$C_{20}H_{14}N_2O_2$

C2	0.2255 (2)	0.7702 (5)	1.2483 (1)	5.81 (6)
C3	0.1242 (2)	0.8970 (4)	1.2016 (2)	6.14 (6)
C4	0.1033 (2)	0.8350 (4)	1.1193 (2)	5.42 (5)
C5	0.1857 (1)	0.6421 (3)	1.0796 (1)	3.96 (4)
C6	0.2893 (1)	0.5164 (3)	1.12609 (9)	3.49 (3)
C7	0.1730 (2)	0.5604 (4)	0.9949 (1)	4.75 (5)
C8	0.2579 (2)	0.3727 (4)	0.9630 (1)	4.25 (4)
C9	0.3601 (1)	0.2605 (3)	1.01407 (9)	3.32 (3)
C10	0.4523 (1)	0.0627 (3)	0.97855 (9)	3.57 (4)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.363 (2)	C10—C10′	1.319 (3)
N1—C6	1.355 (2)	N1—C9	1.328 (2)
C1—C2	1.358 (3)	C1—C6	1.414 (2)
C2—C3	1.397 (3)	C3—C4	1.360 (3)
C4—C5	1.410 (3)	C5—C6	1.411 (2)
C5—C7	1.412 (2)	C7—C8	1.355 (3)
C8—C9	1.413 (2)	C9—C10	1.459 (2)
O1—C1—C6	119.0 (2)	O1—C1—C2	120.8 (2)
C6—N1—C9	117.9 (1)	C2—C1—C6	120.2 (2)
N1—C9—C10	118.6 (1)	N1—C9—C8	121.7 (2)
C9—C10—C10′	124.4 (2)	C8—C9—C10	119.7 (1)
C10′—C10—H7	118.1 (8)	C9—C10—H7	117.4 (8)
O1—C1—C6—N1	−0.3 (2)	N1—C9—C10—C10′	2.9 (3)
C8—C9—C10—C10′	−177.1 (2)	C9—C10—C10′—C9′	180.0

Symmetry code: (′) $1 - x, -y, 2 - z$.

Non-H atoms were refined anisotropically and H atoms were refined isotropically.

Rigaku AFC-7R software was used for data collection, cell refinement and data reduction. The title structure was solved by direct methods using SAPI91 (Fan, 1991) and refined by expanded Fourier techniques using the full-matrix least-squares technique of DIRDIF92 (Beurskens et al., 1992). All calculations were performed using TEXSAN (Molecular Structure Corporation, 1992).

References

Bernstein, J. (1975). *Acta Cryst.* B31, 1268–1271.
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Boustra, J. A., Schouten, A. & Kroon, J. (1984). *Acta Cryst.* C40, 428–430.
Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
Finder, C., Newton, M. G. & Allinger, N. L. (1974). *Acta Cryst.* B30, 411–415.
Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Ogawa, K. (1993). *J. Synth. Org Chem. Jpn*, 34, 942–949.
Robertson, J. M. & White, J. G. (1944). *Nature*, 154, 605–606.
Tirado-Rives, J., Fronczek, F. R. & Gandour, R. D. (1985). *Acta Cryst.* C41, 1327–1329.
Wolfgang, H. & Mehmet, A. (1990). *Acta Cryst.* C46, 1157–1158.

Low-Temperature Triphenylmethane

Nora Veldman,[a] Anthony L. Spek,[a] Jacobus J. H. Schlotter,[b] Jan W. Zwikker[b] and Leonardus W. Jenneskens[b]

[a]*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and* [b]*Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Abstract

The crystal structure of triphenylmethane, $C_{19}H_{16}$, has been redetermined at 150 K. It confirms the previously reported room-temperature study [Riche & Pascard-Billy (1974). *Acta Cryst.* B30, 1874–1876], while correcting for the erroneously reported space group from $P2_12_12_1$ to $Pna2_1$. The structure contains two crystallographically independent triphenylmethane molecules, both with a propeller configuration. The deformations from ideal phenyl-ring geometry conform with those expected for rings having electron-releasing substituents.

