is rather flexible, but that the global minimum-energy conformation of the five-membered ring is similar to that observed in the crystal structures. The fragment (O—C—C—N) can change orientation without affecting the ring conformation. The region +*gauche* to *trans* is accessible in the (+)-(2*S*,5*S*)-enantiomer of muscarone. Other possible orientations of the (O—C—C—N) fragment cause steric interactions for some ring conformations. Pseudorotational parameters, calculated by the method described by Rao, Westhof & Sundaralingam (1981) are given in Table 2. The magnitude of the amplitudes [except for (±)-muscarone iodide from 1972] and the preferred conformations correspond to results obtained by *ab initio* calculations for cyclopentanone (Cremer & Pople, 1975). The two crystal structure determinations indicate that the five-membered ring of the muscarone ion prefers one minimum-energy conformation with the carbonyl group in the planar part of the ring, while the side chain adopts both the *gauche* and the *trans* orientation.

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Acta Cryst. (1992). C**48**, 474–477

Structure of the 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Bis(fluoroacetonitrile) Complex

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Abstract. $C_{12}H_{24}O_6.2C_2H_2FN$, $M_r = 382.416$, monoclinic, $P2_1/n$, $a = 8.3125\,(11)$, $b = 8.3049\,(17)$, $c = 15.2308\,(14)$ Å, $\beta = 100.950\,(9)°$, $V = 1032.3\,(3)$ Å^3, $Z = 2$, $D_x = 1.23$ g cm^{-3}, $\lambda = 0.70930$ Å, $\mu = 0.10$ mm^{-1}, $F(000) = 408$, room temperature, $R_F = 0.065$, $wR = 0.040$ for 1039 reflections. The 18-crown-6 molecule has approximate D_{3d} symmetry. The two fluoroacetonitrile molecules are situated one

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above and one below the plane of the ether O atoms. Unusual long H···O interactions are found between the host and both guests.

Introduction. The interactions of 18-crown-6 (and several other polyethers) with neutral organic guest molecules have become of increasing interest during the past decade. The complex formation of neutral molecules with polyethers is made possible mainly by the formation of intermolecular hydrogen bonds. The crystal structure of the title complex was investigated to find the relative conformation of 18-crown-6 ring in the complex and the effect of the F atom of CH_2FCN on the shape of the cavity and on the interaction between the host and the guest.

Experimental. The 18-crown-6.2CH_2FCN complex was prepared by mixing the 18-crown-6 (0.35 g, 1.3 mmol) with an excess of fluoroacetonitrile (1 ml, 18 mmol) in dimethyl ether (10 ml). Recrystallization from ethyl acetate was necessary in order to obtain good crystals for crystallographic investigation. M.p. 362–367 K. Since the complex is very hygroscopic, a white cubic crystal (dimensions 0.40 × 0.40 × 0.40 mm) was sealed in a capillary. A summary of crystal structure data is given in Table 1. Diffraction intensities were collected on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, using the $\theta/2\theta$-scan technique with profile analysis (Grant & Gabe, 1978) at a scan speed of 2° $\min^{-1}$. Three standards were measured every 100 reflections and no crystal decay was observed. The long-range instability of the three standards is around 1.5%. Space group determined by systematic absences. Unit-cell parameters obtained by least-squares refinement of the setting angles for 25 reflections ($40 < 2\theta < 45°$). Lorentz and polarization factors were applied but no correction for absorption was made.

The structure was solved by direct methods and refined by full-matrix least squares with counting statistics weights. H-atom positions were found by Fourier difference synthesis and refined isotropically. All the calculations were performed using the *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) crystal structure package. The final atomic positional parameters are listed in Table 2.* An *ORTEP* (Johnson, 1965) view of the complex and a stereoview of the unit-cell packing are shown in Figs. 1 and 2, respectively.

