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Rearrangements of cationic organic σ- and π-complexes

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Abstract. The structure-kinetic and stereochemical aspects of rearrangements of cationic σ- and π-complexes of unsaturated organic compounds with electrophilic reagents containing no metal atoms and the effects of the medium and phase state on these rearrangements are considered. The bibliography includes 299 references.

I. Introduction

In recent decades the structures and reactivities of cationic organic σ- and π-complexes† generated under 'long lifetime' conditions have been intensively studied.[1–33] 'Long-lived' σ- and π-complexes attract the steady attention of researchers, because they are close structural analogues of the intermediates of some organic reactions of great theoretical and practical importance. These reactions include electrophilic aromatic substitution,[20,36–38] acid-catalysed transformations of organic compounds,[39–41] electrophilic addition,[42] and solvolysis with anchimeric assistance.[43]

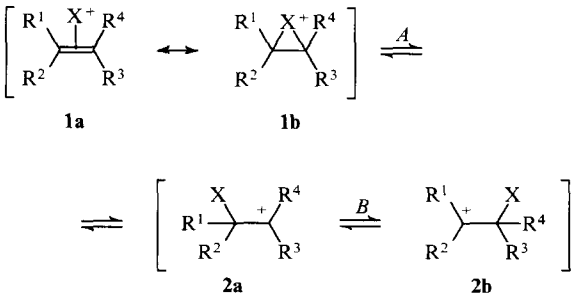
The wide use of modern physical methods has produced extensive information on the structures and reactivities of cationic σ-complexes.[1–33] However, studies of the structures and reactivities of cationic π-complexes are few, and their results are often ambiguous (see, for example, Refs 2, 23, 25, 29). Experimental data on the interconversion of cationic σ- and π-complexes (Scheme 1, path *A*) are even more scarce, despite the fact that in many cases this interconversion is the key step and determines the composition of the reaction products.[20,42,43]

† We use the term 'σ-complex' in its traditional sense [20] to denote a species that is formed by one-centred σ-bonding of an electrophilic agent to an unsaturated system via two electrons of the π-system. The term π-complex corresponds to an adduct formed by *n*-centred bonding ($n > 1$) of an electrophilic agent to the π-system of an unsaturated compound.[34,35]

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Scheme 1



1a **1b** **2a** **2b**

In principle, data on the energy of interconversion of cationic and anionic σ- and π-complexes can be obtained from quantum-chemical calculations (see Refs 44–47). However, this approach has essential limitations caused, in particular, by the unreliability of the calculation techniques.[46,48] This is clearly demonstrated by the results of quantum-chemical calculations on the simplest σ- and π-complexes, the ethyl cation and its π-analogue, for which the of relative energy varied over very wide limits (from 23.5 to −33.2 kcal mol^{-1}), depending on the chosen method of calculation.

The purpose of the present review is to consider the state of investigations, first of all, of the experimental ones, on rearrangements of cationic σ- and π-complexes. This is necessary for the development of approaches to the control of numerous organic reactions involving these complexes as intermediates. We shall confine the discussion to complexes formed by compounds and electrophilic reagents containing no metal ions. Considerable attention is paid to degenerate rearrangements of σ- and π-complexes in which the initial and the final species have identical energies. In conformity with the Marcus concept [49,50] and other similar approaches,[51] the kinetic characteristics of the degenerate processes are fundamental in the structural kinetic theory.

II. Types of rearrangements of σ- and π-complexes

Three main types of rearrangements of σ- and π-complexes can be distinguished, namely, σ,σ-, σ,π-, and π,π-rearrangements (see Fig. 1). One-step rearrangements of σ-complexes (*a*) as well as two-step rearrangements involving the formation of π-complexes as unstable intermediates (*b*) belong to the first type. The rearrangements characterised by similar stabilities of σ and π-complexes may be assigned to the σ,π-type (*c*). Finally, one-step

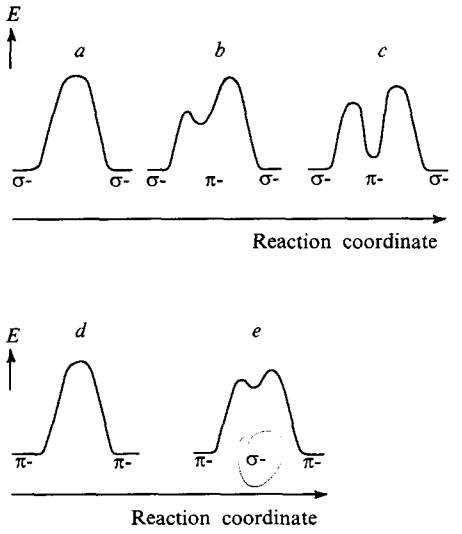


Figure 1. Dependence of the energy on the reaction coordinate for some types of rearrangements of σ- and π-complexes.

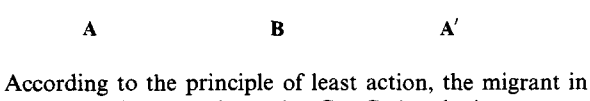
rearrangements of π-complexes (*d*) or two-step rearrangements involving the formation of unstable σ-complexes (*e*) may be referred to as π,π-rearrangements.

A more detailed classification of σ,σ-rearrangements includes allowance for the number of cleaved (*n*) and of formed (*m*) σ-bonds (an *n*σ,*m*σ-rearrangement). If one takes into account the possibility of coordination of the apical group (migrant) with different numbers of atoms of the complex core, then interconversions of π-complexes may be defined as π(*n*η),π(*m*η)-rearrangements. In conformity with this the interconversion of σ- and π-complexes may be referred to as a *n*σ,π(*m*η)-rearrangement.

III. σ,σ-Rearrangements

The most significant and extensively studied of σ,σ-rearrangements of cationic σ-complexes are those occurring through the 1,2-shift of a migrant (R_m) to the electron-deficient carbon atom, viz. the carbocationic centre (C_t) (Scheme 2).

Scheme 2



According to the principle of least action, the migrant in a 1,2-shift should move along the C_0-C_t bond via a state of π-bonding (an intermediate or transition state **B**),[20,22] and, with certain assumptions, the kinetic parameters of these rearrangements can characterise the relative stabilities of σ- and π-complexes. The main tool for the investigation of these rearrangements which occur at high rates is dynamic NMR,[15,16,20,21,52] while slow transformations are mostly studied by the radioactive tracer method.[15-17,20,53] Degenerate rearrangements of 'long-lived' cationic σ-complexes with a variety of migrants of σ-, π-, or *n*-type have been studied. The kinetic characteristics of the 1,2-shifts of these migrants are presented in Tables 1-4.

An important point is that the published data[15,17,20,21] indicate that the nature of the counter-ion or the solvent does not significantly affect the rates of intramolecular rearrangements of 'long-lived' cationic σ-complexes. Therefore, we shall consider initially the structure-kinetic regularities of these rearrangements. An approach consisting in separating a σ-complex into two structural fragments, the migrant (R_m) and the core (the rest of the ion), and in establishing the relationships between the structures of these fragments and the rate of the rearrangement was successful in identifying these regularities.[3,15,20,21]

1. The structural effects of the core

It is apparent that, in the absence of complicating factors, the rate of rearrangement for a given migrant should increase with the electrophilicity of the carbocationic centre C_t (see Ref. 76). In fact, for 1,2-shifts of migrants of σ-(H,Me), π-(Ph), and *n*-(Cl) types in arenonium ions (see Tables 1-4), the following linear correlations have been identified:

$$y = a_i + b_i\zeta\,, \qquad (1)$$

where y is $\lg k$ (k is the rate constant), free energy of activation ($\Delta G^{\neq}$), or activation energy (E_a); ζ, the chemical shift of the C_t atom (δC_t^+), reflecting the degree of electron deficiency,[138] or q_i^+ the total or π-charge.[78-81,97,102,111,125,129,134]

Borodkin et al.[102] reported a simplified interpretation of dependences of this sort in terms of the method of vacant molecular orbitals.[139] A more rigorous quantum-chemical analysis of the variation of the coefficients a_i and b_i with variation of the migrants R_m was later carried out.[140-143] The a_i and b_i coefficients in the relationship (1) behave so that the relative abilities of R_m of different types (H, Me, Ph, Cl, NO_2) to migrate do not form a universal sequence.[21,78,129]

It is noteworthy that $\Delta G^{\neq} = 0$ for the extrapolation curves is achieved at various values of δC_t^+. This apparently indicates the possibility of inversion of the relative arrangement of energy levels of the σ-complexes (**A**, **A'**) and the π-complex (**B**) (or the corresponding transition state **B**) (see Scheme 2) with increase in the charge on the carbonium centre; the tendency of the migrants R_m to form π-complexes increases in the sequence $H < Me < Ph < NO_2 < Cl$.[78,129]

The degree of electron deficiency on the C_t atom in a series of related σ-complexes can be characterised, as well as by δC^+ and q_i^+, by the σ^+-constants of the substituents[78,102,125] or by the ν(CO) stretching frequencies of the ketones resulting from the replacement of the C_t^+-Me fragment in the σ-complex by a C = O fragment.[78,125,144] The validity of linear correlation dependences of this type has been confirmed using the 1,2-shifts of hydrogen atoms,[78] Me[144] and Ph[125] groups in arenium ions as examples.

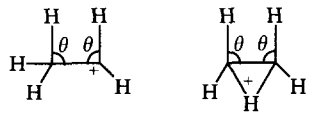
The relationships of type (1) ($\zeta = \delta C_t^+$ or q_π^+) do not hold for rearrangements of 1-R_m-1,2-dimethyl-3,4,5,6-tetrafluorobenzenium ions (R_m = H, Cl)[80,135] or 1-R_m-1,2,3,4-tetramethylbiphenylenium ions (R_m = H, Me).[82,98] In the former case the quality of the correlation can be substantially improved by using the difference between the chemical shifts of the C_t atom of the arenium ion and its precursor, the corresponding arene, instead of δC_t^+ (see Ref. 135). Morozov et al.[145] have shown that by taking into account the logarithms of the basicity constants of arenes ($\lg K$), obtained by the imaginary abstraction of the migrant R_m^+ from the cation, as well as the q_π^+ parameter, one can quantitatively describe rearrangements of arenium ions of both the benzoid and nonbenzoid types in the framework of the two-parameter correlation

$$\Delta G^{\neq} = a + b\,q_i + c\lg K\,. \qquad (2)$$

This approach was later extended to the rearrangements of aliphatic carbocations.[146]

More serious limitations arise when one attempts to use type (1) relationships for quantitative descriptions of the rearrangements of σ-complexes with different types of cores. For example, in the case of 1-R_m-1,2-dimethylacenaphthylenium ions (R_m = H, Me,[85] Cl[134]), the differences between experimentally determined $\Delta G^{\neq}$ values and those calculated from type (1) relationships can reach 5-7 kcal mol^{-1}. An increase in the

activation barrier with decrease in the size of the ring against which the migration occurs has also been found for the isomeric σ-complexes **24a** and **25** (see Table 1). A similar increase in ΔG is observed on going from the 2-butyl cation ($\Delta G^{\neq}_{-140\,°C} < 1.9$ kcal mol^{-1})‡ (see Refs 15, 54) to the cyclobutyl ion (**5a**) (see Table 1).[57] Using MINDO/3 and ab initio calculations, Chandrasekhar and Schleyer[149] have determined the dependence of the difference between the energies of the σ-complex (**C**) and the π-complex (**D**) on the magnitude of the angle θ and have shown that the activation barrier to the 1,2-shift of a hydrogen atom increases as this angle decreases.

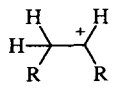


C **D**

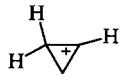


c **d**

One of the reasons for the increase in the activation barrier to the 1,2-shift is the increase in the antibonding interaction between the atomic orbitals in the occupied MO (**c** and **d**) corresponding to structures **C** and **D**, which is due to the shortening of the C_0-C_t bond (1.49 and 1.40 Å, respectively). MINDO/3 and ab initio calculations of the barriers to the 1,2-shifts of hydrogen in acyclic and in cyclic σ-complexes **5a**, **6a**, **9a**, **77 – 79** confirm the conclusions suggested by the above-mentioned model.



R = H (**77**), Me (**78**)



79

Apart from the 'ring effect' against whose background the migration occurs, the influence of other factors (in particular, orbital orientation) also can lead to deviations from type (1) dependences.[17, 21, 22, 103, 150 – 153] An unfavourable mutual orientation of the C_0-R_m bond and the vacant atomic *p*-orbital makes the transition state more strained[153] (see Ref. 71) and the rate of the rearrangement decreases. The allowance for the aromatic or antiaromatic character of the transition state can be important[21] (see Ref. 71). The latter is probably responsible to a substantial degree for the increase in the activation barriers to the 1,2-shifts of hydrogen and methyl groups in the ions **24a, b** and **37** compared with those expected from calculations using dependences of type (1).[82, 83, 98] This retarding factor is even more pronounced in the case of 1-R_m-1,2,3,4-tetramethylcyclobutenyl cations for which no rearrangements occurring via 1,2-shifts of migrants (R_m = H, Me, Ph) can be detected even under quite rigorous conditions (see Tables 1 – 3), although other rearrangements associated with the reconstruction of the system of bonds in these ions occur quite readily.[15, 88, 89] (see Ref. 71).

The aggregate of the charge factor and other factors can be taken into account (at least, for identical migrants) by choosing a 'chemical' parameter, the free energy of activation (or lg *k*, E_a) of the 1,2-shift of the standard migrant as a generalised parameter.§ The legitimacy of using this approach to the quantitative description of rearrangements of different cationic σ-complexes has been shown for the first time for the 1,2-shifts of hydrogen atom and methyl group chosen as the standard group.[155] It turned out that for a wide range of rearranging ions, 1-R_m-1,2,3,4,5,6 hexamethylbenzenium, 2,7- and 3,6-substituted 9-R_m-9,10-dimethylphenanthrenium, 1-R_m-1,2-dimethyl-acenaphthylenium, and 1,4-di-X-2-R_m-2,3-dimethylnorbornyl ions the following correlation relationships hold:[78]

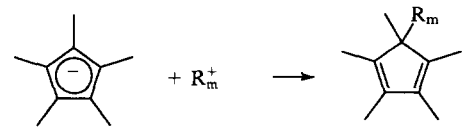
$$\Delta G^{\neq}(R_m) = a_1 + b_1 \Delta G^{\neq}(Me), \quad (3)$$

$$\lg k(R_m) = a_2 + b_2 \lg k(Me), \quad (4)$$

$$E_a(R_m) = a_3 + b_3 E_a(Me). \quad (5)$$

Later the range of rearranging σ-complexes covered by analogous dependences has been extended by including the data for rearrangements of 2-R_m-2,3-dimethylbutyl, 2-R_m-1,2,3,4-tetramethylnaphthalenium, and 2-R_m-1,2,3,4-tetramethylbiphenylenium ions and neutral structures, i.e. 5-R_m-1,2,3,4,5-pentamethyl-1,3-cyclopentadienes (**80**),[156] which can be regarded as neutral σ-complexes formed by linking a 1,2,3,4,5-pentamethylcyclopentadienyl anion to an R_m^+ cation (Scheme 3).[98]

Scheme 3



80a – d

R_m = H (**a**),[156, 157] Me (**b**),[158] Ph (**c**),[159] NO_2 (**d**).[160]

It should be noted that when the whole set of data is processed, the above-presented correlation relationships can describe a very wide range of rearrangement rates $\Delta\Delta G^{\neq}(Me) \approx 40$ kcal mol^{-1} including structures with formal charges between 0 and 1.

