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Trifluoromethyl derivatives of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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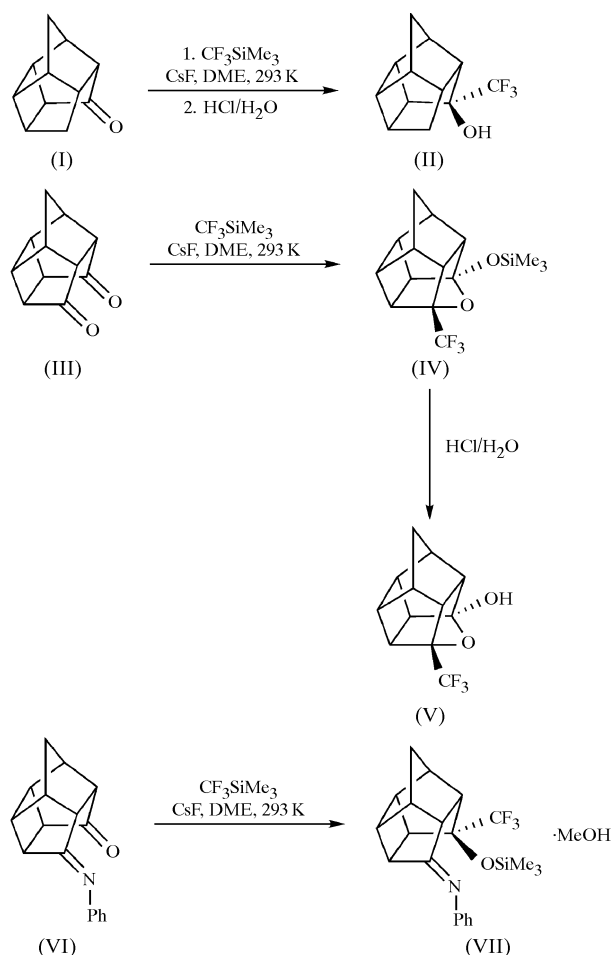
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Three cage-like polycyclic compounds, viz. *exo*-8-(trifluoromethyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-*endo*-8-ol, C₁₂H₁₃F₃O, 5-(trifluoromethyl)-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecan-3-ol, C₁₂H₁₁F₃O₂, and *N*-[*exo*-11-(trifluoromethyl)-*endo*-11-(trimethylsilyloxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-ylidene]aniline methanol solvate, C₂₁H₂₄F₃NOSi·CH₄O, were obtained from the corresponding oxo derivatives by nucleophilic trifluoromethylation with (trifluoromethyl)trimethylsilane in 1,2-dimethoxyethane solution in the presence of CsF. The crystal structures show that the addition of trifluoromethanide occurs exclusively from the *exo* face of the polycyclic ketones. Further examination of the crystal structures, together with that of the starting pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione, C₁₁H₁₀O₂, showed that increasing substitution at the 8- and/or 11-positions in the cage molecules increases the non-bonded intramolecular C...C distances at the mouth of the cage and changes the puckering of the five-membered rings involving the 8- and 11-positions from an envelope towards a distorted half-chair conformation. Intermolecular co-operative O—H...O hydrogen bonds in the *endo*-8-ol compound link the molecules into tetramers.

Comment

Fluorinated organic compounds are of interest because of their modified physico-chemical and biological properties in comparison with their non-fluorinated analogues (Hiyama, 2000; Maienfisch & Hall, 2004). One of the most frequently used methods for the synthesis of fluorinated molecules is trifluoromethylation (Singh & Shreeve, 2000). For nucleophilic trifluoromethylation, (trifluoromethyl)trimethylsilane (CF₃SiMe₃; Ruppert's reagent) has become the reagent of choice (Prakash & Mandal, 2001). In our recent studies, ketones with the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane skeleton (so called 'cage' ketones; Marchand, 1995) were used as starting materials for the reaction with CF₃SiMe₃

