

# Mass Spectrometry of Oligomeric Cyanines and Squaraines of the Indole Series: Fast Atom Bombardment-Induced Chemical Reactions\*

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*In memoriam W. Grahn (1942 - 2001)*

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Fast Atom Bombardment Mass Spectrometry (FAB-MS), Indocyanines, Squaraines

Fast atom bombardment (FAB) has been used for mass spectrometric characterization of oligomeric cyanines and squaraines of the indole series which are linked by different aromatic spacers. Markedly different results were obtained for the oligomers and for the corresponding monomers. In addition to the expected mono-anions and mono-cations, ions of high relative abundance were detected which can only be explained on the basis of FAB-induced chemical reactions of the initial oligomers. Formation of allenes, hydrogenation and dehydrogenation, respectively, is characteristic for this class of compounds under FAB-conditions.

## Introduction

Oligomeric cyanines and squaraines of definite length and structural uniformity are of current interest for their potential application in third-order non-linear optical materials [1]. In this context and for systematic studies, a number of different oligomers as well as the corresponding monomeric units have been synthesized [2, 3]. Fast atom bombardment (FAB) has been used for the mass spectrometric characterization of the ionic and zwitter-ionic compounds.

## Mass Spectrometry

The classical technique of electron impact ionization (EI) is restricted to the investigation of volatile compounds. For the analysis of ionic and highly polar compounds of low and high molecular weight a number of different ionization techniques are available today which are generally called “soft ionization” techniques. They are characterized by the formation of highly abundant positively or negatively

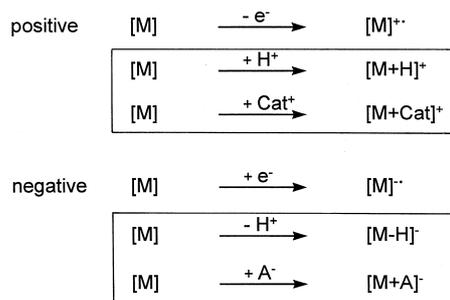


Fig. 1. Types of molecular ions obtained by soft ionization techniques. M = neutral molecule, Cat = cation, A = anion.

charged molecular ions and by negligible fragmentation. In principle, there are three different ionization processes that can be made responsible for the formation of molecular ions: a) electron ionization (less frequent), b) protonation or deprotonation and c) attachment of cations or anions to the neutral molecule (Fig. 1). In the case of ionic compounds, the respective cations or anions are obtained preferentially. The knowledge and consideration of these processes is indispensable for the correct molecular weight determination.

Among these soft ionization techniques FAB has found widespread application because of its experi-

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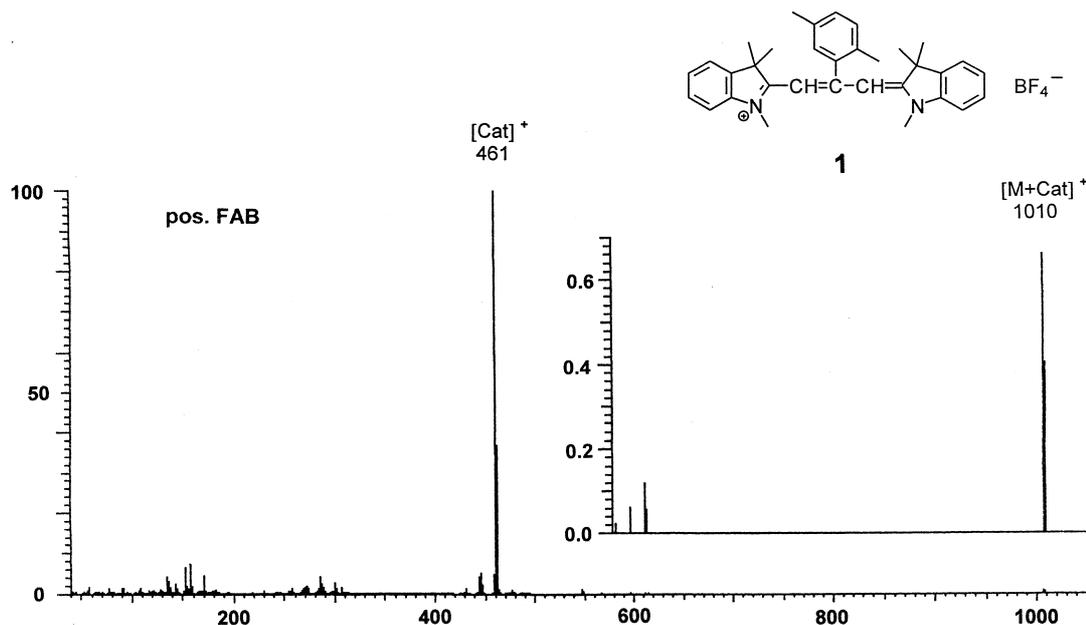
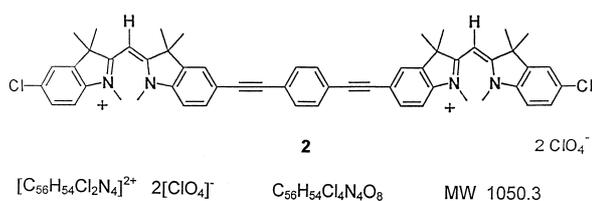


