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Mass Spectral Fragmentation Study of Substituted 1,3-Diphenyl--2-pyrazolines

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The electron impact induced fragmentation of twenty two 1,3--diphenyl-2-pyrazolines mono-, di- and trisubstituted in one or in both phenyl rings was studied by deuterium labelling, high and low resolution mass spectrometry, and ion kinetic energy spectroscopy. The fragmentation patterns are discussed taking into account especially the nature of the substituent and the position of substitution.

The results, compared with those for the unsubstituted compound, showed that in general the phenyl ring substitution does not affect its fragmentation. The formation of stable quinoid-type ions directs many fragmentation pathways of methoxy substituted compounds.

INTRODUCTION

The mass spectral behaviour of 1,3-diphenyl-2-pyrazolines and its derivatives with a monosubstituted phenyl ring has been the subject of our previous papers[1,2].

A closer study of the mass spectra of 1,3-diphenyl-2-pyrazoline and of its isotopically (^{13}C, ^{15}N and ^{2}H) labelled as well as phenyl ring substituted derivatives, taking into account the metastable transitions and exact mass measurements, provided the possibility of completely elucidating their fragmentation following the electron impact. In the postulated fragmentation pathway of 1,3-diphenyl-2-pyrazoline all the ions in the mass spectrum (except *m/e* 103) originate from the molecular ions furnishing the base peak of the spectrum. In general, the effect of phenyl ring substituion, as indicated by the study of thirty compounds monosubstituted in one or both phenyls, does not affect the fragmentation pattern of the parent compound, although *ortho* substitution produces some special effect, as demonstrated by the example of *ortho* methoxy and nitro substitution.

In the present study this result is being confirmed by the example of several new compounds, 1,3-diphenyl-2-pyrazolines monosubstituted in one or both phenyl rings, as well as disubstituted or trisubstituted in one or both phenyl

rings. Their mass spectra turned out to be characteristic, thus allowing unambiguous identification of isomers. We investigated their fragmentation mechanisms using the data obtained from their labelled analogues and metastable ion decompositions.

RESULTS

In addition to the mass spectra of 31 substituted 1,3-diphenyl-2-pyrazolines reported in our previous papers[1,2] the following 22 substituted 1,3-diphenyl-2-pyrazolines have now been examined:

1. monosubstituted in one phenyl ring:
   - 1-phenyl-3-(4″-methylsulfonylphenyl)-2-pyrazoline *1*
   - 1-(4′-methylsulfonylphenyl)-3-phenyl-2-pyrazoline *2*
   - 1-phenyl-3-(4″-methylthiophenyl)-2-pyrazoline *3*
   - 1-phenyl-3-(4″-acetylaminophenyl)-2-pyrazoline *4*
   - 1-(4′-carbamoylphenyl)-3-phenyl-2-pyrazoline *5*
   - 1-phenyl-3-(4″-dimethylaminophenyl)-2-pyrazoline *6*
2. monosubstituted in both phenyl rings:
   - 1-(4′-chlorophenyl)-3-(4″-methylsulfonylphenyl)-2-pyrazoline *7*
   - 1-(4′-methylsulfonylphenyl)-3-(4″-chlorophenyl)-2-pyrazoline *8*
   - 1-(4′-methoxycarbonylphenyl)-3-(4″-chlorophenyl)-2-pyrazoline *9*
   - 1-(4′-sulfamoylphenyl)-3-(4″-chlorophenyl)-2-pyrazoline *10*
   - 1-(3′-sulfamoylphenyl)-3-(4″-chlorophenyl)-2-pyrazoline *11*
3. disubstituted in one phenyl ring:
   - 1-phenyl-3-(2″,4″-dimethoxyphenyl)-2-pyrazoline *12*
   - 1-phenyl-3-(2″,5″-dimethoxyphenyl)-2-pyrazoline *13*
   - 1-phenyl-3-(2″,6″-dimethoxyphenyl)-2-pyrazoline *14*
   - 1-phenyl-3-(2″,6″-dimethoxy-d_6-phenyl)-2-pyrazoline *15*
   - 1-phenyl-3-(3″,4″-dimethoxyphenyl)-2-pyrazoline *16*
   - 1-phenyl-3-(3″,5″-dimethoxyphenyl)-2-pyrazoline *17*
4. disubstituted in both phenyl rings:
   - 1-(2′,6′-dimethylphenyl)-3-(2″,5″-dimethoxyphenyl)-2-pyrazoline *18*
   - 1-(2′,6′-dimethylphenyl)-3-(2″,6″-dimethoxyphenyl)-2-pyrazoline *19*
5. trisubstituted in one phenyl ring:
   - 1-phenyl-(2″,4″,6″-trimethoxyphenyl)-2-pyrazoline *20*
   - 1-phenyl-(3″,4″,5″-trimethoxyphenyl)-2-pyrazoline *21*
   - 1-phenyl-(2″,4″,6″-trimethylphenyl)-2-pyrazoline *22*

