Cubane derivatives

2.* Synthesis and structures of some esters of 1,4-cubanedicarboxylic acid

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New esters of 1,4-cubanedicarboxylic acid, 1,4-$(ROCO)_2C_8H_6$ (R = Et (**3a**), Pr (**3b**), CMe_3 (**3c**), C_6H_{13} (**3d**), CH_2CF_3 (**3e**), or $CH(CF_3)_2$ (**3f**)) were synthesized. The structures of esters **3a**, **3b**, **3e**, and **3f** were established by X-ray diffraction analysis. The cubane framework of compound **3b** is somewhat distorted, whereas the C—C bond lengths and bond angles in the other compounds remain virtually ideal.

Key words: 1,4-cubanedicarboxylic acid, esters, X-ray diffraction analysis.

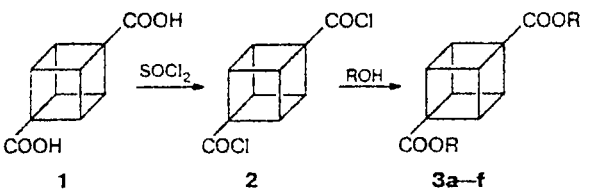
Previously,[1] we have reported the synthesis of a number of esters of 1,4-cubanedicarboxylic acid and studied them by X-ray structural analysis. It was found that in the case of dimethyl and bis-isopropyl esters of 1,4-cubanedicarboxylic acid, the cubane framework is almost undistorted, whereas in bis(2-fluoro-2,2-dinitroethyl) ester, the cubane framework is substantially distorted, which may be a result of the effects of the electron-withdrawing NO_2 groups and the fluorine atom. It should be noted that the specificity of the geometric characteristics of the cubane framework (the bond angles are close to 90°) affects the nature of the C—C bonds of cubane, which, according to the data of precision studies of the electron density distribution, are bent so that the maxima of the electron density are located above the bonds on the outside of the cubane framework.[2] As part of continuing studies along this line, we synthesized a new series of esters of 1,4-cubanedicarboxylic acid in which, on the one hand, the chain length of the substituent is increased and, on the other hand, the fluorine content of the R group is increased with the aim of revealing the possible effect on the character of bonding of carbon atoms in the cubane fragment.

Results and Discussion

Esters of 1,4-cubanedicarboxylic acid were synthesized according to the Scheme 1.

All the compounds synthesized, **3a—f**, were obtained in the crystalline form and were characterized by elemental analysis and IR and NMR spectroscopy (Table 1). Compounds **3a**, **3b**, **3e**, and **3f** were studied by X-ray diffraction analysis. As in the case of the methyl and isopropyl derivatives, which we have studied previously, the cubane framework of diethyl ester **3a** is rather symmetrical (Fig. 1; Tables 2 and 3; the C—C bond lengths are in the range of 1.560(2)—1.580(2) Å, and the CCC bond angles are in the range of 89.2(1)—90.8(1)°). However, the cubane framework in dipropyl 1,4-cubanedicarboxylate **3b** is substantially distorted (Fig. 2, Tables 2 and 3). The C—C bond lengths are in the range of 1.518(19)—1.627(13) Å, which exceeds substantially the experimental error, whereas in esters **3a** and **3b**, the bond lengths between the carbon atom of the cubane framework and the carbon atom of the carbonyl group have similar values (1.488(2) Å and 1.495(17) Å, respectively). The CCC bond angles in the cubane framework of ester **3b** also differ from the ideal values in the regular cube (85.6(10)—94.0(8)°). However, we failed to reveal particular distortion centers in the molecule of the isopropyl derivative, unlike

Scheme 1



1 **2** **3a—f**

R = C_2H_5 (**3a**); C_3H_7 (**3b**); $C(CH_3)_3$ (**3c**); C_6H_{13} (**3d**); CH_2CF_3 (**3e**); $CH(CF_3)_2$ (**3f**)

* For Part 1, see Ref. 1.

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Table 1. Principal characteristics of esters of 1,4-cubanedicarboxylic acid