Fig. 2. Positive FAB mass spectrum of the monomeric indocyanine **1**,  $[C_{33}H_{37}N_2]^+ [^{11}BF_4]^-$ , MW 548.3, matrix: 3-nitrobenzyl alcohol.



Scheme 1. Dimeric tolane-bridged indocyanine **2**.

mental and instrumental simplicity and the fact that conventional mass spectrometers can be used without expensive modifications. The desorption of preformed ions from a liquid matrix by impact of fast atoms such as xenon or caesium represents the basic principle of FAB. For the desorption it is essential for the analyte to be dissolved in a liquid matrix. Commonly used matrices are 3-nitrobenzyl alcohol and glycerol. In most cases, the application of an organic matrix results in a superposition of the matrix signals and those of the investigated sample. In general, this imposes no problem for interpreting the spectra. However, another effect inherent to FAB may cause difficulties: Chemical reactions of the sample induced during or by the FAB exposition itself can lead to unexpected peaks in the mass spectrum. First experimental proofs of such induced chemical reactions were reported in 1982

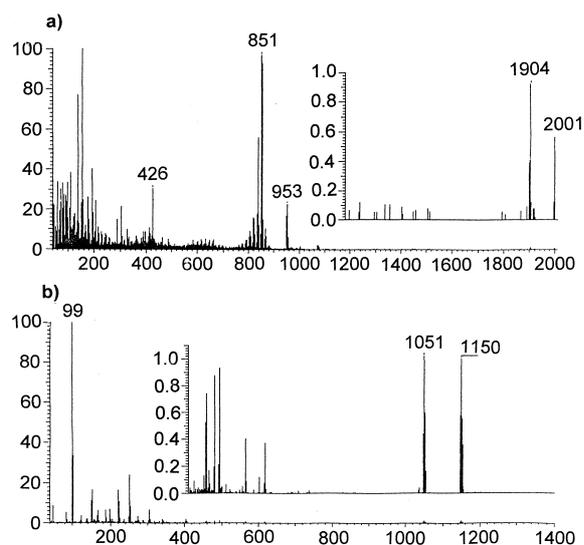


Fig. 3. FAB-mass spectra of dimeric indocyanine **2**, matrix: 3-nitrobenzyl alcohol, a) positive and b) negative ionization mode. The marked ion masses correspond to the monoisotopic ion masses of the isotope pattern. a)  $m/z$  426  $[Cat]^{++}$ ,  $m/z$  851  $[Cat_{allene}]^+$ ,  $m/z$  951  $[M-ClO_4]^+$ ,  $m/z$  1904  $[M_{allene}+M-ClO_4]^+$ ,  $m/z$  2001  $[2M-ClO_4]^+$ , b)  $m/z$  99  $[ClO_4]^-$ ,  $m/z$  1051  $[M_{allene}+ClO_4]^-$ ,  $m/z$  1150  $[M+ClO_4]^-$ .

