Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.376 (3)	C1′—C2′	1.398 (3)
C4—C5	1.391 (5)	C4′—C5′	1.391 (5)
C1—C6*t*	1.485 (3)	C1′—C6*t*′	1.481 (3)
N2—C3*t*	1.345 (3)	N2′—C3*t*′	1.349 (3)
C5*t*—C6*t*	1.436 (3)	C5*t*′—C6*t*′	1.445 (3)
C2—F2	1.363 (3)	C2′—F2′	1.332 (3)
C3—C4	1.379 (4)	C3′—C4′	1.381 (5)
C6—C1	1.399 (3)	C6′—C1′	1.394 (3)
N1—N2	1.347 (2)	N1′—N2′	1.344 (3)
N4—C5*t*	1.330 (3)	N4′—C5*t*′	1.329 (3)
C5*t*—N5	1.327 (3)	C5*t*′—N5′	1.329 (3)
C2—C3	1.380 (3)	C2′—C3′	1.376 (4)
C5—C6	1.391 (4)	C5′—C6′	1.383 (3)
C6*t*—N1	1.318 (3)	C6*t*′—N1′	1.307 (3)
C3*t*—N4	1.341 (3)	C3*t*′—N4′	1.340 (3)
C3*t*—N3	1.336 (3)	C3*t*′—N3′	1.331 (3)
C1*A*—O1*A*	1.398 (3)	C1*B*—O1*B*	1.383 (3)
C1—C2—C3	124.3 (2)	C1′—C2′—C3′	122.5 (2)
C4—C5—C6	120.1 (3)	C4′—C5′—C6′	120.4 (3)
C2—C1—C6*t*	123.3 (2)	C2′—C1′—C6*t*′	121.4 (2)
C6*t*—N1—N2	121.4 (2)	C6*t*′—N1′—N2′	121.5 (2)
C3*t*—N4—C5*t*	116.7 (2)	C3*t*′—N4′—C5*t*′	116.8 (2)
C5*t*—C6*t*—C1	123.2 (2)	C5*t*′—C6*t*′—C1′	121.7 (2)
N4—C5*t*—N5	118.0 (2)	N4′—C5*t*′—N5′	118.3 (2)
C3—C2—F2	116.4 (2)	C3′—C2′—F2′	117.8 (2)
C3—C4—C5	120.2 (2)	C3′—C4′—C5′	119.6 (3)
C6—C1—C2	116.5 (2)	C6′—C1′—C2′	117.1 (2)
C1—C6*t*—N1	117.3 (2)	C1′—C6*t*′—N1′	118.7 (2)
N2—C3*t*—N4	125.7 (2)	N2′—C3*t*′—N4′	125.6 (2)
C5*t*—C6*t*—N1	119.3 (2)	C5*t*′—C6*t*′—N1′	119.6 (2)
N4—C3*t*—N3	117.3 (2)	N4′—C3*t*′—N3′	117.4 (2)
C1—C2—F2	119.3 (2)	C1′—C2′—F2′	119.7 (2)
C2—C3—C4	118.0 (2)	C2′—C3′—C4′	119.4 (3)
C5—C6—C1	120.8 (2)	C5′—C6′—C1′	121.0 (3)
C6—C1—C6*t*	120.2 (2)	C6′—C1′—C6*t*′	121.5 (2)
N1—N2—C3*t*	117.0 (2)	N1′—N2′—C3*t*′	117.1 (2)
N4—C5*t*—C6*t*	119.7 (2)	N4′—C5*t*′—C6*t*′	119.3 (2)
N2—C3*t*—N3	116.9 (2)	N2′—C3*t*′—N3′	117.0 (2)
C6*t*—C5*t*—N5	122.2 (2)	C6*t*′—C5*t*′—N5′	122.3 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5′—H52′···N4	1.07 (4)	1.98 (4)	3.035 (3)	168 (3)
N5—H52···N4′	0.89 (3)	2.12 (3)	2.995 (3)	168 (3)
N3′—H31′···N2^{i}	0.80 (4)	2.26 (4)	3.043 (3)	164 (4)
N3—H31···N2′^{ii}	0.89 (3)	2.17 (3)	3.037 (3)	168 (3)
N5—H51···O1*A*^{i}	0.87 (3)	2.02 (3)	2.832 (2)	155 (3)
N3′—H32′···O1*A*^{i}	0.90 (4)	2.21 (3)	3.079 (4)	1622 (3)
N3—H32···O1*B*^{iii}	0.91 (3)	2.16 (3)	3.020 (4)	157 (2)
N5′—H51′···O1*B*^{iii}	0.84 (2)	2.30 (3)	2.923 (2)	132 (3)
O1*A*—H1*A*···N1^{iv}	0.77 (6)	2.09 (6)	2.824 (3)	161 (5)
O1*B*—H1*B*···N1′^{v}	0.941 (2)	2.043 (2)	2.971 (3)	168.0 (1)