Analogous dependences have also been found for other migrants (Ph[159] and NO_2[160]) using the methyl group as the standard migrant. The fact that dependences of types (3) – (5) are valid for both cationic and uncharged σ-complexes indicates a fundamental inherent alliance between rearrangements of carbocations and those of neutral compounds. An analysis of the behaviour of type (3) dependences for the H, Me, Ph, and NO_2 migrants has shown[159] that as the activity grows [the $\Delta G^{\neq}(Me)$ value decreases], the selectivity [$\Delta G^{\neq}(R_m^1) - \Delta G^{\neq}(R_m^2)$] diminishes until the isoselectivity points located in the region of low $\Delta G^{\neq}(Me)$ values are reached, which is in conformity with the 'activity – selectivity' ¶ principle (see Refs 161 – 164).

2. Influence of the nature of the migrant

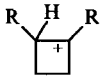
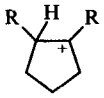
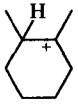
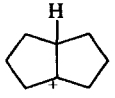
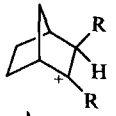
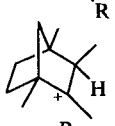
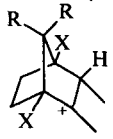
Predicting the rates of rearrangements of carbocations that occur via 1,2-shifts of various atoms or groups is one of the fundamental problems in the theory of molecular rearrangements,[15, 20, 21, 166, 167] and, it is also one of the most complex problems, since both the structure of the core of the carbocation (electrophilic agent) and the nature of the migrant atom subjected to the attack vary over wide limits. As was noted above, quantum-chemical calculations do not allow the rates of carbocation rearrangements to be predicted reliably enough (see Refs 168 – 180). We believe that the approach based on the use of correlation relationships and experimentally determined parameters characterising the nature of the migrant is a more promising approach to the quantitative description of the rearrangements of cationic σ-complexes. In this connection, illustrative data have been obtained for the 1,2-shifts of isosteric migrants, *meta*- and *para*-substituted phenyl groups. The rearrangements of 9-(X-phenyl)-9,10-dimethylphenanthrenium

‡ The value of $\Delta G^{\neq}$ probably refers to the interconversion of the 2-butyl cation and the corresponding π-complex of type **B** (see Scheme 2 and Refs 25, 147, 148).

§ The fruitfulness of using 'chemical' parameters in organic chemistry is well known. Typical examples are Hammet and Brønsted equations, etc.[154]

¶ Note that the behaviour of the migrants C_6F_5S or C_6F_5Se in similar rearrangements does not obey the 'activity-selectivity' principle.[165]

Table 1. Kinetic characteristics of the 1,2-shift of hydrogen atom for degenerate rearrangements of σ-complexes.

Structural formula	σ-Complex	R (X or Y)	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**3a**	Me	$SO_2ClF-SO_2F_2$ [b]			3.1±0.1 (−138 °C)	54
	3b	CD_3	$SO_2ClF-SO_2F_2$ [b]			3.0±0.1 (−138 °C)	54
	3c	Et	$SO_2ClF-SO_2F_2$ [b]			4.4±0.2 (−116 °C)	54
	3d	Ph	HSO_3F-SO_2ClF			> 10.2 (−80 °C)	55
	**4a**	Ph	HSO_3F-SO_2ClF			> 16.8 (37 °C)	55
	4b	*p*-MeC_6H_4	$CF_3SO_3H-SO_2ClF$			> 14.7 (0 °C)	56
	**5a**	H	$SbF_5-SO_2ClF-SO_2F_2$			> 10 (−61 °C)	57
	5b	Me	SbF_5-SO_2ClF			⩽ 6.6±0.5 (−95 °C)	58
	**6a**	H	$HSO_3F-SbF_5-SO_2ClF$ or $HF-SbF_5-SO_2ClF$			> 5.5 (−130 °C)	59, 60
			$SbF_5-SO_2ClF-SO_2F_2$			⩽ 4.7 (−150 °C)	61
	6b	Me	$SO_2ClF-SO_2F_2$ [b]			3.1±0.1 (−139°C)	54
	**7**		$SO_2ClF-SO_2F_2$ [b]			3.7±0.1 (−137 °C)	54
	**8**		$HSO_3F-SbF_5-SO_2ClF$			4.0 [d]	62
	**9a**	H	$SbF_5-SO_2-SO_2F_2$	10.8 ± 0.6 [e]	12.3 [e]	11.5 (25 °C)	64
	9b	Me	HSO_3F-SO_2ClF			⩾ 12.0 [d]	65
	**10**		HSO_3F-SO_2ClF			> 14.1 (−10 °C)	66
	**11a**	R = H, X = H	HSO_3F-SO_2ClF			7.2 (25 °C)	65
	11b	R = H, X = Me	HSO_3F-SO_2ClF			7.3 (−115 °C)	66, cf. 65, 67

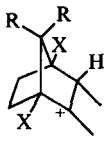
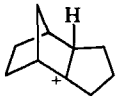
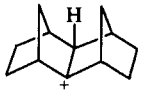
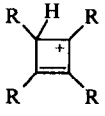
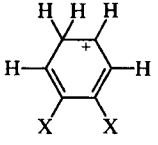
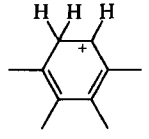
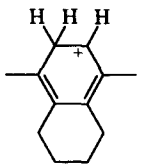
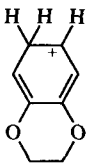
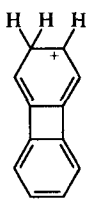
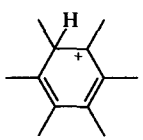
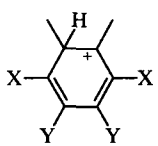
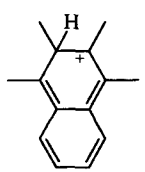
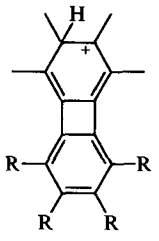
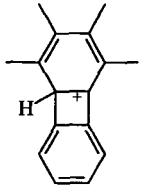
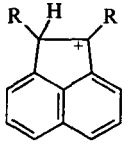
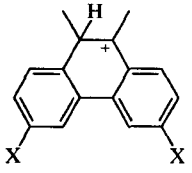
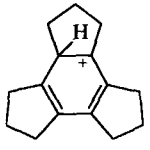
	**11c**	R = Me, X = Me	HSO_3F-SO_2ClF			7.4 (−110 °C)	67
	**12**		SbF_5-SO_2ClF			7.2±0.5 (−110 °C)	68
	**13**		HSO_3F-SO_2ClF			7.0[d]	62, 69
	**14**		SbF_5-SO_2ClF			⩾15 (0 °C)	62
	**15a**	H	$HSO_3F-SbF_5-SO_2ClF$ (SO_2)			> 15.8 (20 °C)[c]	70
	15b	Me	CH_2Cl_2 (AlC_4^- anion)			> 19.2 (80 °C)[c]	71
	**16a**	H	$HF-SbF_5-SO_2ClF-SO_2F_2$	10.0±1	15.3±1.6	6.6 (25 °C)	72, 73
	16b	Me	$HF-SbF_5-SO_2ClF$	5.3±0.8	8.5±0.6	11.2 (25 °C)	74
	16c	F	$HF-SbF_5-SO_2ClF$	5.7±0.8	8.6±0.7	11.4 (25 °C)	74
	16d	OH	$HSO_3F-SbF_5-SO_2ClF$			> 13.6 (−20 °C)[c]	75
	16e	OMe	$HF-BF_3$			> 14.7 (20 °C)	76
	**17**		$HF-BF_3$	11.6	13.0	11.3 (25 °C)	76

Table 1 (continued)

Structural formula	σ-Complex	R (X or Y)	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**18**		$HF-BF_3$	11.2	13.0	10.9 (25 °C)	76
	**19**		$HF-BF_3$			> 16.3 (0 °C)	76
	**20**		$HSO_3F-SbF_5-SO_2ClF$			~12.4 (−32 °C)	77
	**21**		$HF-BF_3$ or $HF-SbF_5$ $HSO_3F-SbF_5-SO_2ClF$	11.3 11.8±0.2	13.3 13.5±0.2	10.6 (25 °C) 10.8 (25 °C)	76 78
	**22a**	X = Cl, Y = Me	$HF-SbF_5-SO_2ClF$			~10.9 (−60 °C)	79
	22b	X = Cl, Y = Cl	$HF-SbF_5-SO_2ClF$	8.5±0.2	11.1±0.2	10.8 (25 °C)	80
	22c	X = F, Y = F	$HF-SbF_5-SO_2ClF$	10.2±0.2	12.6±0.2	10.5 (25 °C)	80
	**23**		$CF_3SO_3H-SbF_5$			12.8 (62 °C)	81

	**24a**	H	$CF_3SO_3H-SO_2ClF$	12.6±0.1	12.6±0.1	12.8 (25 °C)	82
	24b	Me	$HCl-Al_2Cl_6-CH_2Cl_2$			~15 (3 °C)	83
	**25**		$CF_3SO_3H-SO_2ClF$			> 14.6 (−2 °C)	82
	**26a**	H	$HSO_3F-SbF_5-SO_2ClF$			> 16.9 (40 °C)[c]	84
	26b	Me	$HSO_3F-SbF_5-SO_2ClF$	13.8±0.3	13.3±0.3	13.1 (25 °C)	85 (cf 84)
	**27a**	H	$HSO_3F-SbF_5-SO_2ClF-SO_2F_2$	8.7±0.3	12.8±0.3	8.7 (25 °C)	78
	27b	Br	$HSO_3F-SbF_5-SO_2ClF-SO_2F_2$	8.8±0.2	12.8±0.2	8.8 (25 °C)	78
	27c	Me	$HSO_3F-SO_2ClF-SO_2F_2$	9.8±0.3	12.8±0.4	9.8 (25 °C)	78
	27d	CF_3	$HSO_3F-SbF_5-SO_2ClF-SO_2F_2$	7.5±0.3	13.5±0.5	6.5 (25 °C)	78
	**28**		$HSO_3F-SbF_5-SO_2ClF$			8.2 (−30 °C)	86

Note. From this point on, free valence lines in structural formulae denote methyl groups. For the sake of simplicity, π-,σ-delocalisation is not shown in the structural formulae.

[a] The values of $\Delta G^{\neq}$ have been calculated from the equation: $\Delta G^{\neq} = 2.3RT[\lg(kT/h) - \lg k_{1,2}]$ (the corresponding temperatures are given in parentheses), $\lg A_{1,2} = \lg A - \lg f$, where f is the statistical factor taken as $f=4$ for the ion **16a**, $f=2$ for the cations **16b,c**, **17**, **18**, **20**, **21**.

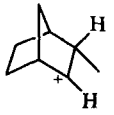
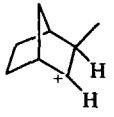
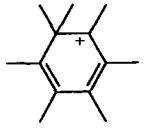
[b] The acid is not specified, it is probably SbF_5.

[c] Based on the data, it was assumed that $k < 10\,s^{-1}$.

[d] The temperature is not given.

[e] According to the published data,[61,63] the values of the kinetic parameters given in the Table refer to the 1,2-shift of the *exo*-H atom; the value of $\Delta G^{\neq}$ for the 1,2-shift of the *endo*-H atom exceeds 20 kcal mol^{-1}.

Table 2. Kinetic characteristics of the 1,2-shifts of alkyl groups in degenerate rearrangements of σ-complexes.

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**29**		$SO_2ClF-SO_2F_2$ [b]			3.8±0.1 (−136 °C)	54
	**30**					>20 [c]	4
	**31**					14.5 [c]	4
	**32a**	H	HSO_3F-SO_2ClF			8.3(25 °C) [d]	87
	32b	Me	HSO_3F-SO_2ClF			9.4 (−94 °C)	67
	**33a**	H	HSO_3F-SO_2ClF			9.4 (−67 °C) [e]	67
	33b	Me	HSO_3F-SO_2ClF			~12.9 (−50 °C) [f]	67
	**34a**	Me	CH_2Cl_2 ($AlCl_4^-$ anion)			>16.1 (25 °C) [g]	71
			94% H_2SO_4			>19.2 (80 °C)	88, 89
			HSO_3F			>27.5 (70 °C)	88, 89
	**35**		HSO_3Cl	18.2±0.6	12.9±0.4	18.1 (25 °C)	90
			9.4 M H_2SO_4	15.2 18.3±1.8 [h]	11.7 13.0±1.2 [h]	18.0 (25 °C)	91
			CF_3COOH ($AlCl_4^-$ anion)	18.4±0.8	13.1±0.6	17.9 (25 °C)	92
				16.5±0.1	11.5±0.1	18.3 (25 °C)	93

