CROATICA CHEMICA ACTA CCACAA 49 (4) 727—737 (1977)

YU ISSN 0011-1643
CCA-1045 547.32
Original Scientific Paper

The Mass and Ion Kinetic Energy Spectra of Fluoro-Chloro Substituted Norbornanes and Nortricyclanes

*B. Kralj, V. Kramer, M. Trkman, and *J. Marsel*

*J. Stefan Institute, University of Ljubljana, and *Dept. of Chemistry, Faculty of Natural Sciences and Technology, University of Ljubljana, Ljubljana, Yugoslavia*

Received March 4, 1977

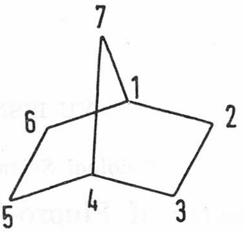
The mass and ion kinetic energy spectra of difluoro- and fluoro-chloro-norbornanes and fluoro-chloro-nortricyclanes have been examined. In several instances the similarity of the mass spectra makes it impossible to distinguish the diastereoisomers from each other. In contrast, however, their ion kinetic energy spectra differ clearly and allow unambiguous differentiation of the stereoisomers.

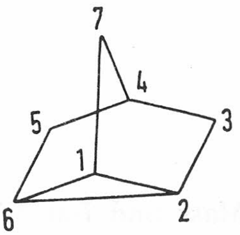
INTRODUCTION

The widespread application of mass spectrometry in the past decade can be attributed to progress in instrumental techniques and/or to the growth of additional information hidden in the decomposition modes of different ions in a mass spectrometer. In particular, sensitive studies of metastable ions, which frequently accompany the decomposition of ions in the gaseous phase, have added a new dimension to the interpretation of mass spectra and reaction mechanisms. Special devices were developed in recent years to meet requirements for recording low intensity metastable ions. For instance, by scanning the electric sector voltage and recording the ions decomposing in the field-free region preceding the electric sector of a double focusing mass spectrometer (i. e. metastable ions) with a sensitive detector (i. e. electron multiplier), ion kinetic energy (IKE) spectra[1] can be obtained. These spectra provide a great deal of information concerning the reactions of gaseous ions. Furthermore, the energy spectra of metastable ions in many cases exhibit a unique fingerprint of isomeric compounds whose mass spectra are almost identical. Efforts in this new field of mass spectrometry were reviewed recently in an excellent monograph[2].

For this investigation we have scanned the mass and ion kinetic energy spectra of several diastereoisomeric difluoronorbornanes (**1—6**), fluoro-chloronorbornanes (**7—10**) and chloro-fluoronortricyclanes (**11** and **12**). The mass spectra of compounds **1—10**, beyond mass 50, are given in the Table I. Many less important peaks are omitted, e. g. those which belong to purely isotopic ions. The mass spectra of isomeric pair **11** and **12** are represented in Figure 6.

Mass spectral fragmentation of several norbornane derivatives has been thoroughly studied[3-8] (see also the references cited therein) using a variety of methods, e. g. deuterium labelling, metastable ion abundances, ionization and appearance potential measurements. However, none concerns the advantages of ion kinetic energy spectra in the differentiation of stereoisomeric halogenated





1 2-*exo*-3-*exo*-difluoronorbornane,
2 2-*exo*-3-*endo*-difluoronorbornane,
3 2-*exo*-5-*exo*-difluoronorbornane,
4 2-*exo*-5-*endo*-difluoronorbornane,
5 2-*exo*-7-*syn*-difluoronorbornane,
6 2-*exo*-7-*anti*-difluoronorbornane,
7 2-*exo*-fluoro-5-*exo*-chloronorbornane,
8 2-*exo*-fluoro-5-*endo*-chloronorbornane,
9 2-*exo*-fluoro-7-*anti*-chloronorbornane,
10 2-*exo*-fluoro-7-*syn*-chloronorbornane,
11 3-*exo*-fluoro-5-*exo*-chloronortricyclane,
12 3-*exo*-fluoro-5-*endo*-chloronortricyclane

