Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	1.94 (2)	2.803 (1)	153 (1)
N3—H3···O2^{ii}	1.99 (2)	2.845 (1)	170 (2)

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, -y, 1 - z$.

Although, from the cell parameters, the crystal symmetry appears to be very close to orthorhombic, Weissenberg and precession film data, together with diffractometer data, showed it to be monoclinic with a β angle very close to 90°.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATRED* (Brookhaven National Laboratory & Birmingham University, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

We thank Dr J. R. Traynor for the synthesis and provision of a sample of the title compound.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1294). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1938–1941

Highly Strained C—C Bonds: 3-(1′-Hydroxy-4′-isopropyl-2′,2′-dimethyl-1′,2′-dihydrobenzocyclobuten-1′-yl)-3-methyl-2-butanone Ethylene Acetal, (I), and (3*S**,1′*S**)-3-Acetoxy-2-(1′-hydroxy-1′,2′-dihydrobenzocyclobuten-1′-yl)-2-methylpentane, (II)†

Katsumi Iida, Etsuya Kawata, Kaori Komada, Masaichi Saito, Shigekazu Kumakura and Michikazu Yoshioka

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan. E-mail: skuma@chem.saitama-u.ac.jp

(Received 5 January 1998; accepted 22 July 1998)

Abstract

The crystal structures of the title compounds, $C_{20}H_{30}O_3$ (I) and $C_{16}H_{22}O_3$ (II), are described. The benzocyclobutene rings in (I) and (II) are approximately planar. The lengths of the Csp^3—Csp^3 bonds in the cyclobutene rings of (I) and (II) are 1.659 (2) and 1.596 (2) Å, respectively. The C—C bond elongation observed in (I) may be ascribed to steric congestion and/or electronic effects on the bond exerted by the methyl groups and the alkyl side chain attached to the cyclobutenol moiety, together with a ring strain expected for a four-membered ring system.

Comment

Crystallographic and electronic structures of benzene derivatives fused to a strained small ring have been extensively studied (Boese & Bläser, 1988; Bläser *et al.*, 1989, 1994). In the crystal of benzocyclobutene, an elongated Csp^3—Csp^3 bond of 1.576 (1.580) Å was observed in the cyclobutene moiety which is coplanar to the benzene ring (Boese & Bläser, 1988). Recently, much longer Csp^3—Csp^3 bonds [1.710 (5)–1.724 (5) Å] were observed in the cyclobutene rings fused to naphthalene and anthracene rings (Toda *et al.*, 1996). In crystals of several benzocyclobutenol derivatives, C—C single bonds longer than 1.60 Å were also found in their cyclobutenol moieties (Courtois *et al.*, 1975, 1977, 1987; Ianelli *et al.*, 1990; Ianelli *et al.*, 1992*a*,*b*; Ianelli, Nardelli, Belletti, Jamart-Grègoire,

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† IUPAC names: 3-{8-hydroxy-4-isopropyl-7,7-dimethylbicyclo[4.2.0]octa-1(6),2,4-trien-8-yl}-3-methyl-2-butanone ethylene acetal, (I), and 4-{8-hydroxybicyclo[4.2.0]octa-1(6),2,4-trien-8-yl}-4-methylpent-3-yl acetate, (II).

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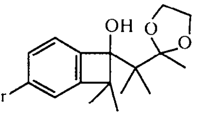
ISSN 0108-2701 © 1998

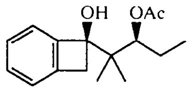
Mouaddib, Zouaoui & Caubère, 1992). Kaupp & Boy (1997) recently reviewed overlong C—C single bonds.

We have previously reported on the thermal isomerization of benzocyclobutenols obtained from photochemical reactions of *ortho*-alkylphenylketones (Yoshioka *et al.*, 1991, 1992, 1993, 1997). In order to clarify the bonding mode of benzocyclobutene rings, X-ray structure analysis was carried out on the title compounds. *Ab initio* molecular orbital and density functional calculations were also performed on benzocyclobutene and its derivatives to examine steric and electronic effects on the bonding character by the ring substituents.

