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Interactions between Carbocations and Anions in Crystals

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I. Introduction

Crystal engineering[1] and the prediction of crystal packing[2−4] have been reviewed recently. Computational approaches to the problem of crystal structure prediction are not yet generally feasible despite recent advances for flexible[5] and rigid[6] molecules. The principles of crystal packing, as given by Brock and Dunitz,[4] are (1) maximize density and minimize free volume, (2) satisfy H-bond donors, acceptors, and any other special types of intermolecular interactions, and (3) minimize electrostatic energy. The hydrogen bond is the most important directed interaction,[7] and it is already widely used in crystal engineering.[1,8−10] Weaker donor−acceptor interactions occur between carbonyl and nucleophilic groups[11] or between a variety of heteroatoms.[12] We report here some empirical rules about cation···anion interactions (see Chart 1) in salts of carbocations with dicoordinate (**A**), tricoordinate (**B**), tetracoordinate (**C**), or pentacoordinate carbon atoms (**D**), halogen atoms (**E**), or hydrogen atoms (**F**, **G**) presumably bearing any amount of positive charge.

Such interactions were already discussed in individual cases,[13−15] but their general occurrence was never investigated in a broader set of structures from the Cambridge Structural Database (CSD).[16] The present review is related to the studies of the initial phases of the reaction pathway of nucleophilic addition to ketenes[17] (cf. **A**) and carbonyl compounds with a sp^2 C atom[17] (cf. **B**), of S_N2 reactions[18] (cf. **C** and **D**), and of Hal···Hal interactions (cf. **E**).[19] It is different from previous reviews in this field because it involves species with opposite charges, i.e., principle 3 comes into play, and because carbocations are generally better electrophiles than carbonyl compounds. On the other hand, the nucleophiles considered here are necessarily somewhat weaker than in the structures of neutral molecules in order to avoid a recombination reaction.[20]

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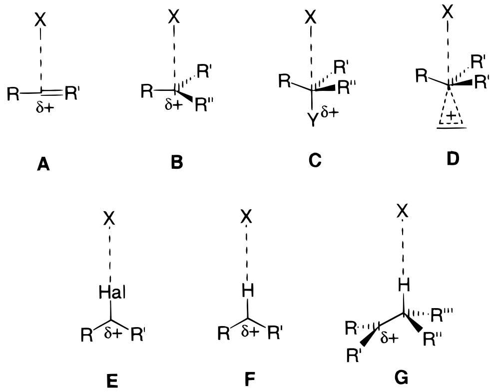
Thomas Laube (born on September 20, 1952, in Berlin, West Germany) studied chemistry (as well as three semesters of mathematics) and received his diploma in chemistry in 1980 from the Free University of Berlin, West Germany (under the supervision of Professor H. Kurreck). He then moved to Zürich, Switzerland, and finished his Ph.D. thesis at the ETH Zürich in 1984 (under the supervision of Professor D. Seebach and Professor J. D. Dunitz). Since 1985, he has worked on the structure of electron-deficient compounds. On the basis of his Habilitationsschrift ("Influence of Electronic Effects on the Structure of Alicyclic Carbocations and Related Molecules"), he holds the title of Privatdozent (since April 1989) at the ETH Zürich where he was senior assistant till June 1994. From October 1995 to August 1996 he worked as a visiting scientist with Professor G. A. Olah and Professor R. Bau at the University of Southern California in Los Angeles. Since June 1997, he has been working at Cilag AG in Schaffhausen, Switzerland. His major research interests concern the experimental investigation of the structures of carbocations and mathematical problems related to this area.

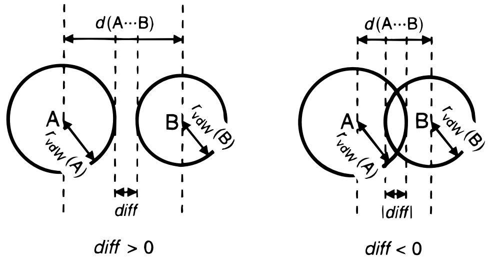
Chart 1. Types of Contacts between Carbocations and Anions[a]



[a] The positive charge is indicated by $\delta+$ and not simply by $+$ because a significant amount of the charge can be delocalized to the substituents. All groups, R^i can be any substituent, Hal is a halogen atom. In most cases X is an anion or belongs to an anion, in a few cases it belongs to a neutral molecule. Y is a positively charged heteroatom or a group $-CR^3R^4-C^+R^5R^6$ which can transfer some positive charge by hyperconjugation to the tetracoordinate C atom under consideration.

The data of most structures were obtained from CSD[16] (version 5.07; database creation date April 1, 1994), and a few structures were included later. Details about the analysis of the data from the CSD with help of the programs SYBYL[21] and SCHAKAL92[22] are given in Appendix D. We were interested only in the less stabilized and less delocalized cations; thus the 129 structures considered here were selected manually from the ~4000 resulting structures of the very general searches, because a question for all kinds of carbocations cannot be formulated in the CSD system. Many of the initially found structures were metal complexes with organic ligands and thus omitted. Also most guanidinium ions, heterocyclic (e.g. pyridinium, quinolinium, imidazolium, adeninium, pyrylium ions) and polycyclic cations (i.e. annulenium ions) and all radical cations were omitted. As they are borderline cases, tropylium, tritylium, and *N*-acylpyridinium ions and some cations with three heteroatom substituents are included in the present review.

Chart 2. Graphical Representation of Positive and Negative Values of *diff*



For all structures investigated in the following sections, the chemical formulas and the reference codes[16] (the names consisting of six letters and two optional digits; refcodes) are given in the corresponding section, the primary references of the structures are given in Appendix A, and additional information and the stereodiagram of the packing with important distances are found in the Supporting Information.

Because of the different atom types X (see Chart 1) in the various structures, the $C^{\delta+}\cdots X$ or other intermolecular distances cannot be compared directly. Thus we use the variable *diff* instead of the distance $d(\text{A}\cdots\text{B})$ for the discussion of a contact between two atoms of the types A and B, which is defined as follows (r_{vdW} is the van der Waals radius[23]):

$$diff = d(\text{A}\cdots\text{B}) - r_{\text{vdW}}(\text{A}) - r_{\text{vdW}}(\text{B})$$

The van der Waals radii (in Å) used here for the various atom types are as follows: C = 1.70, F = 1.47, Cl = 1.75, Br = 1.85, I = 1.98, O = 1.52, N = 1.55, S = 1.80, Se = 1.90, H = 1.20. Usually *diff* refers to the $C^{\delta+}\cdots X$ contact. In ambiguous cases *diff* is specified as $diff_{\text{A}\cdots\text{B}}$. The variable *diff* can be greater than, equal to, or less than zero, see Chart 2.

Unfortunately it is difficult to apply the newer results about the ellipsoidal van der Waals surfaces of electronegative atoms X as described by Nyburg and Faerman.[24] Only the van der Waals surfaces of several atom types X in C−X bonds were analyzed in that work, while the anions considered here contain often Sb−X, B−X or Cl−X bonds, e.g. in the anions $SbCl_6^-$, BF_4^-, ClO_4^-. Finally, the ellipsoidal van der Waals surface of carbon is presently not known, and its shape might still depend on the carbon charge.

II. Results

In this section only the direct results of the analysis of the crystal packings will be presented. These results are grouped into 18 classes of carbocations. This classification is mainly based on the substituents at the cationic C atoms and allows the comparison of different classes.

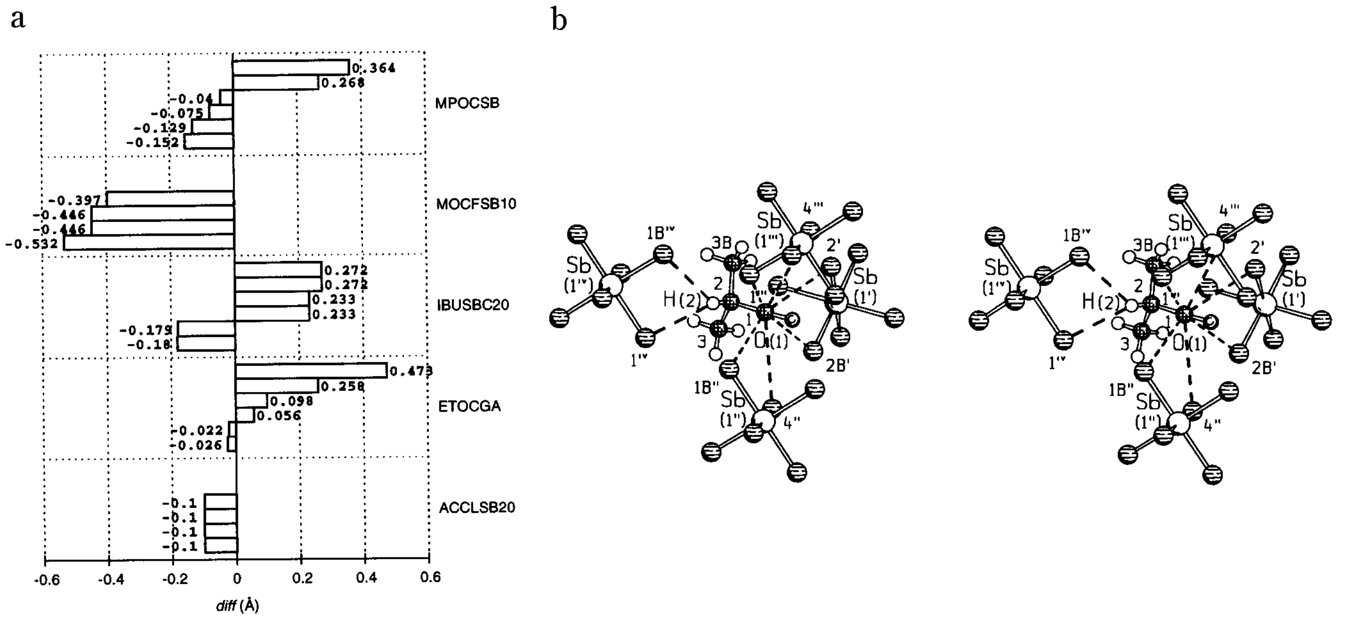
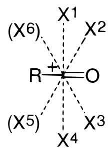


Figure 1. (a) Interactions of the cationic C atoms of acyl cations with counterions (**1**), see also Table 1; and (b) stereo ball-and-stick diagram[22] of the structure of **4** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)···Cl(1B^{II}) 3.27, C(1)···Cl(1^{III}) 3.27, C(1)···Cl(2^{I}) 3.68, C(1)···Cl(2B^{I}) 3.68, C(1)···Cl(4^{II}) 3.72, C(1)···Cl(4^{III}) 3.72, Cl(1^{IV})···H(2) 2.92, Cl(1B^{IV})···H(2) 2.92.

A. Acyl Cations

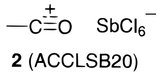
The five ordered and error-free salts considered here show interactions between the cationic sp C atom and 4−6 nucleophilic atoms from counterions, which are approximately arranged on a circle with the C atom in the center and the CO bond in perpendicular direction (see Table 1 and Figure 1; for an example, see Figure 1b).



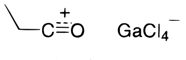
1

The sterically least demanding acetyl cation (crystal structures of **2** and **5**) shows four short contacts with *diff* between −0.53 and −0.10 Å, while the more substituted cations show six somewhat weaker contacts with *diff* between −0.18 and +0.47 Å.

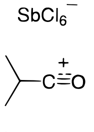
Table 1. Important Features of the Crystal Packing of Acyl Cations (1)



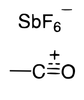
2 (ACCLSB20)



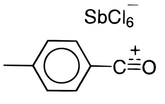
3 (ETOCGA)



4 (IBUSBC20)



5 (MOCFSB10)

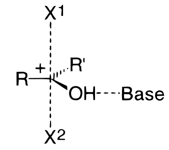


6 (MPOCSB)

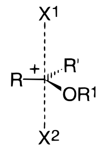
	refcode	R	X	no. of C$^+$···X contacts
2	ACCLSB20	Me	Cl	4
3	ETOCGA	Et	Cl	6
4	IBUSBC20	*i*-Pr	Cl	6
5	MOCFSB10	Me	F	4
6	MPOCSB	*p*-Tolyl	Cl	6

B. Protonated and O-Alkylated Ketones

In nearly all cases, C$^{\delta+}$···X interactions are observed on both faces (see Tables 2 and 3 and Figure 2a; −0.25 Å < *diff* < +0.46 Å; for an example, see Figure 2b). All protonated ketones form a O−H···base hydrogen bond.

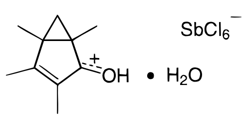


7

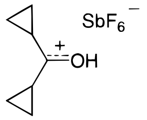


8

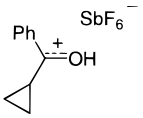
Table 2. Important Features of the Crystal Packing of Protonated Ketones (7)



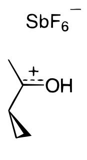
9 (DOMFUG)



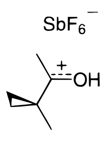
10 (DONBAJ)



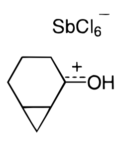
11 (DONBEN)



12 (JICPOA)



13 (JICPUG)



14 (JICRAO)

	refcode	R	R′	X^1	X^2	base
9	DOMFUG	C$_{sp^3}$	C$_{sp^2}$	Cl	Cl	O
10	DONBAJ	c-Pr[a]	c-Pr[a]	F	F	F
11	DONBEN	Ph	c-Pr[a]	F	F/-[b]	F
12	JICPOA	Me	c-Pr[a]	F	F	F
13	JICPUG	Me	1-Me-c-Pr[c]	F	F	F
14	JICRAO	C$_{sp^3}$	2-R-c-Pr[d]	Cl	Cl	Cl

[a] Cyclopropyl. [b] Two entries for two molecules in the asymmetric unit. [c] 1-Methyl-1-cyclopropyl. [d] A 2-substituted cyclopropyl group.

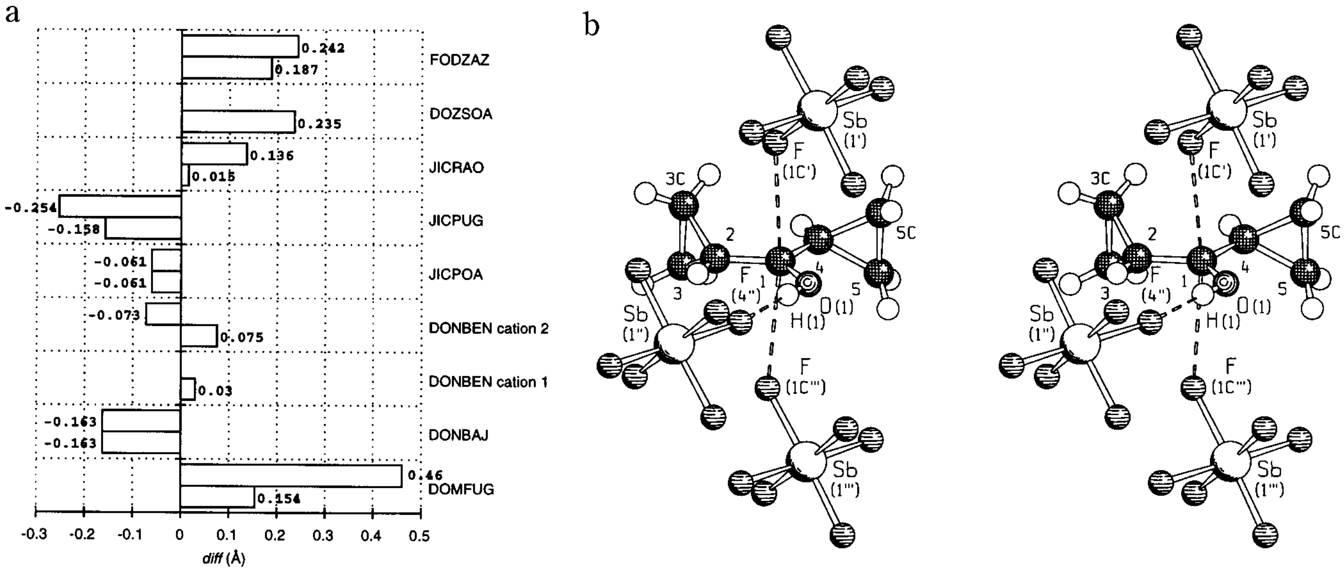
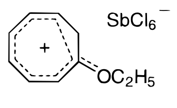
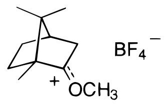


Figure 2. (a) Interactions of the cationic C atoms of protonated or *O*-alkylated ketones with counterions (**7** or **8**); see also Tables 2 and 3; and (b) stereo ball-and-stick diagram[22] of the structure of **10** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: H(1)···F(4^{II}) 1.83, C(1)···F(1C^{I}) 3.01, C(1)···F(1C^{III}) 3.01.

Table 3. Important Features of the Crystal Packing of O-Alkylated Ketones (8)



15 (DOZSOA)

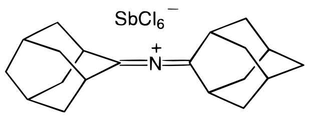


16 (FODZAZ)

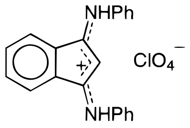
	refcode	R	R′	R^1	X^1	X^2
15	DOZSOA	C$_{sp^3}$	C$_{sp^2}$	Et	Cl	C$_{sp^2}$^{a}
16	FODZAZ	C$_{sp^3}$	C$_{sp^3}$	Me	F	F

[a] Intramolecular.

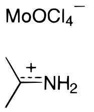
Table 4. Important Features of the Crystal Packing of Iminium Ions (17)



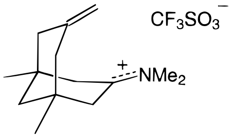
18 (DATZIH)



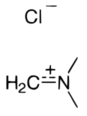
19 (DOYBIC)



20 (JAJRIV)



21 (KESDER)



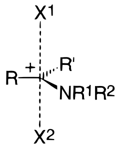
22 (VAPREJ)

	refcode	R, R′	R^1, R^2	X^1	X^2	$n_{Y-H\cdots Z}$^{a} (Y,Z) or other contacts
18	DATZIH	2 C$_{sp^3}$	=C$_{sp^2}$	–^{b}	–^{b}	–
19	DOYBIC^c	2 C$_{sp^2}$	H, Ph	–	–	1 (N,O)
20	JAJRIV	2 Me	2 H	Cl	–	2 (N,Cl); 3 (C,Cl); 1 (C,O)
21	KESDER	2 C$_{sp^3}$	2 Me	O/O/F^d	C$_{sp^2}$^{e}	f
22	VAPREJ	2 H	2 Me	Cl	Cl	8 (C,Cl); 2 N−C$_{sp^3}$···Cl

[a] Number of Y−H···Z hydrogen bonds. [b] Sterically hindered. [c] A symmetrical allylic cation. [d] Three entries for three molecules in the asymmetric unit. [e] Intramolecular. [f] Each cation has four to six C−H···O or C−H···F bonds.

C. Iminium Ions

The less delocalized iminium ions (**17**; R^1, R^2 = H or C$_{sp^3}$) show in nearly all cases C$^{\delta+}$···X interactions

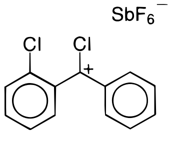


17

on both faces (see Table 4 and Figure 3a; −0.05 Å < *diff* < +0.30 Å; for an example, see Figure 3b). Protons bonded to the iminium N are involved in hydrogen bonds. Weaker C−H···base hydrogen bonds are observed at sp^3 C atoms bonded directly to the C=N fragment.

D. Monochloro-Substituted Cations

So far, the only example (a diphenylchloromethyl cation; **23**; see Figure 4) shows C$^{\delta+}$···X interactions on both sides of the cationic C atom (*diff* +0.06 and +0.29 Å), and the Cl atom is involved in very strong interactions with other halogen atoms ($diff_{Cl\cdots F}$ = −0.44 Å).



23 (YAMWOY)

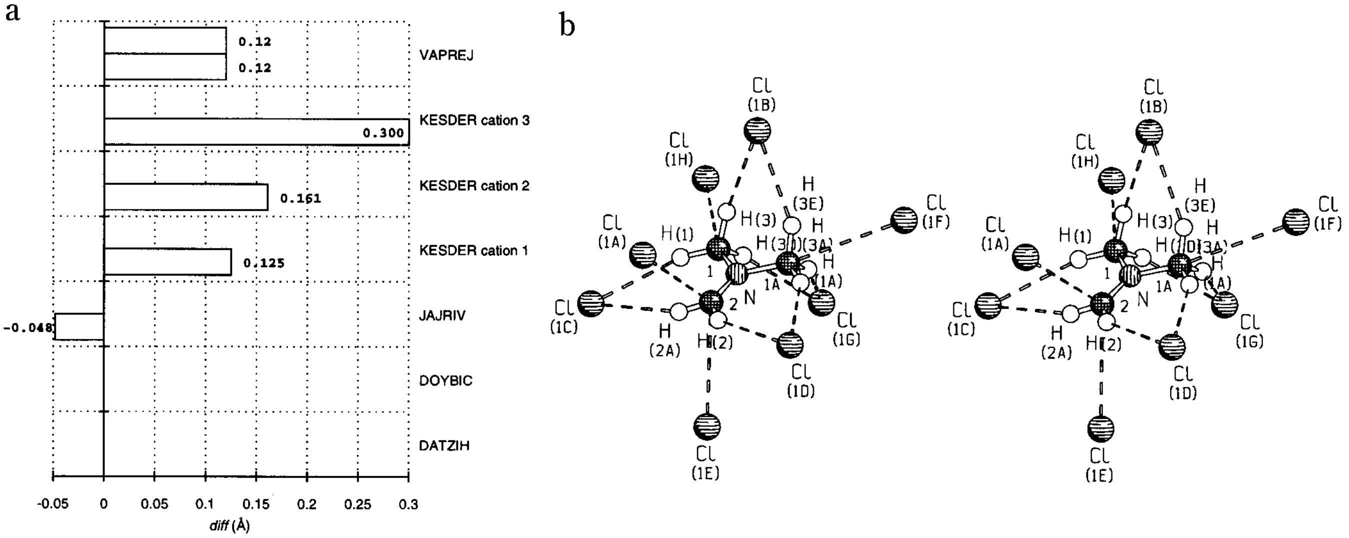


Figure 3. (a) Interactions of the cationic C atoms of iminium ions with counterions (**17**); see also Table 4; and (b) stereo ball-and-stick diagram[22] of the structure of **22** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)···Cl(1H) 3.42, C(1A)···Cl(1F) 3.42, C(2)···Cl(1A) 3.57, C(2)···Cl(1E) 3.57, H(1)···Cl(1C) 2.82, H(2)···Cl(1D) 2.86, H(3)···Cl(1B) 2.80, H(3D)···Cl(1G) 2.80, H(2A)···Cl(1C) 2.86, H(1A)···Cl(1D) 2.82, H(3A)···Cl(1G) 2.80, H(3E)···Cl(1B) 2.80.

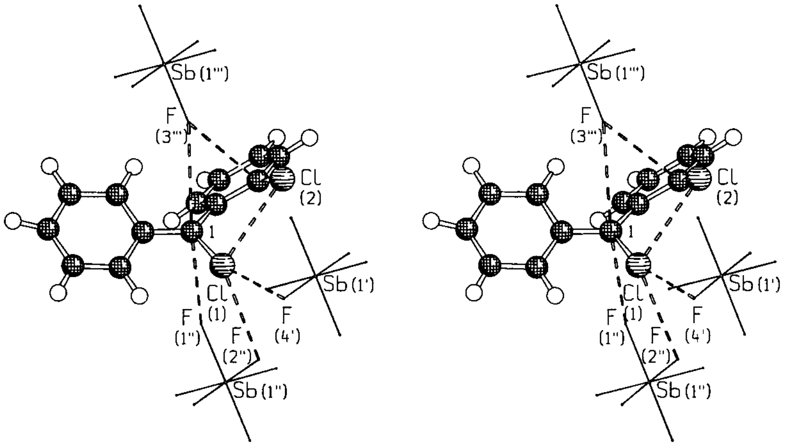
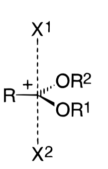


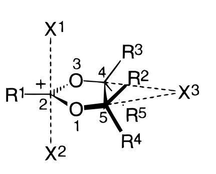
Figure 4. Stereo ball-and-stick diagram[22] of the structure of **23** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)···F(1^{II}) 3.23, C(1)···F(3^{III}) 3.46, Cl(1)···Cl(2) 3.08, Cl(1)···F(4^{I}) 2.78, Cl(1)···F(2^{II}) 3.10, C(3)···F(3^{III}) 3.35.