Table 1. *X-ray crystallography parameters*

Max. $(\sin\theta)/\lambda$ (Å^{-1})	0.537
Range of *hkl* indices	$-8\rightarrow8$, $0\rightarrow8$, $0\rightarrow16$
No. of reflections measured	2100
No. of unique reflections	1330
R_{int} (%)	1.7
No. of unique reflections $I_{\text{net}} > n\sigma(I_{\text{net}})$	1039 with $n = 2.5$
Last least-squares cycle calculated with	27 atoms, 175 parameters, 1039 out of 1330 reflections
Goodness-of-fit (last cycle)	10.33
R_F (all reflections)	0.081
wR (all reflections)	0.041
Max. shift/σ	0.60
Last difference map, deepest hole and highest peak (e Å^{-3})	−0.200 0.230
Secondary-extinction coefficient	0.082553

Table 2. *Atomic parameters x, y, z and* B_{iso}

E.s.d.'s refer to the last digit printed. B_{iso} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{iso}(Å^2)
F	0.7401 (4)	0.7496 (3)	0.0710 (17)	9.69 (16)
O(1)	0.2221 (3)	0.8819 (3)	1.0583 (20)	5.56 (16)
O(2)	0.2519 (4)	0.8541 (4)	0.8755 (19)	5.94 (16)
O(3)	0.4958 (4)	1.0409 (4)	0.8158 (17)	6.42 (17)
N	0.5971 (7)	0.5839 (6)	−0.1179 (3)	12.3 (3)
C(1)	0.1341 (7)	0.7696 (8)	0.9978 (5)	6.9 (4)
C(2)	0.1037 (7)	0.8387 (9)	0.9064 (5)	7.4 (4)
C(3)	0.2312 (8)	0.9242 (8)	0.7886 (5)	7.3 (4)
C(4)	0.3893 (8)	0.9335 (9)	0.7606 (4)	7.4 (4)
C(5)	0.3452 (8)	0.9529 (9)	1.2036 (4)	7.0 (4)
C(6)	0.2497 (8)	0.8273 (8)	1.1482 (4)	6.7 (3)
C(7)	0.5995 (6)	0.6722 (7)	−0.0625 (3)	7.1 (3)
C(8)	0.6051 (7)	0.7908 (8)	0.0069 (4)	5.6 (3)

Discussion. The title complex lies on a crystallographic centre of inversion. The two fluoroacetonitrile molecules are situated one above and one below the cavity of the crown-ether ring (Fig. 1). The intermolecular distances between the methylene C atom of the nitrile and the O atoms of the crown ether are 3.50 [C(8) to O(1)], 3.53 [C(8) to O(2)′] and 3.29 Å [C(8) to O(3)]. As shown in Table 3, the sequence of torsion angles in the ether is in accordance with a pseudo D_{3d} conformation of the 18-crown-6 ring. The average bond distances and angles between the atoms of the crown-ether ring are similar to those observed in the other complexes with neutral guests containing C—H acidic groups such as 18-crown-6.bis(malononitrile) (Kaufman, Knöchel, Kopf, Oehler & Rudolph, 1977), 18-crown-6.-adiponitrile, 18-crown-6.cyanoacetic acid.water (Elbasyouny, Brügge, von Deuten, Dickel, Knöchel, Koch, Kopf, Melzer & Rudolph, 1983), 18-crown-6.-bis(nitromethane) (de Boer, Reinhoudt, Harkema, van Hummel & de Jong, 1982; Rogers & Green, 1986), 18-crown-6.bis(dimethyl sulfone) (Bandy, Truter & Vögtle, 1981), 18-crown-6.dimethyl sulfate (Weber, 1983), 18-crown-6.dimethyl acetylenedicarboxylate (Goldberg, 1975) and 18-crown-6.bis-(acetonitrile) (Weller, Borgholte, Stenger, Vogler & Dehnicke, 1989). They are also in accordance with

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54439 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

those of complexes of 18-crown-6 with inorganic and some other neutral organic molecules (Goldberg, 1984).

However, H···O intermolecular distances in the title complex are not comparable to those found in the literature complexes listed above. As shown in Figs. 1 and 2, the H atoms [H(8*A*) and H(8*B*)] of the fluoroacetonitrile form two very weak H···O interactions of equal distances (2.89 Å) to O atoms 1 and 3 of the crown-ether ring. It is interesting to note that these H···O intermolecular distances are nearly 0.3 Å longer than the sum of the van der Waals radii (2.60 Å; Pauling, 1960). These distances are also longer than the H···O distances found in the literature for similar complexes (Table 4). For the literature complexes, the C—H···O distances are rather similar and range from 2.2 to 2.6 Å while the distance for the title complex is 2.89 Å. These results show that for the 18-crown-6.bis(fluoroacetonitrile) complex, the host-guest interactions are weaker than those of related complexes and the fluoroacetonitrile is less strongly pulled into the crown-ether pocket than the guests of related complexes.