R	Molecular formula	M.p. /°C	^{1}H NMR, δ, *J*/Hz ($CDCl_3$, Me_4Si)	IR (KBr pellets), ν/cm^{-1}	Found / Calculated (%)		
					C	H	F
C_2H_5	$C_{14}H_{16}O_4$	87—88	1.29 (t, 6 H, CH_3, $^3J_{CH-CH}$ = 6.9); 4.17 (q, 4 H, OCH_2, $^3J_{CH-CH}$ = 6.9); 4.21 (s, 6 H, CH)	2999, 2993, 1316 (CH_{cubane}); 2906, 1445 (CH_2);1715 (C=O); 1091, 1364 (CH_3); 1220 (C—O—C)	67.72 / 67.73	6.44 / 6.50	—
n-C_3H_7	$C_{16}H_{20}O_4$	68—69	0.99 (t, 6 H, CH_3, $^3J_{CH-CH}$ = 6.9); 1.69 (q, 4 H, C—CH_2, $^3J_{CH-CH}$ = 6.9); 4.10 (t, 4 H, OCH_2, $^3J_{CH-CH}$ = 6.9); 4.23 (s, 6 H, CH)	2999, 1328 (CH_{cubane}); 2969, 1457 (CH_2); 1715 (C=O); 1397 (CH_3); 1223, 1094 (C—O—C)	70.12 / 69.55	7.31 / 7.30	—
$C(CH_3)_3$	$C_{18}H_{24}O_4$	115—117	4.1 (s, 6 H, CH); 1.5 (s, 18 H, CH)	3002, 1322, 1166, 1088 (CH_3), 1706 (C=O), 1238 (C—O—C)	68.34 / 71.03	790 / 7.96	—
n-C_6H_{13}	$C_{22}H_{32}O_4$	45—46	0.90 (m, 6 H, CH_3, $^3J_{CH-CH} \approx 6.0$); 1.21—1.50 (br.m, 12 H, CH_2); 1.66 (quintet, 4 H, $OCH_2CH_2CH_2$, $^3J_{CH-CH} \approx 6.0$); 4.11 (m, 4 H, OCH_2, $^3J_{CH-CH} \approx 6.0$); 4.21 (s, 6 H, CH)	3007.3002, 1322 (CH_{cubane}), 2951, 2930, 2852, 1466, 1394, 1376 (CH_2, CH_3); 1712 (C=O); 1217, 1097 (C—O—C)	74.01 / 73.29	8.91 / 8.95	—
$C_2H_2F_3$	$C_{14}H_{10}F_6O_4$	92—93	4.30 (s, 6 H, CH_{cubane}); 4.50 (q, 4 H, CH_2, $^3J_{HF}$ = 8.5)	3020, 2918, 1463, 1421 (CH_2); 3002, 1325 (CH_{cubane}); 1733 (C=O)	46.81 / 47.20	2.80 / 2.83	31.76 / 32.00
$CH(CF_3)_2$	$C_{16}H_8F_{12}O_4$	158—158.5	4.41 (s, 6 H, CH); 5.76 (sextet, 2 H, $CH(CF_3)_2$, $^3J_{HF}$ = 5.9)	3029, 2984, 1364 (CH_{cubane}); 1763 (C=O); 1286, 1088 (C—F); 1106 (C—O—C)	40.05 / 39.04	1.57 / 1.64	46.20 / 46.32

Table 2. Bond lengths (*d*) in compounds **3a**,**b**,**e**,**f**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Molecule **3a**		C(1)—C(2)	1.537(14)	C(5)—C(13)	1.507(18)	C(4)—C(1A)	1.566(3)
O(1)—C(5)	1.329(2)	C(1)—C(9)	1.495(17)	C(7)—C(8)	1.595(15)	C(6)—H(6B)	0.927(34)
C(1)—C(4)	1.563(2)	C(2)—H(2A)	0.942(25)	Molecule **3e**		Molecule **3f**	
C(1)—C(3A)	1.563(2)	C(3)—H(3A)	0.972(37)	O(1)—C(5)	1.192(3)	O(1)—C(4)	1.355(6)
C(2)—C(1A)	1.560(2)	C(5)—C(6)	1.627(13)	F(1)—C(7)	1.308(4)	F(1)—C(6)	1.320(10)
C(3)—H(3)	0.965(22)	C(6)—C(7)	1.518(19)	C(1)—C(2)	1.560(3)	C(1)—C(2)	1.553(5)
C(4)—C(5)	1.488(2)	C(7)—H(7A)	0.873(32)	C(1)—C(4A)	1.566(3)	C(1)—C(3A)	1.544(8)
O(1)—C(6)	1.459(2)	O(1)—C(10)	1.440(15)	C(2)—C(2A)	1.573(4)	C(2)—C(2A)	1.549(8)
C(1)—H(1)	0.986(21)	O(4)—C(13)	1.332(13)	C(3)—C(3A)	1.555(4)	C(3)—C(2B)	1.579(5)
C(2)—C(4)	1.557(2)	C(1)—C(4)	1.602(19)	C(6)—C(7)	1.481(4)	C(5)—C(6A)	1.491(7)
C(2)—C(3A)	1.564(2)	C(2)—C(3)	1.626(21)	O(2)—C(5)	1.346(3)	O(1)—C(5)	1.416(8)
C(3)—C(1A)	1.563(2)	C(3)—C(4)	1.556(14)	F(2)—C(7)	1.336(4)	F(2)—C(6)	1.321(8)
C(6)—C(7)	1.477(3)	C(4)—C(6)	1.533(17)	C(1)—C(3)	1.566(3)	C(1)—H(1A)	0.892(43)
O(2)—C(5)	1.200(2)	C(5)—C(8)	1.529(20)	C(2)—C(4)	1.564(3)	C(2)—C(3)	1.579(5)
C(1)—C(2A)	1.560(2)	C(6)—H(6A)	0.944(29)	C(3)—C(4)	1.580(3)	C(3)—C(4)	1.473(8)
C(2)—H(2)	0.925(21)	C(8)—H(8A)	1.032(25)	C(4)—C(5)	1.481(3)	C(5)—C(6)	1.491(7)
C(3)—C(4)	1.580(2)	O(2)—C(9)	1.117(16)	C(6)—H(6A)	1.013(32)	O(2)—C(4)	1.173(5)
C(3)—C(2A)	1.564(2)	O(4)—C(14)	1.455(16)	O(2)—C(6)	1.439(3)	F(3)—C(6)	1.327(6)
Molecule **3b**		C(1)—C(7)	1.587(15)	F(3)—C(7)	1.327(3)	C(1)—C(2B)	1.553(5)
O(1)—C(9)	1.332(12)	C(2)—C(8)	1.612(17)	C(1)—H(1A)	1.008(28)	C(2)—H(2A)	0.843(41)
O(3)—C(13)	1.232(15)	C(3)—C(5)	1.563(15)	C(2)—H(2A)	1.082(36)	C(3)—C(1A)	1.544(8)
		C(4)—H(4A)	0.994(29)	C(3)—H(3A)	0.957(26)	C(5)—H(5A)	0.925(49)

