The Cubane Cage – A Sensitive Probe for Assessing Substituent Effects on a Four-Membered Ring, Part II[+]

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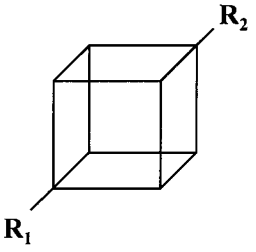
Keywords: Cage compounds / Cubanes / Donor–acceptor systems / Solid-state structures / Substituent effects

The crystal structures of methyl 4-methoxycubane-1-carboxylate (**1**), 1-acetamido-4-fluorocubane (**2**), methyl 4-acetoxycubane-1-carboxylate (**3**), 1,4-difluorocubane (**4**), 1,4-dichlorocubane (**5**), and *N*,*N*-diisopropylcubane-1,4-dicarboxamide (**6**) have been investigated by means of X-ray diffraction analysis. Fluorine and chlorine substituents cause a shortening of the vicinal bonds, as is seen in the 4-halocubane-1-carboxylates. The cage bonds vicinal to the ester substituent, with a favorable orientation with regard to the π-acceptor influence of this group become longer than the CH–CH bonds. Furthermore, the influence on bond length with respect to the orientation of this group relative to bonds within the cubane skeleton has been investigated experimentally. The effect of the methoxy group has also been found to depend on the orientation. The cage bond antiperiplanar to the methyl group is shortened, while the cage bonds in *gauche* orientation to this group are lengthened. As seen in the case of the halogen-substituted derivatives, the bonds bearing the acetoxy substituent are shortened due to the σ-acceptor property of this group. Ab initio calculations on compounds **1**, **2**, **4**, and **5** performed at the 6-31G* level confirm the experimental results.

In contrast to the situation with three-membered rings, substituent effects in cyclobutane derivatives are too weak to be detected unambiguously.[1] However, as a strained polycyclic cage compound, the cubane system has proved suitable for assessing substituent effects on four-membered rings. We have previously reported on the various geometric distortions within the cubane skeleton that result from the attachment of halogen atoms and of a methyl carboxylate group.[2]

To extend these investigations concerning the influence of substituent effects on the cubane cage, we have now determined the crystal structures of methyl 4-methoxycubane-1-carboxylate (**1**), 1-acetamido-4-fluorocubane (**2**), methyl 4-acetoxycubane-1-carboxylate (**3**), and *N*,*N*-diisopropylcubane-1,4-dicarboxamide (**6**), i.e. cubane derivatives substituted with methoxy, acetamido, acetoxy, and amide groups (Scheme 1). Since methyl carboxylate derivatives are readily accessible, the influence of the orientation of this group relative to the cubane skeleton has been investigated experimentally. Furthermore, the crystal structures of 1,4-difluorocubane (**4**) and 1,4-dichlorocubane (**5**) demonstrate that the strong electronic effects of two fluorine or two chlorine atoms in the 1,4-positions lead to large distortions of the cubane skeleton.



	R$_1$	R$_2$
1	COOMe	OMe
2	NHCOMe	F
3	COOMe	OCOMe
4	F	F
5	Cl	Cl
6	CON(iPr)$_2$	CON(iPr)$_2$
7	COOH	COOH
8	COOMe	F
9	Br	Br
10	I	I
12	COOMe	I

Scheme 1. 1,4-Disubstituted cubane derivatives

Syntheses

The syntheses of the cubane derivatives 1-acetamido-4-fluorocubane (**2**) and methyl 4-acetoxycubane-1-carboxylate (**3**) have been described previously.[3]

Methyl 4-methoxycubane-1-carboxylate (**1**) and 1,4-difluorocubane (**4**) were prepared as described by Della and Head.[3][4] To avoid contamination of the fluorides with chlorine substituents, *n*-hexane was used as solvent instead of dichloromethane. 1,4-Dichlorocubane (**5**) was obtained by treatment of cubane-1,4-dicarboxylic acid (**7**) with lead tetraacetate and lithium chloride. Transformation of acid **7** into the twofold acid chloride and subsequent solvolysis with diisopropylamine yielded *N*,*N*-diisopropylcubane-1,4-dicarboxamide (**6**).[5]

[+] Part 1: Ref.[2]

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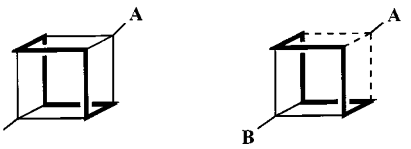


Scheme 2. Different bond types in 1,4-disubstituted cubanes

Substituent Effects

The 1,4-disubstituted derivatives can be subdivided into two groups, i.e. those in which the two substituents are the same, and those that have dissimilar substituents (Scheme 2).