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

All H atoms of the phenyl ring were positioned from geometrical constraints, while the remaining H atoms were located on difference synthesis maps. One hydroxyl H atom (H1*B*) was fixed in position. All H atoms were refined isotropically.

Data collection: CAD-4 software. Programs used to solve structure: *SHELX*76 (Sheldrick, 1976). Programs used to prepare figures: *SNOOPI* (Karaulov, 1992), *PLUTO* (Motherwell & Clegg, 1988). Additional molecular geometry calculations: *XANADU* (Roberts & Sheldrick, 1975), *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Janes, R. W., Lisgarten, J. N. & Palmer, R. A. (1989). *Acta Cryst.* **C45**, 129–132.

Karaulov, S. (1992). *SNOOPI. Molecular Plotting Progam.* Univ. of Wales, Cardiff, Wales.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Roberts, P. & Sheldrick, G. M. (1975). *XANADU. Program for Crystallographic Calculations.* Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

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Thiooxalic Acid 2-Amide-1-hydrazide-2-hydrazone

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Abstract

The results of an X-ray analysis reveal that the title compound, $C_2H_7N_5S$, has zwitterionic character (2), instead of the initially assumed form of a neutral tautomer (1). The bonding in (2) can be described as a resonance of several dipolar limiting structures. Their particular contributions to the zwitterionic resonance hybrid were estimated through calculations using the HOSE model based on the observed bond lengths. The two predominant resonance contributors, together with four intramolecular hydrogen bonds, account for the almost perfect planarity of the molecules.

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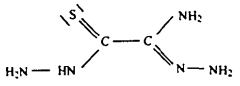
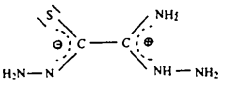
Comment

The reaction of sodium cyanodithioformate dimethyl formamide solvate, NaSC(S)CN.3dmf, with 50% hydrazine hydrate gives a product with empirical formula $C_2H_7N_5S$, which was first described as 'monothiooxalic acid hydrazide hydrazone amide' (Kibbel & Schröder, 1986). However, recent results concerning the reactivity and spectroscopic data disagree with this structural concept and suggest a characterization of the substance as a tautomer of (1), namely as zwitterionic thiooxalic acid 2-amide-1-hydrazide-2-hydrazone, (2) (Dehne, Scheunemann, Michalik, Hartung, Heinemann & Kibbel, 1994). In order to decide between the neutral (1) and the zwitterionic form, (2), of the title compound, an X-ray analysis was performed.



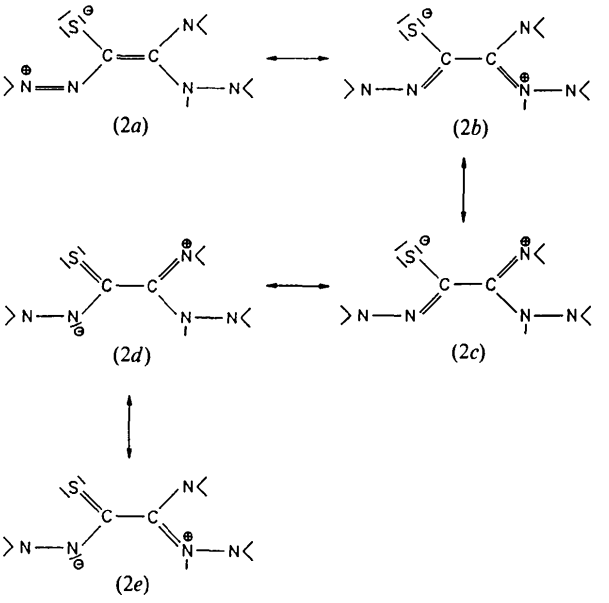
(1)



(2)