The normalized and uncorrected 70 eV mass spectra of the compounds *1*—*11* and *15* are listed in table I. Peaks with an intensity of 1% or more related to the base peak are tabulated. For comparison, the spectra od *12*—*14* and *16*—*22* are presented as bar graphs in figure 1.

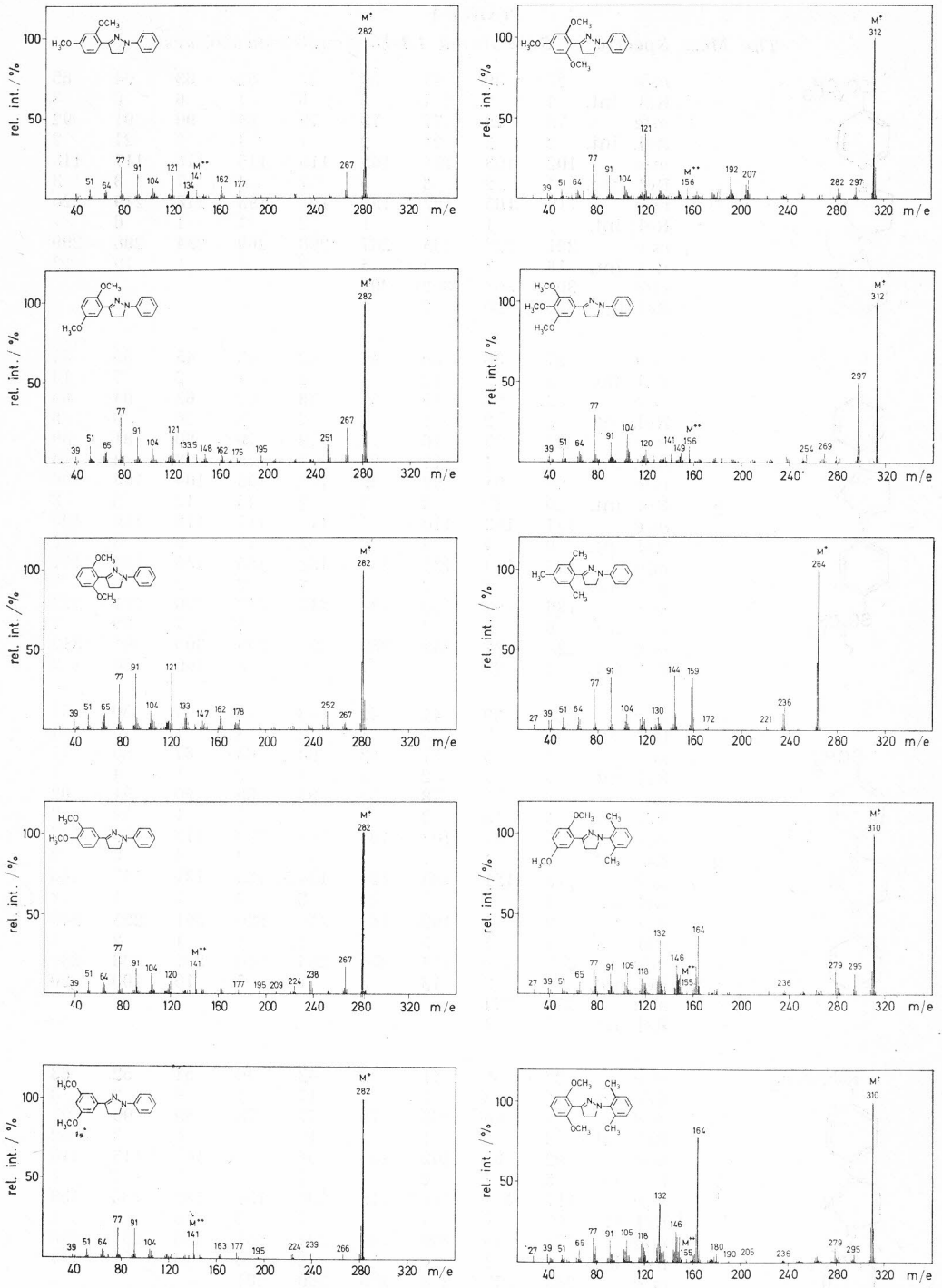
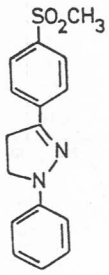