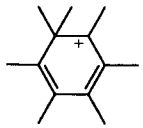
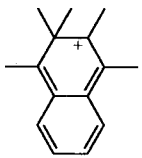
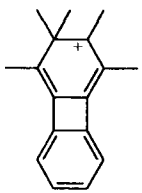
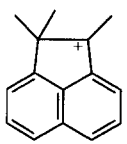
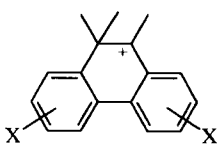
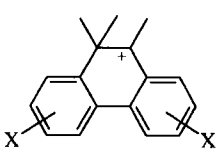
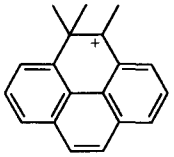
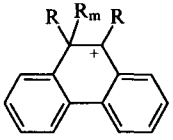
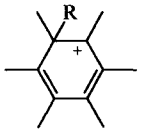
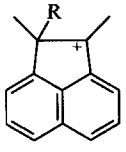
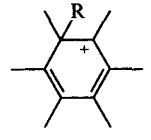
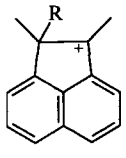
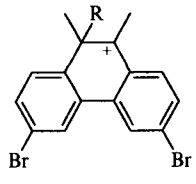
	**35**		CH_2Cl_2 ($SbCl_6^-$ anion)	17.4±0.2	12.4±0.1	17.9 (25 °C)	94, 95
			$SOCl_2$ ($AlCl_4^-$ anion)	10.5±0.2	4.8±0.2	21.4 (25 °C)	93, 95
			Crystal (BF_4^- anion)	16.4±0.5	10.2±0.5	19.9 (25 °C)	95
			Crystal (BPh_4^- anion)	15.1±0.5	9.2±0.5	20.0 (25 °C)	95
			Crystal ($SbCl_6^-$ anion)	18.3±0.2	13.5±0.2	17.3 (25 °C)	94, 95
			Crystal ($AlCl_4^-$ anion), on Al_2O_3	15.0±0.2	10.3±0.2	18.4 (25 °C)	96
	**36**		CF_3SO_3H, $HSO_3F-SO_2ClF-SO_2F_2$			22.7 (−125 °C)	97
	**37**		CF_3SO_3H	19.4±0.4	13.5±0.2	18.5 (25 °C)	98
	**38**		CF_3SO_3H	18.5±0.3	12.9±0.2	18.4 (25 °C)	85
			Crystal ($AlCl_4^-$ anion)	22.5±0.5	13.7±0.4	21.3 (25 °C)	99, 100
	**39a**	H	$HCl-Al_2Cl_6-CH_2Cl_2$	12.1±0.2	13.2±0.2	11.5 (25 °C)	101
			HSO_3F-SO_2ClF	12.2±0.1	13.3±0.1	11.5 (25 °C)	102
	39b	3,6-Br_2	HSO_3F-SO_2ClF	11.2±0.2	12.5±0.1	11.6 (25 °C)	102
	39c	3,6-Me_2	HSO_3F-SO_2ClF	13.4±0.3	12.8±0.2	13.4 (25 °C)	102
	**39d**	3,6-$(CF_3)_2$	HSO_3F-SO_2ClF	7.9±0.1	11.5±0.1	9.7 (25 °C)	102
	39e	2,7-Br_2	HSO_3F-SO_2ClF	10.2±0.2	12.3±0.2	10.9 (25 °C)	102
	39f	4,5-Me_2	CF_3SO_3H, HSO_3F-SO_2ClF	14.1±0.2	12.8±0.2	14.1 (25 °C)	103

Table 2 (continued)

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**40**		HSO_3F-SO_2ClF	11.7±0.1	12.8±0.1	11.7 (25 °C)	102
	**41a**	R_m = Me, R = Et	$HCl-Al_2Cl_6-CH_2Cl_2$			~12 (25 °C)	104
	41b	R_m = Et, R = Me	$HCl-Al_2Cl_6-CH_2Cl_2$			10.1 (25 °C)	104
	41c	R_m = Et, R = Et	$HCl-Al_2Cl_6-CH_2Cl_2$	10.1	12.4	10.6 (25 °C)	104, 105
	**42**	Et	CF_3COOH			16.0 (25 °C)	105, 106
	**43**	Et	CF_3SO_3H	16.3±0.3	12.3±0.2	17.0 (25 °C)	107
	**44**	$CH_2-CH=CH_2$	HSO_3F			> 12.8 (−50 °C)	108
	**45**	$CH_2-CH=CH_2$	HSO_3F			> 15.9 (0 °C)	108
	**46**	$CH_2-CH=CH_2$	HSO_3F-SO_2ClF			8.1 (−90 °C)	108

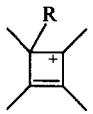
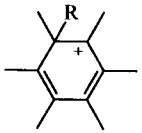
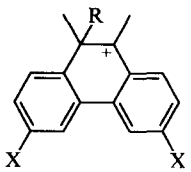
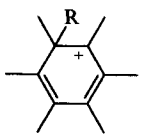
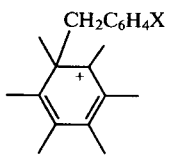
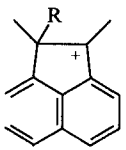
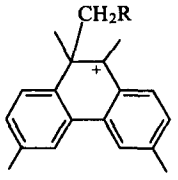
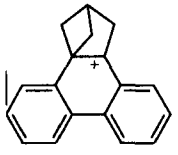
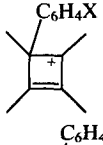
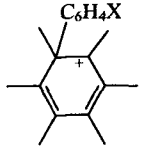
	**34b**	$CH_2-CH=CH_2$	HSO_3F-SO_2ClF			> 12.9 (−90 °C)	109
	**47**	CH_2Cl	HSO_3F or CF_3COOH			> 19.5 (60 °C)	106, 110
	**48a**	Me	CF_3SO_3H	17.7±0.5	12.7±0.4	17.8 (25 °C)	111
	48b	CF_3	HSO_3F	13.8±0.3	13.0±0.2	13.5 (25 °C)	111
	48c	Br	HSO_3F	16.2±0.4	13.0±0.3	15.9 (25 °C)	111
	**49**	$CHCl_2$	$CHCl_3$ ($Al_2Cl_7^-$ anion)			> 18.3 (40 °C)	105, 106
	50	CH_2CHO	HSO_3F			> 11.7 (−70 °C)	105, 106
	**51a**	H	HSO_3F-SO_2ClF	12.4±0.3	13.9±0.3	10.9 (25 °C)	112
	51b	*p*-Me	$HSO_3F-SO_2ClF-SO_2F_2$	10.4±0.3	13.4±0.3	9.6 (25 °C)	113
	51c	*p*-CF_3	HSO_3F-SO_2ClF	14.5±0.3	13.4±0.2	13.7 (25 °C)	113
	51d	*p*-Cl	HSO_3F-SO_2ClF	12.6±0.4	13.7±0.4	11.4 (25 °C)	113
	51e	*m*-F	HSO_3F-SO_2ClF	13.4±0.2	13.2±0.2	12.8 (25 °C)	113
	**52**	$CH_2C_6H_4Cl$-*p*	HSO_3F			14.7 (0 °C)	107, 114

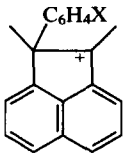
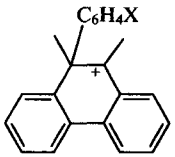
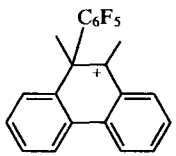
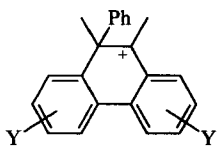
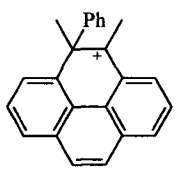
Table 2 (continued)

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**53a**	Ph	HSO_3F-SO_2ClF	7.9±0.2	11.6±0.2	9.5 (25 °C)	115
	53b	$C_6H_4CF_3$-*m*	HSO_3F-SO_2ClF	9.2±0.1	12.2±0.1	10.0 (25 °C)	115
	53c	C_6H_4Cl-*p*	HSO_3F-SO_2ClF	8.8±0.1	12.3±0.1	9.5 (25 °C)	115
	53d	C_6H_4Cl-*m*	HSO_3F-SO_2ClF	8.2±0.2	11.5±0.2	10.0 (25 °C)	115
	53e	3,5-$Cl_2C_6H_3$	HSO_3F-SO_2ClF	9.8±0.1	12.6±0.1	10.1 (25 °C)	115, 116
	**54**		HSO_3F-SO_2ClF			≤6.6 (−105 °C)	117

[a] See footnote 'a' to Table 1; the values were taken as $f = 4$ for ion **35**, $f = 3$ for ion **29**, $f = 2$ for cations **36–40**, **41c**.
[b] The acid is not given, it is probably SbF_5.
[c] The value has been evaluated (the temperature was not given). [d] For the shift of the *exo*-methyl group; for the shift of the *endo*-methyl group, $\Delta G^{\neq}_{-64\,°C} > 10.7$ kcal mol^{-1} (see Refs 4, 87).
[e] For the shift of the *exo*-methyl group; for the shift of the *endo*-methyl group, $\Delta G^{\neq}_{-64\,°C} = 19.5$ kcal mol^{-1} (see Ref 63).
[f] Apparently, for the shift of the *exo*-methyl group.
[g] Based on the published data, it was assumed that $k < 10\,s^{-1}$.
[h] The values were calculated by Koptyug and Shubin[15] based on the kinetic data reported in the literature.[91]

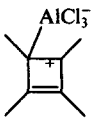
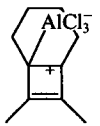
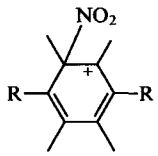
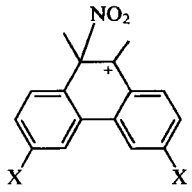
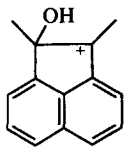
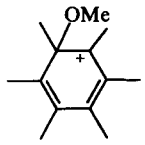
Table 3. Kinetic characteristics of 1,2-shifts of aryl groups for degenerate rearrangements of σ-complexes

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**55a**	H	94% H_2SO_4			>17.5 (50 °C) [b]	15, 89
			PhCl ($Al_2Cl_7^-$ anion)			>20.3 (100 °C) [b]	15, 89
	55b	*p*-FSO_2	HSO_3F			>18.6 (70 °C) [b]	15, 89
	**56a**	H	$CF_3SO_3H-SO_2ClF$	16.8±0.2	12.5±0.2	17.2	118
			Crystal ($AlCl_4^-$ anion)	13.6±0.1	5.9±0.1	23.0	119
	56b	*p*-Me	$CF_3SO_3H-SO_2ClF$	16.0±0.8	12.6±0.9	16.3	120, cf 121
	56c	*p*-Cl	$CF_3SO_3H-SO_2ClF$	17.9±0.3	12.8±0.3	17.9	120, cf 121
	56d	*m*-CF_3	$CF_3SO_3H-SO_2ClF$	20.0±0.3	12.8±0.3	20.0	120, cf 121

	**57a**	H	CF_3SO_3H	11.4±0.2	11.7±0.2	12.8	122, cf 123
	57b	*p*-Me	$CF_3SO_3H-SO_2ClF$	9.4±0.1	11.6±0.1	11.1	122, cf 123
	57c	*p*-Cl	CF_3SO_3H	12.2±0.3	11.8±0.2	13.6	122, cf 123
	57d	*m*-Cl	CF_3SO_3H	14.4±0.2	12.0±0.1	15.5	122, cf 123
	57e	*p*-CF_3	CF_3SO_3H	17.1±0.1	13.1±0.1	16.7	122, cf 123
	57f	*m*-CF_3	CF_3SO_3H	16.4±0.2	12.9±0.1	16.3	122, cf 123
	**58a**	H	$HCl-Al_2Cl_6-CH_2Cl_2$	8.9±0.1	12.1±0.1	9.7	124
			HSO_3F-SO_2ClF	9.0±0.2	12.2±0.2	9.8	124
			HSO_3F-SO_2ClF	9.4±0.1	12.5±0.1	9.8	125
	58b	*p*-Me	HSO_3F-SO_2ClF	6.5±0.2	11.0±0.2	8.9	124
	58c	*p*-MeO	HSO_3F-SO_2ClF			6.5	106
	58d	*p*-Cl	HSO_3F-SO_2ClF	9.8±0.1	12.4±0.1	10.3	124
	58e	*p*-F	HSO_3F-SO_2ClF	9.3±0.1	12.5±0.1	9.7	124
	58f	*m*-F	HSO_3F-SO_2ClF	11.5±0.1	12.6±0.1	11.8	124
	58g	*p*-CF_3	HSO_3F-SO_2ClF	11.7±0.2	12.0±0.1	12.8	124
	**59**		HSO_3F			> 19.1 (60°C)	106, 124
	**60a**	3,6-Br_2	HSO_3F-SO_2ClF	8.2±0.2	11.6±0.2	9.8	125
	60b	3,6-Me_2	HSO_3F-SO_2ClF	10.7±0.1	11.9±0.1	11.9	125
	60c	3,6-$(CF_3)_2$	$HSO_3F-SO_2ClF-SO_2F_2$	6.4±0.2	12.7±0.3	6.5	125
	60d	2,7-Br_2	$HSO_3F-SO_2ClF-SO_2F_2$	7.3±0.1	11.8±0.2	8.7	125
	**61**		HSO_3F-SO_2ClF	9.4±0.2	12.4±0.2	9.9	125

[a] See footnote 'a' to Table 1; $f = 2$ for the ions **56a–d**. [b] Based on the published data,[89] it was assumed that $k < 10\,s^{-1}$.

Table 4. Kinetic characteristics of 1,2-shifts of the migrants $AlCl_3^-$, NO_2, OR, SO_3H, and Hal for degenerate rearrangements of σ-complexes

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**62**		$Cl_2CHCHCl_2$	20.3	16.1	15.8 (25 °C)	126
	**63**		$Cl_2CHCHCl_2$			19.8 (92 °C)	126
	**64a**	Me	HSO_3F-SO_2	16.8±1.5			127,
				13.3±1.3 [b]	13.1±1.2 [b]	12.9 (25 °C)[b]	cf 128
			HSO_3F-SO_2ClF	13.2±0.3	13.5±0.2	12.2 (25 °C)	129
			$HSO_3F-SbF_5-SO_2ClF$	12.6±0.4	12.9±0.4	12.4 (25 °C)	129
	64b	Cl	HSO_3F-SO_2ClF or $CF_3SO_3H-SO_2ClF$			9.0 (−100 °C)	79
			HSO_3F-SO_2ClF			8.9 (−90 °C)	79
	**65a**	H	$CF_3SO_3H-SO_2ClF-SO_2F_2$			7 (−105 °C)	129
	65b	Me	HSO_3F-SO_2ClF			9.9 (−89 °C)	129
			$CF_3SO_3H-SO_2ClF$			9.8 (−85 °C)	129
	**66**		HSO_3F-SO_2ClF	15.4±0.3	16.4±0.3	10.5 (25 °C)	130
	**67**		HSO_3F			>11.7 (−75 °C)	106, 131