The molecular structure with the atomic numbering is depicted in Fig. 1. The molecule as a whole is approximately planar. The maximum deviation from the least-squares plane through the non-H atoms is 0.110 (2) Å for N5; all other non-H-atoms are less than 0.1 Å out of this plane. The planar molecular fragments S1,C1,C2,N1,N2 [only significant deviation: 0.017 (2) Å for C1] and N4,N3,C2,C1,N5 [maximum deviation: 0.024 (3) Å for N4] make a dihedral angle of 7.3 (1)°. The observed geometrical parameters (Table 2) confirm the zwitterionic character of (2). Both atoms C1 and C2 are sp^2 hybridized with bond-angle sums of 359.9 and 360.0°, respectively. The bond length C1—C2 [1.488 (3) Å] approaches the standard value for a C_{sp^2}—C_{sp^2} single bond [1.466 Å; all standard values used in the discussion are quoted from Rademacher (1987)]. The C1···S1 distance [1.730 (2) Å] is exactly the mean of the standard values for the distance between a C_{sp^2} and an S atom bonded by a single and a double bond (1.76 and 1.70 Å, respectively). All three C···N bond lengths are similar and do not differ significantly from the C_{sp^2}=N_{sp^2} standard value of 1.29 Å. The N1—N2 bond length [1.370 (3) Å] is a little longer than the mean of the standard values for a single and a double bond between two N atoms given as 1.35 Å, whereas the N3—N4 distance [1.408 (3) Å] is significantly longer and close to the value for a single bond (1.45 Å).

Considering the observed geometric molecular parameters, the bonding situation in (2) can only be sufficiently described by a resonance of the dipolar limiting structures (2*a*)–(2*e*). Their individual contributions to the resonance hydrid were estimated by calculations using the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983). For this reason, all bond lengths were corrected for libration according to the riding-motion model (Busing & Levy, 1964). This resulted in the HOSE stabilization energy for the five resonance contributors amounting to 151 (3) kJ mol^{-1}. As expected from chemical intuition, a clear dominance could be ascribed to limiting structures (2*b*) [31.4 (9)%] and (2*c*) [29.5 (8)%], whereas (2*d*) [14.7 (4)%] and (2*e*) [15.1 (4)%] are of much less importance, and (2*a*) [9.3 (2)%] can nearly be neglected.



(2*a*) (2*b*) (2*d*) (2*c*) (2*e*)

There is a total of four intramolecular interactions with some hydrogen-bonding characteristics. These interactions, geometrically described in Table 2, contribute to the aforementioned planar conformation of the molecule. As can be seen from the data in Table 2, both N3—H31 and N5—H52 are involved

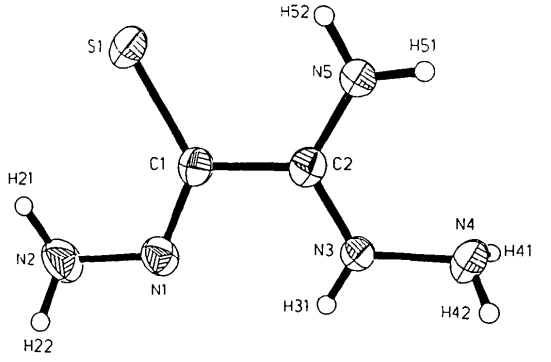


Fig. 1. The molecular structure and atomic numbering scheme. Displacement ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radii.

in three-centre bifurcated hydrogen bonds. The corresponding angles $A_1\cdots H\cdots A_2$ (A_1/A_2 = N1/N2^{i} and S1/N4^{iii}) complete the description of the bifurcated-bond configuration and amount to 94.8 (8) and 110 (1)°, respectively.

The molecular packing of (2) is shown in Fig. 2. The molecules form corrugated sheets parallel to the *ac* plane which are stacked one on the other in the *b* direction. There are three short intermolecular contacts between non-H atoms which can be considered as hydrogen bonds (*cf.* Table 2).

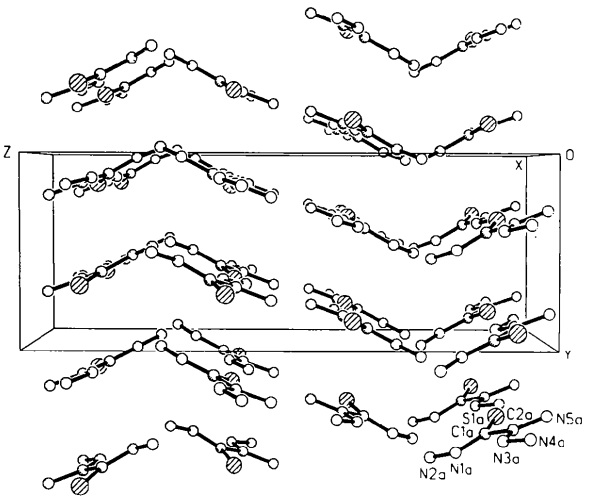


Fig. 2. Molecular packing with H atoms omitted for clarity.