Comment

Commercially available triphenylchloromethane contains some triphenylmethane as an impurity (capillary GC–MS) and has to be purified by recrystallization prior to use. Good quality crystals of triphenylmethane, (I), were obtained as a by-product. The room-temperature X-ray structure of this compound has been reported previously by Riche & Pascard-Billy (1974). Unfortunately, the space group was reported incorrectly as $P2_12_12_1$ rather than the correct $Pna2_1$ (see below), which was presumably used in the study. This error appears to have propagated into the Cambridge Structural Database (Allen, Kennard & Taylor, 1983; Version 5, October 1994), where additional errors were introduced in the coordinates of atoms C36 and C37 on the basis of the incorrect space group symmetry, resulting in nonsensical connectivity. The present low-temperature study clarified the case and confirms the previously reported structural results with improved precision.

(I)
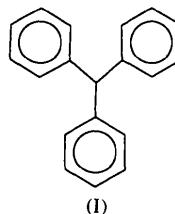
The asymmetric unit contains two crystallographically independent triphenylmethane molecules. They are related by an approximate non-crystallographic glide plane at $y = 0.517$, with a glide component of 0.175 in the a-axis direction. Both molecules have their phenyl rings in a propeller configuration, with cis-H—C_{sp^3}—C—C torsion angles of 54.9 (6), 34.8 (7) and 31.9 (6)°, and −50.0 (7), −39.5 (7) and −20.1 (7)°, for molecules 1 and 2, respectively. Such a configuration is similar to those observed in some of the polymorphs of the related triphenylphosphine oxide (Spek, 1987; Brock, Schweizer & Dunitz, 1985). All six phenyl rings show the characteristic electron-releasing substituent effect on the ring geometry (Domenicano, Vaciago & Coulson, 1975), with endocyclic α angles smaller than 120° [range 117.6 (4)–118.0 (4)°] and β angles larger than 120° [range 120.1 (4)–121.9 (5)°].

Fig. 2. Projection of the structure down the c axis, illustrating the packing and the pseudo-symmetry. Molecule 2 (C20–C38) is shown with filled C atoms.

Experimental

Crystals of the title compound were obtained by recrystallization of commercially available triphenylchloromethane (containing triphenylmethane as an impurity) from petroleum ether (boiling range 363–393 K; Hauser & Hudson, 1946).

Crystal data

$C_{19}H_{16}$	Mo $K\alpha$ radiation
$M_r = 244.34$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$Pna2_1$	reflections
$a = 25.4909$ (4) Å	$\theta = 10.1–13.9°$
$b = 14.5860$ (12) Å	$\mu = 0.07$ mm^{-1}
$c = 7.400$ (2) Å	$T = 150$ K
$V = 2751.4$ (8) Å^3	Block
$Z = 8$	0.75 × 0.63 × 0.25 mm
$D_x = 1.180$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4T/RA	$R_{int} = 0.0508$
diffractometer	$\theta_{max} = 25°$
$\omega/2\theta$ scans	$h = -26 \rightarrow 30$
Absorption correction:	$k = -17 \rightarrow 0$
none	$l = -8 \rightarrow 0$
4053 measured reflections	3 standard reflections
2633 independent reflections	frequency: 60 min
1539 observed reflections	intensity decay: 2%
$[I > 2\sigma(I)]$	