Table 3. Bond angles (ω) in compounds **3a,b,e,f**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Molecule **3a**		C(2)—C(4)—C(5)	125.8(1)	C(2)—C(3)—C(4)	90.5(10)	C(1)—C(3)—C(4)	89.7(2)
C(5)—O(1)—C(6)	117.6(1)	O(1)—C(5)—O(2)	124.0(1)	C(4)—C(3)—C(5)	90.2(7)	C(4)—C(3)—C(3A)	90.1(1)
C(4)—C(1)—C(2A)	90.8(1)	O(2)—C(5)—C(4)	124.9(2)	C(1)—C(4)—C(6)	89.9(9)	C(2)—C(4)—C(5)	127.8(2)
C(4)—C(1)—C(3A)	89.6(1)	Molecule **3b**		C(3)—C(5)—C(6)	88.7(8)	C(2)—C(4)—C(1A)	90.6(2)
C(2A)—C(1)—C(3A)	90.1(1)	C(9)—O(1)—C(10)	118.2(8)	C(6)—C(5)—C(8)	88.9(9)	C(5)—C(4)—C(1A)	124.3(2)
C(4)—C(2)—C(1A)	90.6(1)	C(2)—C(1)—C(4)	92.1(9)	C(6)—C(5)—C(13)	124.1(9)	O(1)—C(5)—C(4)	125.6(2)
C(4)—C(2)—C(3A)	89.7(1)	C(4)—C(1)—C(7)	87.0(9)	C(4)—C(6)—C(5)	88.7(7)	O(2)—C(6)—C(7)	106.5(2)
C(1A)—C(2)—C(3A)	89.9(1)	C(4)—C(1)—C(9)	123.3(9)	C(5)—C(6)—C(7)	89.9(8)	Molecule **3f**	
C(4)—C(3)—C(1A)	89.6(1)	C(1)—C(2)—C(3)	88.6(8)	C(1)—C(7)—C(8)	87.0(7)	C(4)—O(1)—C(5)	117.4(3)
C(4)—C(3)—C(2A)	90.1(1)	C(3)—C(2)—C(8)	85.6(10)	C(2)—C(8)—C(5)	92.7(9)	C(2)—C(1)—C(3A)	90.4(3)
C(1A)—C(3)—C(2A)	90.2(1)	C(2)—C(3)—C(5)	90.9(9)	C(5)—C(8)—C(7)	90.8(8)	C(1)—C(2)—C(3)	89.9(3)
C(1)—C(4)—C(3)	89.2(1)	C(1)—C(4)—C(3)	88.8(8)	O(1)—C(9)—C(1)	107.7(8)	C(3)—C(2)—C(2A)	89.2(3)
C(1)—C(4)—C(5)	125.3(1)	C(3)—C(4)—C(6)	92.4(8)	O(1)—C(10)—C(11)	109.6(10)	C(2)—C(3)—C(1A)	89.8(3)
C(3)—C(4)—C(5)	125.1(1)	C(3)—C(5)—C(8)	90.7(9)	Molecule **3e**		C(2)—C(3)—C(2B)	89.1(4)
O(1)—C(5)—C(4)	111.1(1)	C(3)—C(5)—C(13)	125.8(10)	C(5)—O(2)—C(6)	115.3(2)	C(1A)—C(3)—C(2B)	89.8(3)
O(1)—C(6)—C(7)	107.6(2)	C(8)—C(5)—C(13)	127.0(9)	C(2)—C(1)—C(4A)	89.6(2)	O(1)—C(4)—C(3)	111.2(3)
C(4)—C(1)—H(1)	123.3(11)	C(4)—C(6)—C(7)	92.0(10)	C(1)—C(2)—C(4)	90.6(2)	O(1)—C(5)—C(6)	108.0(4)
H(1)—C(1)—C(2A)	127.4(12)	C(1)—C(7)—C(6)	91.0(9)	C(4)—C(2)—C(2A)	89.2(2)	C(6)—C(5)—C(6A)	112.4(6)
H(1)—C(1)—C(3A)	124.6(11)	C(6)—C(7)—C(8)	90.4(10)	C(1)—C(3)—C(3A)	90.3(1)	C(2)—C(1)—C(2B)	91.0(4)
C(4)—C(2)—H(2)	125.7(12)	C(2)—C(8)—C(7)	90.8(8)	C(2)—C(4)—C(3)	89.5(2)	C(2B)—C(1)—C(3A)	90.4(3)
H(2)—C(2)—C(1A)	124.6(12)	O(1)—C(9)—O(2)	124.9(12)	C(3)—C(4)—C(5)	123.9(2)	C(1)—C(2)—C(2A)	90.6(4)
H(2)—C(2)—C(3A)	125.3(12)	O(2)—C(9)—C(1)	127.3(11)	C(3)—C(4)—C(1A)	89.4(1)	C(2)—C(3)—C(4)	125.9(3)
C(4)—C(3)—H(3)	126.0(12)	C(13)—O(4)—C(14)	117.3(9)	O(1)—C(5)—O(2)	123.2(2)	C(4)—C(3)—C(1A)	125.0(3)
H(3)—C(3)—C(1A)	124.7(12)	C(2)—C(1)—C(7)	94.0(8)	O(2)—C(5)—C(4)	111.2(2)	C(4)—C(3)—C(2B)	125.9(3)
H(3)—C(3)—C(2A)	125.2(12)	C(2)—C(1)—C(9)	125.6(10)	C(2)—C(1)—C(3)	90.2(2)	O(1)—C(4)—O(2)	122.9(5)
C(1)—C(4)—C(2)	90.5(1)	C(7)—C(1)—C(9)	124.5(9)	C(3)—C(1)—C(4A)	90.2(2)	O(2)—C(4)—C(3)	125.8(5)
C(2)—C(4)—C(3)	89.6(1)	C(1)—C(2)—C(8)	88.2(7)	C(1)—C(2)—C(2A)	90.5(2)	O(1)—C(5)—C(6A)	108.0(4)