Experimental

Crystal data

$C_2H_7N_5S$
M_r = 133.19
Orthorhombic
Pbca
a = 8.411 (2) Å
b = 7.094 (1) Å
c = 19.349 (4) Å
V = 1154.5 (4) Å^3
Z = 8
D_x = 1.533 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 82 reflections
θ = 10.0–15.5°
μ = 0.456 mm^{-1}
T = 293 K
Needle
0.60 × 0.15 × 0.10 mm
Yellow
Crystal source: recrystallized from water

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
2792 measured reflections
1017 independent reflections
701 observed reflections [$F_o^2 > 2\sigma(F_o^2)$]

R_{int} = 0.0575
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 8$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R(F)$ = 0.0333
$wR(F^2)$ = 0.0804
S = 1.004
1017 reflections
102 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.261 e Å^{-3}
$\Delta\rho_{min}$ = −0.180 e Å^{-3}
Extinction correction: empirical, $F_{corr} = kF_c(1 + 0.001\chi F_c^2\lambda^3/\sin 2\theta)^{-1/4}$
Extinction coefficient: χ = 0.021(2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.08589 (6)	0.16190 (10)	0.61326 (3)	0.0369 (2)
N1	−0.1396 (2)	0.0218 (3)	0.69960 (9)	0.0303 (5)
N2	−0.0152 (3)	−0.0282 (3)	0.74147 (11)	0.0374 (5)
N3	−0.3853 (2)	0.1269 (3)	0.62573 (9)	0.0277 (5)
N4	−0.5220 (2)	0.1600 (4)	0.58554 (11)	0.0350 (5)
N5	−0.2255 (2)	0.2178 (3)	0.53745 (9)	0.0342 (5)
C1	−0.1027 (2)	0.1079 (3)	0.64297 (11)	0.0242 (5)
C2	−0.2444 (2)	0.1540 (3)	0.60010 (10)	0.0244 (5)

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.730 (2)	N3—N4	1.408 (3)
N1—C1	1.292 (3)	N5—C2	1.304 (3)
N1—N2	1.370 (3)	C1—C2	1.488 (3)
N3—C2	1.299 (3)		
C1—N1—N2	116.1 (2)	C2—C1—S1	120.0 (2)
C2—N3—N4	120.6 (2)	N3—C2—N5	121.2 (2)
N1—C1—C2	112.6 (2)	N3—C2—C1	119.0 (2)
N1—C1—S1	127.3 (2)	N5—C2—C1	119.8 (2)
N2—N1—C1—C2	179.0 (2)	N1—C1—C2—N3	8.2 (3)
N2—N1—C1—S1	1.7 (3)	S1—C1—C2—N3	−174.3 (2)
N4—N3—C2—N5	2.1 (3)	N1—C1—C2—N5	−170.8 (2)
N4—N3—C2—C1	−176.8 (2)	S1—C1—C2—N5	6.8 (3)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···S1	0.90 (2)	2.50 (2)	2.949 (2)	112 (2)
N3—H31···N1	0.78 (3)	2.33 (2)	2.621 (2)	103 (2)
N5—H51···N4	0.89 (3)	2.47 (3)	2.694 (3)	94 (2)
N5—H52···S1	0.80 (3)	2.65 (3)	3.028 (2)	111 (3)
N3—H31···N2^{i}	0.78 (3)	2.26 (3)	3.001 (3)	161 (2)
N4—H42···S1^{ii}	0.87 (3)	2.87 (3)	3.341 (2)	116 (2)
N5—H52···N4^{iii}	0.80 (3)	2.40 (3)	3.056 (3)	139 (2)

Symmetry codes: (i) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (ii) $x-1, y, z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

The structure was solved by direct methods. Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program used to solve structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976); *SCHAKAL* (Keller, 1990). Software used to perform geometrical calculations: *EDIT* (Jaskólski, 1982).

The authors would like to thank the Fonds der Chemischen Industrie for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Dehne, H., Scheunemann, A., Michalik, M., Hartung, H., Heinemann, F. & Kibbel, H. U. (1994). *Phosphorus Sulfur Silicon*, **86**, 177–179.