TABLE I

The Mass Spectra of Difluoronorbornanes **1—6** *and Fluoro-Chloronorbornanes* **7—10**

m/e	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
51	15	11	11	12	20	18	11	16	40	35
52	3				4	3	3	4	10	9
53	27	21	15	16	25	22	14	20	45	49
54	14	9	4	4	14	14	7	14	18	20
55	5	4			14	19	4	8	20	23
57	9	7	9	10	15	13	5	6	18	17
59	35	25	24	27	40	32	11	16	31	32
65	6	5	8	9	9	7	11	14	37	36
66	6	5	16	15	10	6	23	26	44	30
67	85	100	32	42	45	30	67	62	100	100
68	100	90	3	4	8	6	6	7	9	9
72	51	34	13	20	43	43	5	9	26	31
77	9	6	4	6	12	12	7	11	22	20
79	14	12	5	8	25	25	11	19	54	59
81	14	12	5	10	100	100	4	9	30	64
84	4	3	5	7	6	7	5	8	8	15
85	15	12	84	95	38	30	76	73	30	40
86	19	16	100	100	25	28	100	100	34	38
88							4	7	21	45
90	15	12	3	4	15	24			16	16
97	15	10	8	12	19	20	7	14	29	35
99	35	22	11	18	31	41	9	17	48	58
102							4	4	12	11
106							3	4	18	23
112	3	2	2	3	7	7	5	7	15	22
113							16	21	75	93
117	6	5	3	3	6	6				
128							6	11	6	12
132 $M^{+\cdot}$	6	4	15	20	4	7				
148 $M^{+\cdot}$							15	20	21	43
150							5	7	7	15

norbornanes. Therefore it was of interest to apply this method for the investigation of the compounds listed above.

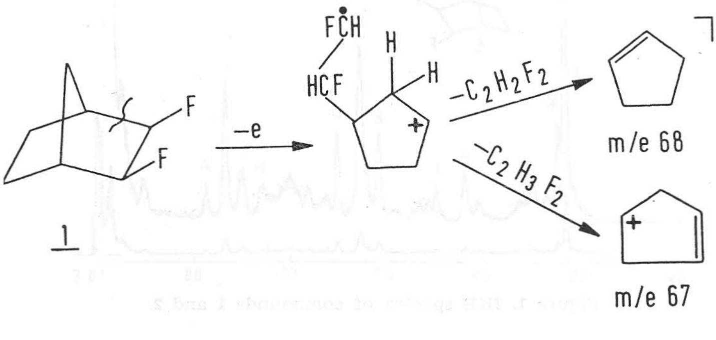
Because the main intention of this paper is to show the applicability of IKE spectra in studying stereoisomeric compounds, we will give here rather simplified fragmentation schemes without an elucidation of formal ion structures. Of course, all important ion species, i. e. their elemental composition, were determined by exact mass determinations. The fragmentation pathways, mentioned in this study, were found by appropriate measurements on metastable ions. A majority of the energy peaks in the IKE spectra were mass analysed, but only those metastable transitions are given in Tables II—IV which are the main contributors to a particular energy peak.

RESULTS AND DISCUSSION

Difluoronorbornanes **1 — 6**

The main feature of their normal mass spectra is that several fragmentation reactions are common to all isomers, but the abundances of the resulting ions differ greatly if positional isomers are compared. Thus, no confusion arises in differentiation of positional isomers. However, comparison of the mass spectra of diastereoisomers shows that an unambiguous diferentiation between them becomes very uncertain.

Peaks representing molecular ions are of medium intensity and do not exceed 20% of the intensities of the base peak. The molecular ion at *m/e* 132 can lose alternatively the following species: $CH_3^{\cdot}$, HF, $CH_2F^{\cdot}$, $CHF_2^{\cdot}$, $C_2H_4F^{\cdot}$, $C_2H_3F_2^{\cdot}$ and $C_2H_2F_2$ forming ions at *m/e* 117, 112, 99, 81, 85, 67 and 68, respectively. It was also estimated that all the prominent peaks in the mass spectra, as well as in the metastable mode, arise, directly from the molecular ion. The species $CH_3^{\cdot}$, HF and $CH_2F^{\cdot}$ also appear frequently as leaving groups in secondary fragmentations. On electron impact the bicyclic system needs to be opened unless the ionization of fluorine atoms takes place. Opening one of the rings then allows different eliminations, including hydrogen rearrangements, depending on which C—C bond rupture occurs. Thus in the case of diastereoisomeric pair **1** and **2**, the most abundant ions *m/e* 67 and 68 will occur in higher probability if, in the course of ionization, bonds C 1—2 or 3—4 are broken. By this means in both instances the elimination of $C_2H_2F_2$ or $C_2H_3F_2^{\cdot}$ from $M^{+\cdot}$ becomes the most probable reaction. The resultant ions probably have a cyclopentene-like structure (Scheme 1).