(Romański & Mloston, 2005). The addition of trifluoromethanide was expected to occur from the *exo* face of the cage ketone, analogously to previously reported reactions with other nucleophiles [e.g. Grignard reagents (Marchand *et al.*, 2001), trimethylsilyl cyanide (Bott, Marchand, Vidyanand & Sachleben, 1995) and amines (Bott, Marchand, Kumar *et al.*, 1995)]. Treatment of the ketone pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one, (I), with Ruppert's reagent in 1,2-dimethoxyethane (DME) in the presence of CsF led to a single product, which, after acidic hydrolysis, was identified as the trifluoromethylated alcohol, (II), with an *exo*-oriented trifluoromethyl group. Under the same conditions, the corresponding diketone, (III), was converted to the silylated acetal, (IV), regardless of the ratio of (III) and CF₃SiMe₃ (1:1 or 1:2).



After hydrolysis of compound (IV), the hemiacetal (V) was obtained as a stable product. Obviously, the addition of trifluoromethanide to one of the carbonyl groups of (III) is followed immediately by ring closure, which results in the subsequent silylation of the second O atom. It is noteworthy that the non-cyclic hexane-2,5-dione reacts with one equivalent of CF₃SiMe₃ to give the corresponding 1:1 adduct without cyclization to the tetrahydrofuran-2-ol derivative (Singh *et al.*, 2001), whereas the reaction with two equivalents of CF₃SiMe₃ leads to the formation of the bistrifluoromethylated diol.

In the case of the iminoketone (VI), the addition of CF₃SiMe₃ occurred chemoselectively at the keto group,

yielding product (VII), again with the CF_3 group in the *exo* position. In contrast to the reaction with the parent dione (III), no cyclization *via* attack of the O atom at the imine C atom was observed and the silylated adduct (VII) was isolated as the only product. The chemoselectivity observed in this reaction can be explained by the fact that typical imines are much less electrophilic than the corresponding carbonyl compounds and do not undergo trifluoromethylation with CF_3SiMe_3 (Singh & Shreeve, 2000).

The crystal structures of (II), (V) and (VII) were determined in order to confirm the stereochemical outcome of the reactions described above. For comparison, the structure of the parent dione (III) was also determined. Compound (II) (Fig. 1) crystallizes in a non-centrosymmetric space group, although the presence of glide planes dictates that the compound in the crystal is racemic. The absolute structure has not been determined and the direction of the polar axis was chosen arbitrarily. The asymmetric unit in the structure of (VII) contains one molecule of the cage compound plus one disordered methanol molecule. The alternate positions for the methanol molecule are approximately equally occupied, and each arrangement affords an intermolecular $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bond with the imine N atom of the same neighbouring cage molecule.

Compound (III) crystallizes with three molecules in the asymmetric unit (molecule *A* is defined by atoms O1, O2 and C1–C11, molecule *B* by atoms O21, O22 and C21–C31, and molecule *C* by atoms O41, O42 and C41–C51), and they all have the same molecular conformation (Fig. 2). The weighted r.m.s. fit of the atomic coordinates of the three molecules is 0.030, 0.032 and 0.011 Å for the fit between molecules *A* and *B*, *A* and *C*, and *B* and *C*, respectively. The atomic coordinates of the three molecules were tested carefully for a relationship from a higher-symmetry space group by using the program *PLATON* (Spek, 2003), but none could be found. Although the compound is racemic because the molecule has internal mirror symmetry, it crystallizes in a polar space group. The absolute structure, and hence space group $P3_1$ instead of $P3_2$, was chosen arbitrarily. The validation routine of *PLATON* also revealed that the crystal is merohedrally twinned by a twofold rotation about a^* . The twin fraction for the major twin component refined to a value of 0.780 (2). Refinement of the

model without allowing for twinning led to a significantly higher $R[F^2 > 2\sigma(F^2)]$ value of 0.067.