Refinement

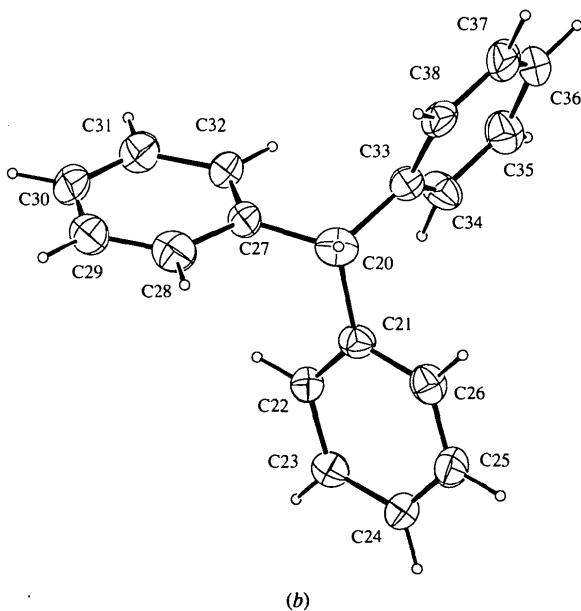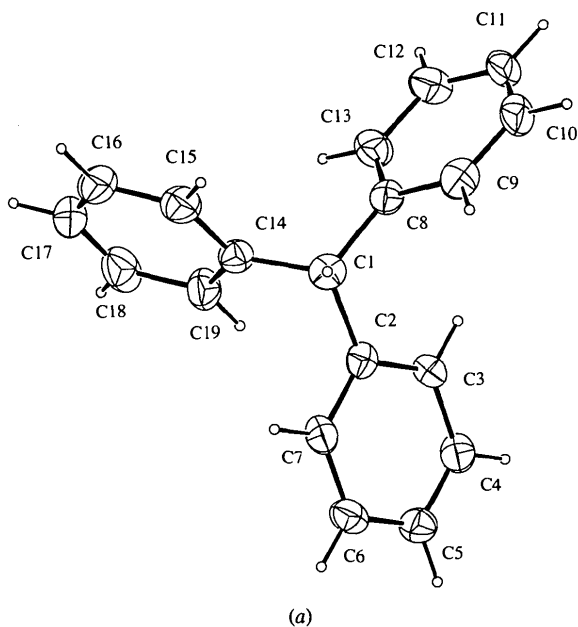|	
Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.054$	$\Delta\rho_{max} = 0.231$ e Å^{-3}
$wR = 0.129$	$\Delta\rho_{min} = -0.251$ e Å^{-3}

(a)

(b)

Fig. 1. Displacement ellipsoid plots (50% probability level) of the two crystallographically independent triphenylmethane molecules; (a) molecule 1 and (b) molecule 2.
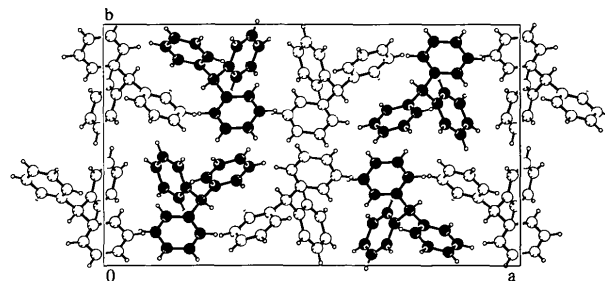
$C_{19}H_{16}$