Although the peak intensity ratio 68/67 in the mass spectra shows a visible difference between stereoisomers **1** and **2** (Table I), in the IKE spectra (Figure 1) the difference becomes far more pronounced. Here the energy peak J, reflecting the loss of $C_2H_3F_2^{\cdot}$ from the metastable molecular ion, increases greatly for the endo-isomer.

This situation makes the competitive simple cleavage of $C_2H_2F_2$ less probable (peak K).

The similarity of the mass spectra of **3** and **4** makes it impossible to distinguish these isomers from each other. Here the formation of base peaks at *m/e* 86, and the accompanying *m/e* 85, follows a similar route to that found in **1** and **2**, namely, by loss of C_2H_3F or $C_2H_4F^{\cdot}$ directly from $M^{+\cdot}$ ion. Their energy spectra (Figure 2), however, exhibit prominent differences, which are especially evident in metastable decompositions assigned by D, I and J (Table II). Again the endo-isomer (**4**) shows more pronounced loss of $C_2H_4F^{\cdot}$ (I) than C_2H_3F (L) in the metastable mode.

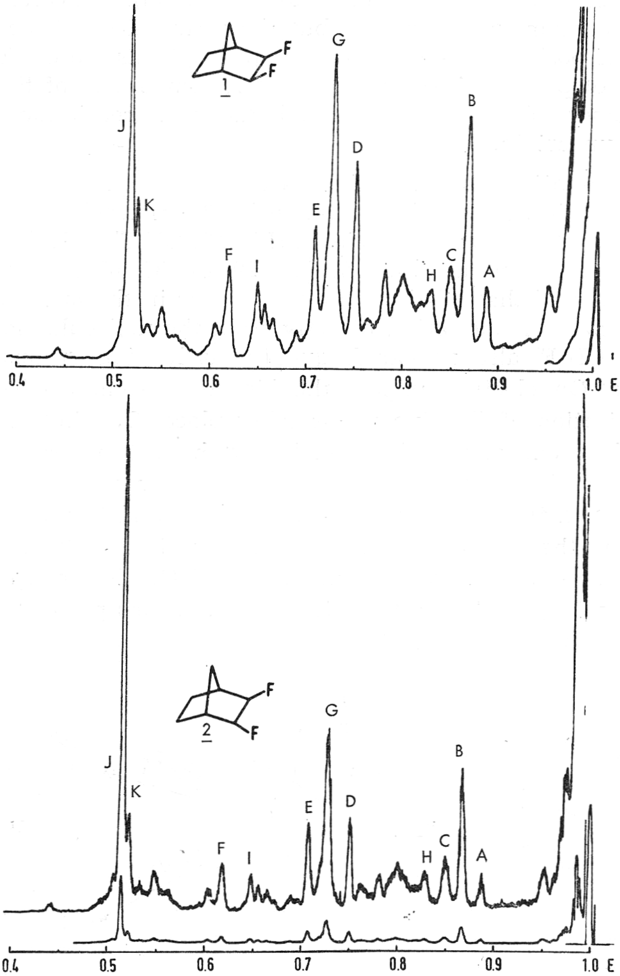


Figure 1. IKE spectra of compounds 1 and 2.

TABLE II

Metastable Decompositions in the IKE Spectra of Difluoronorbornanes **1—6**

Peak	$m_1^+ \rightarrow m_2^+ + m_3$	Peak	$m_1^+ \rightarrow m_2^+ + m_3$
A	$132^+ \rightarrow 117^+ + CH_3^{\cdot}$	G	$73^+ \rightarrow 53^+ + HF$
B	$112^+ \rightarrow 97^+ + CH_3^{\cdot}$	H	$117^+ \rightarrow 97^+ + HF$
C	$132^+ \rightarrow 112^+ + HF$	I	$132^+ \rightarrow 85^+ + C_2H_4F^{\cdot}$
D	$132^+ \rightarrow 99^+ + CH_2F^{\cdot}$	J	$132^+ \rightarrow 67^+ + C_2H_3F_2^{\cdot}$
E	$112^+ \rightarrow 79^+ + CH_2F^{\cdot}$	K	$132^+ \rightarrow 68^+ + C_2H_2F_2$
F	$132^+ \rightarrow 81^+ + CHF_2^{\cdot}$	L	$132^+ \rightarrow 86^+ + C_2H_3F$