E. O,O-Substituted Cations

In nearly all of the cases, C$^{\delta+}$···X interactions are observed on both faces of the cationic C (see Tables 5 and 6 and Figures 5a and 6a). For the protonated acids and lactonium ions, one finds -0.37 Å $<$ *diff* $< +0.32$ Å. All protonated carboxylic acids form O−H···base hydrogen bonds (for an example, see Figure 5b). The 1,3-dioxolan-2-ylium ions (see Table 6; -0.47 Å $<$ $diff_{C(2)\cdots X}$ $< +0.06$ Å; for an example, see Figure 6b) show an additional interaction between the sp^3 C ring atoms (4 and 5) and a nucleophilic atom (-0.21 Å $<$ $diff_{C(4,5)\cdots X3}$ $< +0.78$ Å), even in the sterically hindered cases (crystal structures of **35** and **36**).[25]

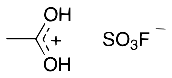


24

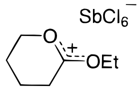


25

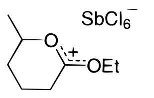
Table 5. Important Features of the Crystal Packing of Protonated Carboxylic Acids and Lactonium Ions (24)



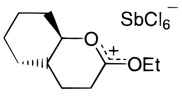
26 (ACETFS)



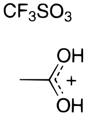
27 (JOPSEM)



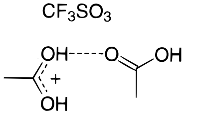
28 (JOPSOW)



29 (JOPSUC)



30 (VOJGAC)



31 (VOJGEG)

	refcode	R	R^1	R^2	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z)
26	ACETFS	Me	H	H	O	O	2 (O,O); 3 (C,O)
27	JOPSEM[b]	−(C$_{sp^3}$)$_4$−		Et	Cl	Cl	−
28	JOPSOW[b]	−(C$_{sp^3}$)$_4$−		Et	Cl	Cl	−
29	JOPSUC[b]	−(C$_{sp^3}$)$_4$−		Et	Cl	Cl	−
30	VOJGAC	Me	H	H	O	O	2 (O,O); 1 (C,O)
31	VOJGEG[c,d]	Me	H	H	O	F	2 (O,O)
31	VOJGEG[c,e]	Me	H	H	O	−	2 (O,O)

[a] Number of Y−H···Z hydrogen bonds. [b] A lactonium ion. [c] Two cations and two AcOH molecules in the asymmetric unit. [d] Cation with C4. [e] Cation with C6.

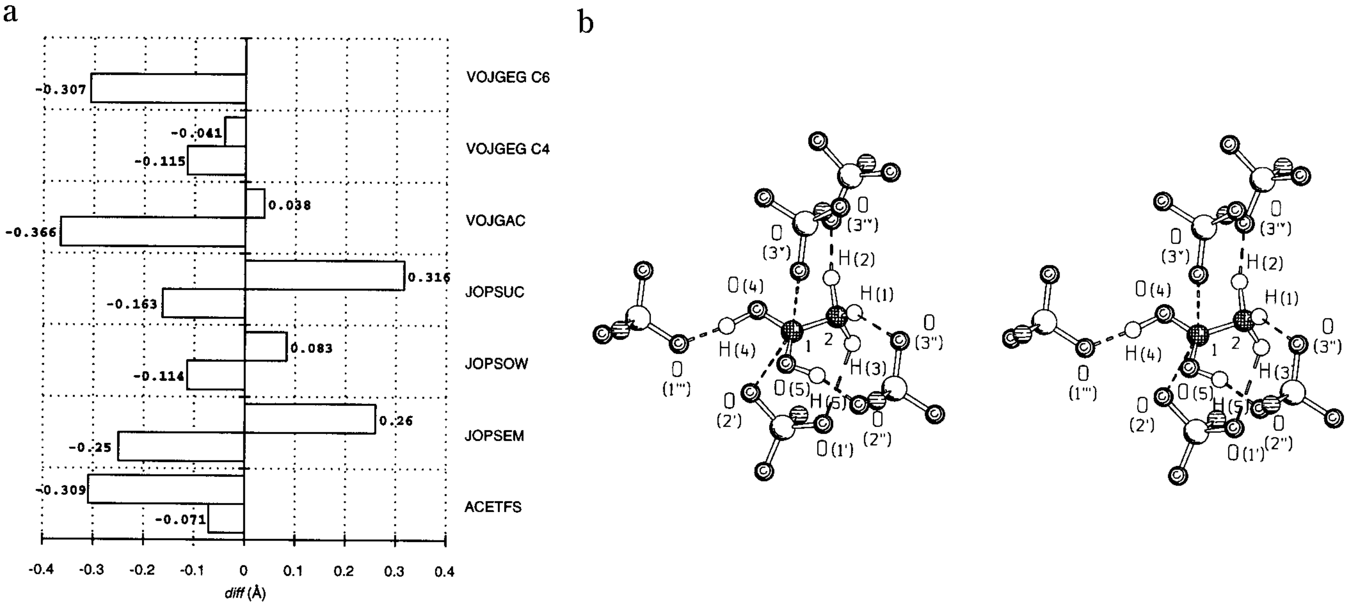


Figure 5. (a) Interactions of the cationic C atoms of protonated carboxylic acids and lactonium ions with counterions (**24**); see also Table 5; and (b) stereo ball-and-stick diagram[22] of the structure of **26** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: H(4)···O(1^{III}) 1.51, C(1)···O(2^{I}) 3.15, C(1)···O(3^{V}) 2.91, H(1)···O(3^{II}) 2.59, H(2)···O(3^{IV}) 2.35, H(5)···O(2^{II}) 1.58, H(3)···O(1^{I}) 2.65.

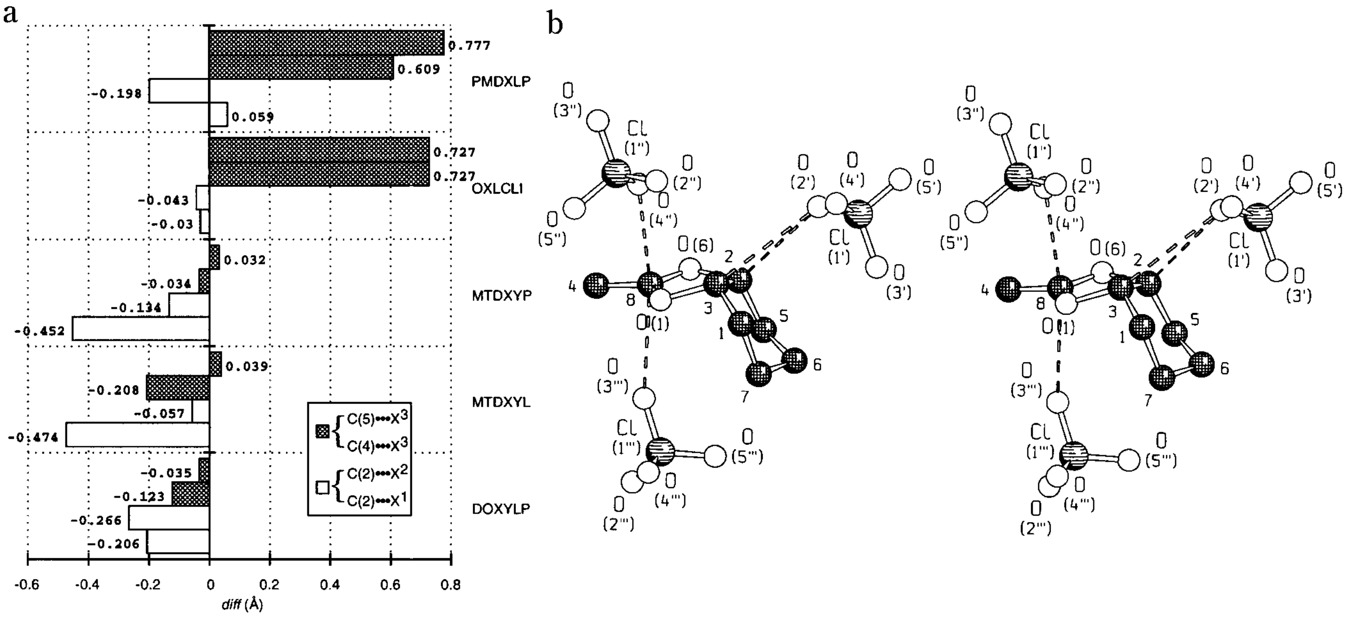
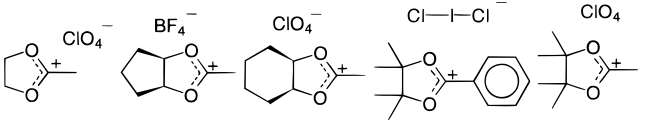


Figure 6. (a) Interactions of the C atoms C(2), C(4), and C(5) of 1,3-dioxolan-2-ylium ions with counterions (**25**); see also Table 6; and (b) stereo ball-and-stick diagram[22] of the structure of **34** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(8)···O(4^{II}) 2.77, C(8)···O(3^{III}) 3.09, C(2)···O(2^{I}) 3.19, C(3)···O(2^{I}) 3.25.

Table 6. Important Features of the Crystal Packing of 1,3-Dioxolan-2-ylium Ions (25)



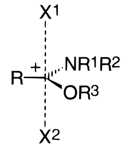
32(DOXYLP) **33**(MTDXYL) **34**(MTDXYP) **35** (OXLCLI) **36**(PMDXLP)

	refcode	R^1	R^2, R^3	R^4, R^5	X^1, X^2	X^3
32	DOXYLP	Me	2 H	2 H	2 O	O
33	MTDXYL	Me	$-(CH_2)_3-$	2 H	2 F	F
34	MTDXYP	Me	$-(CH_2)_4-$	2 H	2 O	O
35	OXLCLI	Ph	2 Me	2 Me	2 Cl	I[a]
36	PMDXLP	Me	2 Me	2 Me	2 O	O[a]

[a] Contact sterically hindered because of the persubstituted atoms C(4) and C(5).

F. N,O-Substituted Cations

At least on one side of the cationic C atom, a $C^{\delta+}\cdots X$ interaction is observed in all cases (see Table 7 and Figure 7a; -0.11 Å < *diff* < $+0.33$ Å; for an example, see Figure 7b). Protons bonded to the N or O atoms are involved in hydrogen bonds.



37

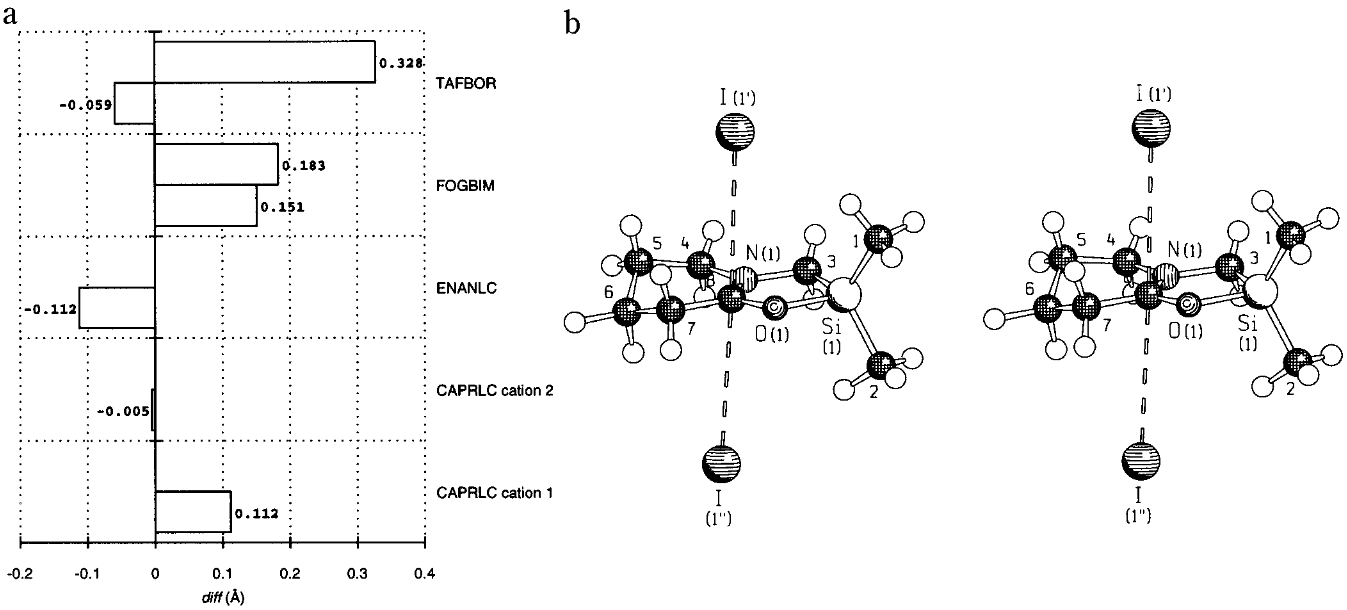
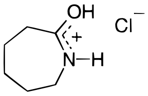
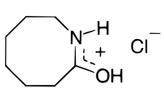


Figure 7. (a) Interactions of the cationic C atoms of N,O-substituted cations with counterions (**37**); see also Table 7; and (b) stereo ball-and-stick diagram[22] of the structure of **40** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: $C(8)\cdots I(1^{I})$ 3.83, $C(8)\cdots I(1^{II})$ 3.86.

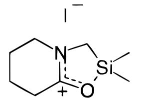
Table 7. Important Features of the Crystal Packing of N,O-Substituted Cations (37)



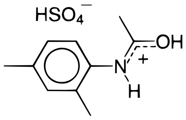
38 (CAPRLC)



39 (ENANLC)



40 (FOGBIM)



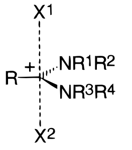
41 (TAFBOR)

	refcode	R	R^1, R^2	R^3	X^1	X^2	$n_{\text{Y–H}\cdots\text{Z}}$[a] (Y,Z)
38	CAPRLC[b]	C_{sp^3}	H, C_{sp^3}	H	Cl	—[c]	1 (N,Cl); 1 (O,Cl)
39	ENANLC[b]	C_{sp^3}	H, C_{sp^3}	H	Cl	—[c]	1 (N,Cl); 1 (O,Cl)
40	FOGBIM	C_{sp^3}	2 C_{sp^3}	SiR'$_3$	I	I	—
41	TAFBOR	Me	H, aryl	H	O	O[d]	1 (N,O); 1 (O,O)

[a] Number of Y–H···Z hydrogen bonds. [b] A protonated lactam. [c] Sterically hindered. [d] Weak.

G. N,N-Substituted Cations

The $C^{\delta+}\cdots X$ interactions seem to occur at least on one side only in those cases where the N atoms have no hydrogens and the cations are not strongly delocalized (see Table 8 and Figure 8a; crystal structures of **44**, **47**, and **54**; −0.03 Å < *diff* < +0.41 Å; for an example, see Figure 8b). If the N atoms have



42

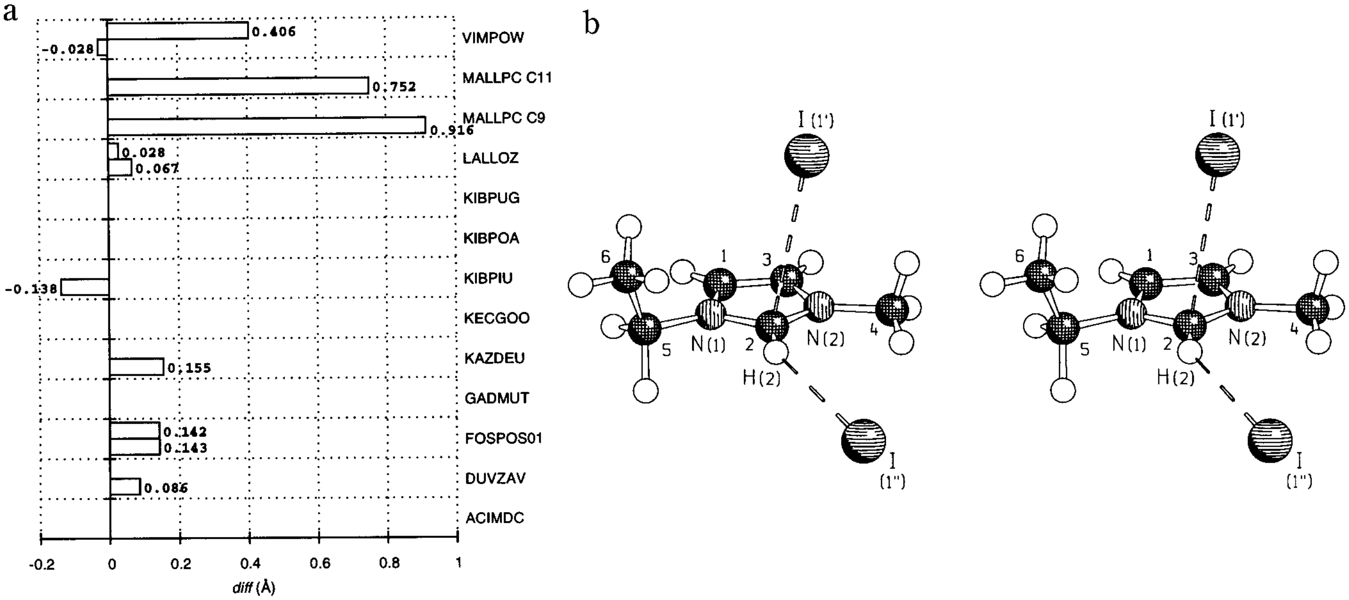
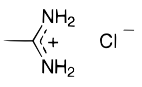
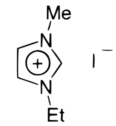


Figure 8. (a) Interactions of the cationic C atoms of N,N-substituted cations with counterions (**42**); see also Table 8; and (b) stereo ball-and-stick diagram[22] of the structure of **44** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: $H(2)\cdots I(1^{II})$ 2.93, $C(2)\cdots I(1^{I})$ 3.77.

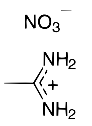
Table 8. Important Features of the Crystal Packing of N,N-Substituted Cations (42)



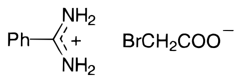
43 (ACIMDC)



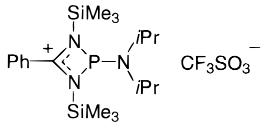
44 (DUVZAV)



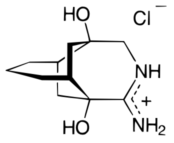
45 (FOSPOS01)



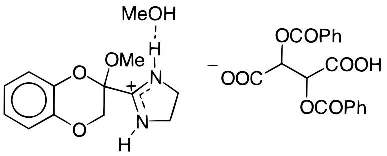
46 (GADMUT)



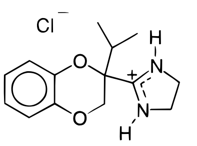
47 (KAZDEU)



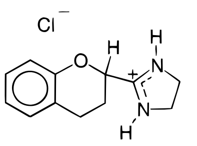
48 (KECGOO)



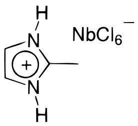
49 (KIBPIU)



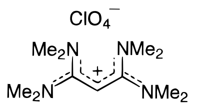
50 (KIBPOA)



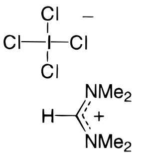
51 (KIBPUG)



52 (LALLOZ)



53 (MALLPC)



54 (VIMPOW)

	refcode	R	R^1, R^2	R^3, R^4	X^1	X^2	$n_{\mathrm{Y-H\cdots Z}}$[a] (Y,Z)
43	ACIMDC	Me	2 H	2 H	–	–	4 (N,Cl)
44	DUVZAV	H	Et, C_{sp^2}	Me, C_{sp^2}	I	–	1 (C,I)
45	FOSPOS01	Me	2 H	2 H	O	O	4 (N,O)
46	GADMUT	Ph	2 H	2 H	–	–	4 (N,O)
47	KAZDEU	Ph	*b*	*b*	O	–	–
48	KECGOO	C_{sp^3}	H, C_{sp^3}	2 H	–	–	2 (N,Cl); 1 (N,O)
49	KIBPIU	C_{sp^3}	H, C_{sp^3}	H, C_{sp^3}	O	–	2 (N,O)
50	KIBPOA	C_{sp^3}	H, C_{sp^3}	H, C_{sp^3}	–	–	2 (N,Cl)
51	KIBPUG	C_{sp^3}	H, C_{sp^3}	H, C_{sp^3}	–	–	2 (N,Cl)
52	LALLOZ	Me	H, C_{sp^2}	H, C_{sp^2}	Cl	Cl	2 (N,Cl)
53	MALLPC[c]	C_{sp^2}	2 Me	2 Me	O[d]	–	–
54	VIMPOW	H	2 Me	2 Me	Cl	Cl[e]	1 (C,Cl)

[a] Number of Y–H···Z hydrogen bonds. [b] $SiMe_3$, PR_2. [c] A symmetrical allyl cation. [d] Very weak. [e] Weak.

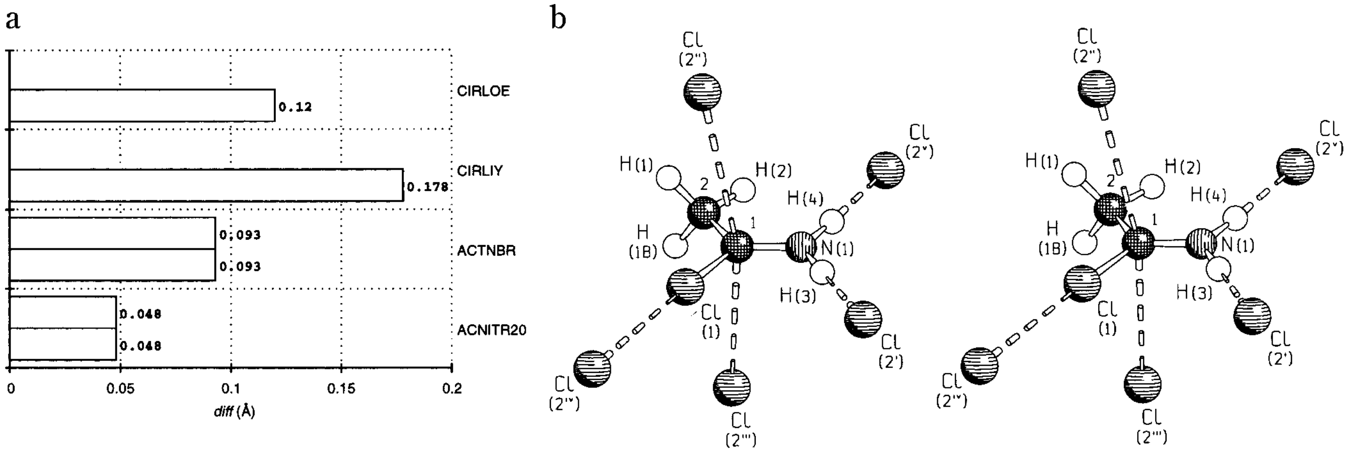
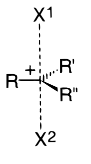


Figure 9. (a) Interactions of the cationic C atoms of haloiminium ions and disulfur- and diselenium-substituted cations with counterions (**55**); see also Table 9; and (b) stereo ball-and-stick diagram[22] of the structure of **56** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: Cl(2^{I})···H(3) 2.01, H(4)···Cl(2^{V}) 2.04, C(1)···Cl(2^{II}) 3.50, C(1)···Cl(2^{III}) 3.50, Cl(1)···Cl(2^{IV}) 3.33.

hydrogens, they are always involved in N–H···base hydrogen bonds, and C$^{\delta+}$···X interactions occur only occasionally.

H. Other Cations with Two Heteroatom Substituents

Haloiminium ions (see Table 9 and Figure 9a; crystal structures of **56** and **57**; for an example, see Figure 9b) show C$^{\delta+}$···X interactions on both faces (*diff* +0.05 Å, +0.09 Å), and N protons are involved in hydrogen bonds. The C$^+$–Hal···Hal contacts here are also remarkably strong, as mentioned in section D about monochloro-substituted cations. In the very similar disulfur- and diselenium-substituted cations, contacts between the cationic C and the Ph ring of another cation are observed on one side in each case (*diff* 0.18 Å and 0.12 Å). Weak C–H···base hydrogen bonds are found at sp^3 C atoms bonded to the cationic C and the S or Se atoms, and S···Cl or Se···Cl contacts are also found.

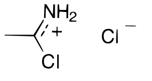


55

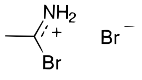
I. N,N,N-Substituted Cations

Hydrogen atoms bonded to the N atoms of guanidinium ions are almost always involved in N–H···

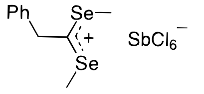
Table 9. Important Features of the Crystal Packing of Haloiminium Ions and Disulfur- and Diselenium-Substituted Cations (55)



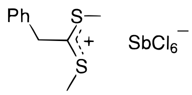
56 (ACNITR20)



57 (ACTNBR)



58 (CIRLIY)



59 (CIRLOE)

	refcode	R	R′	R″	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z) and other contacts
56	ACNITR20	Me	NH_2	Cl	Cl	Cl	2 (N,Cl); 1 C−Cl···Cl$^-$
57	ACTNBR	Me	NH_2	Br	Br	Br	2 (N,Br); 1 C−Br···Br$^-$
58	CIRLIY	Bzl[b]	SeMe	SeMe	C_{sp^2}	−	7 (C,Cl); 4 Se···Cl
59	CIRLOE	Bzl[b]	SMe	SMe	C_{sp^2}	−	6 (C,Cl); 4 S···Cl

[a] Number of Y−H···Z hydrogen bonds. [b] Bzl = benzyl.

