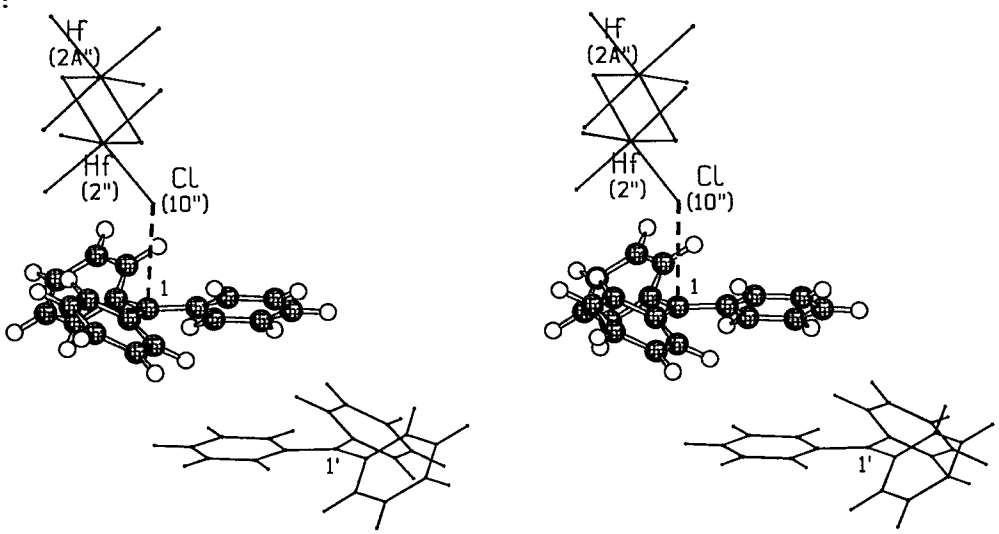
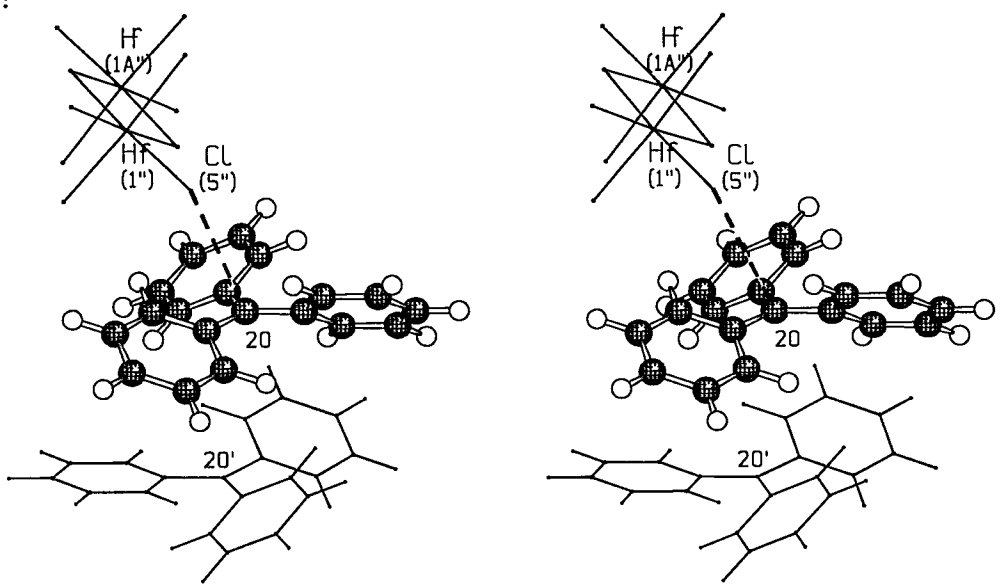
cation #1:



C(1) - Cl(10^{II}) 3.544 | *diff* = 0.094

cation #2:

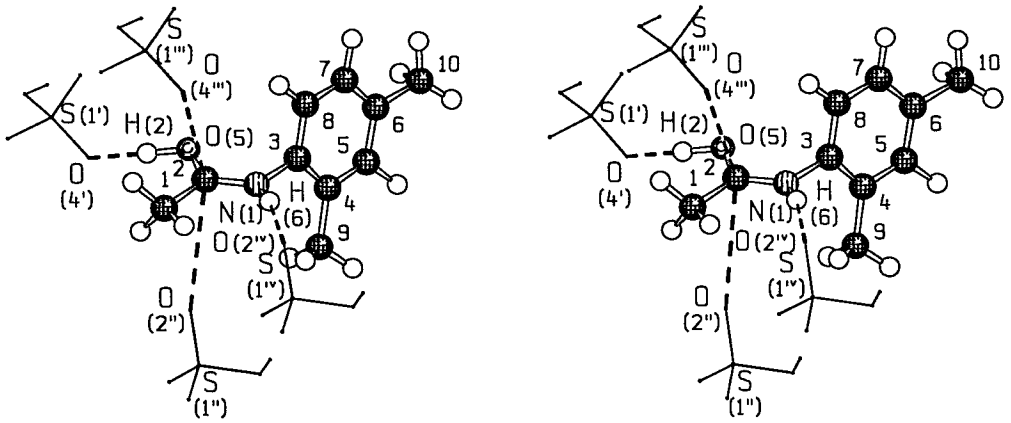


Cl(5^{II}) - C(20) 3.808 | *diff* = 0.358 weak

TAFBOR

2,4-Dimethyl-1-(1'-hydroxyethylamide-)-benzene monohydrogensulfate
C10 H14 N1 O1 1+,H1 O4 S1 1-
A.I.Gubin,G.D.Khakimzhanova,N.N.Nurakhmetov,M.Zh.Buranbaev,R.Sh.Erkasov
Kristallografiya, 34, 240,1989

TAFBOR P21/c Z= 4 NATOMS= 32 DIFF AS=2 R-FACTOR= 0.052
ERROR y(H2) is 0.235, not 0.135
12 C-H BONDS: S.D.= 0.061; MEAN = 1.016; RANGE: 0.929 - 1.115

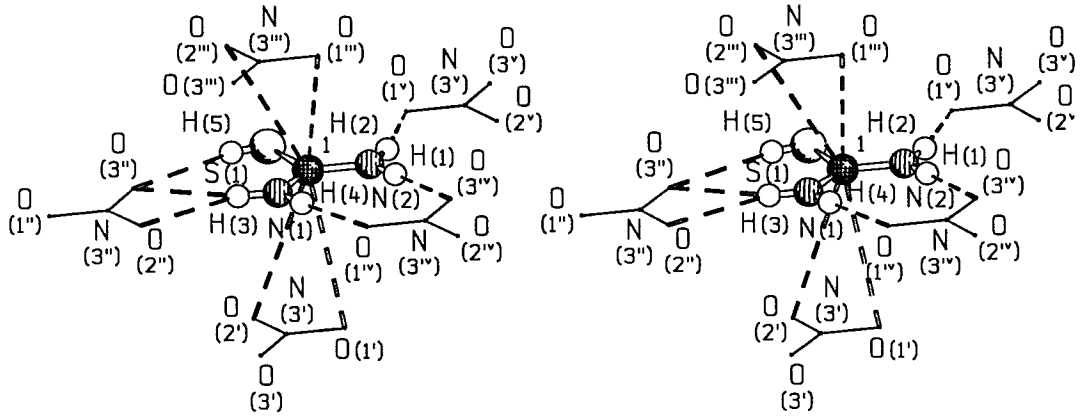


O(4^{I})	- H(2)	1.483	*diff* = -1.237	(H bond)
C(2)	- O(4^{III})	3.161	*diff* = -0.059	
C(2)	- O(2^{II})	3.548	*diff* = 0.328	weak
H(6)	- O(2^{IV})	1.972	*diff* = -0.748	(H bond)

THIURN01

Thiourea nitrate
Mo radiation
C1 H5 N2 S1 1+,N1 O3 1-
D.Feil,W.Song Loong
Acta Crystallogr.,Sect.B, 24, 1334,1968

THIURN P21/m Z= 2 NATOMS= 13 DIFF AS=0 R-FACTOR= 0.049



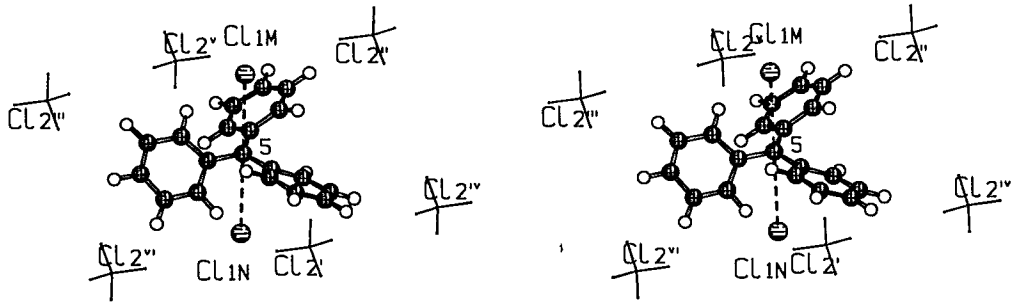
H(1)	- O(3^{IV})	2.021	*diff* = -0.699	(H bond)
H(2)	- O(1^{V})	2.092	*diff* = -0.628	(H bond)
H(3)	- O(2^{II})	2.409	*diff* = -0.311	(H bond)
H(3)	- O(3^{II})	2.362	*diff* = -0.358	(H bond)
H(4)	- O(1^{IV})	2.118	*diff* = -0.602	(H bond)
C(1)	- O(1^{I})	3.500	*diff* = 0.280	
C(1)	- O(2^{I})	3.528	*diff* = 0.308	weak
C(1)	- O(1^{III})	3.500	*diff* = 0.280	
C(1)	- O(2^{III})	3.528	*diff* = 0.308	weak
H(5)	- O(3^{II})	2.615	*diff* = -0.105	(H bond)

TIPMEP

Triphenylmethyl perchlorate
high temp. form
C19 H15 1+,Cl1 O4 1-
A.H.Gomes de Mesquita,C.H.MacGillavry,K.Eriks
Acta Crystallogr., 18, 437,1965

TIPMEP F4132 Z= 16 NATOMS= 40 UNSP AS=0 R-FACTOR= 0.084
DISORD ONE PERCHLORATE GROUP, CLO4(A), IS DISORDERED
15 C-H BONDS: S.D.= 0.003; MEAN = 1.086; RANGE: 1.080 - 1.088

Cl(1M) and Cl(1N) belong to disordered ClO_4 anions.

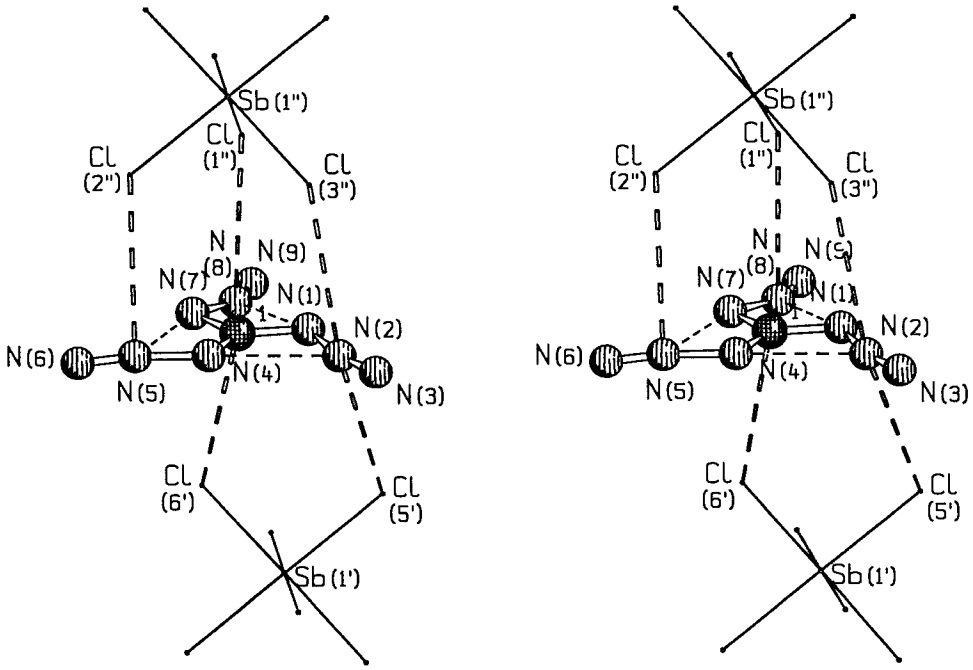


Cl(1M)	- C(5)	4.094	
C(5)	- Cl(1N)	4.094	

TRAZSB

Triazidocarbonium hexachloroantimonate
C1 N9 1+,Cl6 Sb1 1-
U.Muller,H.Barnighausen
Acta Crystallogr.,Sect.B, 26, 1671,1970

TRAZSB P21/c Z= 4 NATOMS= 17 DENS AS=3 R-FACTOR= 0.068



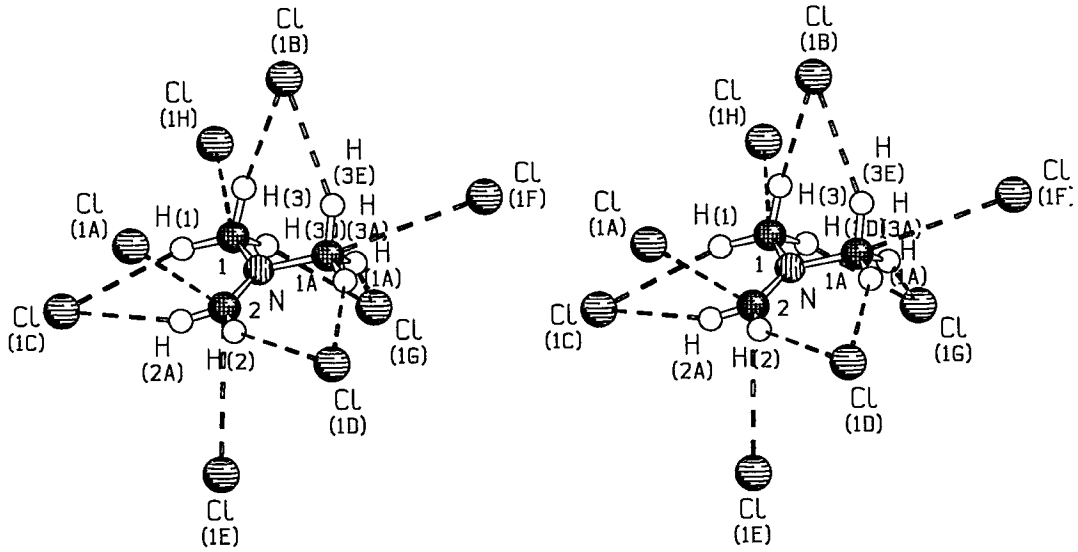
C(1)	- $Cl(6^{I})$	3.348	*diff* = -0.102	strong
N(1)	- N(8)	2.463	*diff* = -0.637	**extremely strong**

N(5)	- N(7)	2.465	*diff* = -0.635	**extremely strong**
N(2)	- N(4)	2.408	*diff* = -0.692	**extremely strong**
N(2)	- Cl(3^{II})	3.409	*diff* = 0.109	
N(2)	- Cl(5^{I})	3.499	*diff* = 0.199	
N(5)	- Cl(2^{II})	3.462	*diff* = 0.162	
N(8)	- Cl(1^{II})	3.384	*diff* = 0.084	

VAPREJ

Dimethylmethyleneammonium chloride
C3 H8 N1 1+,Cl1 1-
A.B.Burg
Inorg.Chem., 28, 1295,1989