Similarly, the mass spectra of compounds **5** and **6** cannot be distinguished with certainty. Of particular interest is the formation of the base peak at *m/e* 81 which here also originates directly from the molecular ion. Because a $CHF_2^{\cdot}$ species is lost, an energetically very favourable rearrangement must occur. In this respect their fragmentation pattern greatly deviates from that of compounds **1**—**4**, where the expulsion of $CHF_2^{\cdot}$ gives rise to very low abundance peaks.

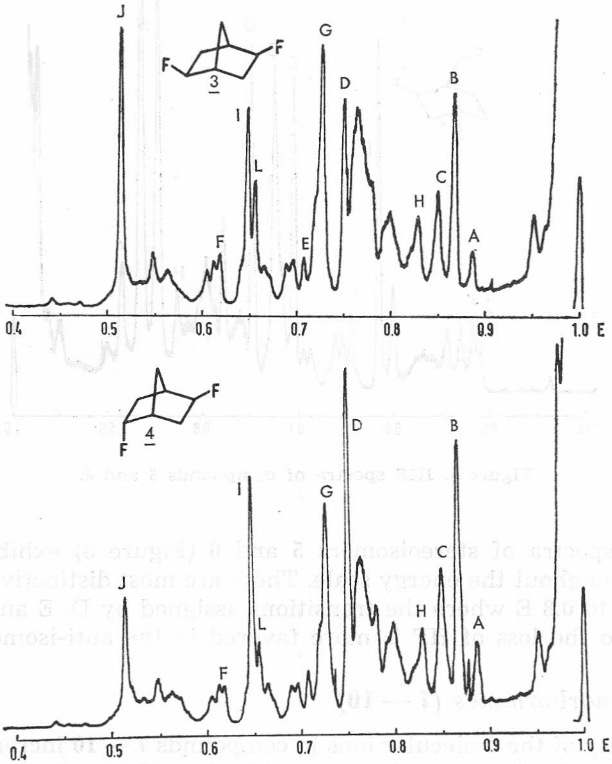


Figure 2. IKE spectra of compounds 3 and 4.