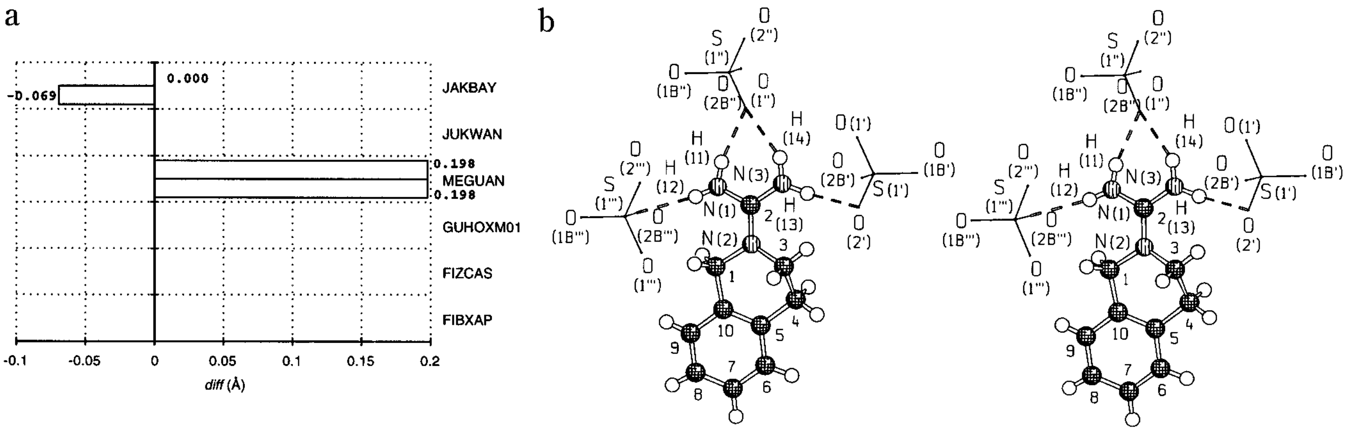
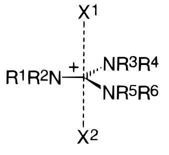
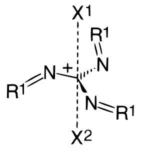


Figure 10. (a) Interactions of the cationic C atoms of guanidinium ions with counterions (**60**); see also Table 10; and (b) stereo ball-and-stick diagram[22] of the structure of **66** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: H(11)···O(1^{II}) 2.00, H(12)···O(2B^{III}) 2.09, O(2^{I})···H(13) 1.99, H(14)···O(1^{II}) 2.11.

base hydrogen bonds, and $C^{\delta+}\cdots X$ interactions occur rarely in such cations (see Table 10 and Figure 10a; for an example, see Figure 10b).[26] Such interactions are found in only one example of a persubstituted guanidinium ion (crystal structure of **67**), so a generalization is not possible.[27] In the other cases of N,N,N-substituted cations (see Table 11 and Figure 11a; for an example, see Figure 11b), a $C^{\delta+}\cdots X$ contact is observed at least on one side of the cation (−0.10 Å < *diff* < +0.26 Å), but other contacts can occur as well.



60

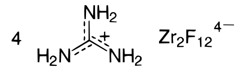


61

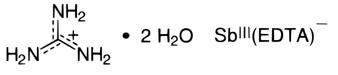
J. Other Cations with Three Heteroatom Substituents

A $C^{\delta+}\cdots X$ interaction is observed in almost all cases at least on one side of the cationic C atom (see Table 12 and Figure 12a; −0.30 Å < *diff* < +0.28 Å; for an example, see Figure 12b). Protons bonded to the N

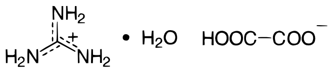
Table 10. Important Features of the Crystal Packing of Guanidinium Ions (60)



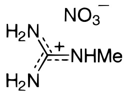
62 (FIBXAP)



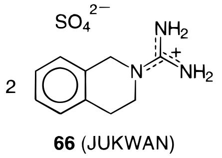
63 (FIZCAS10)



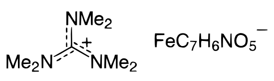
64 (GUHOXM10)



65 (MEGUAN)



66 (JUKWAN)



67 (JAKBAY)

	refcode	R^1, ..., R^6	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z)
62	FIBXAP	6 H	−	−	5 (N,F)/6 (N,F)[b]
63	FIZCAS10	6 H	−	−	6 (N,O)
64	GUHOXM01	6 H	−	−	6 (N,O)
65	MEGUAN	5 H, 1 Me	O	O	5 (N,O)
66	JUKWAN	4 H, 2 C_{sp^3}	−	−	4 (N,O)
67	JAKBAY	6 Me	O	O	−

[a] Number of Y−H···Z hydrogen bonds. [b] Two entries for two molecules in the asymmetric unit.

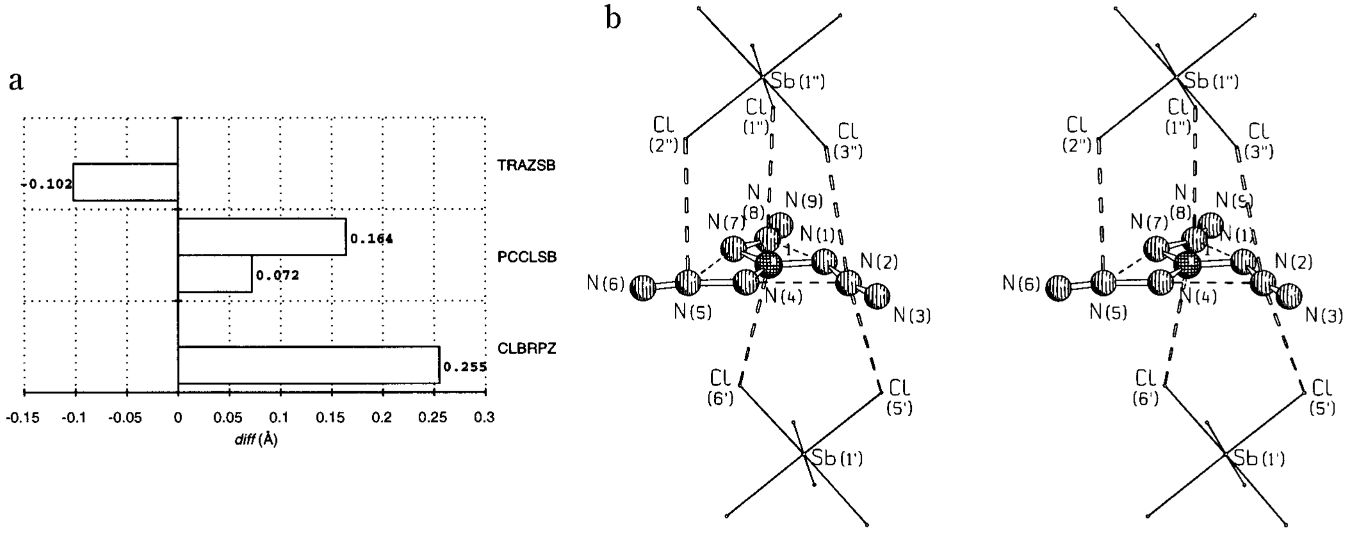
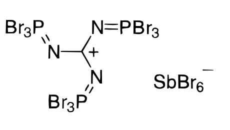
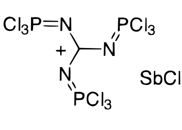


Figure 11. (a) Interactions of the cationic C atoms of carbocations with three NR^1 substituents with counterions (**61**); see also Table 11; and (b) stereo ball-and-stick diagram[22] of the structure of **70** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)$\cdots$Cl(6^I) 3.35, N(1)$\cdots$N(8) 2.46, N(2)$\cdots$N(4) 2.41, N(2)$\cdots$Cl(3^{II}) 3.41, N(2)$\cdots$Cl(5^I) 3.50, N(5)$\cdots$Cl(2^{II}) 3.46, N(8)$\cdots$Cl(1^{II}) 3.38.

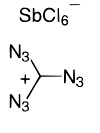
Table 11. Important Features of the Crystal Packing of Carbocations with Three N=R^1 Substituents (61)



68 (CLBRPZ)



69 (PCCLSB)

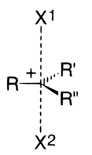


70 (TRAZSB)

	refcode	=R^1	X^1	X^2
68	CLBRPZ	=P(Br$_{0.78}$Cl$_{0.22}$)$_3$[a]	Br	–[b]
69	PCCLSB	=PCl$_3$	Cl	Cl
70	TRAZSB	=N$_\beta$=N$_\gamma$	Cl	–[c]

[a] The halogen atoms are statistically disordered. [b] Two P–Br$\cdots$Br–Sb contacts. [c] Three N$_\beta\cdots$Cl–Sb contacts.

or S atoms are involved in hydrogen bonds. The F,S,S-substituted cation (crystal structure of **84**) is remarkable because of its strong S$\cdots$F and C$_{sp^3}\cdots$F contacts.



71

K. *N*-Acylpyridinium Ions

One contact between the carbonyl C atom and a nucleophilic or electron-rich atom is always observed

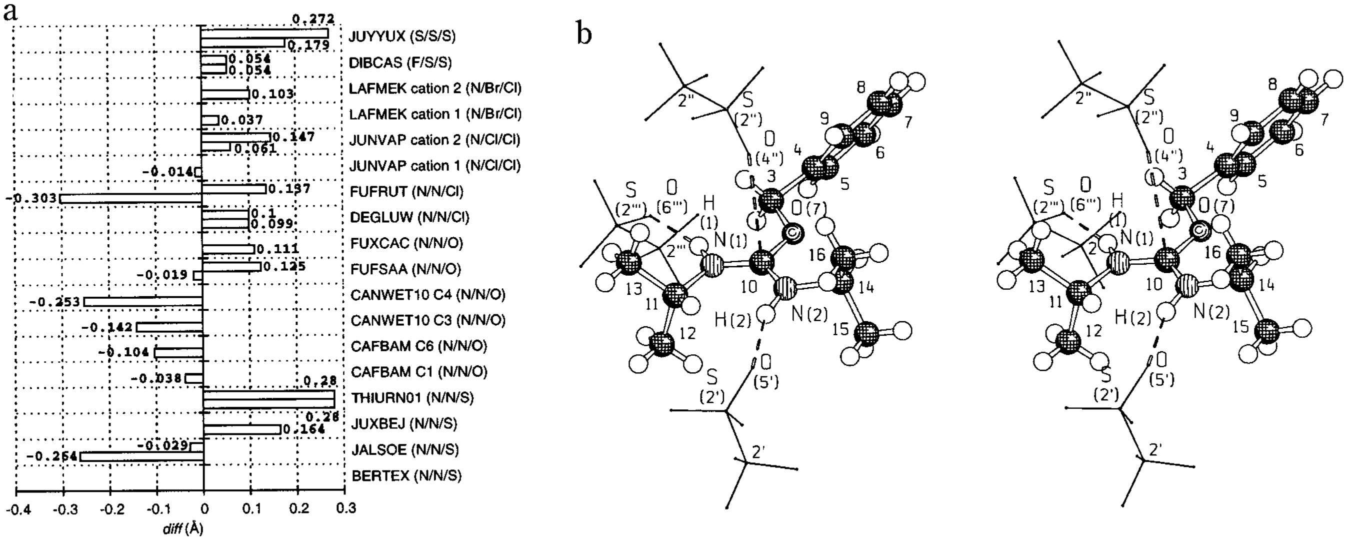
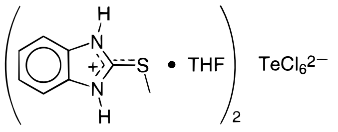
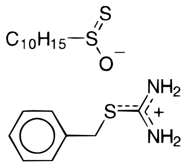


Figure 12. (a) Interactions of the cationic C atoms of carbocations with three heteroatom substituents (the heteroatoms are given in parentheses) with counterions (**71**); see also Table 12. N,N,N-Substituted carbocations are excluded because they are treated in Figures 10a and 11a. (b) Stereo ball-and-stick diagram[22] of the structure of **79** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(10)$\cdots$O(4^{II}) 3.33, O(5^I)$\cdots$H(2) 1.96, H(1)$\cdots$O-(6^{III}) 2.02.

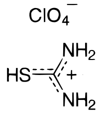
Table 12. Important Features of the Crystal Packing of Carbocations with Three Heteroatom Substituents (71) (N,N,N-Substituted carbocations are excluded because they are listed in Tables 10 and 11)



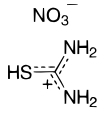
72 (BERTEX)



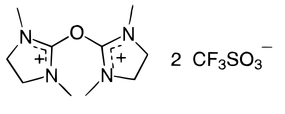
73 (JALSOE)



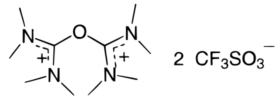
74 (JUXBEJ)



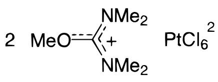
75 (THIURN01)



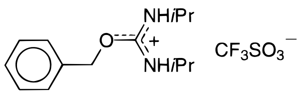
76 (CAFBAM)



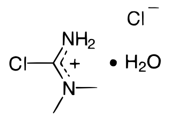
77 (CANWET10)



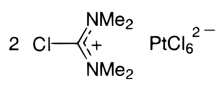
78 (FUFSAA)



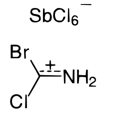
79 (FUXCAC)



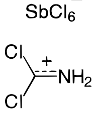
80 (DEGLUW)



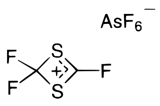
81 (FUFRUT)



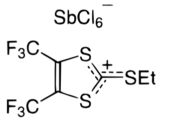
82 (LAFMEK)



83 (JUNVAP)



84 (DIBCAS)



85 (JUYYUX)

	refcode	R[a]	R′ [a]	R″ [a]	X^1	X^2	$n_{\mathrm{Y-H\cdots Z}}$[b] (Y,Z) or other contacts[c]
72	BERTEX	NHar	NHar	SMe	−	−	1 (N,Cl); 1 (N,O)
73	JALSOE	NH$_2$	NH$_2$	SBzl	O	C$_{sp^2}$[d]	2 (N,O); 2 (N,S)
74	JUXBEJ	NH$_2$	NH$_2$	SH	O	−	4 (N,O); 1 (S,O)
75	THIURN01	NH$_2$	NH$_2$	SH	O	O	4 (N,O); 1 (S,O)
76	CAFBAM	NR$_2$	NR$_2$	OR	O	−	−
77	CANWET10	NMe$_2$	NMe$_2$	OR	O	−	−
78	FUFSAA	NMe$_2$	NMe$_2$	OMe	Cl	O	−
79	FUXCAC	NH*i*-Pr	NH*i*-Pr	OBzl	O	−	2 (N,O)
80	DEGLUW	NH$_2$	NMe$_2$	Cl	Cl	O	2 (N,Cl)
81	FUFRUT	NMe$_2$	NMe$_2$	Cl	Cl	Cl	−
82	LAFMEK	NH$_2$	Br	Cl	Cl	−	2 (N,Cl)
83	JUNVAP	NH$_2$	Cl	Cl	Cl	Cl/−[e]	2 (N,Cl)
84	DIBCAS	F	SC$_{sp^3}$	SC$_{sp^3}$	F	F	4 S⋯F; 2 C$_{sp^3}$⋯F
85	JUYYUX	SEt	SC$_{sp^2}$	SC$_{sp^2}$	Cl	Cl	−

[a] ar = aryl, Bzl = benzyl. [b] Number of Y−H⋯Z hydrogen bonds. [c] Different kinds of contacts are separated by a semicolon. [d] Intramolecular. [e] Two entries for the two molecules in the asymmetric unit.

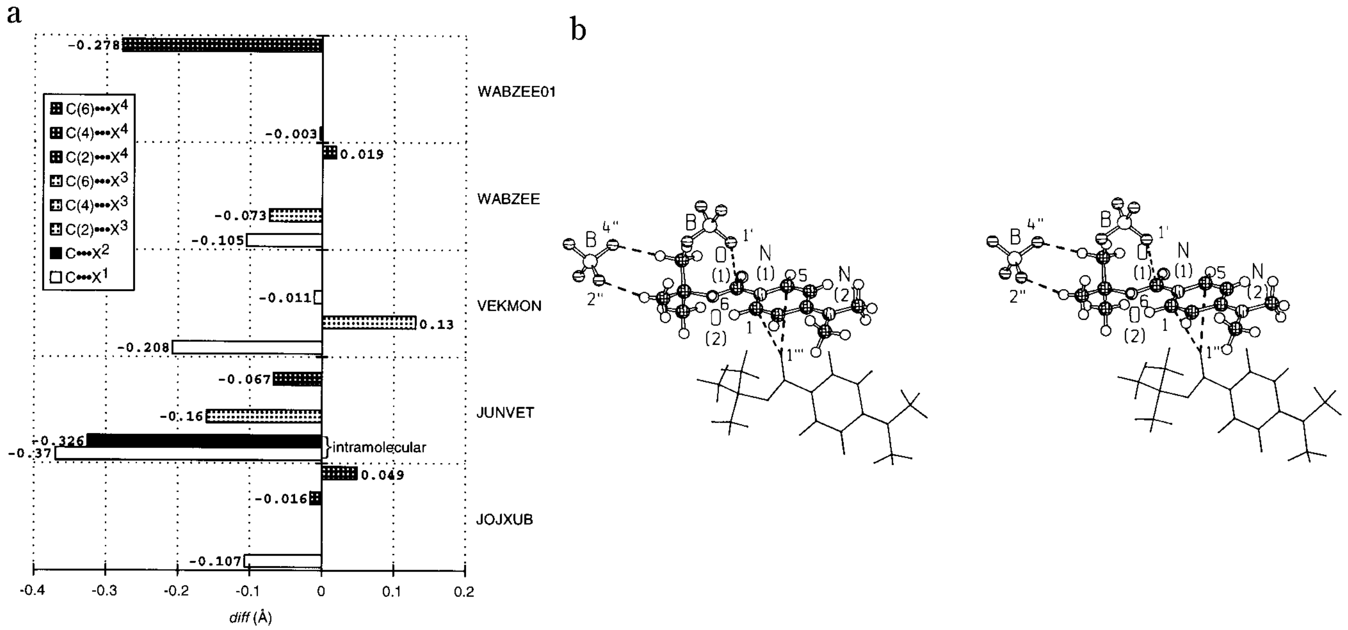
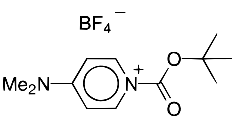
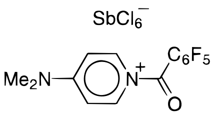


Figure 13. (a) Interactions of the carbonyl and electron-deficient pyridinium C atoms of *N*-acylpyridinium ions with counterions (**86**); see also Table 13; and (b) stereo ball-and-stick diagram[22] of the structure of **87** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(6)⋯F(1$^{\mathrm{I}}$) 3.06, C(1)⋯O(1$^{\mathrm{III}}$) 3.20, C(5)⋯O(1$^{\mathrm{III}}$) 3.27, F(4$^{\mathrm{II}}$)⋯H(7) 2.59, F(2$^{\mathrm{II}}$)⋯H(10) 2.67.

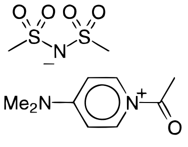
Table 13. Important Features of the Crystal Packing of *N*-acylpyridinium Ions (86)



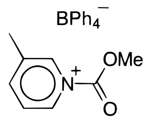
87 (JOJXUB)



88 (JUNVET)



89 (VEKMON)

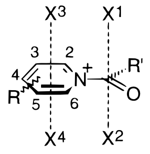


90a (WABZEE)
90b (WABZEE01)

	refcode	R	R′	X^1	X^2	X^{3a}	X^{4a}
87	JOJXUB	4-NMe$_2$	O*t*-Bu	F	–	–	2,6: O
88	JUNVET	4-NMe$_2$	C$_6$F$_5$	F[b]	2 F[b]	4: Cl	4: Cl
89	VEKMON	4-NMe$_2$	Me	O	–	2,6: O	–
90a	WABZEE[c]	3-Me	OMe	C$_{sp^2}$	–	2: C$_{sp^2}$	6: C$_{sp^2}$
90b	WABZEE01[c]	3-Me	OMe	C$_{sp^2}$	–	–	6: C$_{sp^2}$

[a] “*i*: X” means a C$_{pyridinium}$(*i*)···X contact, “*i,j*: X” two such contacts. [b] (Partly) intramolecular. [c] Contacts to a BPh$_4$ counterion, see also Figure 32.

(see Table 13 and Figure 13a; -0.21 Å < *diff* < 0.00 Å; for an example, see Figure 13b). Additionally, one or two contacts between the electron-deficient pyridinium C atoms 2, 4, or 6 and a nucleophilic or electron-rich atom are also found (-0.28 Å < *diff* < $+0.13$ Å).

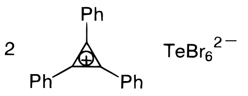


86

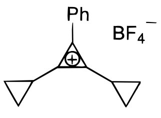
L. Cyclopropenyl Cations

All sterically nonhindered cyclopropenyl cations show some C$^{\delta+}$···X contacts on one side of the cation, and occasionally on both sides (see Table 14 and

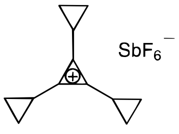
Table 14. Important Features of the Crystal Packing of Cyclopropenyl Cations (91)



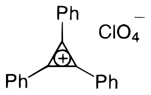
92 (CUGBAH)



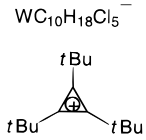
93 (DIJTIZ)



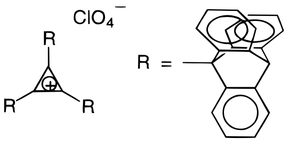
94 (DIJTOF)



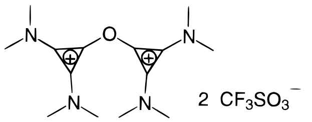
95 (PHPRPC10)



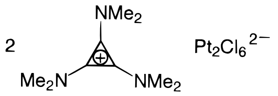
96 (SIYDOT)



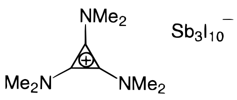
97 (VAWXEW10)



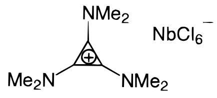
98 (CAFBEQ)



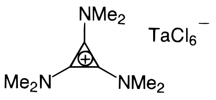
99 (DMCPRP10)



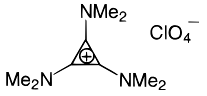
100 (FAFGUO)



101 (KOWGOS)



102 (KOWGUY)



103 (MACPRP10)

	refcode	R^1, R^2, R^3	X^{1a}	X^{2a}
92	CUGBAH	3 Ph	1,2: Br/3: Br[b]	–
93	DIJTIZ	Ph, 2 c-Pr[c]	1–3: C$_{sp^2}$	–
94	DIJTOF	3 c-Pr[c]	1–3: F	1–3: F
95	PHPRPC10	3 Ph	1–3: O	1–3: O
96	SIYDOT	3 *t*-Bu	1,2: Cl	–
97	VAWXEW10	3 9-triptycyl	–[d]	–[d]
98	CAFBEQ	2 NMe$_2$, OR	1,2: O/1: O[b]	1,3: O/2: O[b]
99	DMCPRP10	3 NMe$_2$	1–3: Pt/1–3: Pt[b,e]	–
100	FAFGUO	3 NMe$_2$	1: I	2: I
101	KOWGOS	3 NMe$_2$	1–3: Cl	1–3: Cl
102	KOWGUY	3 NMe$_2$	1–3: Cl	1–3: Cl
103	MACPRP10	3 NMe$_2$	1,2: O	–

[a] “*i*: X” means a C$_{cyclopropenyl}$(*i*)···X contact, “*i,j*: X” two such contacts. [b] Two entries for two molecules in the asymmetric unit. [c] c-Pr = cyclopropyl. [d] Hindered by intramolecular C$_{cyclopropenyl}$···H contacts. [e] Type of the interaction not known.