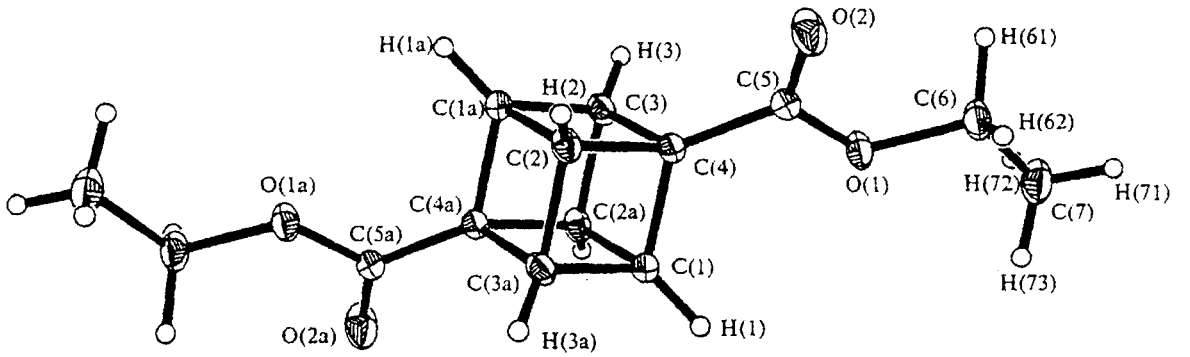

Fig. 1. Structure of molecule **3a**.

