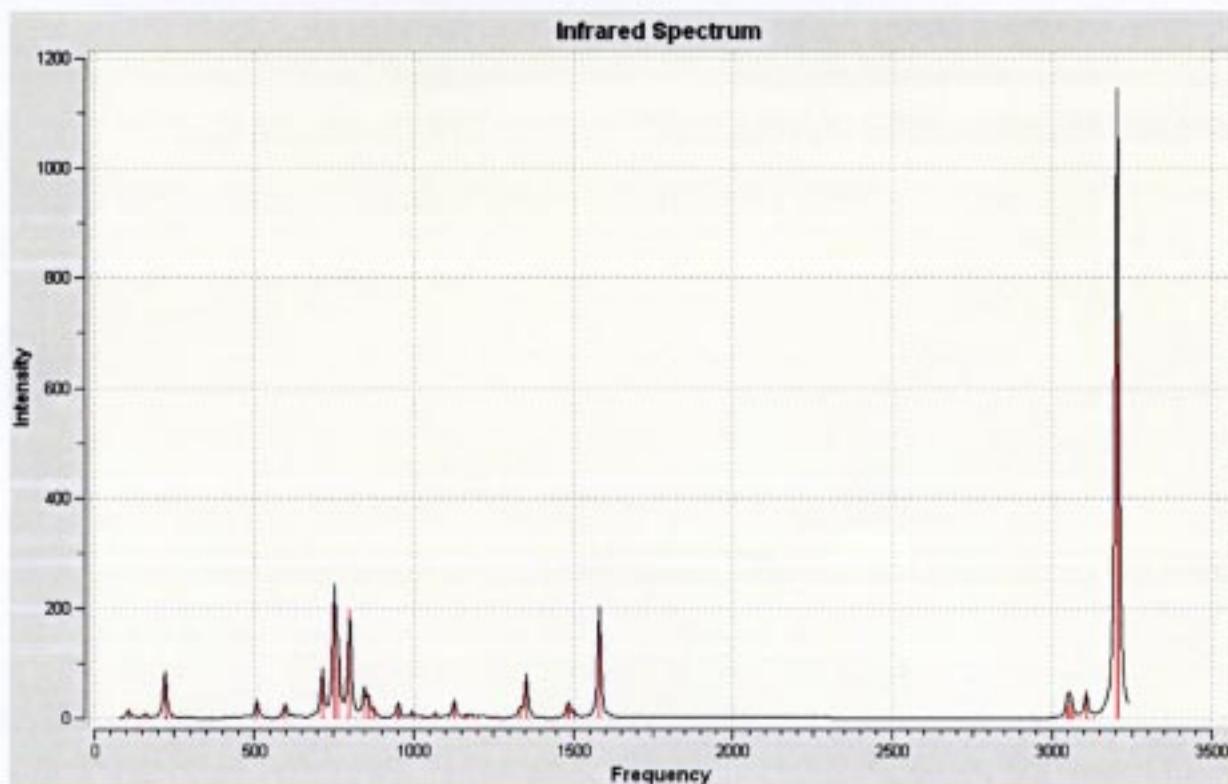


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.388202
3	6	0	1.205573	0.000000	2.112627
4	6	0	2.431587	-0.000791	1.461576
5	6	0	2.434134	-0.000888	0.060771
6	6	0	1.235984	-0.000293	-0.659370
7	1	0	-0.929566	-0.002719	-0.564691
8	1	0	3.366235	-0.004323	2.017831
9	1	0	3.380839	-0.006046	-0.473948
10	1	0	1.264126	-0.004783	-1.746325
11	6	0	0.837444	0.042041	3.585254
12	1	0	1.604068	-0.300073	4.283532
13	6	0	-1.127588	0.041252	2.404855
14	1	0	-2.103937	-0.301590	2.056299
15	6	0	0.237420	1.455551	3.873618
16	1	0	0.926769	2.237487	3.552997
17	1	0	0.056163	1.585517	4.942893
18	6	0	-1.100684	1.455315	3.069375
19	1	0	-1.959948	1.586122	3.731001
20	1	0	-1.140927	2.236830	2.309733
21	6	0	-0.428813	-0.818696	3.468032
22	1	0	-0.284330	-1.873595	3.227385
23	8	0	-1.215413	-0.788985	4.774895
24	1	0	-2.111736	-1.220748	4.683169
25	1	0	-0.732684	-1.255378	5.515015



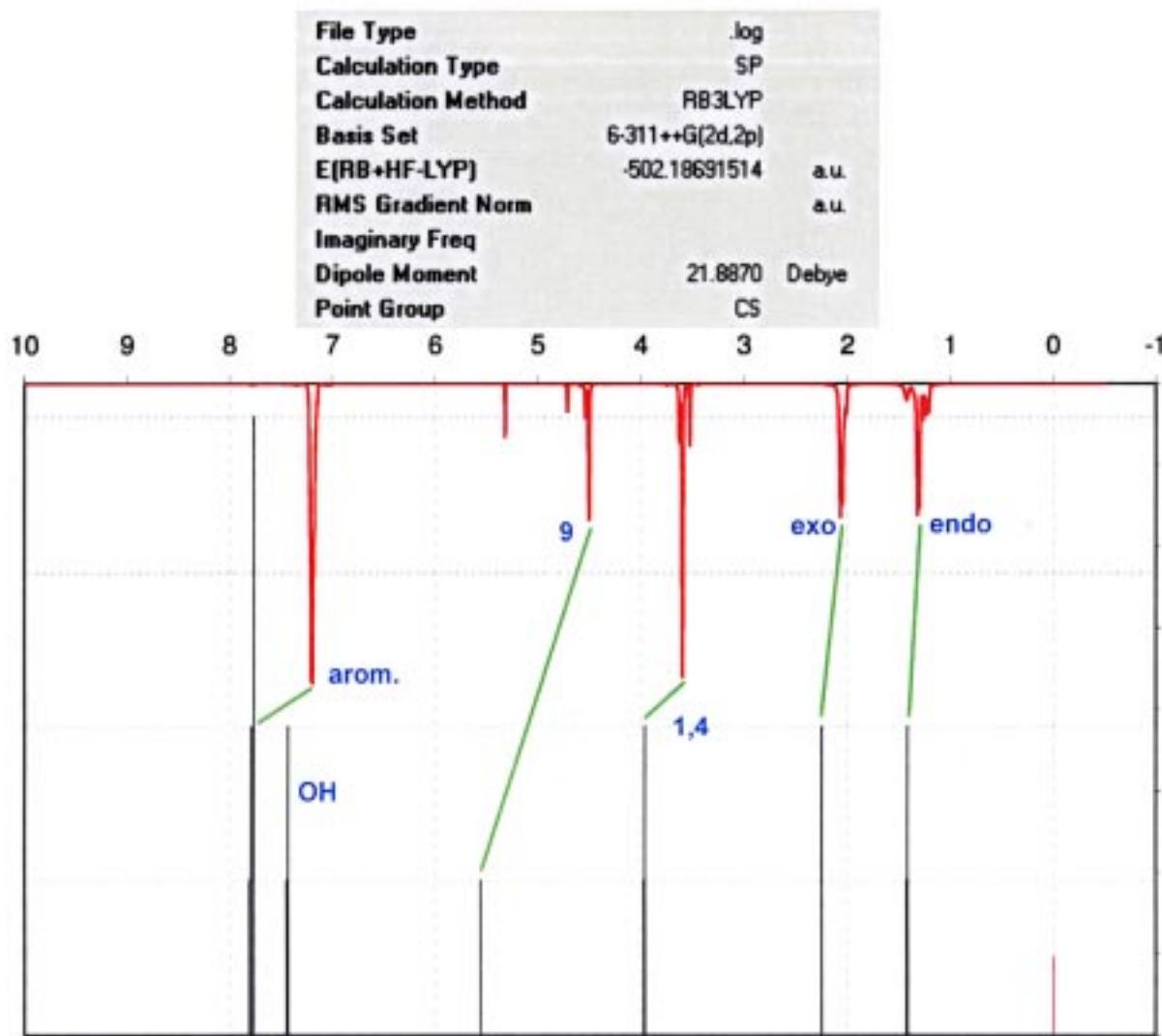
X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol

Thomas Laube

J. Am. Chem. Soc.

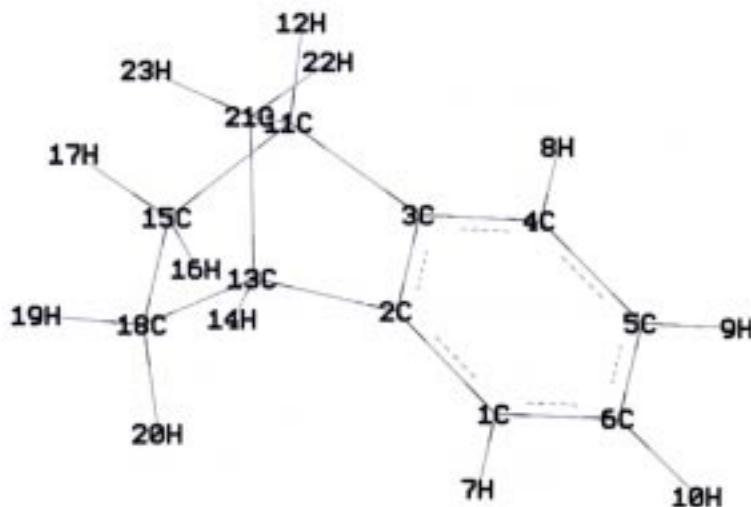
Zero-point correction=	0.212655 (Hartree/Particle)
Thermal correction to Energy=	0.222056
Thermal correction to Enthalpy=	0.223000
Thermal correction to Gibbs Free Energy=	0.178584
Sum of electronic and zero-point Energies=	-501.956914
Sum of electronic and thermal Energies=	-501.947513
Sum of electronic and thermal Enthalpies=	-501.946568
Sum of electronic and thermal Free Energies=	-501.990985

NMR chemical shift calculation with the GIAO method (TMS absolute shielding value *in water* at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6206); abscissa: chemical shift in ppm; red function: experimental ^1H -NMR spectrum; black lines: calculated ^1H -NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.



No.	nucleus	delta / ppm (relative to TMS ^b)	H atom no. (chemical numbering)
9,10	H	7.8	6,7
7,8	H	7.8	5,8
24	H	7.5	(OH)
25	H	7.4	(OH)
22	H	5.6	9
12,14	H	4.0	1,4
17,19	H	2.3	2,3-exo
16,20	H	1.4	2,3-endo

Structure and IR spectrum of 6

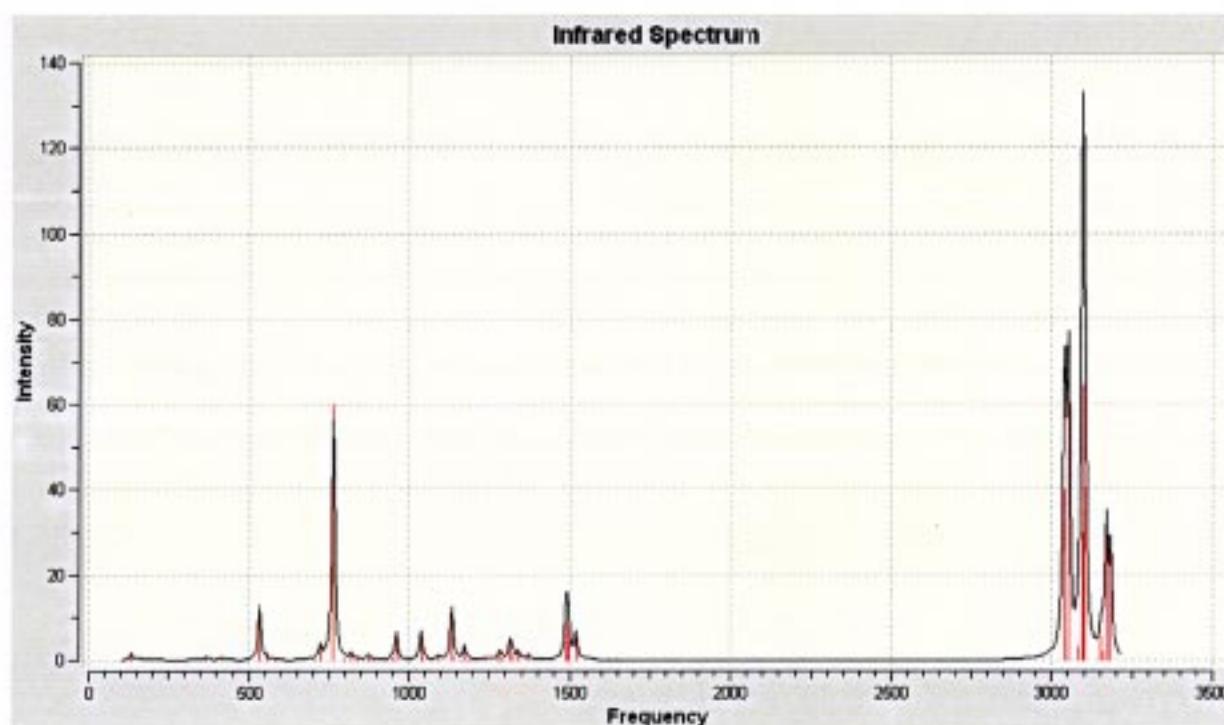


File Type	log	
Calculation Type	FREQ	
Calculation Method	RB3LYP	
Basis Set	6-311+G(d,p)	
E(RB+HF-LYP)	-426.49758086	a.u.
RMS Gradient Norm	0.00000059	a.u.
Imaginary Freq	0	
Dipole Moment	0.8376	Debye
Point Group	CS	

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.010372	1.447927	1.412502
2	6	0	-0.196396	0.271277	0.703353
3	6	0	-0.196396	0.271277	-0.703353
4	6	0	-0.010372	1.447927	-1.412502
5	6	0	0.157300	2.641673	-0.697021
6	6	0	0.157300	2.641673	0.697021
7	1	0	-0.004871	1.454966	2.497806
8	1	0	-0.004871	1.454966	-2.497806
9	1	0	0.283677	3.575888	-1.233155
10	1	0	0.283677	3.575888	1.233155
11	6	0	-0.365144	-1.172310	-1.136901
12	1	0	-0.704336	-1.324220	-2.161625
13	6	0	-0.365144	-1.172310	1.136901
14	1	0	-0.704336	-1.324220	2.161625
15	6	0	0.968568	-1.906643	-0.781461
16	1	0	1.836602	-1.398028	-1.204025
17	1	0	0.954715	-2.925922	-1.176706
18	6	0	0.968568	-1.906643	0.781461
19	1	0	0.954715	-2.925922	1.176706
20	1	0	1.836602	-1.398028	1.204025
21	6	0	-1.285073	-1.691281	0.000000

22	1	0	-2.270781	-1.221214	0.000000
23	1	0	-1.397828	-2.779571	0.000000



Zero-point correction=	0.199685 (Hartree/Particle)
Thermal correction to Energy=	0.207390
Thermal correction to Enthalpy=	0.208335
Thermal correction to Gibbs Free Energy=	0.167418
Sum of electronic and zero-point Energies=	-426.297896
Sum of electronic and thermal Energies=	-426.290191
Sum of electronic and thermal Enthalpies=	-426.289246
Sum of electronic and thermal Free Energies=	-426.330163

Precise crystal structures used for data shown in Figure 3

ZAPYOE01
 syn-1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-1,4:5,8:9,12-trimethanotriphenylene
 at 123 K.
 C21 H24
 R.Rathore, S.V.Lindeman, A.S.Kumar, J.K.Kochi
 J.Am.Chem.Soc., 120, 6012, 1998