Data for the structures of 137 molecules having the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane skeleton and a large variety of substituents at various sites are recorded in the Cambridge Structural Database (November 2004 release; Allen, 2002). Of these, 52 are substituted only at the 8- and/or 11-positions, and in 30 of these structures, there is no bridging route through the substituents that links the 8-position to the 11-position, so that these positions form the open mouth of the cage. The cage geometry of representative examples of these compounds has been discussed by Flippen-Anderson *et al.* (1991), and the cage geometry of compounds (II), (III), (V) and (VII) is generally consistent with those observations. In particular, the cage C9–C10 bond, which lies across from the cyclobutane ring, and is parallel to and immediately adjacent to the $\text{C8} \cdots \text{C11}$ axis, is long at around 1.59 Å [excluding compound (V); Table 3]. The long C9–C10 bond is probably a consequence of the stretching strain introduced by the open mouth of the cage formed by the adjacent atoms C8 and C11. When atoms C8 and C11 are held closer together by the oxo bridge in (V), the C9–C10 bond is at its shortest. Interestingly, the C1–C7 bond, which is also immediately adjacent to the $\text{C8} \cdots \text{C11}$ axis, is elongated only in (III). Flippen-Anderson *et al.* also remarked that the C–C bonds linking the substituted C atoms to the cyclobutane ring are often unusually short. In the present structures, the corresponding bonds, C7–C8 and C1–C11, are similarly short when the substituent bond involves a π system, as in the dione, (III), and for the imine-substituted C atom of (VII). In most other cases, shortening of these bonds is not observed, although the C7–C8 bond in (II), which involves the substituted C atom, is slightly shorter than the C1–C11 bond, which involves the unsubstituted C atom. The C3–C4–C5 bond angle involving the capping C atom has an average value of 95.3 (5)° across the four structures and is consistent with the observations of Flippen-Anderson *et al.*

The $\text{C8} \cdots \text{C11}$ non-bonded intramolecular distances at the mouth of the cage reflect the congestion caused by various degrees of substitution at these atoms. In (V), the oxo bridge between atoms C8 and C11 holds these atoms together at a distance of 2.172 (2) Å (Fig. 3). In the dione (III), the environment about atoms C8 and C11 is sp^2 -planar, so that the

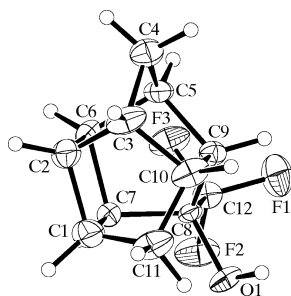


Figure 1
View of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary size and only one of the disordered hydroxy H atoms is shown.

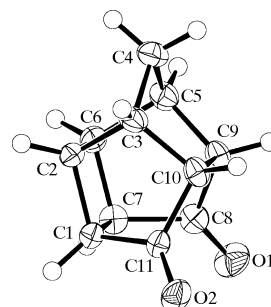


Figure 2
View of one of the three symmetry-independent molecules (molecule *A*) of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

steric restraints introduced by the ketone O atoms are small, and the C8...C11 distance ranges from 2.562 (4) to 2.574 (5) Å across the three symmetry-independent molecules. Compound (II) is disubstituted at atom C8 but not substituted at atom C11, and the C8...C11 distance is considerably longer at 2.749 (7) Å. In compound (VII), the C8...C11 distance is only 2.682 (2) Å, even though atom C11 is now also substituted and the trimethylsilyloxy substituent at atom C8 occupies the *endo*-position (Fig. 4). The shorter distance results from the reduced steric crowding afforded by the sp^2 -planar character of atom C11 in (VII), compared with the more bulky situation in (II), where atom C11 forms part of a tetrahedral methylene group.

The degree and type of substitution at atoms C8 and C11 also affects the puckering of the five-membered rings that form the sides of the cage and in which these atoms reside (Table 4). For five-membered rings, the puckering parameter φ_2 ideally has a value of $n \times 36^\circ$ for an envelope conformation

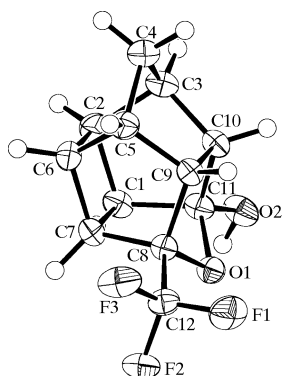


Figure 3
View of the molecule of (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