VAPREJ Pmmn Z= 2 NATOMS= 13 DIFF AS=2 R-FACTOR= 0.066
8 C-H BONDS: S.D.= 0.060; MEAN = 1.028; RANGE: 0.925 - 1.079



C(1)	- Cl(1H)	3.417	*diff* = -0.033	
C(1A)	- Cl(1F)	3.417	*diff* = -0.033	
C(2)	- Cl(1A)	3.570	*diff* = 0.120	
C(2)	- Cl(1E)	3.570	*diff* = 0.120	
H(1)	- Cl(1C)	2.822	*diff* = -0.128	(H bond)
H(2)	- Cl(1D)	2.855	*diff* = -0.095	(H bond)
H(3)	- Cl(1B)	2.801	*diff* = -0.149	(H bond)
H(3D)	- Cl(1G)	2.801	*diff* = -0.149	(H bond)
H(2A)	- Cl(1C)	2.855	*diff* = -0.095	(H bond)
H(1A)	- Cl(1D)	2.822	*diff* = -0.128	(H bond)
H(3A)	- Cl(1G)	2.801	*diff* = -0.149	(H bond)
H(3E)	- Cl(1B)	2.801	*diff* = -0.149	(H bond)

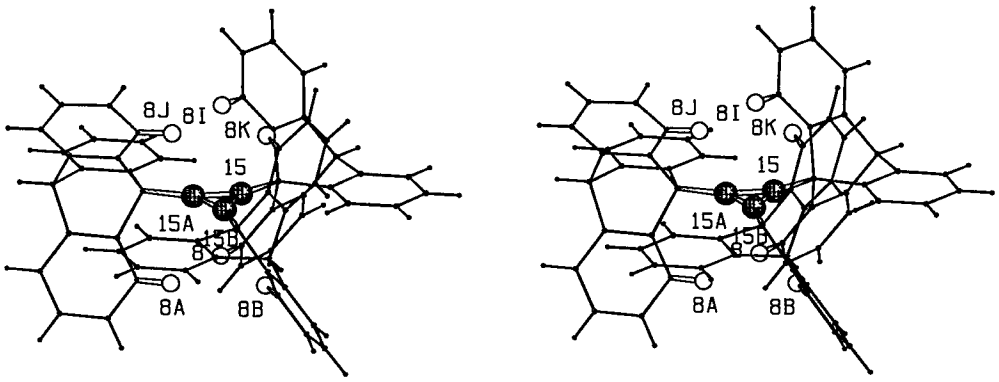
VAWXEW10

tris(9-Triptycyl)cyclopropenium perchlorate
C63 H39 1+,Cl1 O4 1-
J.M.Chance,J.H.Geiger,Y.Okamoto,R.Aburatani,K.Mislow
J.Am.Chem.Soc., 112, 3540,1990

VAWXEW10 P63/m Z= 2 NATOMS=102 DIFF AS=2 R-FACTOR= 0.057

DISORD The perchlorate anion is disordered and could not satisfactorily be modelled

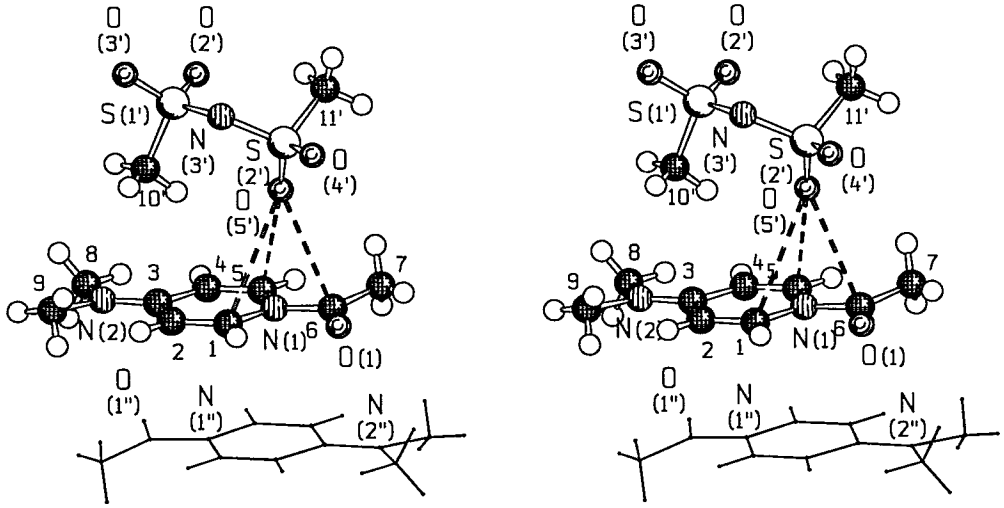
39 C-H BONDS: S.D.= 0.001; MEAN = 0.960; RANGE: 0.958 - 0.961



VEKMON

1-Acetyl-4-dimethylaminopyridinium dimesylamide
at -90 deg.C
C9 H13 N2 O1 1+,C2 H6 N1 O4 S2 1-
P.G.Jones,K.Linoh,A.Blaschette
Z.Naturforsch.,Teil B, 45, 267,1990

VEKMON P-1 Z= 2 NATOMS= 40 DIFF AS=1 R-FACTOR= 0.031
REMARK CSD 54129 has been used
19 C-H BONDS: S.D.= 0.049; MEAN = 0.947; RANGE: 0.741 - 0.960

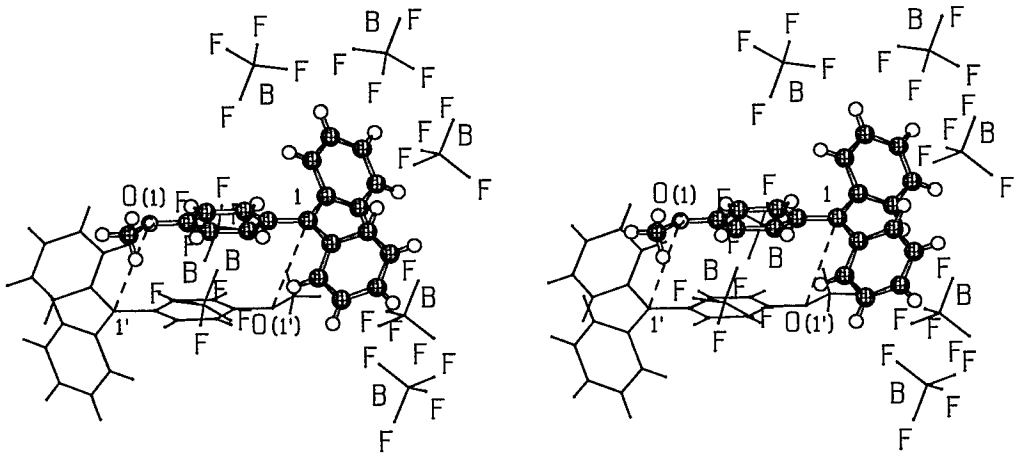


C(1)	- O(5^{I})	3.350	*diff* = 0.130	
C(5)	- O(5^{I})	3.209	*diff* = -0.011	
C(6)	- O(5^{I})	3.012	*diff* = -0.208	strong

VIGXUE

p-Methoxyphenyldiphenylcarbenium tetrafluoroborate
4-Methoxytritylium tetrafluoroborate
C20 H17 O1 1+,B1 F4 1-
C.Bleasdale,W.Clegg,S.B.Ellwood,B.T.Golding
Acta Cryst.,C (Cr.Str.Comm.), 47, 550,1991

VIGXUE P21/n Z= 4 NATOMS= 43 DIFF AS=1 R-FACTOR= 0.063
17 C-H BONDS: S.D.= 0.001; MEAN = 0.960; RANGE: 0.959 - 0.960

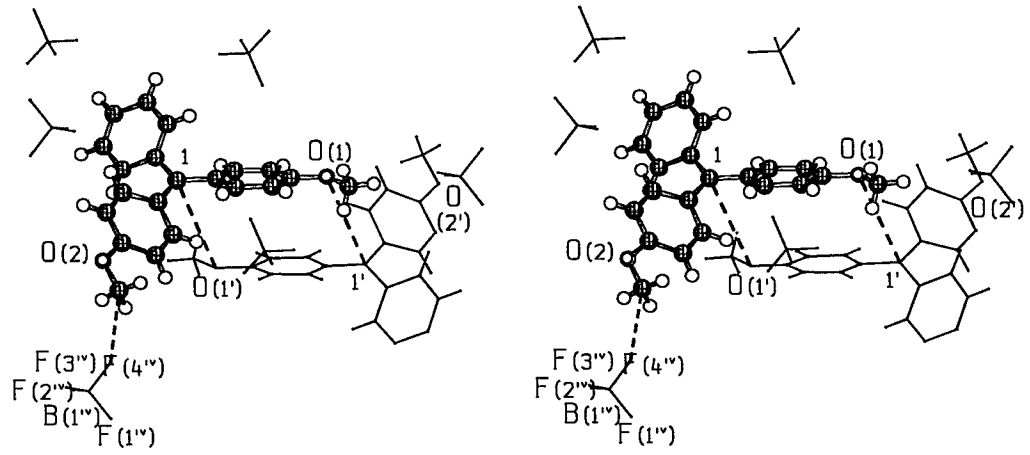


C(1)	- O(1^{I})	3.714	*diff* =	0.494	weak
O(1)	- C(1^{I})	3.714	*diff* =	0.494	weak

VIGYAL

bis(p-Methoxyphenyl)phenylcarbenium tetrafluoroborate
bis(4-Methoxy)tritylium tetrafluoroborate
C21 H19 O2 1+,B1 F4 1-
C.Bleasdale,W.Clegg,S.B.Ellwood,B.T.Golding
Acta Cryst.,C (Cr.Str.Comm.), 47, 550,1991

VIGYAL P21/n Z= 4 NATOMS= 47 DIFF AS=3 R-FACTOR= 0.106
19 C-H BONDS: S.D.= 0.001; MEAN = 0.960; RANGE: 0.959 - 0.961



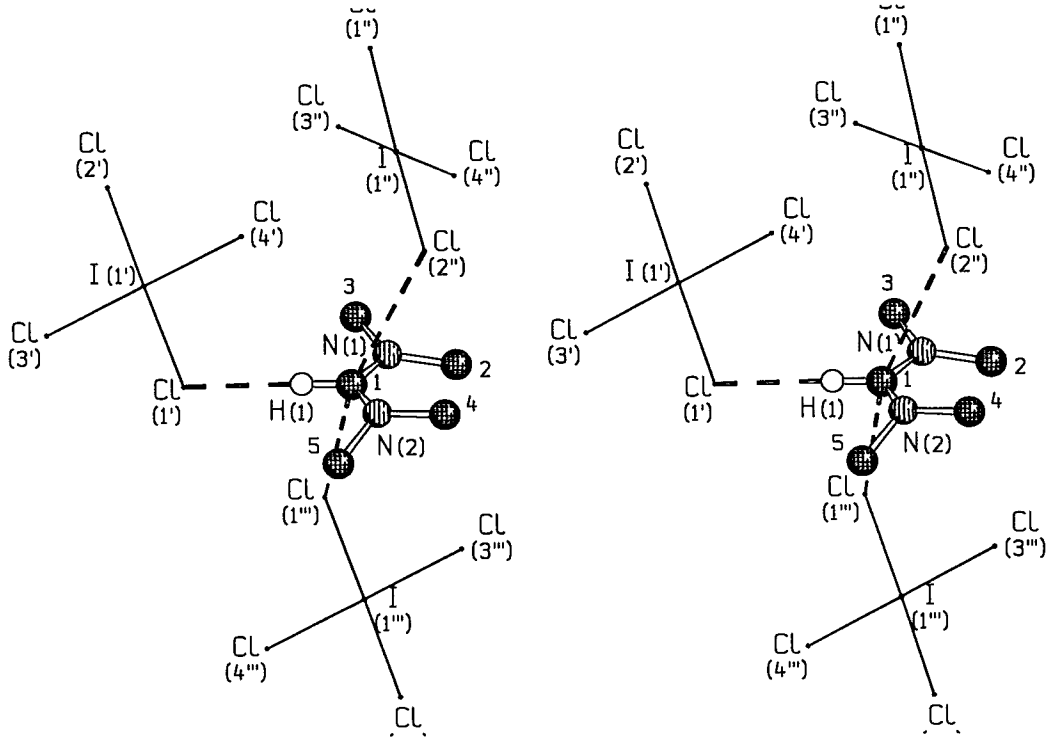
C(21)	- F(4^{IV})	3.130	*diff* =	-0.040	
C(1)	- O(1^{I})	3.807	*diff* =	0.587	very weak
O(1)	- C(1^{I})	3.807	*diff* =	0.587	very weak

VIMPOW

N,N-Dimethylformamidinium iodine-tetrachloride
C5 H13 N2 1+,Cl4 I1 1-
A.I.Gubin,A.I.Ill'in,E.G.Pugina,V.P.Kostinyuk,M.Zh.Buranbaev
Kristallografiya, 35, 501,1990

VIMPOW P21/c Z= 4 NATOMS= 12 DIFF AS=0 R-FACTOR= 0.117

H(1) was added in the present paper.

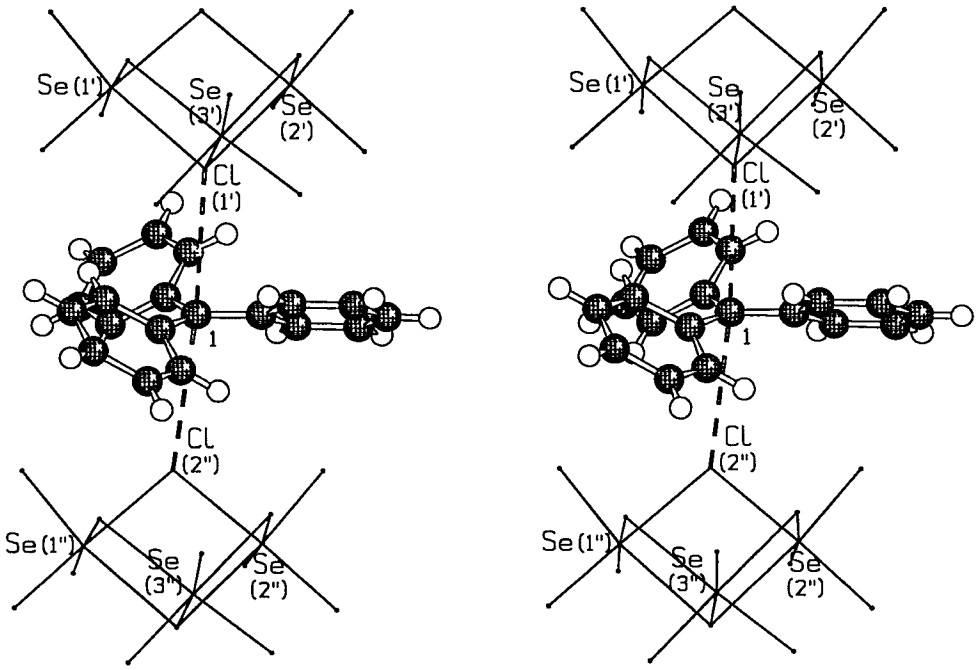


C(1)	- $Cl(1^{III})$	3.422	*diff* = -0.028	
C(1)	- $Cl(2^{II})$	3.856	*diff* = 0.406	weak
$Cl(1^{I})$	- H(1)	2.522	*diff* = -0.428	(H bond)

VIRDAB

Triphenylcarbonium (μ_3-chloro)-tris(μ_2-chloro)-nonachloro-tri-selenium
at 140 deg.K
C19 H15 1+,Cl13 Se3 1-
F.-P.Ahlers,E.Luhrs,B.Krebs
Z.Anorg.Allg.Chem., 594, 7,1991