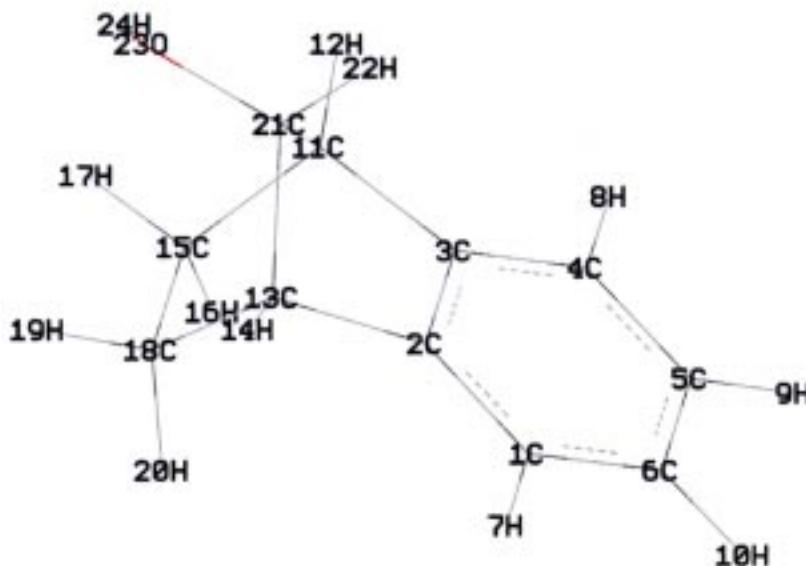
ZIWVIK
 9,10-Dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene
 at 223 K: monoclinic polymorph

C18 H22 O2
R.Rathore, J.K.Kochi
J.Org.Chem., 60, 4399, 1995

ZIWVIK01
anti-9,10-Dimethoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene
at 123 K: triclinic polymorph

P.L. Magueres, S.V. Lindeman, J.K. Kochi
Organometallics, 20, 115, 2001

Structure and IR spectrum of 18



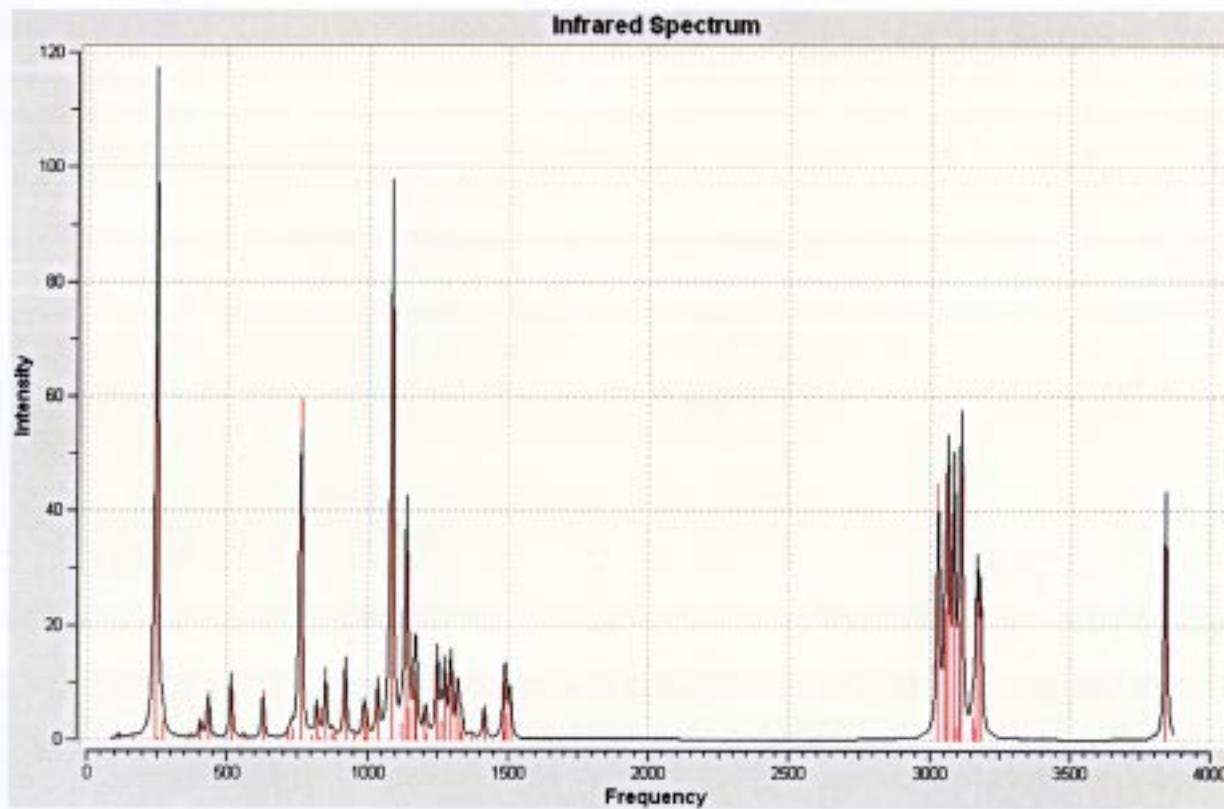
File Type	.log
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Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-501.74155412 a.u.
RMS Gradient Norm	0.00000047 a.u.
Imaginary Freq	0
Dipole Moment	1.2137 Debye
Point Group	C1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.744565	1.414774	-0.083431
2	6	0	0.551269	0.706745	-0.102886
3	6	0	0.549994	-0.701022	-0.114797
4	6	0	1.741783	-1.411281	-0.103227
5	6	0	2.946107	-0.696958	-0.089168
6	6	0	2.947582	0.698180	-0.079913
7	1	0	1.753130	2.499949	-0.075953
8	1	0	1.748059	-2.496368	-0.112555
9	1	0	3.888567	-1.233450	-0.090207
10	1	0	3.891105	1.232779	-0.073596
11	6	0	-0.898182	-1.137032	-0.102867
12	1	0	-1.101035	-2.151556	-0.444444
13	6	0	-0.896474	1.141399	-0.081080
14	1	0	-1.093460	2.165624	-0.401820
15	6	0	-1.476290	-0.790638	1.306526
16	1	0	-0.865238	-1.222054	2.100845
17	1	0	-2.490466	-1.180971	1.401804
18	6	0	-1.476253	0.770100	1.320052

X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol
Thomas Laube J. Am. Chem. Soc.

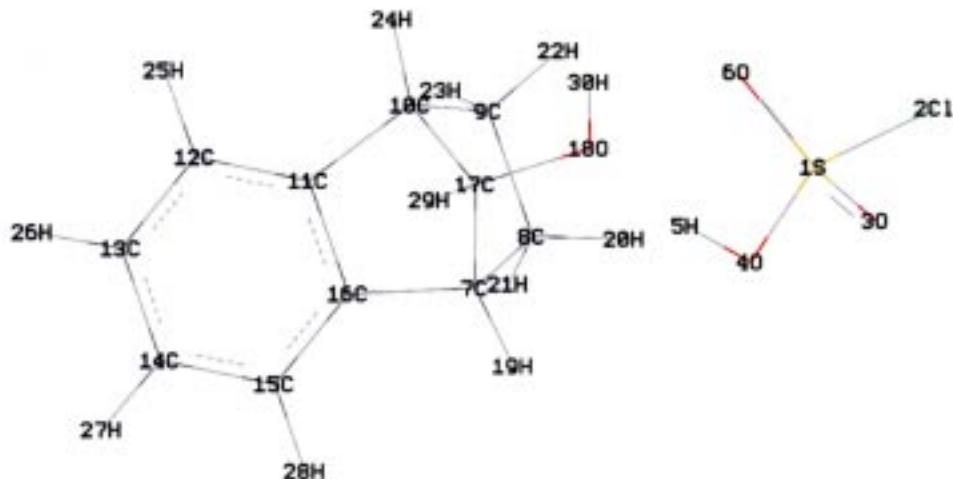
19	1	0	-2.491983	1.156015	1.422054
20	1	0	-0.868886	1.189074	2.123800
21	6	0	-1.504462	0.002602	-0.956757
22	1	0	-1.103142	0.008633	-1.976166
23	8	0	-2.922896	-0.069334	-0.972507
24	1	0	-3.261304	0.605785	-1.568415



Zero-point correction= 0.203937 (Hartree/Particle)
Thermal correction to Energy= 0.212957
Thermal correction to Enthalpy= 0.213901
Thermal correction to Gibbs Free Energy= 0.170235
Sum of electronic and zero-point Energies= -501.537617
Sum of electronic and thermal Energies= -501.528597
Sum of electronic and thermal Enthalpies= -501.527653
Sum of electronic and thermal Free Energies= -501.571319

Structure and IR and NMR spectrum of $18 \cdot \text{ClSO}_3\text{H}$ (gas phase)

The optimization started from the complex geometry as found in the asymmetric unit of the crystal structure and was consecutively carried out at the AM1, B3LYP/6-31G(d), and B3LYP/6-311+G(d,p) levels. The other diastereomeric complex (atom 2 = Cl and atom 3 = O exchanged) had on the AM1 level a slightly higher energy and was therefore not further optimized.



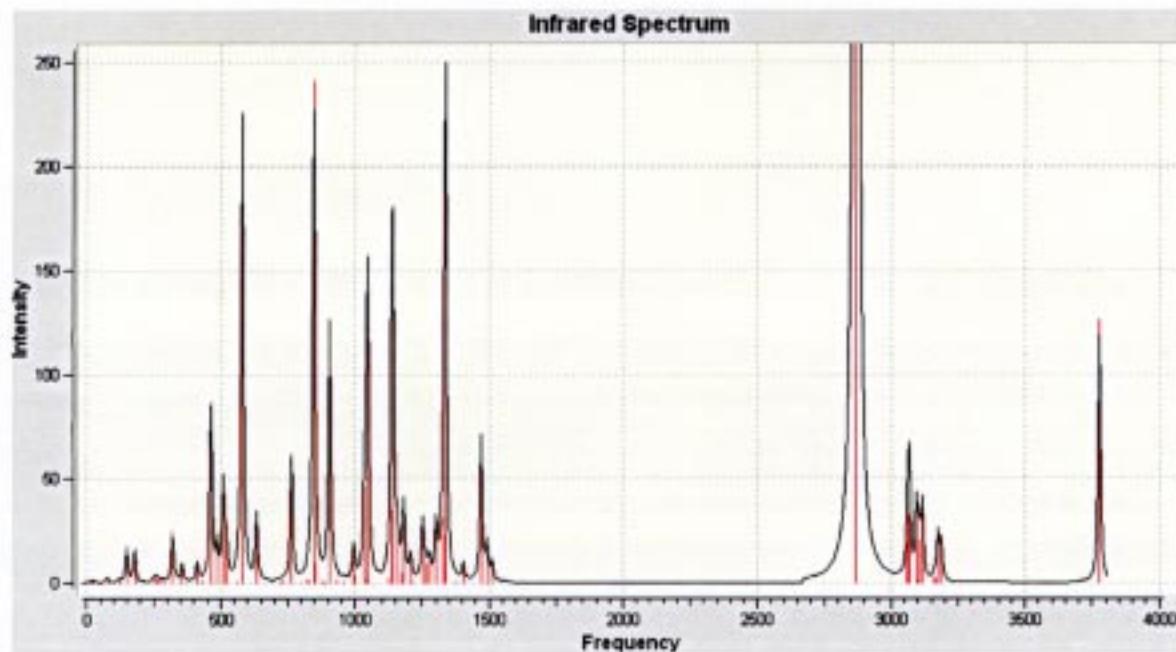
File Type	.log
Calculation Type	FREQ
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-1586.47171098 a.u.
RMS Gradient Norm	0.00000251 a.u.
Imaginary Freq	0
Dipole Moment	5.4499 Debye
Point Group	C1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	3.688949	-0.633570	0.289460
2	17	0	4.432577	1.137536	-0.579492
3	8	0	4.708456	-1.636005	0.138901
4	8	0	2.491653	-0.976994	-0.686359
5	1	0	1.650111	-0.508387	-0.360927
6	8	0	3.159180	-0.252109	1.587670
7	6	0	-1.486646	-0.283466	-0.925696
8	6	0	-1.362848	1.172035	-1.481249
9	6	0	-1.604352	2.059260	-0.220064
10	6	0	-1.842991	1.013799	0.915077
11	6	0	-3.150797	0.311462	0.617322
12	6	0	-4.400839	0.366592	1.216475
13	6	0	-5.437336	-0.396188	0.665361

X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol
 Thomas Laube *J. Am. Chem. Soc.*

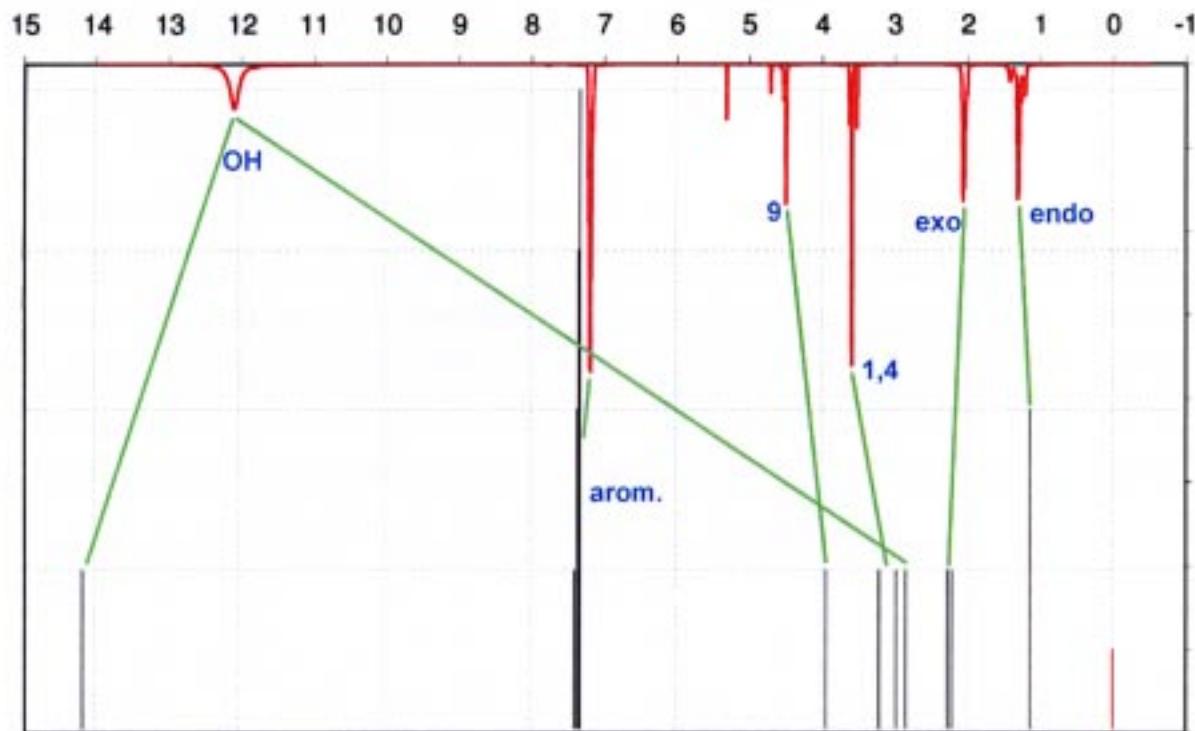
14	6	0	-5.219425	-1.187944	-0.462639
15	6	0	-3.959037	-1.238942	-1.069876
16	6	0	-2.931032	-0.488081	-0.519001
17	6	0	-0.874414	-0.119470	0.483510
18	8	0	0.508233	0.274600	0.408982
19	1	0	-1.052230	-1.057811	-1.557821
20	1	0	-0.367219	1.341459	-1.894431
21	1	0	-2.091898	1.350833	-2.272215
22	1	0	-0.726898	2.669292	0.001115
23	1	0	-2.461660	2.724753	-0.326428
24	1	0	-1.726734	1.398762	1.928932
25	1	0	-4.577211	0.979414	2.094215
26	1	0	-6.420154	-0.375349	1.122743
27	1	0	-6.035040	-1.774565	-0.870300
28	1	0	-3.795918	-1.858539	-1.945332
29	1	0	-0.968519	-1.019919	1.095914
30	1	0	0.874507	0.398793	1.295650



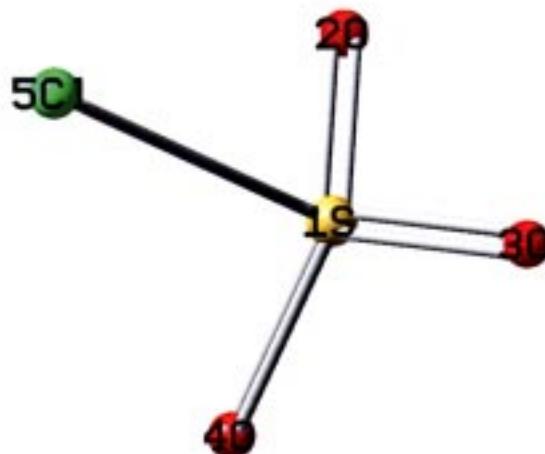
Zero-point correction=	0.230712 (Hartree/Particle)
Thermal correction to Energy=	0.246361
Thermal correction to Enthalpy=	0.247305
Thermal correction to Gibbs Free Energy=	0.183604
Sum of electronic and zero-point Energies=	-1586.240999
Sum of electronic and thermal Energies=	-1586.225350
Sum of electronic and thermal Enthalpies=	-1586.224406
Sum of electronic and thermal Free Energies=	-1586.288107

NMR chemical shift calculation with the GIAO method (TMS absolute shielding value at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6287); abscissa: chemical shift in ppm; red function: experimental ^1H -NMR spectrum; black lines: calculated ^1H -NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.

