APPENDIX A

X-ray Crystallographic Data for:

4,4-Difluoro-3-(trifluoromethyl)-tricyclo[4.2.1.$0^{2,5}$]non-7-ene-3-carboxylic acid (**2.10**)

X-ray Experimental for Compound 2.10:

The crystal was cut from a larger crystal and had approximate dimensions: 0.48 x 0.24 x 0.19 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 347 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 39 seconds per frame. The data were collected at -120 °C using an Oxford Cryostream low temperature device. Details of crystal data, data collection, and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atom positions were located in a ΔF and refined with isotropic displacement parameters. The function, $\Sigma w(|F_0|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_0))^2 + (0.0455*P)^2 + (0.4828*P)]$ and $P = (|F_0|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.102, with R(F) equal to 0.0455 and a goodness of fit, S = 0.998. Definitions used for calculating R(F), $R_w(F^2)$, and the goodness of fit, S, are given below.[4] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1+ (6(4)x10^{-6})*F_c^2\lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in Tables 1 through 6.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343-350.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

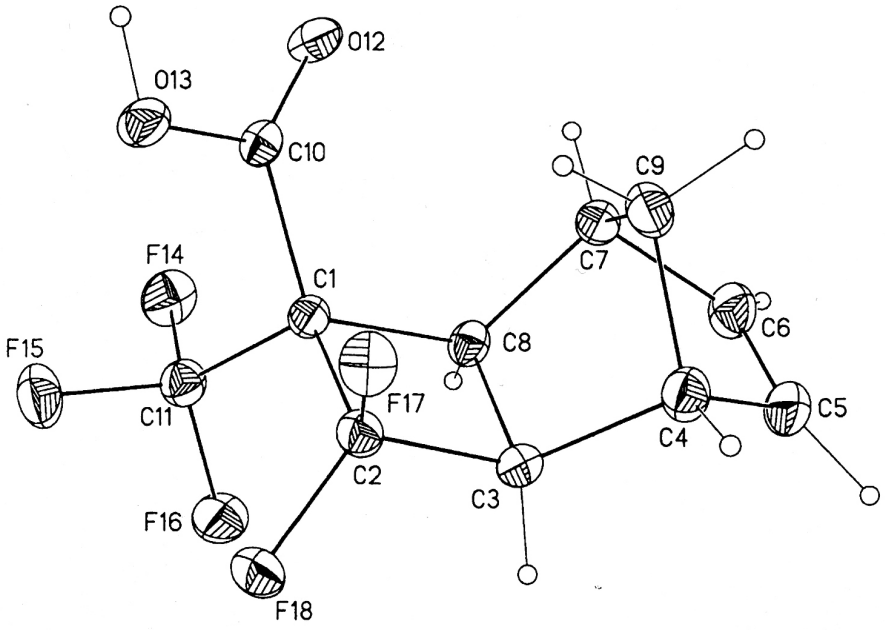
5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C11 H9 F5 O2	
Formula weight	268.18	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 6.7504(2) Å	α= 90°.
	b = 19.0686(5) Å	β= 110.485(2)°.
	c = 8.9486(2) Å	γ = 90°.
Volume	1079.03(5) $Å^3$	
Z	4	
Density (calculated)	1.651 Mg/m^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	544	
Crystal size	0.48 x 0.24 x 0.19 mm	
Theta range for data collection	3.29 to 27.49°.	
Index ranges	-8<=h<=8, -22<=k<=24, -11<=l<=11	
Reflections collected	4338	
Independent reflections	2414 [R(int) = 0.0188]	
Completeness to theta = 27.49°	97.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2414 / 0 / 200	
Goodness-of-fit on F^2	0.998	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0915	
R indices (all data)	R1 = 0.0585, wR2 = 0.1016	
Extinction coefficient	$6(4)x10x10^{-6}$	
Largest diff. peak and hole	0.382 and -0.251 $e.Å^{-3}$	

Structure 1. View of **2.10** showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary size.



Structure 2. View of the H-bound dimers formed by **2.10**. The dimer lies around a crystallographic inversion center at 0, 1/2, ½. The geometry of the interaction is: O13-H13····O12 (related by –x, 1-y, 1-z), O····O 2.697(2)Å, H····O 1.85(3)Å, O-H····O 174(2)°. Thermal ellipsoids are scaled to the 30 % probability level. Hydrogen atoms are drawn to an arbitrary size.