Jaskólski, M. (1982). *EDIT. Program to Edit Atomic Information from Atom Data Files.* Univ. of Poznań, Poland.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Keller, E. (1990). *SCHAKAL88. Fortran Program for the Graphic Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.

Kibbel, H. U. & Schröder, J. (1986). East German Patent 233 562; *Chem. Abs.* **105**, 133362.

Krygowski, T. M., Anulewicz, R. & Kruszewski, J. (1983). *Acta Cryst.* B**39**, 732–739.

Rademacher, P. (1987). *Strukturen organischer Moleküle.* Weinheim: VCH.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Stoe & Cie (1991*a*). *DIF4. Diffractometer Control Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991*b*). *REDU4. Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1995). C**51**, 445–447

1,3,5,7-Tetrakis(trifluoromethyl)-2,6-dioxabicyclo[3.3.0]octane-3,7-diol

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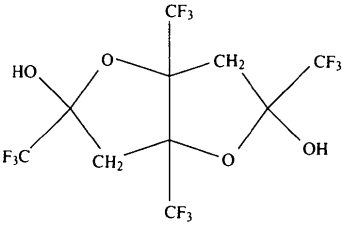
Abstract

There are two molecules in the asymmetric unit of $C_{10}H_6F_{12}O_4$ that differ primarily in their packing and hydrogen bonding. The molecules are linked in groups of four by the hydrogen bonding between the hydroxyls about an inversion center. In one of the independent molecules, one hydroxyl is a hydrogen donor and the other is an acceptor, while in the second molecule the hydroxyls act as both donor and acceptor.

Comment

A number of crystal structures of substituted 2,6-dioxabicyclo[3.3.0]octanes have been reported, *e.g.* the methyl glycoside of 2-*C*-benzyl-3-keto-L-*lyxo*-hexulosonic acid lactone (Hvoslef & Nordenson, 1976), 3a,6a-dimethyl-2,3,3a,5,6,6a-hexahydrofuro[3,2-*b*]-furan-2,5-dione (Caira, Watson, Kagan & Singh, 1984), 1,4:3,6-dihydro-D-glucitol (van Koningsveld, Peters & Jansen, 1984), methyl 3,6-anhydro-β-D-glucofuranoside (Kopf & Koll, 1984) and β,β-D-*thero*-3,4-hexodiulose (Angyal, Craig & Kusmann, 1989). Comparison of the nonplanar fused rings shows a range of conformations. In the title compound the torsion angles O2—C1—C5—O6 and C4—C5—C1—C8 about the bridge are 94.1 and $-138.2°$, respectively, for one molecule, and 94.1 and $-138.5°$, respectively, for the other molecule in the asymmetric unit. In the references listed above these torsion angles range from 82.3 to 110.1° and from -141.4 to $-123.4°$, respectively.



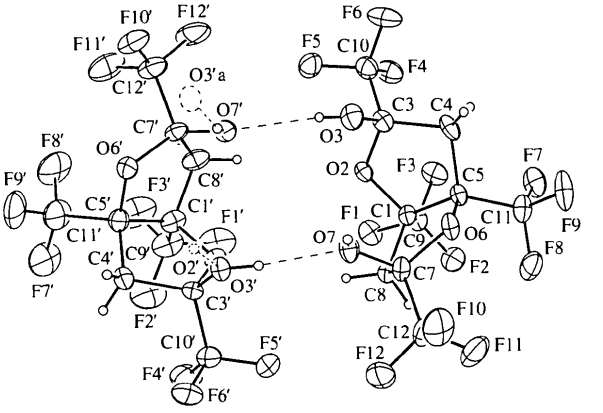


Fig. 1. A displacement ellipsoid plot of the title compound with ellipsoids drawn at the 20% probability level. Dotted lines represent hydrogen bonds and O3'a is a symmetry-related atom. atom.

Experimental

Strontium hexafluoroacetylacetone [$Sr(HFA)_2$], from a reaction between excess H(HFA) and strontium, was purified by washing with excess H(HFA) (Purdy, Berry, Holm, Fatemi & Gaskill, 1989). After recovery of the H(HFA) from the filtrate on the vacuum line, the orange residue was dissolved in ether, transferred to a stoppered vial and set aside in the 'dri-lab'. Three years later, the ether had evaporated and small colorless crystals formed.

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