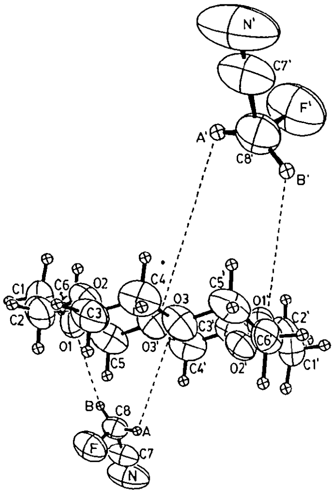

Fig. 1. *ORTEP* diagram of the structure of 18-crown-6.-$2CH_2FCN$, with atomic numbering scheme.

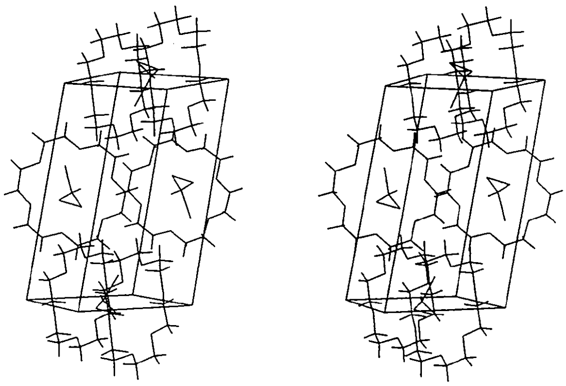

Fig. 2. Stereoview of the unit-cell packing for 18-crown-6.-$2CH_2FCN$.

Table 3. *Bond distances* (Å), *bond angles* (°) *and selected torsional angles* (°)

F—C(8)	1.383 (5)	N—C(7)	1.115 (8)
O(1)—C(1)	1.414 (7)	C(1)—C(2)	1.482 (10)
O(1)—C(6)	1.418 (6)	C(3)—C(4)	1.459 (10)
O(2)—C(2)	1.406 (8)	C(5)—C(6)	1.475 (10)
O(2)—C(3)	1.426 (7)	C(7)—C(8)	1.439 (8)
O(3)—C(4)	1.416 (7)		
O(3)—C(5′)	1.410 (7)		
C(1)—O(1)—C(6)	112.8 (4)	O(3)—C(4)—C(3)	110.8 (5)
C(2)—O(2)—C(3)	112.9 (4)	O(3′)—C(5)—C(6)	109.3 (5)
C(4)—O(3)—C(5′)	113.8 (5)	O(1)—C(6)—C(5)	107.3 (5)
O(1)—C(1)—C(2)	109.4 (5)	N—C(7)—C(8)	177.8 (7)
O(2)—C(2)—C(1)	110.2 (5)	F—C(8)—C(7)	105.0 (4)
O(2)—C(3)—C(4)	109.6 (4)		
C(1)—O(1)—C(6)—C(5)	−178.7 (6)	O(2)—C(3)—C(4)—O(3)	−65·4 (4)
C(6)—O(1)—C(1)—C(2)	177.4 (6)	C(5′)—O(3)—C(4)—C(3)	175.8 (6)
O(1)—C(1)—C(2)—O(2)	67.8 (4)	C(4)—O(3)—C(5′)—C(6′)	174.9 (6)
C(3)—O(2)—C(2)—C(1)	−178.4 (6)	O(3)—C(5′)—C(6′)—O(1′)	68.8 (4)
C(2)—O(2)—C(3)—C(4)	−179.0 (6)	N—C(7)—C(8)—F	−104.1 (6)

Table 4. H···O *and* C···O *intermolecular distances* (Å) *in crystalline complexes of* 18-*crown*-6

Guest	H···O	C···O	Stoichiometry
CH_2FCN^a	2.89	3.503 (7)	1:2
	2.89	3.287 (7)	
		3.537 (6)	
$CH_2(CN)_2{}^b$	2.235 (28)	3.257 (3)	1:2
	2.694 (36)		
$(CH_2)_4(CN)_2{}^c$	2.575		1:1
	2.427		
$CH_2(CN)COOH.H_2O^c$	2.514/2.752		1:1:1
	2.530/2.960		
$CH_3NO_2{}^d$	2.30	3.27	1:2
	2.45	3.24	
	2.35	3.32	
$(CH_3)_2SO_2{}^e$	2.48 (4)	3.363 (4)	1:2
	2.62 (4)	3.314 (4)	
	2.47 (4)	3.321 (4)	
$CC(COOCH_3)_2{}^f$	2.32	3.08	1:1
	2.45	3.38	
		3.39	
CH_3CN^g	2.43 (6)	—	1:2
	2.53 (6)	—	
	2.67 (6)	—	
$(CH_3)_2SO_4{}^h$	2.325 (8)	3.220 (7)	1:1
	2.332 (8)	3.227 (8)	
	2.560 (8)	3.310 (8)	
	2.586 (8)	3.318 (8)	