[4, 5]. Meanwhile a whole series of different reactions are known [6]. This paper reports two new

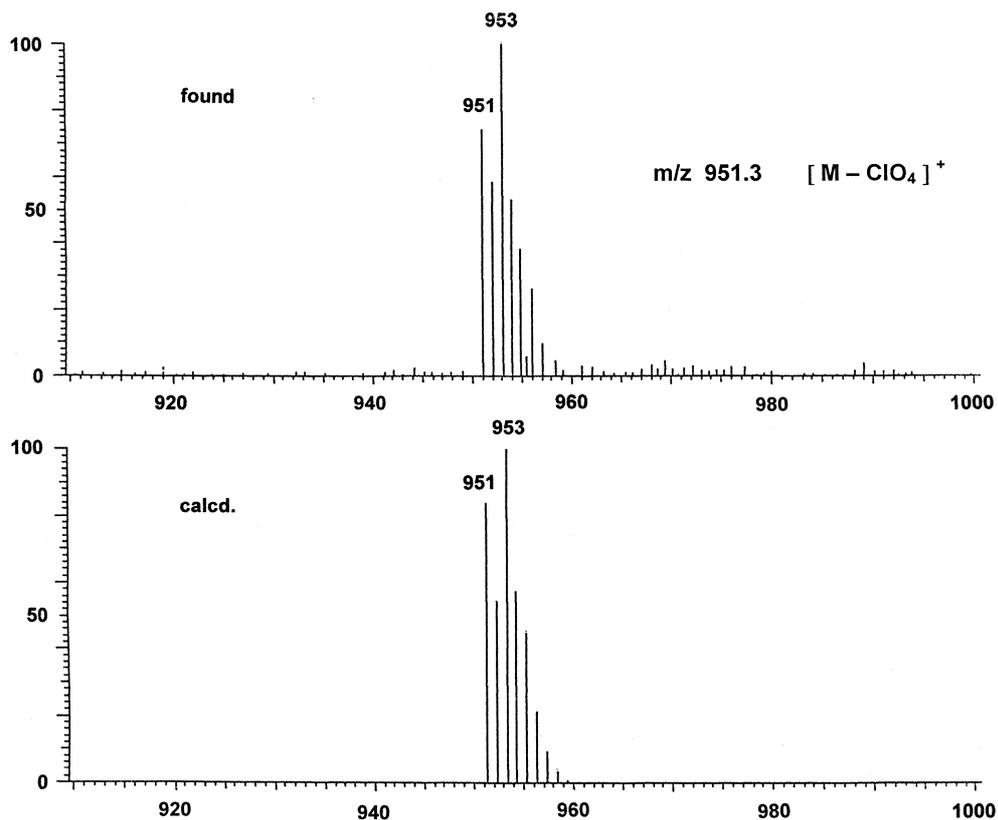


Fig. 4. Experimental (exp.) and calculated (calc.) isotopic pattern of the mono-cation  $[M - \text{ClO}_4]^+$  of compound **2**.

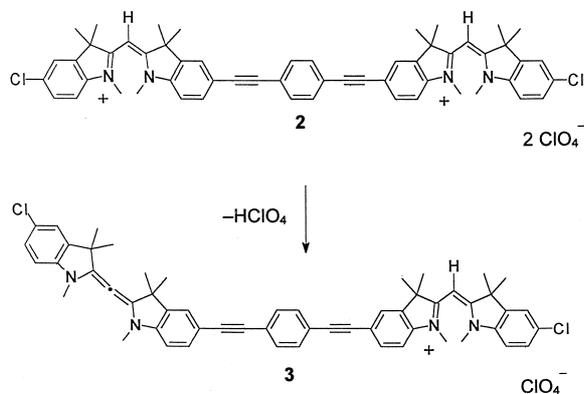
types of impact-induced reactions prior to desorption.