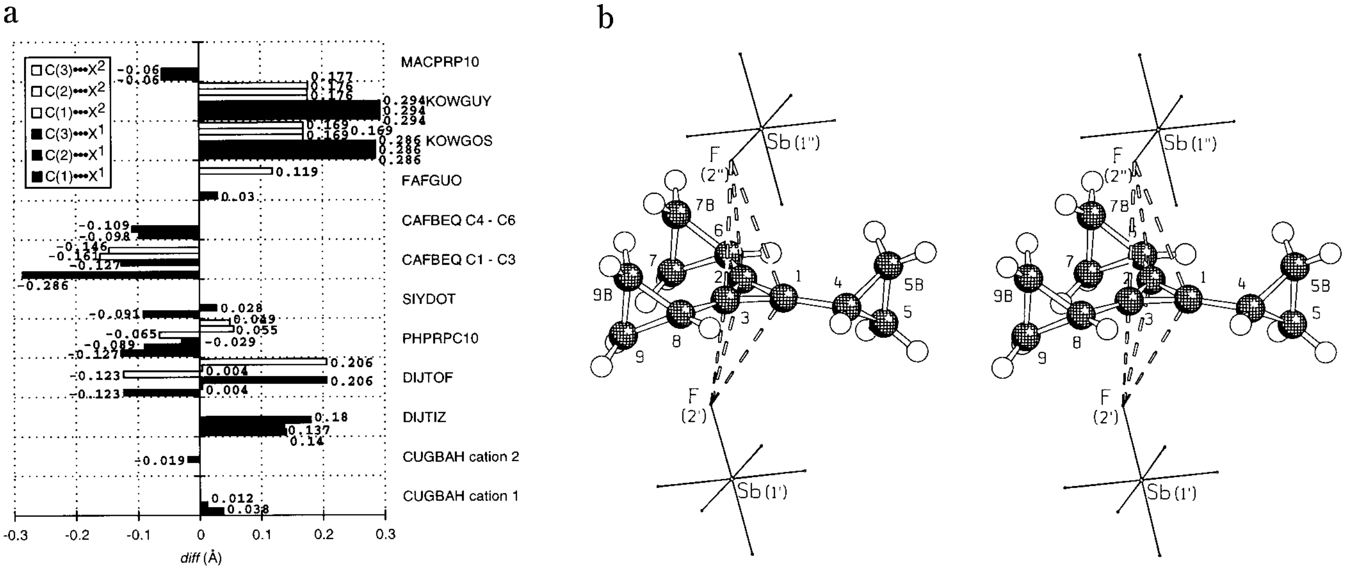
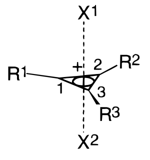


Figure 14. (a) Interactions of the cationic C atoms of cyclopropenyl cations with counterions (**91**); see also Table 14; and (b) stereo ball-and-stick diagram[22] of the structure **94** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: $F(2^I)\cdots C(2)$ 3.05, $C(2)\cdots F(2^{II})$ 3.05, $F(2^I)\cdots C(3)$ 3.17, $C(3)\cdots F(2^{II})$ 3.17, $F(2^I)\cdots C(1)$ 3.38, $C(1)\cdots F(2^{II})$ 3.38.

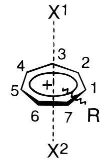
Figure 14a; −0.29 Å < *diff* < +0.29 Å; for an example, see Figure 14b).



91

M. Tropylium Ions

Tropylium ions occasionally show some $C^{\delta+}\cdots X$ contacts on both sides of the cation (see Table 15; for an example, see Figure 15). Sometimes the H atoms on the tropylium ring are involved in C−H···base hydrogen bonds.

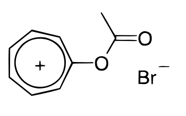


104

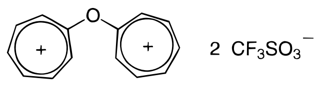
N. Cyclohexadienyl Cations (σ Complexes)

The persubstituted cations resulting from the formal addition of smaller cations to hexamethylbenzene (crystal structures of **112**−**114**) show interactions between some C atoms of the pentadienylium

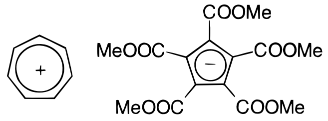
Table 15. Important Features of the Crystal Packing of Tropylium Ions (104)



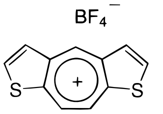
105 (ACTRPB)



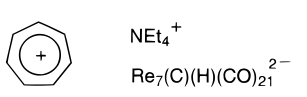
106 (CADZUC)



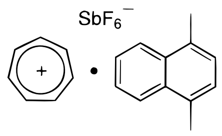
107 (DIVXEL)



108 (DTHTRO)



109 (GEGGAA)



110 (SASNOP)

	refcode	R	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z) or other contacts
105	ACTRPB	1-OAc	Br	O	6 (C,Br)[b]; 1 $C_{acetyl\ sp^2}\cdots Br$
106	CADZUC	1-OR	O	F[c]	–
107	DIVXEL	–	C_{sp^2}, O[d]	C_{sp^2}, O[d]	–
108	DTHTRO	*e*	F	π system[f]	–
109	GEGGAA	–	O[d]	O[d]	–
110	SASNOP	–	π system[g]	π system[g]	5 (C,F)[b]

[a] Number of Y−H···Z hydrogen bonds. [b] Involving only $C_{tropylium}$−H bonds. [c] Weak. [d] Several contacts. [e] Two condensed thiophene rings. [f] Thiophene ring from another cation. [g] 1,4-Dimethylnaphthalene.

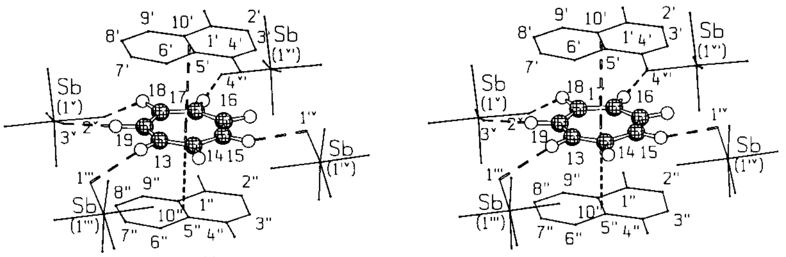
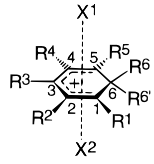


Figure 15. Stereo ball-and-stick diagram[22] of the structure of **110** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: $F(1^{III})\cdots H(13)$ 2.43, $F(1^{IV})\cdots H(15)$ 2.29, $F(4^{VI})\cdots H(17)$ 2.34, $F(2^{V})\cdots H(18)$ 2.52, $F(3^{V})\cdots H(19)$ 2.66, center of the tropylium ion to the centers of the upper and lower dimethylnaphthalene molecules, 3.39 and 3.38, respectively.

fragment and nucleophilic atoms on both sides of the cation (see Table 16 and Figure 16a; -0.08 Å < *diff* < +0.23 Å; for an example, see Figure 16b). The cations derived from 1,3,5-triaminobenzenes show at least one interaction between a substituent at the sp^3-hybridized C(6) and a counterion (C(6)−H···base hydrogen bond or C(6)−C_{sp^3}···X).

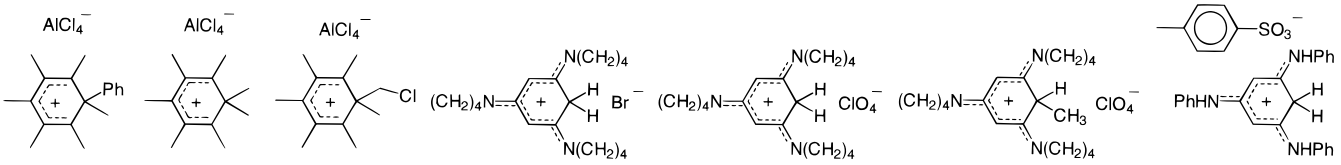


111

O. Cyclobutenyl Cations

The data for cyclobutenyl cations are listed in Table 17 and Figure 17a. The only example of a cyclobute-

Table 16. Important Features of the Crystal Packing of Cyclohexadienyl Cations (111)



112 (COMBIP) **113** (HEBZCA) **114** (SAXCAV) **115** (FEDZIX) **116** (FEDZOD) **117** (FEDZUJ) **118** (WAZYOL)

	refcode	$R^1, ..., R^{5a}$	$R^6, R^{6'}$	X^{1b}	X^{2b}	$n_{Y-H\cdots Z}{}^c$ (Y,Z) or other contacts
112	COMBIP	5 Me	Ph, Me	1,2: Cl	3,4: Cl	–
113	HEBZCA	5 Me	2 Me	2,3: Cl	2,3: Cl	–
114	SAXCAV	5 Me	CH_2Cl, Me	2,3: Cl	3: Cl	–
115	FEDZIX	R, H, R, H, R	2 H	–	–	1 (C(6),Br)
116	FEDZOD	R, H, R, H, R	2 H	–	–	2 (C(6),O)
117	FEDZUJ	R, H, R, H, R	H, Me	–	–	1 (C(6),O); 1 C(6)−C_{sp^3}···O
118	WAZYOL	R′, H, R′, H, R′,	2 H	–	–	2 (C(6),O); 3 (N,O)

[a] R = 1-pyrrolidinyl, R′ = NHPh. [b] "*i*: X" means a $C_{cyclohexadienyl}(i)\cdots X$ contact, "*i*,*j*: X" two such contacts. [c] Number of Y−H···Z hydrogen bonds.

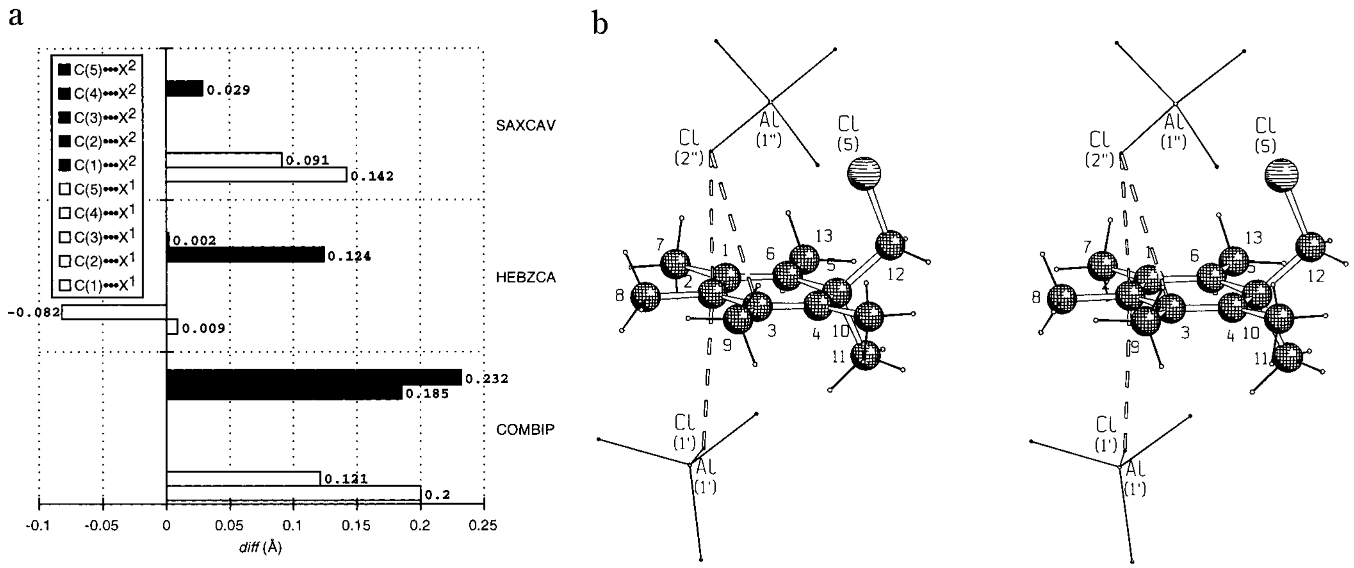
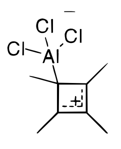
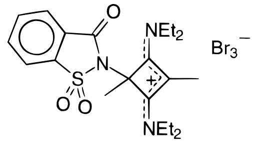


Figure 16. (a) Interactions of the cationic C atoms of cyclohexadienyl cations with counterions (**111**); see also Table 16; and (b) stereo ball-and-stick diagram[22] of the structure of **114** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: $C(2)\cdots Cl(1^{I})$ 3.48, $C(2)\cdots Cl(2^{II})$ 3.54, $C(3)\cdots Cl(2^{II})$ 3.59.

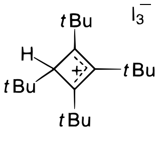
Table 17. Important Features of the Crystal Packing of Cyclobutenyl Cations (119)



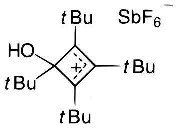
120 (CBUALC)



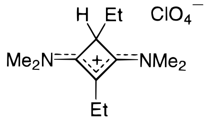
121 (COVSUB10)



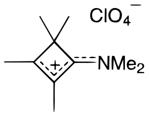
122 (DEJKEI)



123 (DEJKIM)



124 (MAECBA)



125 (MTMCBA)

	refcode	R^1, R^2, R^3	R^4, $R^{4'}$	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z)
120	CBUALC[b]	3 Me	Me, $AlCl_3^-$	Cl	Cl[c]	–
121	COVSUB10	NEt_2, Me, NEt_2	R, Me	O[c]	Br[d]	–
122	DEJKEI	3 *t*-Bu	H, *t*-Bu	–[e]	–[e]	–
123	DEJKIM	3 *t*-Bu	OH, *t*-Bu	–[e]	–[e]	1 (O,F)
124	MAECBA	NMe_2, Et, NMe_2	H, Et	O	–[e]	
125	MTMCBA	NMe_2, Me, Me	2 Me	O	O	–

[a] Number of Y–H···Z hydrogen bonds. [b] A zwitterion. [c] Intramolecular. [d] Weak. [e] Sterically hindered.

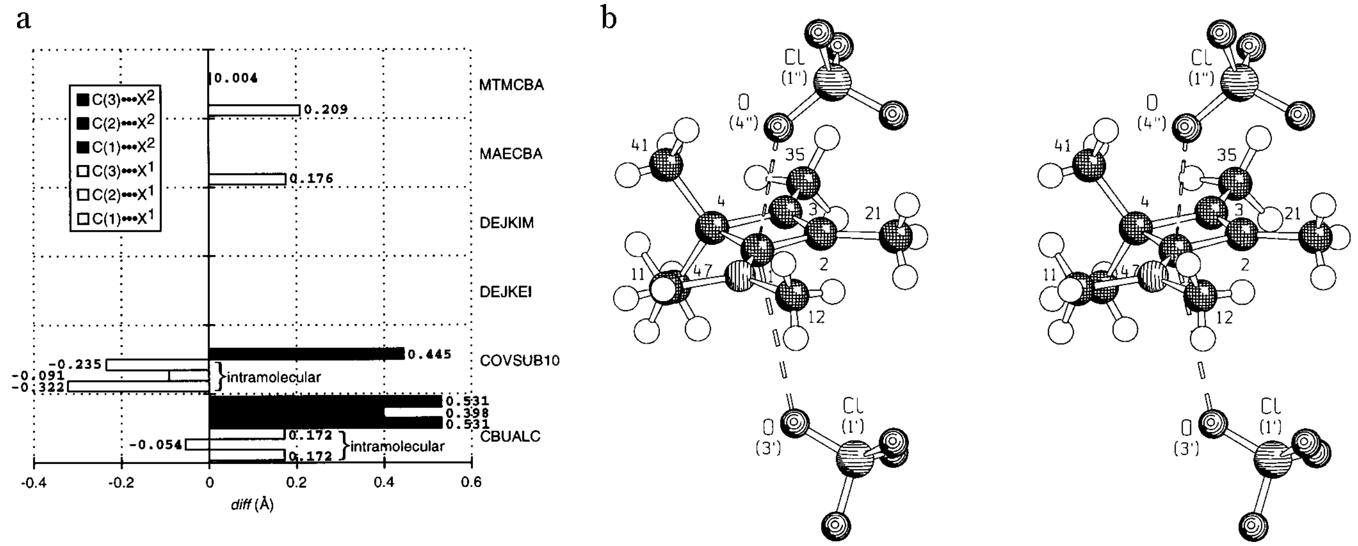
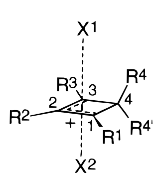


Figure 17. (a) Interactions of the cationic C atoms of cyclobutenyl cations with counterions (**119**); see also Table 17; and (b) stereo ball-and-stick diagram[22] of the structure of **125** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)···O(3^I) 3.43, C(1)···O(4^{II}) 3.22.

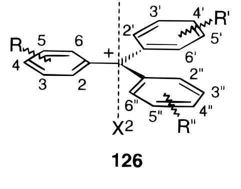
nyl cation which is sterically not hindered on both sides (crystal structure of **125**, see Figure 17b) shows two interactions of the cationic π system with nucleophilic atoms (*diff* 0.00 Å, 0.21 Å). The systems that are hindered on one side show one intermolecular contact with nucleophilic atoms on the free side (crystal structures of **120**, **121**, and **124**; closest contacts 0.18 Å < *diff* < 0.45 Å).



119

P. Trityl Cations

In six different salts, the unsubstituted trityl cation shows, at least on one side of the cation, a contact between the central C atom and a nucleophilic atom from a counterion (see Table 18 and Figure 18a; +0.03 Å < *diff* < +0.47 Å; for an example, see Figure 18b and also Figure 35 in Appendix C). Substituents acting as π donors reduce these interactions particularly if they are involved in hydrogen bonds (see crystal structure of **127**).



126

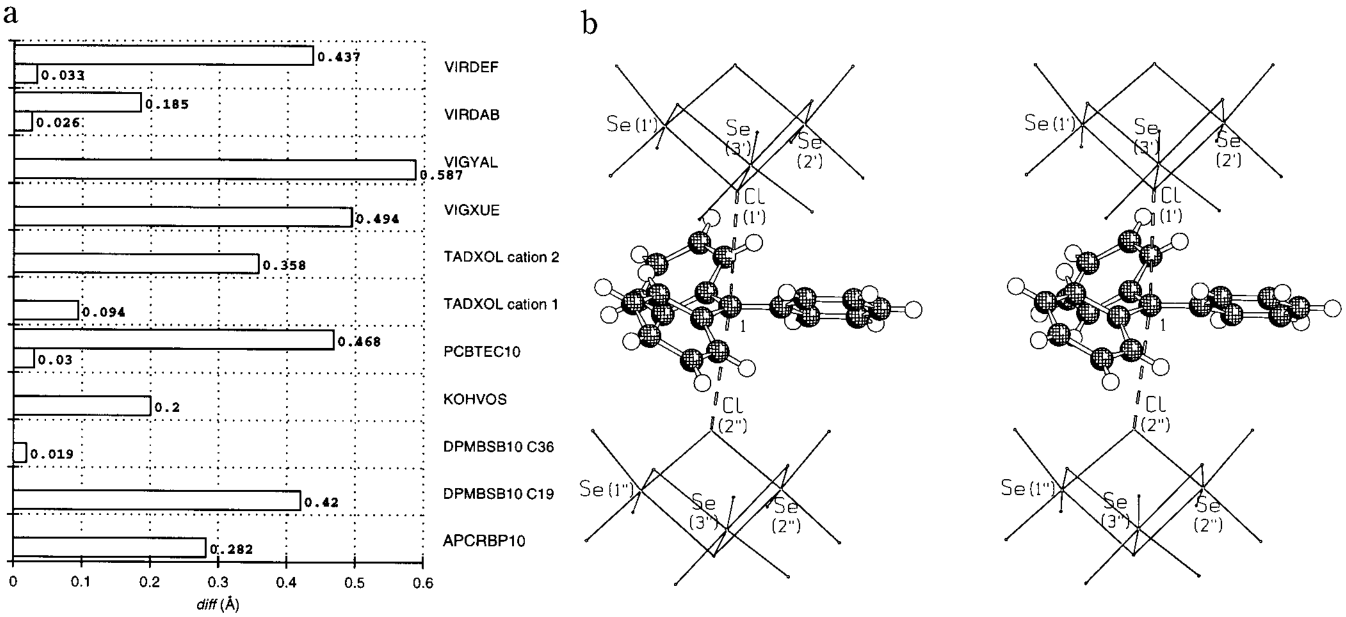
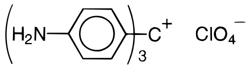
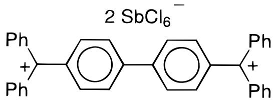


Figure 18. (a) Interactions of the cationic C atoms of trityl cations with counterions (**126**); see also Table 18; and (b) stereo ball-and-stick diagram[22] of the structure of **136** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(1)···Cl(1^{I}) 3.48, C(1)···Cl(2^{II}) 3.64.

Table 18. Important Features of the Crystal Packing of Trityl Cations (126)



127 (APCRBP10)

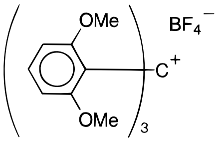


128 (DPMBSB10)

$AuCl_4^-$

Ph_3C^+

129 (KOHVOS)



130 (KUBLUO)

$Te_3Cl_{13}^-$

Ph_3C^+

131 (PCBTEC10)

$Hf_2Cl_{10}^{2-}$

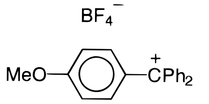
$2\ Ph_3C^+$

132 (TADXOL)

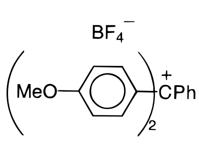
ClO_4^-

Ph_3C^+

133 (TIPMEP)



134 (VIGXUE)



135 (VIGYAL)

$Se_3Cl_{13}^-$

Ph_3C^+

136 (VIRDAB)

$Se_3Br_{13}^-$

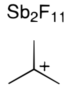
Ph_3C^+

137 (VIRDEF)

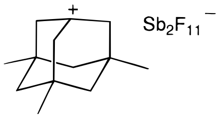
refcode	R, R′, R″	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z)
127 APCRBP10	4,4′,4″-(NH$_2$)$_3$	C$_{sp^2}$	–	3 (N,O)
128 DPMBSB10	4-aryl	Cl	–	–
129 KOHVOS	–	Cl	–	–
130 KUBLUO	2,6,2′,6′,2″,6″-(OMe)$_6$	–[b]	–	–
131 PCBTEC10	–	Cl	Cl[c]	–
132 TADXOL	–	Cl	–	–
133 TIPMEP	–	O[d]	O[d]	–
134 VIGXUE	4-OMe	O[d]	–	–
135 VIGYAL	4,4′-(OMe)$_2$	O[e]	–	–
136 VIRDAB	–	Cl	Cl	–
137 VIRDEF	–	Br	Br[c]	–

[a] Number of Y–H···Z hydrogen bonds. [b] Sterically hindered. [c] Weak. [d] From disordered ClO$_4$ anions. [e] Very weak.

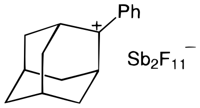
Table 19. Important Features of the Crystal Packing of Aliphatic, Alicyclic, and Benzylic Cations without 3c–2e Bonds (138)



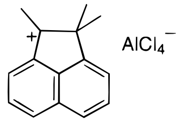
139 (PESGID)



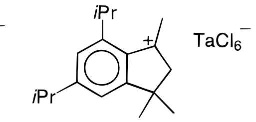
140 (DOPRIJ)



141 (SUNMOD)



142 (DIFMEK)



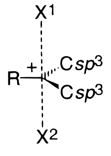
143 (SODREI)

	refcode	R	X^1	X^2	$n_{Y-H\cdots Z}$[a] (Y,Z) or other contacts
139	PESGID	C$_{sp^3}$	F	F	9 (C,F)
140	DOPRIJ	C$_{sp^3}$	F	–[b]	–
141	SUNMOD	Ph	F	–[c]	–
142	DIFMEK	aryl	Cl[d]	Cl[d]	2 C$_{methyl}$···F
143	SODREI	aryl	Cl	Cl	6 C$_{aryl}$···Cl

[a] Number of Y–H···Z hydrogen bonds. [b] Interaction impossible because of the cage structure. [c] Sterically hindered. [d] Weak.

Q. Aliphatic, Alicyclic, and Benzylic Cations without Three-Center, Two-Electron (3c-2e) Bonds

The only aliphatic cation (crystal structure of **139**, see Table 19 and Figure 19a,b) shows interactions



138

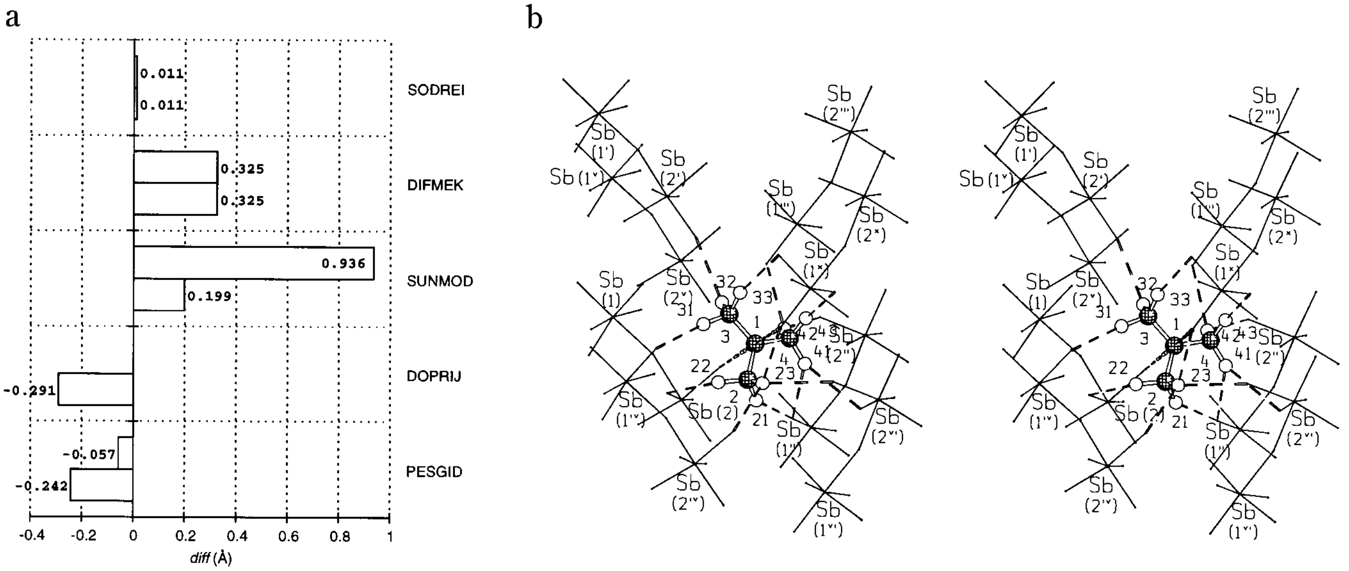


Figure 19. (a) Interactions of the cationic C atoms of aliphatic, alicyclic, and benzylic cations without 3c-2e bonds with counterions (**138**); see also Table 19; and (b) stereo ball-and-stick diagram[22] of the structure of **139** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: F(23)···C(1) 2.93, C(1)···F(11^{X}) 3.11, H(21)···F(12^{II}) 2.59, F(24)···H(22) 2.60, H(23)···F(23^{IV}) 2.62, H(23)···F(25^{VI}) 2.62, H(23)···F(11^{X}) 2.56, H(31)···F(15^{IV}) 2.36, H(32)···F(21^{I}) 2.54, H(33)···F(13^{X}) 2.63, H(41)···F(12^{II}) 2.58, H(41)···F(24^{VI}) 2.66, H(42)···F(25^{II}) 2.40, H(42)···F(11^{III}) 2.65, H(43)···F(14^{X}) 2.29.