References: (*a*) this work; (*b*) Kaufmann *et al.* (1977); (*c*) Elbasyouny *et al.* (1983); (*d*) Rogers & Green (1986); (*e*) Bandy *et al.* (1981); (*f*) Goldberg (1975); (*g*) Weller *et al.* (1989); (*h*) Weber (1983).

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Structure of (*E*)-5-(Methoxymethylene)-2,4-imidazolidinedione

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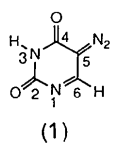
(*Received* 30 *October* 1990; *accepted* 15 *July* 1991)

Abstract. $C_5H_6N_2O_3$, $M_r = 142.11$, monoclinic, $P2_1/n$, $a = 3.862\,(1)$, $b = 16.329\,(2)$, $c = 10.088\,(1)$ Å, $\beta = 98.77\,(2)°$, $V = 628.7\,(2)$ Å^3, $Z = 4$, $D_x = 1.50$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71069 Å, $\mu = 1.18$ cm^{-1}, $F(000) = 296$, $T = 296$ K, $R = 0.035$ for 1124 independent reflections with $I > 3\sigma(I)$. The structure is a hydantoin derivative with a methoxymethylene group substituted at the 5-position. Excluding the H atoms, the molecule is planar to within 0.032 Å. All of the N and O atoms are involved in an intermolecular hydrogen-bonding network *via* N—H···O and C—H···O interactions. The packing arrangement is a linear ribbon motif with the ribbons stacked to form the short *a* axis.

Introduction. 5-Diazouracil (1) and its derivatives have been of enormous medicinal interest (Previc & Richardson, 1969). Reaction of (1) with methanol gives 5-diazo-6-methoxydihydrouracil (2) (Thurber & Townsend, 1972). The structure of (2) has been confirmed by X-ray crystallography (Abraham, Cochran & Rosenstein, 1971). Morpholine, a secondary amine, also adds to the 1,6-double bond in (1) to give 5-diazo-6-morpholinodihydrouracil (3) (Mathur & Shechter, 1990). Thermolysis of (3) in the presence of catalytic amounts of rhodium acetate in isobutyronitrile at 378 K gives 5-morpholinouracil (4) (Mathur & Shechter, 1990). Similar treatment of (2), however, yields a compound whose spectral properties do not match the expected 5-methoxyuracil (5) (Mathur & Shechter, 1991). An X-ray analysis of this solid reveals the product to be (*E*)-5-(methoxymethylene)-2,4-imidazolidinedione (6) and its structure is reported herein.



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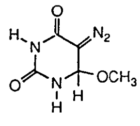

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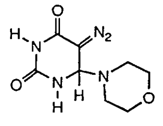

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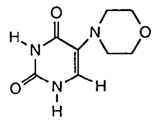

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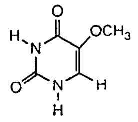

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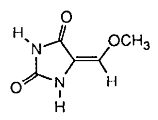

(6)

Experimental. The synthesis of the title compound (6) is reported elsewhere (Mathur & Shechter, 1991). Only the *E* isomer was isolated. Formation of only one isomer in the synthesis of other methylenehydantoins has been previously reported (Tan, Ang & Fong, 1986). The compound crystallized from water as clear orange rectangular rods. The crystal used for data collection was cut from a long rod and was 0.23 × 0.46 × 0.50 mm in size.

Examination of the diffraction pattern with a Rigaku AFC-5S diffractometer indicated a monoclinic crystal system with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$, which uniquely determine the space group as $P2_1/n$. At room temperature the unit-cell constants are based on a symmetry-restricted least-squares fit of the setting angles for 25 reflections in the 2θ range 28 to 30° with graphite-monochromated Mo $K\alpha$ radiation.

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