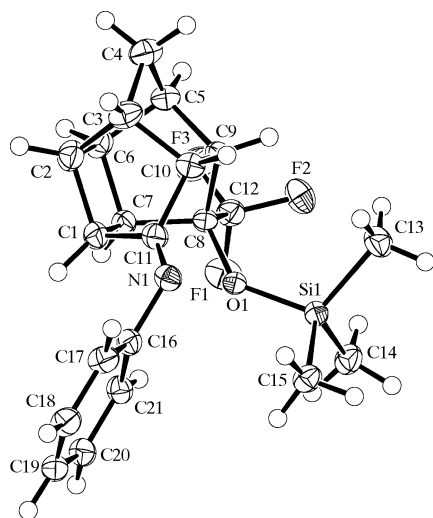


Figure 4
View of the molecule of (VII), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size and the disordered methanol molecule has been omitted for clarity.

and $(n \times 36) + 18^\circ$ for a half-chair conformation (n is an integer). In compound (V), which displays the shortest C8...C11 distance and has the constraint of the oxo bridge, the rings defined by the atom sequences C5–C9 and C1–C2–C3–C10–C11 have almost ideal envelope conformations, puckered on atoms C9 and C10, respectively. In (III), the corresponding rings in molecule *A* also have similar envelope conformations, but the increase in the C8...C11 distance caused by the opening out of the mouth of the cage has moved atoms C8 and C11 out of the planes of atoms C5, C6 and C7 and atoms C1, C2 and C3, respectively, so that the envelope conformations have become distorted towards half-chair conformations twisted on C8–C9 and C10–C11, respectively. The other two symmetry-independent molecules have almost identical conformations. In (II), the five-membered ring containing the substituted C atom, C8, has an almost ideal half-chair conformation twisted on C8–C9, while the ring containing the unsubstituted C atom can best be described by a half-chair conformation twisted on C10–C11 but distorted somewhat towards an envelope conformation puckered on atom C10. The corresponding five-membered rings in compound (VII) are best described as being distorted half-chairs twisted on C8–C9 and C10–C11, with the puckering distorted to a point almost half-way between that of a half-chair and an envelope puckered on atoms C9 and C10, respectively.

A significant feature of the structure of (II) is the O–H...O hydrogen bonding (Table 1). The hydroxy O atom is within hydrogen-bonding distance of the hydroxy O atoms of two neighbouring molecules. Although no obvious positions for the hydroxy H atom could be detected in the peak lists obtained from any difference Fourier maps, a contoured map showed a hint of residual electron density on opposing sides of

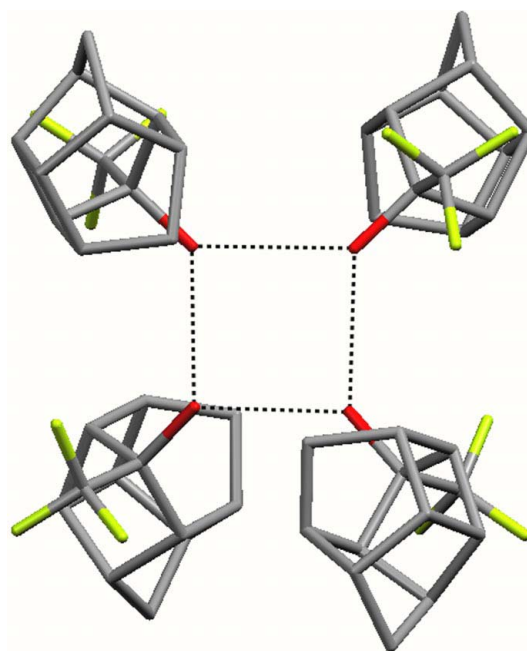


Figure 5
The hydrogen-bonded tetramer in the structure of (II). All H atoms have been omitted for clarity.

the O atom and in positions that would be consistent with O—H···O hydrogen bonds to both neighbouring molecules. Including either one of these positions for the hydroxy H atom in the model generates unreasonably short intermolecular O—H···H—O distances, because the symmetry relationships between adjacent molecules always result in the hydroxy H atoms in these adjacent molecules pointing at one another. Introducing equally occupied disordered sites for the hydroxy H atom, with the O—H vectors pointing in opposite directions and at both neighbouring hydroxy O atoms, alleviates the close contact issue, because neither H-atom site in the H···H contact would need to be occupied simultaneously. The propagation of the interactions leads to a loop of co-operative O—H···O hydrogen bonds, which link four molecules into a tetrameric unit (Fig. 5). The disorder of the H-atom positions represents two alternative directions of the O—H···O pattern around the loop. The hydrogen-bonding pattern can be described by the graph-set motif $R_4^4(8)$ (Bernstein *et al.*, 1995).