VIRDAB P-1 Z= 2 NATOMS= 50 DIFF AS=2 R-FACTOR= 0.030
REMARK CSD 54775 has been used
15 C-H BONDS: S.D.= 0.001; MEAN = 0.960; RANGE: 0.959 - 0.960

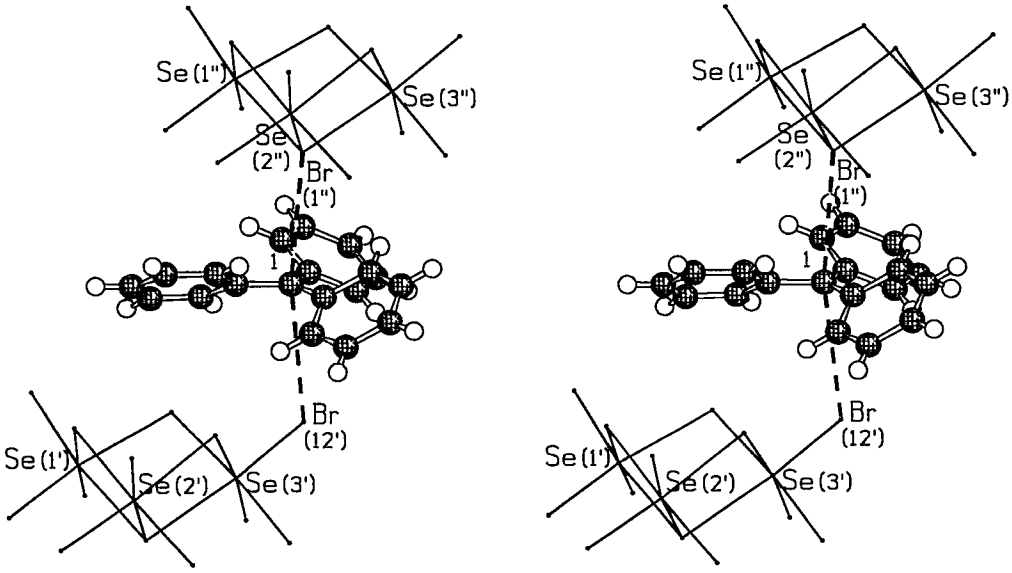


C(1)	- Cl(1^{I})	3.476	*diff* =	0.026	
C(1)	- Cl(2^{II})	3.635	*diff* =	0.185	

VIRDEF

Triphenylcarbonium (μ_3-bromo)-tris(μ_2-bromo)-nonabromo-tri-selenium
at 140 deg.K
C19 H15 1+,Br13 Se3 1-
F.-P.Ahlers,E.Luhrs,B.Krebs
Z.Anorg.Allg.Chem., 594, 7,1991

VIRDEF P21/c Z= 4 NATOMS= 50 DIFF AS=4 R-FACTOR= 0.058
REMARK CSD 54775 has been used
15 C-H BONDS: S.D.= 0.001; MEAN = 0.960; RANGE: 0.958 - 0.961

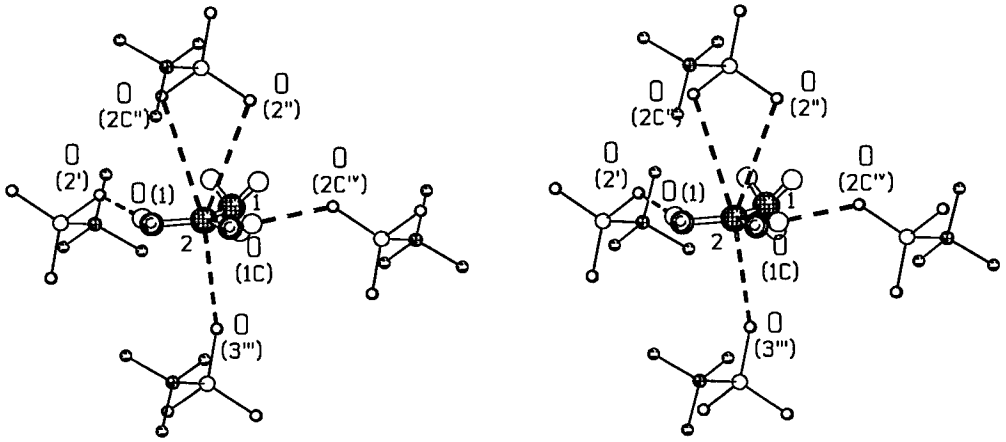


C(1)	- Br(12^{I})	3.987	*diff* =	0.437	weak
C(1)	- Br(1^{II})	3.583	*diff* =	0.033	

VOJGAC

Acetacidinium trifluoromethanesulfonate
at -130 deg.C
C2 H5 O2 1+,C1 F3 O3 S1 1-
K.Bartmann,D.Mootz
Z.Anorg.Allg.Chem., 601, 31,1991

VOJGAC P21/m Z= 2 NATOMS= 17 DIFF AS=0 R-FACTOR= 0.048
3 C-H BONDS: S.D.= 0.075; MEAN = 0.880; RANGE: 0.773 - 0.933



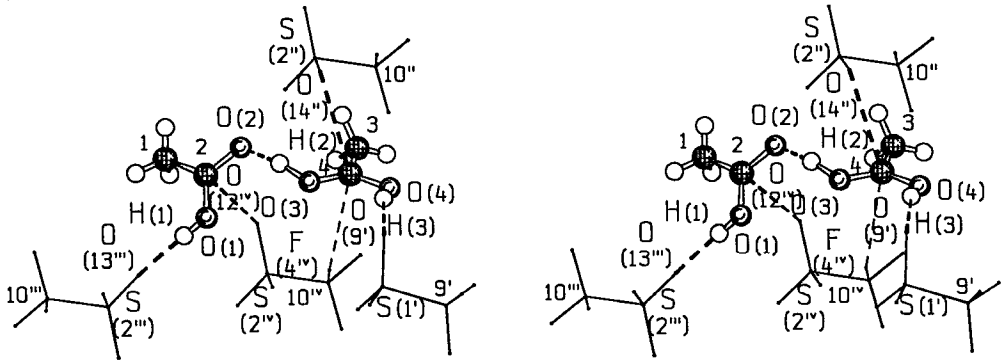
C(2)	- O(3^{III})	2.854	*diff* = -0.366	**very strong**
H(3)	- O(2^{I})	2.020	*diff* = -0.700	(H bond)
H(3C)	- O(2C^{IV})	2.020	*diff* = -0.700	(H bond)
C(2)	- O(2^{II})	3.258	*diff* = 0.038	
C(2)	- O(2C^{II})	3.258	*diff* = 0.038	

VOJGEG

Acetacidinium acetic acid trifluoromethanesulfonate
at -130 deg.C
C2 H5 O2 1+,C2 H4 O2,C1 F3 O3 S1 1-
K.Bartmann,D.Mootz
Z.Anorg.Allg.Chem., 601, 31,1991

VOJGEG P-1 Z= 4 NATOMS= 50 DIFF AS=1 R-FACTOR= 0.047
12 C-H BONDS: S.D.= 0.056; MEAN = 0.956; RANGE: 0.894 - 1.073

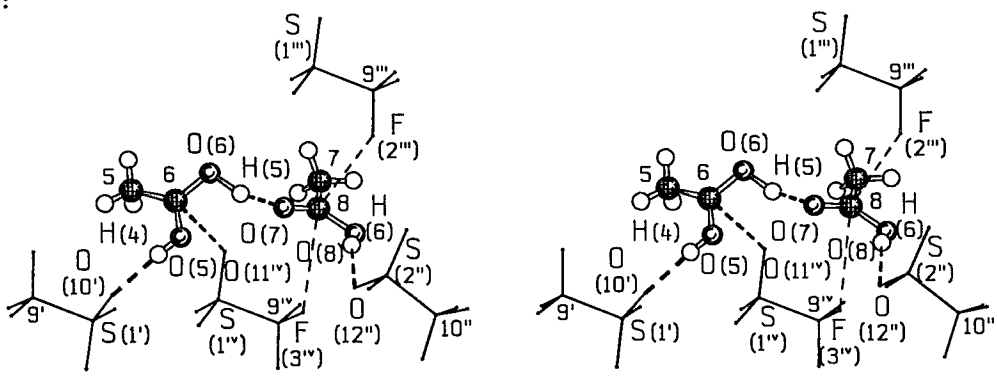
cation #1:



O(2)	- H(2)	1.418	*diff* = -1.302	(H bond)
H(3)	- O(9^{I})	1.941	*diff* = -0.779	(H bond)
H(1)	- O(13^{III})	1.764	*diff* = -0.956	(H bond)

C(4)	- O(14^{II})	3.105	*diff* = -0.115	strong
C(4)	- F(4^{IV})	3.129	*diff* = -0.041	
C(2)	- O(12^{IV})	2.982	*diff* = -0.238	strong

cation #2:

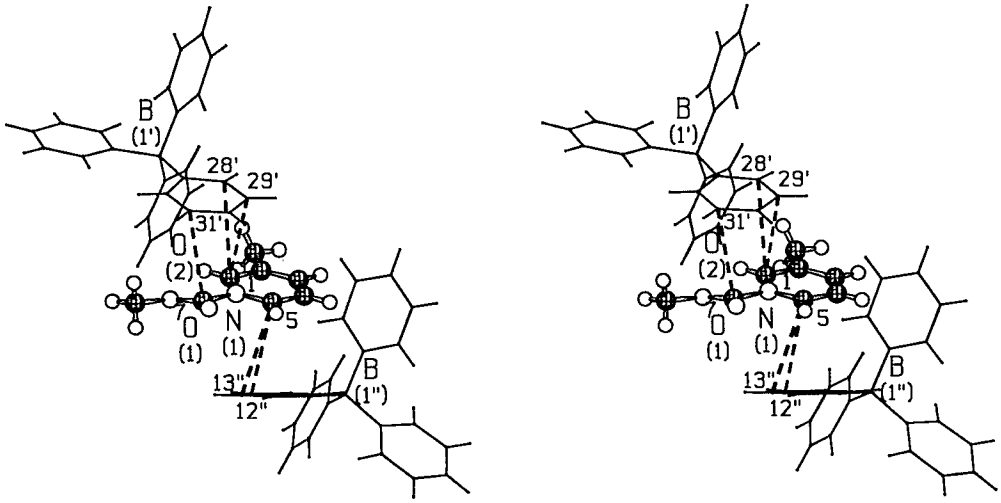


O(7)	- H(5)	1.348	*diff* = -1.372	(H bond)
H(4)	- O(10^{I})	1.760	*diff* = -0.960	(H bond)
H(6)	- O(12^{II})	2.054	*diff* = -0.666	(H bond)
C(8)	- F(2^{III})	3.089	*diff* = -0.081	
C(8)	- F(3^{IV})	3.358	*diff* = 0.188	
C(6)	- O(11^{IV})	2.913	*diff* = -0.307	**very strong**

WABZEE

N-Methoxycarbonyl-3-methylpyridinium tetraphenylborate
at 173 deg.K, polymorph I
C24 H20 B1 1-,C8 H10 N1 O2 1+
G.L.Bryant Junior,J.A.King Junior
Acta Cryst.,C (Cr.Str.Comm.), 49, 551,1993

WABZEE P21/n Z= 4 NATOMS= 66 DIFF AS=1 R-FACTOR= 0.052
REMARK CIF entry ST1001
30 C-H BONDS: S.D.= 0.000; MEAN = 0.960; RANGE: 0.958 - 0.960

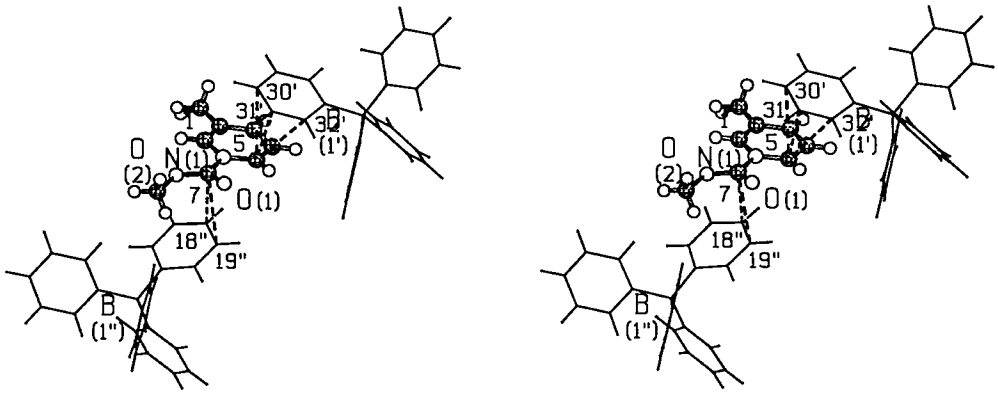


C(7)	- C(31^{I})	3.295	*diff* = -0.105	strong
C(1)	- C(28^{I})	3.418	*diff* = 0.018	
C(1)	- C(29^{I})	3.327	*diff* = -0.073	
C(5)	- C(12^{II})	3.446	*diff* = 0.046	
C(5)	- C(13^{II})	3.419	*diff* = 0.019	

WABZEE01

N-Methoxycarbonyl-3-methylpyridinium tetraphenylborate
at 213 deg.K, polymorph II
C24 H20 B1 1-,C8 H10 N1 O2 1+
G.L.Bryant Junior,J.A.King Junior
Acta Cryst.,C (Cr.Str.Comm.), 49, 551,1993

WABZEE01 P21/n Z= 4 NATOMS= 66 DIFF AS=2 R-FACTOR= 0.055
REMARK CIF entry ST1001
30 C-H BONDS: S.D.= 0.034; MEAN = 0.966; RANGE: 0.959 - 1.148

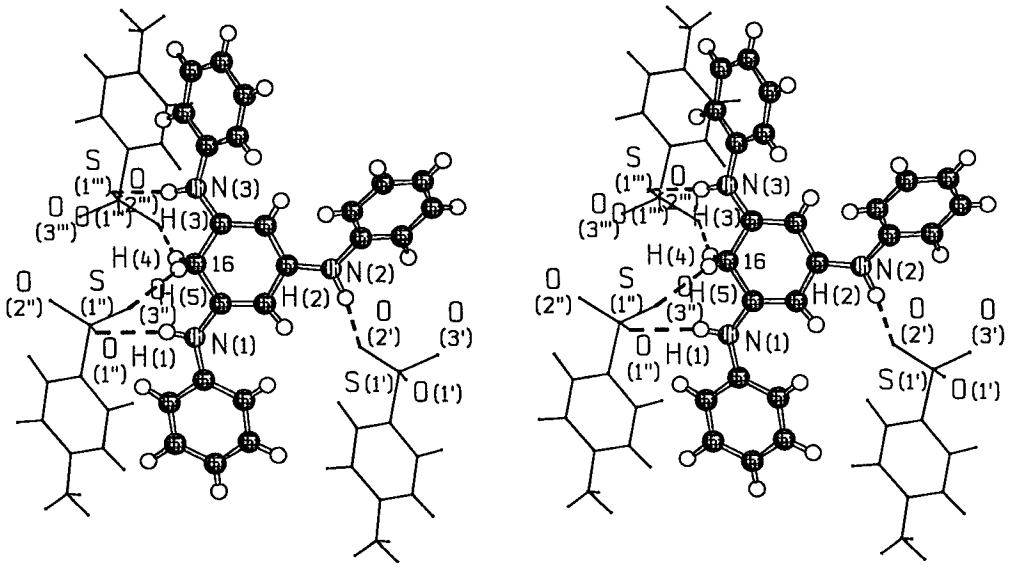


C(7)	- $C(18^{II})$	3.397	*diff* = -0.003	
C(7)	- $C(19^{II})$	3.416	*diff* = 0.016	
C(5)	- $C(30^{I})$	3.369	*diff* = -0.031	
C(5)	- $C(31^{I})$	3.122	*diff* = -0.278	strong
C(5)	- $C(32^{I})$	3.337	*diff* = -0.063	