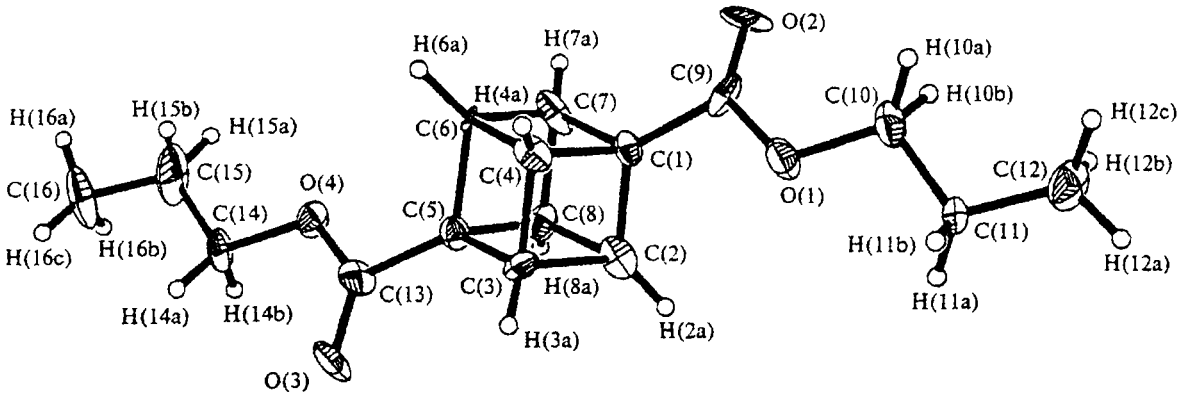

Fig. 2. Structure of molecule **3b**.

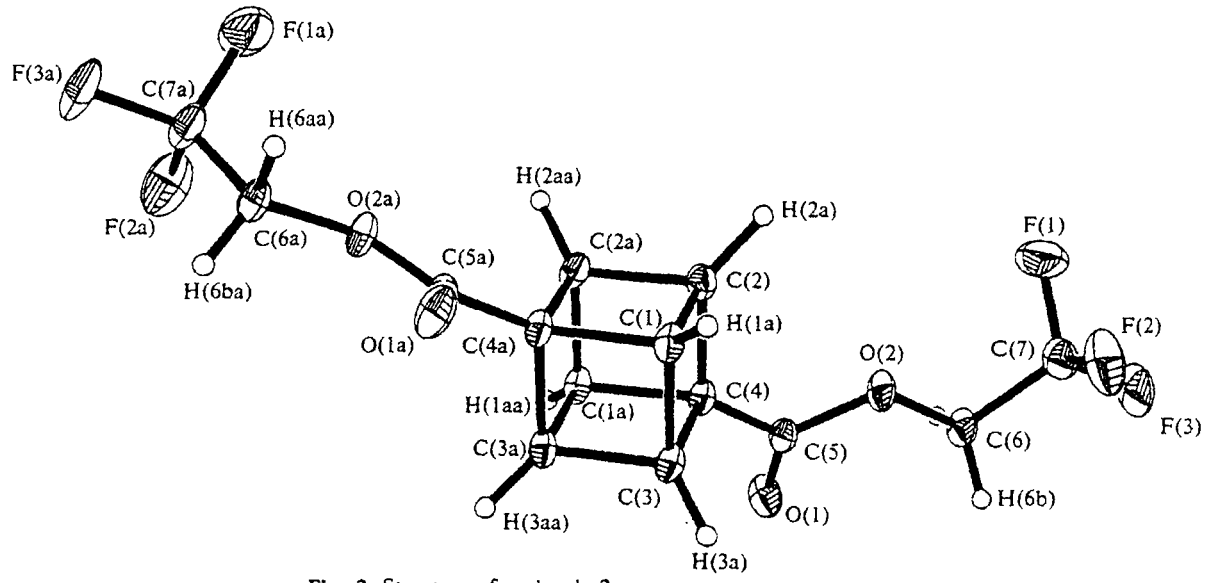

Fig. 3. Structure of molecule **3e**.

