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Fast Atom Bombardment Mass Spectra of Disulphonated Oxonole Dyes

R. Borsdorf, R. Haessner

Sektion Chemie der Karl-Marx-Universität, DDR-7010
Leipzig, Talstrasse 35, German Democratic Republic

H. Ruotsalainen

Department of Chemistry, University of Oulu, Oulu, Finland

and

G. Bach

VEB Filmfabrik Wolfen, Direktorat F/E, DDR-4440 Wolfen 1,
Puschkinplatz 1, German Democratic Republic

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SUMMARY

Fast Atom Bombardment Mass Spectrometry (FABMS) can be used to elucidate the structure of involatile oxonole dyes. The spectra of three selected compounds are presented. Excellent spectra are obtained in the negative ion mode, whereas only little information is obtainable from the positive ion spectra. Fragmentation takes place mainly along the methine chain of the dyes. In the lower mass region, isocyanate and sulphanilic acid peaks are the dominating fragment ions.

1. INTRODUCTION

In photographic materials, oxonole dyes are used as filter compounds. They absorb light scattered from the silver halide grains and prevent

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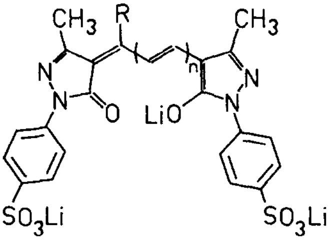
the formation of a halo. Most of these dyes contain sulphonic acid groups to aid solubility in water. They are removed from the photographic layers during the development procedure. The sulphonated dyes are involatile and for that reason their structure cannot be determined by conventional mass spectroscopic techniques. Even methylation of the sulphonic acid groups[1] fails to give satisfactory mass analysis. Recent investigations have however demonstrated the successful application of FABMS to the investigation of sulphonated dyestuffs (azo dyestuffs,[2-4] xanthene[5] and merocyanine[6] dyes) and their precursors (naphthalene sulphonic acids[7]). The FAB mass spectra of oxonole dyes presented in this paper confirm the wide applicability of this technique for the analysis of dyestuffs.

2. RESULTS AND DISCUSSION

The FAB spectra of the three oxonole dyes **1–3** was studied. The principal features evident in the negative and positive ion spectra of these compounds are summarised in Tables 1 and 2 respectively. Because of the high solubility of the oxonole dyes in glycerol, the pure glycerol cluster ion peaks $(n.\text{gly} - \text{H})^-$ or $(n.\text{gly} + \text{H})^+$ respectively are comparatively weak. For the same reason, no strong dye–glycerol clusters are observed[8] in the molecular ion region, as has been reported in studies of other dyestuffs.[2-4,6,7]



1–3

Oxonole	*n*	*R*	*Mol. wt*
1	0	H	536
2	1	H	562
3	1	CH_3	576

TABLE 1
Negative Ion Molecular Information and Fragmentation in the FAB Spectra of Oxonole Dyes

Fragment	*Fragment or mol. wt*			*Relative intensity (% of base peak)*		
	1	**2**	**3**	**1**	**2**	**3**
$(M-H)^-$	535	561	575	—[b]	0·5	6
$(M-Li)^-$	529	555	569	5	15	9
$(M-2Li+H)^-$	523	549	563	3	2	3
$(M-3Li+2H)^-$	517	543	557	4	1	—[b]
$(M-Li-SO_3)^-$	449	475	489	—[b]	—[b]	2
$(M-2Li+H-SO_3)^-$	443	469	483	5	3	—[b]
$(M-3Li+2H-SO_3)^-$	437	463	477	—[b]	1·5	—[b]
4	367	393	407	4	2·5	—[b]
5	351	377	391	3·5	—[b]	2
6	345	371	385	2	1	1
7	367	367	367	4	—[b]	18
8	351	351	351	3·5	—[b]	17
9	—[a]	—[a]	299	—[a]	—[a]	14
10	—[a]	—[a]	293	—[a]	—[a]	25
11	—[a]	279	279	—[a]	8	15
12	265	265	265	8	10	12
13	259	259	259	15	21	14
14	253	253	253	—[b]	9	16
15	252	252	252	—[b]	8	15
$(O{=}C{=}N{-}C_6H_4{-}SO_3)^-$	198	198	198	100	100	100
$(H_2N{-}C_6H_4{-}SO_3)^-$	172	172	172	20	24	37
$(\cdot HN{-}C_6H_4{-}SO_3)^-$	171	171	171	40	43	59
$(C_6H_5SO_3)^-$	157	157	157	40	12	70
$(\cdot C_6H_4{-}SO_3)^-$	156	156	156	67	60	58

[a] Impossible fragment constitution.
[b] Possible constitution, but not observed.