WAZYOL

N,N',N''-Triphenyl-2,4,6-triamino-1H-benzenium p-toluenesulfonate
C24 H22 N3 1+,C7 H7 O3 S1 1-
D.T.Glatzhofer,M.A.Khan
Acta Cryst.,C (Cr.Str.Comm.), 49, 2128,1993

WAZYOL P21/n Z= 4 NATOMS= 67 DIFF AS=2 R-FACTOR= 0.036
REMARK CIF entry BR1033
26 C-H BONDS: S.D.= 0.043; MEAN = 0.952; RANGE: 0.873 - 1.070

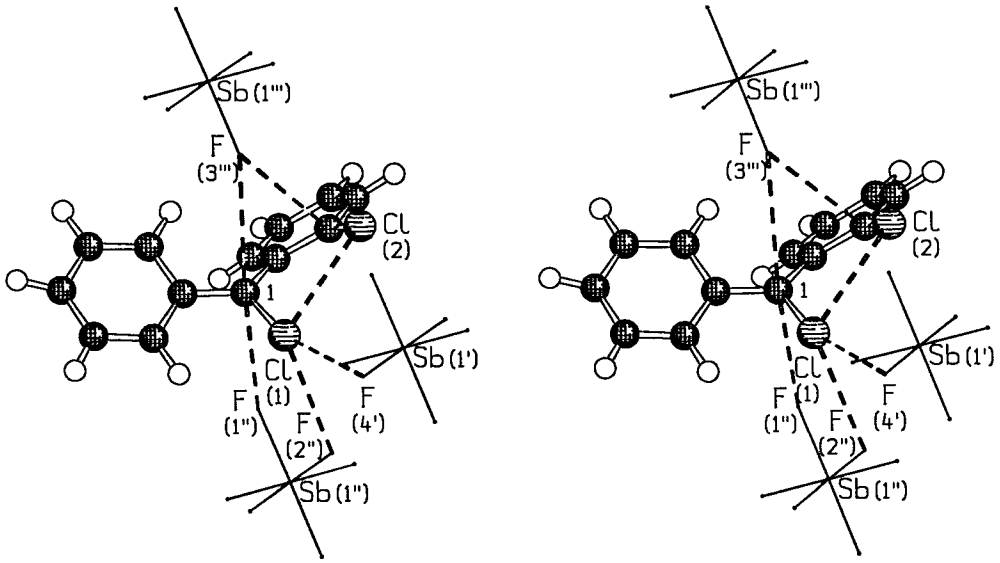


H(1)	- $O(1^{II})$	2.183	*diff* = -0.537	(H bond)
$O(2^{I})$	- H(2)	1.824	*diff* = -0.896	(H bond)
H(3)	- $O(1^{III})$	2.071	*diff* = -0.649	(H bond)
H(4)	- $O(2^{III})$	2.437	*diff* = -0.283	(H bond)
H(5)	- $O(3^{II})$	2.341	*diff* = -0.379	(H bond)

YAMWOY

Chloro-(2-chlorophenyl)-phenylcarbenium hexafluoroantimony(v)
at -80deg.C
C13 H9 Cl2 1+,F6 Sb1 1-
T.Laube,E.Bannwart,S.Hollenstein
J.Am.Chem.Soc., 115, 1731,1993

YAMWOY P-1 Z= 2 NATOMS= 31 DIFF AS=3 R-FACTOR= 0.062
9 C-H BONDS: S.D.= 0.100; MEAN = 1.015; RANGE: 0.784 - 1.082

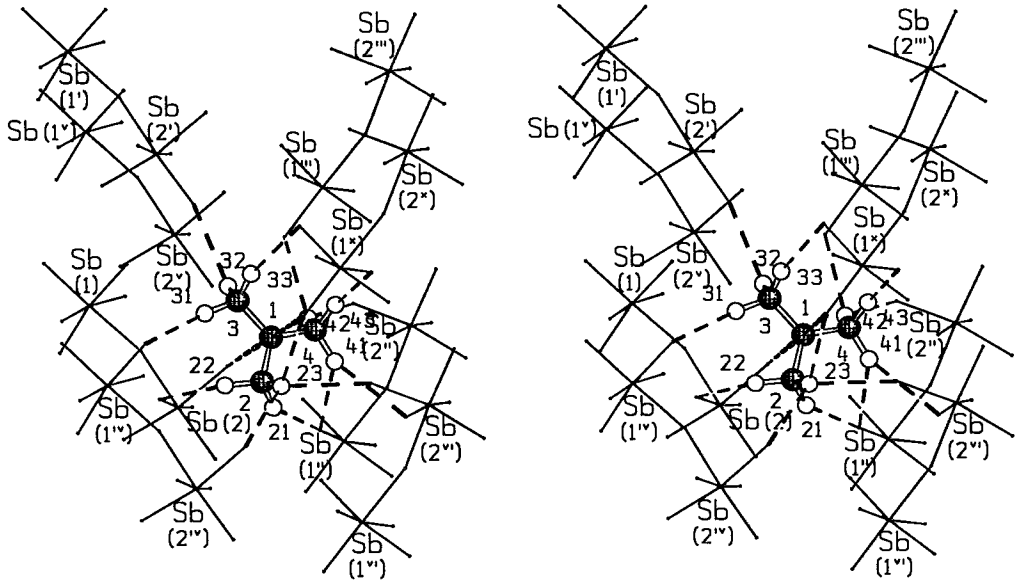


C(1)	- $F(1^{II})$	3.228	*diff* = 0.058	
C(1)	- $F(3^{III})$	3.455	*diff* = 0.285	
Cl(1)	- Cl(2)	3.081	*diff* = -0.419	**very strong**
Cl(1)	- $F(4^{I})$	2.782	*diff* = -0.438	**very strong**
Cl(1)	- $F(2^{II})$	3.097	*diff* = -0.123	strong

C(3)	- $F(3^{III})$	3.349	*diff* = 0.179

PESGID

tert-Butyl (μ_2-fluoro)-bis(pentafluoro-antimony)
at -80 deg. C
C4 H9 1+,F11 Sb2 1-
S.Hollenstein,T.Laube
J.Am.Chem.Soc., 115, 7240,1993
Only one set of the disordered methyl hydrogens is used at C(2) and C(3).

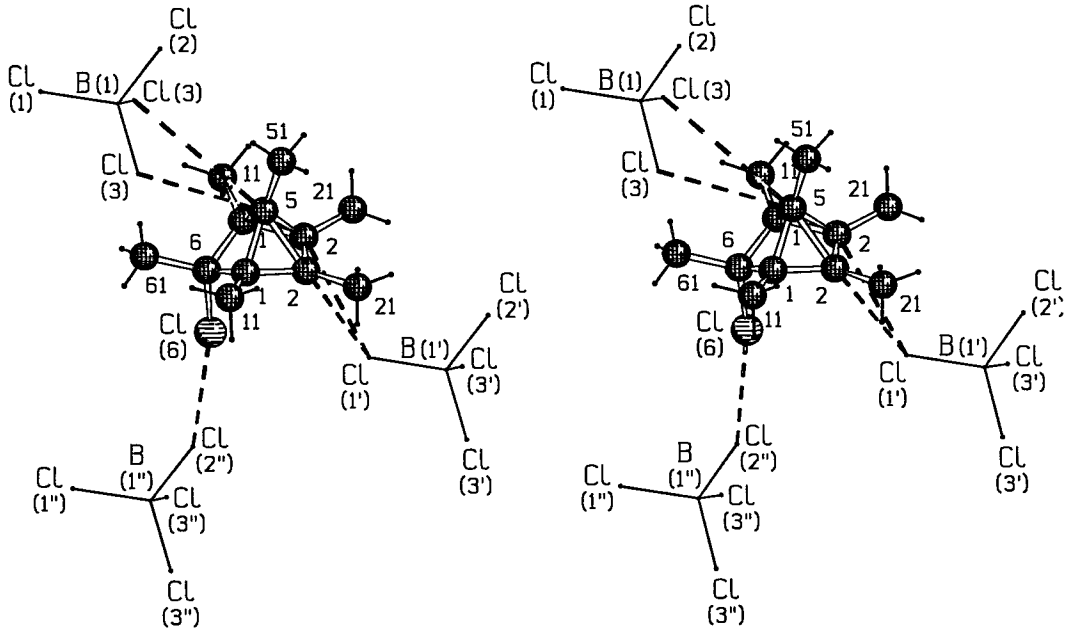


F(23)	- C(1)	2.928	*diff* = -0.242 strong
C(1)	- $F(11^{X})$	3.113	*diff* = -0.057
H(21)	- $F(12^{II})$	2.592	*diff* = -0.078 (H bond)
F(24)	- H(22)	2.604	*diff* = -0.066 (H bond)
H(23)	- $F(23^{IV})$	2.622	*diff* = -0.048 (H bond)
H(23)	- $F(25^{VI})$	2.617	*diff* = -0.053 (H bond)
H(23)	- $F(11^{X})$	2.562	*diff* = -0.108 (H bond)
H(31)	- $F(15^{IV})$	2.355	*diff* = -0.315 (H bond)
H(32)	- $F(21^{I})$	2.543	*diff* = -0.127 (H bond)
H(33)	- $F(13^{X})$	2.627	*diff* = -0.043 (H bond)
H(41)	- $F(12^{II})$	2.575	*diff* = -0.095 (H bond)
H(41)	- $F(24^{VI})$	2.661	*diff* = -0.009 (H bond)
H(42)	- $F(25^{II})$	2.399	*diff* = -0.271 (H bond)
H(42)	- $F(11^{III})$	2.652	*diff* = -0.018 (H bond)
H(43)	- $F(14^{X})$	2.287	*diff* = -0.383 (H bond)

PONHOP

(*deloc*-2,3,5)-6-*endo*-Chloro-1,2,3,4,5,6-*exo*-hexamethylbicyclo[2.1.1]hex-2-en-5-yl tetrachloroborate
at -165deg.C
C12 H18 Cl1 1+,B1 Cl4 1-
T.Laube,C.Lohse
J.Am.Chem.Soc., 116, 9001,1994

The cation and the anion lie on a crystallographic mirror plane. For a chemical numbering see the original publication.

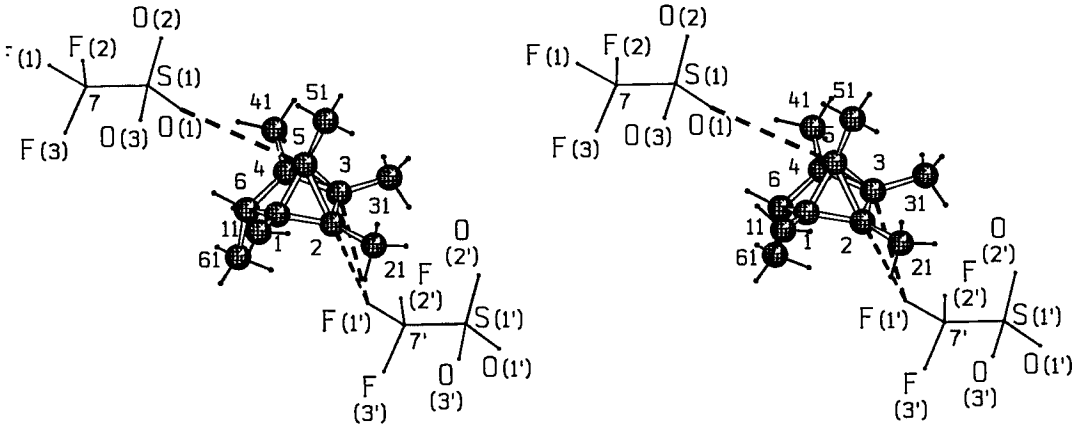


Cl(3)	- C(5)	3.992	*diff* = 0.542	very weak	(2x)
C(2)	- Cl(1^{I})	3.451	*diff* = 0.001		(2x)
Cl(6)	- Cl(2^{II})	3.353	*diff* = -0.147	strong	

PONHUV

(*deloc*-2,3,5)-1,2,3,4,5,6-*endo*-Hexamethylbicyclo[2.1.1]hex-2-en-5-yl trifluoromethanesulfonate
at -78deg.C
C12 H19 1+,C1 F3 O3 S1 1-
T.Laube,C.Lohse
J.Am.Chem.Soc., 116, 9001,1994

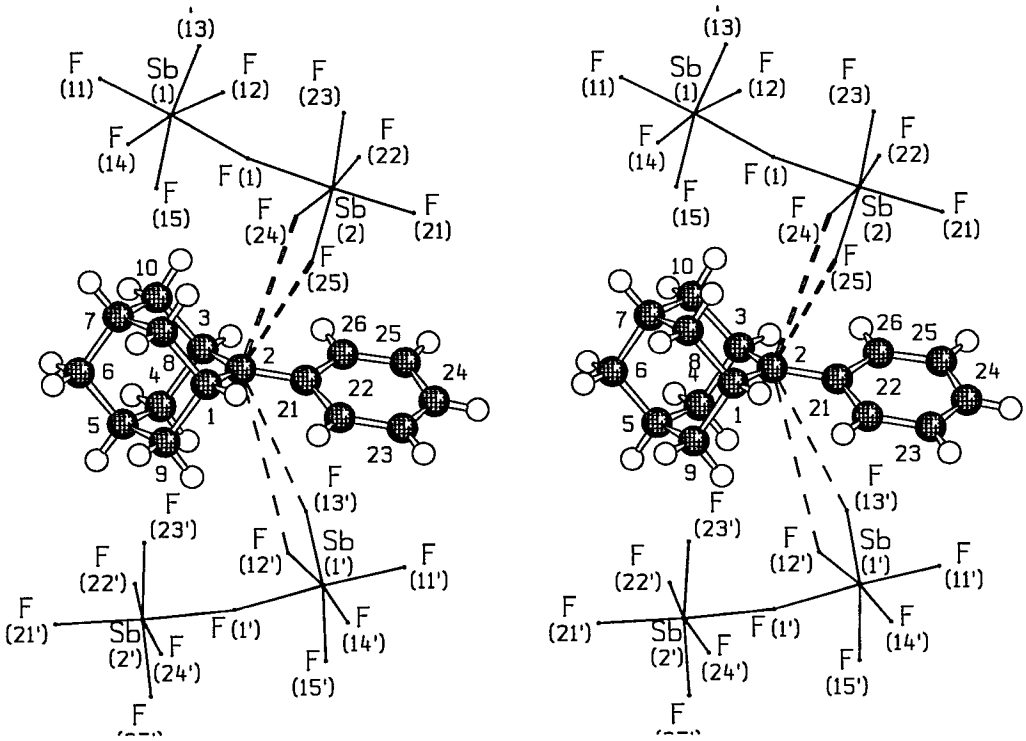
Only the major orientations of the disordered methyl groups and of the triflate anion are used.