The hydroxy group in (V) forms an intermolecular hydrogen bond with the oxo O atom of a neighbouring molecule (Table 2) and thereby links pairs of molecules across a centre of inversion into dimers, which can be described by the hydrogen-bonding motif $R_2^2(8)$.

Experimental

The starting ketones, (I) and (III), were prepared according to published procedures (Cookson *et al.*, 1964; Romański *et al.*, 2005). Crystals of (III) suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution at room temperature (m.p. 413–415 K). Compound (VI) was prepared by heating (III) with aniline in boiling benzene, in an analogous manner to a literature protocol (Sasaki *et al.*, 1974), and was used for further reaction without purification. The reactions of ketones (I) and (III), as well as aminoketone (VI), with trimethyl(trifluoromethyl)silane were performed in absolute 1,2-dimethoxyethane (DME) under an argon atmosphere in the presence of catalytic amounts (*ca* 10 mol%) of caesium fluoride, which had been dried by preheating at 423 K for several hours (Romański & Młostoń, 2005). After evaporation of the solvent, the residues obtained from ketones (I) and (III) were hydrolyzed by stirring with 4 *N* HCl to give (II) and (V), respectively. Suitable crystals of these compounds were obtained by slow evaporation of their hexane/dichloromethane and methanol solutions, respectively, at room temperature [m.p. 399–400 and 389–390 K for (II) and (V), respectively]. In the case where (VI) was the starting ketone, the product (VII), obtained after evaporation of DME, was also crystallized by slow evaporation of a methanol solution at room temperature (m.p. 414–415 K).

Compound (II)

Crystal data

$C_{12}H_{13}F_3O$	Mo $K\alpha$ radiation
$M_r = 230.23$	Cell parameters from 1354 reflections
Tetragonal, $I\bar{4}c2$	$\theta = 2.0$ – 27.5°
$a = 14.1311$ (3) Å	$\mu = 0.13$ mm $^{-1}$
$c = 20.2206$ (6) Å	$T = 160$ (1) K
$V = 4037.81$ (17) Å 3	Block, colourless
$Z = 16$	$0.30 \times 0.23 \times 0.20$ mm
$D_x = 1.515$ Mg m $^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.062$
φ and ω scans with κ offsets	$\theta_{max} = 27.5^\circ$
23 516 measured reflections	$h = -18 \rightarrow 16$
1262 independent reflections	$k = -18 \rightarrow 16$
1036 reflections with $I > 2\sigma(I)$	$l = -26 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0974P)^2 + 4.4956P]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.174$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.39$ e Å $^{-3}$
1258 reflections	$\Delta\rho_{min} = -0.22$ e Å $^{-3}$
146 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A···O1 ⁱ	0.84	2.05	2.701 (6)	133
O1—H1B···O1 ⁱⁱ	0.84	1.95	2.673 (6)	144

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

Compound (III)

Crystal data

$C_{11}H_{10}O_2$	Mo $K\alpha$ radiation
$M_r = 174.20$	Cell parameters from 3543 reflections
Trigonal, $P3_1$	$\theta = 2.0$ – 30.0°
$a = 18.0861$ (4) Å	$\mu = 0.10$ mm $^{-1}$
$c = 6.4388$ (1) Å	$T = 160$ (1) K
$V = 1824.00$ (6) Å 3	Block, colourless
$Z = 9$	$0.35 \times 0.30 \times 0.20$ mm
$D_x = 1.427$ Mg m $^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.054$
φ and ω scans with κ offsets	$\theta_{max} = 30.0^\circ$
28 695 measured reflections	$h = -25 \rightarrow 25$
3543 independent reflections	$k = -25 \rightarrow 25$
3128 reflections with $I > 2\sigma(I)$	$l = -8 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.1521P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.28$ e Å $^{-3}$
3542 reflections	$\Delta\rho_{min} = -0.21$ e Å $^{-3}$
353 parameters	
H-atom parameters constrained	