To assess the substituent effects on the bonds of the cubane skeleton, different bond types were inspected, as outlined in Scheme 2. In the case of molecules with two substituents of the same type, there are only two bond types, namely CH−CA and CH−CH bonds. In molecules with dissimilar substituents, CH−CB bonds are also present. In the latter molecules, with different substituents A and B, the electronic effects of the two groups on the cage bonds can be compared within the same system.

As reported for methyl 4-halocubane-1-carboxylates,[2] the contrasting effects of halogen and ester groups on the vicinal cubane bond lengths, due to their opposite electronic influences, could be demonstrated. In methyl 4-fluorocubane-1-carboxylate (**8**),[2] as a representative of this class, the cage bonds vicinal to the ester substituent with a favorable orientation (see Scheme 3 and the appertaining discussion) with regard to the π-acceptor influence of this group, are lengthened compared to the average of the non-substituted bonds (Figure 1). In contrast, the bonds adjacent to the fluorine substituent are shortened (Figure 1). Comparable influences can be observed in 1-acetamido-4-fluorocubane (**2**) (Figure 1, Table 1).

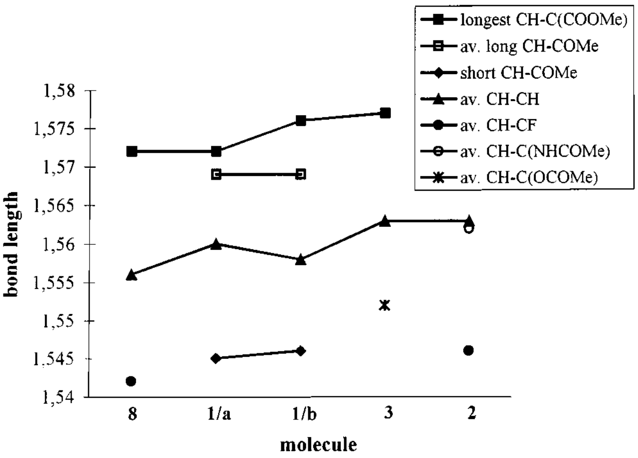
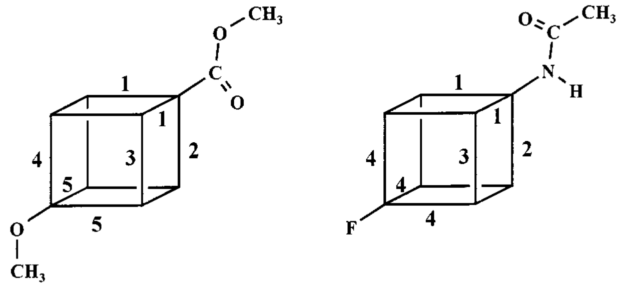


Figure 1. Diagram showing the effects of the different substituents on molecules **1**−**3**; data for **8**[2] are included for comparison

The cubane derivative **3** also bears a methyl carboxylate substituent. In accordance with findings for other ester-substituted cubane derivatives,[2][6] the cage bonds vicinal to this group with a favorable orientation with regard to the π-acceptor influence are lengthened to 1.577(2) Å (Figure 1) compared to the CH−CH bonds [av. 1.563(2) Å]. In contrast, as seen in the case of the halogen-substituted derivatives, the bonds bearing the acetoxy substituent are shortened to an average of 1.552(2) Å due to the σ-acceptor property of this group (Figure 1).