O(1)	- C(5)	3.500	*diff* = 0.280	
C(2)	- F(1^{I})	3.136	*diff* = -0.034	
C(3)	- F(1^{I})	3.147	*diff* = -0.023	

SUNMOD

2-Phenyl-2-adamantyl (μ_2-fluoro)-bis(pentafluoro-antimony)
at 183 K
C16 H19 1+,F11 Sb2 1-
S.Hollenstein,T.Laube
Helv.Chim.Acta, 77, 1773,1994

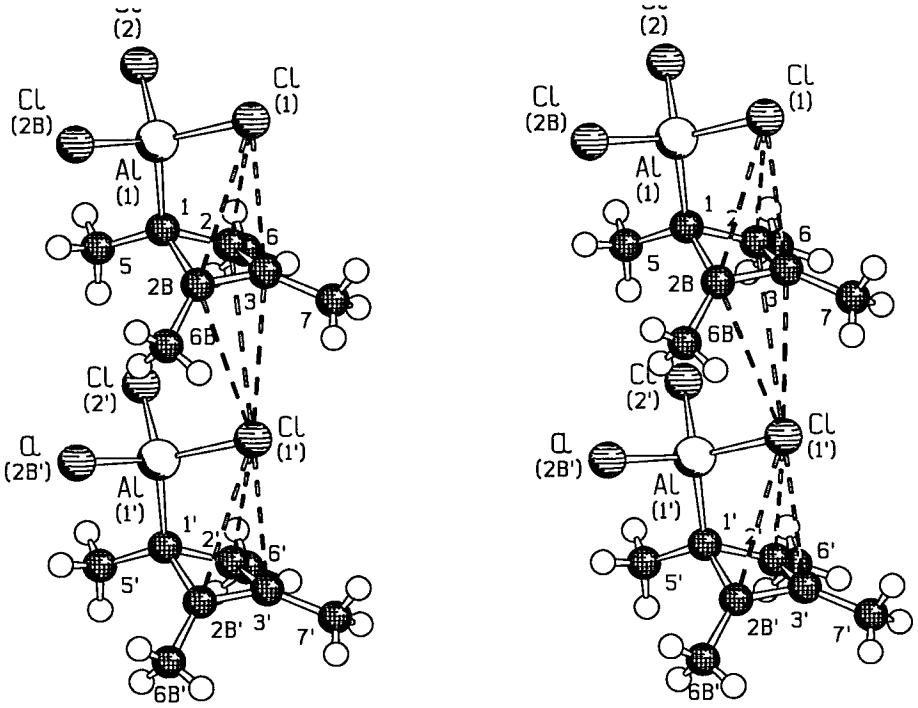


F(24)	- C(2)	3.596	*diff* =	0.426	weak
F(25)	- C(2)	3.369	*diff* =	0.199	
F(12^{I})	- C(2)	4.150	*diff* =	0.980	very weak
F(13^{I})	- C(2)	4.106	*diff* =	0.936	very weak

CBUALC

1,2,3,4-Tetramethyl-1-trichloroaluminium-cyclobutadiene
C8 H12 Al1 Cl3
C.Kruger,P.J.Roberts,Y.-H.Tsay,J.B.Koster
J.Organomet.Chem., 78, 69,1974

CBUALC Pnma Z= 4 NATOMS= 24 DIFF AS=2 R-FACTOR= 0.054
12 C-H BONDS: S.D.= 0.046; MEAN = 0.895; RANGE: 0.841 - 1.007



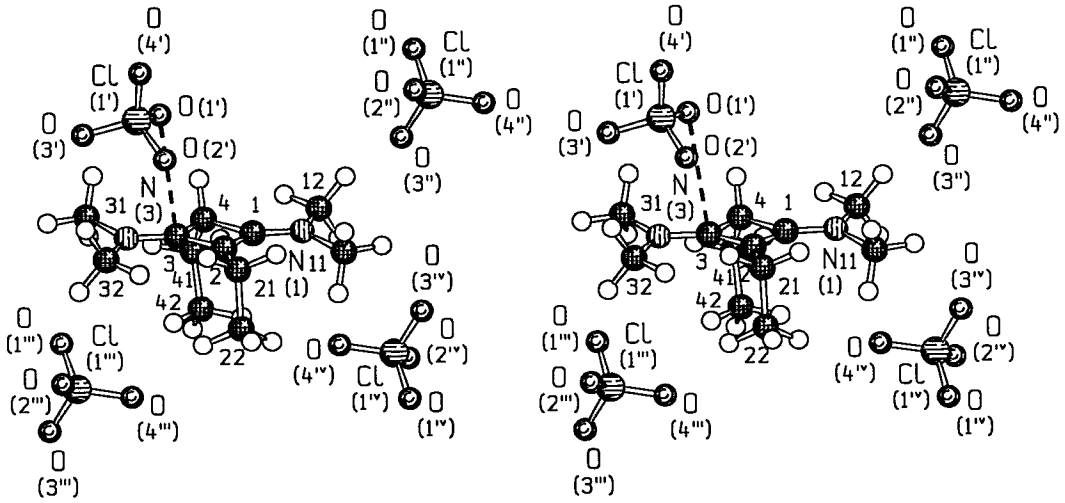
Cl(1)	- C(2)	3.622	*diff* = 0.172	
Cl(1)	- C(2B)	3.622	*diff* = 0.172	
Cl(1)	- C(3)	3.396	*diff* = -0.054	
C(2)	- Cl(1^{I})	3.981	*diff* = 0.531	very weak
C(2B)	- Cl(1^{I})	3.981	*diff* = 0.531	very weak
C(3)	- Cl(1^{I})	3.848	*diff* = 0.398	weak
Cl(1^{I})	- C(2^{I})	3.622	*diff* = 0.172	
Cl(1^{I})	- C($2B^{I}$)	3.622	*diff* = 0.172	
Cl(1^{I})	- C(3^{I})	3.395	*diff* = -0.055	

MAECBA

N,N-Dimethyl-3-dimethylamino-2,4-diethyl-cyclobutylideneimmonium perchlorate
C12 H23 N2 1+,C11 O4 1-
F.Chentli-Benchikha,J.P.Declercq,G.Germain,M.van
Meerssche,T.Debaerdemaeker,O.Dideberg,A.Michel,J.P.Putzeys
Acta Crystallogr.,Sect.B, 33, 3428,1977

MAECBA P21/c Z= 4 NATOMS= 19 DIFF AS=2 R-FACTOR= 0.082
ERROR ATOM LABELS N1,C11,C12 IN TAB 5 SHOULD BE INTER- CHANGED WITH
N3,C31,C32 RESPECTIVELY.ALSO INTERCHANGE C11 AND C12 IN TABLE 11- (I)-3

All H atoms were computed in the present paper.

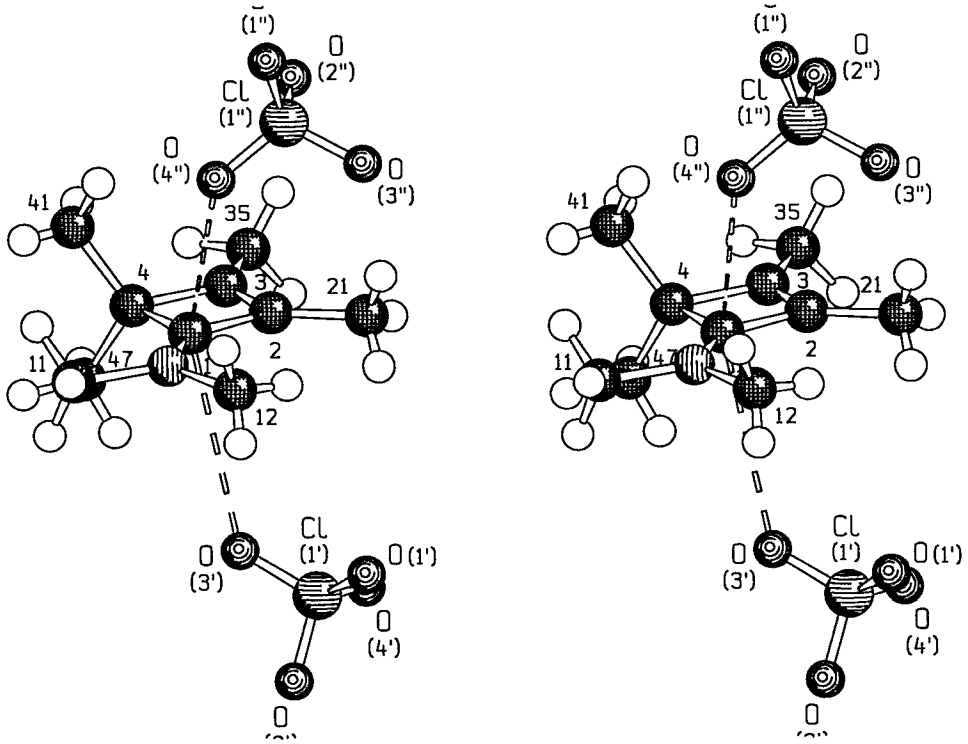


C(3) - O(1^{I}) 3.396 | *diff* = 0.176

MTMCBA

N,N-Dimethyl-2,3,4,4-tetramethyl-cyclobutenylideneammonium perchlorate
C10 H18 N1 1+,Cl1 O4 1-
F.Chentli-Benchikha,J.P.Declercq,G.Germain,M.van
Meerssche,T.Debaerdemaeker,O.Dideberg,A.Michel,J.P.Putzeys
Acta Crystallogr.,Sect.B, 33, 3428,1977

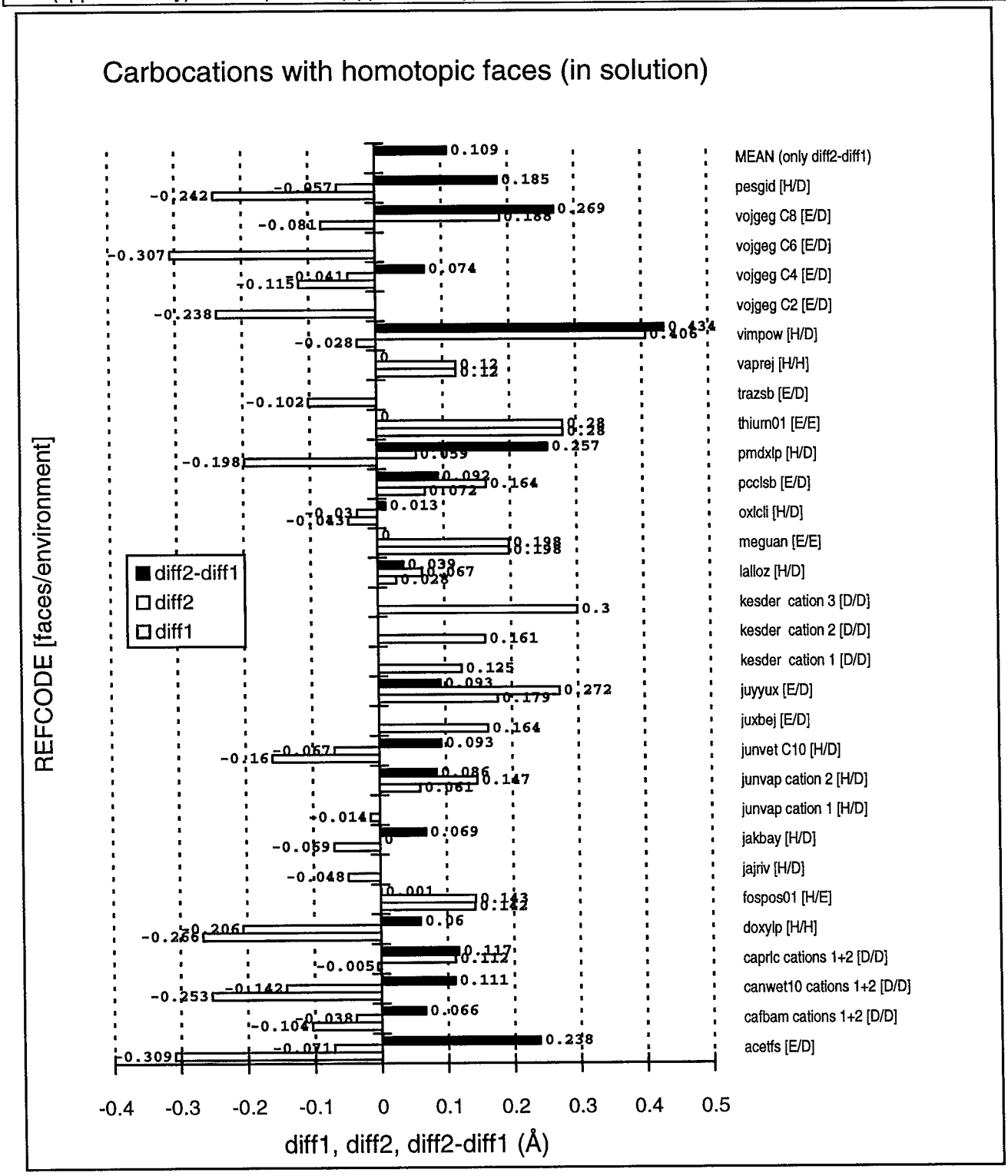
MTMCBA P212121 Z= 4 NATOMS= 34 DIFF AS=2 R-FACTOR= 0.060
18 C-H BONDS: S.D.= 0.112; MEAN = 0.954; RANGE: 0.719 - 1.070



C(1) - O(3^{I}) 3.429 | *diff* = 0.209
C(1) - O(4^{II}) 3.224 | *diff* = 0.004

Figure S1. Interactions of homotopic faces of cationic Csp^2 atoms of carbocations with counterions. Two possibilities exist: (a) the cations have homotopic faces (ignoring their environment in the crystal) and show interactions in most cases on both faces, (b) there is more than one cation in the asymmetric unit (Z' > 1) and the equivalent faces of different cations are considered.

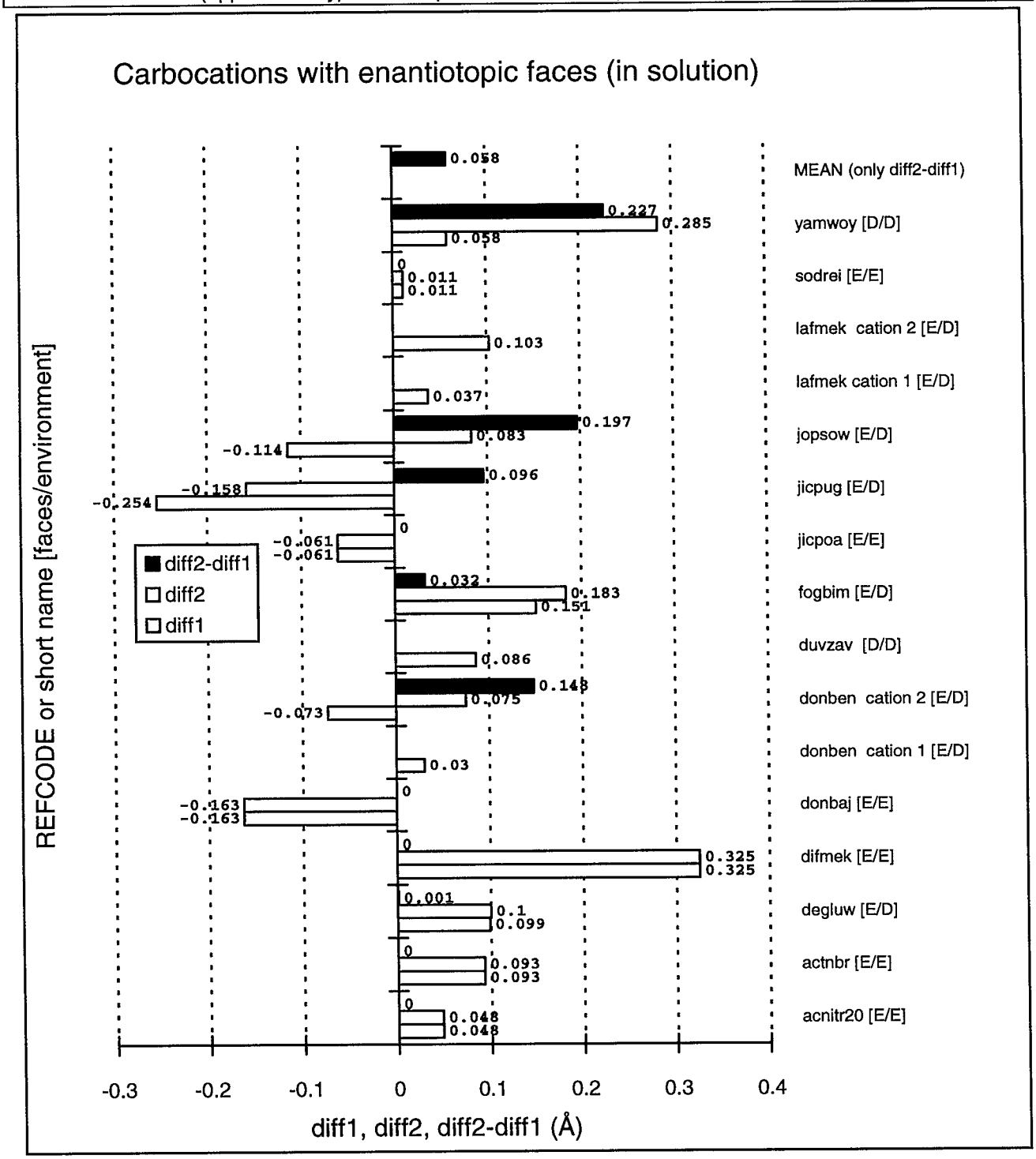
[*Faces* of the cation in the crystal / their *environment* in the crystal]:
H = (approximately) homotopic, E = (approximately) enantiotopic, D = diastereotopic or not symmetry-related.