The benzocyclobutene rings observed in both compounds, (I) and (II), are approximately planar. Their benzene moieties are slightly deformed from the usual aromatic rings; the endocyclic valence angles of aromatic-C atoms at the ring junction are larger than 120° and those next to the junction show smaller angles. Such deformation of bond angles was commonly observed in the crystallographic data of 26 benzocyclobutene derivatives retrieved from the Cambridge Structural Database (1996) [the mean bond angles at the ring junction and next to the ring junction are 122.9 (15) and 115.2 (18)°, respectively].



(I)

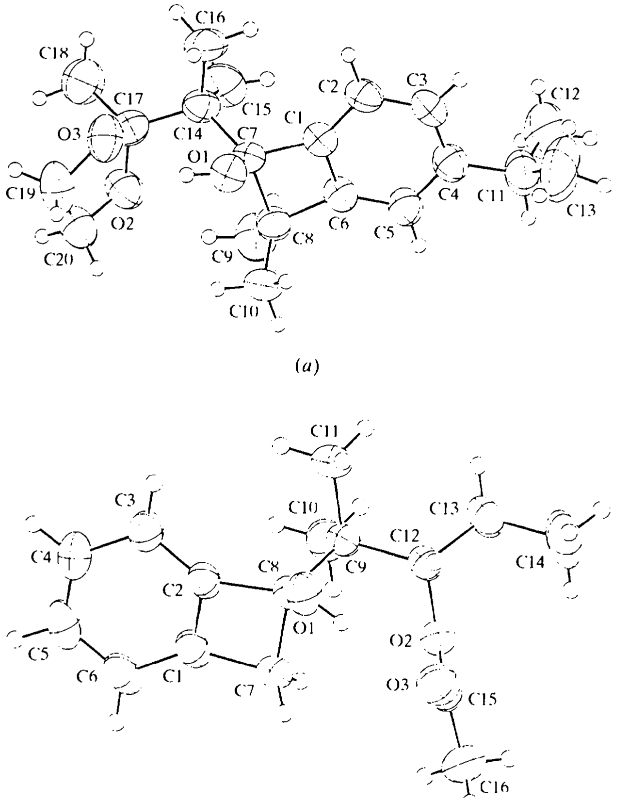


(II)

The C7—C8 bond in compound (I) has a length of 1.659 (2) Å, significantly longer than 1.596 (3) Å in compound (II) as well as 1.576 Å (1.580 Å) in benzocyclobutene itself (Boese & Bläser, 1988). Similar bond elongation was found previously for the C—C single bond [1.652 (9) and 1.650 (10) Å] of the cyclobutene ring in 2-(1′-hydroxy-4′-isopropyl-2′,2′-dimethyl-1′,2′-dihydrobenzocyclobuten-1′-yl)-2-methyl-4-hexen-3-ol (compound III) (Yoshioka *et al.*, 1997), which is in a similar environment to that in compound (I). The cyclobutenol moieties in both (I) and (III) have two methyl groups and a bulky alkyl side chain on their respective positions.

In order to examine the electronic effects of the ring substituents, *ab initio* calculations were carried out on benzocyclobutene and benzocyclobutenol by employing HF, MP2, B3LYP, BLYP, and SVWN methods with a 6-31G* basis set (*GAUSSIAN*94; Frisch *et al.*, 1996). Slight deformations are observed in the benzene rings of these molecules which are similar in extent to those observed in compounds (I) and (II). The lengths of the C—C single bonds in their cyclobutene moieties, corresponding to C7—C8 bonds in compounds (I) and (II), are calculated as follows; 1.572 (HF), 1.575 (MP2), 1.582 (B3LYP), 1.595 (BLYP) and 1.562 Å (SVWN) for benzocyclobutene, and 1.573 (HF), 1.579 (MP2), 1.590 (B3LYP), 1.607 (BLYP) and 1.574 Å (SVWN) for benzocyclobutenol. On comparison of these values on each level of calculation, an hydroxy group seems to cause slight elongation of the C—C bond in the cyclobutene ring. Furthermore, HF calculations were performed for 2,2-dimethyl-1,2-dihydrobenzocyclobuten-1-ol (DMDHBCB) and 1-*tert*-butyl-2,2-dimethyl-1,2-dihydrobenzocyclobuten-1-ol (tBDMDHBCB) to examine the effect of methyl substituents and the bulky alkyl side chain on the elongated C7—C8 bond observed in compound (I). The lengths calculated for the C—C single bond in their respective cyclobutenol moieties are 1.578 (DMDHBCB) and 1.628 Å (tBDMDHBCB). These calculations suggest that the methyl and *tert*-butyl substituents affect the C—C bond elongation, though the calculations seem to be less reliable than those including CI.