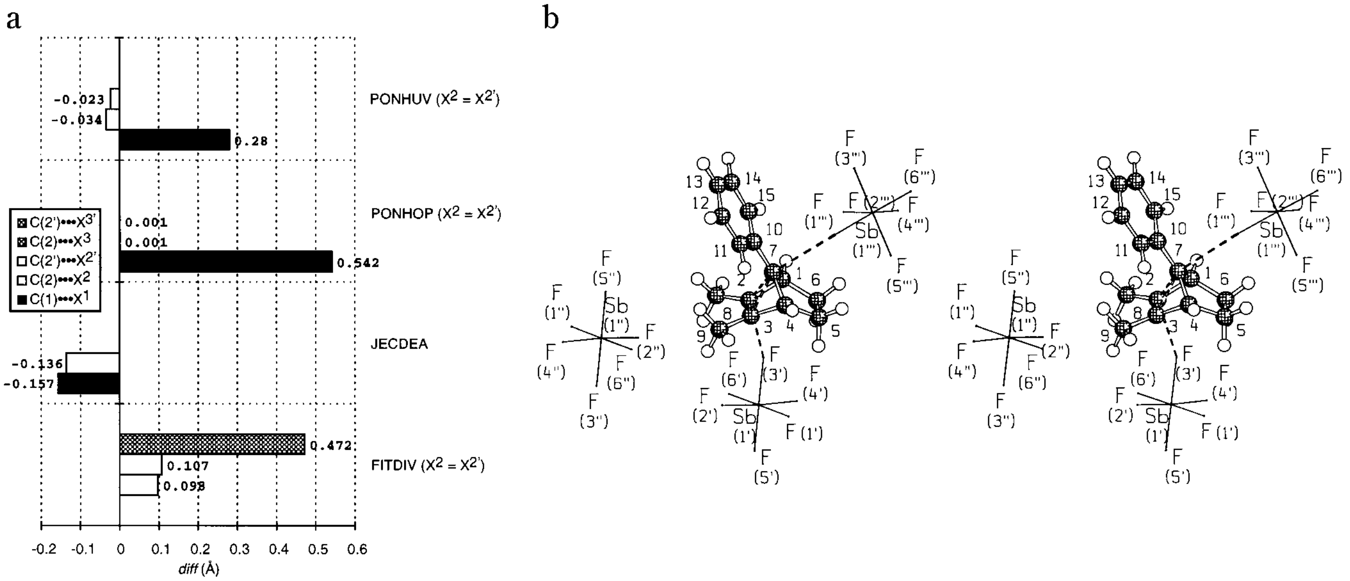
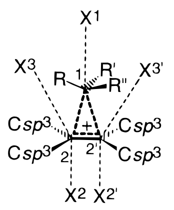


Figure 20. (a) Interactions of the cationic C atoms of carbocations with 3c-2e bonds with counterions (**144**); see also Table 20; and (b) stereo ball-and-stick diagram[22] of the structure of **146** and its environment in the crystal. The following distances (in Å) are represented by dashed bonds: C(2)···C(7) 1.86, C(3)···C(7) 1.86, C(2)···F(3^{I}) 3.03, C(7)···F(1^{III}) 3.01.

between the cationic C atom and F atoms on both sides of the cation (*diff* −0.24 Å, −0.06 Å), and all nine H atoms are involved in C−H···F hydrogen bonds. The cage structure of the 1-adamantyl cation (crystal structure of **140**) allows a C^{+}···F interaction only on the free side of C(1) with *diff* = −0.29 Å. The bent C(2) bridge of the somewhat sterically hindered 2-phenyl-2-adamantyl cation (crystal structure of **141**) allows a C^{+}···F contact on the C(2) side with *diff* = +0.20 Å, the other side is sterically hindered due to the deformation of the cation (*diff* = +0.94 Å). The benzylic cations (crystal structures of **142** and **143**) show C^{+}···Cl interactions on both sides (*diff* +0.33 Å, +0.01 Å).

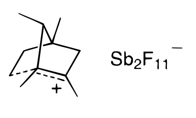
R. Carbocations with 3c-2e Bonds

The pentacoordinate C(1) (see formula **144**) has, in two of the four structures (see Table 20 and Figure 20a; for an example, see Figure 20b), contact to a

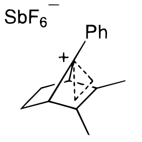


144

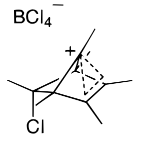
Table 20. Important Features of the Crystal Packing of Carbocations with 3c−2e Bonds (144)



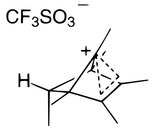
145 (FITDIV)



146 (JECDEA)



147 (PONHOP)



148 (PONHUV)

	refcode	R, R′, R″	X^1	X^2	$X^{2'}$	X^3	$X^{3'}$
145	FITDIV	C_{sp^3}, 2 H	–	F	F[a]	F	–[b]
146	JECDEA	Ph, 2 C_{sp^3}	F	F	–	–[b]	–[b]
147	PONHOP	3 C_{sp^3}	–[b]	Cl	Cl[a]	–[b]	–[b]
148	PONHUV	3 C_{sp^3}	O	F	F[a]	–[b]	–[b]

[a] X^2 and $X^{2'}$ are the same atom. [b] Sterically hindered.

nucleophilic atom X^1 (*diff* −0.16 Å, +0.28 Å). All cations show an interaction between a nucleophilic atom (X^2) and at least one of the two tetracoordinate atoms C(2) and C(2′) from the bottom (−0.14 Å < *diff* < +0.11 Å). The unsymmetrical 3c-2e bond of the substituted 2-norbornyl cation (crystal structure of **145**) allows a weak C(2)···X^3 interaction with *diff* = +0.47 Å, the corresponding C(2′)···$X^{3'}$ interaction is sterically impossible.

III. Discussion

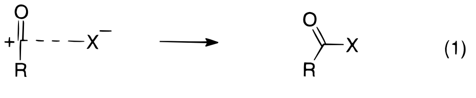
A. Analysis and Interpretation of the Contacts

1. Dicoordinate Carbon Atoms in Carbocations

A statistical analysis of the geometry of the contacts between the cationic C atoms of acylium ions and the nearest anions (see Figure 21) shows that the C−C···X angles (α_1) lie in the range between 85° and 110°. In the closer contacts, α_1 seems to converge to values between 85° and 90°, see left side of Figure 21a. Unfortunately up to now, no other kind of dicoordinate carbocations with ordered anions in the crystal has been investigated by X-ray crystallography.

The $C^{\delta+}$···X contacts may be interpreted in terms of pure electrostatic interactions or charge-transfer complexes. The accumulation of these contacts also allows a dynamical interpretation according to Bürgi and Dunitz,[11] i.e., the structures can be seen as early points on the reaction coordinate of reaction 1 (see also **A** in Chart 1).

Nucleophiles add easily to acyl cations to yield acid derivatives (reaction 1). The circular arrangement



$$\overset{\displaystyle O}{\underset{\displaystyle R}{\overset{\|}{\overset{+}{C}}}}\text{---}X^- \longrightarrow \overset{\displaystyle O}{\underset{\displaystyle R}{C}}\text{—}X \qquad (1)$$

of the nucleophilic atoms corresponds to the rotation-symmetrical electron density in the acylium group which is isoelectronic with a nitrile.

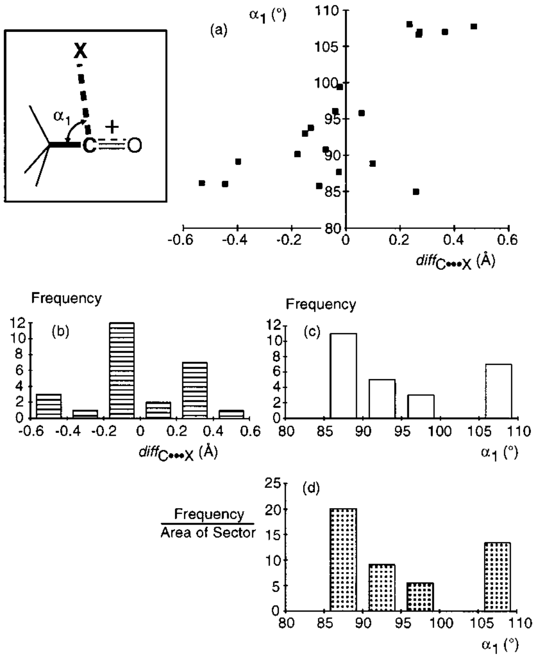


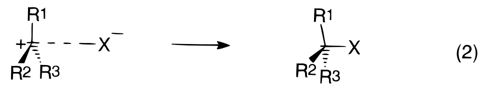
Figure 21. Statistical analysis of the contacts between the dicoordinate C atoms of acylium ions and anions. For the definition of the variables see formula on the inset. (a) Scatterplot of α_1 vs $diff_{C\cdots X}$; (b) histogram of $diff_{C\cdots X}$; (c) histogram of α_1; (d) normalized histogram of α_1 (for the normalization see Appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S7.

2. Tricoordinate Carbon Atoms in Carbocations

A statistical analysis of the geometry of the contacts between the cationic C atoms of tricoordinate carbocations and the nearest anions (see Figure 22) shows that the angles between the symmetry axis of the empty p orbital and the C···X vector (α_2) lie in the range between 0° and 51°. It follows from Figure 22d that the probability density distribution of α_2 is not uniform, but that it has a maximum at 0°, decreases with higher values of α_2, and is very small for $\alpha_2 > 30°$ For the closer contacts, α_2 seems to converge to 0°, see left side of Figure 22a.

A dynamical interpretation is also possible in this case. The limit of 0° for α_2 in the close contacts agrees with the expectation of the beginning formation of a covalent C−X bond. Tricoordinate carbocations are generated in many solvolysis reactions and yield products with a tetracoordinate C atom according to reaction 2 (see also **B** in Chart 1); other products resulting from deprotonation, rearrangement, or fragmentation are of course also possible.

The interaction of these cations, with nucleophilic atoms on both sides, corresponds to the loss of stereochemical information often occurring in S_N1 reactions. The nucleophilic attack on the carbonyl and on the electron-deficient pyridinium C atoms[28] observed in the *N*-acylpyridinium salts may also be seen as examples for reaction 2.



$$\overset{\displaystyle R1}{\underset{\displaystyle R2\ R3}{\overset{+}{C}}}\text{---}X^- \longrightarrow \overset{\displaystyle R1}{\underset{\displaystyle R2\ R3}{C}}\text{—}X \qquad (2)$$

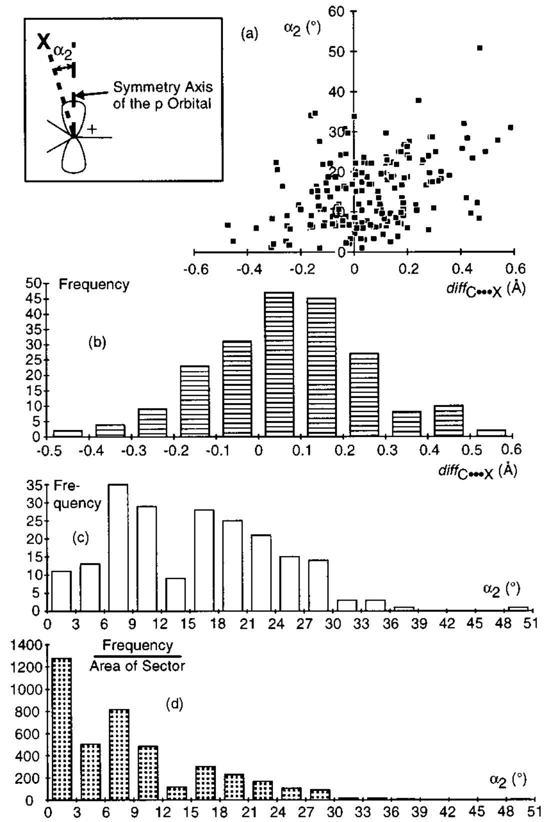


Figure 22. Statistical analysis of the contacts between tricoordinate C atoms and anions. For the definition of the variables see formula on the inset; it is assumed that the direction of the symmetry axis of the empty p orbital at the cationic C atom coincides with the direction of the normal of the least-squares plane defined by the cationic C atom and its three bond partners. (a) Scatterplot of α_2 vs $diff_{C\cdots X}$; (b) histogram of $diff_{C\cdots X}$; (c) histogram of α_2; (d) normalized histogram of α_2 (for the normalization see Appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S8.

3. Tetracoordinate Carbon Atoms in Carbocations

The crystal structures with tetracoordinate carbon atoms (see Figure 23 and Chart 3) are scattered over the various cation types discussed in the section II. The examples with the following groups G are **32**–**36** and **135** (G = O, see also ref 25); **84** (G = S), **103**, **22** (G = NR), and **142**, **117** (G = CR$_2$). A statistical analysis of the geometry of the contacts between the tetracoordinate C atoms of carbocations and the nearest anions shows that the angles between the G–C bond and the C•••X vector (α_3) lie in the range between 130° and 180°. It follows from Figure 23d that the probability density distribution of α_3 is not uniform, but that it has a maximum at 180° and decreases with smaller values of α_3.

This observation agrees with the dynamical interpretation of the structures as points on a S$_N$2 reaction coordinate (backside attack; Walden inversion; see also **C** in Chart 1). The S$_N$2 reaction 3 is less common but known for example as special case 3a in sugar chemistry: neighboring group participation by acetate groups[29] leads to intermediate 1,3-dioxolan-2-

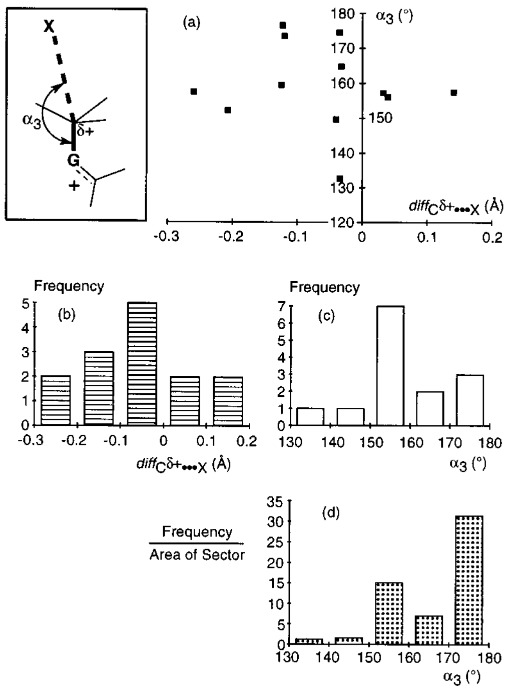
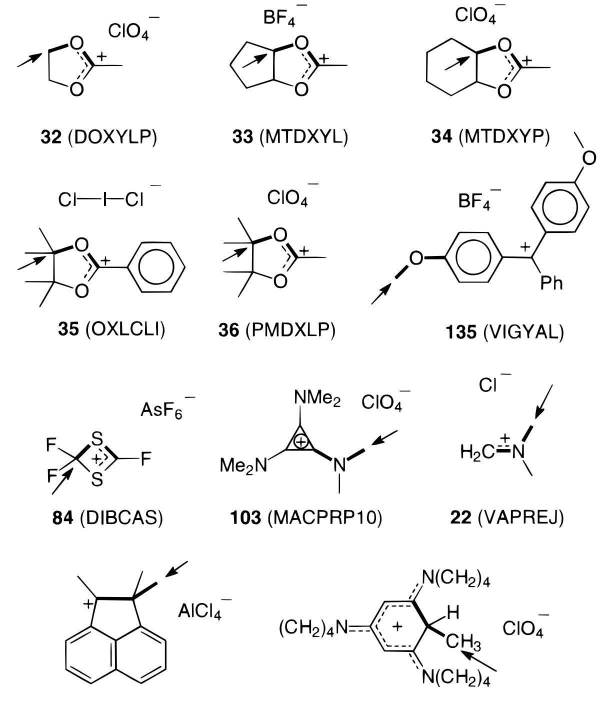


Figure 23. Statistical analysis of the contacts between tetracoordinate C atoms bonded to G (see formula on the inset) and anions. (a) Scatterplot of α_3 vs $diff_{C\cdots X}$; (b) histogram of $diff_{C^{\delta+}\cdots X}$; (c) histogram of α_3; (d) normalized histogram of α_3 (for the normalization see Appendix B). The formulas and refcodes of the structures are given in Chart 3. The numerical data used for this figure can be found in the Supporting Information in Table S9.

Chart 3. Compounds with Contacts between Tetracoordinate C Atoms Bonded to G and Anions (see Figure 23)[a]



32 (DOXYLP) **33** (MTDXYL) **34** (MTDXYP)

35 (OXLCLI) **36** (PMDXLP) **135** (VIGYAL)

84 (DIBCAS) **103** (MACPRP10) **22** (VAPREJ)

142 (DIFMEK) **117** (FEDZUJ)

[a] The thick bonds connect the chain C_{sp^3}–G–C_{sp^2}; the arrow indicates the direction of the attack of X.

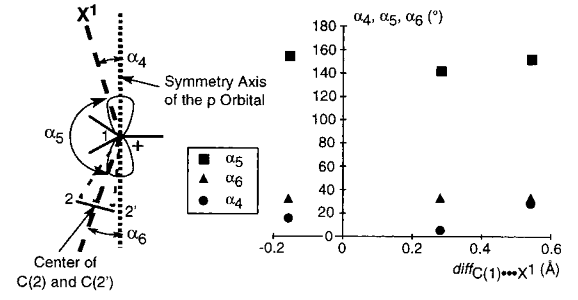
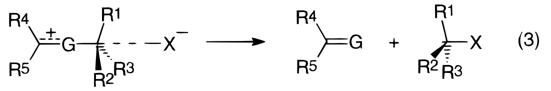


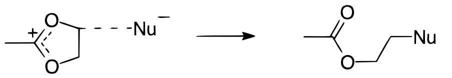
Figure 24. Statistical analysis of the contacts between pentacoordinate atoms C(1) and anions. For the definition of the variables see the formula. The direction of the symmetry axis of the p-like orbital at C(1) is approximately computed as the normal of the least-squares plane defined by C(1) and its three single bond partners, i.e., the bond partners C(2) and C(2′) involved in the 3c-2e bond are ignored. The formulas and refcodes of the structures are given in Chart 4. The numerical data used for this figure can be found in the Supporting Information in Table S10.

ylium ions which undergo ring opening upon nucleophilic attack.[30]



(3)

(G = O, S, NR, CR$_2$)

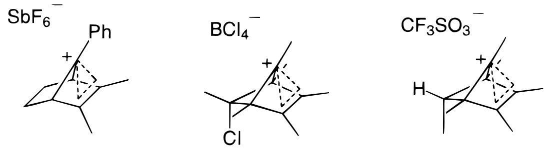


(3a)

4. Pentacoordinate Carbon Atoms in Carbocations

Only three crystal structures of carbocations with pentacoordinate C atoms and anion contacts at these atoms are presently known (**146**−**148**, Chart 4).

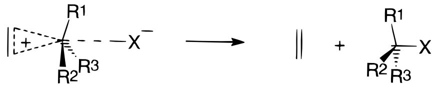
Chart 4



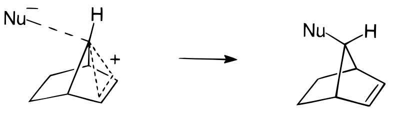
146 (JECDEA) **147** (PONHOP) **148** (PONHUV)

Because of their similar bicyclic structures, the angles α_4, α_5, and α_6 do not scatter very much (see Figure 24).

The S$_N$2-like reaction 4 (see also **D** in Chart 1) is observed in the solvolysis of 7-norbornenyl cations, if the nucleophile comes from the 7-anti direction[13a] (reaction 4a).



(4)

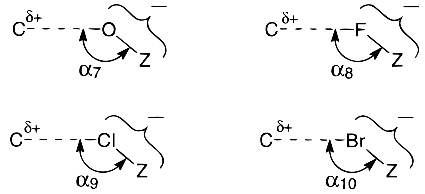


(4a)

5. Oxygen and Halogen Atoms of Anions Coordinated to Cationic Carbon Atoms

The statistical analysis of the angles α_7 to α_{10} (see Chart 5) at the oxygen or halogen atoms of complex anions, which are coordinated to cationic C atoms, shows that there are clear preferences for particular values of these angles.

Chart 5. Definition of the Angles α_7 to α_{10}[a]



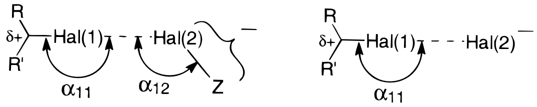
[a] C$^{\delta+}$ can be di-, tri-, tetra-, or pentacoordinate. Z is the direct bond partner of the O or Hal atom in a larger molecule (in most cases an anion).

The following mean values were computed from the data in the histograms in part a of Figure 25A−D: $\langle C^{\delta+}\cdots O{-}Z\rangle \equiv \langle a_7\rangle = 119(3)°$, $\langle C^{\delta+}\cdots F{-}Z\rangle \equiv \langle a_8\rangle = 131(2)°$, $\langle C^{\delta+}\cdots Cl{-}Z\rangle \equiv \langle a_9\rangle = 114(2)°$, $\langle C^{\delta+}\cdots Br{-}Z\rangle \equiv \langle a_{10}\rangle = 107(5)°$. These angles agree with the assumption that the nucleophilicity of oxygen or halogen atom is high in those directions which coincide approximately with the directions of the symmetry axes of lone pair orbitals.

6. Halogen Atoms Bonded to Cationic Carbon Atoms

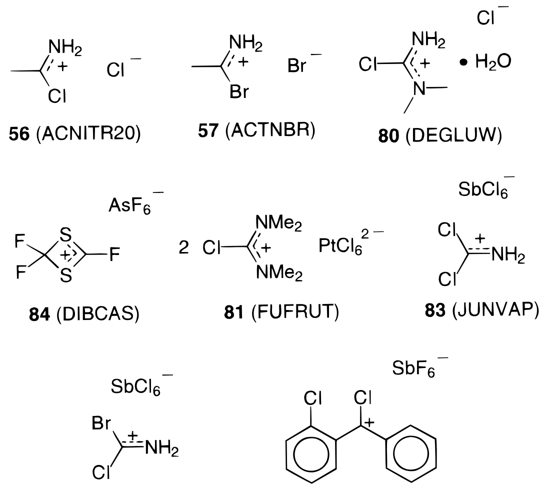
Bent, in his landmark review[31] in 1968, analyzed the structure of crystalline iodine and concluded that “the ‘bond’ angles I−I*⋯I are approximately 90° when the central atom of the interaction, atom I*, is acting as an electron donor, and approximately 180° when the central atom is acting as an electron acceptor”. Many other complexes between neutral molecules, in which a halogen atom acts as an electron acceptor, are listed in Bent’s review. The same argument was used for the explanation of the

Chart 6. Definition of the Angles α_{11} and α_{12}[a]



[a] R and R′ can be any substituent. In the left formula, Z is the direct bond partner of Hal(2) in a larger molecule (in most cases an anion), see Figure 26A. α_{12} is not defined when Hal(2)$^-$ is a halide anion (right formula).