File Type	.log
Calculation Type	SP
Calculation Method	RB3LYP
Basis Set	6-311++G(2d,2p)
E(RB+HF-LYP)	-1586.53488661 a.u.
RMS Gradient Norm	a.u.
Imaginary Freq	
Dipole Moment	5.3160 Debye
Point Group	C1



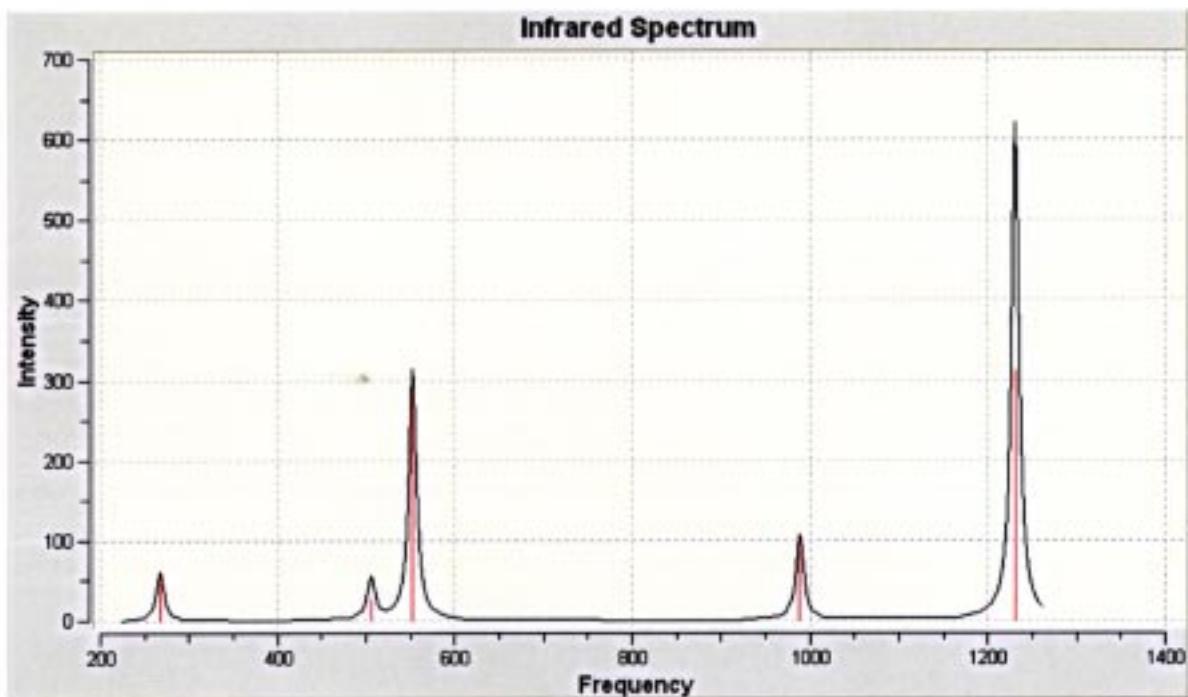
Structure and IR spectrum of ClSO₃⁻ (gas phase)



File Type	.log
Calculation Type	FREQ
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-1084.22958533 a.u.
RMS Gradient Norm	0.00000033 a.u.
Imaginary Freq	0
Dipole Moment	0.2431 Debye
Point Group	CS

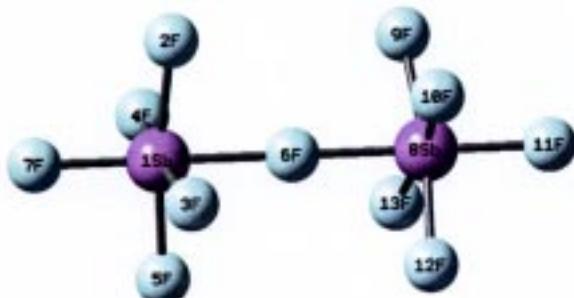
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	0.558946	-0.000001	0.000000
2	8	0	0.852876	1.438022	0.000000
3	8	0	0.852876	-0.719010	1.245369
4	8	0	0.852876	-0.719010	-1.245369
5	17	0	-1.730128	0.000000	0.000000



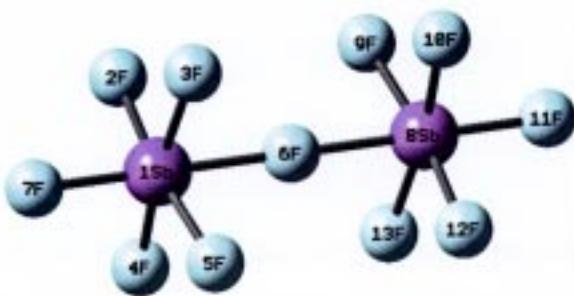
Zero-point correction=	0.013190 (Hartree/Particle)
Thermal correction to Energy=	0.018143
Thermal correction to Enthalpy=	0.019087
Thermal correction to Gibbs Free Energy=	-0.015994
Sum of electronic and zero-point Energies=	-1084.216395
Sum of electronic and thermal Energies=	-1084.211442
Sum of electronic and thermal Enthalpies=	-1084.210498
Sum of electronic and thermal Free Energies=	-1084.245579

Potential energy surface of $\text{Sb}_2\text{F}_{11}^-$



File Type	.log	
Calculation Type	FREQ	
Calculation Method	RB3LYP	
Basis Set	LANL2DZ	
E(RB+HF-LYP)	-1109.57504162	a.u.
RMS Gradient Norm	0.00000233	a.u.
Imaginary Freq	0	
Dipole Moment	0.0005	Debye
Point Group	C1	

Absolute minimum on the potential energy surface (PES)



File Type	.log	
Calculation Type	FREQ	
Calculation Method	RB3LYP	
Basis Set	LANL2DZ	
E(RB+HF-LYP)	-1109.57456704	a.u.
RMS Gradient Norm	0.00000001	a.u.
Imaginary Freq	1	
Dipole Moment	0.0000	Debye
Point Group	D4H	

Transition state on the PES



Any conformation on the PES with $\text{Sb}-\text{F}-\text{Sb} < 180$ degrees

It is remarkable that the computed D_{4h} structures of the similar anions V_2F_{11} , As_2F_{11} and Ta_2F_{11} were described as absolute minima on the potential energy surfaces (Sobczyk, M.; Sawicka, A.; Skurski, P. *Eur. J. Inorg. Chem.* **2003**, 3790-3797). The computed D_{4h} conformation of the Sb_2F_{11} anion was described as global minimum by Sham, I. H. T. et al (*Solid State Sciences* **2002**, 4, 1457-1463). The method used by us (GAUSSIAN 03W: opt=tight, int=ultrafine) shows that the D_{4h} conformation is a transition state. The energy differences, however, are small (0.3 kcal/mole).

Conformations with Sb1-F6-Sb8 = 180 degrees

abs(F3-Sb1-Sb8-F10) / degrees	Energy / hartrees	(E – E _{min}) / (kcal / Mole)
0	-1109.574567	0.298
15	-1109.574736	0.192
30	-1109.574947	0.059
45	-1109.575042	0

Conformations with Sb-F-Sb < 180 degrees (angles in degrees)

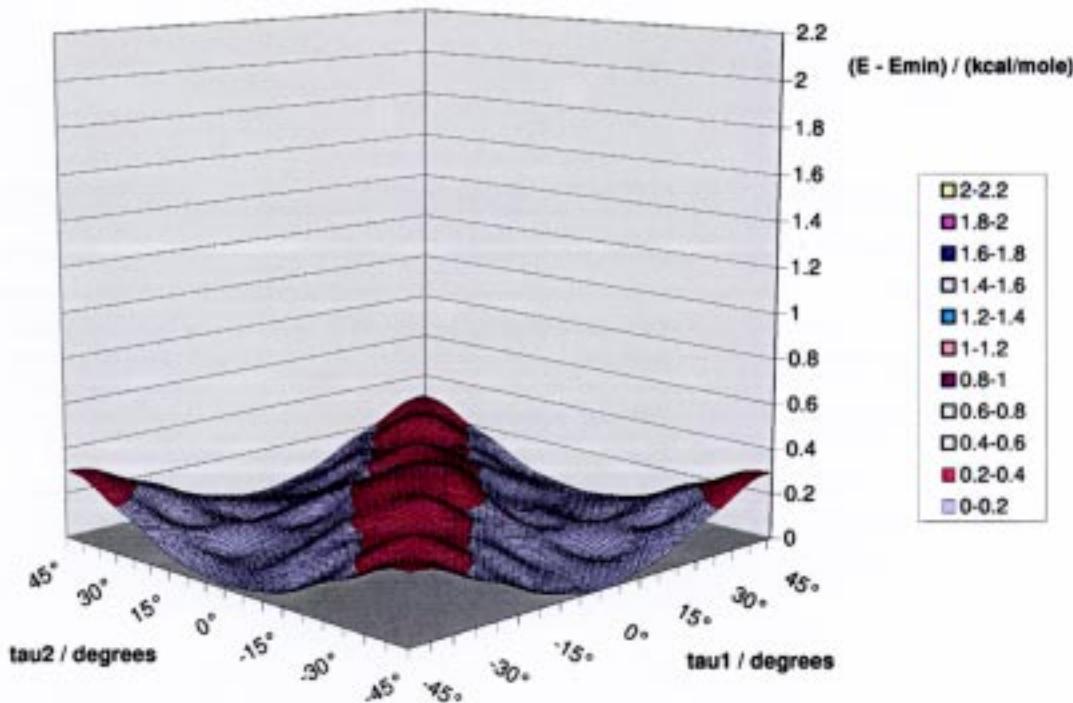
Sb1-F6-Sb8	tau1	tau2	Energy / hartrees	(E – E _{min}) / (kcal / Mole)
150	0	0	-1109.57174	2.072
150	15	-45	-1109.57295	1.312
150	15	-30	-1109.572224	1.768
150	15	-15	-1109.571818	2.023
150	15	0	-1109.572109	1.840
150	15	15	-1109.572834	1.385
150	15	30	-1109.573279	1.106
150	15	45	-1109.572974	1.298
150	30	-45	-1109.572339	1.696
150	30	-30	-1109.571964	1.931
150	30	-15	-1109.572222	1.769
150	30	0	-1109.572872	1.362
150	30	15	-1109.573278	1.107
150	30	30	-1109.573006	1.277
150	30	45	-1109.572346	1.691
150	45	-45	-1109.572042	1.882
150	45	-30	-1109.572341	1.694
150	45	-15	-1109.572954	1.310
150	45	0	-1109.573276	1.108
150	45	15	-1109.572968	1.301
150	45	30	-1109.572345	1.692
150	45	45	-1109.572038	1.885
160	0	0	-1109.573602	0.903
160	15	-45	-1109.574193	0.533
160	15	-30	-1109.573819	0.767
160	15	-15	-1109.573625	0.889
160	15	0	-1109.573803	0.777
160	15	15	-1109.574181	0.540
160	15	30	-1109.574378	0.417
160	15	45	-1109.574201	0.528
160	30	-45	-1109.573836	0.757
160	30	-30	-1109.573646	0.876
160	30	-15	-1109.573817	0.769
160	30	0	-1109.574187	0.536
160	30	15	-1109.574377	0.417
160	30	30	-1109.574203	0.526

160	30	45	-1109.573838	0.755
160	45	-45	-1109.573658	0.868
160	45	-30	-1109.573836	0.757
160	45	-15	-1109.574197	0.530
160	45	0	-1109.574375	0.418
160	45	15	-1109.574199	0.528
160	45	30	-1109.573837	0.756
160	45	45	-1109.573656	0.870
170	0	0	-1109.574357	0.430
170	15	-45	-1109.574757	0.179
170	15	-30	-1109.574492	0.345
170	15	-15	-1109.574358	0.429
170	15	0	-1109.574492	0.345
170	15	15	-1109.574756	0.179
170	15	30	-1109.574886	0.097
170	15	45	-1109.574757	0.178
170	30	-45	-1109.574492	0.345
170	30	-30	-1109.57436	0.428
170	30	-15	-1109.574493	0.344
170	30	0	-1109.574756	0.179
170	30	15	-1109.574885	0.098
170	30	30	-1109.574757	0.178
170	30	45	-1109.574492	0.345
170	45	-45	-1109.57436	0.428
170	45	-30	-1109.574495	0.343
170	45	-15	-1109.574757	0.179
170	45	0	-1109.574885	0.099
170	45	15	-1109.574757	0.179
170	45	30	-1109.574492	0.345
170	45	45	-1109.57436	0.428

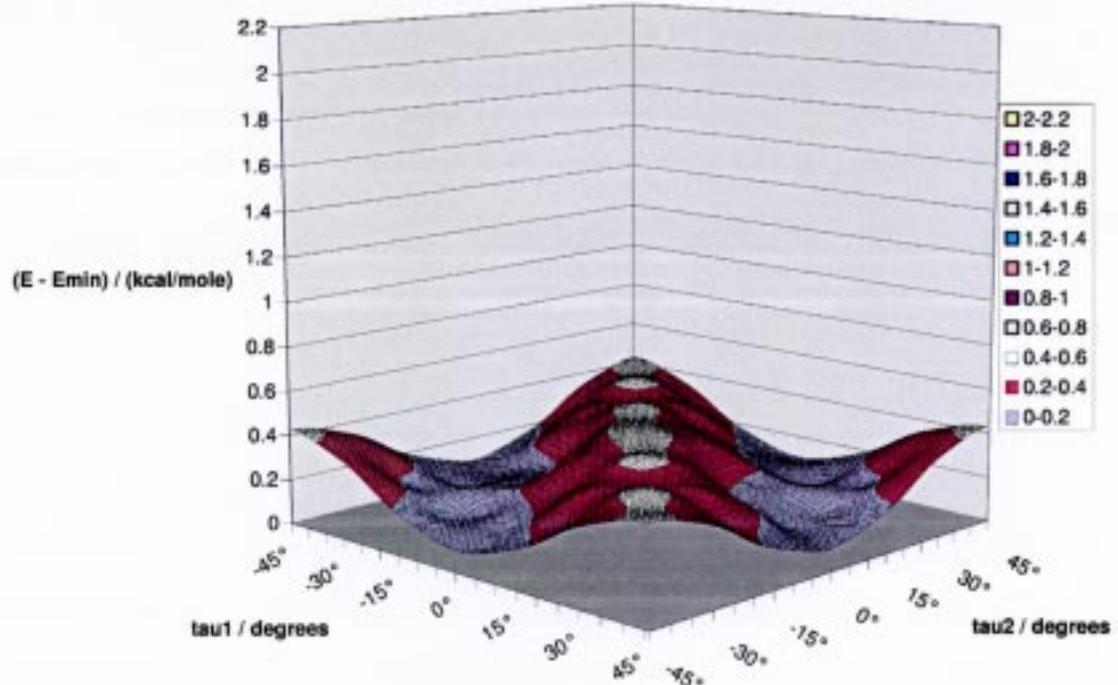
An interpolation of the PES [$(E - E_{\min}) = f(Sb-F-Sb, \tau_1, \tau_2)$] has been carried out with a Fortran program using the NAG subroutine E01TGF (*Interpolating functions, modified Shepard's method, three variables*, NAG Fortran Library Mark 19, NAG:Oxford, 1999). We thus imply for simplicity that the energy is only a function of these three variables. We assume periodicity of τ_1, τ_2 on $[-45^\circ, 45^\circ]$ each and we assume $(E - E_{\min}) = f(360^\circ - Sb-F-Sb, \tau_1, \tau_2)$ for $Sb-F-Sb > 180^\circ$ for reliable interpolation close to $Sb-F-Sb = 180^\circ$. An interpolation with a Fourier-like sum of cosine functions failed for $Sb-F-Sb$ close to 180° . Plots of $(E - E_{\min}) = f(180^\circ, \tau_1, \tau_2)$, $(E - E_{\min}) = f(170^\circ, \tau_1, \tau_2)$, $(E - E_{\min}) = f(160^\circ, \tau_1, \tau_2)$, $(E - E_{\min}) = f(150^\circ, \tau_1, \tau_2)$ are shown. Although the interpolant reproduces all energies used for its construction, the dents and ripples indicate that the energy values may have an uncertainty of ± 0.1 kcal/mole.