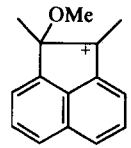
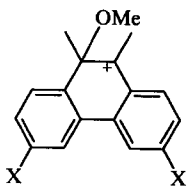
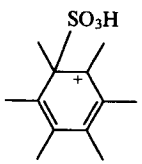
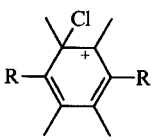
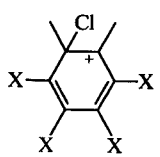
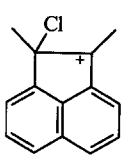
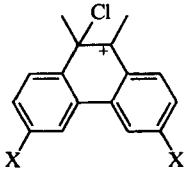
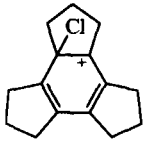
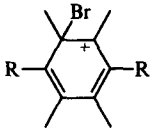
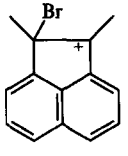
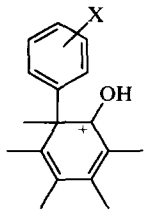
	**68**		HSO_3F-SO_2ClF (1:1)	13.0±0.5	14.8±0.5	10.3 (25 °C)	132
			HSO_3F-SO_2ClF (1:3)	12.2±0.4	14.5±0.4	9.9 (25 °C)	132
			HSO_3F-SO_2ClF (1:6)	9.4±0.3	12.3±0.3	10.1 (25 °C)	132
			HSO_3F-SO_2ClF (1:8)			9.1 (−110 °C)	132
			HSO_3F-SO_2 (1:4)			10.4 (−55 °C)	132
			HF			10.1 (−57 °C)	132
			$CF_3SO_3H-SO_2ClF$ (1:4)			9.0 (−102 °C)	132
			$HSO_3F-n SbF_5-SO_2ClF$ [c]	13.5±0.9	13.6±0.3	12.4 (25 °C)	132
				15.2±0.3	16.0±0.3	10.8 (25 °C)	132
				15.2±0.3	16.4±0.3	10.3 (25 °C)	132
				14.8±0.2	16.2±0.2	10.2 (25 °C)	132
				14.4±0.2	16.2±0.2	9.8 (25 °C)	132
			$(HSO_3F-SbF_5)/SO_2ClF$ (1:2)			14.3 (0 °C)	132
	**69a**	H	HSO_3F-SO_2ClF			<9.2 (−100 °C)[d]	133
	69b	Br	HSO_3F-SO_2ClF			<9.2 (−100 °C)[d]	133
	69c	Me	HSO_3F-SO_2ClF			<10.3 (−80 °C)[d]	133
	**70**		HSO_3F	19.2±0.4	15.4±0.3	15.6 (25 °C)	128
	**71a**	Me	HSO_3F	15.7±0.3	13.5±0.2	14.7 (25 °C)	134
			$HCl-Al_2Cl_6-CH_2Cl_2$	14.9±0.9	13.0±0.7	14.6 (25 °C)	134
	71b	Cl	HSO_3F			13.2 (−15 °C)	79
	**72a**	Cl	$HF-SbF_5-SO_2ClF$	10.7±0.2	12.0±0.1	11.8 (25 °C)	135
	72b	F	$HF-SbF_5-SO_2ClF$			12.3 (−42 °C)	135
	**73**		HSO_3F-SO_2ClF	10.5±0.2	13.5±0.2	9.5 (25°C)	134

Table 4 (continued)

Structural formula	σ-Complex	R or X	Acid, solvent	E_a/kcal mol^{-1}	lg $A_{1,2}$	$\Delta G^{\neq}$/kcal mol^{-1} [a]	Ref.
	**74a**	H	$CF_3SO_3H-SO_2ClF-SO_2F_2$	~5.6		~6.3 (−110 °C)	134
	74b	Me	$CF_3SO_3H-SO_2ClF$	6.6±0.1	11.5±0.1	8.3 (25 °C)	134
	**75**		$HSO_3F-SbF_5-SO_2ClF$			11.6 (−40 °C)	86
	**75a**	Me	HSO_3F-SO_2ClF	10.3±0.3	13.6±0.4	9.2 (25 °C)	136
	75b	Cl	HSO_3F-SO_2ClF			~7.4 (−110 °C)	79
	**76**		HSO_3F-SO_2ClF	5.1±0.2	12.3±0.2	5.8 (25 °C)	137
			$AlBr_3-CH_2Cl_2$	3.9±0.2	11.1±0.2	6.2 (25 °C)	137

[a] See footnote 'a' to Table 1; f = 2 for the ions **62**, **64a**, **70**, **71a**, **75a**.
[b] Calculated by Koptyug and Shubin[15] based on the kinetic data reported in the literature[127], see Ref 106.
[c] In these experiments, $0 < n < 1$, the value of n increases from bottom to top. The acid:diluent ratio is 1:2.
[d] Based on the published data,[133] it was assumed that $k < 10$ s^{-1}.

(**58a–g**),[124] 1-(X-phenyl)-1,2,3,4,5,6-hexamethylbenzenium (**56a–d**),[120,121] and 1-(X-phenyl)-1,2-dimethylacenaphthylenium (**57a–f**)[122,123] ions have been used to demonstrate the validity of the relationships $\lg(k_X/k_H) = \rho\sigma_X^+$. Judging by the absolute values of $\rho^+_{-50\,°C}$ (−4.5, −4.47, and −6.64, respectively), the series of the relative migration ability are not universal even in the case of structurally similar migrants, i.e. substituted phenyl groups. Analogous dependences hold for the nondegenerate rearrangements of 1-(X-phenyl)-2-hydroxy-1,3,4,5,6-pentamethylbenzenium ions (**81a–f**) ($\rho^+_{-50\,°C} = -3.37$)[181] and also for the 1,2-shifts of $XC_6H_4CH_2$ groups in 1-(X-benzyl)-1,2,3,4,5,6-hexamethylbenzenium cations ($\rho^+_{-50\,°C} = -4.42$)[113] and 9-(X-benzyl)-9,10-dimethylphenanthrenium cations ($\rho^+_{-50\,°C} = -1.08$).[115] Borodkin et al.[115,120] have analysed the behaviour of the sensitivity constants ρ^+ for the 1,2-shifts of XC_6H_4 and $XC_6H_4CH_2$ groups as a function of the structure of the core in terms of the O'Ferrall–Jencks model.

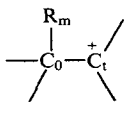


81a–f

X = H (**a**), *p*-Me (**b**), *p*-MeO (**c**), *p*-CF_3 (**d**), *m*-CF_3 (**e**), *p*-Cl (**f**).

A comparison of the selectivity (ρ^+) and activity [$\lg k$(Ph)] parameters for the rearrangements of ions **56a–d**, **57a–f**, **58a–g**, and **81a–f** shows that the 'activity-selectivity' principle (cf Refs 161–164) is not obeyed even for the isosteric XC_6H_4 migrants.[113] One may expect an antiparallel relationship between the activity and the selectivity when only one of the factors influencing the reaction rate is varied (for example, the inductive or the resonance effect)[22] (cf Ref 164). Comparing the activation free energies of the 1,2-shifts of the CH_2R groups (R = H, Me, Cl) in arenium ions with the chemical shifts of the carbocationic centre indicates that the 'activity-selectivity' principle is obeyed in the case of σ-migrants whose migration ability for ions with a fixed core is mainly determined by the inductive effect of the substituent R.[111] The $XC_6H_4CH_2$ groups behave anomalously in the series of migrants of the CH_2R type. This is shown by the intersection of the lines corresponding to the *p*-$ClC_6H_4CH_2$, $C_6H_5CH_2$, and CH_3CH_2 groups which intersect in the region of experimentally accessible values of δC^+ and $\Delta G^{\neq}$ (see Ref. 115). The violation of the 'activity-selectivity' principle in this case, as also for XC_6H_4 groups, may be associated with the simultaneous influence of the inductive and resonance effects of the substituents R (or X), the ratio between whose contributions probably varies with the activity parameter.[113,115]

A substantially more complicated problem arises in developing approaches to the quantitative description of the migration ability of different types of migrant (see Refs 140–143). Borodkin et al.[182] took the first step in this direction. They assumed that the activation free energy of the 1,2-shifts of different migrants in the cationic σ-complexes can be expressed as the sum of two constituents one of which (E_1) reflects the consumption of energy for elongation of the C_0-R_m bond and for deformation of the $C_t-C_0-R_m$ bond angle when the transition state is achieved, and the other (E_2) is the gain in energy resulting from the interaction of the migrant with the carbocationic centre.



$$\Delta G^{\neq} = a + b_1E_1 + c_1E_2. \quad (6)$$

The energy required to cleave the $C-R_m$ bond in the compounds CH_3R_m [$E_b(CH_3R_m)$] [or the force constant of the deformation vibration of the $C_t-C_0-R_m$ fragment (K_{def})] and the proton affinity of compounds CH_3R_m (*PA*) have been suggested as characteristic parameters of the E_1 and E_2 energies. It would be more reasonable to use the affinity of CH_3R_m to the CH_3^+ cation, but these data are quite limited. In terms of this simplified model, allowing for the limited relationship of the charge on the carbocationic centre (q^+) to the value of chemical shift of the C_t atom,[138] we obtain:

$$\Delta G^{\neq}(R_m) = a + bD + cq_t^+[d + e(PA)(CH_3R_m)], \quad (7)$$

where $D = E_b(CH_3R_m)$ or K_{def}; $q_t^+ = f + g\delta C^+$.

A comparison of the free energies of activation of the 1,2-shifts of the migrants in 1-R_m-1,2,3,4,5,6-hexamethylbenzenium, 9-R_m-9,10-dimethylphenanthrenium, 9-R_m-9,10-dimethylpyrenium, and 2-R_m-1,2,3,4-tetramethylnaphthalenium ions (R_m = Me, Et, XC_6H_4, Cl, Br) (see Tables 2–4) with the corresponding values of $E_b(CH_3R_m)$, $(PA)(CH_3R_m)$, and $\delta C^+(CH_3)$ produces the following correlation:†

$$\Delta G^{\neq}_{25\,°C} = 0.9 + 0.329E_b - 0.00129(PA)(\delta C^+ - 130), \quad (8)$$

$$r = 0.987,\ s = 0.7,\ n = 29.$$

The activation free energies of the 1,2-shifts of hydrogen atoms do not obey the correlation (8). This may be due to the fact that the deformation of the C_t-C_0-H fragment occurs more easily than that of other fragments, which results in an increase in the migration ability of hydrogen and probably reflects the well known tendency of hydrogen to form bridged structures (see Refs 183–187). However, when the parameter E_1 is characterised by the force constant of the deformation vibration of the $C_t-C_0-R_m$ fragment, the correlation is more general:

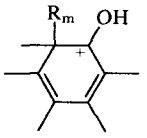
$$\Delta G^{\neq}_{25\,°C} = 17.1 + 14.5K_{def} - 0.00127(PA)(\delta C^+ - 130), \quad (9)$$

$$r = 0.963,\ s = 0.7,\ n = 33.$$

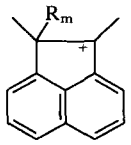
For a series of cationic σ-complexes with a fixed core ($q_t^+ \approx$ const, $\delta C^+ \approx$ const), the relationships (8) and (9) are transformed into simpler dependences:

$$\Delta G^{\neq} = a + bD + d(PA). \quad (10)$$

This makes it possible to verify the applicability of these dependences to the quantitative description of nondegenerate rearrangements of arenonium ions and of rearrangements of carbocations that differ from arenium ions in the type of core. A comparison of the activation free energies of the 1,2-shifts of migrants in 1-R_m-2-hydroxy-1,3,4,5,6-pentamethylbenzenium ions (**81, 82**)[181,188,189] and 1-R_m-1,2-dimethylacenaphthylenium ions (**83**) with the corresponding $E(CH_3R_m)$, K_{def}, and (*PA*) parameters produces correlation relationships whose characteristics are presented in Table 5.[100,190] The values of the free energies of activation of degenerate and nondegenerate 1,2-shifts of the migrants R_m in arenium ions and in 1-R_m-1,2-dimethylacenaphthylenium cations calculated from type (7) and (10) relationships are in good agreement with experimental data: the discrepancy between $\Delta G^{\neq}$ values normally does not exceed 1 kcal mol^{-1}, the range of their variation being ~ 20 kcal mol^{-1}.[100]



82a–c



83a–c

† The chemical shifts of the corresponding ions with the standard migrant, the Me group, were taken as the values of δC^+.

Table 5. The parameters of correlations of type (10) for 1,2-shifts of the R_m migrants in 1-R_m-2-hydroxy-1,3,4,5,6-pentamethylbenzenium and 1-R_m-1,2-dimethylacenaphthylenium ions at 25 °C.

Ions	Parameter					
	D	*a*	*b*	*d*	*r*	*s*
81a–f, 82a–c	E_b	14.5	0.312	−0.121	0.98	0.3
81a–f, 82a–c	K_{def}	31.0	16.6	−0.142	0.96	0.5
38, 43, 57a–f, 73, 76	E_b	20.7	0.406	−0.268	0.97	1.1
26b, 38, 43, 57a–f, 73	K_{def}	43.4	30.4	−0.358	0.92	1.3

3. Influence of the medium on the rates of degenerate σ,σ-rearrangements

When the data on the rearrangements of cationic σ-complexes are compared in terms of structure-kinetics relationships the question of how the medium influences the rate of an 1,2-shift is of importance. The influence of the liquid medium (solvent and counter-ion) has been most extensively studied for the 1,2-shift of a methyl group in the heptamethylbenzenium ion (**35**). The rate constants of the rearrangement of this ion turned out to be virtually identical in the following media: HSO_3F,[191] HSO_3Cl,[90,191] H_2SO_4,[91,191,192] CF_3COOH,[92] HCOOH,[191] HSO_3F-SbF_5 (9:1),[191] a 20% solution of SO_3 in HSO_3F,[192] CH_2Cl_2 (with $AlCl_4^-$ as the anion),[93,191] $HC(SO_2F)_3$,[193] $SOCl_2$ (with $SbCl_6^-$ as the anion),[94,95] $PhNO_2$ (with the $AlCl_4^-$ anion),[191] C_6F_6 (with the $Al_2Cl_7^-$ anion),[21] $PhNO_2$ (with the Ph_4B^- anion).[21] The same conclusion applies to the rearrangements of 9,9,10-trimethylphenanthrenium (**39a**),[101,102,104,194,195] 3,6,9,9,10-pentamethylphenanthrenium (**39c**),[102,193] and 1,1,2-trimethylacenaphthylenium (**38**)[85] ions. No appreciable influence of the medium on the rates of 1,2-shifts of hydrogen has been detected for 1-*H*-1,2,3,4,5,6-hexamethylbenzenium (**21**),[21,76,78] 9*H*-3,6,9,10-tetramethylphenanthrenium (**27c**),[78] 2-*H*-1,2,3,4-tetramethylbiphenylenium (**24a**),[82] 1-*H*-1,2-dimethylacenaphthylenium (**26b**),[84,85] 2,3-dimethyl-2-norbornyl (**11a**),[65] 1-*H*-1,2-dimethyl-3,4,5,6-tetra-X-benzenium (X=Cl, F (**22b**),[80] 1,2,3,4-tetramethylnaphthalenium (**23**),[81] 2-methyl-2-butyl,[21,152,196–198] or 4-R-1,2,3,4,5-pentamethylcyclopentenyl (R = H, Me)[21,199] ions. Likewise, very low sensitivities of the rearrangement rates to variation of the medium have been found for the 1,2-shifts of XC_6H_4 groups in 1-phenyl-1,2,3,4,5,6-hexamethylbenzenium (**56a**),[118] 9-phenyl-9,10-dimethylphenanthrenium (**58a**),[124,125] and 9,9,10-tri-(*p*-X-phenyl)phenanthrenium[200] ions as well as for the 1,2-shifts of halogen atoms in 1-chloro-1,2,3,4,5,6-hexamethylbenzenium (**71a**)[134] and 1-bromo-1,2-dimethylacenaphthylenium (**76**)[137] cations (see Table 4). The rate of the 1,2-shift of the $AlCl_3^-$ group in the ion **62** is also virtually unchanged on going from CH_2Cl_2 to $CHCl_2CHCl_2$.[126]

The lack of influence of the medium on the rates of the 1,2-shifts in the π-delocalised carbocations considered above is probably due to the fact that the location of the 'centre of gravity' of the positive charge on the cation varies only slightly on going from the ground state to the transition state.[21]

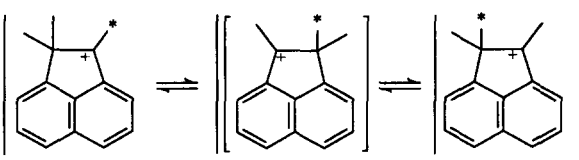
As would be expected, in the case of migrants susceptible to specific solvation the influence of the medium on the rates of rearrangements becomes dominant. For example, the rate of the degenerate rearrangement of the 1-nitro-1,2,3,4,5,6-hexamethylbenzenium ion (**64a**) in the $HSO_3F-SbF_5-SO_2ClF$ system, which occurs via the 1,2-shift of the nitro group, decreases as the concentration of SbF_5 increases.[129] Similar effects have been observed for OH,[130] OMe,[132] and Alk–OCO [201] groups (see Ref. 202). It is likely that in these cases, owing to specific solvation of the migrant by the medium, the magnitude of the positive charge on the migrant increases and this leads to a diminution of the rate of rearrangement.