Chart 7



56 (ACNITR20) **57** (ACTNBR) **80** (DEGLUW)

84 (DIBCAS) **81** (FUFRUT) **83** (JUNVAP)

82 (LAFMEK) **23** (YAMWOY)

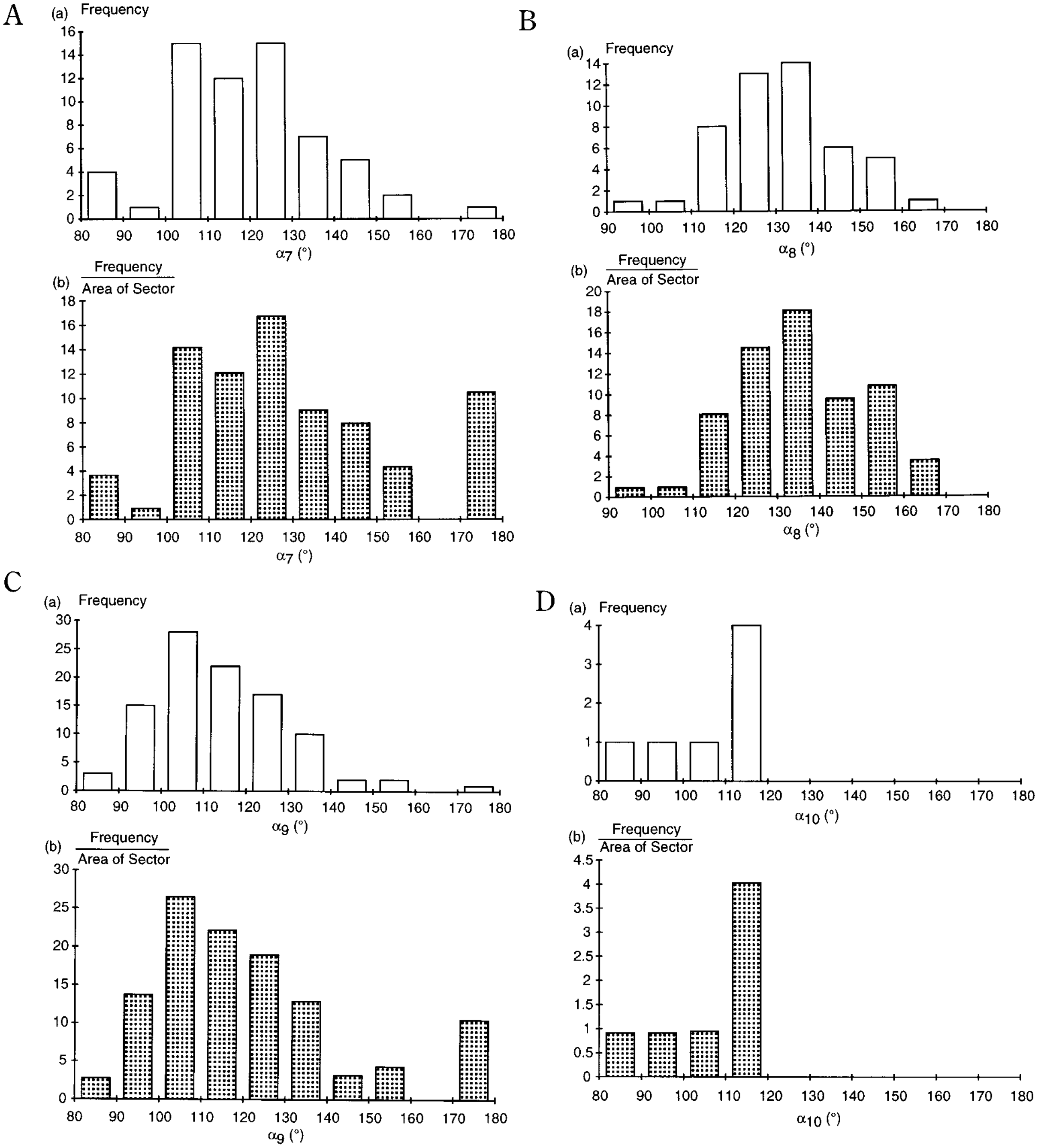


Figure 25. (A) Histogram of the angles α_7 (anions: SO_3F^-, $CF_3SO_3^-$, ClO_4^-, NO_3^-, HSO_4^-, $(CH_3SO_2)_2N^-$, $R-S(=S)-O^-$, an iron–carbonyl complex). (a) Histogram of α_7; (b) normalized histogram of α_7 (for the normalization see appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S3. (B) Histogram of the angles α_8 (anions or groups containing F–Z: AsF_6^-, SbF_6^-, $Sb_2F_{11}^-$, BF_4^-, $CF_3SO_3^-$, intermolecular contact with a C–F group). (a) Histogram of α_8; (b) normalized histogram of α_8 (for the normalization see appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S4. (C) Histogram of the angles α_9 (anions $SbCl_6^-$, $AlCl_4^-$, $GaCl_4^-$, $PtCl_6^{2-}$, $MoOCl_4^-$, $AuCl_4^-$, $NbCl_6^-$, $TaCl_6^-$, ICl_2^-, ICl_4^-, $Te_3Cl_{13}^-$, $R-WCl_5^-$, $Hf_2Cl_{10}^{2-}$, BCl_4^-, $R-AlCl_3^-$). (a) Histogram of α_9; (b) normalized histogram of α_9 (for the normalization see appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S5. (D) Histogram of the angles α_{10} (anions $SbBr_6^-$, Br_3^-, $TeBr_6^{2-}$, $Se_3Br_{13}^-$). (a) Histogram of α_{10}; (b) normalized histogram of α_{10} (for the normalization see appendix B). The refcodes and the numerical data used for this figure can be found in the Supporting Information in Table S6.

angles α_7 to α_{10} at the donor O and Hal atoms discussed in the previous section (III.A.5).

The statistical analysis of the angles α_{11} and α_{12} in carbocation···anion contacts (see Charts 6 and 7) is shown in Figure 26A–D.

The $C^{\delta+}$–Hal(1)···Hal(2)–Z (Z is missing if Hal(2) is a halide anion) contacts observed in all structures with the $C^{\delta+}$–Hal(1) fragment discussed here are remarkable because of the nearly linear $C^{\delta+}$–Hal(1)···Hal(2) (mean value $\langle a_{11}\rangle = 166(3)°$), but bent Hal(1)···Hal(2)–Z fragments (mean value $\langle a_{12}\rangle = 108(4)°$). This geometry agrees with a nucleophilic attack[32] of Hal(2) on Hal(1), i.e., the beginning of reaction 5. For the interpretation of the contacts in

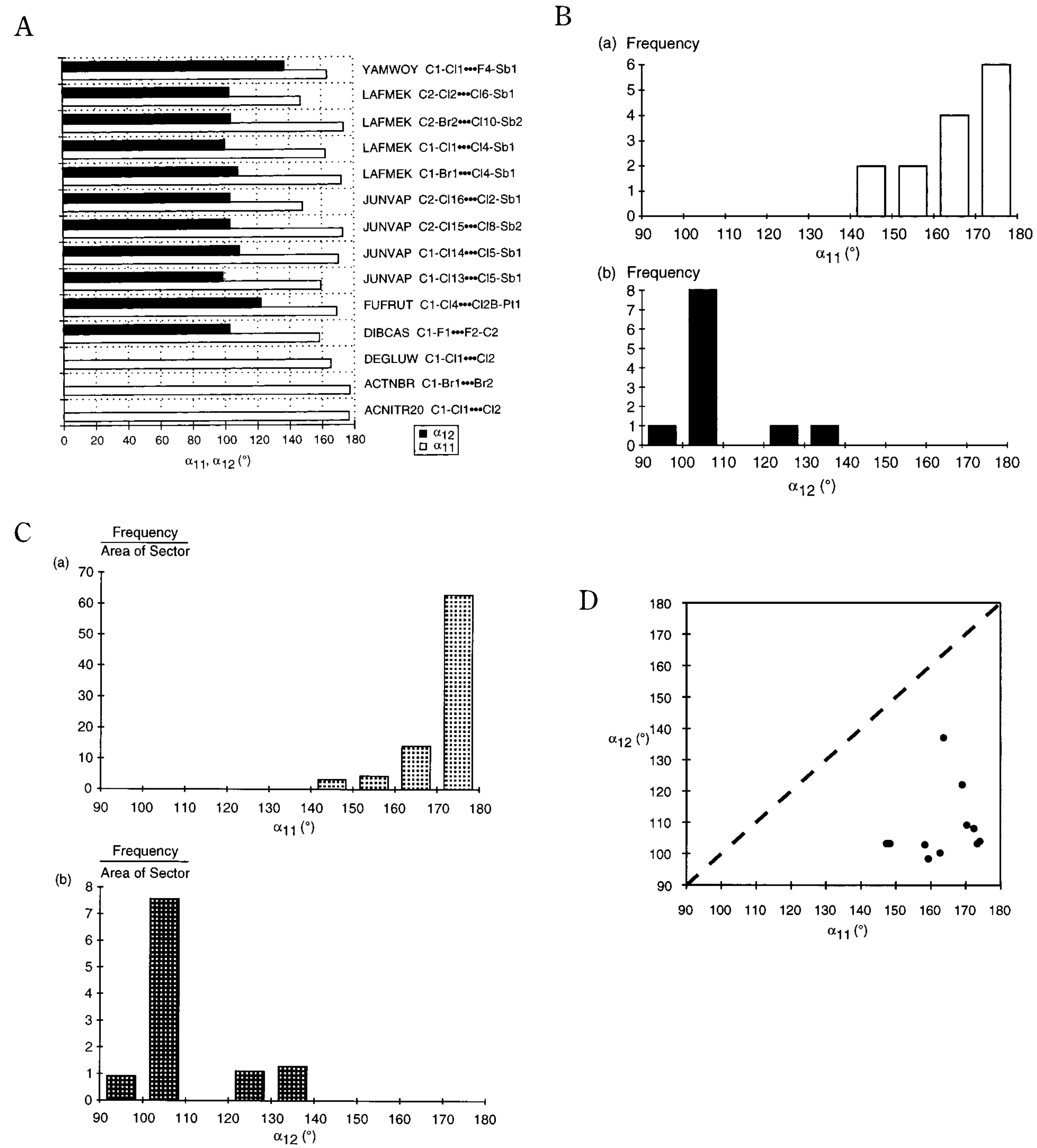
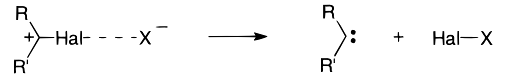
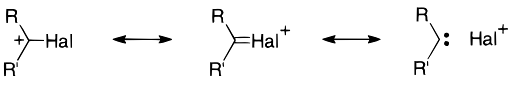


Figure 26. (A) Halogen···halogen interactions involving halogen substituted carbocations. The angles α_{11} and α_{12} are defined in Chart 6. The atoms $C^{\delta+}$–Hal(1)···Hal(2)[–Z] are given behind the refcodes; the formulas are shown in Chart 7; for the atom numbering and the numerical data see Table S2 in the Supporting Information. (B) Histograms of the angles α_{11} and α_{12}. (C) Normalized histograms of the angles α_{11} and α_{12}. For the normalization see Appendix B. (D) Scatterplot of α_{11} vs α_{12}. The dashed line is the function $\alpha_{12} = \alpha_{11}$.

the examples discussed here, it is helpful that one can make some assumptions about the charges of the halogen atoms (see eq 5a). Such an assumption is not straightforward if Hal···Hal contacts between neutral molecules are investigated. Hal(1) may have some positive charge due to the neighboring $C^{\delta+}$, while Hal(2) often belongs to an anion or is an anion and thus may have some negative charge.[33] Therefore it is probable that Hal(1) acts as an electrophile and Hal(2) as a nucleophile. Thus the analysis of the Hal···Hal interactions in charged species seem to support the hypothesis of specific attractive forces (nucleophile–electrophile interactions) between Hal atoms in the present debate on the nature of these interactions.[32b] It must be mentioned that the high



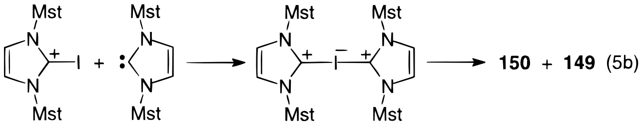
(5)



(5a)

nucleophilicity of Hal atoms in particular directions agrees with the ellipsoidal van der Waals surfaces[24] ("polar flattening" of the van der Waals surface).

Which examples can be found for reaction 5? $CH_2I^+\cdots I^-$ is discussed as intermediate in the photochemical carbene generation from CH_2I_2 in the presence of olefins,[34] leading to cyclopropanes and I_2. However, there is evidence in the recent literature that this reaction follows a concerted I_2 elimination.[35] An example for the reverse direction of reaction 5 has been studied: Kuhn et al. found that an imidazol-2-ylidene yields upon reaction with iodine the corresponding 2-iodoimidazolium iodide.[36] Several crystal structure analyses of 2-iodoimidazolium cations with iodine-containing anions have been reported. Arduengo et al.[37] found a $C^{\delta+}-I(1)\cdots I(2)-I(3)-I^-$ interaction with $I(1)\cdots I(2) = 3.310$ Å (i.e., $diff_{I\cdots I} = -0.65$ Å), $C^{\delta+}-I(1)\cdots I(2) = 173.1°$, $I(1)\cdots I(2)-I(3) = 90.2°$, and they also reported the structure of the corresponding stable carbene.[38] Similar values are observed in the structure of Kuhn et al.:[36] $(C^{\delta+}-)I\cdots I^- = 3.348$ Å (i.e., $diff_{I\cdots I} = -0.61$ Å), $C^{\delta+}-I\cdots I^- = 176.0°$. A particularly interesting example with respect to the carbene formation is the bis(carbene) adduct of I^+, **151**, which can be considered as an intermediate in the degenerate reaction of the iodo-substituted carbocation **149** with the carbene **150**, see reaction 5b. The crystal structures of **149** and **151** have been reported by Arduengo et al.[39]



149 **150** **151**

Mst = Mesityl = 2,4,6-Trimethylphenyl

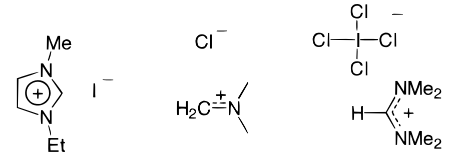
The C–I bond lengths in **149** are 2.042–2.115 Å (several crystallographically independent ions), and in **151**, 2.287 and 2.365 Å (C–I–C = 177.5°). Thus these structures can be considered as points on the reaction coordinate of eq 5.

7. Hydrogen Atoms in C^+–H Fragments

Hydrogen bonds of the type $RR'C^+-H\cdots X$ are structurally closely related to the $RR'C^+-Hal(1)\cdots Hal(2)$ contacts discussed in the previous section (III.A.6). There are three examples of N-substituted carbocations in the data set investigated in the present study, see Table 21 and Figure 27.

Such $C-H\cdots X$ hydrogen bonds can be seen as initial phases of a deprotonation leading to a carbene, see reaction 6, and a resonance contribution according to eq 6a could explain some positive charge on the H atom. Formally, the positive charge on the H atoms of the ammonium ion can be explained similarly (equation 6b). Indeed the deprotonation of the formamidinium ion **152** with LDA (reaction 6c) has been reported recently, and even the crystal structure of the resulting carbene **153** could be determined.[40] The ion **152** is very similar to the cation in **54** (Table 21) which is involved in a $C-H\cdots Cl$ hydrogen bond. Arduengo et al. have shown that imidazole-derived carbenes are very stable,[38] and the $C-H\cdots I$ hydrogen bond in **44** also seems to indicate the beginning of a deprotonation leading to an imidazol-2-ylidene. The reaction of the imidazolium ion **154** with the imid-

Table 21. Structural Data of $C^+-H\cdots X$ Hydrogen Bonds in Ion Pairs of the Type $RR'C^+-H\cdots X$, Where R or R′ are Amino Groups and X Is or Belongs to an Anion



44 (DUVZAV) **22** (VAPREJ) **54** (VIMPOW)

	refcode	R, R′ [a]	X	$diff_{H\cdots X}$ [b]	$C^+-H\cdots X$ [c]
44	DUVZAV	2 NR^1R^2	I	−0.25	144
22	VAPREJ	H, NMe_2	Cl	−0.10	146
54	VIMPOW	2 NMe_2	Cl	−0.43	170

[a] See also reaction 6 or **F** in Chart 1. [b] In angstroms. [c] In degrees.

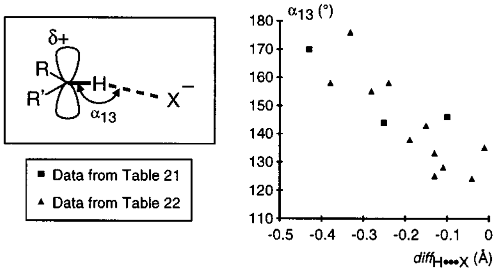


Figure 27. Statistical analysis of the $C^{\delta+}-H\cdots X$ contacts. For the definition of the variables see the formula on the inset. The numerical values are given in Tables 21 and 22 and in Tables S11 and S12 of the Supporting Information; the formulas are shown in Tables 21 and 22.

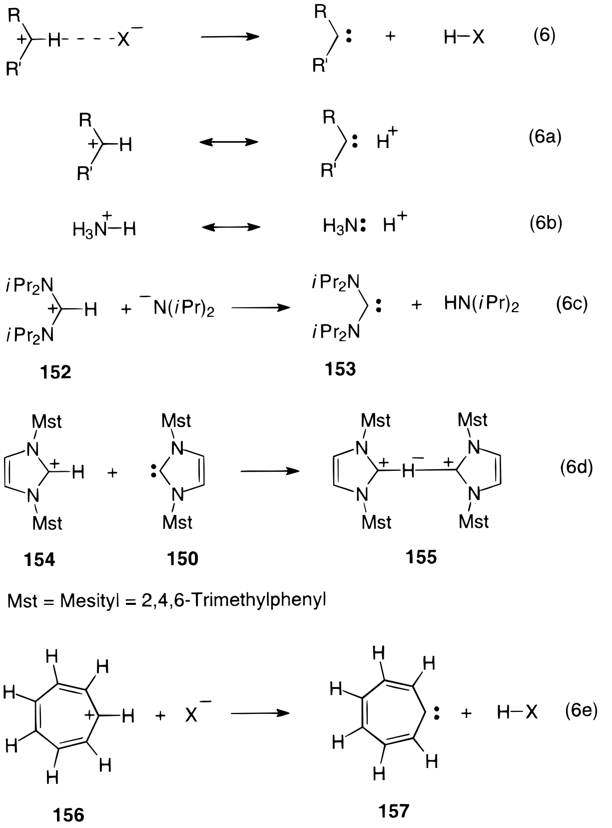
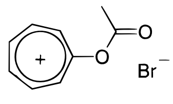
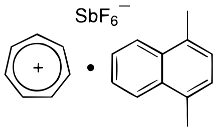


Table 22. Ranges of Structural Data of $C^{\delta+}$−H···X Hydrogen Bonds, where $C^{\delta+}$−H Belongs to a Tropylium Ring and X Is or Belongs to an Anion



105 (ACTRPB)



110 (SASNOP)

	refcode	X	$diff_{H\cdots X}$ [a]	$C^{\delta+}$−H···X [b]
105	ACTRPB	Br	−0.28 to −0.04	124 to 155
110	SASNOP [c]	F	−0.38 to −0.01	135 to 176

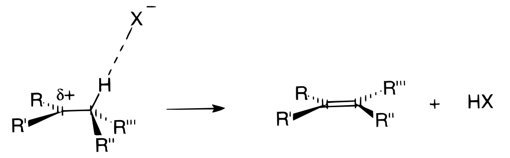
[a] In angstroms. [b] In degrees. [c] See Figure 15.

azol-2-ylidene **150** (reaction 6d) leads to the stable bis(carbene)−proton complex **155** whose crystal structure has been determined.[41] The unsymmetrical C−H···C hydrogen bond in **155** is characterized by the CH bond lengths of 1.16(5) and 2.03(5) Å and a CHC angle of 173°. The protonation of carbenes, i.e., the reversal of reaction 6, leads to carbocations and has been studied e.g. by Scaiano et al.[42]

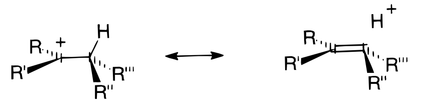
Tropylium ions also have C−H···X contacts, as can be seen e.g. in Figure 15. Table 22 and Figure 27 show that the geometrical data are similar to those in the N-substituted carbocations discussed above. The stronger hydrogen bonds in both kinds of systems are nearly linear. An extrapolation from the structural features of the N-substituted cations and their reactions discussed above leads to the conclusion that the C−H···X contacts in tropylium ions can also be interpreted as initial phases of the deprotonation (eq 6e). The crystal structures of several iron[43] and platinum[44] complexes of the carbene **157** are known. They are characterized by a σ-bond-like coordination of **157** via the carbene lone pair to the metal center. Cycloheptatrienylidene (**157**) and its complexes have also been studied by NMR[45] and theoretical[46] methods.

8. Hydrogen Atoms in C^+–C–H Fragments

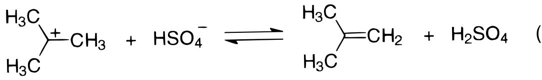
The hydrogen bonds of the types $C^{\delta+}$−O−H···X and $C^{\delta+}$−N−H···X occurring in many structures of protonated ketones or carboxylic acids or iminium, amidinium, or guanidinium ions will not be discussed in the present review as they are only special cases of the widely investigated O−H···X and N−H···X hydrogen bonds.[7,8] Hydrogen bonds of the type $C^{\delta+}$−C−H···X are more interesting due to the high Brønsted acidity of the cations, but they occur less frequently because media of higher acidity are required to avoid deprotonation according to reaction 7 if compared with O−H···X and N−H···X hydrogen bonds. The C−H acidity can be explained by C−H hyperconjugation according to eq 7a.



(7)



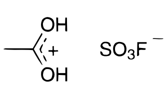
(7a)



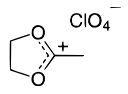
(7b)

The most prominent example for reaction 7 is the reversible deprotonation of the *tert*-butyl cation in sulfuric acid[47] (reaction 7b). The range for the observed $diff_{H\cdots X}$ values is practically the same as in the examples discussed in section III.A.7, see Figure 28 and Table 23. One would expect that the C−H acidity and the ability to form H bonds depend on the torsion angle τ due to the hyperconjugation. Figure 28a shows that the strong H bonds occur preferentially with |τ| around 30°, but this result is mainly due to the strong H bonds in some cyclohexadienylium ions with little torsional flexibility. The dependence of the C−H···X angles on $diff_{H\cdots X}$ is very

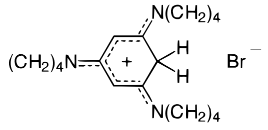
Table 23. Important Features of Structures with $C^{\delta+}$−C−H···X Hydrogen Bonds in Ion Pairs of the Type RR′$C^{\delta+}$−CR″R‴−H···X, Where X Is or Belongs to an Anion



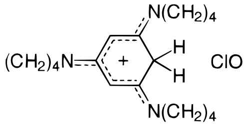
26 (ACETFS)



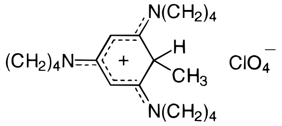
32 (DOXYLP)



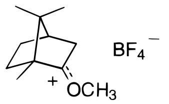
115 (FEDZIX)



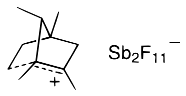
116 (FEDZOD)



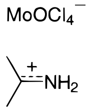
117 (FEDZUJ)



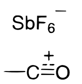
16 (FODZAZ)



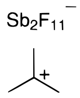
145 (FITDIV)



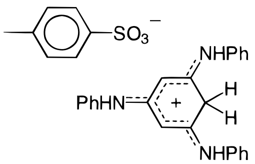
20 (JAJRIV)



5 (MOCFSB10)



139 (PESGID)



118 (WAZYOL)

	refcode	X	R, R′	R″, R‴
26	ACETFS	O	2 OH	2 H
32	DOXYLP	O	2 OR^1	2 H
115	FEDZIX	Br	NR^1R^2, C_{sp^2}	H, C_{sp^2}
116	FEDZOD	O	NR^1R^2, C_{sp^2}	H, C_{sp^2}
117	FEDZUJ	O	NR^1R^2, C_{sp^2}	C_{sp^3}, C_{sp^2}
16	FODZAZ	F	O, C_{sp^3}	H, C_{sp^3}
145	FITDIV [a]	F	2 C_{sp^3}	H, C_{sp^3}
		F	2 C_{sp^3}	2 H
20	JAJRIV	Cl	NH_2, C_{sp^2}	2 H
		O	NH_2, C_{sp^2}	2 H
5	MOCFSB10	F	=O	2 H
139	PESGID	F	2 C_{sp^3}	2 H
118	WAZYOL	O	NR^1R^2, C_{sp^2}	H, C_{sp^2}

[a] The more precise data from the redetermined structure (refcode FITDIV01) have been used.