## Results and Discussion

### Indocyanines

The ionic monomers show an optimal behavior under FAB conditions as is demonstrated for compound **1** in Fig. 2 as an example: high relative abundance of the cation, no considerable superposition with the matrix spectrum, and additional molecular weight information by formation of the adduct ion  $[M + \text{Cat}]^+$ . Complementary information is obtained in the negative ion mode which shows an abundant signal for the anion.

As a rule, using FAB multiply charged ionic compounds are detected as singly charged species. The observation of doubly charged ions is rather an exception. In the positive ion spectrum of the dimeric compound **2** (Scheme 1) the expected ions are observed for  $[M - \text{ClO}_4]^+$  at  $m/z$  951.3 and – with re-



Scheme 2. Formation of the allene mono-cation **3** by FAB-induced dehydrogenation of the original dimeric bis-cation **2**.

markable intensity – the bis-cation  $[\text{Cat}]^{++}$  at  $m/z$  426 (Fig. 3a). In all cases, the observed isotopic pattern is in good agreement with the theoretical one. An example is given in Fig. 4. A surprising result is the ion at  $m/z$  851 which is the base peak

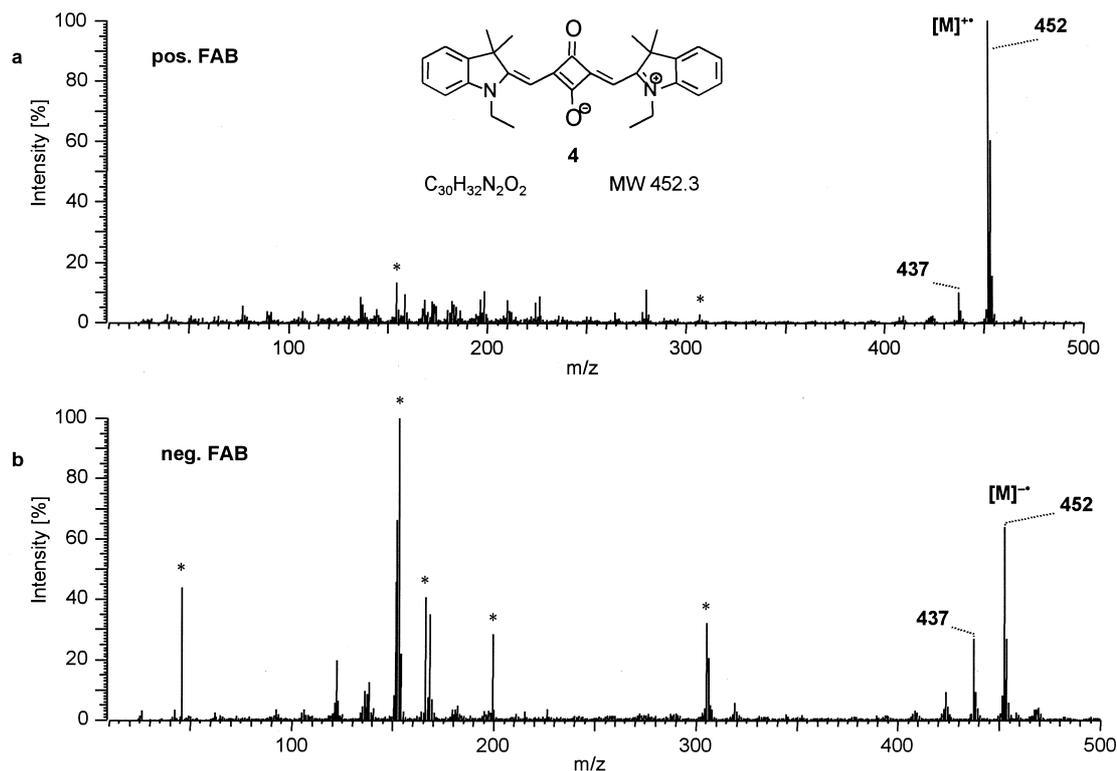
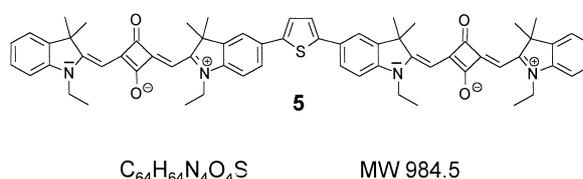