Figure 1. Normalized 70 eV mass spectra of methoxy and methyl substituted 1,3-diphenyl-2--pyrazolines (*12*, *13*, *14*, *16* and *17*, left, top to bottom; *20*, *21*, *22*, *18* and *19*, right, top to bottom).

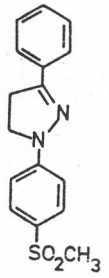
TABLE I

The Mass Spectra of Substituted 1,3-Diphenyl-2-pirazolines



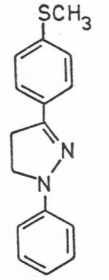
1

m/e	27	39	41	50	51	52	63	64	65
Rel. int.	1	2	1	2	6	1	6	6	3
m/e	75	76	77	78	79	89	90	91	92
Rel. int.	2	3	21	2	1	4	3	21	2
m/e	102	103	104	105	110.5	115	116	117	118
Rel. int.	1	2	8	5	1	4	7	3	3
m/e	119	165	182	191	192	193	218	219	220
Rel. int.	1	1	1	1	2	1	1	6	7
m/e	221	222	235	237	268	269	284	298	299
Rel. int.	16	3	2	5	1	4	1	10	12
m/e	300	301	302	303					
Rel. int.	100	20	7	1					



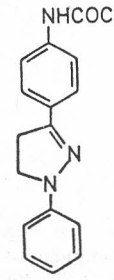
2

m/e	27	38	39	41	42	43	45	50	51
Rel. int.	3	2	12	3	2	3	2	7	13
m/e	52	53	55	57	58	62	63	64	65
Rel. int.	5	2	2	3	2	3	26	9	8
m/e	74	75	76	77	78	79	80	81	89
Rel. int.	2	4	11	29	7	5	8	2	6
m/e	90	91	92	96	102	103	104	105	106
Rel. int.	20	19	8	3	2	15	12	5	3
m/e	107	108	110.5	115	116	117	118	119	120
Rel. int.	9	4	4	8	5	18	9	5	11
m/e	123	130	131	132	152	155	156	165	171
Rel. int.	3	3	2	2	2	2	2	2	3
m/e	186	192	193	194	212	219	220	221	222
Rel. int.	6	3	4	2	3	5	7	29	7
m/e	235	237	238	269	298	299	300	301	312
Rel. int.	2	25	5	7	6	8	100	20	8



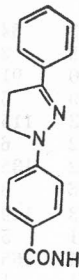
3

m/e	27	39	41	42	43	45	47	50	51
Rel. int.	1	2	3	1	2	3	1	1	4
m/e	52	55	57	63	64	65	67	69	71
Rel. int.	1	2	2	2	4	2	1	4	1
m/e	76	77	78	81	83	89	90	91	92
Rel. int.	1	13	2	2	1	1	1	14	2
m/e	95	97	103	104	105	108	115	116	117
Rel. int.	1	1	1	4	2	2	4	6	2
m/e	118	121	133	134	134.5	135	137	147	148
Rel. int.	1	1	1	11	2	2	1	1	4
m/e	149	150	163	164	219	220	221	225	240
Rel. int.	4	1	5	1	1	1	1	2	1
m/e	251	252	253	254	255	266	267	268	269
Rel. int.	2	2	13	3	1	5	10	100	20
m/e	270	271							
Rel. int.	7	1							