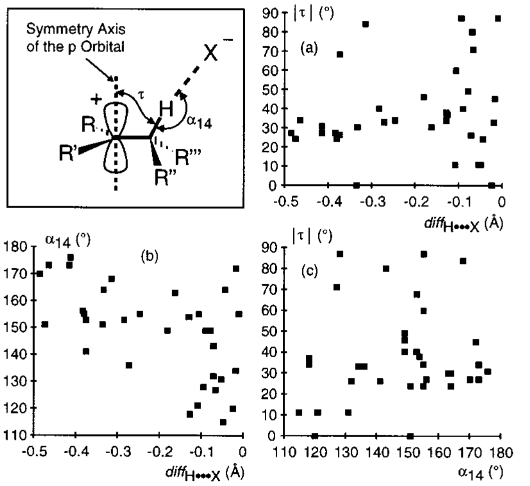


Figure 28. Statistical analysis of the $C^{\delta+}-C-H\cdots X$ contacts. For the definition of the variables see formula on the inset. The torsion angle τ is approximately calculated from R−C−C−H or R′−C−C−H by adding ±90°, and it is selected with the smallest possible absolute value. The refcodes and the formulas are shown in Table 23; the numerical value are given in Table S13 in the Supporting Information.

similar in the $C^{\delta+}-H\cdots X$ and $C^{\delta+}-C-H\cdots X$ cases (Figures 27 and 28b), i.e., the stronger H bonds also in this case tend to be linear. There is no correlation between $|\tau|$ and α_{14} (Figure 28c).

B. Topicity of the Faces of Cationic Carbon Atoms

In an isolated molecule or ion (i.e., in the gas phase), homotopic faces are related by a symmetry operation of the first kind (proper symmetry operation), while enantiotopic faces are related by a symmetry operation of the second kind (improper symmetry operation). Diastereotopic faces are not related by any symmetry operation. A very general introduction to symmetry elements of molecules in crystals is given in Appendix C.

In a crystal, a rigid cation with homotopic faces may or may not lie on a *crystallographic* symmetry element of the first kind.[48] In the first case, the two faces of the cation and their near and far environment are related by this symmetry element, while in the second case, the two faces of the cation are only related by a *noncrystallographic* (i.e., local) symmetry element, which applies only to the cation, but not necessarily also to its environment. In most cases, such a noncrystallographic symmetry element is only an approximate symmetry element because of the slight molecular deformations due to lattice forces. Similarly, the enantiotopic faces of a rigid cation in a crystal may or may not lie on a crystallographic symmetry element of the second kind. In the first case, the two faces of the cation and their near and far environment are also related by this symmetry element, while in the second case, only an approximate, noncrystallographic symmetry element is found.[49] Nevertheless, one would expect that, in the case of absence of crystallographic symmetry elements, homotopic, or enantiotopic faces of a cation have approximately equal or enantiotopic environments and $C^{\delta+}\cdots X$ contacts, at least within short distance ranges, since such faces are energetically equivalent and thus equally attractive for an interaction with a counterion. Diastereotopic faces of a cation have necessarily different environments in the gas phase and in a crystal because of the absence of symmetry elements. For flexible cations, the situation may be even more complicated: a flexible molecule may adopt such a conformation, that homotopic faces become effectively enantiotopic[50] or diastereotopic[51] in the crystal, see also Appendix C.

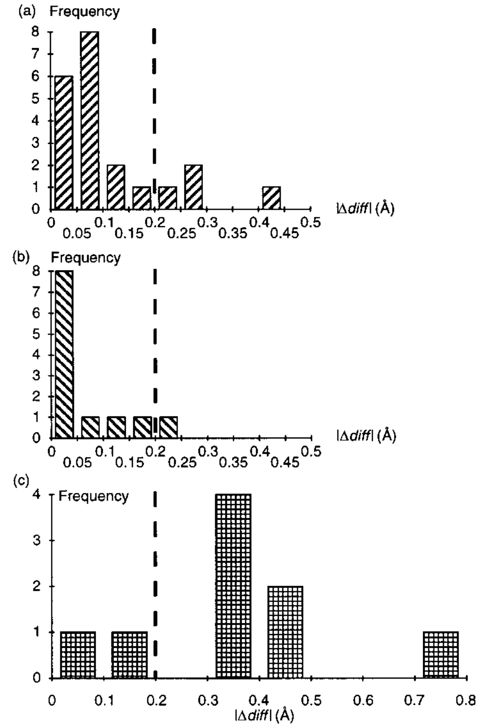


Figure 29. Histograms of the absolute values of the differences between the *diff* values of $C^{\delta+}\cdots X$ contacts on different sides of cationic C_{sp^2} atoms ($|\Delta(diff)|$). (a) Cations with homotopic faces in solution or in the gas phase; (b) cations with enantiotopic faces in solution or in the gas phase; (c) cations with diastereotopic faces. The empirical border of 0.2 Å distinguishes the distributions for cations with symmetry-related faces (a and b; $|\Delta(diff)| \leq 0.2$ Å) from cations without symmetry-related faces (c; $|\Delta(diff)| > 0.2$ Å). The refcodes and numerical values are given in Figures S1−S3 in the Supporting Information.

We have analyzed the *diff* values of $C^{\delta+}\cdots X$ contacts on both faces of a variety of cations. Because a crystal packing is always a compromise between the principles given in the Introduction, favorable $C^{\delta+}\cdots X$ contacts may be sometimes impossible because they would lead to large empty spaces in the crystal[52] or because other attractive interactions are also possible.[53] In the cases, where $C^{\delta+}\cdots X$ interactions are observed on both faces, we find the following mean absolute differences of *diff* values for the two faces ($|\Delta(diff)|$): homotopic 0.11(3) Å, enantiotopic 0.06(3) Å, diastereotopic 0.31(5) Å (see Figure 29 and Figures S1−S3 in the Supporting Information). While the former two values are near to the ideal value zero, the latter is, as expected, significantly different from zero. Compared with homotopic faces, the value for enantiotopic faces is perhaps nearer to zero, because

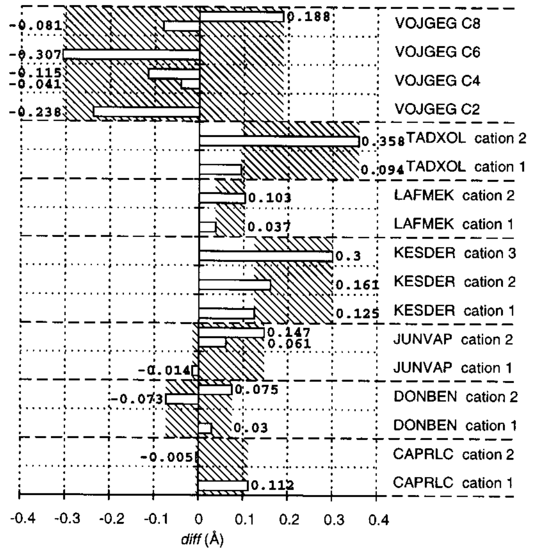
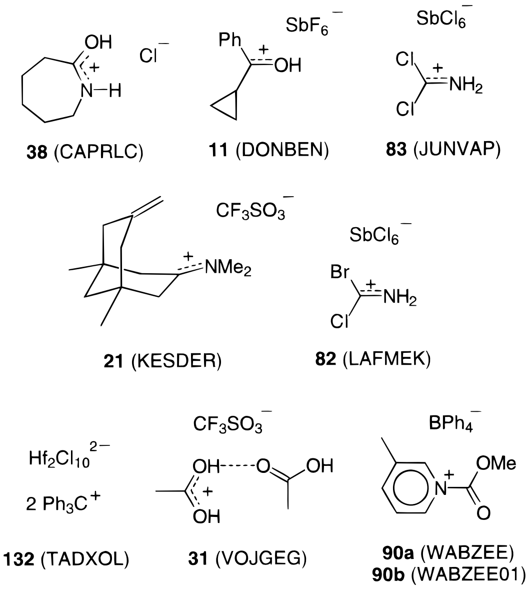


Figure 30. Crystal structures of carbocation salts with $Z' > 1$. The diagonally hatched areas show the ranges of the *diff* values for each structure. The crystal structure of **31** is a special case because it has two cations and two activated neutral molecules in the asymmetric unit.

crystallographic mirror planes are more often occupied by molecules than crystallographic C_2 axes,[4] which lead in both cases to examples with $|\Delta(diff)| = 0$ and therefore lower the corresponding value of $|\Delta(diff)|$. By taking the great scatter of the data into account, one can conclude that $|\Delta(diff)| > 0.2$ Å

Chart 8



38 (CAPRLC) **11** (DONBEN) **83** (JUNVAP)

21 (KESDER) **82** (LAFMEK)

132 (TADXOL) **31** (VOJGEG) **90a** (WABZEE) **90b** (WABZEE01)

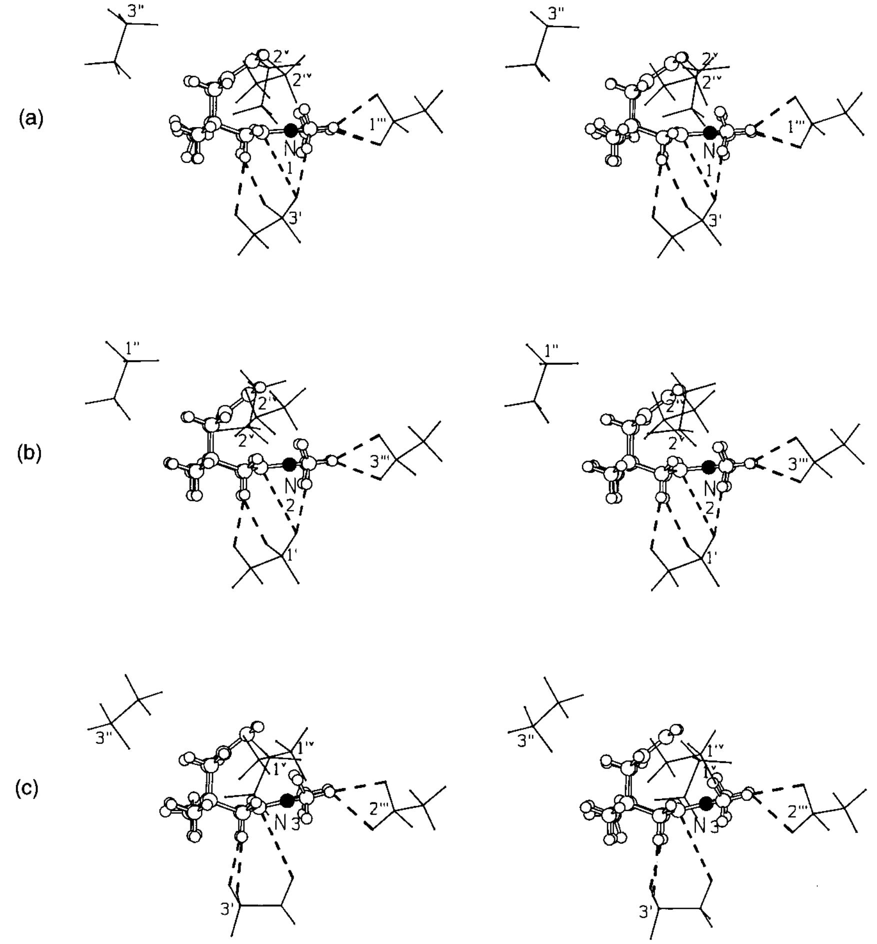


Figure 31. Stereoplots[22] of the nearest environments of the three crystallographically independent cations in the structure of **21** ($Z' = 3$). The N atom of each cation is drawn as a black sphere and labeled. Each cation is shown with its five closest triflate anions (wire models). The S atom of each anion is labeled with an arabic number for the differentiation of the three crystallographically independent anions in the asymmetric unit and a roman superscript indicating the relative position of the anion with respect to the cation. The $C^+\cdots X$ contacts are indicated by five dashes; H bonds, by three dashes. (a) Cation 1; (b) cation 2; (c) cation 3.

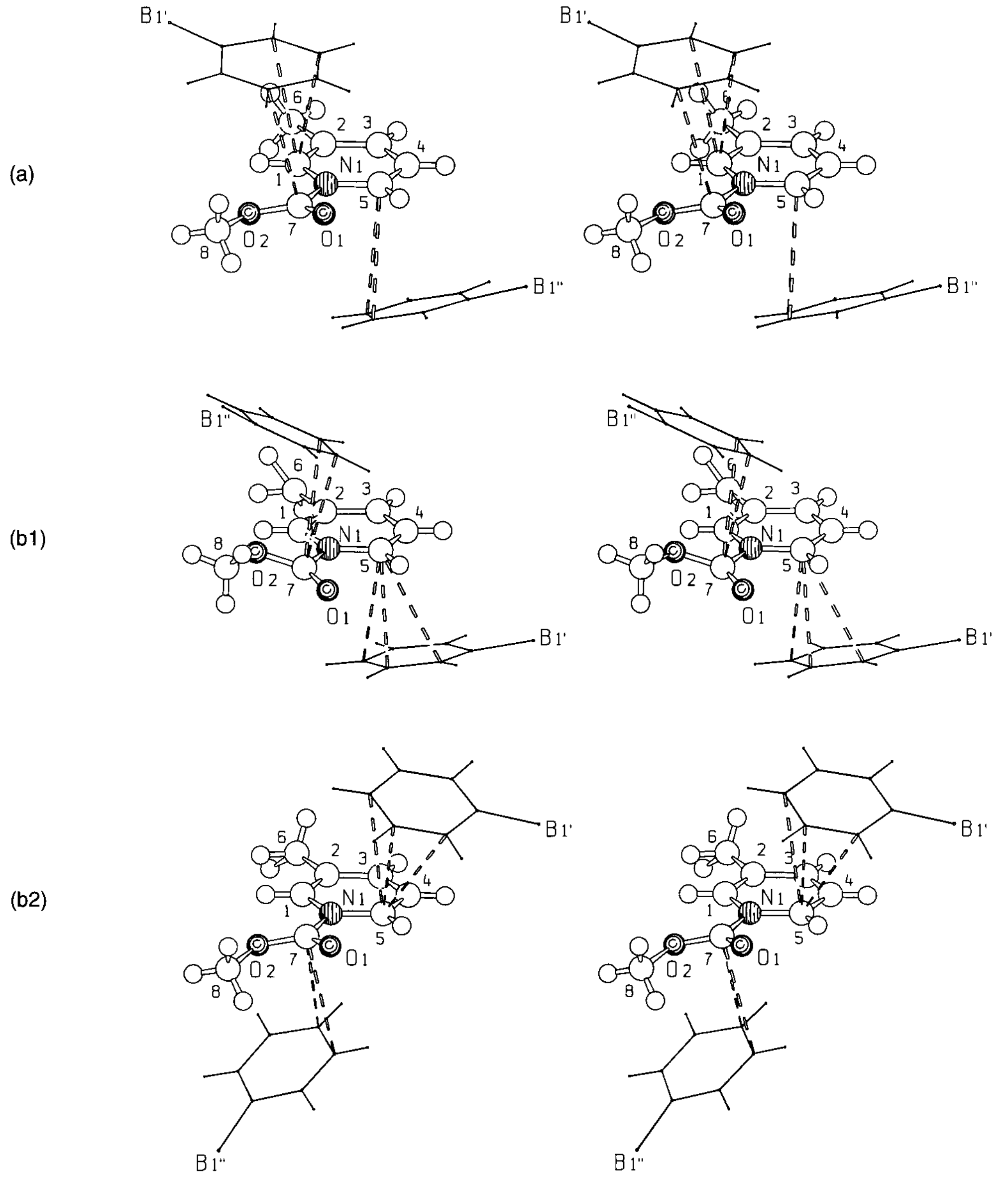


Figure 32. Stereoplots[22] of the nearest environment of a cation in two polymorphic forms. (a) Polymorph I, **90a**; (b1) and (b2) polymorph II, **90b**. Both polymorphs crystallize in the centrosymmetric space group $P2_1/n$. The packing (b2) has been generated from (b1) by inversion and new orientation. Only the closest phenyl ring and the B atom of each tetraphenylborate anion are drawn (wire models). The orientation of the pyridine ring is the same for all three diagrams. The C atoms of the cations are labeled by their numbers. The $C^{\delta+}\cdots C_{anion}$ contacts indicated by dashed bonds lie in the range from 3.12 to 3.45 Å. Comparison of a and b1 shows the similar arrangements of the rings in both polymorphs despite the different sings of the torsion angles C1–N1–C7–O2. These torsion angles have the same sign in a and b2.

corresponds in many cases to energetically different faces. These findings support the earlier published assumption about a qualitative correlation between the diastereoselectivity of solvolysis reactions of norbornyl and norbornenyl cations and their crystal structures.[13a]

How unique is the arrangement of other ions around a carbocation? This question is related to the problem of $C^{\delta+}\cdots X$ contacts at homotopic or enantiotopic faces. It is best answered by a visual inspection of the environment of carbocations in structures with $Z' > 1$ (more than one molecule in the asymmetric unit) or in polymorphic structures (Chart 8). Equivalent faces of two or more cations may be considered as homotopic, because they are related by a proper symmetry operation including a noncrystallographic translation or because they yield identical product molecules upon addition of a nucleophile. Arguing from analogy one could claim that two faces in two cations are enantiotopic if they are related by an improper symmetry operation or if they yield enantiomeric product molecules upon addition of a nucleophile. The result of the analysis of carbocations with $Z' > 1$ is shown in Figure 30. The *diff* values for each cation type scatter in most cases within a range of 0.2 Å (hatched areas in Figure 30). The packing of the cations, the $C^{\delta+}\cdots X$ contacts and the hydrogen bonds are always similar, even in a case with $Z' = 3$, see Figure 31. The only example of polymorphism in the present data set is depicted in Figure 32. The nearest environment is also in this case similar despite different conformations of the cations: the positively charged region around N1 in both polymorphs is embedded between the phenyl

Table 24. Literature Citations from the Cambridge File[16] (The refcodes are given in parentheses)

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3 (ETOCGA)	Le Carpentier, J.-M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 1430
4 (IBUSBC20)	Le Carpentier, J.-M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 1430
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11 (DONBEN)	Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692
12 (JICPOA)	Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912
13 (JICPUG)	Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912
14 (JICRAO)	Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912
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22 (VAPREJ)	Burg, A. B. *Inorg. Chem.* **1989**, *28*, 1295
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29 (JOPSUC)	Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *Can. J. Chem.* **1991**, *69*, 2024
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90b (WABZEE01)	Bryant, G. L., Jr.; King, J. A., Jr. *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* **1993**, *49*, 551
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96 (SIYDOT)	Weller, F.; Pauls, I.; Dehnicke, K.; Becker, G. *Z. Naturforsch., Teil B* **1991**, *46*, 519
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99 (DMCPRP10)	Cowman, C. D.; Thibeault, J. C.; Ziolo, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 3209
100 (FAFGUO)	Pohl, S.; Saak, W.; Mayer, P.; Schmidpeter, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 825
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115 (FEDZIX)	Effenberger, F.; Reisinger, F.; Schonwalder, K. H.; Bauerle, P.; Stezowski, J. J.; Jogun, K. H.; Schollkopf, K.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1987**, *109*, 882
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118 (WAZYOL)	Glatzhofer, D. T.; Khan, M. A. *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* **1993**, *49*, 2128
120 (CBUALC)	Kruger, C.; Roberts, P. J.; Tsay, Y.-H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69
121 (COVSUB10)	Estienne, J. *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* **1986**, *42*, 1614
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130 (KUBLUO)	Kahr, B.; Jackson, J. E.; Ward, D. L.; Sei-Hum Jang; Blount, J. F. *Acta Crystallogr., Sect. B (Str. Sci.)* **1992**, *48*, 324
131 (PCBTEC10)	Krebs, B.; Paulat, V. *Z. Naturforsch., Teil B* **1979**, *34*, 900
132 (TADXOL)	Calderazzo, F.; Pallavicini, P.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1990**, 2743
133 (TIPMEP)	Gomes de Mesquita, A. H.; MacGillavry, C. H.; Eriks, K. *Acta Crystallogr.* **1965**, *18*, 437
134 (VIGXUE)	Bleasdale, C.; Clegg, W.; Ellwood, S. B.; Golding, B. T. *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* **1991**, *47*, 550
135 (VIGYAL)	Bleasdale, C.; Clegg, W.; Ellwood, S. B.; Golding, B. T. *Acta Crystallogr., Sect. C (Cr. Str. Comm.)* **1991**, *47*, 550
136 (VIRDAB)	Ahlers, F.-P.; Luhrs, E.; Krebs, B. *Z. Anorg. Allg. Chem.* **1991**, *594*, 7
137 (VIRDEF)	Ahlers, F.-P.; Luhrs, E.; Krebs, B. *Z. Anorg. Allg. Chem.* **1991**, *594*, 7

Table 24 (Continued)

139 (PESGID)	Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* **1993**, *115*, 7240
140 (DOPRIJ)	Laube, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 349
141 (SUNMOD)	Laube, T.; Hollenstein, S. *Helv. Chim. Acta* **1994**, *77*, 1773
142 (DIFMEK)	Borodkin, G. I.; Nagi, Sh. M.; Gatilov, Yu. V.; Shubin, V. G. *Dokl. Akad. Nauk SSSR* **1985**, *280*, 881
143 (SODREI)	Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1991**, 841
145 (FITDIV)	Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560. Redetermination: Laube, T. *Helv. Chim. Acta* **1994**, *77*, 943
146 (JECDEA)	Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224
147 (PONHOP)	Laube, T.; Lohse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9001
148 (PONHUV)	Laube, T.; Lohse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9001

rings of anions, although the anions have different orientations in the two polymorphs.

C. Empirical Rules about Carbocation···Anion Contacts

Some empirical rules can now be formulated which allow the prediction and analysis of important cation···anion interactions in salts of localized or weakly delocalized and sterically nonhindered carbocations. These rules belong to principles 2 and 3 given in the Introduction (section I). These principles seem to be valid in the same sequence also for carbocation salts. As in the previous sections, X is in most cases an anion or belongs to an anion, in a few cases it belongs to a neutral molecule. For the definition of other general groups or atoms (R, Y, Z) see the corresponding sections.

(a) Hydrogen bonds, $C^{\delta+}\cdots X$ and $C^{\delta+}-Hal\cdots X$ contacts are of nearly comparable importance, i.e., they occur in most of the cases where they are possible. In the present data set, $C^{\delta+}\cdots X$ contacts are found in 113 of 129 structures with a cationic center, and $C^{\delta+}-Hal\cdots X$ contacts are found in all eight structures with a $C^{\delta+}-Hal$ fragment. The exceptions for the $C^{\delta+}\cdots X$ contacts are mentioned in rule d, see below.

(b) Hydrogen bonds of the types $C^{\delta+}-O-H\cdots X$ and $C^{\delta+}-N-H\cdots X$ occur wherever possible.

(c) Cationic sp C atoms (e.g., acyl cations) are surrounded by 4−6 X atoms, see section II.A.

(d) Cationic sp^2 C atoms have, at least on one side, a $C^{\delta+}\cdots X$ contact. The following exceptions were observed:

(d1) Cations with ≥2 NR_2 substituents or with ≥2 $C^{\delta+}-N-H\cdots X$ hydrogen bonds and no other electron-attracting substituents such as halogens have only occasional $C^{\delta+}\cdots X$ contacts.

(d2) In strongly donor-substituted cyclohexadienylium ions, only the C(6) substituents are involved in interactions with X atoms, see section II.N.

(d3) Highly donor-substituted allyl cations show only weak $C^{\delta+}\cdots X$ contacts.

(e) At sp^3 C atoms, $C^{\delta+}\cdots X$ contacts are rare except in 1,3-dioxolan-2-ylium ions where they always occur at C(4) or C(5), see section II.E.

(f) Cations containing a 3c-2e bond show at least one $C^{\delta+}\cdots X$ contact with either C(2) or C(2′) (see **144** and Table 20), while the pentacoordinate C(1) is only occasionally involved in such contacts, see section II.R.

(g) Halogen atoms at cationic centers are involved in $C^{\delta+}-Hal(1)\cdots Hal(2)-Z$ interactions (observed mean angles $C^{\delta+}-Hal(1)\cdots Hal(2) = 166(3)°$, $Hal(1)\cdots Hal(2)-Z = 108(4)°$, see section III.A.6).

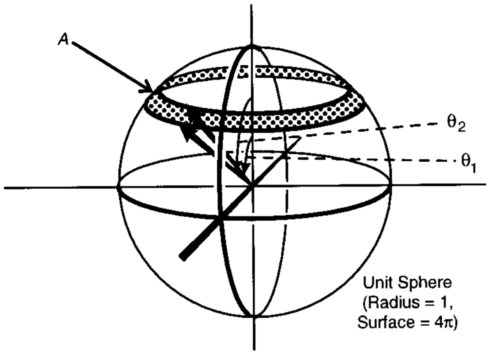

Figure 33. A unit sphere with a sector defined by the angles θ_1 and θ_2. The area *A* of this sector (rastered area) is used for the normalization of the histograms.

(h) *N*-Acylpyridinium ions show at the carbonyl C and at C(2), C(4), or C(6) of the pyridinium ring $C^{\delta+}\cdots X$ contacts, see section II.K.

(i) Differences >0.2 Å between the *diff* values of $C^{\delta+}\cdots X$ contacts from two directions may indicate different accessibility of the cationic C from the corresponding directions, i.e., different behavior in kinetically controlled reactions in solution; differences <0.2 Å are not significant, see section III.B.

(j) Nucleophilic atoms X in the environment of a cationic C atom are located near the symmetry axis of the empty carbon p orbital (**A**, **B**) or approximately in anti position to a potential leaving group (**C**, **D**). The atoms X point preferentially with a lone pair toward the cationic C atom. The currently available data mentioned in j1−j5 may be used for the estimation of parameters in unknown structures.