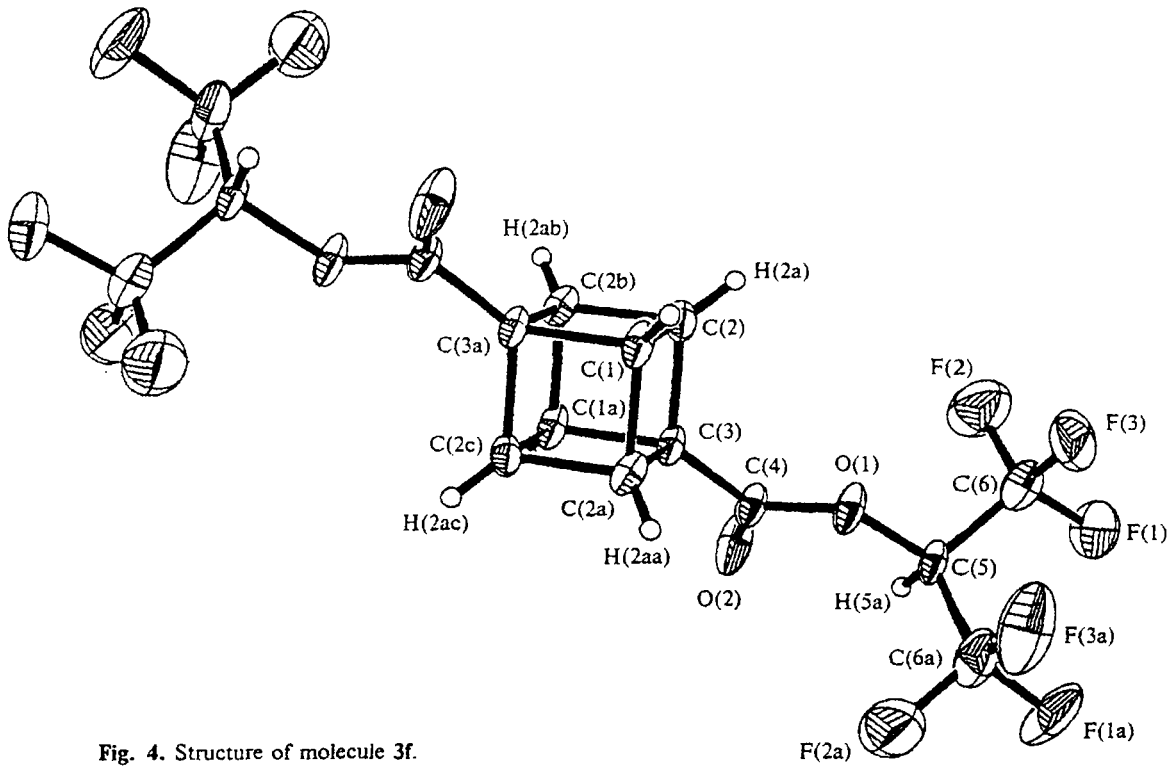

Fig. 4. Structure of molecule **3f**.

$1,4\text{-}(F(NO_2)_2CCH_2OCO)_2C_8H_6$ studied previously,[1] in which the most substantial distortions are observed for the bonds with the participation of the carbon atoms that are bonded to the substituents.

In the structures of molecules **3e** and **3f** (Figs. 3 and 4; Tables 2 and 3), which contain one and two trifluoromethyl groups in the substituents, respectively, no noticeable distortions of the cubane framework are observed. Thus, the C—C bond lengths and the CCC bond angles of the cubane framework (1.555(4)—1.580(3) Å and 89.5(2)—90.6(2)° in **3e** and 1.544(8)—1.579(5) Å and 89.1(4)—91.0(4)° in **3f**) are in the ranges similar to those observed in the symmetrical molecules of ester **3a** and of the methyl and isopropyl deriva-

Table 4. Crystallographic parameters for compounds **3a,b,e,f**

Parameter	**3a**	**3b**	**3e**	**3f**
Space group	$P2_1/c$	$Pca2_1$	$C2/c$	$C2/m$
a/Å	10.733(2)	10.797(3)	19.959(4)	9.365(2)
b/Å	5.391(2)	5.402(2)	7.482(2)	10.506(2)
c/Å	10.736(2)	25.407(6)	9.627(2)	10.458(2)
β/deg	96.66(2)	90	97.21(3)	115.58(2)
V/Å^3	617.0(2)	1481.8(6)	1426.2(7)	928.0(3)
Z	2	4	4	2
ρ_{calc}/g cm^{-3}	1.336	1.239	1.659	1.761
μ/cm^{-1}	0.98	0.88	1.70	2.02
Radiation	Mo-Kα (λ = 0.71073 Å)			
θ-2θ scanning range/deg	2—54	2—52	3—58	2—56
Number of measured reflections	1337	1652	2067	1258
Number of reflections c $I > 4.0\sigma$	1093	691	1161	1189
Weighting scheme	$w^{-1} = \sigma^2(F) + kF^2$,			
k	0.0001	0.0005	0.0023	0.0003
R	0.046	0.087	0.052	0.072
Rw	0.059	0.101	0.080	0.090

Table 5. Atomic coordinates (×10^4) and equivalent isotropic temperature factors for compounds **3a,b,e,f**