The interpolated function is used only for obtaining a coarse insight into the shape of the PES and an estimation of the relative energy range of the observed conformations.

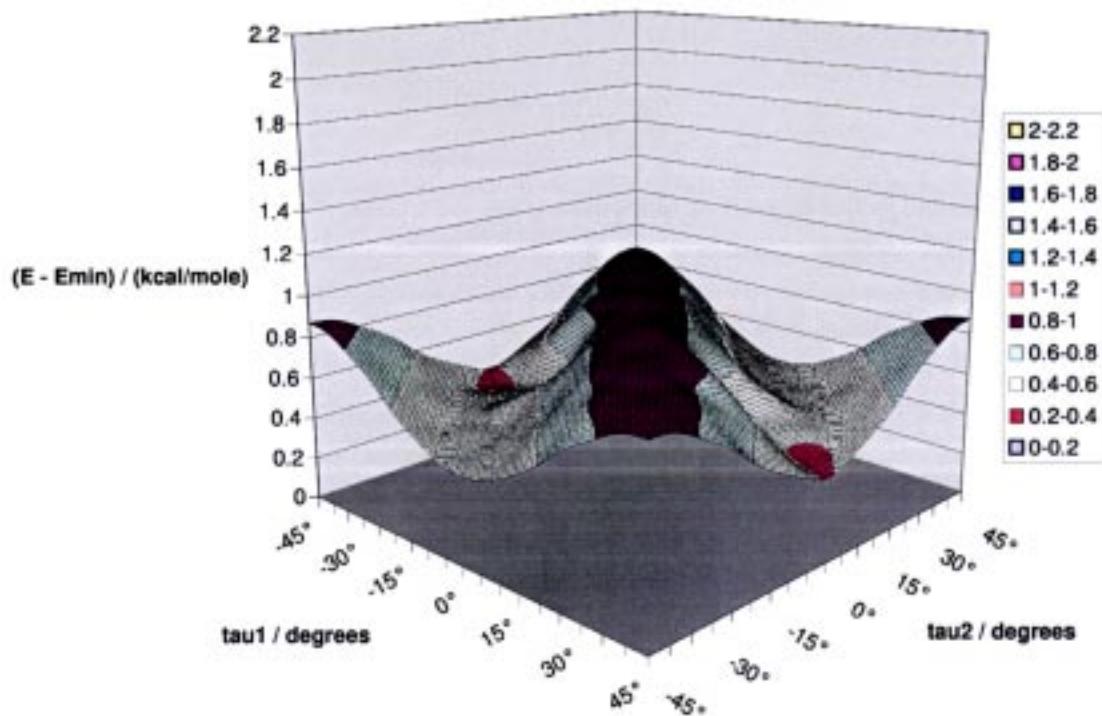
Sb-F-Sb = 180 degrees



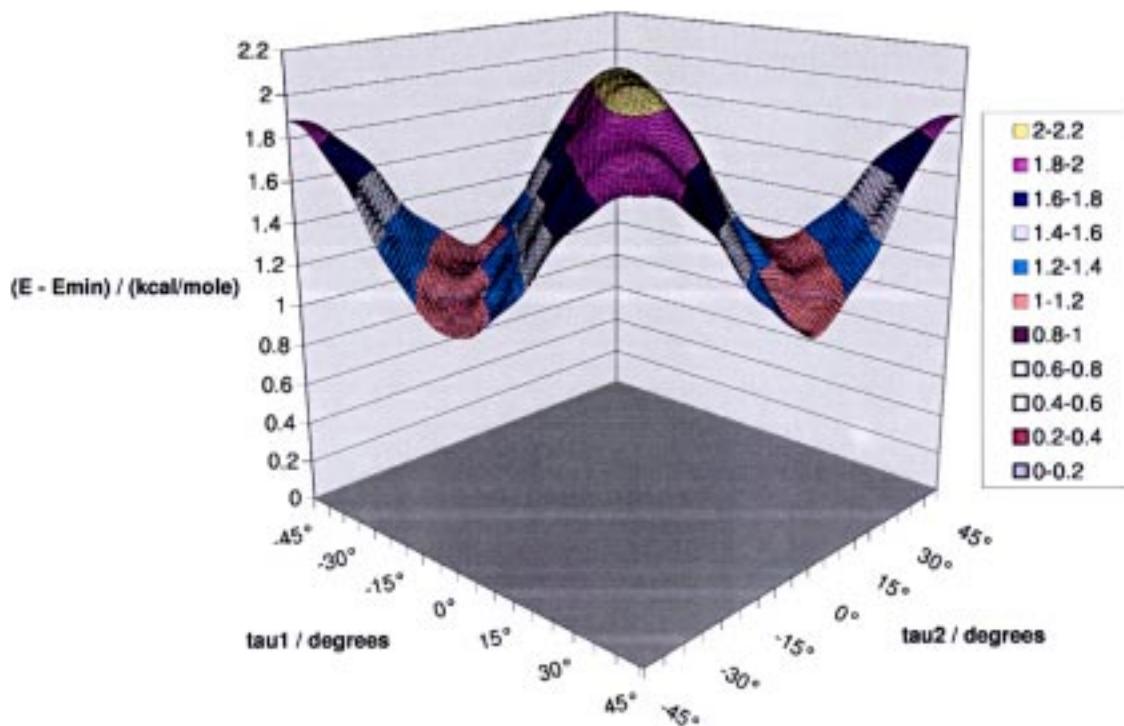
Sb-F-Sb = 170 degrees



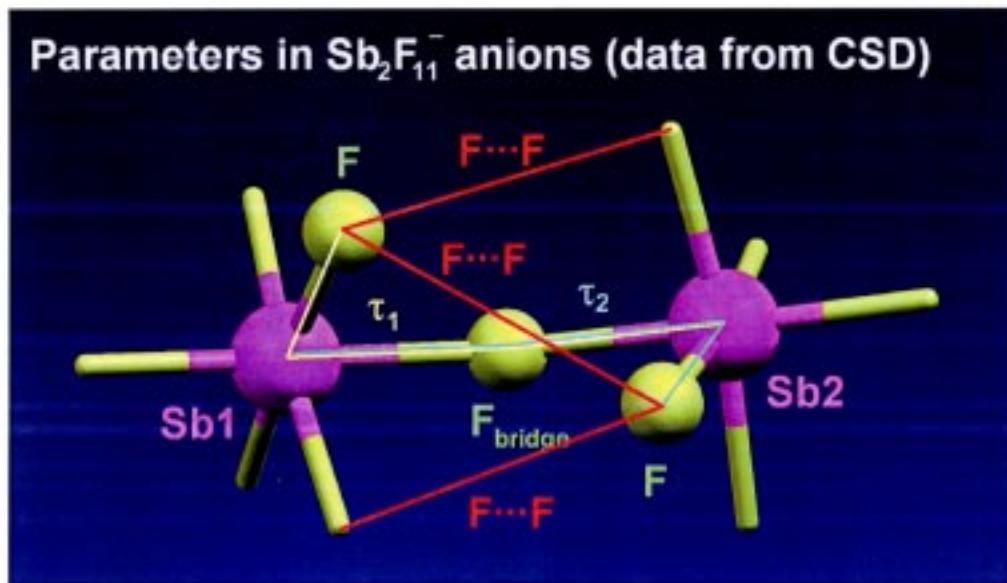
Sb-F-Sb = 160 degrees



Sb-F-Sb = 150 degrees



Crystal structures containing the $\text{Sb}_2\text{F}_{11}^-$ anion in general positions from the Cambridge File (CSD) and their estimated relative energies (calculated with the interpolant described above).



Refcode	Sb1	Sb2	F1(bridging)	F11	F12	F13	F14	F15	F21	F22	F23
DOPRIJ	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
DOPRIJ10	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F9	F11
FITDIV	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
FITDIV01	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
GOBDEG	Sb2	Sb1	F6	F7	F8	F9	F10	F11	F1	F2	F3
HOKFES	Sb5	Sb6	F19	F20	F21	F22	F23	F24	F25	F26	F27
HOLMOK	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
MAZNUW	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
PESGID	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
QEZTAQ	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
QEZTEU	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
SUNMOD	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
TOQLOA	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9
WEBJES	Sb2	Sb3	F7	F8	F9	F10	F11	F12	F13	F14	F15
YEQRUH	Sb1	Sb2	F4	F5	F6	F7	F8	F5C	F1	F2	F3
ZOJZUT	Sb1	Sb2	F1	F2	F3	F4	F5	F6	F7	F8	F9

Refcode	*RFAC	*SIGF	$\text{Sb2}\text{-F(br)}\text{-Sb1}\text{-F}$ / deg	$\text{Sb1}\text{-F(br)}\text{-Sb2}\text{-F}$ / deg	$\text{Sb1}\text{-F(br)}\text{-Sb2}$ / deg	$(E - E_{\text{min}}) / (\text{kcal/mole})$
DOPRIJ	0.07	3	27.6	29.3	146.9	1.54
DOPRIJ10	0.045	2	28.6	26.5	145.6	1.65
FITDIV	0.08	3	16.8	-41.4	162.9	0.45
FITDIV01	0.058	2	20.2	42.5	157.1	0.75
GOBDEG	0.048	3	-39.3	-14.8	146.2	1.56
HOKFES	0.048	2	-18.3	39.0	150.0	1.55
HOLMOK	0.028	1	19.0	36.1	148.5	1.33
MAZNUW	0.037	2	-1.8	-35.7	154.7	0.73
PESGID	0.029	2	-31.2	-20.1	149.0	1.21
QEZTAQ	0.022	2	-19.6	-23.0	151.6	1.01
QEZTEU	0.022	2	-22.8	22.7	161.1	0.82
SUNMOD	0.065	3	-15.6	17.2	165.9	0.58
TOQLOA	0.031	3	38.6	17.8	153.0	0.94
WEBJES	0.043	2	-6.4	-23.4	149.5	1.30
YEQRUH	0.023	2	0.0	45.7	150.7	1.02
ZOJZUT	0.035	2	2.0	39.8	147.6	1.30

Refined conformation in the crystal structure of $\text{Me}-\mathbf{1}^+ \text{Sb}_2\text{F}_{11}^-$

Character in F label	τ_1	τ_2	$\text{Sb1-F}_{\text{bridge}}-\text{Sb2}$	$(E - E_{\min}) / (\text{kcal/mole})$
a	$ \text{F13a-Sb1-F1a-Sb2} = 44.6^\circ$	$ \text{Sb1-F1a-Sb2-F24a} = 0^\circ$	$\text{Sb1-F1a-Sb2} = 168.2^\circ$	0.13
b, b'	$ \text{F15b-Sb1-F1b-Sb2} = 43.9^\circ$	$ \text{Sb1-F1b-Sb2-F22b} = 3.6^\circ$	$\text{Sb1-F1b-Sb2} = 154.3^\circ$	0.74

Reference codes (refcodes) of the crystal structures for which the energy of the $\text{Sb}_2\text{F}_{11}^-$ anion conformation has been estimated with the interpolating function:

DOPRIJ

3,5,7-Trimethyl-adamantyl (μ_2 -fluoro)-bis(pentafluoro-antimony) at -160deg.C.
 C13 H21 1+,F11 Sb2 1-

T.Laube

Angew.Chem.,Int.Ed.Engl., 25, 349,1986

-----+-----+-----+-----+-----+-----+

DOPRIJ10

3,5,7-Trimethyl-adamantyl (μ_2 -fluoro)-bis(pentafluoro-antimony) at 103 K.
 C13 H21 1+,F11 Sb2 1-

T.Laube,E.Schaller

Acta Crystallogr.,Sect.B:Struct.Sci., 51, 177,1995

-----+-----+-----+-----+-----+-----+

FITDIV

1,2,4,7-anti-Tetramethyl-2-norbornyl (μ_2 -fluoro)-bis(pentafluoro-antimony) at -80 deg.C.
 C11 H19 1+,F11 Sb2 1-

T.Laube

Angew.Chem.,Int.Ed.Engl., 26, 560,1987

-----+-----+-----+-----+-----+-----+

FITDIV01

1,2,4,7-anti-Tetramethylbicyclo(2.2.1)heptan-2-yl cation undecafluoro-di-antimony at 110 K.
 C11 H19 1+,F11 Sb2 1-

T.Laube

Helv.Chim.Acta, 77, 943,1994

-----+-----+-----+-----+-----+-----+

GOBDEG

(Perfluoroisopropyl)oxonium (μ_2 -fluoro)-bis(pentafluoro-antimonate) at 173 K.

C3 H2 F7 O1 1+,F11 Sb2 1-

R.Minkwitz,S.Reinemann

Z.Anorg.Allg.Chem., 625, 121,1999

-----+-----+-----+-----+-----+-----+

HOKFES

catena-(tris(mu²-cis-Difluoro(tetrafluoro)antimonato(v))-bis(tetracarbonyl-molybdenum(ii)) (μ_2 -fluoro)-bis(pentafluoro-antimonate(v)))

at 180.2 K.

(C16 F36 Mo4 O16 Sb6 2+)n,2n(F11 Sb2 1-)

R.Brochler,D.Freidank,M.Bodenbinder,I.H.T.Sham,H.Willner,S.J.Rettig,J.Trotter,F.Aubke
 Inorg.Chem., 38, 3684,1999

-----+-----+-----+-----+-----+-----+

HOLMOK

Hexacarbonyl-iron(ii) bis(undecafluorodiantimonate(v))

C6 Fe1 O6 2+,2(F11 Sb2 1-)

E.Bernhardt,B.Bley,R.Wartchow,H.Willner,E.Bill,P.Kuhn,I.H.T.Sham,M.Bodenbinder,R. Brochler,F.Aubke
 J.Am.Chem.Soc., 121, 7188,1999

-----+-----+-----+-----+-----+-----+

MAZNUW

Chloro-pentacarbonyl-rhodium(iii) bis(undecafluoro-diantimonate(v))
C5 Cl1 O5 Rh1 2+,2(F11 Sb2 1-)

H.Willner,C.Bach,R.Wartchow,Changqing Wang,S.J.Rettig,J.Trotter,V.Jonas,W.Thiel, F.Aubke
Inorg.Chem., 39, 1933,2000

-----+-----+-----+-----+-----+-----+
PESGID

t-Butyl cation (μ_2 -fluoro)-decafluoro-di-antimonate(v)
at -80 deg.C.