MEAN of (*diff*2-*diff*1) = $\overline{|\Delta(diff)|}$ = 0.109 Å (n=21, esd of $\overline{|\Delta(diff)|}$ = 0.024 Å)

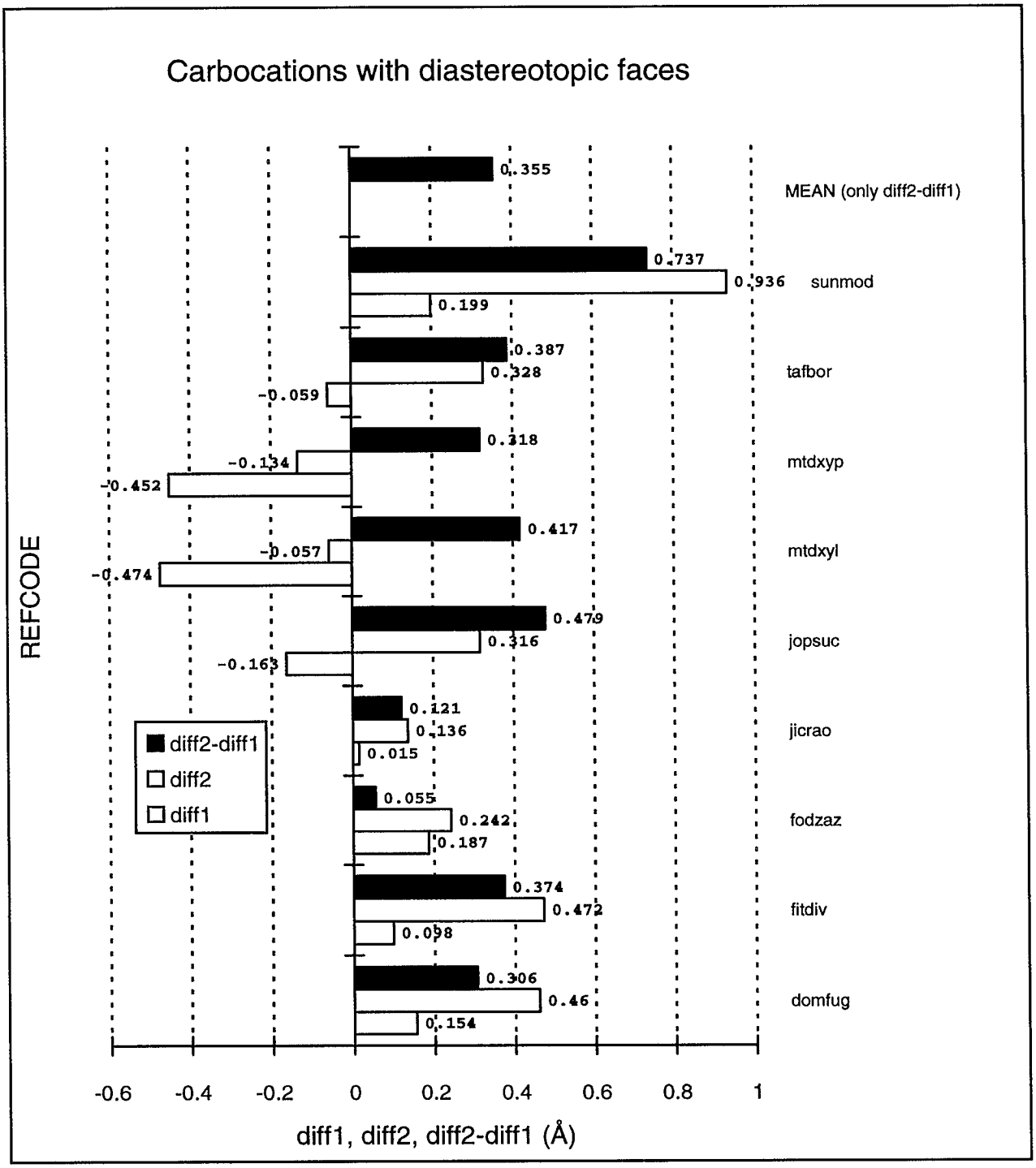
Figure S2. Interactions of enantiotopic faces of cationic Csp^2 atoms of carbocations with counterions. If the cationic C is situated on a crystallographic mirror plane, (*diff*2-*diff*1) is necessarily equal to zero.

[*Faces* of the cation in the crystal / their *environment* in the crystal]:
E = (approximately) enantiotopic, D = diastereotopic or not symmetry-related.



MEAN of (*diff*2-*diff*1) = $\overline{|\Delta(diff)|}$ = 0.058 Å (n=12 esd of $\overline{|\Delta(diff)|}$ = 0.025 Å)

Figure S3. Interactions of diastereotopic faces of cationic Csp^2 atoms of carbocations with counterions.



MEAN of (*diff*2-*diff*1) = $\overline{|\Delta(diff)|}$ = 0.355 Å (n=9; esd of $\overline{|\Delta(diff)|}$ = 0.066 Å)

without "sunmod": MEAN of (*diff*2-*diff*1) = $\overline{|\Delta(diff)|}$ = 0.307 Å (n=8; esd of $\overline{|\Delta(diff)|}$ = 0.052 Å)

Table S2. The angles in $C^{\delta+}$—$Hal^1\cdots Hal^2$—Z contacts observed in all structures with the $C^{\delta+}$—Hal^1 fragments: $C^{\delta+}$—$Hal^1\cdots Hal^2 = \alpha_1$, $Hal^1\cdots Hal^2$—$Z = \alpha_2$ (angles in degrees; the roman superscripts for the symmetry operations as given in the drawings were omitted):

acnitr20									
C1	-	CL1	...	CL2	176.45				
actnbr									
C1	-	BR1	...	BR2	176.98				
degluw									
C1	-	CL1	...	CL2	165.41				
dibcas									
C1	-	F1	...	F2	158.36				
F1	...	F2	-	C2	102.97				
C1	-	F1	...	F2	158.36				
F1	...	F2	-	C2	102.97				
fufrut									
C1	-	CL4	...	CL2B	169.11				
CL4	...	CL2B	-	PT1	122.22				
junvap									
C1	-	CL13	...	CL5	159.41				
CL13	...	CL5	-	SB1	98.60				
C1	-	CL14	...	CL5	170.32				
CL14	...	CL5	-	SB1	109.00				
C2	-	CL15	...	CL8	173.15				
CL15	...	CL8	-	SB2	103.27				
C2	-	CL16	...	CL2	148.19				
CL16	...	CL2	-	SB1	103.30				
lafmek									
C1	-	BR1	...	CL4	172.21				
BR1	...	CL4	-	SB1	108.17				
C1	-	CL1	...	CL4	162.56				
CL1	...	CL4	-	SB1	100.32				
C2	-	BR2	...	CL10	173.88				
BR2	...	CL10	-	SB2	103.90				
C2	-	CL2	...	CL6	147.28				
CL2	...	CL6	-	SB1	103.13				
yamwoy									
C1	-	CL1	...	F4	163.67				
CL1	...	F4	-	SB1	137.31				

Statistical evaluation (IMSL STAT/LIBRARY Version 1.1; confidence levels: 99.9 %):

$C^{\delta+}$—$Hal^1\cdots Hal^2 = \alpha_1$

Univariate Statistics from UVSTA

	1
Mean	165.5
Variance	91.8
Std. Dev.	9.6
Skewness	-0.7
Kurtosis	-0.6
Minimum	147.3
Maximum	177.0
Range	29.7
Coef. Var.	0.1
Count	14.0
Lower CLM	154.7
Upper CLM	176.3
Lower CLV	32.7
Upper CLV	517.8

$Hal^1\cdots Hal^2$—$Z = \alpha_2$

Univariate Statistics from UVSTA

	1
Mean	108.
Variance	132.
Std. Dev.	11.
Skewness	2.
Kurtosis	2.
Minimum	99.
Maximum	137.
Range	39.
Coef. Var.	0.
Count	11.
Lower CLM	93.
Upper CLM	124.
Lower CLV	42.
Upper CLV	1042.

Table S3. The angles $C^{\delta+}\cdots O—Z$ observed in all structures (angles in degrees; the roman superscripts for the symmetry operations as given in the drawings were omitted):

acetfs			
C1	- O2	- S1	108.48
C1	- O3	- S1	129.39
cafbam			
C1	- O4	- S1	109.06
C6	- O3	- S1	113.71
cafbeq			
C1	- O2	- S1	149.36
C1	- O4	- S1	123.59
C2	- O4	- S1	121.55
C3	- O2	- S1	125.59
C4	- O3	- S1	124.53
C5	- O6	- S2	111.94
canwet10			
C3	- O13	- S1	107.27
C4	- O22	- S2	114.44
doxylp			
C1	- O2	- CL1	117.31
C1	- O5	- CL1	112.86
C3	- O5	- CL1	100.28
C2	- O5	- CL1	110.60
fospos01			
C1	- O3	- N3	82.55
fuxcac			
C10	- O4	- S2	121.82
jakbay			
C8	- O1	- C1	121.37
C8	- O2	- C2	128.98
jalsoe			
C11	- O1	- S1	103.83
juxbej			
C1	- O1	- CL1	112.56
kazdeu			
C1	- O1	- S1	158.32
kesder cation 1			
C3	- O7	- S3	107.81
kesder cation 2			
C17	- O1	- S1	107.36
macprp10			
C2	- O2	- CL1	108.32
C3	- O2	- CL1	126.71
mallpc			
C11	- O3	- CL1	135.62
C9	- O2	- CL1	144.82
meguan			
C2	- O2	- N4	89.10
mtdxyp			
C8	- O4	- CL1	122.95
C8	- O3	- CL1	151.16
C2	- O2	- CL1	136.06
C3	- O2	- CL1	122.06
phprpc10			
C18	- O4	- CL1	116.58
C19	- O2	- CL1	111.81
C20	- O2	- CL1	102.22
C18	- O3	- CL1	94.49
C19	- O3	- CL1	101.12
C19	- O4	- CL1	100.21
C20	- O4	- CL1	105.63
pmdxlp			
C2	- O3	- CL1	120.09
C2	- O6	- CL1	118.76
C3	- O5	- CL1	127.39
C4	- O5	- CL1	115.12
tafbor			
C2	- O4	- S1	114.19
C2	- O2	- S1	146.54
thiurn01			
C1	- O1	- N3	83.41
C1	- O2	- N3	82.40
vekmon			
C6	- O5	- S2	138.03

C1	- O5	- S2	138.53
C5	- O5	- S2	174.76
vojgac			
C2	- O3	- S1	145.20
C2	- O2	- S1	100.61
C2	- O2C	- S1	100.61
vojgeg			
C4	- O14	- S2	122.17
C2	- O12	- S2	130.34
C6	- O11	- S1	123.15

ponhuv			
C5	- O1	- S1	142.37
maecba			
C3	- O1	- CL1	104.48
mtmcba			
C1	- O3	- CL1	132.79
C1	- O4	- CL1	130.44

Statistical evaluation (IMSL STAT/LIBRARY Version 1.1; confidence levels: 99.9 %):

Univariate Statistics from UVSTA

	1
Mean	119.1
Variance	338.3
Std. Dev.	18.4
Skewness	0.4
Kurtosis	0.4
Minimum	82.4
Maximum	174.8
Range	92.4
Coef. Var.	0.2
Count	62.0
Lower CLM	111.0
Upper CLM	127.2
Lower CLV	198.4
Upper CLV	665.7

Table S4. The angles $C^{\delta+}\cdots F—Z$ observed in all structures (angles in degrees; the roman superscripts for the symmetry operations as given in the drawings were omitted):

dibcas			
C1	- F5	- AS1	114.51
C1	- F5	- AS1	114.50
C1	- F5	- AS1	114.50
C1	- F5	- AS1	114.50
C2	- F4	- AS1	153.11
C2	- F4	- AS1	153.11
dijtof			
C1	- F2	- SB1	111.46
C2	- F2	- SB1	134.69
C3	- F2	- SB1	116.36
donbaj			
C1	- F1C	- SB1	134.20
C1	- F1C	- SB1	134.20
donben			
C11	- F9	- SB2	123.19
C12	- F2	- SB1	130.95
C12	- F6	- SB1	128.11
doprij			
C1	- F25	- SB2	165.47
fitdiv			
C1	- F6	- SB1	147.12
C2	- F6	- SB1	131.11
C2	- F7	- SB2	125.44
C2	- F8	- SB2	98.18
fodzaz			
C2	- F4	- B1	121.55
C2	- F2	- B1	144.92
jecdea			
C2	- F3	- SB1	122.51
C7	- F1	- SB1	128.65
jicpoa			
C1	- F1	- SB1	121.91
C1	- F1A	- SB1	121.91
jicpug			
C1	- F2	- SB1	123.12
C1	- F4	- SB1	125.81
jojxub			
C6	- F1	- B1	139.00
junvet			
C1	- F4	- C6	148.29
kesder cation 3			
C31	- F7	- C45	131.28
mocfsb10			
C2	- F1	- SB1	151.93
C2	- F2	- SB1	148.86
C2	- F4	- SB1	135.08
C2	- F4C	- SB1	135.08
mtdxyl			
C1	- F1	- B1	153.86
C1	- F2	- B1	125.68
C2	- F4	- B1	141.06
C3	- F4	- B1	120.65
vojgeg			
C4	- F4	- C10	133.51
C8	- F2	- C9	137.81
C8	- F3	- C9	128.51
yamwoy			
C1	- F1	- SB1	134.56
C1	- F3	- SB1	141.90
pesgid			
C1	- F11	- SB1	119.14
C1	- F23	- SB2	130.24
ponhuv			
C2	- F1	- C7	151.36
C3	- F1	- C7	137.15
sunmod			
C2	- F24	- SB2	108.88
C2	- F25	- SB2	117.43

Statistical evaluation (IMSL STAT/LIBRARY Version 1.1; confidence levels: 99.9 %):

Univariate Statistics from UVSTA

	1		
Mean	131.1	Range	67.3
Variance	193.9	Coef. Var.	0.1
Std. Dev.	13.9	Count	49.0
Skewness	0.2	Lower CLM	124.2
Kurtosis	-0.3	Upper CLM	138.1
Minimum	98.2	Lower CLV	107.1
Maximum	165.5	Upper CLV	421.7