As an example, the negative and positive ion spectra of the extensively used oxonole derivative **3** are shown in Figs 1 and 2 respectively. Figure 3 shows an amplification in the molecular ion region of Fig. 2.[7]

The negative ion spectra of all the dyes show a molecular anion $(M-Li)^-$, but only dyes **2** and **3** show $(M-H)^-$, with low intensity. The recognition of the molecular weight may be difficult, because the lithium cation can be exchanged by a proton, so that peaks corresponding

TABLE 2
Molecular Ion Information in the FAB Spectra of Positive Ions of Oxonole Dyes (rel. int. [%] in comparison to the base peak (gly + Li)$^+$)

Ion	*Ion wt*			*Relative intensity* (% *of base peak* (*gly* + *Li*)$^+$)		
	1	**2**	**3**	**1**	**2**	**3**
$(M + Li)^+$	543	569	583	0·05	0·2	0·1
$(M + H)^+$	537	563	577	0·1	0·2	0·2
$(M - Li + 2H)^+$	531	557	571	0·06	0·1	0·05
$(M - 2Li + 3H)^+$	525	551	565	—	—	0·1
$(M + H + gly)^+$	629	655	669	0·03	—	—
$(M - Li + 2H + gly)^+$	623	649	663	—	—	0·1
$(M - 2Li + 3H + gly)^+$	617	643	657	—	—	0·05
$(M - Li + 2H - SO_3H)^+$	450	476	490	—	0·2	—

to $(M - 2Li + H)^-$ and $(M - 3Li + 2H)^-$ are also observed. The intensity of these different peaks depends on the concentration of the dyestuff in the glycerol matrix. Sometimes it can be very useful to use another alkali-metal salt, such as the sodium or potassium salt, of the same dye for a second comparative mass analysis.

Interesting ions in the negative mass spectra are the fragment ions formed by bond cleavage along the methine chain. Because of the bond

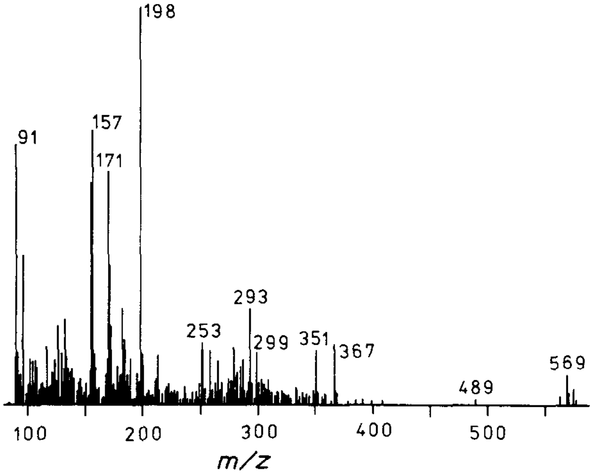


Fig. 1. Negative ion FAB mass spectrum of dye **3**.

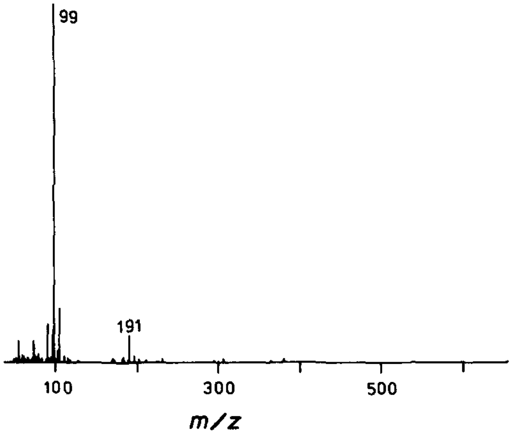


Fig. 2. Positive ion FAB mass spectrum of dye **3**.

order equivalence in the methine chain, fragmentations are expected at all the bonds and, in fact, all possible fragments are observed (as indicated in Table 1). Once again, the ions (frag – Li)$^-$ and (frag – H)$^-$ are observed and the intensities of these again depend on the dye concentration.

The monomethine fragments at *m*/*e* 367 and *m*/*e* 351 in the spectrum of the trimethine dye **3** are of special interest. These are not due to

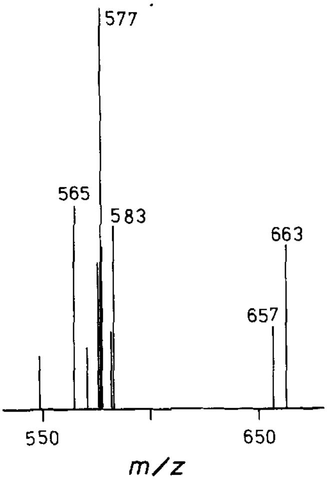
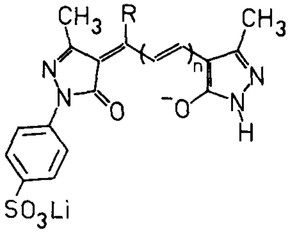


Fig. 3. Part of Fig. 2 amplified about 400 times in the molecular ion region.

contamination of dye **3** with dye **1**, since dye **3** shows no absorption in its visible spectrum in the region of 450 nm, at which wavelength the absorption maxima of dye **1** occur. The thermal rearrangement of tri- and penta-methine oxonole dyes to mono- and tri-methine dyes respectively is known to occur, and evidently this reaction also takes place during measurement of the FAB spectra.