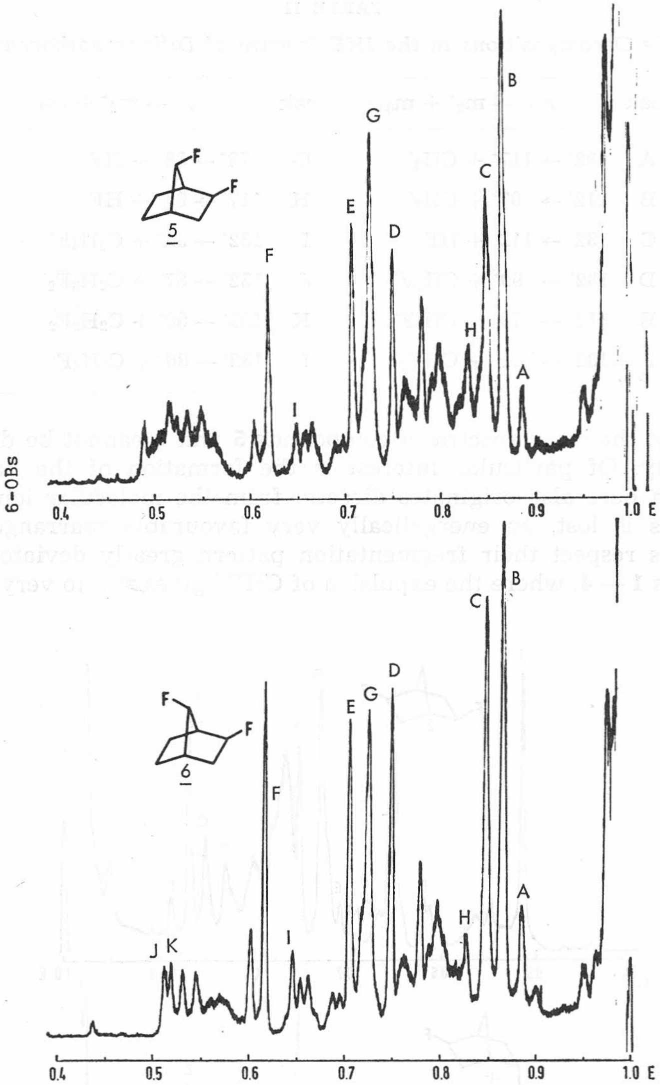


Figure 3. IKE spectra of compounds 5 and 6.

The IKE spectra of stereoisomers **5** and **6** (Figure 3) exhibit appreciable differences throughout the energy scale. These are most distinctive in the region of about 0.6 E to 0.8 E where the transitions assigned by D, E and F take place (Table II). Also the loss of HF is more favored in the anti-isomer (**6**, peak C).

Fluoro-chloronorbornanes (**7** — **10**)

The stability of the molecular ions in compounds **7** — **10** increases noticeably in comparison to the difluoronorbornanes. Also here the positional isomers show

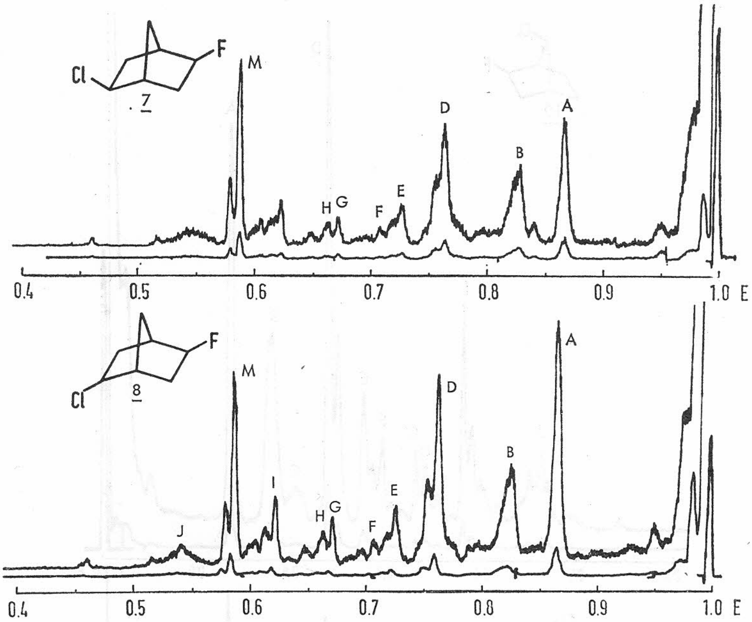


Figure 4. IKE spectra of compounds 7 and 8.

clear differences in their normal mass spectra (Table I). Stereoisomers exhibit visible differences in **9** and **10**, but they are insufficiently distinctive for the certain identification of **7** and **8**. Replacement of a fluorine with a chlorine atom in this system causes perceptible alterations in the fragmentation behaviour. Loss of C_2H_3Cl in **7** and **8** leads to the base peaks at *m/e* 86. In **9** and **10** this process, as expected from these structures, is not nearly so important. This loss gives rise in the metastable mode in **7** to a more abundant energy peak compared to that in **8** (compare relative peak intensities in Figure 4). This enables an unambiguous differentiation of both stereoisomers. In the IKE spectra of **9** and **10** (Figure 5) this process practically disappears. Further, the molecular ions of **7** — **10** can alternatively lose HF, $Cl^{\cdot}$ and $CH_2Cl^{\cdot}$ forming ions 128, 113 and 99, respectively. The corresponding processes are also found in their IKE spectra and are assigned in Table III. Also these energy peaks show more pronounced differences between stereoisomers than in the normal mass spectra.

The ion *m/e* 67, which becomes the base peak in **9** and **10**, is the product of a secondary fragmentation, i. e. loss of chlorine from the $(M—C_2H_3F)^{+\cdot}$ ion. This intermediate ion at *m/e* 102 is in all instances of low abundance. Also the energy peak which should reflect this decomposition of $M^{+\cdot}$ (at 0.688 E) is absent. The observed instability of 102 indicates that its structure must be different from that in difluoronorbornanes (e .g. **3** and **4**) where an identical species from $M^{+\cdot}$ is lost. Loss of chlorine from *m/e* 102 leads to a small energy peak (H) in all instances. Thus, the consecutive decomposition $M^{+\cdot}$—C_2H_3F—Cl is practically completed in the ion source.