Table 1. Experimental and calculated bond lengths of the cage bonds in cubane derivatives **1** and **2**



Bond	**1** Exp.	**1** 6-31G*	**2** Exp.	**2** 6-31G*
av. 1	1.574(3)	1.564	1.565(2)	1.558
2	1.557(2)	1.549	1.557(2)	1.555
av. 3	1.559(3)	1.559	1.563(2)	1.561
av. 4	1.546(2)	1.548	1.546(2)	1.548
av. 5	1.569(3)	1.565	–	–

The crystals of methyl 4-methoxycubane-1-carboxylate (**1**) were found to contain two independent molecules (**1/a** and **1/b**) within the asymmetric unit. These differ in the orientations of the ester and methoxy substituents in relation to the cubane cage. As depicted in Figure 1, the bonds influenced by the π-acceptor properties of the ester group are significantly lengthened compared to the CH−CH bond lengths. The effect of the methoxy group also depends on orientation. The cage bond of type 4 (Table 1), antiperiplanar to the methyl group, is shortened to 1.546(2) Å due to the σ-acceptor property of the methoxy group, which is similar to that of a halogen substituent. Both cage bonds of type 5 (Figure 1, Table 1), in *gauche* orientation to the methyl group, are lengthened because of the π-donating property.

Quantum chemical calculations on methyl 4-fluorocubane-1-carboxylate (**8**),[2] methyl 4-methoxycubane-1-carboxylate (**1**), and 1-acetamido-4-fluorocubane (**2**), performed under complete geometry optimization at the 6-31G* level, confirm the experimental results concerning the bond-shortening influence of fluorine on the vicinal skeletal bonds (Table 1). Furthermore, the calculations demonstrate the conformation-dependent effect of the methoxy group on the vicinal bonds, as found experimentally for compound **1** (Table 1).

The opposite effects of the halogen and carbonyl groups, due to their different electronic influences, can also be observed in the symmetrically 1,4-disubstituted cubane derivatives **4**−**6**. The electronic influence of the amide group in molecule **6** is akin to the corresponding influence of the ester group (Figure 2).

Fluorine and chlorine substituents cause a significant distortion along the 1,4-diagonal in the molecules **4** and **5** ow-

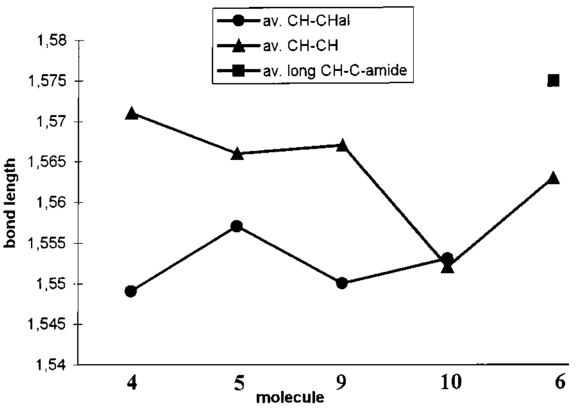
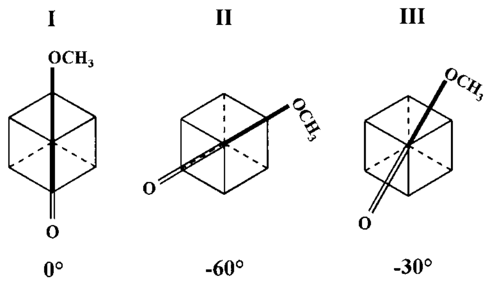


Figure 2. Diagram showing the substituent effects on the cage bonds of molecules **4**–**6**; bond lengths in molecules **9** and **10** are taken from the literature[7][8]

ing to a shortening of the substituted cage bonds [av. 1.549(2) Å in **4** and 1.557(2) Å in **5**] compared to the CH–CH bond lengths [av. 1.571(2) Å and 1.566(2) Å, respectively] (Figure 3, Table 2). This effect is not significant in 1,4-dibromocubane (**9**) and 1,4-diiodocubane (**10**).[7][8] With fluorine and chlorine atoms at both substituted cage corners, the significant distortion of the cubane skeleton can be detected by means of X-ray diffraction analysis.

In the cubane derivative **6**, substituted with amide groups, the cage bonds with a favorable orientation with regard to the π-acceptor influence of these groups are lengthened [av. 1.575(2) Å] compared to the average of the CH–CH bond lengths [1.563(2) Å] (Figure 2).

Ab initio quantum chemical calculations on the fluorine and chlorine derivatives **4** and **5**, performed at the 6-31G* level with full geometry optimization, confirm the cubane cage distortion found experimentally (Table 2).