(j1) For **A**, $diff_{C\cdots X}$ is greater than −0.5 Å, and the observed $C-C^{+}\cdots X$ angles lie in the range 85° to 110°; see section III.A.1.

(j2) For **B**, $diff_{C\cdots X}$ is greater than −0.5 Å, the observed probability density of the angles ∠(symmetry axis of the empty p orbital, $C^{\delta+}\cdots X$) is maximal at 0° and becomes very small for angles >30°; see section III.A.2.

(j3) For **C**, $diff_{C\cdots X}$ is greater than −0.3 Å, the observed $X\cdots C^{\delta+}-Y$ angles lie in the range 130° to 180°; see section III.A.3.

(j4) For **D**, $diff_{C\cdots X}$ is greater than −0.2 Å, the three observed angles $X\cdots C^{+}\cdots$(center of the former double bond) in bicyclo[2.*n*.1]alkenyl cations ($n = 1,2$) lie in the range 142° to 156°; see section III.A.4.

(j5) The mean $C^{\delta+}\cdots X-Z$ angles are for X = O, 119(3)°, F, 131(2)°, Cl, 114(2)°, Br, 107(5)°, see section III.A.5.

(k) Hydrogen atoms in $C^{\delta+}-H\cdots X$ and $C^{\delta+}-C-H\cdots X$ fragments can be involved in $H\cdots X$ contacts

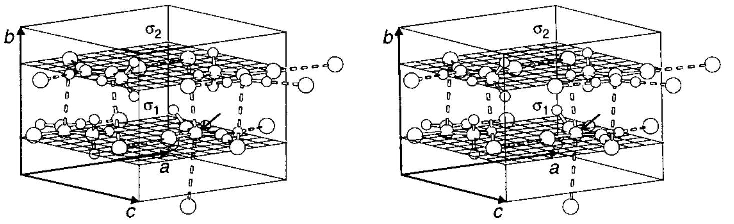

Figure 34. Stereo ball-and-stick diagram[22] of the crystal structure of **56** (see also Figure 9b). The heavy atoms of the cations and the anions lie on the crystallographic mirror planes σ_1 and σ_2 at $y = {}^1/_4$ and $y = {}^3/_4$ (drawn as nets). The cationic carbon atom of one cation is marked by an arrow, and all its closest counterions are shown as in Figure 9b. The only symmetry element of this cation, the mirror plane σ_1, is also a symmetry element of the space group *Pnma* (no. 62). Thus the cations and the anions lie on special positions with the site symmetry $C_s \equiv m$, and the near and far environment on both sides of the cation are exactly related by this mirror plane.

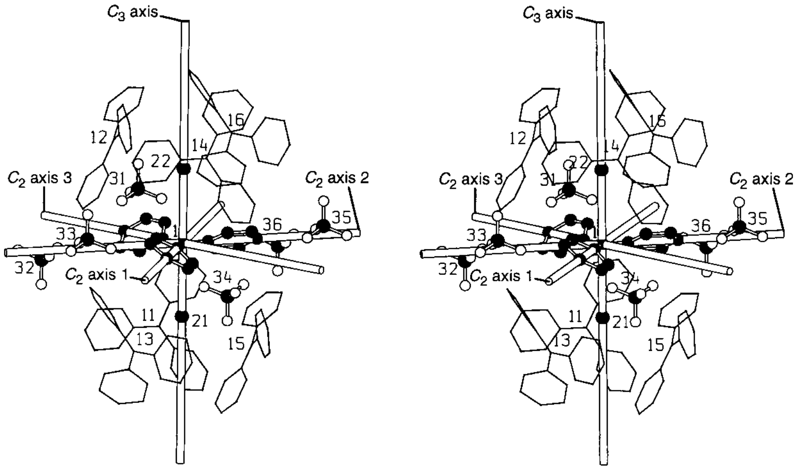

Figure 35. Stereo ball-and-stick diagram[22] of the crystal structure of **133** (space group $F4_132$, no. 210). The carbon atoms of the central trityl cation (number 1) and the chlorine atoms of the perchlorate anions (numbers 21, 22, and 31−36) are drawn as black spheres, the symmetry-related cations (numbers 11−16) are shown as wire models. The cation lies on a special position with the site symmetry $D_3 \equiv 32$, and the C_n axes of the central cation are drawn as thick sticks. The anions lie on two different special positions which have both the site symmetry $T \equiv 23$. Half of them are ordered (examples numbers 31−36), and the other half of them are orientationally disordered (examples numbers 21 and 22; oxygen atoms not drawn). The three phenyl rings and each side of each phenyl ring are related by an exact rotation axis, i.e., these symmetry elements are also valid for the near and far environment. For a crystal structure in which a trityl cation lies on a general position see Figure 18b.

which are up to 0.5 Å shorter than the sum of the van der Waals radii; see sections III.A.7 and III.A.8.

It must be emphasized that these rules have some fuzzy character, i.e., there is no guarantee that a particular interaction will always occur because competing donor−acceptor or steric interactions may come into play. It is possible that these rules must be extended in the future, when more such structures become available.

IV. Conclusion

Common important features were observed in the crystal packing of many salts of localized or weakly delocalized carbocations. The interactions of the cationic C atoms and their neighboring atoms with nucleophilic or electron-rich atoms in the environment can be described by qualitative and quantitative empirical rules, which allow some predictions for unknown structures. The occasional extreme diastereoselectivities observed for carbocation reactions in solution are correlated with their structure and packing. Although the multifunctionality of many carbocations leads often to competing effects (hydrogen bonds, $C^{\delta+}\cdots X$, and $C^{\delta+}-Hal\cdots X$ interactions), crystal engineering will perhaps be possible also with such highly polar compounds.

V. Acknowledgments

I thank Professor George A. Olah and Professor Robert Bau for their generous support and hospitality during my stay at the University of Southern California. It is a great pleasure to thank Ms. Anjana Mitra (University of Southern California) for her help and patience in improving the style of the manuscript. The CSD searches have been carried out on a computer of the ETH Zürich (Switzerland).

VI. Appendices

A. References for the Crystal Structures

The references for all crystal structures analyzed in the review are listed in numerical order in Table 24.

B. Normalization of the Angle Histograms

If points are randomly but uniformly scattered on the surface of a unit sphere, a histogram of their angles θ do not show a uniform distribution, because

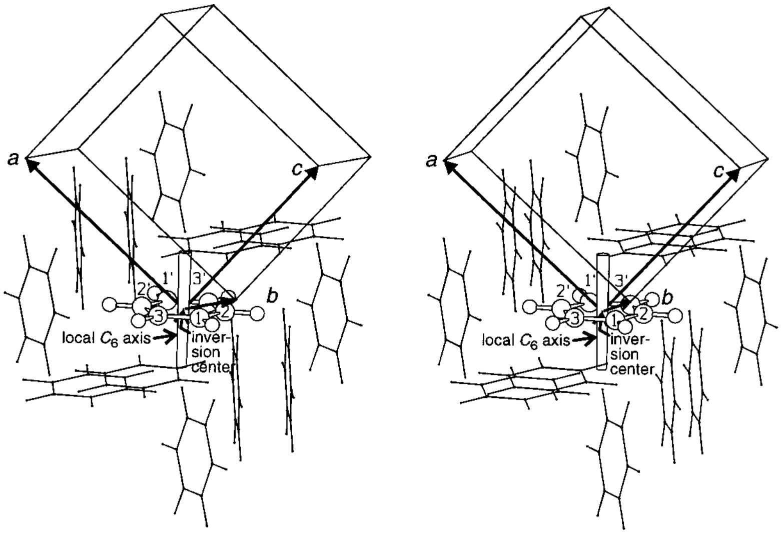

Figure 36. Stereo ball-and-stick diagram[22] of the crystal structure of benzene[54] (space group *Pbca*, no. 61). The free benzene molecule belongs to the point group $D_{6h} \equiv 6/mmm$, but only the inversion center is retained in the crystal, and the primed atoms are related to the unprimed ones by this inversion center.[55] However, the molecule has approximate D_{6h} symmetry (the local C_6 axis is drawn as thick stick). The environment of the molecule has only the inversion symmetry belonging to the space group.

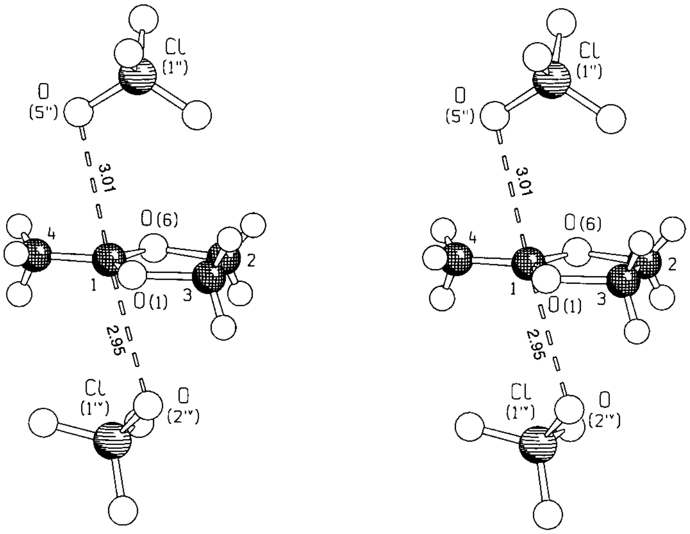

Figure 37. Stereo ball-and-stick diagram[22] of the crystal structure of **32** (space group $P2_1/c$, no. 14; distances in Å). If one ignores the conformation of the C(4) methyl group because of the fast rotation, the cation has homotopic faces in solution (point group $C_{2v} \equiv mm2$). The cation lies in the crystal on a general position, and thus no exact symmetry element relates the faces of the cationic C(1) to each other. The arrangement of the two perchlorate anions in the crystal, however, leads to approximately equal near environments on both faces of C(1) with similar C(1)···O distances.

the probability of finding points at θ about 90° is much higher than at θ about 0° or θ about 180° due to the area of a sector defined by the angles θ_1 and θ_2, see Figure 33.

Therefore the frequency observed in each angle bin (defined by the angles θ_1 and θ_2) must be divided by the area A of the corresponding sector of a unit sphere (rastered area in Figure 33). The area A of such a sector is

$$A = \int_0^{2\pi} \int_{\theta_1}^{\theta_2} \sin\theta \, d\theta \, d\varphi = 2\pi(\cos\theta_1 - \cos\theta_2)$$

A thus normalized histogram of uniformly distributed points shows (in the limit of an infinite number of points) equal frequencies in all bins, i.e., the normalized histograms represent the *probability density of finding a point on the surface of the sphere* depending on θ. No φ dependence is taken into account, i.e., rotation symmetry is assumed in all cases.

C. Symmetry Elements of a Molecule in a Crystal

1. General and Special Positions

A finite, i.e., nonpolymeric molecule in a crystal can lie on a point group symmetry element which belongs to the space group of that particular crystal. In this case one part of the molecule is exactly related to another part of the same molecule. In addition to the parts of the molecule, the near and far environments of these parts in the crystal are also related by the same symmetry element. In this case the position of the molecule is called a *special position* (which has by definition a site symmetry higher than $C_1 \equiv 1$). The symmetry element of the special

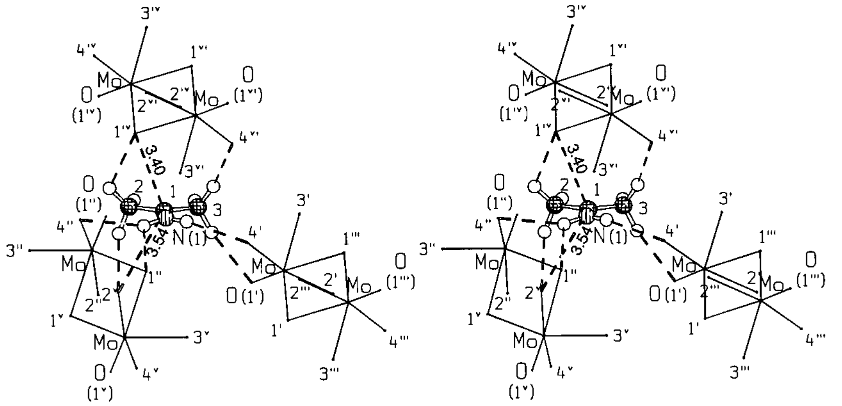

Figure 38. Stereo ball-and-stick diagram[22] of the crystal structure of **20** (space group $P2_1/c$, no. 14; distances in Å; the carbon atoms of the cation and the chlorine atoms of the anions are labeled by their numbers only). If one ignores the conformation of the methyl groups because of the fast rotation, the cation has homotopic faces in solution (point group $C_{2v} \equiv mm2$). Although the cation lies on a general position and not even an approximate symmetry element can be found which relates the anions on both faces of C(1) to each other, the first shell of neighboring atoms is involved in comparable C(1)···Cl contacts and H bonds on the two faces of the cation.

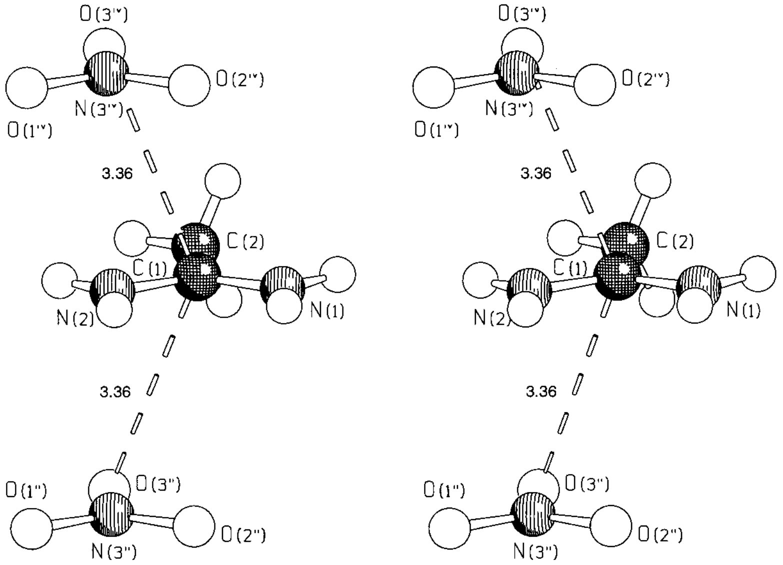

Figure 39. Stereo ball-and-stick diagram[22] of the crystal structure of **45** (space group $P2_1/m$, no. 11; distances in Å). If one ignores the conformation of the methyl group because of the fast rotation, the cation has homotopic faces in solution (point group $C_{2v} \equiv mm2$). In the crystal, however, the cation lies on a mirror plane and thus belongs to the point group $C_s \equiv m$. Its near and far environment in the crystal must be considered as enantiotopic. Only a very approximate C_2 axis can be constructed through C(1) and C(2), which refers also to the next counterions.

position also necessarily belongs to the point group of the free, isolated molecule with the same conformation for example in the gas phase. Generally, the site symmetry of the special position of a molecule can be equal to (see Figures 34 and 35) or lower than (see Figure 36) the point symmetry of the molecule. A site symmetry higher than the point symmetry of the free molecule is possible only in special cases, see below.

If a molecule in a crystal does not lie on a symmetry element of the space group of that crystal, it is said to lie on a *general position* (which has only the trivial site symmetry $C_1 \equiv 1$). This does not exclude the possibility that the molecule belongs to a point group of higher symmetry. If present, however, such a higher symmetry can only be an approximate symmetry in the crystal because interactions with neighboring molecules will lead to slight but different deformations of those parts of the molecule which are exactly symmetry related in the free molecule.

2. Rigid Molecules

In an ordered crystal, a rigid molecule, belonging as a free molecule to the point group C_1, can only lie on a general position. In the case of orientational disorder, such a molecule can lie on a special position because a superposition of the molecule with itself in another orientation can have higher symmetry than the single molecule. Orientational disorder is of course also possible on a general position.

A rigid molecule belonging as a free molecule to a point group higher than C_1 can in an ordered crystal lie on a general (see Figures 37 and 38) or on a special position (see Figure 34, 36, and 39). If the special position has the same symmetry as the molecule, this symmetry is also valid for the near and far environ-

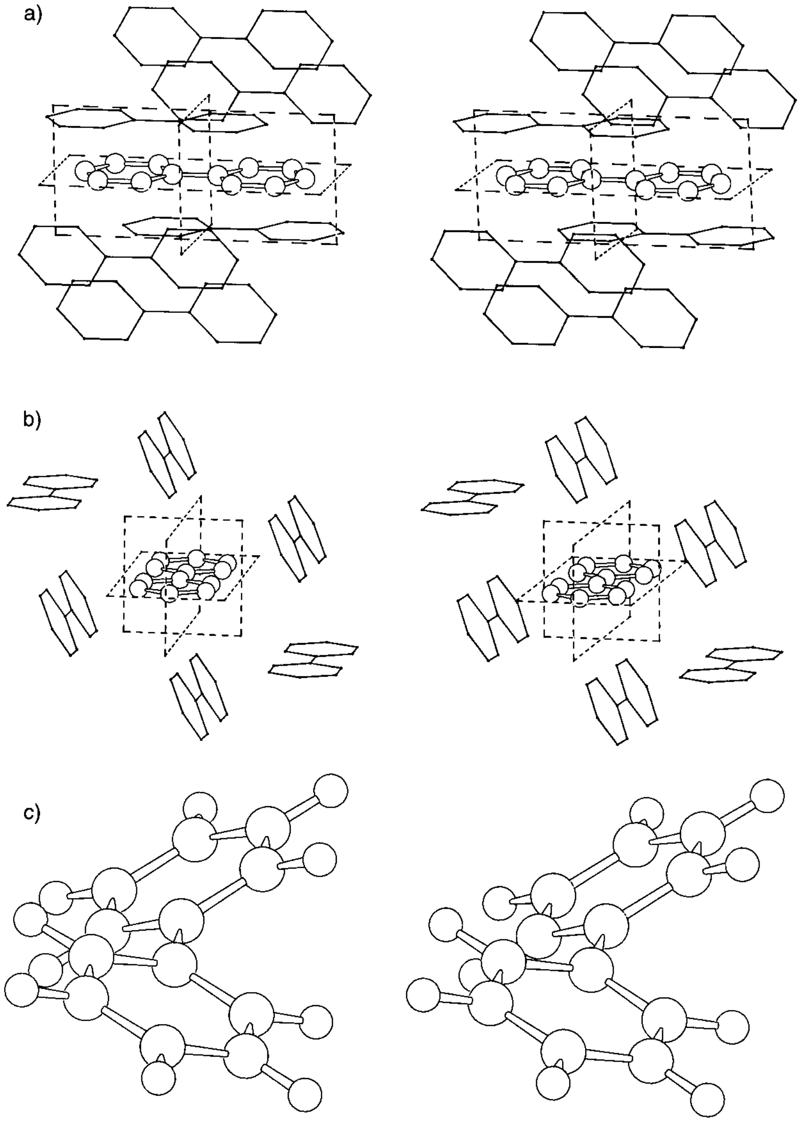

Figure 40. Stereo ball-and-stick diagram[22] of the crystal structure of biphenyl[56] (space group $P2_1/a$, no. 14); the hydrogen atoms were omitted in the two different views shown in a and b. The molecule has in this crystal structure approximate $D_{2h} \equiv mmm$ symmetry, and the three mirror planes are indicated by dashed rectangles. The molecule lies on an exact inversion center, and thus the molecules in the environment are only related by this inversion center, but not by any of the mirror planes or the 2-fold axes on the intersection lines of the mirror planes. The free molecule is twisted along the central C−C bond[57] and belongs only to the point group $D_2 \equiv 222$, see c.

ment of the molecule in the crystal (see Figure 34). If the special position has a lower symmetry than the molecule, the environment also has only the lower symmetry, but it can have, approximately, any higher symmetry (see Figure 39).

3. Nonrigid Molecules

Flexible molecules in a crystal can adopt a conformation of higher energy if compared with the ground-state conformation in the gas phase (see Figure 40). The point group of the molecule may or may not change on going from the gas phase to the crystalline state. For an example where the symmetry in the crystal is higher than in the free molecule, see Figure 40; an example where the symmetry is equal in both cases is shown in Figure 35, and examples where the symmetry in the crystal is lower than in the free molecules are shown in Figures 41 and 42.

D. Analysis of the Data from the CSD

No upper limits for the *R* values or the average esd's of the C−C bonds were applied in the very general QUEST searches for carbocations because we do not derive precise structural parameters from this study. Severe cases of disorder, i.e., when the cationic C atoms could not be located reliably, were excluded. The result files ("dat" format) of the QUEST searches were converted with GSTAT into ASCII files ("cor" format).

The analysis of the crystal packings could not be carried out with public domain or commercially available programs known to the author. Therefore a sequence of locally developed FORTRAN77 programs (cor2csd, csd2mol, dat2cry, cry2mol) was used for the generation of the suitable sections of the crystal packing and for the search for hydrogen bonds and nucleophile−electrophile interactions. The re-

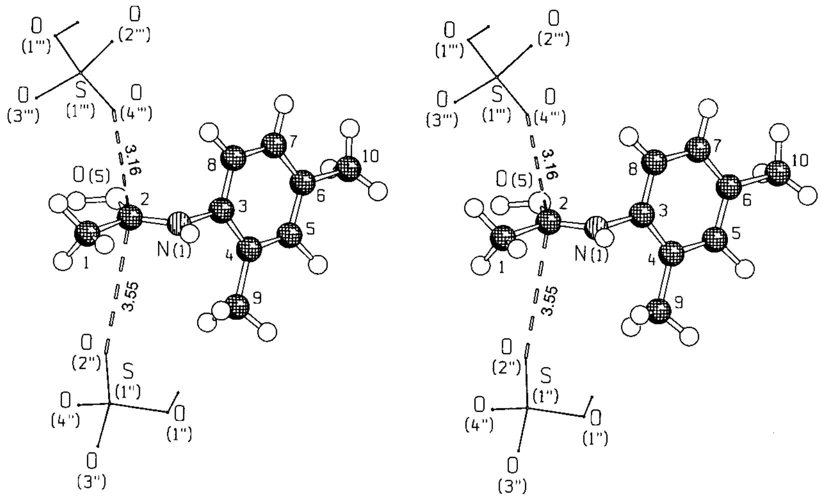

Figure 41. Stereo ball-and-stick diagram[22] of the crystal structure of **41** (space group $P2_1/c$, no. 14; distances in Å). Due to the conformational flexibility, the two faces of the cationic C(2) are enantiotopic in solution. The fixed conformation in the crystal makes the faces effectively diastereotopic, and a nucleophilic attack of O(2″) or O(4‴) would lead to diastereomeric products, if the conformation of the phenyl ring could be fixed. The C(9) methyl group hinders the approach of a nucleophile from the lower face, as can be concluded from the significantly different C(2)···O distances.

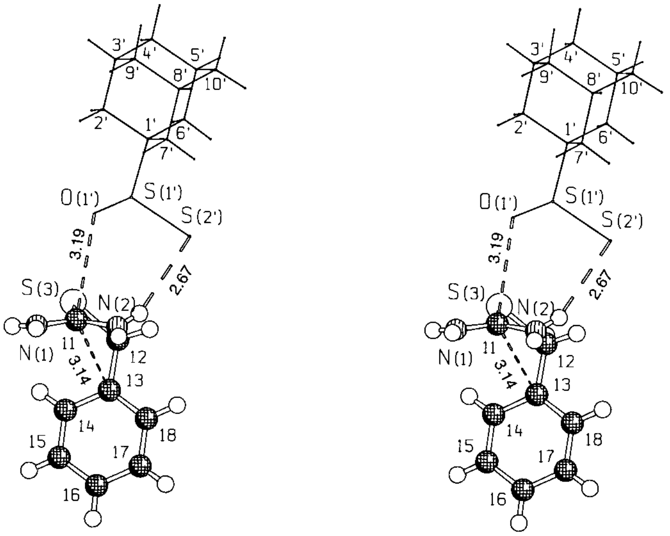

Figure 42. Stereo ball-and-stick diagram[22] of the crystal structure of **73** (space group $P\bar{1}$, no. 2; distances in Å). Due to the conformational flexibility, the two faces of the cationic C(11) are expected to be homotopic in solution, at least over longer periods of time, because the C(11)···C(13) interaction can be seen as a π or aryl participation with a slight bonding character. The two faces of C(11) are in the crystal not related by any exact or approximate symmetry element, and a nucleophilic attack of C(13) or O(1′) on C(11) would lead to different products, which are not even isomeric. This means that the faces are considered as heterotopic in the crystal.

sults were written into files in the SYBYL[21] "mol" format, read into SYBYL, and processed interactively. Usually the smallest part of the crystal packing showing the desired features was saved as another SYBYL "mol" file. These files were converted into the SCHAKAL92[22] "dat" format, and the final stereodrawings were generated with SCHAKAL92. The important intermolecular distances, which are drawn as dashed bonds, were computed with the LB command of SCHAKAL92, trapped as an ASCII file, and converted into a format, which uses the same symmetry operation descriptors as shown in the drawings.

Supporting Information Available. A listing of the refcodes of all structures with important features, stereodiagrams of the crystal packings, literature citations; bar diagrams and tables of distances and angles (118 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(50) Crystal structures of examples **74** and **75**.
(51) Crystal structures of examples **105**, **76**, **77**, and **73**.
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