C4 H9 1+,F11 Sb2 1-

S.Hollenstein,T.Laube

J.Am.Chem.Soc., 115, 7240,1993

-----+-----+-----+-----+-----+-----+
QEZTAQ

Tetracarbonyl-palladium(ii) bis((μ_2 -fluoro)-decafluoro-di-antimony(v))
at 180.2 K.

C4 O4 Pd1 2+,2(F11 Sb2 1-)

H.Willner,M.Bodenbinder,R.Brochler,G.Hwang,S.J.Rettig,J.Trotter,B.von
Ahsen,U.Westphal,V.Jonas,W.Thiel,F.Aubke
J.Am.Chem.Soc., 123, 588,2001

-----+-----+-----+-----+-----+-----+
QEZTEU

Tetracarbonyl-platinum(ii) bis((μ_2 -fluoro)-decafluoro-di-antimony(v))
at 180.2 K.

C4 O4 Pt1 2+,2(F11 Sb2 1-)

H.Willner,M.Bodenbinder,R.Brochler,G.Hwang,S.J.Rettig,J.Trotter,B.von
Ahsen,U.Westphal,V.Jonas,W.Thiel,F.Aubke
J.Am.Chem.Soc., 123, 588,2001

-----+-----+-----+-----+-----+-----+
SUNMOD

2-Phenyladamantan-ylium (μ_2 -fluoro)-decafluoro-di-antimony(v)
at 183 K.

C16 H19 1+,F11 Sb2 1-

T.Laube,S.Hollenstein

Helv.Chim.Acta, 77, 1773,1994

-----+-----+-----+-----+-----+-----+
TOQLOA

Chloro-pentacarbonyl-iridium bis((μ_2 -fluoro)-bis(pentafluoroantimonate))
C5 Cl1 Ir1 O5 2+,2(F11 Sb2 1-)

C.Bach,H.Willner,Changqing Wang,S.J.Rettig,J.Trotter,F.Aubke
Angew.Chem.,Int.Ed.Engl., 35, 1974,1996

-----+-----+-----+-----+-----+-----+
WEBJES

Hexacarbonyl-(hexafluoroantimonato(v))-tungsten(ii) undecafluoro-di-antimonate(v) at 180.2 K.

C6 F6 O6 Sb1 W1 1+,F11 Sb2 1-

R.Brochler,I.H.T.Sham,M.Bodenbinder,V.Schmitz,S.J.Rettig,J.Trotter,H.Willner,F.Aubke
Inorg.Chem., 39, 2172,2000

-----+-----+-----+-----+-----+-----+
YEQRUH

(Trifluoromethyl)dimethyloxonium (μ_2 -fluoro)-decafluoro-di-antimony
at 171 K.

C3 H6 F3 O1 1+,F11 Sb2 1-

R.Minkwitz,S.Reinemann,R.Seelbinder,D.Konikowski,H.Hartl,I.Brudgam,J.Hegge,B.Hoge,J.A.Sheehy,K.O.Chr
iste

Inorg.Chem., 40, 4404,2001

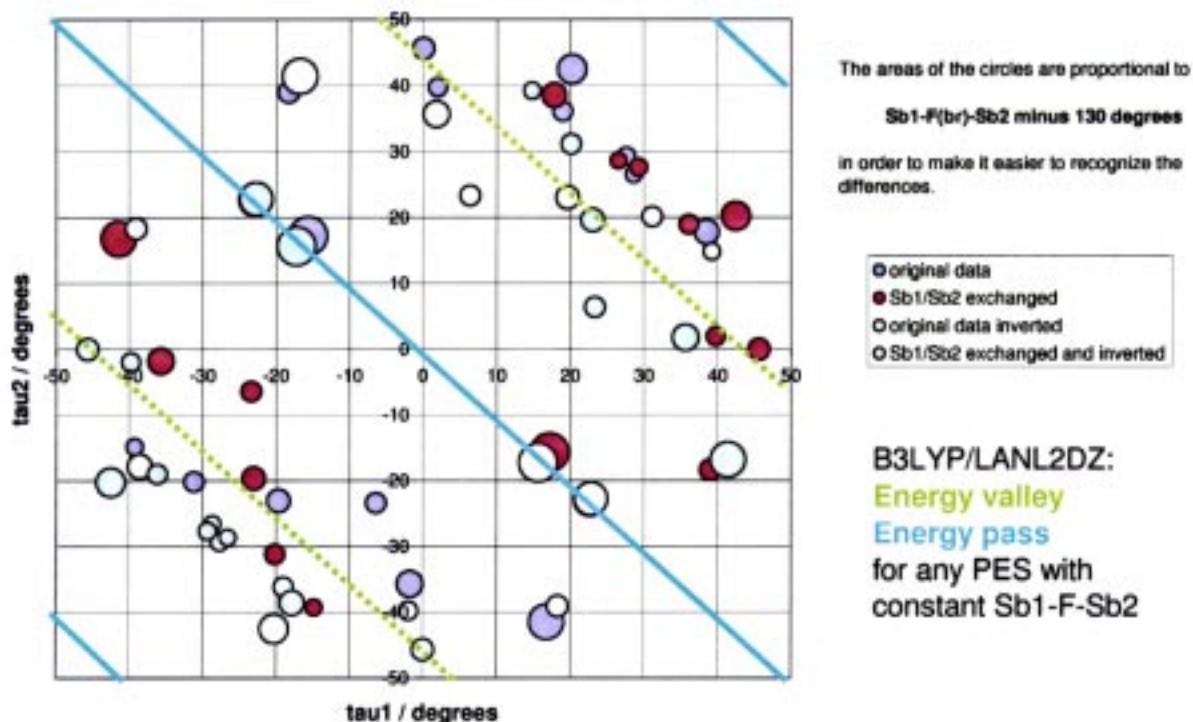
-----+-----+-----+-----+-----+-----+
ZOJZUT

Dicarbonyl-mercury(ii) bis((μ_2 -fluoro)-decafluoro-di-antimony(v))
at 195 K.

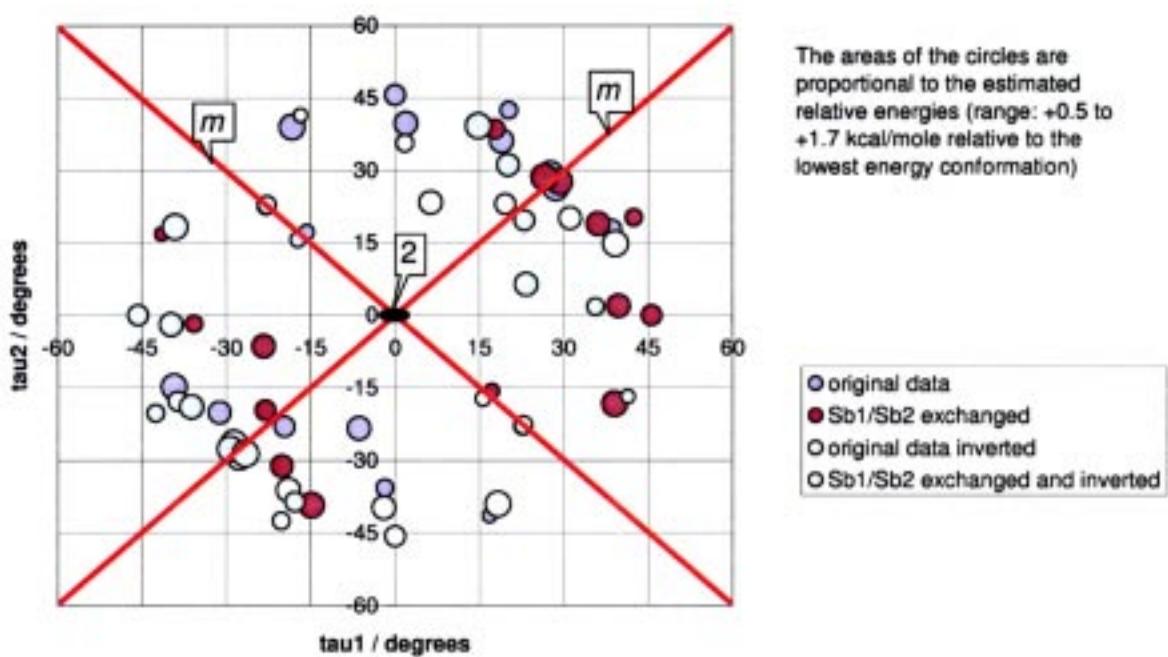
C2 Hg1 O2 2+,2(F11 Sb2 1-)

M.Bodenbinder,G.Balzer-Jollenbeck,H.Willner,R.J.Batchelor,F.W.B.Einstein,C.Wang, F.Aubke
Inorg.Chem., 35, 82,1996

Angle Sb1-F(bridge)-Sb2 in crystal structures with Sb₂F₁₁(-) anions

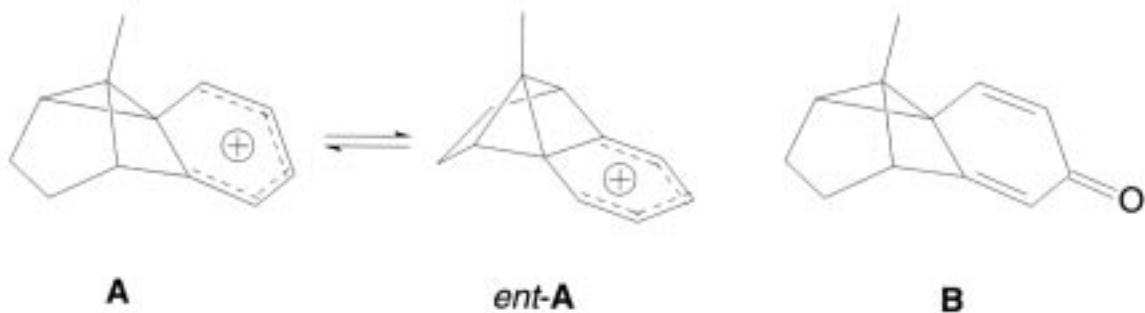


Estimated relative energies (quadratic 3D interpolation of the PES based on B3LYP/LANL2DZ calculations of isolated ions) of Sb₂F₁₁(-) conformations found in single crystal structures

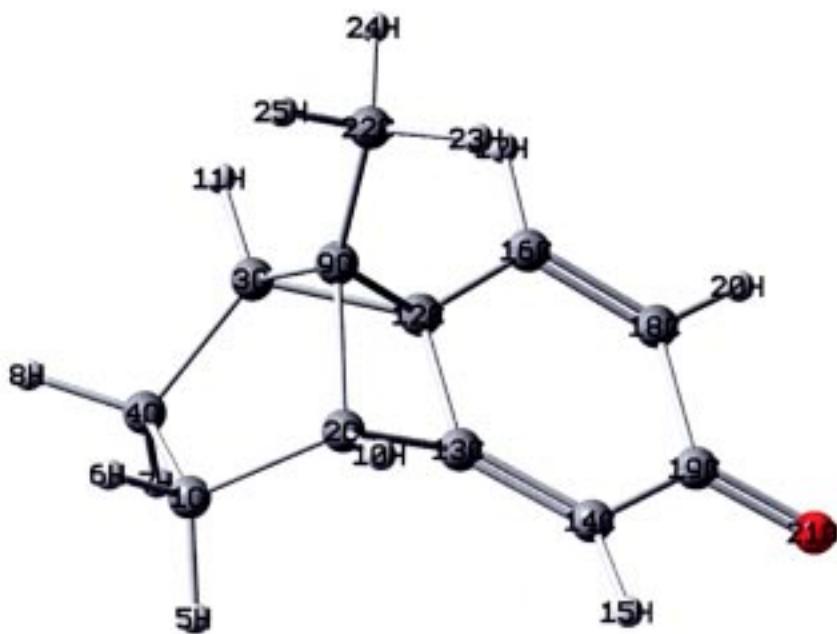


Neutral model for a classical isomer of Me- $\mathbf{1}^+$

The alternative description of the structure of Me-1^+ would be an equilibrium between two enantiomeric isomers without a (3c, 2e) bond, **A** and *ent*-**A**:



Because the structure of **A** could perhaps only be computed using a molecular mechanics program without parameters for bridged structures (DFT methods lead to the bridged structure), we computed the structure of the very similar neutral ketone **B** with the same DFT method used for most other calculations in this paper, B3LYP/6-311+G(d,p). The presence of the carbonyl group leads to a slight electron deficiency in the conjugated system, but bridging does not occur. The DFT structure of the strained molecule **B** is probably more accurate than a structure computed with lower level methods (molecular mechanics, semi-empirical). The distances corresponding to C4a-C9 and C8a-C9 in Me-1^+ are C12-C9 = 1.63 and C13-C9 = 2.09 Å in **B**, and these values are mentioned in the manuscript as estimates for **A**.



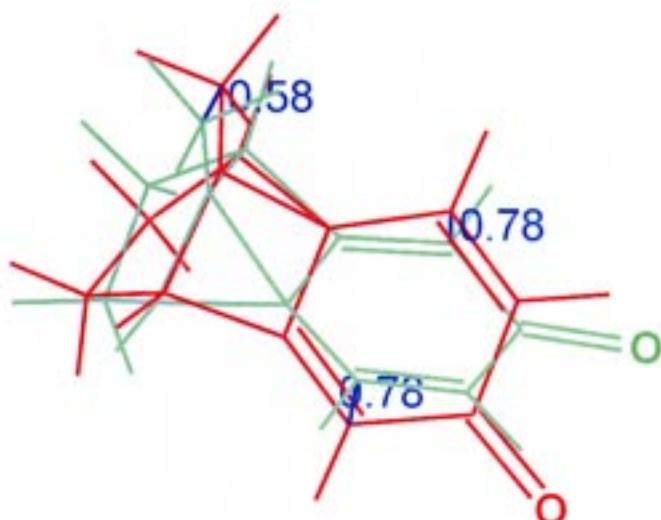
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	539.78631274 a.u.
RMS Gradient Norm	0.00000032 a.u.
Imaginary Freq	0
Dipole Moment	7.4083 Debye
Point Group	C1

Standard orientation:

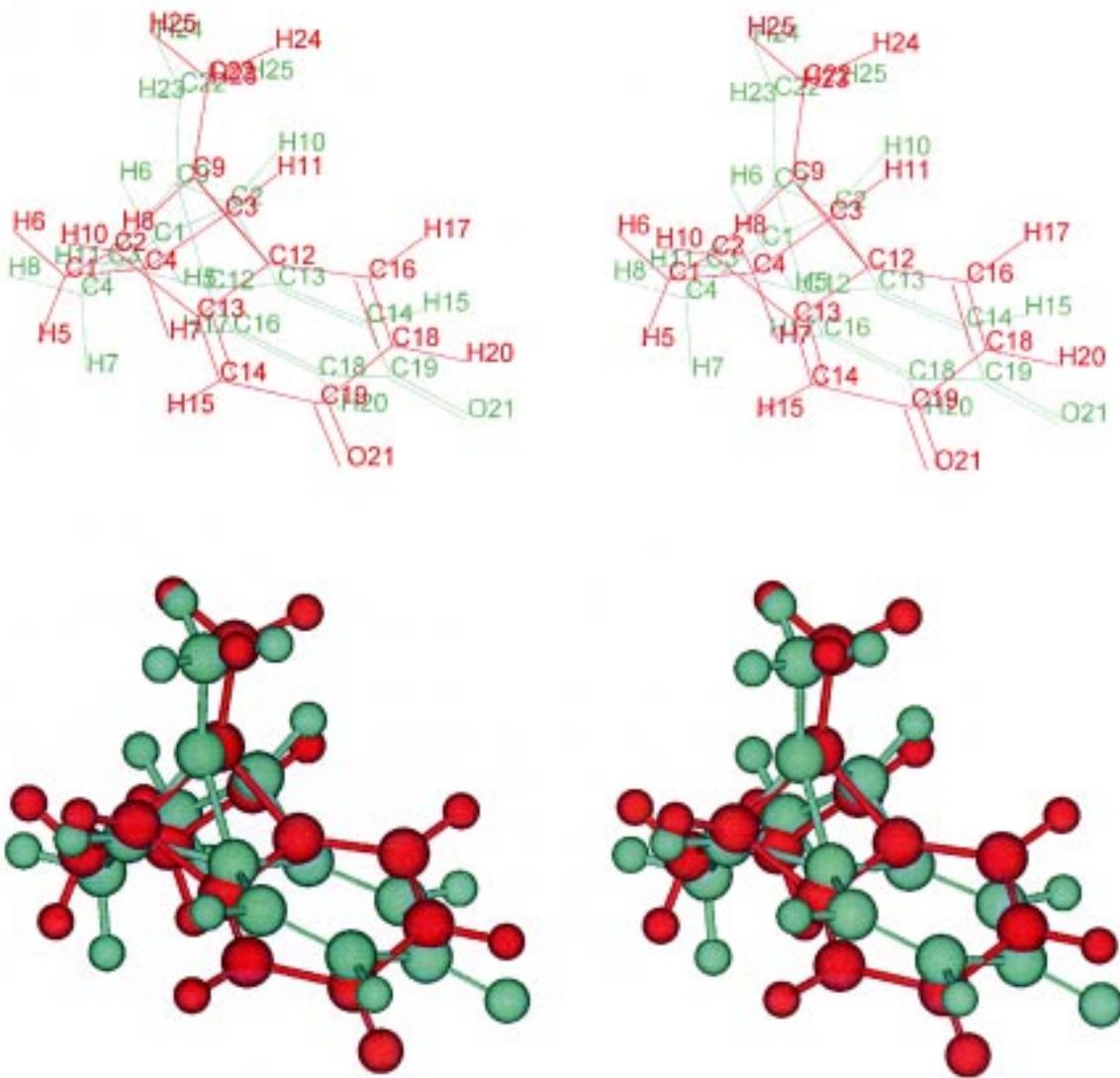
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.156395	-1.624921	-0.054331
2	6	0	-1.203823	-0.854720	0.880297
3	6	0	-1.558394	0.552715	-0.946000
4	6	0	-2.173418	-0.786625	-1.361801
5	1	0	-1.825196	-2.652767	-0.215372
6	1	0	-3.154268	-1.663145	0.393395
7	1	0	-1.592304	-1.254286	-2.160006
8	1	0	-3.190656	-0.644907	-1.736006
9	6	0	-1.404741	0.654446	0.520389
10	1	0	-1.249538	-1.138860	1.930830
11	1	0	-1.798488	1.452584	-1.503908
12	6	0	-0.105887	0.525402	-0.453067
13	6	0	0.189362	-0.685875	0.302996
14	6	0	1.440368	-1.077262	0.615604
15	1	0	1.655897	-1.895840	1.293041
16	6	0	0.990556	1.376471	-0.865604
17	1	0	0.798683	2.301759	-1.400998
18	6	0	2.251904	0.951892	-0.632142
19	6	0	2.576762	-0.313075	0.081476
20	1	0	3.110576	1.527637	-0.960240
21	8	0	3.747027	-0.651579	0.251817
22	6	0	-1.726546	1.777329	1.453614
23	1	0	-1.053268	1.782881	2.315348
24	1	0	-1.645141	2.744001	0.951033
25	1	0	-2.750998	1.678909	1.829766

Zero-point correction=	0.206249 (Hartree/Particle)
Thermal correction to Energy=	0.216748
Thermal correction to Enthalpy=	0.217692
Thermal correction to Gibbs Free Energy=	0.170403
Sum of electronic and zero-point Energies=	-539.580064
Sum of electronic and thermal Energies=	-539.569565
Sum of electronic and thermal Enthalpies=	-539.568620
Sum of electronic and thermal Free Energies=	-539.615909

The largest distances between corresponding C atoms (blue) after least squares adjustment of all C atoms are 0.78 and 0.58 Å (red: **B**; green: *ent*-**B**; both molecules are treated as rigid bodies).



Stereo diagrams of **B** (red) and *ent*-**B** (green) after least squares adjustment of the corresponding C atoms

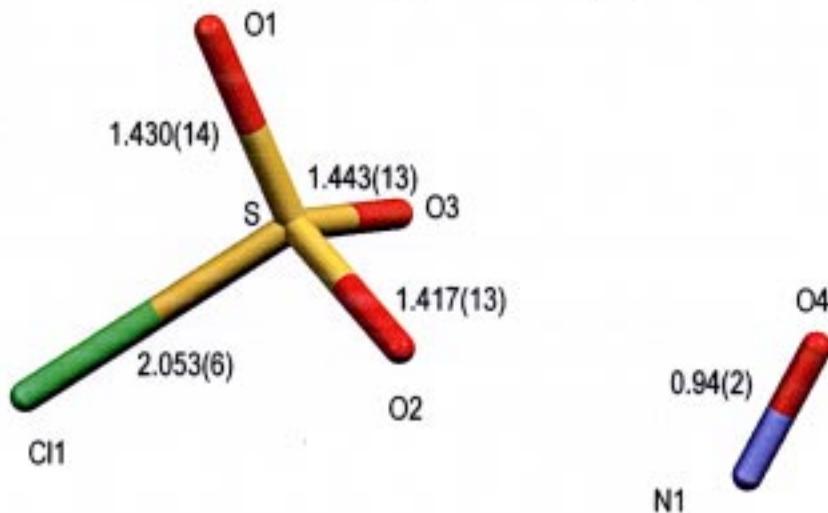


If there would be static or dynamic disorder between classical ions **A** and *ent*-**A** in the crystal, the thermal ellipsoids should be elongated along the directions connecting corresponding positions (some of them are marked above with blue lines). Despite the generally large ADPs of the cation Me-1⁺, this case can be excluded. A disorder between nearly symmetrically bridges structures cannot be excluded on the basis of the X-ray data.

Additional data about related structures reported in the literature

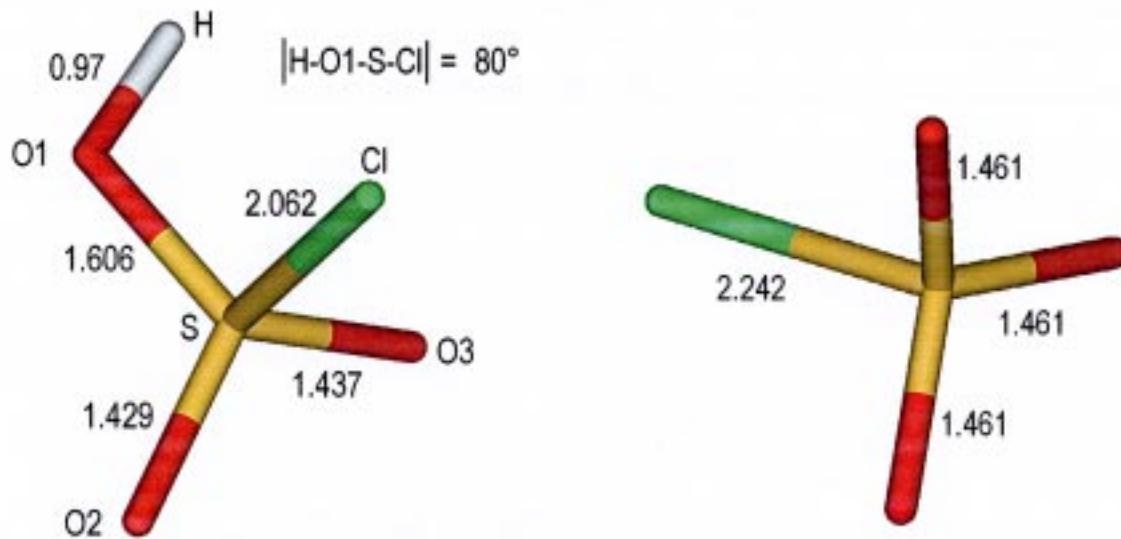
Crystal structure of $\text{NO}^+ \text{SO}_3\text{Cl}^-$

T. Höhle, F. C. Mijlhoff,
Recl. Trav. Chim. Pays-Bas **1967**, *86*, 1153



ab initio structures of HSO_3Cl and SO_3Cl^-

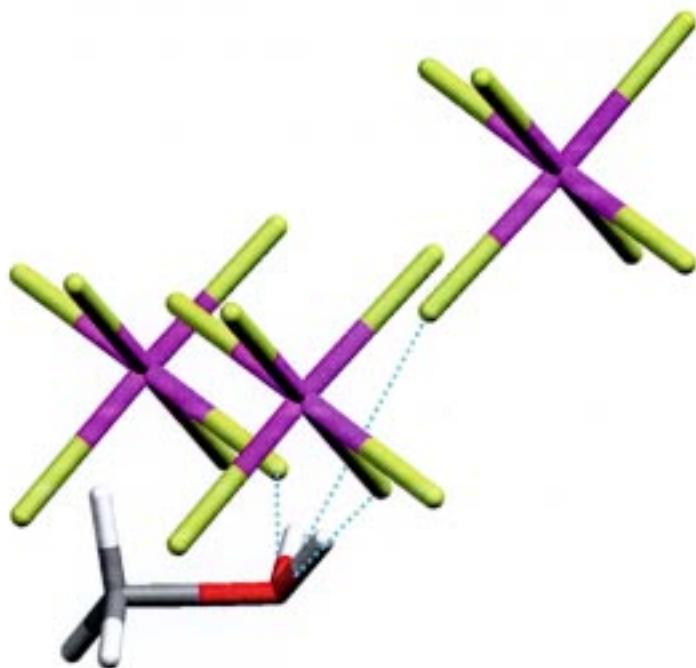
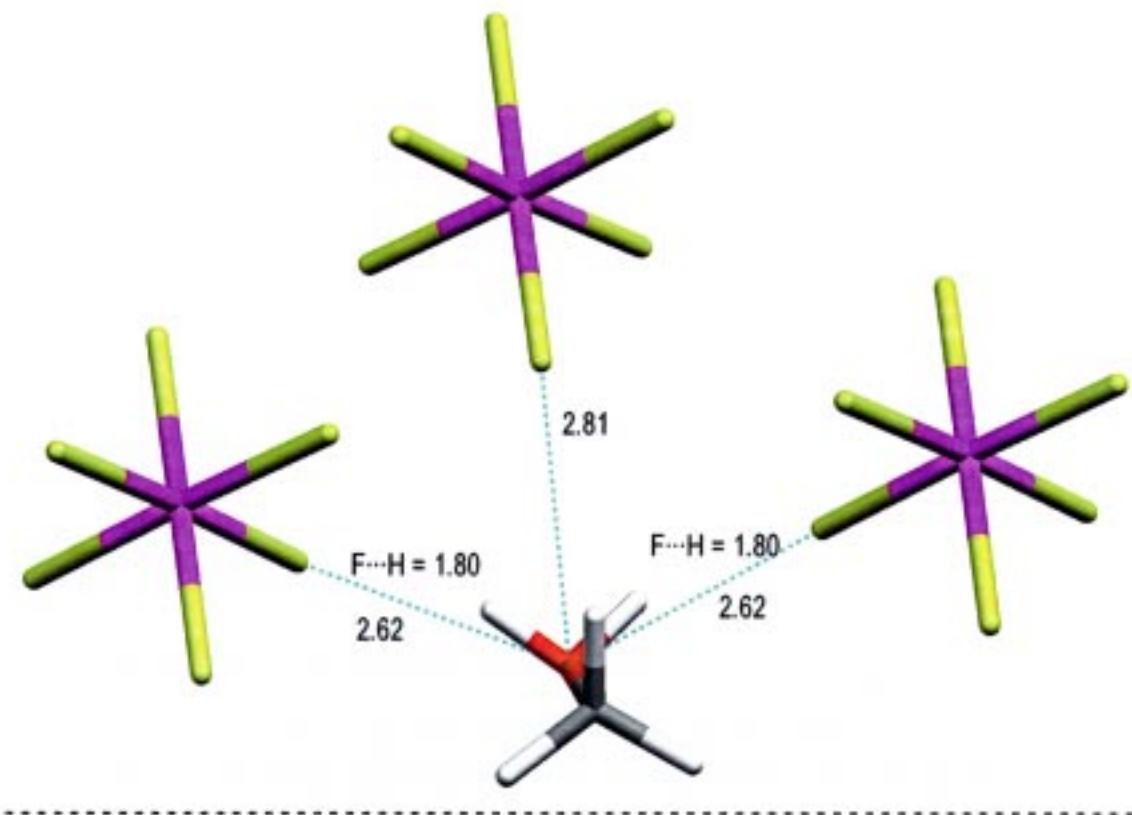
R. Steudel, A. H. Otto,
Eur. J. Inorg. Chem. **2000**, 2379
calculated at MP2 / 6-311++G(d,p) level



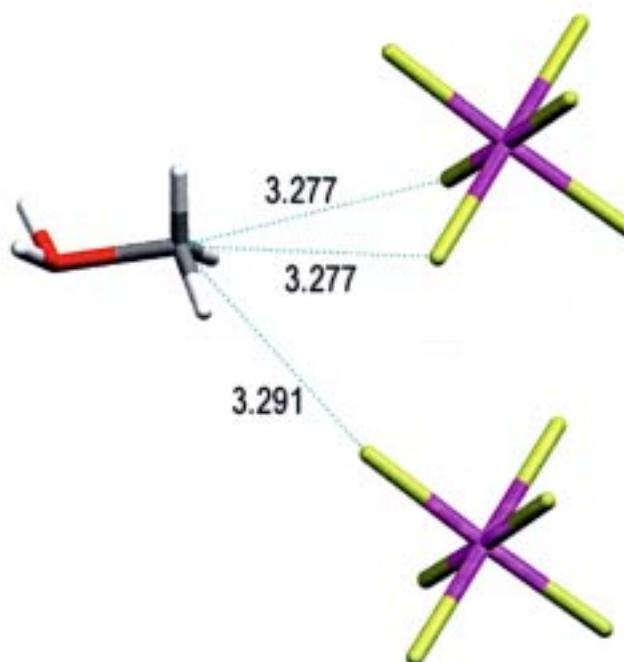
R. Minkwitz, S. Schneider, Z. anorg. allg. Chem. 1998, 624, 1989

$\text{MeOH}_2^+ \text{AsF}_6^-$: C-O = 1.45(1) Å

(Cambridge File: CH₃-OH: av. C-O = 1.413(5) Å)



View from the side on the cation.