Scheme 3. Principal orientation of the ester group with respect to the cubane skeleton

Table 2. Experimental and calculated bond lengths in the dihalocubanes **4** and **5**

	4		5	
	Exp.	6-31G*	Exp.	6-31G*
CH–CHal	1.549(2)	1.547	1.557(2)	1.551
CH–CH	1.571(2)	1.563	1.566(2)	1.560

As has been reported for the nitro group,[9] the methyl carboxylate and amide substituents adopt favoured orientations in relation to the cubane cage (Scheme 3). In conformation **I** (0°), the carbonyl fragment is in an eclipsed orientation to a cage bond. Therefore, the plane of the ester is oriented parallel to the cage bond. Another orientation with the ester plane in a parallel position is depicted as conformer **II**. Here, in contrast to **I**, the methoxy fragment

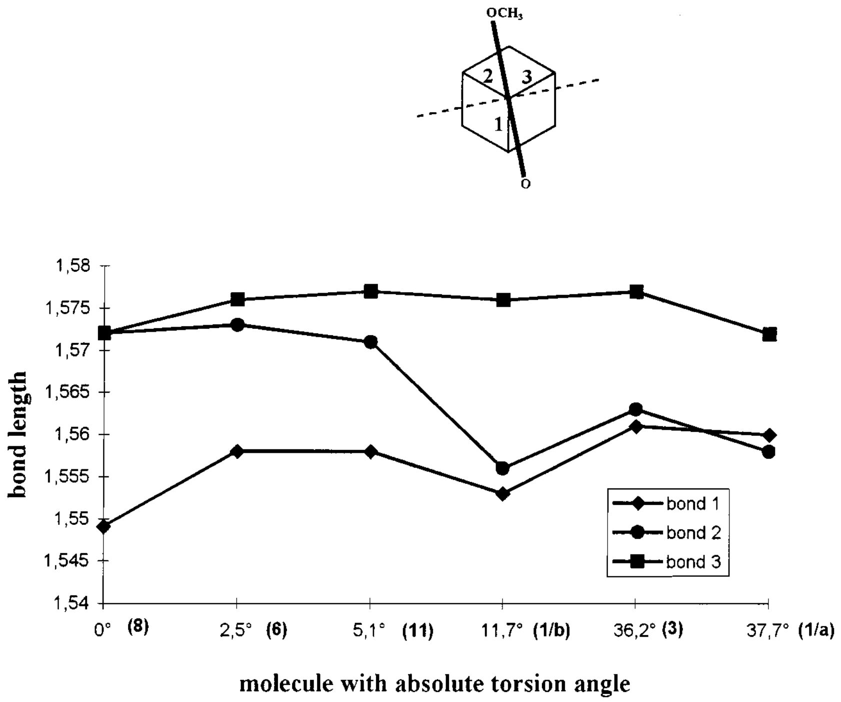


Figure 3. Bond-length alternation as a function of the torsion angle for the ester and amide groups

adopts an eclipsed orientation to a skeletal bond. The third principal orientation is shown as conformation **III**. In the projection of **III** in Scheme 3, the ester plane is positioned perpendicular to one skeletal bond with the π-system of the carbonyl fragment being parallel to this cage bond.

In the crystalline state of the cubane derivatives **1**, **3**, **6**, **8**, and methyl 3,4-difluorocubane-1-carboxylate (**11**),[10] the ester and amide groups have orientations of type **I**, orientations close to type **III**, and orientations between these two extremes. In the present cases, orientation of type **II** is not observed. Figure 3 depicts the variation in bond length as a function of the absolute torsion angle of the carbonyl fragment relative to cage bond 1 (Figure 3). While in the 0° position (molecule **8**), bonds 2 and 3 (Figure 3) are lengthened and bond 1 is short, the lengthening of bond 2 decreases as the torsion angle increases. In the case of compounds **1/a** and **3**, where the orientation is close to type **III** (Scheme 3), only bond 3 is affected by the π-accepting properties of the carbonyl fragment. Hence, only bond 3 is lengthened in this case, while bonds 1 and 2 are short.

This orientation dependence has also been found for conformations **I** and **III** in the case of cubanes substituted by four and five ester groups.[6] In the crystal stuctures of other 1,4-disubstituted derivatives bearing various ester groups,[11] a carboxylic acid group,[12] or a nitro substituent,[13] the same behavior can be recognized.