Table S5. The angles $C^{\delta+}\cdots Cl—Z$ observed in all structures (angles in degrees; the roman superscripts for the symmetry operations as given in the drawings were omitted):

acclsb20			
C1	- CL3	- SB1	104.25
C1	- CL3B	- SB1	104.25
C1	- CL3D	- SB1	104.25
C1	- CL3F	- SB1	104.25
combip			
C3	- CL1	- AL1	117.51
C4	- CL1	- AL1	96.57
C5	- CL3	- AL1	106.33
C6	- CL3	- AL1	127.34
difmek			
C1	- CL2	- AL1	106.96
C1	- CL2	- AL1	106.96
C14	- CL3	- AL1	111.48
C14A	- CL3	- AL1	111.48
domfug			
C2	- CL1	- SB1	126.77
C2	- CL4	- SB1	116.80
dozsoa			
C1	- CL1	- SB1	116.56
dpmbsb10			
C19	- CL5	- SB1	126.43
C36	- CL11	- SB2	120.27
etocga			
anion 1			
C1	- CL1	- GA1	92.66
C1	- CL4	- GA1	96.03
anion 2			
C1	- CL1	- GA1	88.65
C1	- CL2	- GA1	96.23
anion 3			
C1	- CL2	- GA1	98.57
C1	- CL4	- GA1	87.18
fufrut			
C1	- CL1	- PT1	136.10
C1	- CL4	- C1	87.46
fufsaa			
C1	- CL3E	- PT1	131.80
hebzca			
C7	- CL3	- AL1	126.75
C8	- CL3	- AL1	107.57
C7	- CL2	- AL1	112.87
C8	- CL2	- AL1	135.81
ibusbc20			
anion 1			
C1	- CL2	- SB1	104.51
C1	- CL2B	- SB1	104.51
anion 2			
C1	- CL1	- SB1	105.95
C1	- CL4	- SB1	93.57
anion 3			
C1	- CL1B	- SB1	105.95
C1	- CL4	- SB1	93.57
jajriv			
C1	- CL1	- MO1	114.29
jicrao			
C1	- CL1	- SB1	127.00
C1	- CL4	- SB1	114.09
jopsem			
C5	- CL4	- SB2	130.52
C5	- CL2	- SB1	99.14
C5	- CL3	- SB1	103.46
jopsow			
C5	- CL6	- SB2	117.07
C5	- CL1	- SB1	117.93
jopsuc			
C5	- CL4	- SB1	138.47
C5	- CL5	- SB1	138.26
junvap			
C1	- CL7	- SB2	117.35
C2	- CL6	- SB1	115.63
C2	- CL5	- SB1	105.26
junvet			
C10	- CL3	- SB1	116.59
C10	- CL5	- SB1	117.65
juyyux			
C1	- CL2	- SB1	129.16
C1	- CL3	- SB1	106.47
kohvos			
C1	- CL1	- AU1	100.13
kowgos			
C1	- CL1	- NB1	98.73
C1	- CL1D	- NB1	102.06
C1	- CL2	- NB2	107.87
kowguy			
C1	- CL1	- TA1	98.71
C1	- CL1D	- TA1	101.99
C1	- CL2	- TA2	107.88
lafmek			
C1	- CL9	- SB2	117.95
C2	- CL3	- SB1	117.34
lalloz			
C1	- CL1	- NB1	109.71
C1	- CL4E	- NB2	113.58

mpocsb
anion 1
C1 - CL1 - SB1 104.34
C1 - CL5 - SB1 95.18
anion 2
C1 - CL1 - SB1 100.80
C1 - CL2 - SB1 104.21
anion 3
C1 - CL3 - SB1 94.85
C1 - CL6 - SB1 108.26

oxlcli
C1 - CL1 - I1 97.63
C1 - CL2 - I1 178.86

pcbtec10
C1 - CL10 - TE3 120.41

pcclsb
C1 - CL5 - SB1 133.56
C1 - CL3 - SB1 132.07

saxcav
C2 - CL1 - AL1 115.48
C2 - CL2 - AL1 137.43
C3 - CL2 - AL1 115.99

siydot
C12 - CL3 - W1 137.57
C13 - CL3 - W1 127.38

sodrei
C9 - CL4 - TA1 128.79
C9 - CL4 - TA1 128.79
C4 - CL3 - TA1 154.35
C4 - CL3 - TA1 154.35
C5 - CL3 - TA1 141.46
C5 - CL3 - TA1 141.46
C6 - CL3 - TA1 120.80
C6 - CL3 - TA1 120.80

tadxol
C1 - CL10 - HF2 122.54
C20 - CL5 - HF1 120.63

trazsb
C1 - CL6 - SB1 108.59

vimpow
C1 - CL2 - I1 113.36
C1 - CL1 - I1 111.54

ponhop
C2 - CL1 - B1 127.40
C2 - CL1 - B1 127.40
C5 - CL3 - B1 98.66
C5 - CL3 - B1 98.66

cbualc
C2 - CL1 - AL1 101.21
C2B - CL1 - AL1 101.21
C3 - CL1 - AL1 117.35

Statistical evaluation (IMSL STAT/LIBRARY Version 1.1; confidence levels: 99.9 %):

Univariate Statistics from UVSTA

	1
Mean	114.4
Variance	253.8
Std. Dev.	15.9
Skewness	1.0
Kurtosis	1.6
Minimum	87.2
Maximum	178.9
Range	91.7
Coef. Var.	0.1
Count	100.0
Lower CLM	109.0
Upper CLM	119.8
Lower CLV	165.4
Upper CLV	425.2

Table S6. The angles $C^{\delta+}\cdots Br—Z$ observed in all structures (angles in degrees; the roman superscripts for the symmetry operations as given in the drawings were omitted):

```
clbrpz
C1    - BR2   - SB1      112.41


covsub10
C10   - BR1   - BR3       84.21
C10   - BR1   - BR2       97.26


cugbah
C3    - BR4   - TE1      118.94
C1'   - BR3   - TE1      104.97
C2'   - BR3   - TE1      111.66


virdef
C1    - BR12  - SE3      119.22
```

Statistical evaluation (IMSL STAT/LIBRARY Version 1.1; confidence levels: 99.9 %):

```
 Univariate Statistics from UVSTA
                              1
      Mean                107.
      Variance            160.
      Std. Dev.            13.
      Skewness             -1.
      Kurtosis             -1.
      Minimum              84.
      Maximum             119.
      Range                35.
      Coef. Var.            0.
      Count                 7.
      Lower CLM            78.
      Upper CLM           135.
      Lower CLV            40.
      Upper CLV          3211.
```

Table S7. Dependence of the angles C-C(+)···X on the *diff* values of C(+)···X in acylium salts (the roman superscripts for the symmetry operations as given in the drawings were omitted).

Refcode and atom names		C-C(+)···X/°	diff(C(+)···X)/Å
acclsb20	C2 - C1 - CL3	85.81	-0.1
acclsb20	C2 - C1 - CL3B	85.81	-0.1
acclsb20	C2 - C1 - CL3D	85.81	-0.1
acclsb20	C2 - C1 - CL3F	85.81	-0.1
etocga	C2 - C1 - CL1	85.05	0.258
etocga	C2 - C1 - CL2	99.36	-0.022
etocga	C2 - C1 - CL1	88.89	0.098
etocga	C2 - C1 - CL4	87.74	-0.026
etocga	C2 - C1 - CL2	95.75	0.056
etocga	C2 - C1 - CL4	107.74	0.473
ibusbc20	C2 - C1 - CL1	90.11	-0.18
ibusbc20	C2 - C1 - CL1B	90.11	-0.179
ibusbc20	C2 - C1 - CL2	108.08	0.233
ibusbc20	C2 - C1 - CL2B	108.08	0.233
ibusbc20	C2 - C1 - CL4	106.95	0.272
ibusbc20	C2 - C1 - CL4	106.96	0.272
mocfsb10	C1 - C2 - F1	89.05	-0.397
mocfsb10	C1 - C2 - F2	86.1	-0.532
mocfsb10	C1 - C2 - F4	85.96	-0.446
mocfsb10	C1 - C2 - F4C	85.97	-0.446
mpocsb	C2 - C1 - CL1	90.73	-0.075
mpocsb	C2 - C1 - CL5	106.68	0.268
mpocsb	C2 - C1 - CL1	96.06	-0.04
mpocsb	C2 - C1 - CL2	93	-0.152
mpocsb	C2 - C1 - CL3	106.96	0.364
mpocsb	C2 - C1 - CL6	93.73	-0.129

Table S8. Dependence of the angles between the symmetry axis of the p-like AO at the C(+) atom and the C(+)···X vector on the *diff* values of C(+)···X in salts of tricoordinated carbocations (see also next page). The direction of the p symmetry axis is approximately computed as the normal of the (least squares) plane defined by C(+) and its three bond partners (the roman superscripts for the symmetry operations as given in the drawings were omitted).

Refcodes and atom names		Angle/°	diff(C(+)···X)/Å
acetfs	p axis of C1 - C1 - O2	18.8	-0.071
acetfs	p axis of C1 - C1 - O3	1.19	-0.309
acnitr20	p axis of C1 - C1 - CL2	7.9	0.048
acnitr20	p axis of C1 - C1 - CL2	7.9	0.048
actnbr	p axis of C1 - C1 - BR2	6.39	0.093
actnbr	p axis of C1 - C1 - BR2	6.39	0.093
cafbam	p axis of C1 - C1 - O4	16.45	-0.038
cafbam	p axis of C6 - C6 - O3	17.16	-0.104
cafbeq	p axis of C1 - C1 - O2	20.58	-0.286
cafbeq	p axis of C1 - C1 - O4	34.17	-0.161
cafbeq	p axis of C2 - C2 - O4	34.71	-0.146
cafbeq	p axis of C3 - C3 - O2	27.65	-0.127
cafbeq	p axis of C4 - C4 - O3	18.66	-0.098
cafbeq	p axis of C5 - C5 - O6	7.38	-0.109
canwet10	p axis of C3 - C3 - O13	16.42	-0.142
canwet10	p axis of C4 - C4 - O22	9.18	-0.253
caprlc	p axis of C1 - C1 - CL1	19.71	0.112
caprlc	p axis of C21 - C21 - CL2	17	-0.005
cirliy	p axis of C1 - C1 - C8	6.9	0.178
cirloe	p axis of C1 - C1 - C8	6.49	0.12
clbrpz	p axis of C1 - C1 - BR2	22.3	0.255
combip	p axis of C3 - C3 - CL1	11.73	0.232
combip	p axis of C4 - C4 - CL1	10.59	0.185
combip	p axis of C5 - C5 - CL3	22.01	0.121
combip	p axis of C6 - C6 - CL3	24.26	0.2
covsub10	p axis of C10 - C10 - BR1	23.5	0.445
cugbah	p axis of C3 - C3 - BR4	2.02	-0.019
cugbah	p axis of C1A - C1A - BR3	22.36	0.038
cugbah	p axis of C2A - C2A - BR3	20.06	0.012
degluw	p axis of C1 - C1 - CL2	10.31	0.1
degluw	p axis of C1 - C1 - O1	19.39	0.099
dibcas	p axis of C1 - C1 - F5	18.38	0.054
dibcas	p axis of C1 - C1 - F5	18.38	0.054
dibcas	p axis of C1 - C1 - F5	18.38	0.054
dibcas	p axis of C1 - C1 - F5	18.38	0.054
difmek	p axis of C1 - C1 - CL2	18.22	0.325
difmek	p axis of C1 - C1 - CL2	18.22	0.325
dijtiz	p axis of C1 - C1 - C12	9.35	0.14
dijtiz	p axis of C2 - C2 - C13	2.47	0.137
dijtiz	p axis of C3 - C3 - C12	13.56	0.18
dijtof	p axis of C1 - C1 - F2	27.48	0.206
dijtof	p axis of C2 - C2 - F2	10.63	-0.123
dijtof	p axis of C3 - C3 - F2	19.34	0.004
dijtof	p axis of C1 - C1 - F2	27.48	0.206

dijtof	p axis of C2 - C2 - F2	10.63	-0.123
dijtof	p axis of C3 - C3 - F2	19.34	0.004
domfug	p axis of C2 - C2 - CL1	16.02	0.154
domfug	p axis of C2 - C2 - CL4	12.33	0.46
donbaj	p axis of C1 - C1 - F1C	5.91	-0.163
donbaj	p axis of C1 - C1 - F1C	5.91	-0.163
donben	p axis of C11 - C11 - F9	17.52	0.03
donben	p axis of C12 - C12 - F2	6.31	0.075
donben	p axis of C12 - C12 - F6	7.26	-0.073
doprij	p axis of C1 - C1 - F25	22.38	-0.291
doxylp	p axis of C1 - C1 - O2	16.26	-0.266
doxylp	p axis of C1 - C1 - O5	11.72	-0.206
dozsoa	p axis of C1 - C1 - CL1	10.49	0.235
dpmbsb10	p axis of C19 - C19 - CL5	13.65	0.42
dpmbsb10	p axis of C36 - C36 - CL11	11.83	0.019
duvzav	p axis of C2 - C2 - I1	10.21	0.086
enanlc	p axis of C1 - C1 - CL1	10.61	-0.112
fafguo	p axis of C1 - C1 - I1A	10.35	0.03
fafguo	p axis of C2 - C2 - I4A	23.8	0.119
fitdiv	p axis of C1 - C1 - F6	4.41	0.107
fitdiv	p axis of C2 - C2 - F6	11.88	0.098
fitdiv	p axis of C2 - C2 - F7	50.7	0.472
fodzaz	p axis of C2 - C2 - F2	37.72	0.242
fodzaz	p axis of C2 - C2 - F4	26.83	0.187
fogbim	p axis of C8 - C8 - I1	12.3	0.183
fogbim	p axis of C8 - C8 - I1	15.84	0.151
fospos01	p axis of C1 - C1 - O3	22.32	0.143
fospos01	p axis of C1 - C1 - O3	22.32	0.142
fufrut	p axis of C1 - C1 - CL1	2.11	-0.303
fufrut	p axis of C1 - C1 - CL4	9.56	0.137
fufsaa	p axis of C1 - C1 - CL3E	6.75	-0.019
fufsaa	p axis of C1 - C1 - O1	7.53	0.124
fuxcac	p axis of C10 - C10 - O4	8.23	0.111
hebzca	p axis of C7 - C7 - CL2	14.99	0.009
hebzca	p axis of C7 - C7 - CL3	17.91	0.124
hebzca	p axis of C8 - C8 - CL2	8.87	-0.082
hebzca	p axis of C8 - C8 - CL3	8.51	0.002
jajriv	p axis of C1 - C1 - CL1	24.09	-0.048
jakbay	p axis of C8 - C8 - O1	6.35	-0.069
jakbay	p axis of C8 - C8 - O2	4.67	0
jalsoe	p axis of C11 - C11 - O1	8.8	-0.029
jecdea	p axis of C2 - C2 - F3	13.9	-0.136
jecdea	p axis of C7 - C7 - F1	15.21	-0.157
jicpoa	p axis of C1 - C1 - F1A	15.97	-0.061
jicpoa	p axis of C1 - C1 - F1	15.97	-0.061
jicpug	p axis of C1 - C1 - F2	6.26	-0.158
jicpug	p axis of C1 - C1 - F4	2.87	-0.254
jicrao	p axis of C1 - C1 - CL1	6.73	0.015
jicrao	p axis of C1 - C1 - CL4	19.21	0.136
jopsem	p axis of C5 - C5 - CL4	6.55	-0.25
jopsem	p axis of C5 - C5 - CL2	32.11	0.415
jopsem	p axis of C5 - C5 - CL3	22.79	0.26
jopsow	p axis of C5 - C5 - CL1	6.28	0.083