In view of the data considered above, the problem of controlling the rates of 1,2-shifts of migrants by using ordered media is of great interest. The first attempts along these lines were undertaken by Borodkin et al.,[203] who studied the rearrangement of the 1,1-dimethyl-2-ethyl-acenaphthylenium ion to the 1-ethyl-1,2-dimethylacenaphthylenium cation (**43**). However, it was found that the rate of this rearrangement virtually does not change on going from liquid to frozen CF_3SO_3H as the solvent. Later it was shown[204] by CPMAS ^{13}C NMR that the rates of hydride shifts in norbornyl and 2-butyl cations are also almost insensitive to the change in the phase state of solutions in SbF_5 (see Ref. 205).

Data on the strong influence of an ordered medium on the rates of 1,2-shifts in cationic σ-complexes were obtained for the first time for the crystalline tetrachloroaluminate of the hexamethylbenzenium ion.[93] The values of the kinetic parameters (E_a, lg*A*) of the 1,2-shift of the methyl group in this cation in the crystalline state were found to be appreciably lower than those in solution (see Table 2). At −77 °C an isokinetic point was observed and at higher temperatures the rate constants of the rearrangement were larger in the case of the liquid phase. Variation of the counter-ions in crystalline heptamethylbenzenium salts ($AlCl_4^-$, BF_4^-, BPh_4^-, $SbCl_6^-$) results in strong changes in both the kinetic parameters (see Table 2) and the rate of the 1,2-shift of the methyl group.[95] Unexpectedly, the intramolecular rearrangement of the $SbCl_6^-$ salt of this ion accelerates on going from solution to the crystalline state (see Table 2).[94,95] This fact and also the decrease in the activation energy found in some other cases are probably due to the Coulomb interaction of the neighbouring counter-ions with the rearranging ion, in particular, the stabilising interaction of the neighbouring anion with the methyl group which carries a partial positive charge in the transition state.[93,95] This is confirmed by the existence of linear correlations of the logarithms of the ratios between the rate constants of the 1,2-shifts of Me and Ph migrants in the ions **35** and **56a** in the crystalline phase and in solution with the values of the difference between the energies of Coulomb interaction of the rearranging ion with their environment in the ground and the transition states.[95] Considerable retardation of the carbocation rearrangements on going from solution to the crystalline state has been found for the tetrachloroaluminate of 1-phenyl-1,2,3,4,5,6-hexamethylbenzenium ion[119] (**56a**, see Table 2).

In the crystalline state the rearrangements of 1-R_m-1,2,3,4,5,6-hexamethylbenzenium ions (R_m = Me, Ph) are degenerate rearrangements as regards both the structure of the ion and the environment, i.e. the rearranging ion preserves its topochemical properties after each act of migration of the R_m group.[206] These rearrangements may be referred to as 'topodegenerate'. Another type of solid-state carbocationic rearrangement, which is degenerate as regards the structure of the ion but nondegenerate as regards the environment ('topo-nondegenerate' rearrangement), has been found in a study of the crystalline tetrachloroaluminate of the 1,1,2-trimethylacenaphthylenium ion (**38**)[99] by the radioactive tracer method. The 1,2-shift of methyl in this ion leads to a structure that is formally identical to the original one (Scheme 4),‡ but has a distorted unit cell. The rate of the rearrangement of ion **38** in the crystalline state is appreciably lower than in solution (see Table 2), which is obviously due to the fact that the structure of ion **38′** does not correspond to the unit cell.

Scheme 4

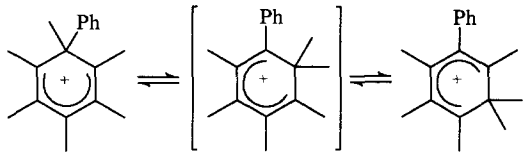


38 **38′**

‡ The vertical line in Scheme 4 conventionally denotes the dissimilar environments of ions **38** and **38′** in the crystal.

One might expect that similar retardation effects would be seen in the case of carbocationic rearrangements that are non-degenerate with respect to both the ion structure and the environment. In fact, the nondegenerate rearrangement of ion **56a** occurring in solution via a 1,2-shift of the methyl group (Scheme 5),[118] does not proceed in the crystalline state to any noticeable degree even under very rigorous conditions (70 °C, 2 h).[119]

Scheme 5



56a

Thus, the selectivity of the process (the k^{Ph}/k^{Me} ratio) increases on passing from solution to the crystalline state.

Surprisingly, the Arrhenius parameters of the rearrangement of heptamethylbenzenium tetrachloroaluminate deposited on Al_2O_3 are intermediate between those found for the reactions in solution and in the crystalline phase (see Table 2).[96] The fact that lg$A$ is larger than in the crystalline state may indicate that this cation possesses a relatively high mobility on the Al_2O_3 surface. By analogy with the crystal-degenerate rearrangement of this ion, the decrease in the activation energy compared with the E_a value for the solution may be caused by the electrostatic interaction of the partial positive charge of the migrant with the nucleophilic centres of alumina and $AlCl_4^-$.

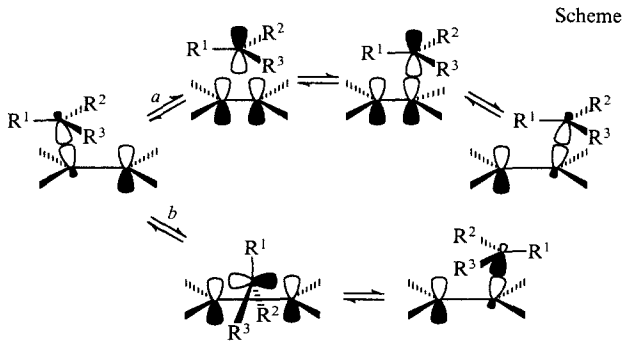
These results show that the transition to ordered or 'partially ordered' media is an effective means of controlling rearrangements in cationic σ-complexes.

4. Stereochemical aspects of cationic σ,σ-rearrangements

The stereochemistry of a migrant is one of the most important aspects of the theory of sigmatropic rearrangements occurring via 1,2-shifts of alkyl or other similar groups. For suprafacial 1,2-shifts of $CR^1R^2R^3$ groups,§ (see Refs 207, 208) the configuration of the C atom bound to R^1, R^2, and R^3 groups can be either retained (Scheme 6, path *a*) or inverted (path *b*).

The stereochemistry of tetragonal migrants involved in 1,2-shifts in 'long-lived' carbocations has been studied for the first time for 1-CH_2R-1,2-dimethylacenaphthylenium ions (R = Me, *p*-ClC_6H_4)[107,114] by an approach based on the fact that the methylene protons are diastereotopic and by using dynamic NMR.[52] A comparison of the rate constants of the rearrangement determined from the variation of the forms of signals of the CH_3 and CH_2R groups showed that they are almost identical. This implies that the 1,2-shifts of C_2H_5 and *p*-$ClC_6H_4CH_2$ groups in ions **43** and **52** occur with retention of the configuration of the methylene C atom, which is consistent with the theory of pericyclic reactions.[207,208]

Scheme 6



§ Antarafacial 1,2-shifts seem to be very unlikely, especially in cyclic systems.[153,207] In a study of degenerate rearrangement of 4,5,9,9,10-pentamethylphenanthrenium ion, it has been found that the 1,2-shift of methyl occurs as a suprafacial process.[103]

Later similar results were obtained for an ion of a different structural type, i.e. the 9-(3′,5′-dichlorobenzyl)-3,6,9,10-tetramethylphenanthrenium cation (**53e**).[116] Assuming that 1,2-shifts in these ions are one-step processes, one can treat these results as experimental evidence for the Miller[209] postulate concerning the stereospecificity of the elementary step of a chemical reaction.[107]

As in the data obtained for 'long-lived' cations, retention of the configuration at the migrating centre has also been observed in the pinacol–pinacolone[210] and other cationoid rearrangements[211–213] whose key step is the 1,2-shift of a migrant to a carbonium centre.

It is noteworthy that the 1,2-shift of the methyl group in the 1,1,2,3,4-pentamethylcyclobutenyl cation (**34a**) does not occur even under very rigorous conditions ($\Delta G^{\neq} > 27.5$ kcal mol^{-1}),[88,89] though according to the theory of pericyclic reactions, this shift is allowed as a suprafacial process with inversion of the configuration of the migrant.

IV. σ,π-Rearrangements

The tendency of cationic σ-complexes to rearrange caused by their 'inherent instability' is closely related to their tendency to form in some cases multicentre migrant—core bonds. Owing to the large deviations of the bond angles from their normal values, the resulting π-complexes are rather strained systems, and the peculiarities of their electronic structures are not adequately characterised by the classical views of the nature of the chemical bond[214] (cf Ref. 35).



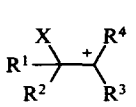
84a **84b**

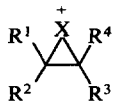
These structures were described for the first time by Dewar[34] in the framework of the method of molecular orbitals. Dewar et al.[35,139] considered the evolution of concepts in the field of the theory of π-complexes. According to the modern views, strong and weak π-complexes are distinguished depending on the ratio between the forward ($\pi-p$) and back (π^*-p) donation.[35] In the case of strong π-complexes (**84a**), the contribution of the forward donation predominates, whereas for weak π-complexes (**84b**), these contributions are comparable.[35] As the electronegativity of the X fragment increases, the role of back donation should diminish.[35,214] The foregoing should be taken into account while considering the relative stabilities of σ- and π-complexes.

According to Dewar and Dougherty,[139] the change in energy on going from a σ- to a π-complex is determined by the following relationship:

$$\Delta E = (E_{C-X} - E_{\pi}) + (E_{C-C} - E_{C=C}),$$

where E_{C-X}, E_{C-C}, and $E_{C=C}$ are the energies of the corresponding bonds and E_{π} is the energy of the bond between the apical group and the core in the π-complex. Despite the fact that the strengths of the C–X bonds in σ- and π-complexes should vary in parallel, the C–X bond in a σ-complex is the stronger and the variation of the E_{C-X} value should be greater than that of E_{π}. Therefore, the stronger the C–X bond, the more stable is the σ-complex. In addition, one might expect that the transition from a σ-complex to a π-complex would lead to an increase in the positive charge on the X fragment.[139] Therefore this transition should be hampered for electronegative groups or atoms X (see Ref. 35). Finally, when X has unshared *p* or *d* electrons, back coordination is possible in the π-complex. The interaction between the occupied AO of the X fragment and the antibonding π-MO will be more effective, the closer their energies. Most of these views are qualitatively confirmed by calculated and experimental data on the relative stabilities of σ- and π-complexes and **85** and **86** (Table 6).


85


86

As shown in Table 6, those X groups whose central atoms are elements of the third or higher periods and have lower electronegativities and relatively less strong C–X bonds tend to stabilise a π-complex.[215] Depending on the chosen quantum-chemical approximation, the ΔE values are in some cases substantially different. The order of relative stabilities of σ- and π-complexes is indicated somewhat better.

It should be emphasised that experimental data on the relative stabilities of the cationic σ- and π-complexes are scarce and mostly refer to the gaseous phase. The construction of a 'chemical scale' of relative stabilities of σ- and π-complexes based on the data on rearrangements of long-lived carbocations occurring via 1,2-shifts is of great interest. During a 1,2-shift the migrant passes through a π-bonded state, and if the distinctions between the transition state and the π-complex are small (see Refs 44, 218), the $\Delta G^{\neq}_{1,2}$ values should reflect the relative stabilities of σ- and π-complexes. To construct this 'chemical scale', which is essentially a kinetic scale, relationship (8) (obtained for degenerate rearrangements of arenium ions by extrapolating the δC^+ values to the region of carbocations of the aliphatic series) has been used. The $\Delta E_{\sigma,\pi}$ values thus found are in agreement with the experimental and quantum-chemical data on the relative stabilities of σ- and π-complexes (see Table 6). The negative values of $\Delta E_{\sigma,\pi}$ indicate that, for aliphatic systems, π-complexes are more stable than σ-complexes. In fact, stable cyclic cations **86** ($R^1 = R^2 = R^3 = R^4 = H$) with $X^+ = RS^+$,[222] RO^+,[223] Ph^+,[224] I^+, Br^+, Cl^{+2} have been detected experimentally.

Borodkin et al.[225] suggested a similar scale based on 1-R-1,2-dimethylacenaphthylenium ions as model systems and a relationship of type (10).

The relative stabilities of the σ- and π-complexes **85** and **86** are substantially affected by the substituents $R^1 - R^4$ at basal C(1), C(2) atoms. As can be seen from the data of Table 6, the relative stabilities of σ-complexes **85** increase as the number of methyl groups at these atoms increases. Previously it has been noted that the 2,3-dimethyl-2-butyl cation **3a** is an open ion that undergoes a very rapid degenerate rearrangement (see Table 1). As estimates for the gaseous phase have shown, in the of case the ethyl cation the equilibrium *A* (see Scheme 1) is shifted toward the π-complex ($\Delta G^\circ = 0.8 \pm 0.1$ kcal mol^{-1}).[226] This is consistent with the results of high-level ab initio calculations.[170] A similar situation might also be expected for 2-butyl cation (**87**). In fact, the ^{13}C NMR spectrum of ion **87** shows a signal at δ 173.4 ppm (see Ref. 25) corresponding to the C(2) and C(3) atoms; no exchange broadening of this signal has been detected up to −140°C.[54] This gives the upper limit of 2.4 kcal mol^{-1} for the free energy of activation of a hypothetical rearrangement occurring via the 1,2-hydride shift (see Ref. 54).