$S = 0.971$
2631 reflections
343 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Molecule 1				
C1	0.0624 (2)	0.7729 (3)	0.3771 (6)	0.0287 (14)
C2	0.0266 (2)	0.8311 (3)	0.2590 (7)	0.0263 (14)
C3	−0.0275 (2)	0.8197 (3)	0.2496 (7)	0.0287 (14)
C4	−0.0576 (2)	0.8750 (3)	0.1389 (6)	0.0343 (17)
C5	−0.0352 (2)	0.9409 (3)	0.0341 (7)	0.0370 (17)
C6	0.0189 (2)	0.9532 (3)	0.0401 (6)	0.0350 (16)
C7	0.0493 (2)	0.8988 (3)	0.1511 (6)	0.0327 (17)
C8	0.0308 (2)	0.7126 (3)	0.5080 (6)	0.0283 (16)
C9	0.0121 (2)	0.7520 (3)	0.6684 (6)	0.0373 (17)
C10	−0.0191 (2)	0.7014 (4)	0.7843 (7)	0.0440 (19)
C11	−0.0316 (2)	0.6121 (4)	0.7458 (7)	0.0440 (19)
C12	−0.0122 (2)	0.5722 (3)	0.5901 (7)	0.0450 (17)
C13	0.0189 (2)	0.6228 (3)	0.4747 (7)	0.0377 (17)
C14	0.1011 (2)	0.7171 (3)	0.2701 (6)	0.0293 (16)
C15	0.1501 (2)	0.6961 (3)	0.3404 (7)	0.0397 (17)
C16	0.1851 (2)	0.6395 (4)	0.2488 (9)	0.052 (2)
C17	0.1704 (2)	0.6041 (4)	0.0829 (9)	0.054 (2)
C18	0.1228 (2)	0.6249 (3)	0.0078 (8)	0.0483 (19)
C19	0.0882 (2)	0.6810 (3)	0.0994 (7)	0.0377 (17)
Molecule 2				
C20	0.2348 (2)	0.2715 (3)	0.3806 (7)	0.0353 (17)
C21	0.2045 (2)	0.1999 (3)	0.2713 (7)	0.0307 (16)
C22	0.1504 (2)	0.2028 (3)	0.2529 (7)	0.0310 (16)
C23	0.1247 (2)	0.1394 (3)	0.1443 (7)	0.0357 (17)
C24	0.1523 (2)	0.0728 (3)	0.0557 (7)	0.0367 (17)
C25	0.2065 (2)	0.0692 (3)	0.0747 (7)	0.0407 (17)
C26	0.2315 (2)	0.1319 (3)	0.1807 (6)	0.0353 (17)
C27	0.1985 (2)	0.3253 (3)	0.5061 (6)	0.0310 (16)
C28	0.1811 (2)	0.2829 (3)	0.6657 (7)	0.0423 (17)
C29	0.1453 (2)	0.3251 (4)	0.7762 (7)	0.049 (2)
C30	0.1260 (2)	0.4102 (4)	0.7360 (8)	0.0517 (19)
C31	0.1429 (2)	0.4534 (3)	0.5800 (8)	0.0490 (19)
C32	0.1790 (2)	0.4109 (3)	0.4668 (7)	0.0350 (17)
C33	0.2679 (2)	0.3318 (3)	0.2592 (6)	0.0303 (16)
C34	0.2479 (2)	0.3648 (3)	0.0956 (7)	0.0380 (17)
C35	0.2778 (2)	0.4201 (3)	−0.0126 (7)	0.0407 (17)
C36	0.3280 (2)	0.4437 (3)	0.0350 (7)	0.048 (2)
C37	0.3489 (2)	0.4102 (4)	0.1914 (8)	0.048 (2)
C38	0.3191 (2)	0.3542 (3)	0.3041 (7)	0.0360 (17)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Molecule 1		Molecule 2	
C1—C2	1.522 (7)	C20—C21	1.530 (7)
C1—C8	1.536 (7)	C20—C27	1.528 (7)
C1—C14	1.504 (7)	C20—C33	1.514 (7)
C2—C3	1.391 (7)	C21—C22	1.386 (7)
C2—C7	1.396 (7)	C21—C26	1.381 (7)
C3—C4	1.382 (7)	C22—C23	1.389 (7)
C4—C5	1.361 (7)	C23—C24	1.367 (7)
C5—C6	1.391 (7)	C24—C25	1.390 (7)
C6—C7	1.380 (7)	C25—C26	1.363 (7)
C8—C9	1.402 (6)	C27—C28	1.405 (7)
C8—C13	1.367 (6)	C27—C32	1.375 (6)
C9—C10	1.383 (7)	C28—C29	1.371 (7)
C10—C11	1.371 (8)	C29—C30	1.368 (8)
C11—C12	1.382 (7)	C30—C31	1.384 (8)
C12—C13	1.379 (7)	C31—C32	1.390 (7)
C14—C15	1.387 (7)	C33—C34	1.399 (7)
C14—C19	1.407 (7)	C33—C38	1.386 (7)