jopsow	p axis of C5 - C5 - CL6	6.6	-0.114
jopsuc	p axis of C5 - C5 - CL4	6.71	-0.163
jopsuc	p axis of C5 - C5 - CL5	17.79	0.316
junvap	p axis of C1 - C1 - CL7	3.34	-0.014
junvap	p axis of C2 - C2 - CL6	6.73	0.061
junvap	p axis of C2 - C2 - CL5	18.89	0.147
junvet	p axis of C10 - C10 - CL3	9.18	-0.067
junvet	p axis of C10 - C10 - CL5	9.09	-0.16
juxbej	p axis of C1 - C1 - O1	7.22	0.164
juyyux	p axis of C1 - C1 - CL2	16.72	0.179
juyyux	p axis of C1 - C1 - CL3	16.7	0.272
kazdeu	p axis of C1 - C1 - O1	8.63	0.155
kesder	p axis of C3 - C3 - O7	22.85	0.125
kesder	p axis of C17 - C17 - O1	21.96	0.161
kesder	p axis of C31 - C31 - F7	10.84	0.3
kibpiu	p axis of C9 - C9 - O6	15.3	-0.138
kohvos	p axis of C1 - C1 - CL1	6.06	0.2
kowgos	p axis of C1 - C1 - CL1	28.71	0.289
kowgos	p axis of C1 - C1 - CL1D	25.02	0.169
kowgos	p axis of C1D - C1D - CL1D	28.7	0.289
kowgos	p axis of C1D - C1D - CL1C	25.02	0.169
kowgos	p axis of C1C - C1C - CL1	25.02	0.169
kowgos	p axis of C1C - C1C - CL1C	28.7	0.289
kowgos	p axis of C1 - C1 - CL2	17.36	0.286
kowgos	p axis of C1C - C1C - CL2C	17.36	0.286
kowgos	p axis of C1D - C1D - CL2D	17.36	0.286
kowguy	p axis of C1 - C1 - CL1	28.65	0.295
kowguy	p axis of C1 - C1 - CL1D	25.02	0.176
kowguy	p axis of C1C - C1C - CL1	25.02	0.176
kowguy	p axis of C1C - C1C - CL1C	28.65	0.295
kowguy	p axis of C1D - C1D - CL1D	28.65	0.295
kowguy	p axis of C1D - C1D - CL1C	25.02	0.177
kowguy	p axis of C1 - C1 - CL2	17.39	0.294
kowguy	p axis of C1C - C1C - CL2C	17.39	0.294
kowguy	p axis of C1D - C1D - CL2D	17.39	0.294
lafmek	p axis of C1 - C1 - CL9	2.97	0.037
lafmek	p axis of C2 - C2 - CL3	9.58	0.103
lalloz	p axis of C1 - C1 - CL1	15.42	0.028
lalloz	p axis of C1 - C1 - CL4E	16.88	0.067
macprp10	p axis of C2 - C2 - O2	11.68	-0.06
macprp10	p axis of C2B - C2B - O2B	11.68	-0.06
meguan	p axis of C2 - C2 - O2	18.79	0.198
meguan	p axis of C2 - C2 - O2	18.79	0.198
mtdxyl	p axis of C1 - C1 - F1	11.94	-0.057
mtdxyl	p axis of C1 - C1 - F2	6.66	-0.474
mtdxyp	p axis of C6 - C8 - O4	2.95	-0.452
mtdxyp	p axis of C6 - C8 - O3	11.45	-0.134
oxlcli	p axis of C1 - C1 - CL1	2.4	-0.03
oxlcli	p axis of C1 - C1 - CL2	6.85	-0.043
pcbtec10	p axis of C1 - C1 - CL1	7.22	0.03
pcbtec10	p axis of C1 - C1 - CL10	8.29	0.468
pcclsb	p axis of C1 - C1 - CL5	3.23	0.072
pcclsb	p axis of C1 - C1 - CL3	3.93	0.164

phprpc10	p axis of C18 - C18 - O4	1.13	-0.127
phprpc10	p axis of C19 - C19 - O2	22.04	-0.089
phprpc10	p axis of C20 - C20 - O4	11.26	-0.065
phprpc10	p axis of C20 - C20 - O2	24.5	-0.029
phprpc10	p axis of C18 - C18 - O3	22.1	0.055
phprpc10	p axis of C19 - C19 - O3	22.2	0.067
phprpc10	p axis of C19 - C19 - O4	18.72	0.049
pmdxlp	p axis of C2 - C2 - O6	16.8	0.059
pmdxlp	p axis of C2 - C2 - O3	10.58	-0.198
saxcav	p axis of C2 - C2 - CL1	1.04	0.029
saxcav	p axis of C2 - C2 - CL2	15.18	0.091
saxcav	p axis of C3 - C3 - CL2	18.65	0.142
siydot	p axis of C12 - C12 - CL3	13.81	-0.091
siydot	p axis of C13 - C13 - CL3	19.82	0.028
sodrei	p axis of C9 - C9 - CL4	5.92	0.011
sodrei	p axis of C9 - C9 - CL4	5.92	0.011
tadxol	p axis of C1 - C1 - CL10	13.61	0.094
tadxol	p axis of C20 - C20 - CL5	19.06	0.358
tafbor	p axis of C2 - C2 - O2	20.1	0.328
tafbor	p axis of C2 - C2 - O4	10.03	-0.059
thiurn01	p axis of C1 - C1 - O1	23.93	0.28
thiurn01	p axis of C1 - C1 - O2	24.93	0.308
thiurn01	p axis of C1 - C1 - O1	23.93	0.28
thiurn01	p axis of C1 - C1 - O2	24.93	0.308
trazsb	p axis of C1 - C1 - CL6	15.36	-0.102
vaprej	p axis of C2 - C2 - CL1	29.76	0.12
vaprej	p axis of C2 - C2 - CL1	29.76	0.12
vigxue	p axis of C1 - C1 - O1	25.01	0.494
vigyal	p axis of C1 - C1 - O1	31.05	0.587
vimpow	p axis of C1 - C1 - CL2	25.84	0.406
vimpow	p axis of C1 - C1 - CL1	15.76	-0.028
virdab	p axis of C1 - C1 - CL2	8.97	0.185
virdab	p axis of C1 - C1 - CL1	3.48	0.026
virdef	p axis of C1 - C1 - BR1	6	0.033
virdef	p axis of C1 - C1 - BR12	9.54	0.437
vojgac	p axis of C2 - C2 - O3	5.92	-0.366
vojgac	p axis of C2 - C2 - O2	23.62	0.038
vojgac	p axis of C2 - C2 - O2C	23.62	0.038
vojgec	p axis of C2 - C2 - O12	5.73	-0.238
vojgec	p axis of C4 - C4 - O14	21.79	-0.115
vojgec	p axis of C4 - C4 - F4	7.88	-0.041
vojgec	p axis of C6 - C6 - O11	8.41	-0.307
vojgec	p axis of C8 - C8 - F2	7.06	-0.081
vojgec	p axis of C8 - C8 - F3	18.57	0.188
yamwoy	p axis of C1 - C1 - F1	12.34	0.058
yamwoy	p axis of C1 - C1 - F3	19.85	0.285
pesgid	p axis of C1 - C1 - F11	10.64	-0.057
pesgid	p axis of C1 - C1 - F23	1.69	-0.242
ponhop	p axis of C2 - C2 - CL1	33.77	0.001
ponhop	p axis of C5 - C5 - CL3	27.86	0.542
ponhuv	p axis of C2 - C2 - F1	30.77	-0.034
ponhuv	p axis of C3 - C3 - F1	29.79	-0.023
ponhuv	p axis of C5 - C5 - O1	5.43	0.28

sunmod	p axis of C2 - C2 - F24	28.39	0.426
sunmod	p axis of C2 - C2 - F25	26.34	0.199
maecba	p axis of C3 - C3 - O1	9.83	0.176
mtmcba	p axis of C1 - C1 - O4	22.16	0.004
mtmcba	p axis of C1 - C1 - O3	23.3	0.209

Table S9. Dependence of the angles between the G-C(δ+) bond and the C(δ+)···X vector on the *diff* values of C(δ+)···X in salts of carbocations with partially charged sp^3 C atoms C(δ+) (the roman superscripts for the symmetry operations as given in the drawings were omitted).

Refcodes and atom names				G-C(δ+)···X/°	diff(C(δ+)···X)/Å
dibcas	S1	- C2	- F4	157.54	-0.26
difmek	C2	- C14	- CL3	157.4	0.14
difmek	C2	- C14A	- CL3	157.4	0.14
doxylp	O1	- C3	- O5	174.52	-0.035
doxylp	O6	- C2	- O5	176.52	-0.123
fedzuj	C1	- C7	- O1	159.41	-0.124
macprp10	N1	- C3	- O2	173.38	-0.12
mtdxyl	O2	- C2	- F4	152.23	-0.208
mtdxyl	O1	- C3	- F4	156.17	0.039
mtdxyp	O1	- C3	- O2	157.19	0.032
mtdxyp	O6	- C2	- O2	132.51	-0.034
vaprej	N1	- C1	- CL1	164.89	-0.033
vaprej	N1	- C1A	- CL1	164.89	-0.033
vigyal	O2	- C21	- F4	149.75	-0.04

Table S10. Dependence of several angles (partly involving the symmetry axis of the p-like AO at the pentacoordinated C(+) atom) on the *diff* values of C(+)···X in salts of carbocations with a pentacoordinated C atom. The direction of the p symmetry axis is approximately computed as the normal of the (least squares) plane defined by C(+) and its three single bond partners (the bond partners in the 3c-2e bond are ignored).

Refcode	and atom names[a]	Angle/°	diff(C(+)···X)/Å
jecdea	p axis of C7 - C7 - F1	15.21	-0.157
ponhop	p axis of C5 - C5 - CL3	27.86	0.542
ponhuv	p axis of C5 - C5 - O1	5.43	0.28

Refcode	and atom names[a]	Angle/°
jecdea	p axis of C7 - C7 - center(C2,C2')[b]	32.34
ponhop	p axis of C5 - C5 - center(C2,C2')[b]	33.49
ponhuv	p axis of C5 - C5 - center(C2,C2')[b]	33.2

Refcode	and atom names[a]	Angle/°
jecdea	F1 - C7 - center(C2,C2')[b]	155.08
ponhop	CL3 - C5 - center(C2,C2')[b]	152.49
ponhuv	O1 - C5 - center(C2,C2')[b]	142.95

[a] the roman superscripts for the symmetry operations as given in the drawings were omitted. [b] considered as position of the leaving group.

Table S11. Structural data of C^+—H···X hydrogen bonds in ion pairs of the type RR'C^+—H···X, where R or R' are amino groups and X is or belongs to an anion.

Refcode	R, R'[a]	X	C^+–H[b]	H···X[b]	$diff_{H\cdots X}$[b]	C^+–H···X[c]
DUVZAV	2 NR^1R^2[d]	I	1.04	2.93	-0.25	144
VAPREJ	H, NMe_2	Cl	0.93	2.86	-0.10	146
VIMPOW	2 NMe_2	Cl	1.07	2.52	-0.43	170

[a] see also (6) or **F** in Chart 1. [b] in Å. [c] in °. [d] see formula in appendix A.

Table S12. Structural data of $C^{\delta+}$—H···X hydrogen bonds in ion pairs of the type $C^{\delta+}$—H···X, where $C^{\delta+}$—H belongs to a tropylium ring and X is or belongs to an anion.

Refcode	*n*	X	$C(n)^{\delta+}$–H[a]	H···X[a]	$diff_{H\cdots X}$[a]	$C(n)^{\delta+}$–H···X[b]
ACTRPB	2	Br	1.07	2.77	-0.28	155
	3	Br	1.07	2.92	-0.13	125
	4	Br	1.07	2.86	-0.19	138
	5	Br	1.07	3.02	-0.04	124
	6	Br	1.07	2.94	-0.11	128
	7	Br	1.07	2.92	-0.13	133
SASNOP[c]	13	F	1.07	2.43	-0.24	158
	15	F	1.07	2.29	-0.38	158
	17	F	1.07	2.34	-0.33	176
	18	F	1.07	2.52	-0.15	143
	19	F	1.07	2.66	-0.01	135

[a] in Å. [b] in °. [c] see Fig. 15.

Table S13. Structural data of the $C^{\delta+}$—C—H···X contacts (the roman superscripts of the atom names for the symmetry operations as given in the drawings were omitted). For the definition of the variables see formula on the inset in Figure 28. The torsion angle τ is approximately calculated from R—C—C—H or R'—C—C—H by adding ±90°, and it is selected with the smallest possible absolute value.

Refcode	and atom names	C–H[a]	H···X[a]	$diff_{H\cdots X}$[a]	C–H···X[b]	τ[b]
ACETFS	C2-H1···O3	0.98	2.59	-0.129	154	38
ACETFS	C2-H2···O3	1.22	2.35	-0.374	153	68
ACETFS	C2-H3···O1	1.07	2.65	-0.071	132	26
DOXYLP	C4-H1···O3	0.89	2.62	-0.105	155	60
FEDZIX	C11-H111···Br11	1.07	2.59	-0.463	173	34
FEDZIX	C12-H122···Br12	0.98	2.72	-0.333	164	30
FEDZOD	C1-H11···O4	1.03	2.24	-0.484	170	27
FEDZOD	C1-H12···O2	1.07	2.31	-0.414	173	27
FEDZUJ	C1-H1···O3	1.00	2.7	-0.017	172	45
FODZAZ	C3-H3N···F3	1.07	2.26	-0.413	176	31
FODZAZ	C3-H3X···F2	1.07	2.3	-0.374	141	26
FITDIV01	C3-H1···F7	0.93	2.49	-0.18	149	46
FITDIV01	C9-H5···F8	0.96	2.6	-0.07	143	80
FITDIV01	C9-H7···F5	0.96	2.58	-0.09	149	40
JAJRIV	C2-H2···Cl1	1.08	2.82	-0.126	118	37
JAJRIV	C2-H3···Cl2	1.08	2.48	-0.474	151	24
JAJRIV	C3-H5···O1	1.08	2.56	-0.163	163	30
JAJRIV	C3-H6···Cl4	1.08	2.7	-0.247	155	34
MOCFSB10	C1-H2···F1	0.97	2.65	-0.023	120	0
MOCFSB10	C1-H2···F3	0.97	2.34	-0.335	151	0
PESGID	C2-H21···F12	1.08	2.59	-0.078	149	49
PESGID	C2-H22···F24	1.08	2.6	-0.066	127	71
PESGID	C2-H23···F23	1.08	2.62	-0.048	115	11
PESGID	C2-H23···F25	1.08	2.62	-0.053	131	11
PESGID	C2-H23···F11	1.08	2.56	-0.108	121	11
PESGID	C3-H31···F15	1.10	2.36	-0.315	168	84
PESGID	C3-H32···F21	1.09	2.54	-0.127	118	34
PESGID	C3-H33···F13	1.08	2.63	-0.043	164	24
PESGID	C4-H41···F12	1.08	2.58	-0.095	128	87
PESGID	C4-H41···F24	1.08	2.66	-0.009	155	87
PESGID	C4-H42···F25	1.08	2.4	-0.271	136	33
PESGID	C4-H42···F11	1.08	2.65	-0.018	134	33
PESGID	C4-H43···F14	1.08	2.29	-0.383	156	27
WAZYOL	C16-H4···O2	0.96	2.44	-0.283	153	40
WAZYOL	C16-H5···O3	0.91	2.34	-0.379	155	24

[a] in Å. [b] in °.