Fig. 5. FAB mass spectra of the monomeric squaraine **4**, matrix: 3-nitrobenzyl alcohol, a) positive and b) negative ionization mode. Matrix signals are marked with asterisks.

in the spectrum of **2** (Fig. 3a). The formation of this ion can be regarded as a new type of a FAB-induced chemical reaction before desorption. Its mass number and isotopic pattern indicates the presence of an allene cation **3** (Scheme 2).

The process of allene formation is not restricted to dimeric cyanines. Thus, signals for mono- and di-allene cations are displayed in the spectra of trimeric cyanines [2]. The observed formation of allenes may be formulated as a gas-phase fragmentation as well. However, the detection of a mixed cluster between the original compound **2** and its reaction product **3** ( $[M_{\text{allene}}+M-\text{ClO}_4]^+$  at  $m/z$  1901.6 in addition to  $[2M-\text{ClO}_4]^+$  at  $m/z$  2001.6) can be regarded as an indication for an impact-induced process before desorption. This assumption is supported by detection of the molecular ions  $[M+\text{ClO}_4]^-$  at  $m/z$  1149.2 of **2** and  $[M_{\text{allene}}+\text{ClO}_4]^-$  at  $m/z$  1049.6 of **3** in the negative ion mode. Base peak of this spectrum is the common anion  $[\text{ClO}_4]^-$  at  $m/z$  99 (Fig. 3b). An independent proof by subsequent chromatography of the used sample after FAB exposition, as it has



Scheme 3. Thienyl-bridged dimeric squaraine of the indole series **5**.

been reported for cyclophosphates [7], has still to be done.

### Squaraines

A somewhat atypical behaviour can be observed for the monomeric squaraine **4**. Instead of an ionization by protonation and deprotonation, which is the common process for zwitter-ionic compounds, the molecular radical ions  $[M]^{\bullet+}$  and  $[M]^{\bullet-}$  are formed (Fig. 5).

An unexpected and at first confusing result is obtained for the dimeric squaraine **5** (Scheme 3). In Fig. 6 the mass range of the positively and neg-