Compound (V)

Crystal data

$C_{12}H_{11}F_3O_2$	$D_x = 1.642$ Mg m $^{-3}$
$M_r = 244.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2379 reflections
$a = 7.4499$ (3) Å	$\theta = 2.0$ – 27.5°
$b = 12.0228$ (5) Å	$\mu = 0.15$ mm $^{-1}$
$c = 11.6047$ (3) Å	$T = 160$ (1) K
$\beta = 108.082$ (2)°	Block, colourless
$V = 988.08$ (6) Å 3	$0.25 \times 0.22 \times 0.12$ mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{\text{int}} = 0.051$
φ and ω scans with κ offsets	$\theta_{\text{max}} = 27.5^\circ$
20 424 measured reflections	$h = -9 \rightarrow 9$
2271 independent reflections	$k = -15 \rightarrow 15$
1725 reflections with $I > 2\sigma(I)$	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.3171P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$
2269 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
159 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by independent and constrained refinement	Extinction coefficient: 0.018 (4)

Table 2

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for V.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O1^{\text{iii}}$	0.89 (3)	1.93 (3)	2.8070 (18)	167 (3)

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

Compound (VII)

Crystal data

$C_{21}H_{24}F_3NOSi\cdot CH_4O$	$Z = 2$
$M_r = 423.54$	$D_x = 1.366 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.8352$ (2) $\text{\AA}$	Cell parameters from 5859 reflections
$b = 9.3775$ (3) $\text{\AA}$	$\theta = 2.0\text{--}30.0^\circ$
$c = 12.6843$ (5) $\text{\AA}$	$\mu = 0.16 \text{ mm}^{-1}$
$\alpha = 100.2675$ (15) $^\circ$	$T = 160$ (1) K
$\beta = 91.417$ (2) $^\circ$	Tablet, colourless
$\gamma = 94.652$ (2) $^\circ$	$0.22 \times 0.20 \times 0.10 \text{ mm}$
$V = 1029.86$ (6) $\text{\AA}^3$	

Table 3

Comparison of selected geometric parameters ($\text{\AA}$, $^\circ$).

Compound	(II)	(IIIA)	(IIIB)	(IIIC)	(V)	(VII)
C1—C2	1.551 (7)	1.557 (4)	1.547 (4)	1.553 (4)	1.555 (2)	1.575 (2)
C1—C7	1.548 (7)	1.585 (4)	1.592 (4)	1.584 (4)	1.557 (2)	1.564 (2)
C1—C11	1.530 (9)	1.508 (4)	1.513 (4)	1.512 (4)	1.532 (3)	1.506 (2)
C2—C6	1.565 (6)	1.553 (4)	1.553 (4)	1.552 (4)	1.561 (3)	1.558 (2)
C6—C7	1.580 (5)	1.553 (4)	1.554 (4)	1.560 (4)	1.547 (2)	1.562 (2)
C7—C8	1.518 (5)	1.507 (4)	1.503 (4)	1.509 (4)	1.547 (2)	1.535 (2)
C8—C9	1.527 (5)	1.517 (4)	1.516 (4)	1.506 (4)	1.543 (2)	1.538 (2)
C9—C10	1.582 (6)	1.592 (4)	1.599 (4)	1.595 (4)	1.569 (2)	1.586 (2)
C10—C11	1.504 (8)	1.519 (4)	1.519 (4)	1.508 (4)	1.525 (2)	1.505 (2)
C2—C1—C7	89.5 (4)	89.2 (2)	89.6 (2)	89.6 (2)	89.50 (13)	88.74 (12)
C1—C2—C6	91.5 (4)	90.6 (2)	90.7 (2)	90.7 (2)	90.19 (13)	90.78 (13)
C3—C4—C5	94.6 (4)	95.6 (2)	95.4 (2)	95.7 (2)	95.11 (13)	95.16 (14)
C2—C6—C7	87.8 (3)	90.6 (2)	90.8 (2)	90.5 (2)	89.67 (13)	89.46 (13)
C1—C7—C6	91.1 (3)	89.6 (2)	89.0 (2)	89.3 (2)	90.64 (13)	91.01 (12)

Table 4

Selected Cremer & Pople (1975) puckering parameters ($\text{\AA}$, $^\circ$).