The application of the CPMAS ^{13}C NMR method yielded the spectrum of the 2-butyl cation in the solid state; no static structure was detected down to −190 °C.[227] Since the rates of intramolecular sigmatropic processes in carbocations normally diminish on going from the liquid to the solid state (cf Ref. 205), the $\Delta G^{\neq}$ value of this rearrangement in solution should apparently be lower than 2.4 kcal mol^{-1}. The chemical shift due to equilibrium **87** ⇄ **87′** averaged, and Et evaluated using the data for 2-propyl- and 2-methyl-2-butyl cations is equal to (320 + 57.5)/2 = 189 ppm, which differs from the observed value (173.4 ppm).[25] This may be accounted for by assuming that bridged structures **88a,b** are involved in the equilibrium, apart from σ-complexes **87**, **87′** (a σ,π-rearrangement). The relatively small value of the isotopic perturbation on replacement of one hydrogen atom in the methyl group by deuterium ($\delta_{-111\,°C}$ = 11 ppm) compared with the corresponding value (22.5 ppm) for the equilibrium of 2,3-dimethyl-2-butyl cations[228] is consistent with this assumption. Nevertheless,

Table 6. Relative energies of isomeric σ- and π-complexes **85**, **86**.

X	R^1, R^3	R^2, R^4	ΔE/kcal mol^{-1}					$\Delta E_{\sigma,\pi}$ (25 °C)[e]
			MINDO/3[a]	MNDO[b]	ab initio[c] (basis set)	CEPA[d]	Experimental[47]	
H	H	H	−8.00	15.0	7.3 (4-31G)	−7.33		
Me	H	H	−5.91	15.8	0.4 (4-31G)	−11.03 (~−7.9)	~−8	−2.3
Ph	H	H			−35.4			−7.2
p-MeC_6H_4	H	H						−9.6
p-ClC_6H_4	H	H						−7.4
p-$CF_3C_6H_4$	H	H						−4.9
F	H	H	−31.14	18.7	11.4 (4-31G)	−1.41		2.8
Cl	H	H	−29.28	−5.6	−9.2 (4-31G)	−30.00		−8.6
					−14.6 (6-31G**)			
					−27.2 (MP2/6-31G**)			
Br	H	H			−30.1 (STO-3G)			−13.8
I	H	H			−37.0 (STO-3G)			−20.0
OH	H	H	−24.1	−5.0	−9.1 (4-31G)	−22.1	−20	−11.1
SH	H	H	−40.1	−16.7	−20.1 (4-31G)	−48.3	(< −5.3)	−17.5
NH_2	H	H		−31.9	−42.6 (4-31G)		−43	−21.5
PH_2	H	H		−12.1				−9.4
CN	H	H			−1.0 (STO-3G)			
					9.4 (4-31G)			
					9.6 (DZP)			
SiH_3	H	H		5.8	−9			
H	Me	H	−5.1					
H	Me	Me	1.2					

[a] See Refs 17, 171, 217. [b] See Refs 35, 217, 218. [c] See Refs 6, 35, 174, 219–221. [d] See Refs 171, 217.

[e] Calculated from Eqn (8) with the value δC^+ = 309.2, obtained from the data for Pr^{i+} cation with allowance for the increment that reflects the replacement of the methyl group by the hydrogen atom.[138] The value for X = H is not presented, since in this case Eqn (8) does not hold. The E_b and (*PA*) values were taken from the literature.[182, 215, 216]

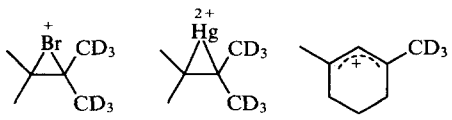


87 **87'**



88a **88b**

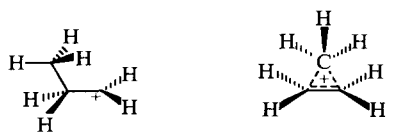
the observed δ value for 2-butyl cations is appreciably greater than those detected in the case of the 'isotopic perturbation of resonance' [17,147,229] in structures **89**, **90**,[230] and **91**[185] (1.81, 3.08, and 0.3 ppm, respectively), which contain more 'perturbing' deuterium atoms. According to the evaluation made by Edward,[148] based on the data on isotopic perturbation, the energy of the π-complex **88** is lower by 0.29 – 0.77 kcal mol^{-1} than that of the σ-complex **87**.



89 **90** **91**

The introduction of more effective electron-donating groups in the core of type **85** carbocations favours an increase in the stability of σ-complexes compared with π-complexes **86**. This is illustrated by the data in Tables 1 and 2.

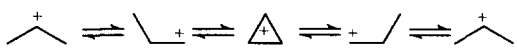
In conformity with the kinetic scale of relative stabilities of σ- and π-complexes, the methyl group shows a moderate tendency to form bridged structures (see Table 6), therefore one might expect that systems with poor delocalisation of the positive charge in the core would contain appreciable quantities of π-complexes in equilibrium with σ-complexes. Cations of the general formula $C_3H_7^+$ are one of these systems. According to detailed ab initio calculations in the STO-3G basis set with refinements in the STO-4-31G basis set, the difference between the energy of the 1-propyl cation (**92**) and that of the corresponding bridged structure **93** is small (<1 kcal mol^{-1}) and the open structure has a distorted geometry with an unusual C – C – C angle (83.4°). This geometry is favourable to the transition to the bridged ion[231] (see Ref. 232).



92 **93**

More recent and rigorous ab initio calculations with allowance for electron correlation (the CTHF method) as well as experimental data for the gaseous phase indicate that the π-complex **93** is more stable than the σ-complex **92** (see Table 6). Experimental data on the relative stability of the σ- and π-complexes under consideration are lacking. However, the results of a study of the isotope distribution of the label in (1,1,1-D_3), (2-D), and (2-^{13}C) enriched isopropyl cations [233,234] suggest easy interconversion of these complexes in accordance with Scheme 7.

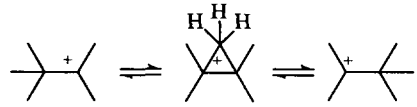
Scheme 7



As has been noted above, the 2,3,3-trimethyl-2-butyl cation undergoes a very rapid degenerate rearrangement ($\Delta G^{\neq}_{-136\,°C}$ = 3.8 kcal mol^{-1}),[54] and, according to the data on isotopic perturbation, the proportion of the π-complex existing in equilibrium with it (Scheme 8) is small.[24]

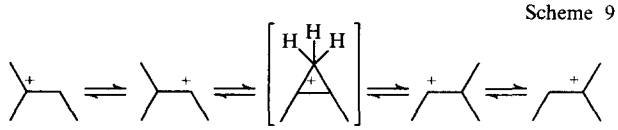
In the case of the 2-methyl-2-butyl cation (**94**), one might expect a situation intermediate between those considered above

Scheme 8



for the 1-propyl and 2,3,3-trimethyl-2-butyl cations. In fact, the ion **94** undergoes degenerate rearrangement via 1,2-H and 1,2-methyl shifts, as shown in Scheme 9, and the activation energy of the rearrangement is 15.3 ± 0.2 kcal mol^{-1}.[196]

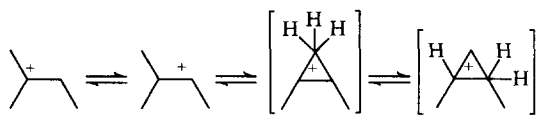
Scheme 9



94 **95** **96**

Taking into account the difference in energy between the tertiary (**94**) and secondary (**95**) ions (10 – 11 kcal mol^{-1}),[27,235] one can infer that the 1,2-shift of the methyl group should occur with an activation energy of less than 5 kcal mol^{-1}, which may be regarded as the upper limit of the relative stability of the σ- and π-complexes **95** and **96**. The assumption that the π-complex **96** is an intermediate rather than a transition state is supported by the following data. At temperatures of >100 °C, 'confusion' of the protons of the CH_3 and CH_2 groups occurs in ion **94**, apart from the above-mentioned rearrangement (E_a = 18.8 ± 1 kcal mol^{-1}).[236] Since the mechanism involving the formation of primary ions is characterised by a higher energy barrier (~ 30 kcal mol^{-1}, see Ref. 24), this rearrangement involves the intermediates **96** and **97**: (Scheme 10).[236]

Scheme 10



94 **95** **96** **97**

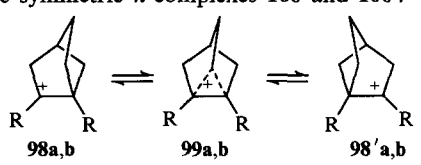
In the case of polycyclic carbocations the specific spatial arrangement of their fragments may result in an increase in the stabilities of π-complexes with respect to σ-complexes even in the presence of apical groups with a low tendency to form multicentre electron-deficient bonds. Systems of the norbornane series, in particular, 2-norbornyl cation, which has been the object of investigation in the series of nonclassical cations for more than 30 years, can serve as examples.[1,7,23,27] As investigations have shown, the 2-norbornyl cation is thermodynamically more stable in the gaseous phase than the secondary aliphatic ions[237] (see Refs 238, 239). Although the numerous quantum-chemical calculations produce contradictory results for this cation (see citations in Ref 240), the most rigorous of these (ab initio 4-21P* with allowance for electron correlation)[240] support the π-complex. The assemblage of data on the ^{1}H and ^{13}C NMR spectra, heats of formation, and effects of the increase in the electron demand and isotopic perturbation obtained for this ion generated in condensed media under 'long lifetime' conditions show its π-complex (nonclassical) nature.[23]

This point of view has been confirmed by the CPMAS ^{13}C NMR data obtained for a frozen solution of 2-norbornyl cation at 5 K.[241] An attempt to interpret these data by invoking the concept of double-well potential and heavy atom tunneling[242] (see Ref. 243) was unsuccessful,[244] since the ^{13}C NMR spectrum of the norbornyl ion did not show the expected splitting of the corresponding signals even at 5 K, and on raising the temperature no broadening of the signals was observed.¶

¶ Recently Kramer and Scouten criticised the concept of a 2-norbornyl cation as a nonclassical ion.[28]

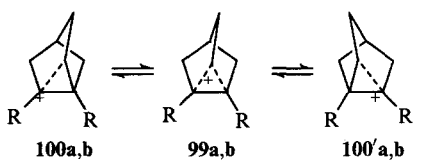
The introduction to the C(1) and C(2) atoms of methyl groups should apparently lead to an increase in the proportion of the σ-complex in equilibrium with the π-complex. The data on the isotopic perturbation for ions **98b** and **99b** (R = CD_3) are consistent with this assumption.[147] Taking into account the data from ^1H and ^{13}C NMR spectroscopy (see Ref. 245), one may infer that interconversion of the ions **98**, **98′** proceeds according to either Scheme 11 or Scheme 12 involving interconversions of the symmetric π-complexes **100** and **100′**.

Scheme 11



98a,b **99a,b** **98′a,b**

Scheme 12



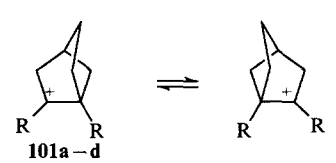
100a,b **99a,b** **100′a,b**

R = Me (**a**), CD_3 (**b**).

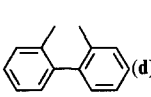
The latter scheme is supported by the results of an X-ray structural study[246] in which the 1,2,4,7-tetramethyl-2-norbornyl cation was shown to be an asymmetric bridged ion with C(1)–C(6) and C(2)–C(6) bond lengths of 1.74 Å and 2.09 Å, respectively. In view of the fact that the mechanisms under consideration differ from one another only in some details of the structures of the interconverting initial cations **98** and **100**, it is difficult at present to choose between these mechanisms.

The addition to the C(1), C(2) atoms of groups more electron-donating than methyl increases the stability of σ-complexes compared with π-complexes. For example, Nickon and Lin[247] have found that the 1,2-dimethoxy-2-norbonyl cation **101a** is classical and undergoes a rapid degenerate rearrangement, in conformity with Scheme 13.

Scheme 13



101a–d

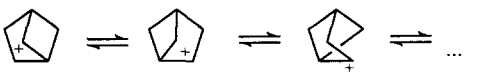
R = MeO (**a**), Ph (**b**), *p*-$MeOC_6H_4$ (**c**), R + R =  (**d**)

A similar situation has been observed for the ions **101b–d** with π-electron delocalisation in the core.[248–251]

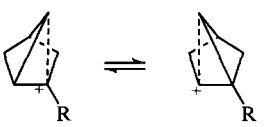
It is of interest to compare the properties of 1,2-R-2-norbornyl ions with those of their closest lower homologues, i.e. 1,2-R-2-bicyclo[2.1.1]hexyl cations. The shortening of the apical group by one unit may lead to a change in the relative proportions of σ- and π-complexes in the equilibrium mixture. The views on the structure of the parent ion of this series, the 2-bicyclo[2.1.1]hexyl cation, have varied and have not yet settled. For example, Seybold et al.[252] who studied the structure of this ion under 'long lifetime' conditions by ^1H NMR, rationalised the results obtained by assuming 'extra fast' equilibrium of nonclassical ions (π-complexes).



MINDO/3 calculations confirmed the bridged structure of the ion.[253] At the same time, analysis of the ^{13}C NMR spectra of 2-bicyclo[2.1.1]hexyl cations[254] and of 2-aryl-2-bicyclo-[2.1.1]hexyl ions[255] (the method of increase in the electron demand) suggested the presence of an equilibrium in which interconverting σ-complexes make the greatest contribution to the averaging of the corresponding NMR signals.



Sorensen and Schmitz[256] attempted to clarify the situation by solving the structure of the 2-bicyclo[2.1.1]hexyl ion. In their opinion, this ion exhibits properties intermediate between those of classical (σ-complexes) and nonclassical (π-complexes) ions, i.e. it is an asymmetric nonclassical ion (asymmetric π-complex) that undergoes degenerate rearrangement:



102a,b **102′a,b**

R = H (**a**), D (**b**).

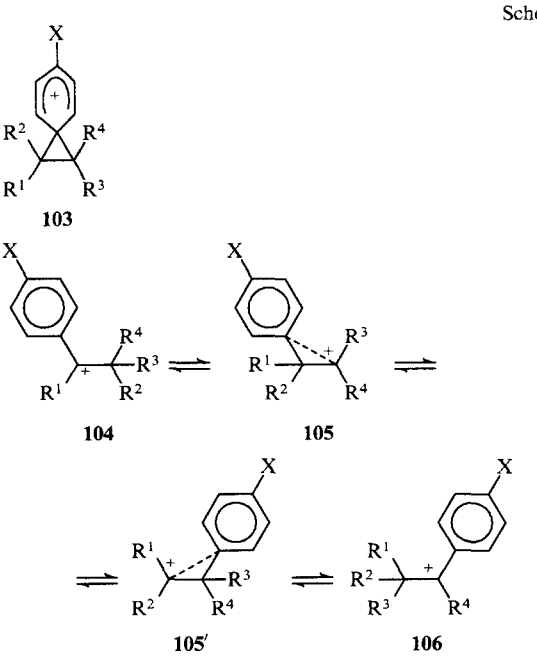
The small magnitude of the isotopic perturbation in the D-analogue of the **102b** ion ($\delta_{-115\,^\circ C}$ = 1.18 ppm)[147] is consistent with this inference.