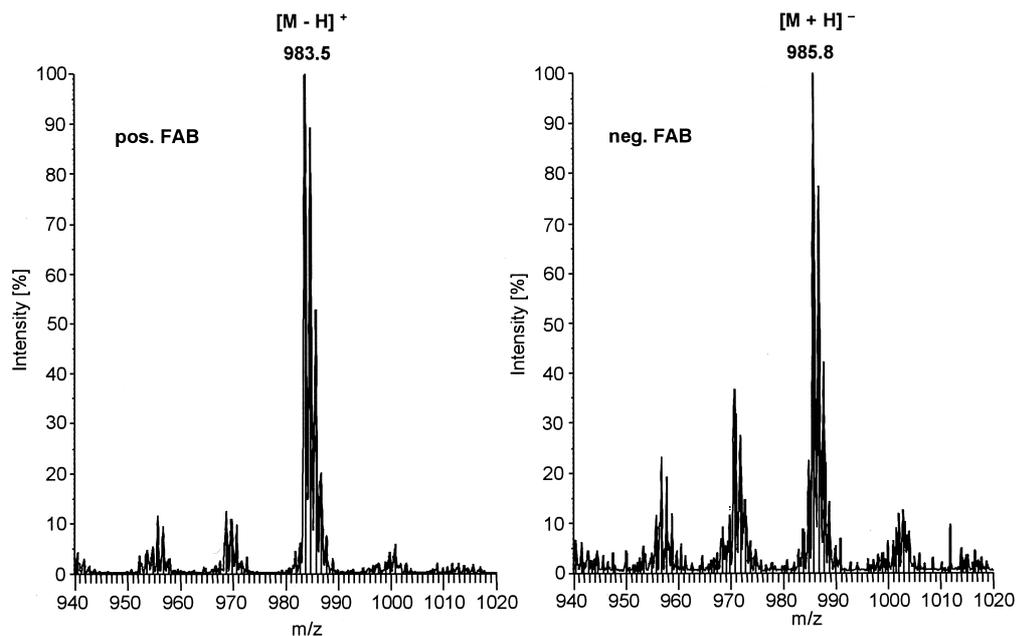
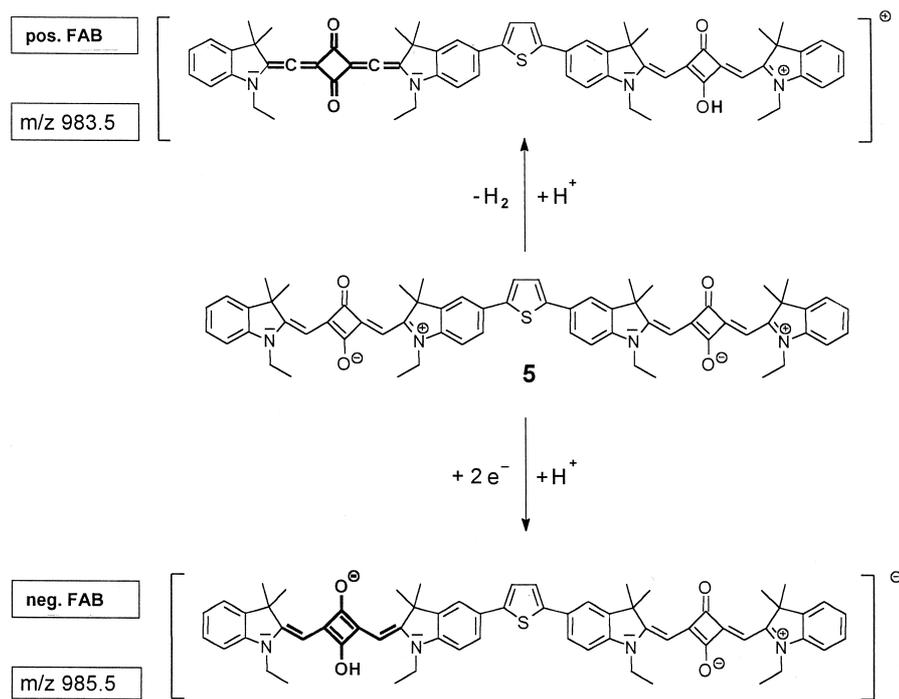


Fig. 6. FAB mass spectra of the molecular ion of **5** in the positive and negative ionization mode. Matrix: 3-nitrobenzyl alcohol.

actively charged molecular ions is displayed. The spectra do not show the expected types of molecular

ions  $[M+H]^+$  and  $[M-H]^-$  (see Fig. 1). Instead, one observes molecular ions corresponding formally to

$[M-H]^+$  and  $[M+H]^-$ . The formation of such molecular ions can only be rationalized by a FAB-induced reaction within the matrix prior to desorption, which has not been reported so far (Scheme 4).

Under FAB conditions, two processes take place simultaneously: first, an elimination of  $H_2$  leading to the formation of a quinoid system, second a reduction of the original zwitter-ionic compound. The dehydrogenated compound is only detectable in the positive mode whereas the hydrogenated reaction product is recorded in the negative mode only. The matrix 3-nitrobenzyl alcohol serves both as the electron and proton donor. The exact analysis of the isotopic pattern demonstrates that the expected molecular ions  $[M+H]^+$  and  $[M-H]^-$  are formed as well, although in small quantities. The main products of

the FAB experiment are the compounds shown in Scheme 4.

### Conclusion

As stated earlier [7] one should consider that the results of FAB mass spectrometry may be complicated by impact induced chemical reactions within the matrix. Of course these chemical reactions depend on the reactivity of the investigated compounds.

### Experimental Section

The FAB measurements were performed on a double-focusing mass spectrometer (MAT 8200, Finnigan MAT, Bremen) using xenon at an energy of 8 kV and 3-nitrobenzyl alcohol as liquid matrix.

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