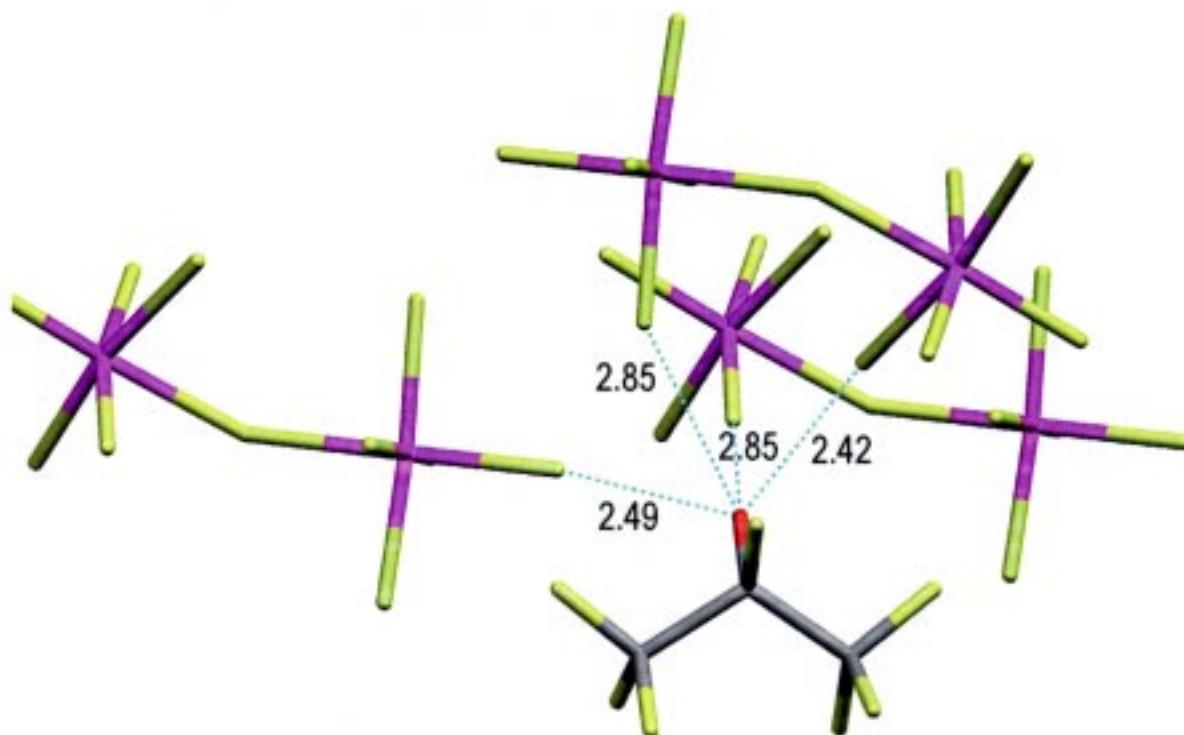


Potential S_N2-like nucleophile-electrophile interactions

R. Minkwitz, S. Reinemann, Z. anorg. allg. Chem. 1999, 625, 121

(CF₃)₂CF-OH₂⁺ Sb₂F₁₁ : C-O = 1.430(13) Å; short O···F ⇒ OH···F

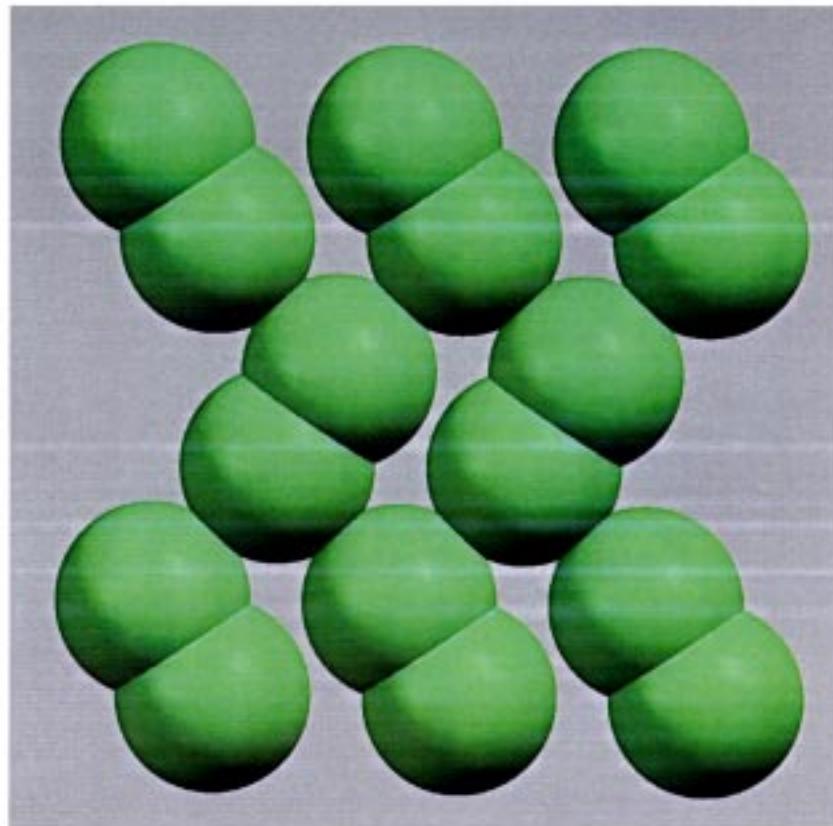
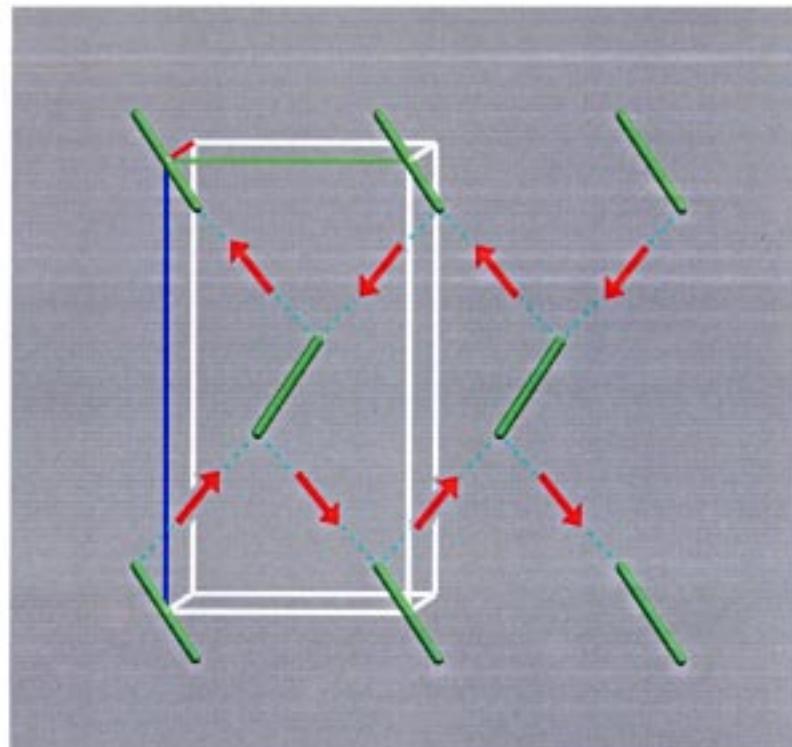
(the hydrogen positions have not been determined in the crystal structure)



H. A. Bent, *Chem. Rev.* 1968, 68, 587: Discussion of I₂ crystal structure

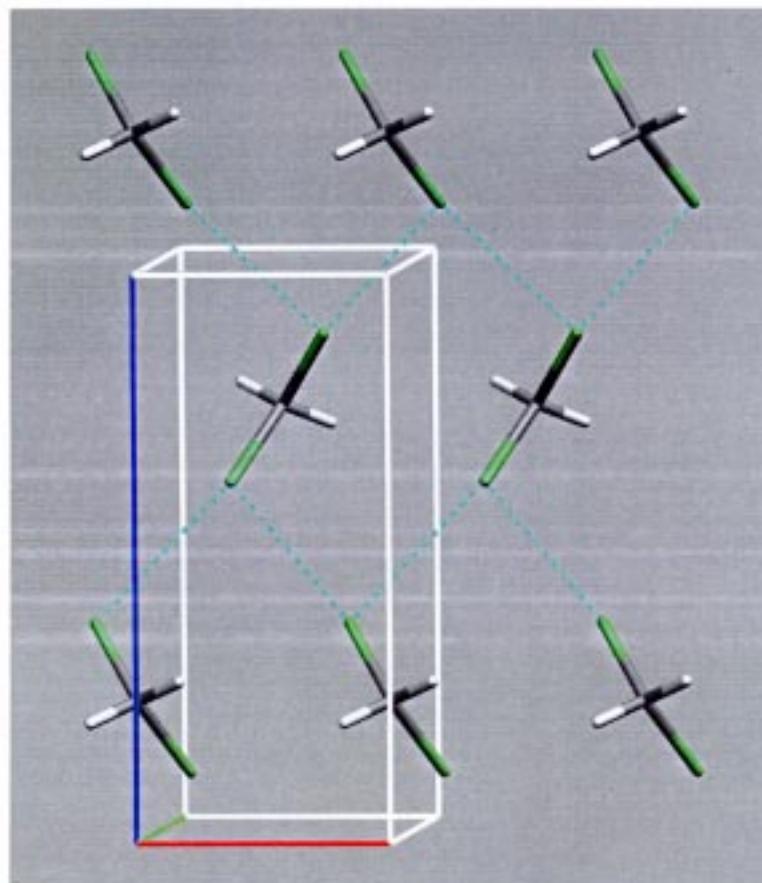
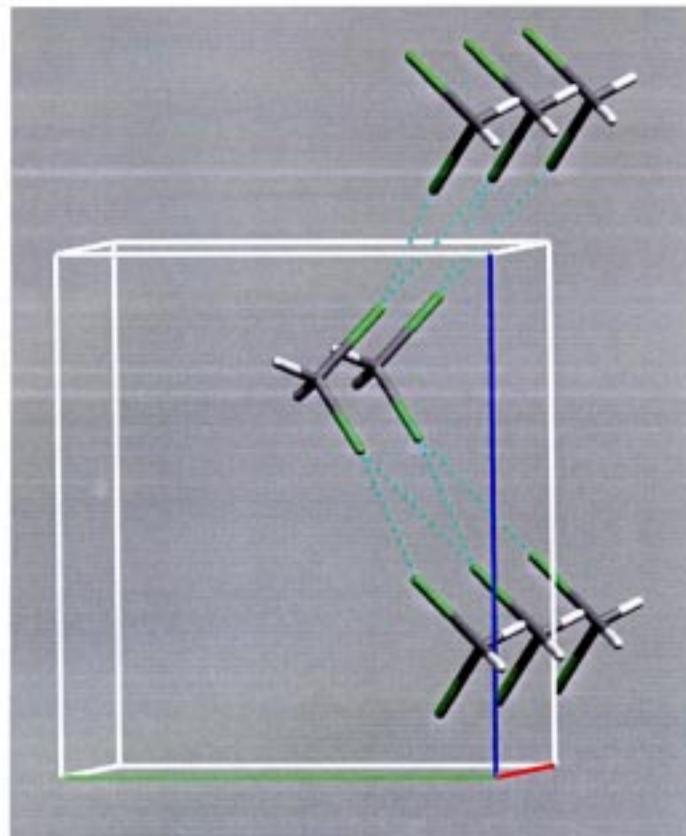
similar: Cl₂ crystal structure (B. M. Powell et al, *Mol. Phys.* 1984, 53, 929)

each halogen atom acts as nucleophile and as electrophile (Nu → El)
 $\text{Cl}\cdots\text{Cl} = 3.258 \text{ Å}$



Crystal structure of methylenechloride

T. Kawaguchi, K. Tanaka, T. Takeuchi, T. Watanabé, *Bull. Chem. Soc. Jpn.* 1973, 46, 62
 $\text{Cl} \cdots \text{Cl} = 3.492 \text{ \AA}$

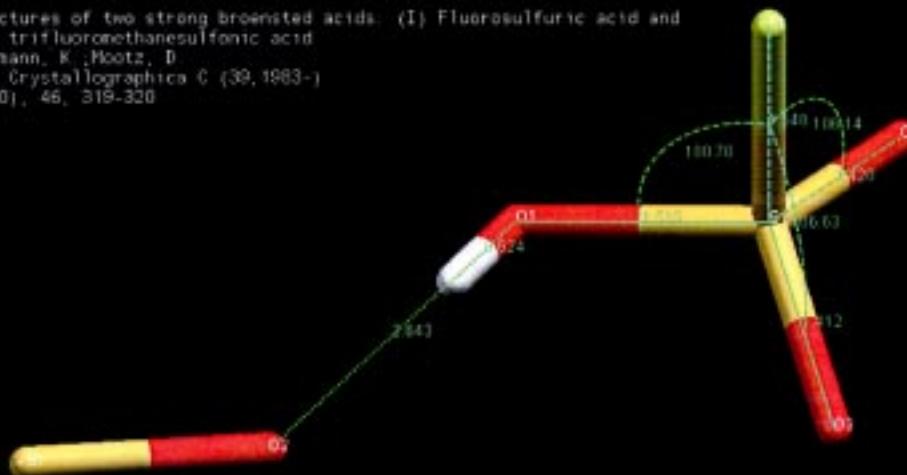


X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol

Thomas Laube

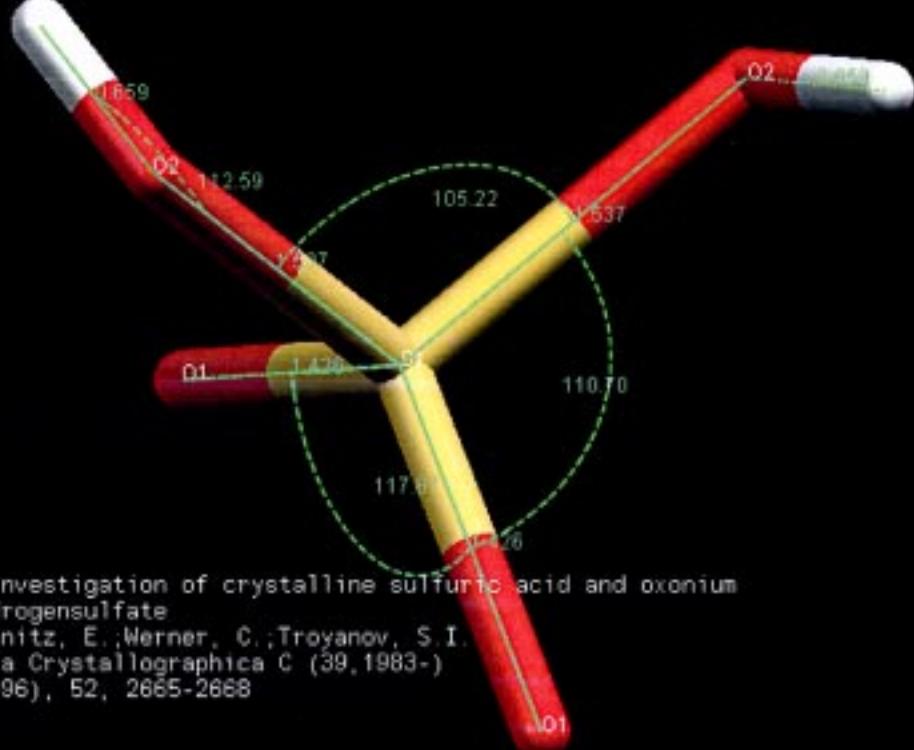
J. Am. Chem. Soc.