The introduction of methyl groups in positions 1 and 2 dramatically lowers the π-complex character of the ion, which is shown by the large isotopic perturbation δ on replacing one of these groups by a CD_3 group ($\delta_{-100\,^\circ C}$ = 36.5 ppm).[256] This value is intermediate between those observed for 1,2-dimethyl-2-norbornyl[257] and 1,2-dimethylcyclopentyl cations.[25,257] Thus, the 1,2-dimethyl-2-bicyclo-[2.1.1]hexyl cation is a σ-complex that undergoes very rapid degenerate rearrangement ($\Delta G^{\neq} < 2.8$ kcal mol^{-1}), the relative proportion of the isomeric π-complex in the equilibrium being probably small.

In conformity with the kinetic scale of the relative stabilities of σ- and π-complexes (see Table 6), the phenyl group exhibits a greater tendency to form bridged structures than alkyl groups. The experimental data obtained so far are not inconsistent with this inference. In fact, the ionisation of 2-chloroethylbenzene in superacids affords a π-complex (**103**, X = R^1 = R^2 = R^3 = R^4 = H).[224,258] Ab initio calculations (STO-3G) confirm the greater stability of this complex compared with the β-phenylethyl cation[172] (see Refs 259, 260).

The evaluation of the relative proportions of σ- and π-complexes for the model structures **103** and **104** (Scheme 14) is complicated by the presence of isomeric ions of the benzyl type (**106**). In fact, the ionisation of 2-chloro-3-

Scheme 14



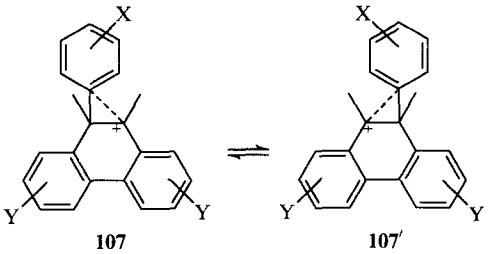
103 **104** **105** **105′** **106**

(*p*-methoxyphenyl)butane in the $HF-SbF_5-SO_2FCl$ system at −78°C affords exclusively 2-(*p*-methoxyphenyl)-2-butyl cations.[261] A similar picture has been observed for 2-chloro-3-phenylbutane.[261] According to the interpretation of Olah et al.,[261] during ionisation of 2-chloro-3-phenyl-2,3-dimethylbutane under these conditions, an equilibrium mixture is formed consisting of an ion of the benzyl type (**104**) and asymmetric π-bridged cations **105** and **105′** that undergo very rapid degenerate rearrangement (see Scheme 14) ($\Delta G^{\neq} < 5$ kcal mol^{-1}). Similarly, ions with substituents X = CF_3, Me, ($R^1 = R^2 = R^3 = R^4$ = Me) are considered to be asymmetric π-bridged structures (**105** and **105′**) existing in a rapid equilibrium with the isomers **104**,[261] (see Ref. 262). The presence of more effective electron-donating substituents X in the phenyl ring (X = MeO) produces the ion **104** of the benzyl type in the SbF_5-SO_2ClF acid system (X = MeO, $R^1 = R^2 = R^3 = R^4$ = Me).[261]

Among the transformations of ions of type **103–106** considered above, the 'extra fast' interconversion of ions **105** ⇄ **105′** is of special interest. The possibility of interaction of the aromatic ring with a carbocationic centre has been shown in a study of the donor-acceptor interaction in 9-(*p*-X-phenyl)-9,10-dimethylphenanthrenium ions (**58**)[263] as well as in 2,7- and 3,6-substituted 9-phenyl-9,10-dimethylphenanthrenium[264] ions. However, the energy of this interaction in the ground state is small, as shown by the low sensitivity of the chemical shift of the C atom carbocationic centre to the effects of substituents X in the XC_6H_4 group[265] and also by the fact that the activation free energies of the rotation barriers of XC_6H_4 groups for substituents with different types of electronic affect (X = Me, Cl, CF_3; $\Delta G^{\neq}_{-100\,°C} = 8.5 \pm 0.1$ kcal mol^{-1}) coincide.[263] The facts that the chemical shifts of the C atoms — carbocationic centres — in 2,7- and 3,6-di-Y-9-R-9,10-dimethylphenanthrenium ions (R = Ph, Me) are close to each other and the difference between them is approximately constant (3–4 ppm) are in agreement with this assumption[102,264] (see Ref. 266).

Although the donor-acceptor interaction in the ground state is weak, the degenerate rearrangements of type **107** ions mentioned above (Scheme 15) can also be considered to be interconversions of asymmetric π-complexes.

Scheme 15



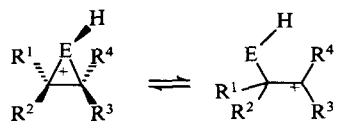
107 **107′**

It is reasonable to assume that owing to the increase in the positive charge on the carbocationic centre on going from ions **107** of the phenanthrene series to cations **105** of the β-arylethyl type, the extent of the donor-acceptor interaction in the ground state increases. This has been confirmed by ab initio calculations, according to which the 3-phenyl-2,3-dimethyl-2-butyl cation has a very distorted geometric structure with an unusually small C(2)–C_{ipso} distance (1.925 Å).[178]

In conformity with the kinetic scale of the relative stabilities of σ- and π-complexes (see Table 6), the migrants EH incorporating Group VI elements E (Scheme 16) show a pronounced tendency to form bridged structures. In the gaseous phase, π-complexes **108a,b** are more stable than isomeric σ-complexes **109a,b**, which is consistent with the data of quantum-chemical calculations (see Table 6).

A number of π-complexes (**108b–e**) have been generated in superacid systems at low temperatures. The oxygen-containing complexes **108c,e** were shown to be converted into the corresponding protonated aldehydes on raising the temperature, apparently via the isomeric σ-complexes **109c,e**.[267] The

Scheme 16



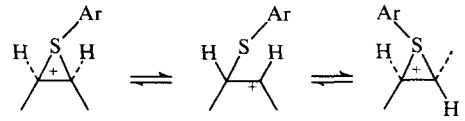
108a–k **109a–k**

	E	R^1	R^2	R^3	R^4
a	O	H	H	H	H
b	S	H	H	H	H
c	O	H	H	H	Me
d	S	H	H	H	Me
e	O	H	H	Me	Me
f	O	H	Me	Me	H
g	O	Me	Me	Me	Me
h	S	Me	Me	Me	Me
i	S	H	Bu^t	H	Bu^t
j	S	Bu^t	H	H	Bu^t
k	S	H	Bu^t	Bu^t	H

authors cited were not able to isolate the π-complexes **108f,g** with a symmetrical arrangement of R^1-R^4 substituents in the individual state under the conditions studied, since these complexes were rapidly converted into the corresponding protonated ketones.[267] This indirectly indicates that the interconversion of σ- and π-complexes **108f,g** ⇄ **109f,g** occurs readily. The analogous sulfur-centred π-complexes **108** are probably more stable than the corresponding isomeric σ-complexes (see Refs 267, 268). This is shown, in particular, by the fact that the ^1H NMR spectra of solutions of salts of π-complexes **108h,j,k** and **108i** are invariably in the temperature ranges from −50 to −80 °C and from 20 to −110 °C, respectively.[268]

There is little information concerning the interconversion of episulfonium ions and of the σ-complexes isomeric to them (see Refs 269, 270). For example, Vorob'eva et al.[271] discovered interconversion of π-complexes **110a** or **112a** kept in CH_2Cl_2 solutions at ambient temperature for ~1 h, which obviously proceeds via opening of the bridge and formation of the σ-complex **111a** as an intermediate (π,σ-rearrangement) (Scheme 17).

Scheme 17



110a,b **111a,b** **112a,b**

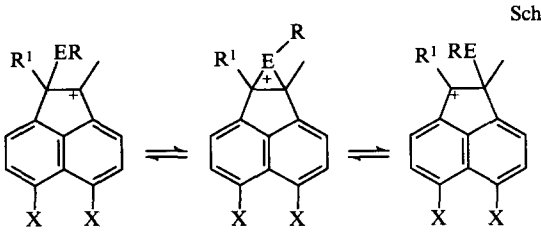
Ar = 2,4-$(O_2N)_2C_6H_3$ (**a**), 4-ClC_6H_4 (**b**).

The cleavage of the episulfonium ring is more difficult for ArS groups containing less electronegative substituents in the aromatic ring. For example, in the case where Ar is *p*-ClC_6H_4, more prolonged storage at ambient temperature (up to 24 h) is required to detect the interconversion shown in Scheme 17. This is probably caused by the fact that the stability of the π-complex relative to that of the σ-complex increases with decrease in the electron-withdrawing ability of the Ar groups.

Borodkin et al.[272] discovered a unique example of interconversion of the episulfonium ion **113f** and of the σ-complexes **114f** and **115f** isomeric to it (Scheme 18, see over).

The extremely high rate of the **113f** ⇄ **115f** interconversion even at −120 °C ($k_{\mathbf{114f}\rightarrow\mathbf{113f}} \geqslant 10^8$ s^{-1})[273] implies easy cleavage of the episulfonium rings in the corresponding π-complexes. A similar σ,π-rearrangement has been found for selenium-centred ions at −80 °C: **113n** ⇄ **115n** ($k \geqslant 10^7$ s^{-1}).[274] The equilibrium between the σ- and π-complexes, **113** ⇄ **115**, is appreciably influenced by the nature of the substituents R, R^1, and X and the element E.[273–275] Analysis of these data resorting to those reported for 1-OR-1,2-dimethylacenaphthylenium ions[130] allowed Borodkin et al.[273–275] to draw the following conclusions:

Scheme 18



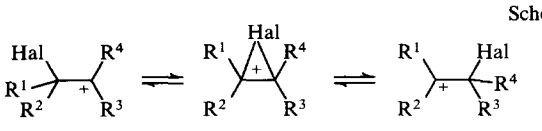
114a–s **113a–s** **115a–s**

	E	R	R^1	X
a	S	Me	Me	H
b	S	Me	CD_3	H
c	S	Ph	Me	H
d	S	Ph	CD_3	H
e	S	Ph	CH_2Cl	H
f	S	C_6F_5	Me	H
g	S	C_6F_5	CD_3	H
h	S	C_6F_5	CH_2Cl	H
i	S	C_6F_5	Me	Br
j	S	C_6F_5	Me	Me
k	S	C_6F_5	CH_2D	Me
l	Se	Ph	Me	H
m	Se	Ph	CD_3	H
n	Se	C_6F_5	Me	H
o	Se	C_6F_5	CD_3	H
p	Se	Ph	CH_2Cl	H
q	Se	Ph	CH_2Cl	H
r	Se	C_6F_5	Me	Me
s	Se	C_6F_5	CH_2D	Me

the proportion of the cationic π-complexes **113** in the equilibrium (see Scheme 18) increases with increase in the electron-donating properties of substituents R and R^1, with increase in the atomic number of the central element, and with diminution of the electron-donating properties of the substituents X. Using the **113f** ⇄ **115f** interconversion of the ions as an example, the authors cited showed that equilibria between cationic σ- and π-complexes with π-electron delocalisation in the ion core are not very sensitive to the effects of the medium.[275,276]

According to the kinetic scale of relative stabilities of σ- and π-complexes (see Table 6), the tendency to form bridged ions in the case of the halogen-centred complexes **116–118** (Scheme 19) should increase in the following sequence: F < Cl < Br < I.

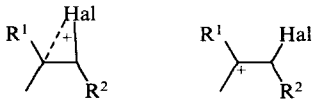
Scheme 19



116a–m **117a–m** **118a–m**

	Hal	R^1	R^2	R^3	R^4
a	Cl	H	H	H	H
b	Cl	Me	Me	Me	Me
c	Br	H	H	H	H
d	Br	Me	H	H	H
e	Br	Me	Me	H	H
f	Br	Me	H	Me	H
g	Br	H	Me	Me	H
h	Br	Me	Me	Me	H
i	Br	Me	Me	Me	Me
j	I	H	H	H	H
k	I	Me	H	Me	H
l	I	H	Me	Me	H
m	I	Me	Me	Me	Me

This is supported by the results of quantum-chemical calculations (see Table 6) and also by the ^1H and ^{13}C NMR spectroscopy data for the ions **116–118**.[2] The influence of substituents has been considered in a general form.[2] The vast majority of the spectral data can be accounted for by assuming the existence of static σ- and π-complexes, however some cases do not fit this concept. Indeed, it is difficult to explain large differences between the chemical shifts of C(1) and C(2) atoms for 1-methyl- and 1,1-dimethylethylenebromonium ions by the presence of symmetrical π-complexes of type **117**. As suggested,[2] this indicates either the formation of asymmetric π-complexes **119a,b** or rapid interconversion of these π-complexes and the corresponding σ-complexes **120a,b**.



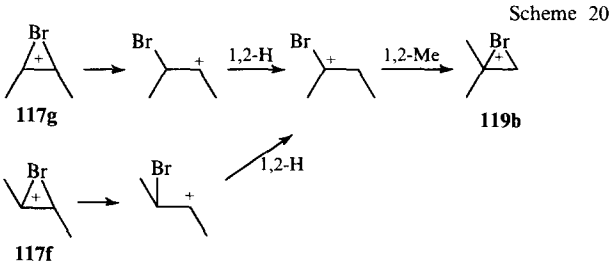
119a–d **120a–d**

	Hal	R^1	R^2
a	Br	H	H
b	Br	Me	H
c	Br	Me	Me
d	Cl	Me	H

This suggestion is supported by the substantial temperature dependence of the chemical shifts of the C(1), C(2) atoms in 1,1-dimethylethylenebromonium ion.[2] A similar interconversion of an asymmetric π-complex and a σ-complex has been suggested in the case of Hal = Br, $R^1 = R^2$ = Me (**119c** ⇄ **120c**). It is noteworthy that at Hal = Cl, R^1 = Me, R^2 = H, the σ-complex **120d** is more stable than the isomeric π-complex.[2]

The most probable structures for symmetrically substituted halogenonium ions must be either static symmetrical π-complexes of type **117** or σ-complexes **116**, **118** existing in a dynamic equilibrium with one another. Judging by the ^1H and ^{13}C NMR spectra, *cis*- and *trans*-2,3-dimethylethylenebromonium ions resulting from the action of SbF_5 on *meso*- or *d,l*-dibromobutanes in SO_2 do not undergo rapid interconversion on the NMR time scale. This allowed Olah et al.[2] to assign these structures to π-complexes. A similar situation occurs in the case of 1,2-dimethylethyleneiodonium ion in which the *cis* : *trans* ratio depends on the precursor used to generate the geometric isomers of the ion in a superacid medium.[2] Nevertheless, the π-complexes **117g** and **117f** are slowly converted at −40 °C into the complex **119b**, apparently, according to Scheme 20:[2]

Scheme 20



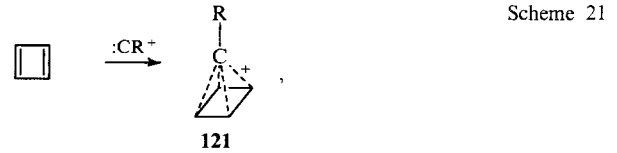
This confirms to the easy cleavage of the bromonium ring in these complexes.