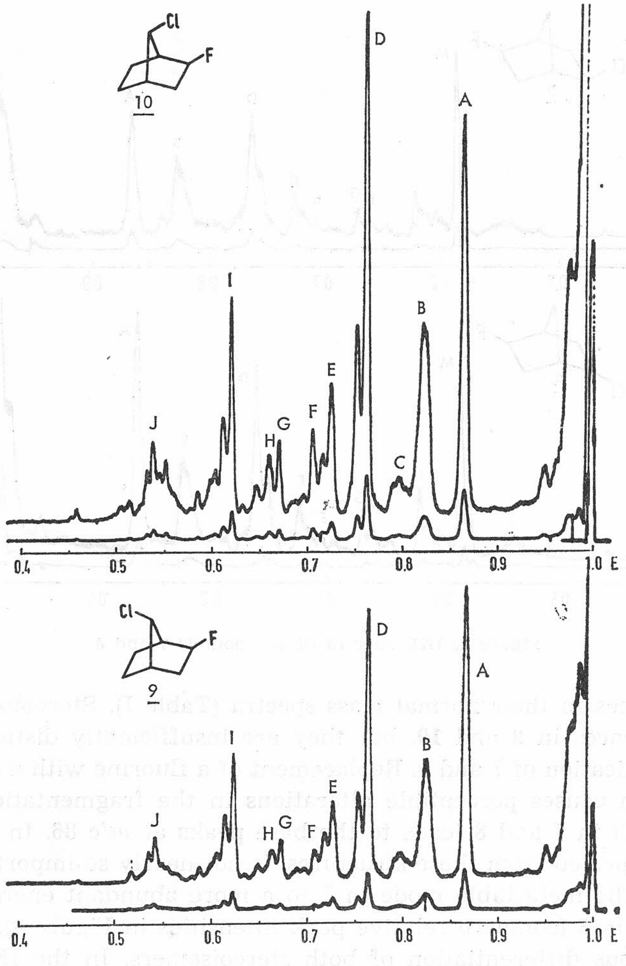


Figure 5. IKE spectra of compounds 9 and 10.

TABLE III

Metastable Decompositions in the IKE Spectra of Fluoro-Chloronorbornanes **7—10**

Peak	$m_1^+ \rightarrow m_2^+ + m_3$	Peak	$m_1^+ \rightarrow m_2^+ + m_3$
A	$148^+ \rightarrow 128^+ + HF$	G	$148^+ \rightarrow 99^+ + CH_2Cl^\cdot$
B	$113^+ \rightarrow 93^+ + HF$	H	$102^+ \rightarrow 67^+ + Cl^\cdot$
D	$148^+ \rightarrow 113^+ + Cl$	I	$128^+ \rightarrow 79^+ + CH_2Cl^\cdot$
	$148^+ \rightarrow 112^+ + HCl$	J	$148^+ \rightarrow 81^+ + CHFCl^\cdot$
E	$128^+ \rightarrow 93^+ + Cl^\cdot$		$148^+ \rightarrow 79^+ + CH_2Cl^\cdot + HF$
F	$120^+ \rightarrow 85^+ + Cl^\cdot$	M	$148^+ \rightarrow 86^+ + C_2H_3Cl$
	$112^+ \rightarrow 79^+ + CH_2F^\cdot$		