The orientation dependence of substituents can only be investigated in the solid state. However, solvolytic experiments in solution[14] and corresponding calculations[15] have also pointed to a strong influence of substituents in the 4-position. Solvolysis rates of 1-cubyl triflates are found to be reduced by halogen, carboxylate, and methoxy substituents in the 4-position since their predominantly electron-withdrawing σ-effects serve to destabilize the intermediate cubyl cation.

Experimental Section

General: Melting points: Dr. Tottoli and Melting Point B 540 apparatus from Büchi; open capillary tubes; all melting points are uncorrected. − NMR: Bruker AC 300 ($CDCl_3$ as internal standard). − TLC: Polygram Sil G/UV$_{254}$ plates (Macherey-Nagel) in closed chambers. − MS: Finnigan 3200 (70 eV) and HP MS 5970 (70 eV) for low resolution. − IR: Bruker IFS 66. − Elemental analysis: Heraeus CHN-O-Rapid.

Table 3. Experimental details of the X-ray diffraction analysis, structure solution, and refinement

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Crystal size [mm]	0.45 × 0.45 × 0.25	0.4 × 0.3 × 0.25	0.5 × 0.3 × 0.15	0.4 × 0.25 × 0.15	0.3 × 0.15 × 0.15	0.5 × 0.2 × 0.15
Crystal form	colorless prisms	colorless prisms	colorless prisms	colorless prisms	colorless needles	colorless needles
Crystal growth	sublimation	CH_2Cl_2	CH_2Cl_2	sublimation	ethyl acetate	ethyl acetate
Temperature [K]	218	218	218	173	218	218
Reflns. recorded	4851	2271	2810	755	919	2646
Unique reflns.	4509	2028	2547	684	851	2502
Obsd. reflns. $I \geq 2.5\sigma(I)$, $2\sigma(I)$*	2716	1433	1973*	600*	723	1785
R_{int}	0.021	0.010	0.036	0.045	0.029	0.011
No. of variables	349	149	194	59	58	186
Solution method[22][23]	SHELXS	MULTAN	SHELXS	SHELXS	MULTAN	MULTAN
Method of refinement[24][25]	MolEN	MolEN	SHELXL	SHELXL	MolEN	MolEN
Refined on	F^2	F^2	F^2	F^2	F^2	F^2
μ [mm^{-1}]	0.09	0.10	0.10	0.14	0.82	0.07
Absorption correction	none	none	none	none	Psi-Scan	none
$\Delta\rho_{max}$ [e/Å^3]	0.30	0.26	0.35	0.40	0.35	0.26
$\Delta\rho_{min}$ [e/Å^3]	−0.08	−0.25	−0.27	−0.64	−0.63	−0.33
R	0.045	0.040	0.048	0.077	0.042	0.042
$R_w(F)$, $R_w(F^2)$*	0.059	0.104*	0.130*	0.189*	0.094*	0.052

Table 4. Experimental results of the X-ray diffraction analysis of compounds **1**−**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{11}H_{12}O_3$	$C_{10}H_{10}NOF$	$C_{12}H_{12}O_4$	$C_8H_6F_2$	$C_8H_6Cl_2$	$C_{22}H_{34}N_2O_2$
Molecular mass	192.2	179.2	220.2	140.1	173.0	358.5
a [Å]	7.303(1)	6.665(1)	5.259(1)	5.384(1)	6.696(1)	9.480(1)
b [Å]	8.120(1)	13.462(2)	20.975(7)	5.554(1)	6.754(1)	7.575(1)
c [Å]	31.810(6)	9.513(1)	9.746(1)	5.245(1)	8.444(1)	14.927(2)
α [°]	90	90	90	98.98(1)	90	90
β [°]	96.47(1)	97.66(1)	99.05(1)	105.69(1)	111.73(1)	103.89(1)
γ [°]	90	90	90	72.12(1)	90	90
Volume [Å^3]	1874.1(9)	845.9(3)	1061.6(4)	143.3(1)	354.7(1)	1040.5(4)
Z	8	4	4	1	2	2
$D_{calcd.}$ [Mg/m^3]	1.36	1.41	1.38	1.62	1.62	1.14
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P-1$	$P2_1/n$	$P2_1/c$