Chem. Name Fluorosulfuric Acid
 Structured F S O2 (9 H)
 Sub HI F1 O3 S1
 ANS ARY3
 D(calc) 2.17
 Title Structures of two strong broensted acids
 (II) trifluoromethanesulfonic acid
 Author(s) Bartmann, K.; Mootz, D
 Reference Acta Crystallographica C (39, 1983-)
 (1990), 46, 319-320



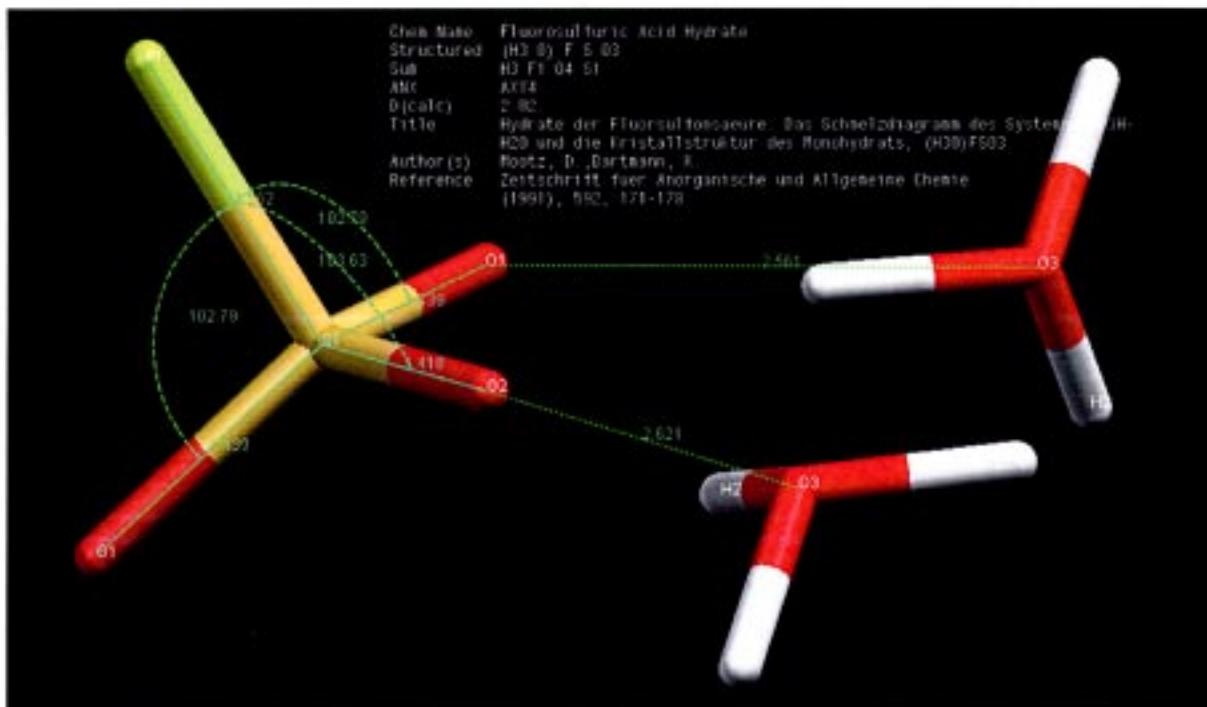
Crystal structure of FSO_3H (Bartmann, K.; Mootz, D. *Acta Crystallogr.* **1990**, C46, 319-320)

Title Reinvestigation of crystalline sulfuric acid and oxonium
hydrogensulfate
Author(s) Kemnitz, E.; Werner, C.; Troyanov, S.I.
Reference Acta Crystallographica C (39,1983-)
(1996), 52, 2665-2688

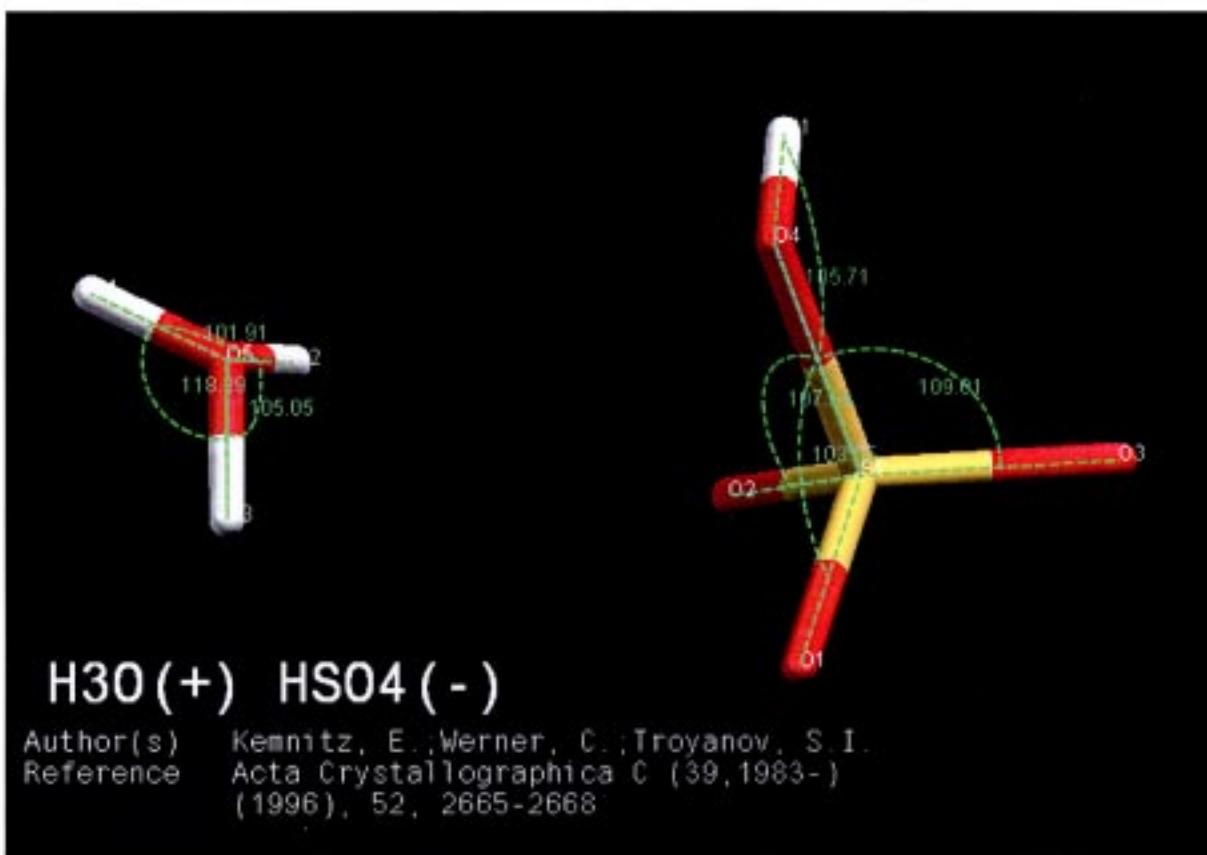


Crystal structure of H₂SO₄ (Kemnitz, E.; Werner, C.; Troyanov, S. I. *Acta Crystallogr.* 1996, C52, 2665-2668)

X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol
Thomas Laube J. Am. Chem. Soc.



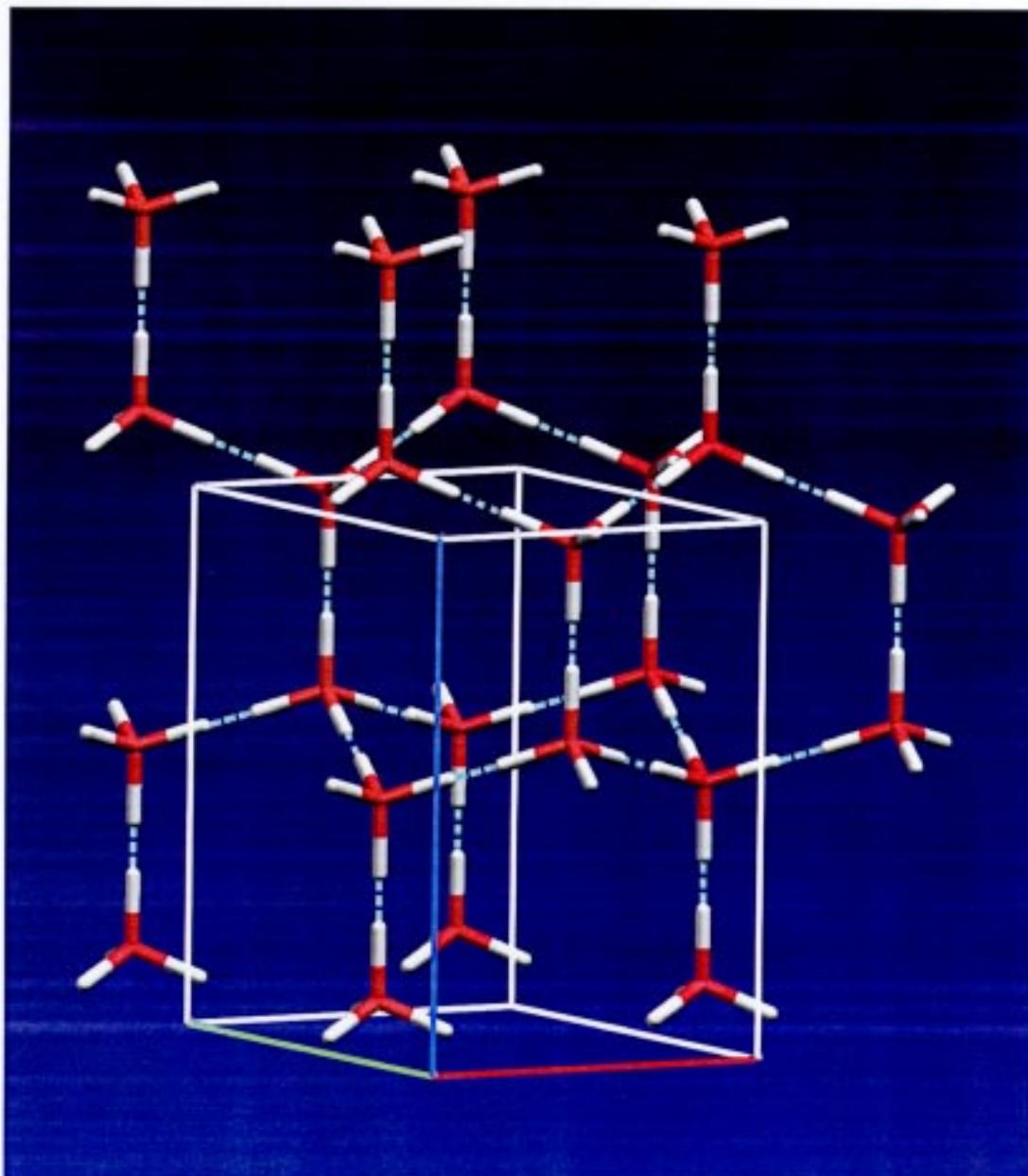
Crystal structure of $\text{H}_3\text{O}^+ \text{FSO}_3^-$ (Mootz, D.; Bartmann, K. *Z. Anorg. Allg. Chem.* 1991, 592, 171-178)



Crystal structure of $\text{H}_3\text{O}^+ \text{HSO}_4^-$ (Kemnitz, E.; Werner, C.; Troyanov, S. I. *Acta Crystallogr.* **1996**, C52, 2665-2668)

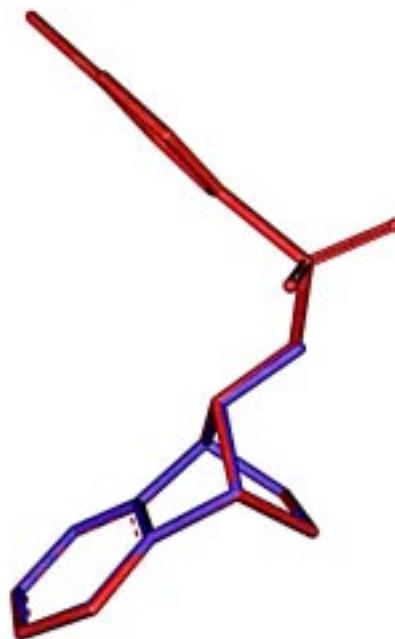
Disordered H bonds: ice I_h

Leadbetter, A.J.; Ward, R.C.; Clark, J.W.; Tucker, P.A.; Matsuo, T.; Suga, H. J.
Chem. Phys. 1985, 82, 424
(D₂O, neutron diffraction; sof(D) = 0.5)

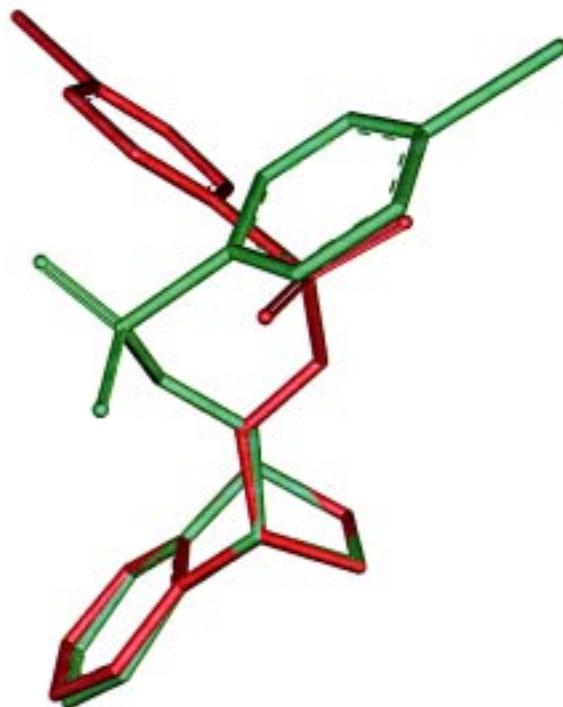


Superpositions of various benzonorbornane derivatives with a leaving group at C9 in *syn* or *anti* position

**Superposition of the benzonorbornenyl-oxonium ion (crystal structure) and the anti-brosylate from Koyoma et al, J. Chem. Soc. B 1969, 940
(least squares adjustment of C1, C2, C3, C4)**

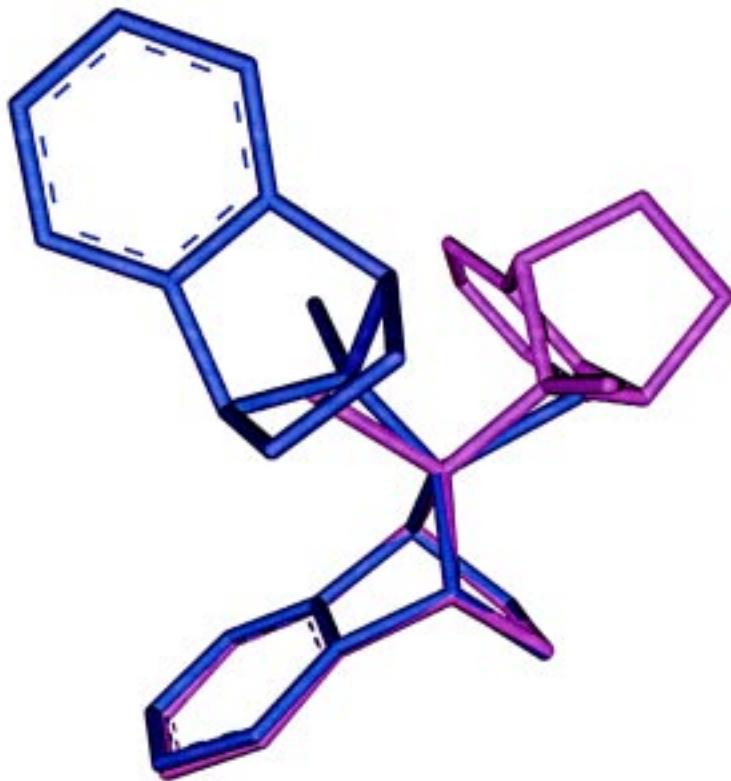


**Superposition of the *syn*-brosylate from Koyoma et al, J. Chem. Soc. B 1968, 935 and the *anti*-brosylate from Koyoma et al, J. Chem. Soc. B 1969, 940
(least squares adjustment of C1, C2, C3, C4)**



C4a...C9, C8a...C9: 2.28, 2.29; 2.35, 2.36 Å

Superposition of the *syn*-chloro part and the *anti*-chloro part
of the chloro-benzonorbornene dimer from
Nakayama et al, *Tetrahedron Lett.* 2000, 8907
(least squares adjustment of C1, C2, C3, C4)



C4a...C9, C8a...C9: 2.335, 2.334; 2.370, 2.371 Å