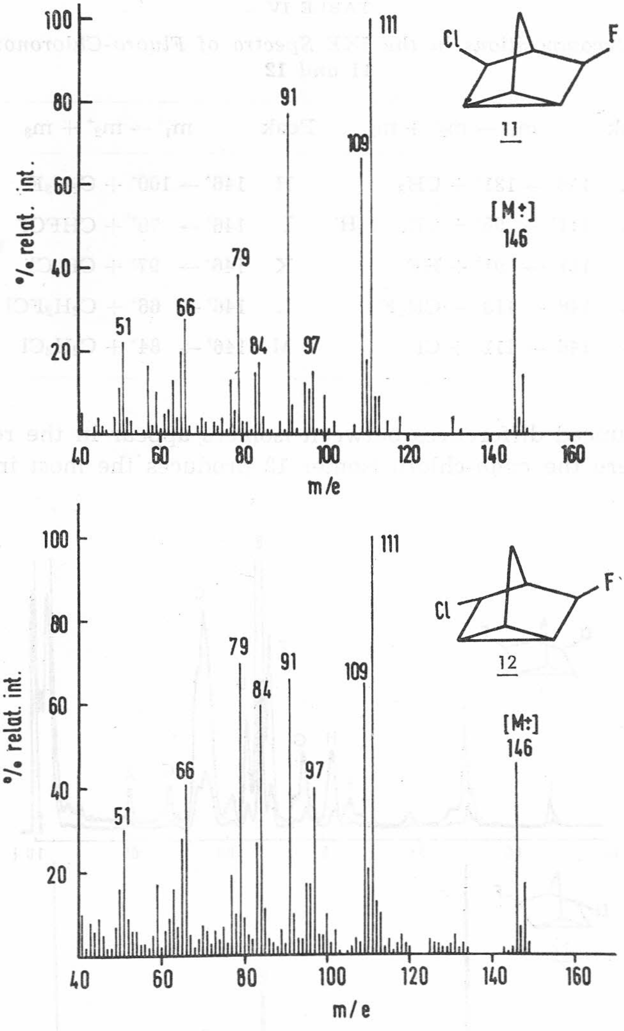


Figure 6. Mass spectra of compounds 11 and 12.

Fluoro-chloronortricyclanes (**11** and **12**)

Like compounds **9** and **10**, stereoisomers **11** and **12** (Figure 6) also exhibit different ion intensities in their mass spectra. They especially differ if the following decompositions, starting from $M^{+\cdot}$ are considered; namely, the loss of $CHFCl^{\cdot}$, C_2H_3Cl and $CH_2Cl^{\cdot}$, forming ions at *m/e* 79, 84 and 97 respectively. The molecular ions are more stable in comparison to those of the compounds given previously. As the metastable measurements show, several ions originate directly from the molecular ion (compare Table IV). Of interest here is the appearance of an intense *m/e* 91, which originates from the consecutive reaction $M^{+\cdot}$—$Cl^{\cdot}$——HF and may be a tropylium cation. The intermediate ion $M^{+\cdot}$—$Cl^{\cdot}$ at *m/e* 111 is the base peak in both instances. However, the intensities of the energy peaks, reflecting the last reaction in the IKE spectra, differ greatly (peak E, Figure 7).

TABLE IV

Metastable Decompositions in the IKE Spectra of Fluoro-Chloronortricyclanes **11** *and* **12**

Peak	$m_1^+ \rightarrow m_2^+ + m_3$	Peak	$m_1^+ \rightarrow m_2^+ + m_3$
A	$146^+ \rightarrow 131^+ + CH_3$	H	$146^+ \rightarrow 100^+ + C_2H_3F$
B	$111^+ \rightarrow 95^+ + CH_3^{\cdot} + H^{\cdot}$	I	$146^+ \rightarrow 79^+ + CHFCl^{\cdot}$
C	$111^+ \rightarrow 91^+ + HF$	K	$146^+ \rightarrow 97^+ + CH_2Cl^{\cdot}$
D	$146^+ \rightarrow 113^+ + CH_2F^{\cdot}$	L	$146^+ \rightarrow 66^+ + C_2H_2FCl$
E	$146^+ \rightarrow 111^+ + Cl$	M	$146^+ \rightarrow 84^+ + C_2H_3Cl$

Further pronounced differences between isomers appear in the reaction $M^{+\cdot}$ — $CHFCl^{\cdot}$, where the *endo*-chloro isomer **12** produces the most intense energy peak (peak I).