An analysis of the ^{13}C NMR spectra of the tetramethylethylenebromonium ion led Olah et al.[2] to the conclusion that these spectra are inconsistent with a π-complex like **117** or the rapid **116** ⇄ **118** interconversion of σ-complexes. The interconversion of both forms of complexes according to Scheme 19[2,277] is the most likely. However, judging by the small value of isotopic perturbation, (δ = 1.81 ppm),[230] the proportion of σ-complexes **116** and **118** equilibrium with the π-complex **117** is very low.

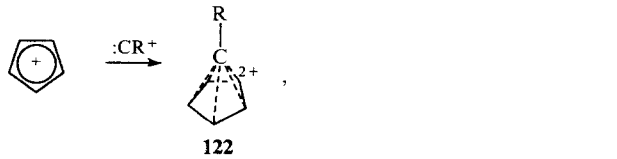
V. π,π-Rearrangements

Carbocations are frequently regarded as a connecting link between organic and organometallic chemistry.[45,278,279] Typical objects for investigation in the latter are π-complexes with multicentre metal-ligand bonds. These bonds are also found in carbocations. 'Long-lived' pyramidal carbocations (π-complexes) in which the coordination number of the carbon atoms can be 5 or more can serve as an example. These π-complexes may be formally regarded as resulting from the interaction of a $:CR^+$ fragment with antiaromatic or other four-electron systems (Scheme 21):[279]

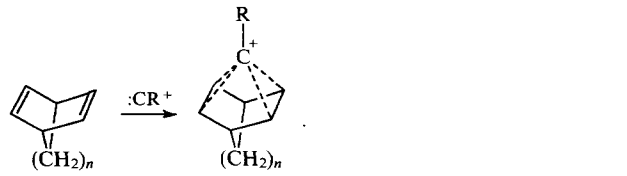
Scheme 21



121



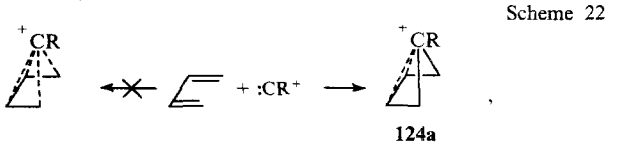
122



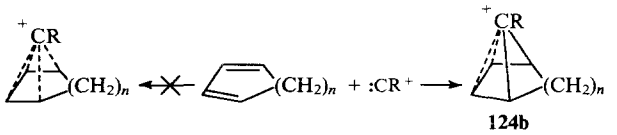
123

The main feature required for the formal construction of these systems from fragments is the similarity of the MO of these fragments as regards their symmetry.[45] If the four-electron component of the diene is not symmetrical, nonclassical ions of type **124a–c**, rather than pyramidal ions, are more stable (Scheme 22):[278,279]

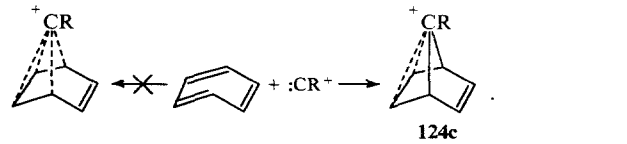
Scheme 22



124a



124b

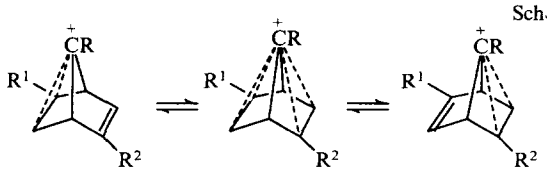


124c

Among the latter set of π-complexes, systems of type **124c** are the most interesting, since in these complexes there is a possibility that bonding of the CR^+ fragment 'switches' from one double bond to the other (π,π-rearrangement of the 'flipping' type[23,280]), in accordance to Scheme 23.

The apical atom in structures **126** has 10 electrons, two of which are located in an antibonding MO, which results in destabilisation of this structure.[45] According to MINDO/2 calculations,[281] the symmetrical structure **126a** corresponds to the transition state rather than to an intermediate state, the energy barrier to the π,π-rearrangement **125a** ⇄ **125'a** being rather high (26 kcal mol^{-1}). The theoretical data have been confirmed experimentally[280,282] (see Ref. 283).

Scheme 23



125a–h **126a–h** **125'a–h**

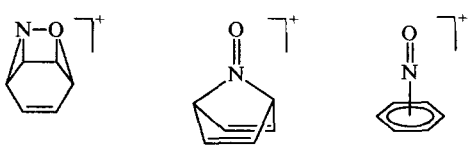
	R	R^1	R^2
a	H	H	H
b	Me	H	H
c	Ph	H	H
d	$HC=CH_2$	H	H
e	OH	H	H
f	OMe	H	H
g	H	Me	H
h	H	H	Me

A kinetic study of the rearrangement of the π-complex **125a** (see Scheme 23) by the radioactive tracer method made it possible to determine the lower limit of the free energy of activation ($\geq$19.6 kcal mol^{-1}).[280] High barriers to π,π-rearrangements are also characteristic of π-complexes **125g** and **125h** (>22.1 kcal mol^{-1} and > 16.6 kcal mol^{-1}, respectively).[280] The introduction in position 7 of a methyl group (π-complex **125b**) leads to a decrease in the activation free energy ($\Delta G^{\neq}_{-14\,°C}$ = 12.4 kcal mol^{-1}),[280] which is obviously due to the larger stabilising effect of this group in the transition state of type **126** compared with that in the ground state. This distinction is probably caused by the greater fraction of the positive charge on the C(7) atom in the symmetrical structure **126**, since, as was mentioned above, the simultaneous interaction of the two double bonds with this atom is unfavourable.

In the case where $R^1 = R^2 = H$ and R = Ph or $CH=CH_2$ rapid interconversion of π-complexes **125** ⇄ **125'** ($\Delta G^{\neq} < 5.2$ and < 8.2 kcal mol^{-1}, respectively) is more likely, whereas the presence in position 7 of a methoxy group having more pronounced electron-donating properties probably results in the formation of the symmetrical π-complex **126f**.[280,284] The latter is consistent with the results of a study of the basicities of 7-substituted norbornene derivatives, where it was shown that the introduction of an OH group in position seven of the 7-norborn-2-enyl cation removes the non-vertical interaction of the carbocationic centre with the double bond.[285]

To draw a parallel between the properties of carbocations and those of organometallic compounds, let us turn our attention to the rearrangements consisting in the migration of a π-bound fragment over a cyclic or open conjugated system. These rearrangements are rather typical of organometallic compounds (see, for example, Ref. 286), however, there is little information on these rearrangements in π-complexes derived from normal (not metal-centred) electrophilic reagents and unsaturated compounds.

Minkin et al.[287] have reported the results of MINDO/3 calculations of the structures of complexes derived from one of the classical electrophilic reagents, i.e. the nitrosonium cation, and benzene, indicating that minima on the potential energy surface correspond to π-complexes **127** and **128**, whereas the top of the hill corresponds to the centrally symmetrical π-complex **129** (see, however, Ref. 288).

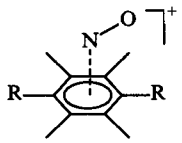


127 **128** **129**

The symmetry of π-complexes **127** and **128** was found to be substantially lower than could have been expected for the gaseous

phase and the solution.[289,290] In the latter case, in view of the isochronism of the protons of the aromatic ring in the ^1H NMR spectrum, the centrally symmetrical π-complex structure **129** was attributed to the complex. Although the π-complexes **127** and **128** possess much lower symmetries than the C_{6v} symmetry detected by NMR, this contradiction was eliminated by quantum-chemical calculations which showed that the complexes **127** and **128** can undergo a rapid degenerate rearrangement (with a barrier of < 3 kcal mol^{-1}) through 'sliding' of the NO group over the aromatic ring plane with 'switching' of the C–N bonds.[287]

Recent X-ray structural studies of π-complexes formed from durene[291] or hexamethylbenzene[291] (see Ref. 292) with the nitrosonium cation (with the $AlCl_4^-$ anion) have shown that the traditional view (see Refs 289, 290) that π-complexes of aromatic compounds with electrophilic reagents are highly symmetrical systems should be reconsidered.[47] It was found that the NO group in these complexes is displaced from the centre of the aromatic ring [towards two (2η) or three (3η) carbon atoms] and is arranged at an angle of ~50° with respect to the plane of the ring.



R = H (**130**), Me (**131**)

According to CNDO/2 calculations carried out using the real geometry of the complex **131**, the values of the positive charge on the basal C atoms of the aromatic ring (and on the methyl groups) are appreciably different.[291] Nevertheless, the ^{13}C NMR spectra recorded both for the liquid (HSO_3F-SO_2ClF, −130 °C)[293] and for the solid state (CPMAS spectra)[291] exhibit only two rather narrow singlets. This may be explained by the degenerate π,π-rearrangement of the complex occurring rapidly on the NMR time scale as 'sliding' of the NO group over the plane of the ring or as the rotation of this ring, about a normal to it, involving 'switching' of the $C_{arom}-N$ bonds, and in the crystalline state the latter mechanism is the more likely.

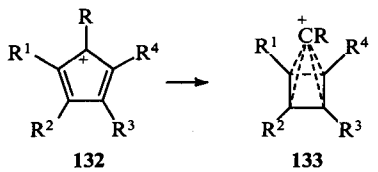
Mefed et al.[293] have studied a polycrystalline specimen of tetrachloroaluminate of complex **131** by relaxation NMR spectroscopy and determined the kinetic parameters of this rearrangement ($E_a = 10.2 \pm 0.6$ kcal mol^{-1}, $\lg A = 13.9 \pm 0.1$ kcal mol^{-1}). As shown by calculations of atomic interactions, the rotation of the hexamethylbenzene ring in the crystalline state should occur more easily ($E_a < 1$ kcal mol^{-1}) than that of the NO group, the latter being tightly clamped by the environment (20 or 150 kcal mol^{-1} depending on the direction of the rotation).

Judging by the NMR spectra, analogous rearrangements via 'sliding' of the NO^+ group over the aromatic ring are also realised in the case of complexes formed from nitrosonium cation and other alkyl-substituted benzene derivatives[292, 294] (see Ref. 295), fluorene,[296] and methyl-substituted naphthalenes.[297,298]

VI. On the possibility of 2-σ,π-rearrangements

The pyramidal cations like **133** can formally result from the rearrangement of cations **132** (Scheme 24) that consists in the cleavage of two σ-bonds to yield a conjugated cyclic π-system reacting with the apical $:CR^+$ fragment (2-σ,π-rearrangement (see Ref. 26).

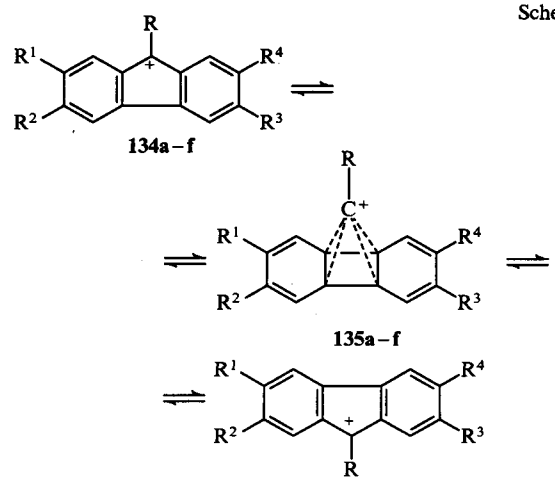
Scheme 24



132 **133**

The possibility of these rearrangements has been verified[299] experimentally for substituted fluorenyl cations **134** (Scheme 25).

Scheme 25



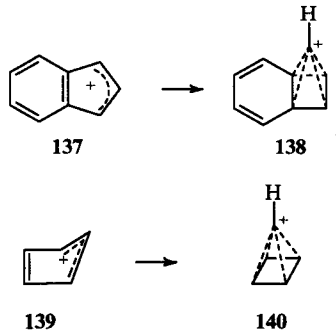
134a–f **135a–f** **136a–f**

	R	R^1	R^2	R^3	R^4
a	Me	D	H	H	H
b	Me	H	D	H	H
c	Me	H	Me	H	H
d	Me	Me	H	H	Me
e	Me	H	Me	Me	H
f	Me	Me	H	Me	H

It was found that the ion **134a** generated in the HSO_3F-SO_2ClF system is not converted into the cation **136b** at −78 °C. Similarly, no 2-σ,π-rearrangement shown in Scheme 25 proceeds in the case of the methyl-substituted fluorenyl ions **134c–f** up to 25°C.

Previously it had been shown that the 9-methyl- and 9-ethylfluorenyl cations are static on the ^1H NMR time scale up to −10°C.[194]

The possibility of the degenerate rearrangement of the fluorenyl cation in conformity with Scheme 25 has been studied by MINDO/3.[299] The energy of the pyramidal structure of type **135** was found to be 73.0 kcal mol^{-1} greater than that of the fluorenyl ion. However, the removal of benzoannelation leads to a decrease in the barrier.



137 **138** **139** **140**

Cation	**137**	**138**	**139**	**140**
ΔH_f/kcal mol^{-1}	247.8	296.9	255.3	269.7
	$\Delta\Delta H_f$ = 49.1		$\Delta\Delta H_f$ = 14.4	

The electronic structure of the fluorenyl ions **134** does not correspond to the ion **139**, but is more in agreement with the structure **141**.[299]



141 **140** **139**

We should note that the thermal rearrangement **139** → **140** is symmetry allowed, whereas the transformation **141** → **140** is a disallowed process.[299]

* * *

Thus, the cationic σ,σ-rearrangements have been most extensively studied to date. The σ,π- and π,π-rearrangements still remain poorly investigated. This reflects the fact that in general the chemistry of 'long-lived' π-complexes derived from ordinary electrophilic reagents and unsaturated systems lags behind the chemistry of σ-complexes. However, the number of studies of the structures and dynamics of π-complexes is rapidly increasing. This is because of the need to extend and deepen our theoretical views of the processes involving cationic π-complexes as well as to use the knowledge of their properties for developing methods of controlling organic reactions.

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