Ring	(II)	(IIIA)	(IIIB)	(IIIC)	(V)	(VII)
$q_2(C5-C6-C7-C8-C9)$	0.463 (4)	0.416 (4)	0.421 (3)	0.427 (3)	0.3268 (18)	0.4517 (18)
$q_2(C1-C2-C3-C10-C11)$	0.502 (6)	0.445 (3)	0.429 (3)	0.426 (3)	0.3374 (19)	0.4768 (19)
$\varphi_2(C5-C6-C7-C8-C9)$	309.3 (5)	316.9 (5)	318.0 (5)	316.8 (5)	147.4 (3)	313.2 (2)
$\varphi_2(C1-C2-C3-C10-C11)$	119.6 (7)	115.0 (4)	115.4 (4)	114.4 (4)	285.3 (3)	117.8 (2)

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{\text{int}} = 0.046$
φ and ω scans with κ offsets	$\theta_{\text{max}} = 30.1^\circ$
26 283 measured reflections	$h = -12 \rightarrow 12$
6025 independent reflections	$k = -13 \rightarrow 13$
4581 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.529P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.136$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
6017 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$
288 parameters	
H-atom parameters constrained	

The merohedral twinning in the structure of (III) was treated by employing the twin matrix $[110/0\bar{1}0/00\bar{1}]$. The asymmetric unit in the structure of (VII) contains one molecule of the cage compound plus one disordered methanol molecule. Two sets of overlapping positions were defined for the atoms of the methanol molecule, and refinement of the site-occupation factors led to a value of 0.53 (1) for the major orientation. Similarity restraints were applied to the C—O bond lengths and the atomic displacement parameters of the C and O atoms of each orientation of the methanol molecule. The hydroxy H atom in (V) was located in a difference Fourier map, and its position and isotropic displacement parameter were refined. In order to obviate unreasonably short intermolecular O—H $\cdots$ H—O distances in compound (II), the hydroxy H atom must be disordered over two equally occupied sites with the O—H vectors pointing in opposite directions. Both positions for the disordered hydroxy H atom in (II) were initially defined to correspond to the direction that would bring each H atom closest to its nearest hydrogen-bond acceptor. The positions were then constrained to an ideal geometry [O—H = 0.84 $\text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$] and subsequently were allowed to rotate freely about the parent O—C bond. The hydroxy H atoms in the disordered methanol molecule of (VII) were treated in the same way. All methyl H atoms in the structure of (VII) were constrained to an ideal geometry [C—H = 0.98 $\text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$] but were allowed to rotate freely about the parent Si—C or O—C bonds. All other H atoms in the structures were placed in geometrically idealized positions and constrained to ride on their parent atoms [C—H = 0.95–1.00 $\text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. Compounds (II) and (III) crystallized in non-centrosymmetric space groups. Owing to the absence of any significant anomalous scatterers in these compounds, attempts to confirm the absolute structure by refinement of the Flack (1983) parameter in the presence of 1052 [for (II)] and 2460 [for (III)] sets of Friedel equivalents led to inconclusive values (Flack & Bernardinelli, 2000) for this parameter [0.3 (14) and 0.4 (9), respectively]. Therefore, the Friedel pairs were merged before the final refinement for (II) and (III), and the absolute structure was assigned arbitrarily. For compounds (II), (III), (V) and (VII), four, one, two and eight low-angle reflections, respectively, were omitted from the final cycles of refinement because their observed intensities were

much lower than the calculated values as a result of being partially obscured by the beam stop.

For all compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); structure solution: *SIR92* (Altomare *et al.*, 1994); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *MERCURY* (Bruno *et al.*, 2002); publication software: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1816). Services for accessing these data are described at the back of the journal.

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