)–C(10)	−6·5 (2)	C(6)–C(7)–C(8)–C(9)	−148·8 (1)
C(2)–C(1)–C(7)–C(6)	−96·5 (1)	C(7)–C(1)–C(2)–C(8)	−21·3 (1)
C(2)–C(1)–C(7)–C(8)	21·3 (1)	C(7)–C(1)–C(12)–C(11)	47·2 (2)
C(2)–C(1)–C(12)–C(11)	−51·8 (2)	C(7)–C(8)–C(9)–C(10)	−50·5 (2)
C(2)–C(3)–C(4)–C(5)	10·1 (2)	C(8)–C(2)–C(1)–C(12)	95·8 (1)
C(2)–C(8)–C(7)–C(6)	92·8 (1)	C(8)–C(7)–C(1)–C(12)	−92·7 (1)
C(2)–C(8)–C(9)–C(10)	48·7 (2)	C(8)–C(9)–C(10)–C(11)	−7·9 (2)
C(3)–C(2)–C(1)–C(7)	91·7 (1)	C(9)–C(10)–C(11)–C(12)	13·3 (2)
C(3)–C(2)–C(1)–C(12)	−151·2 (1)	C(16)–C(11)–C(10)–C(17)	13·2 (2)
C(3)–C(2)–C(8)–C(7)	−96·7 (1)	C(24)–C(5)–C(4)–C(25)	−14·8 (2)

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* Lists of structure factors, anisotropic thermal parameters and atomic parameters of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42158 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In (1) the rocking angles of the C atoms of the four-membered ring are smaller than unity due to fewer non-bonded repulsions between *trans*-vicinal substituents compared to the repulsion between *cis*-vicinal substituents [4·3 (4)° (Allen, 1984)].

As a result of the transannular distance 2·155 (2) Å in the cyclobutane, the seven-membered rings are strained. Both angles at the atoms C(3) and C(4) and the equivalent atoms exceed the angle at sp^2-C atoms of 120° significantly [124·1 (4) and 125·7 (2)°]. Therefore the biphenyl groups deviate from a linear arrangement as they do in the tetrabenzocyclododecene derivative (2) and its *cis–cis-* and *cis–trans*-isomers (Irngartinger, 1972, 1973*a,b*): the exocyclic bond angles at C(4), C(5), C(10) and C(11) [118·3 (3)°] are smaller than 120°. An angle of 169·9 (1) and 169·7 (1)° is given by the axes defined by the atoms C(4), C(27) and C(5), C(22) respectively and the corresponding axes in the second biphenyl group. The 1,4-distances C(16)···C(17) 2·841 (2) and C(24)···C(25) 2·857 (2) Å are much shorter than the corresponding distances C(3)···C(6) 3·167 (2) and C(9)···C(12) 3·168 (2) Å [van der Waals distance 3·4 Å (Pauling, 1976)].

In both biphenyl groups there are twists around the central bonds [C(3)–C(4)–C(5)–C(6) −14·9 (2), C(9)–C(10)–C(11)–C(12) 13·3 (2)°] with different sense of rotation, hence (1) is provided with a *meso*-conformation in the crystal and shows only small deviations from S_4 ($\bar{4}$) symmetry. These distortions bring about the different angles 112·0 (5) and 116·5 (6)° between the bonds from the aromatic rings to the cyclobutane system and the two adjacent bonds of the four-membered ring. The bond lengths [1·415 (2) Å; Fig. 1] between both substituted C atoms in the phenyl rings are the longest ones within the six-membered rings.

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