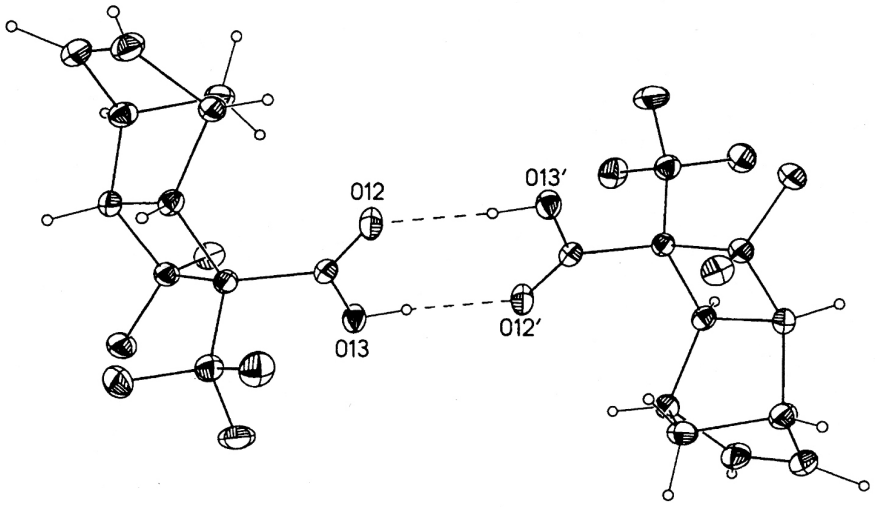


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2305(2)	3607(1)	3784(2)	23(1)
C(2)	4730(2)	3586(1)	4102(2)	26(1)
C(3)	4345(3)	3470(1)	2335(2)	28(1)
C(4)	4800(3)	4081(1)	1362(2)	32(1)
C(5)	3661(3)	3859(1)	-365(2)	38(1)
C(6)	1613(3)	3916(1)	-667(2)	38(1)
C(7)	1299(3)	4179(1)	847(2)	30(1)
C(8)	1891(3)	3531(1)	1956(2)	26(1)
C(9)	3263(3)	4642(1)	1510(2)	33(1)
C(10)	1379(2)	4246(1)	4334(2)	24(1)
C(11)	1523(3)	2961(1)	4411(2)	31(1)
O(12)	-191(2)	4541(1)	3460(1)	33(1)
O(13)	2395(2)	4413(1)	5826(1)	32(1)
F(14)	-595(2)	2961(1)	3925(1)	42(1)
F(15)	2237(2)	2922(1)	6001(1)	44(1)
F(16)	2084(2)	2362(1)	3878(1)	41(1)
F(17)	5809(1)	4172(1)	4781(1)	33(1)
F(18)	5764(2)	3050(1)	5069(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for 1.

C(1)-C(11)	1.523(2)	C(6)-C(7)	1.527(3)
C(1)-C(10)	1.526(2)	C(6)-H(6)	1.01(2)
C(1)-C(2)	1.561(2)	C(7)-C(9)	1.529(3)
C(1)-C(8)	1.567(2)	C(7)-C(8)	1.548(2)
C(2)-F(17)	1.3563(19)	C(7)-H(7)	0.95(2)
C(2)-F(18)	1.3632(18)	C(8)-H(8)	0.981(19)
C(2)-C(3)	1.526(2)	C(9)-H(9A)	0.98(2)
C(3)-C(4)	1.549(2)	C(9)-H(9B)	1.00(2)
C(3)-C(8)	1.574(2)	C(10)-O(12)	1.2125(19)
C(3)-H(3)	0.96(2)	C(10)-O(13)	1.3094(19)
C(4)-C(5)	1.525(3)	C(11)-F(15)	1.335(2)
C(4)-C(9)	1.529(3)	C(11)-F(14)	1.341(2)
C(4)-H(4)	0.988(19)	C(11)-F(16)	1.341(2)
C(5)-C(6)	1.317(3)	O(13)-H(13)	0.85(3)
C(5)-H(5)	1.03(2)		