The structures of the fragment ions **4–15** in the negative ion spectra, as listed in Table 1, are shown.



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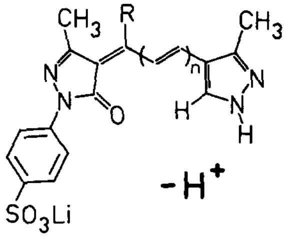

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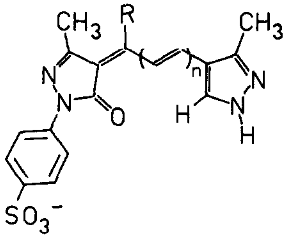

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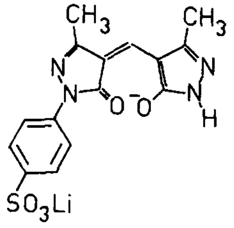

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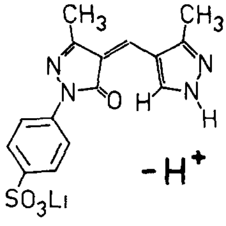

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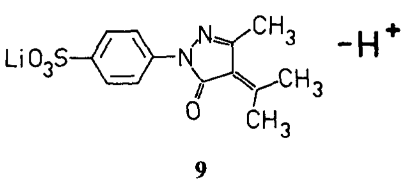

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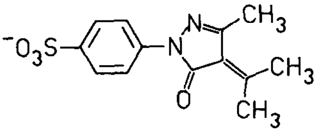

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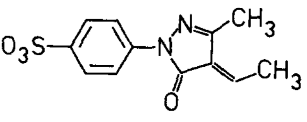

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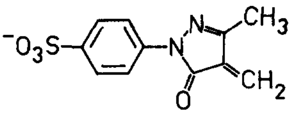

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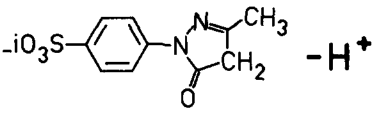

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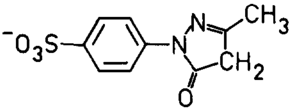

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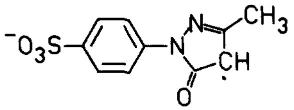

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In the lower mass region of the negative ion spectra, there are observed typical peaks arising from the fragmentation of the pyrazole ring. The sulphonated phenylisocyanate ion $(OCN \cdot C_6H_4SO_3)^-$ is the base peak of the spectra of all the dyes **1**–**3**. This ion, as well as the sulphanilic acid and benzene sulphonic acid fragments, are characteristic features of the pyrazolone system.

From the positive ion spectra, only a much more limited amount of information is obtainable. Thus, the spectra derived show (Table 2) the expected molecular cations $(M + Li)^+$ and $(M + H)^+$, and also the corresponding glycerol cluster ions $(M + Li + gly)^+$ and $(M + H + gly)^+$. Additional to these peaks, the ions corresponding to $(M - Li + 2H)^+$, $(M - 2Li + 3H)^+$ and $(M - Li + 2H + SO_3H)^+$ are observed, the latter only in the spectrum of dye **2**. Typical fragment ions found in the negative ion spectra are not observed in the positive ion mass analysis and the value of the negative ion spectra in the mass analysis of sulphonated dyes is thus clearly demonstrated.

3. EXPERIMENTAL

Purification of the dyestuffs was effected by means of electrophoresis with glass fibre filters of type 15-90 (VEB Feinpapierfabrik Neu Kaliss). Nitrogen was used as inert gas for this operation because of the 0·2M–NH_3 used as electrolyte. Lithium salts were obtained by cation exchange (KPS 200, VEB CKB Bitterfeld).

Samples of the compounds studied were prepared in glycerol solutions at the highest possible concentration. The glycerol solution of a sample was deposited on the stainless steel tip of a sample probe.

The positive and negative ion fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS80RF Autoconsole double-focusing mass spectrometer (Manchester, GB) equipped with a Kratos DS55 data system. A sample in glycerol was bombarded by a xenon atom beam produced by a saddle field source, FAB11NF (Ion Tech. Ltd, Teddington, GB), operated with a tube current of 1·1 mA at an energy of 9 keV.

4. CONCLUSIONS

The results show that sulphonated oxonole dyestuffs may be analysed by FABMS. Negative ion spectra are superior to those in the positive ion mode. In contrast to merocyanine dyes, oxonole dyes have no basic centre and hence positive ions from oxonole dyes are difficult to observe.

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