In the cyclobutene moiety of compound (I), the nonbonded contact between the methyl C9 and the methyl C15 of the side chain is 3.213 (3) Å, which is much smaller than the usual methyl–methyl contact. The C8—C7—C14 and C7—C8—C9 angles are 124.1 (2) and 122.6 (2)°, respectively; these are much larger than the usual tetrahedral angle. These observations indicate that



(*a*)

(*b*)

Fig. 1. The molecular structures of (*a*) (I) and (*b*) (II) with 50% probability displacement ellipsoids and showing the atom-numbering schemes.

severe steric interaction can be anticipated between the side chain and the *cis*-located methyl group. This steric interaction may also play an important role in the bond elongation observed in compound (I). Thus, steric and/or electronic effects of the methyl groups and the alkyl side chain attached to the cyclobutenol ring seem to be crucial to the C7—C8 bond elongation in compound (I) and, hence, play an important role in the thermal isomerization of the compound.

Experimental

The title compounds were obtained by irradiation of the corresponding arylketones by a high-pressure mercury lamp. Recrystallization was from hexane.

Compound (I)

Crystal data

$C_{20}H_{30}O_3$
$M_r = 318.46$
Orthorhombic
$P2_12_12_1$
$a = 9.069\ (5)$ Å
$b = 9.595\ (3)$ Å
$c = 21.624\ (7)$ Å
$V = 1881.7\ (13)$ Å^3
$Z = 4$
$D_x = 1.124$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from all reflections
$\theta = 1–31°$
$\mu = 0.074$ mm^{-1}
$T = 298$ K
Prism
0.3 × 0.3 × 0.2 mm
Colorless

Data collection

Mac Science DIP3000 diffractometer
Area detector scans
Absorption correction: none
17 015 measured reflections
3154 independent reflections

2449 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 30.20°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 30$

Refinement

Refinement on F
$R = 0.068$
$wR = 0.071$
$S = 1.320$
2449 reflections
235 parameters
H-atom parameters constrained
$w = \exp(\sin^2\theta/\lambda^2)/[\sigma^2(F_o) + 0.001(F_o)^2]$

$(\Delta/\sigma)_{\rm max} = 0.0084$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1—C7	1.423 (2)	C3—C4	1.408 (3)
C1—C2	1.376 (3)	C4—C5	1.386 (3)
C1—C6	1.386 (2)	C5—C6	1.377 (3)
C1—C7	1.524 (2)	C6—C8	1.521 (3)
C2—C3	1.386 (3)	C7—C8	1.659 (2)
C2—C1—C6	121.2 (2)	O1—C7—C1	108.4 (2)
C2—C1—C7	144.2 (2)	O1—C7—C8	110.5 (1)
C6—C1—C7	94.5 (2)	C1—C7—C8	85.3 (1)
C1—C2—C3	116.7 (2)	C6—C8—C7	84.4 (1)
C2—C3—C4	123.0 (2)	C6—C8—C9	113.0 (2)
C3—C4—C5	118.7 (2)	C6—C8—C10	113.8 (2)
C4—C5—C6	118.5 (2)	C7—C8—C9	122.6 (2)
C1—C6—C5	122.0 (2)	C7—C8—C10	112.0 (2)
C1—C6—C8	95.8 (2)	C9—C8—C10	109.1 (2)
C5—C6—C8	142.2 (2)		

Compound (II)