Atom	x	y	z	B_{eq}
		3a		
O(1)	2534(1)	627(2)	7405(1)	45(1)
O(2)	3009(1)	−2700(3)	6315(2)	70(1)
C(1)	583(2)	2157(3)	5349(2)	38(1)
C(2)	742(2)	−1376(3)	4326(2)	38(1)
C(3)	−228(1)	−1275(3)	6033(2)	38(1)
C(4)	1111(1)	−485(3)	5699(1)	33(1)
C(5)	2318(1)	−1013(3)	6482(2)	35(1)
C(6)	3718(2)	435(4)	8219(2)	50(1)
C(7)	3754(2)	2472(5)	9143(2)	62(1)
H(1)	1041(17)	3701(42)	5593(18)	47(5)
H(2)	1237(19)	−2322(35)	3859(20)	51(5)
H(3)	−399(19)	−2195(37)	6766(21)	54(6)
H(61)	3774(26)	−1295(60)	8613(27)	97(9)
H(62)	4354(23)	549(45)	7746(22)	69(7)
H(71)	4568(26)	2440(45)	9613(24)	76(7)
H(72)	3104(30)	2238(56)	9674(32)	105(10)
H(73)	3628(25)	4036(56)	8703(26)	87(9)
		3b		
O(1)	6648(7)	1996(14)	489	66(1)
O(2)	7777(10)	5200(14)	684(6)	98(1)
O(3)	9617(10)	−182(15)	−1837(5)	82(1)
O(4)	10903(7)	3028(13)	−1605(4)	63(1)
C(1)	8191(9)	2981(17)	−90(5)	43(1)
C(2)	8467(11)	340(18)	−283(7)	56(1)
C(3)	7986(10)	1154(16)	−864(6)	53(1)
C(4)	7697(11)	3805(17)	−658(6)	54(1)
C(5)	9321(10)	1993(16)	−1021(5)	45(1)
C(6)	8995(12)	4743(14)	−800(5)	38(1)
C(7)	9503(10)	4026(19)	−264(6)	62(1)
C(8)	9804(10)	1310(17)	−475(6)	54(1)
C(9)	7550(9)	3641(16)	412(5)	47(1)
C(10)	5923(12)	2186(18)	963(6)	78(1)
C(11)	5179(16)	−83(18)	1031(6)	73(1)
C(12)	4573(13)	−123(19)	1550(9)	91(1)
C(13)	9945(10)	1503(17)	−1542(6)	58(1)
C(14)	11607(11)	2815(18)	−2091(5)	64(1)
C(15)	12259(15)	4967(20)	−2173(9)	119(1)
C(16)	13189(12)	4965(20)	−2631(7)	105(1)
H(2A)	8242(22)	−1225(23)	−150(21)	81(2)
H(3A)	7498(23)	50(23)	−1083(21)	78(2)
H(4A)	6961(23)	4788(23)	−765(21)	82(2)
H(6A)	9190(23)	6280(23)	−957(21)	83(2)
H(7A)	9958(23)	5106(23)	−97(21)	81(2)
H(8A)	10632(23)	355(23)	−488(22)	82(2)
H(10A)	5517(23)	3702(23)	1049(21)	83(2)
H(10B)	6515(23)	2321(23)	1303(21)	82(2)
H(11A)	5782(23)	−1679(23)	977(21)	81(2)
H(11B)	4496(23)	−174(23)	775(21)	83(2)
H(12A)	4109(23)	−1479(23)	1624(21)	84(2)
H(12B)	5157(23)	13(23)	1777(21)	84(2)
H(12C)	4123(23)	1418(23)	1633(21)	86(2)
H(14A)	11047(23)	2393(23)	−2394(21)	83(2)
H(14B)	12278(23)	1455(23)	−2009(21)	82(2)
H(15A)	12593(23)	5566(23)	−1878(21)	83(2)
H(15B)	11567(23)	6363(23)	−2173(21)	81(2)
H(16A)	13750(23)	6489(23)	−2530(21)	86(2)
H(16B)	13879(23)	3806(23)	−2552(21)	83(2)
H(16C)	12817(23)	4451(23)	−2926(21)	84(2)
		3e		
O(1)	−1733(1)	889(3)	−4099(2)	58(1)
O(2)	−1173(1)	2473(3)	−5549(2)	45(1)
F(1)	−1557(1)	5289(3)	−7323(3)	106(1)
F(2)	−1080(1)	3182(4)	−8289(2)	99(1)
F(3)	−2149(1)	3590(3)	−8737(2)	91(1)
C(1)	534(1)	1654(3)	−3247(2)	38(1)
C(2)	−20(1)	3135(3)	−3321(2)	42(1)
C(3)	−24(1)	176(3)	−3312(2)	36(1)
C(4)	−584(1)	1677(3)	−3389(2)	36(1)
C(5)	−1227(1)	1609(3)	−4342(2)	36(1)
C(6)	−1760(1)	2383(4)	−6582(3)	46(1)
C(7)	−1635(1)	3622(4)	−7721(3)	58(1)
H(1A)	932(13)	1651(34)	−3797(30)	44(7)
H(2A)	−3(17)	4320(48)	−3960(38)	79(11)
H(3A)	−68(12)	−869(35)	−3890(27)	38(6)
H(6A)	−2169(15)	2853(41)	−6173(31)	53(8)
H(6B)	−1842(16)	1247(44)	−6949(36)	68(9)
		3f		
O(1)	2242(3)	0	2994(3)	67(2)
O(2)	−283(4)	0	1418(4)	103(2)
F(1)	4167(6)	1260(4)	1028(5)	155(3)
F(2)	2835(7)	2202(4)	1967(5)	168(3)
F(3)	4954(5)	1258(5)	3281(5)	161(3)
C(1)	1354(6)	0	6199(5)	56(2)
C(2)	848(4)	1054(4)	5047(4)	53(2)
C(3)	320(5)	0	3855(4)	47(2)
C(4)	662(5)	0	2606(5)	56(2)
C(5)	2746(6)	0	1898(5)	55(2)
C(6)	3689(7)	1179(6)	2042(6)	99(3)
H(1A)	2252(63)	0	6996(57)	64(15)
H(2A)	1370(45)	1714(37)	5064(38)	54(11)
H(5A)	1853(67)	0	1041(59)	63(16)