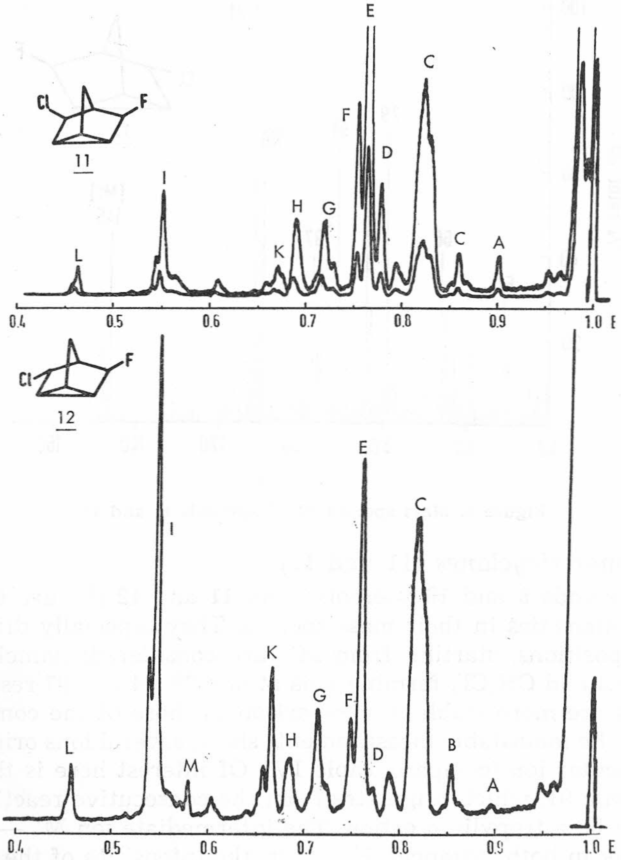


Figure 7. IKE spectra of compounds **11** and **12**.

It is evident from the above discussion that energy spectra can undoubtedly give further insight into electron impact induced fragmentation, making it possible to distinguish more clearly between several stereoisomeric compounds.

EXPERIMENTAL

Mass spectra were recorded on a CEC 21-110 C mass spectrometer at 70 eV, 6 kV accelerating voltage and 150 μA ionizing current. Samples were introduced via a gas inlet system at a temperature of about 100 °C. For recording IKE spectra, the instrument was modified to monitor accelerating and/or electric sector voltage (from zero volts to 2E volts) independently. A channeltron type detecting device, considerably smaller than conventional ion-electron multipliers, was placed on the trajectory of the main ion beam behind the electric sector[9]. This detecting device can be quickly shifted out of the main beam allowing the ions transmitted by the electric sector to pass the magnetic analyser.

Acknowledgement. We wish to thank the Res. Community of Slovenia for financial support. The authors are indebted to Mr. V. Vrščaj for excellent technical assistance.

REFERENCES

1. J. H. Beynon, J. W. Amy, and W. E. Baitinger, *Chem. Commun.* (1969) 723.
2. R. G. Cooks, J. H. Beynon, R. M. Capprioli, and G. R. Lester, *Metastable Ions,* Elsevier, Amsterdam, 1973.
3. J. L. Holmes and D. McGillivray, *Org. Mass Spectrom.* **5** (1971) 1349.
4. P. H. Chen and W. F. Kuhn, *Org. Mass Spectrom.* **6** (1972) 785.
5. J. L. Holmes and D. McGillivray, *Org. Mass. Spectrom.* **7** (1973) 559.
6. R. Robbiani and J. Seibl, *Org. Mass Spectrom.* **7** (1973) 1153.
7. D. C. DeJough and S. R. Shraded, *J. Amer. Chem. Soc.* **88** (1966) 3881.
8. C. A. Bunton and T. W. Pesco, *Org. Mass Spectrom.* **2** (1969) 81.
9. To be published.

IZVLEČEK

Masni spektri in spektri kinetične energije ionov nekaterih fluoro-kloro substituiranih norbornanov in nortriciklanov

B. Kralj, V. Kramer, M. Trkman in J. Marsel

Študirali smo masne spektre in spektre kinetične energije ionov difluoro-in fluoro-kloro-norbornanov ter fluoro-kloro-nortriciklanov. V nekaterih primernih podobnost masnih spektrov onemogoča razlikovanje diastereoizomer. Vendar se nasprotno njihovi spektri kinetične energije ionov jasno razlikujejo in omogočajo nedvoumno razlikovanje izomer.

INSTITUT JOŽEF STEFAN, UNIVERZA V LJUBLJANI
IN
ODDELEK ZA KEMIJO, FAKULTETA ZA NARAVOSLOVJE
IN TEHNOLOGIJO, UNIVERZA V LJUBLJANI

Prispjelo 4. ožujka 1977.