Crystal data

$C_{16}H_{22}O_3$
$M_r = 262.35$
Triclinic
$P\bar{1}$
$a = 7.500\ (2)$ Å
$b = 8.505\ (2)$ Å
$c = 11.852\ (5)$ Å
$\alpha = 85.22\ (7)°$
$\beta = 88.89\ (7)°$
$\gamma = 77.23\ (3)°$
$V = 734.7\ (4)$ Å^3
$Z = 2$
$D_x = 1.186$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from all reflections
$\theta = 1–31°$
$\mu = 0.080$ mm^{-1}
$T = 298$ K
Prism
0.38 × 0.26 × 0.12 mm
Colorless

Data collection

Mac Science DIP3000 diffractometer
Area detector scans
Absorption correction: none
7516 measured reflections
4417 independent reflections

2819 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 30.18°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
$R = 0.060$
$wR = 0.070$
$S = 1.612$
2819 reflections
236 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = \exp(10.0\sin^2\theta/\lambda^2) \times [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$
$(\Delta/\sigma)_{\rm max} = 0.0080$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C8	1.423 (1)	C2—C8	1.535 (1)
C1—C2	1.377 (1)	C3—C4	1.400 (1)
C1—C6	1.388 (1)	C4—C5	1.381 (1)
C1—C7	1.519 (1)	C5—C6	1.395 (1)
C2—C3	1.382 (1)	C7—C8	1.596 (1)
C2—C1—C6	122.8 (1)	C3—C4—C5	122.5 (1)
C2—C1—C7	94.5 (1)	C4—C5—C6	121.6 (1)
C6—C1—C7	142.6 (1)	C1—C6—C5	115.5 (1)
C1—C2—C3	122.2 (1)	C1—C7—C8	86.1 (1)
C1—C2—C8	93.7 (1)	O1—C8—C2	109.4 (1)
C3—C2—C8	144.0 (1)	O1—C8—C7	114.1 (1)
C2—C3—C4	115.3 (1)	C2—C8—C7	85.7 (1)

Weissenberg photographs were recorded on 30 frames of imaging plates mounted on a DIP3000 diffractometer, each of which was taken around the ω axis with an oscillation range of 6°. The unit cells were determined by the routine *SCALEPACK*

(*DENZO*; Otwinowski & Minor, 1994) employing all reflections observed. H atoms in compounds (I) and (II) were placed at calculated positions (C—H 0.96 Å), except for the hydroxyl-H atoms which were found from difference Fourier maps. In compound (I), all H atoms were refined isotropically using a riding model, while H1 was refined with an isotropic displacement parameter. In the final cycle of refinement, isotropic displacement parameters of the methyl H atoms on C12 and C13 were fixed to their values equal to those obtained from the previous cycle. All H atoms in (II) were refined isotropically. In the final cycle of refinement, all H parameters of methyl C14 and C16 were held fixed to those obtained from the previous cycle.

For both compounds, data collection: *XDIP* (Mac Science, 1996); data reduction: *DENZO* (Otwinowski & Minor, 1994); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *CRYSTAN-GM* (Edwards *et al.*, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1055). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1941–1943

A Cytosine and Tryptophan Hybrid Dipeptide: Cytosinyl-L-tryptophan–Water (2/6)

Mitsunobu Doi, Mariko Tarui, Mihoko Ogata, Akiko Asano and Toshimasa Ishida

Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan. E-mail: doit@oysun01.oups.ac.jp

(*Received 17 October 1997; accepted 8 June 1998*)

Abstract

The hybrid dipeptide of the title compound, $2C_{18}H_{19}N_5O_4.6H_2O$, containing cytosine base and L-tryptophan was crystallized in hexahydrated form; the solvent occupies 12% by weight of the asymmetric unit. Two independent molecules were distinguished by the different directions of their indole rings. All polar atoms of the title compound participate in hydrogen-bond formation, and a tight network is built by combination with solvent-mediated hydrogen bonds. A π–π electron interaction was observed between the indole and nucleic base; it is facilitated by hydrogen bonds.

Comment

The title compound, C-Trp, was designed in order to investigate the cooperative interactions between the nucleic acid and polypeptide molecules (Ishida *et al.*,