tives.[1,2] Apparently, this effect (in spite of the presence of the strong electron-withdrawing groups containing fluorine atoms) indicates that in this class of derivatives, the cubane framework would be expected to be distorted when the chain of the substituent is increased by more than two carbon atoms (**3b**) or when NO_2 groups are introduced as was observed in the case of the fluorodinitroethyl analog studied previously.[1]

Experimental

The ^1H NMR spectra were recorded on an NMR spectrometer equipped with a superconducting magnet (295 MHz). The instrument was developed and built at the Institute of Chemical Physics in Chernogolovka of the Russian Academy of Sciences. The IR spectra were measured on a Specord M82 instrument as KBr pellets.

Preparation of 1,4-cubanedicarboxylic acid dichloride (2). Acid **1** (1 g, 5.2 mmol) was added carefully to a freshly distilled thionyl chloride (10 mL) at ~20 °C. The mixture was heated to 40 °C and stirred at this temperature for 3 h. Then the reaction mixture was cooled, and excess thionyl chloride was distilled off at a residual pressure of 10 Torr until the product was obtained as a white powder. The powder was used in subsequent reactions without additional purification. M.p. 133—135 °C (published data:[3] m.p. 135—136 °C).

Preparation of esters 3a—d (general procedure). Alkanol (6 mmol) was added to freshly prepared dichloride **2** (2 mmol) at ~20 °C. The mixture was refluxed for 2.5 h. Then excess alkanol was distilled off at a residual pressure of 10 Torr. The solid residue was recrystallized from hexane, and esters **3a—d** were obtained as colorless crystals in yields of 85—95%.

Preparation of bis-(2,2,2-trifluoroethyl) 1,4-cubanedicarboxylate (3e). A solution of lithium trifluoroethoxide, which was prepared from Li (100 mg, 12.5 mmol) and trifluoroethanol (3 mL), was added to a solution of freshly prepared product **2** (from 1.56 mmol of **1**) in anhydrous THF (50 mL) with cooling to 0 °C. The reaction mixture was stirred at ~20 °C for 1 h and then at 40 °C for 1 h and poured into distilled water (250 mL). The precipitate was filtered off, washed with water, dried, and recrystallized from a 1 : 2 chloroform—hexane mixture. The yield of compound **3e** was 47%.

Preparation of bis-hexafluoroisopropyl 1,4-cubanedicarboxylate (3f). A mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (1 mL, 9 mmol) and lithium hydride (80 mg, 10 mmol) in THF (50 mL) was stirred until LiH was dissolved. Then the reaction mixture was cooled to 0 °C, and freshly prepared dichloride **2** (500 mg, 2.183 mmol) was added. The reaction mixture was kept at ~20 °C for 1 h and then at 40 °C for 1 h, cooled, poured into distilled water (200 mL), and stirred until a precipitate formed. The precipitate was filtered off, dried, and recrystallized from heptane. The yield was 51%.

X-ray diffraction analysis. Crystals of compounds **3a**, **3b**, **3e**, and **3f** suitable for X-ray diffraction analysis were prepared by slow concentration of solutions of the compounds in 5 : 1 CH_2Cl_2—hexane or 3 : 1 THF—hexane mixtures. The experimental data sets for all the compounds were collected on a Siemens R3v/m diffractometer at 22 °C. The unit cell parameters were measured and refined using 24 equivalent reflections. Three strong standard reflections with $0 < \chi < 60°$ were used for monitoring possible movements of the crystal and decomposition of the sample. The standard reflections revealed no significant intensity variation, and therefore, no corrections were applied. All the structures were solved by direct methods, which allowed us to reveal all nonhydrogen atoms. The positional and thermal parameters of the nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from the difference Fourier maps and refined isotropically. The crystallographic parameters of the compounds and selected details of the refinement are given in Table 4. The principal geometric characteristics of molecules **3a**, **3b**, **3e**, and **3f** are given in Tables 2 and 3 The atomic coordinates and equivalent temperature factors are listed in Table 5. All calculations were carried out on a Pentium 100 computer using the SHELXTL PLUS program package (PC Version).[4]

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