Methyl 4-Iodocubane-1-carboxylate (12): This compound was synthesized as described in the literature.[2,4,16]

Methyl 4-Fluorocubane-1-carboxylate (8): Xenon difluoride (1.334 g, 7.88 mmol) was added in one portion to a suspension of iodide **12** (0.500 g, 1.74 mmol) in pure *n*-hexane (12 mL). The resulting mixture was then refluxed under argon for 5 h. After cooling to room temperature, the solution was diluted with 150 mL of ethyl acetate, washed with sodium bisulfite solution (5%), and dried with $MgSO_4$. The solvent was then removed and the residue was redissolved in chloroform. This solution was filtered (silica gel) and then concentrated to dryness. The yellowish crude product was purified by sublimation (30°C/0.015 Torr) to yield 0.185 g (59%) of fluoride **8**. − M.p. 97−99°C [ref.[4] m.p. 97−99°C]. − ^1H NMR ($CDCl_3$): δ = 3.70 (s, 3 H, OCH_3), 4.03−4.09 (m, 3 H, cubyl), 4.28−4.34 (m, 3 H, cubyl) [ref.[4] ($CDCl_3$): δ = 3.71 (s, 3 H), 3.85−4.55 (m, 6 H)].

Methyl 4-Methoxycubane-1-carboxylate (1): A solution of iodide **12** (0.228 g, 0.79 mmol) in pure methanol (24 mL) was irradiated under argon in a Rayonet® reactor (22 h, 10 lamps, 2537 Å, 40−45°C). The reaction was monitored by GC MS, which indicated that the desired product and methyl cubane-1-carboxylate had been generated. The reaction mixture was then neutralized with Na_2CO_3 solution (10%) and the solvent was removed. The residue was taken up in chloroform and the resulting solution was concentrated to dryness. The products were separated by column chromatography on silica gel (elution with *n*-hexane/ethyl acetate, 9:1). Sublimation (20−25°C/0.005 Torr) of the crude methoxy derivative gave 0.047 g (31%) of pure material as a white solid. − M.p. 37−38°C. − ^1H NMR ($CDCl_3$): δ = 3.31 (s, 3 H, OCH_3), 3.69 (s, 3 H $COOCH_3$), 3.96−4.00 (m, 3 H, cubyl), 4.14−4.17 (m, 3 H cubyl). − IR (KBr): $\tilde{\nu}$ = 2992 cm^{-1} (m to s), 2833 (w to m), 1726 (s, C=O), 1436 (m), 1307 (s, C−O−C), 1206, 1123, 1090 (m to s, C−O−C), 1019 (m to s). − MS (70 eV); *m/z* (%): 193 (1) [$(M + 1)^+$], 192 (7) [M^+], 177 (6) [$(M - CH_3)^+$], 161 (10) [$(M - OCH_3)^+$], 133 (100) [$(M - COOCH_3)^+$], 118 (47) [$C_8H_6O^+$], 108 (64) [$C_7H_8O^+$], 105 (41), 103 (14), 102 (10) [$C_8H_6{}^+$]. − $C_{11}H_{12}O_3$ (192.21): calcd. C 68.74, H 6.29; found C 68.73, H 6.31.

1,4-Difluorocubane (4), 1,4-Dichlorocubane (5), and *N*,*N*-Diisopropylcubane-1,4-dicarboxamide (6): Prepared according to procedures described in the literature.[3,17,18] In the synthesis of **4**, *n*-hexane was used as the solvent.

Ab Initio Calculations: Calculations on compounds **2**, **4**, and **5** were carried out using the GAMESS[19] system of programs. In the case of compound **1**, the GAUSSIAN 94[20] system of programs was used.

X-ray Diffraction Analysis: Data collection was carried out with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and $\omega/2\theta$ scans in the range $\theta = 2-28°$. Further details of the structure determination are given in Table 3.[21] Results of the X-ray analyses of compounds **1**−**6** are presented in Table 4. For 1-acetamido-4-fluorocubane (**2**), the hydrogen atoms of the methyl group were refined as "riding atoms".

Acknowledgments

We thank Mrs. U. Wiesinger for her assistance in the data collection. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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Received June 30, 1998
[O98295]