C(11)-C(1)-C(10)	107.03(13)	C(5)-C(4)-C(9)	99.51(14)
C(11)-C(1)-C(2)	112.84(13)	C(5)-C(4)-C(3)	103.46(15)
C(10)-C(1)-C(2)	118.94(13)	C(9)-C(4)-C(3)	101.77(13)
C(11)-C(1)-C(8)	110.56(13)	C(5)-C(4)-H(4)	118.8(11)
C(10)-C(1)-C(8)	117.86(13)	C(9)-C(4)-H(4)	118.6(12)
C(2)-C(1)-C(8)	88.86(11)	C(3)-C(4)-H(4)	112.2(11)
F(17)-C(2)-F(18)	104.97(12)	C(6)-C(5)-C(4)	107.82(16)
F(17)-C(2)-C(3)	117.02(13)	C(6)-C(5)-H(5)	127.3(13)
F(18)-C(2)-C(3)	114.35(14)	C(4)-C(5)-H(5)	124.3(13)
F(17)-C(2)-C(1)	115.12(13)	C(5)-C(6)-C(7)	107.84(16)
F(18)-C(2)-C(1)	113.99(13)	C(5)-C(6)-H(6)	127.9(12)
C(3)-C(2)-C(1)	91.57(11)	C(7)-C(6)-H(6)	124.0(12)
C(2)-C(3)-C(4)	118.56(15)	C(6)-C(7)-C(9)	99.42(15)
C(2)-C(3)-C(8)	89.86(12)	C(6)-C(7)-C(8)	102.78(14)
C(4)-C(3)-C(8)	102.91(13)	C(9)-C(7)-C(8)	102.60(13)
C(2)-C(3)-H(3)	112.1(12)	C(6)-C(7)-H(7)	118.1(11)
C(4)-C(3)-H(3)	113.6(12)	C(9)-C(7)-H(7)	116.6(12)
C(8)-C(3)-H(3)	117.6(11)	C(8)-C(7)-H(7)	114.9(11)

C(7)-C(8)-C(1)	120.45(14)	H(9A)-C(9)-H(9B)	108.6(16)
C(7)-C(8)-C(3)	102.34(13)	O(12)-C(10)-O(13)	124.93(15)
C(1)-C(8)-C(3)	89.55(11)	O(12)-C(10)-C(1)	121.73(14)
C(7)-C(8)-H(8)	113.0(11)	O(13)-C(10)-C(1)	113.28(14)
C(1)-C(8)-H(8)	111.1(11)	F(15)-C(11)-F(14)	106.96(13)
C(3)-C(8)-H(8)	118.4(11)	F(15)-C(11)-F(16)	106.85(14)
C(4)-C(9)-C(7)	94.83(14)	F(14)-C(11)-F(16)	106.65(14)
C(4)-C(9)-H(9A)	114.3(11)	F(15)-C(11)-C(1)	113.28(14)
C(7)-C(9)-H(9A)	115.1(11)	F(14)-C(11)-C(1)	110.38(14)
C(4)-C(9)-H(9B)	112.7(11)	F(16)-C(11)-C(1)	112.35(13)
C(7)-C(9)-H(9B)	110.8(11)	C(10)-O(13)-H(13)	106.8(16)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	23(1)	23(1)	-1(1)	10(1)	0(1)
C(2)	25(1)	28(1)	26(1)	3(1)	9(1)	2(1)
C(3)	30(1)	30(1)	28(1)	2(1)	13(1)	7(1)
C(4)	28(1)	41(1)	30(1)	5(1)	13(1)	2(1)
C(5)	45(1)	46(1)	28(1)	4(1)	18(1)	7(1)
C(6)	41(1)	48(1)	24(1)	2(1)	11(1)	3(1)
C(7)	28(1)	35(1)	26(1)	5(1)	10(1)	8(1)
C(8)	28(1)	26(1)	24(1)	-4(1)	11(1)	-3(1)
C(9)	40(1)	30(1)	29(1)	5(1)	13(1)	-1(1)
C(10)	24(1)	26(1)	24(1)	-2(1)	11(1)	-2(1)
C(11)	34(1)	29(1)	32(1)	0(1)	16(1)	-2(1)
O(12)	28(1)	39(1)	28(1)	-8(1)	6(1)	9(1)
O(13)	34(1)	36(1)	23(1)	-5(1)	7(1)	8(1)
F(14)	35(1)	43(1)	54(1)	-1(1)	23(1)	-10(1)
F(15)	60(1)	41(1)	33(1)	9(1)	21(1)	-4(1)
F(16)	54(1)	23(1)	53(1)	-1(1)	27(1)	-2(1)
F(17)	27(1)	39(1)	30(1)	-2(1)	7(1)	-7(1)
F(18)	33(1)	42(1)	36(1)	13(1)	12(1)	13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1.

	x	y	z	U(eq)
H(3)	4880(30)	3027(11)	2140(20)	35(5)
H(4)	6320(30)	4195(10)	1710(20)	38(5)
H(5)	4390(40)	3634(12)	-1080(30)	55(6)
H(6)	420(30)	3772(11)	-1660(30)	43(6)
H(7)	-20(30)	4390(10)	750(20)	34(5)
H(8)	1000(30)	3121(10)	1510(20)	30(5)
H(9A)	3560(30)	4814(10)	2600(20)	37(5)
H(9B)	3170(30)	5056(11)	800(20)	40(5)
H(13)	1750(40)	4764(14)	6040(30)	63(7)