C15—C16	1.392 (8)		
C16—C17	1.384 (9)		
C17—C18	1.369 (8)		
C2—C1—C8	111.5 (4)	C21—C20—C27	111.5 (4)
C2—C1—C14	113.1 (4)	C21—C20—C33	111.4 (4)
C8—C1—C14	111.5 (4)	C27—C20—C33	113.6 (4)
C3—C2—C7	117.8 (4)	C22—C21—C26	118.0 (4)
C2—C3—C4	120.7 (4)	C21—C22—C23	120.4 (4)
C2—C7—C6	121.0 (5)	C21—C26—C25	121.9 (5)
C9—C8—C13	118.0 (4)	C28—C27—C32	117.6 (4)
C8—C9—C10	120.1 (4)	C27—C28—C29	120.9 (4)
C8—C13—C12	121.9 (5)	C27—C32—C31	121.1 (5)
C15—C14—C19	117.7 (4)	C34—C33—C38	118.0 (4)
C14—C15—C16	121.7 (5)	C33—C34—C35	120.4 (5)
C14—C19—C18	120.9 (5)	C33—C38—C37	120.6 (5)

Observed systematic extinctions are consistent with space groups $Pna2_1$ and $Pnma$. The structure refined successfully in the non-centrosymmetric space group $Pna2_1$. No higher lattice symmetry was indicated with the program *LEPAGE* (Spek, 1988). All non-H atoms were refined with anisotropic displacement parameters. H atoms were refined with fixed geometry, riding on their carrier atoms, with a fixed isotropic displacement parameter amounting to 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atom. No missed symmetry (*MISSYM*; Le Page, 1987) or solvent-accessible voids were detected by procedures implemented in *PLATON* (Spek, 1990, 1994).

Data collection: *CAD-4 Software*, locally modified (Enraf–Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON*. Software used to prepare material for publication: *PLATON*.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Brock, C. P., Schweizer, W. B. & Dunitz, J. D. (1985). *J. Am. Chem. Soc.* **107**, 6964–6970.
Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
Hauser, C. R. & Hudson, B. E. Jr (1946). *Org. Synth.* **23**, 102–107.
Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
Riche, C. & Pascard-Billy, C. (1974). *Acta Cryst.* B**30**, 1874–1876.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1987). *Acta Cryst.* C**43**, 1233–1235.

Spek, A. L. (1988). *J. Appl. Cryst.* **20**, 264–269.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Spek, A. L. (1993). *HELENA. Program for Data Reduction.* University of Utrecht, The Netherlands.

Spek, A. L. (1994). *Am. Crystallogr. Assoc. Abstr.* **22**, 66.

Extremely Long C—C Bonds in Strained 1,1,2,2-Tetraphenylcyclobutaarenes: 3,8-Dichloro-1,1,2,2-tetraphenylcyclobuta-[b]naphthalene, C36H24Cl2, and 3,6,9,10-Tetrachloro-4,5-dimethyl-1,1,2,2,7,7,8,8-octaphenyldicyclobuta[b,h]phenanthrene Toluene Solvate, C68H46Cl4.1.5C7H8

FUMIO TODA,[a] KOICHI TANAKA,[a] ZAFRA STEIN[b] AND ISRAEL GOLDBERG[b]

[a]*Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790, Japan, and* [b]*School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel*

Abstract

Cyclobutaarenes are highly strained compounds which exhibit unusual geometric features. Introduction of diphenyl substituents on the peripheral C atoms of the cyclobutene ring adds stereoelectronic effects and causes further distortion of the ring structure. The interatomic distances observed for the peripheral C—C bonds in the cyclobutene moiety of the two compounds are in the range 1.71–1.72 Å, among the longest of C_{sp^3}—C_{sp^3} bonds previously reported for similar compounds. The core structure of the phenanthrodicyclobutene derivative is severely twisted due to non-bonding interactions between the chlorine substituents.

Comment

A series of low-temperature crystallographic studies of arenes containing fused strained cyclobutene and cyclopropene rings, characterizing the effect of the angular strain on the electronic structure of benzene, have recently been published (Boese & Bläser, 1988; Bläser *et al.*, 1989; Boese *et al.*, 1994). For the benzocyclobutene species, the interatomic dimensions of the four-membered rings were typically found to be near C_{sp^2}—C_{sp^2} = 1.34, C_{sp^2}—C_{sp^3} = 1.52 and C_{sp^3}—C_{sp^3} = 1.58 Å. More recently, a new synthetic route to benzocyclobutene derivatives has been reported,

leading to the preparation of a series of highly strained aromatic compounds which consist of substituted benzocyclobutene, naphthocyclobutene and anthracyclobutene fragments (Toda, Tanaka, Sano & Isozaki, 1994). The title compounds were subjected to a detailed structural analysis (at room temperature) in order to establish the molecular structure of the new materials and to characterize the effect of the severe intramolecular overcrowding on the covalent parameters of the cyclobutene ring.

(I)   (II)
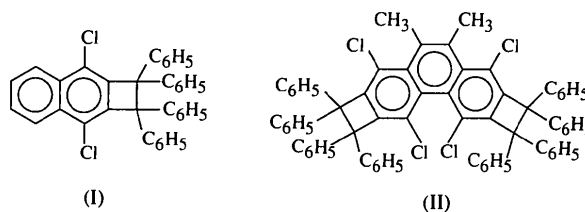
The cyclobutene structure observed in this study is characterized by C_{sp^3}—C_{sp^3} bond distances in the range 1.710 (5)–1.724 (5) Å and C_{sp^3}—C_{sp^2} bond distances varying from 1.526 (4) to 1.538 (4) Å. These values have not been corrected for thermal motion effects and do not account for the presence of 'bent bonds' in the four-membered ring (Boese *et al.*, 1994). In the planar naphthocyclobutene compound, the cyclobutene fusion bond has a normal length of 1.409 (4) Å, while the adjacent bonds in the benzene ring are considerably shortened [1.351 (5) and 1.360 (4) Å]. On the other hand, in the twisted phenanthrodicyclobutene derivative, the fusion-annelated bonds and the adjacent aryl bonds have lengths which are closer in magnitude, within 1.365 (6)–1.368 (5) and 1.369 (5)–1.374 (5) Å, respectively. The intramolecular twist in the latter is best characterized by the C(Cl)—C—C—C(Cl) torsion angle along the concave surface of the molecule of 37.6 (5)°, which represents a severe distortion of the aryl core from planarity. Moreover, while on each side of the molecule the fused cyclobutene and benzene rings are almost coplanar, the dihedral angle formed between the mean planes of the two eight-membered ring pairs is 34.6 (1)°. This allows accommodation of the two inner Cl substituents at a non-bonding distance of 3.099 (2) Å. The stretched C—C outer bonds of the cyclobutene moiety facilitate cleavage of the strained ring at this site by photoirradiation.

The significant stretching of the C_{sp^3}—C_{sp^3} bonds in the cyclobutene fragment is most probably effected by a combination of steric and electronic effects. Some elongation should, undoubtedly, be attributed to steric hindrance between the diphenyl substituents on the peripheral bond. This has been demonstrated by crystal structure analyses of two 1,1,2,2-tetraphenylethane-1,2-diol derivatives, in which the central C_{sp^3}—C_{sp^3} bond distances are 1.59 Å, as compared with the standard