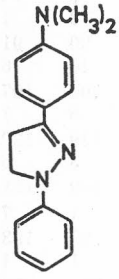
4

m/e	27	39	41	42	43	50	51	52	63
Rel. int.	1	3	2	2	17	1	6	2	3
m/e	64	65	66	76	77	78	89	90	91
Rel. int.	8	5	1	1	19	3	1	3	22
m/e	92	93	102	103	104	105	106	115	116
Rel. int.	5	1	1	2	7	4	3	1	1
m/e	117	118	118.5	119	130	131	132	133	158
Rel. int.	3	6	1	2	2	3	15	3	1
m/e	174	175	208	209	234	235	236	237	238
Rel. int.	1	1	1	4	2	6	18	21	7
m/e	263	277	278	279	280	281			
Rel. int.	2	4	7	100	22	3			



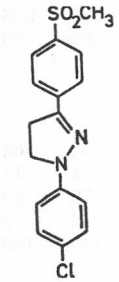
5

m/e	27	28	38	39	40	41	44	45	50
Rel. int.	2	1	2	10	1	2	8	2	8
m/e	51	52	53	62	63	64	65	66	74
Rel. int.	17	5	1	3	15	9	15	2	2
m/e	75	76	77	78	79	88	89	90	91
Rel. int.	7	11	31	5	3	2	11	15	15
m/e	92	93	95.5	102	103	104	105	106	107
Rel. int.	4	2	1	3	14	13	3	2	4
m/e	109	114	115	116	117	118	118.5	119	120
Rel. int.	1	2	12	11	28	9	1	3	3
m/e	121	123.5	124	125	125.5	130	131	131.5	132
Rel. int.	4	10	2	8	2	1	2	2	6
m/e	132.5	133	134	135	142	143	144	147	148
Rel. int.	2	5	4	7	2	2	2	1	3
m/e	149	152	165	166	167	170	189	190	191
Rel. int.	2	1	4	1	1	1	1	2	3
m/e	192	193	194	217	218	219	220	221	234
Rel. int.	3	3	2	2	8	9	2	4	2
m/e	236	237	238	245	246	247	248	249	250
Rel. int.	1	1	1	2	1	44	9	15	3
m/e	262	263	264	265	266	267	268		
Rel. int.	4	75	37	94	100	18	2		



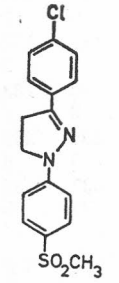
6

m/e	27	39	42	50	51	52	63	64	65
Rel. int.	1	2	3	1	4	1	2	3	2
m/e	75	76	77	78	79	89	90	91	92
Rel. int.	1	1	13	2	1	1	2	8	1
m/e	102	103	104	105	115	116	117	118	119
Rel. int.	2	1	5	3	3	3	2	3	2
m/e	120	121	129	130	131	131.5	132	132.5	133
Rel. int.	1	1	2	3	3	6	9	15	3
m/e	134	143	144	145	146	147	158	159	160
Rel. int.	3	1	5	15	11	2	2	5	21
m/e	161	221	236	237	248	249	250	263	264
Rel. int.	3	1	1	3	1	2	2	3	7
m/e	265	266	267						
Rel. int.	100	20	2						



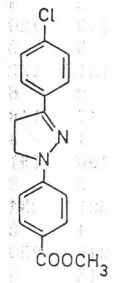
7

m/e	39	50	51	63	64	65	75	76	77
Rel. int.	1	2	2	9	2	2	6	4	2
m/e	79	89	90	91	102	103	104	111	112
Rel. int.	1	6	7	2	2	1	1	10	1
m/e	113	115	116	117	118	125	126	127	138
Rel. int.	3	4	6	4	2	10	1	4	6
h/e	139	140	141	152	182	191	195	218	219
Rel. int.	4	2	1	1	1	1	1	1	1
m/e	253	254	255	256	257	258	269	271	272
Rel. int.	1	2	14	4	5	1	1	6	1
m/e	273	303	332	333	334	335	336	337	338
Rel. int.	2	2	4	7	100	21	38	8	2



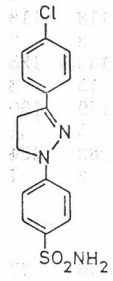
8

m/e	27	39	50	51	52	62	63	64	65
Rel. int.	1	6	4	2	2	2	15	5	4
m/e	74	75	76	77	78	79	80	89	90
Rel. int.	1	6	6	6	3	3	4	4	12
m/e	91	92	96	101	102	103	104	106	107
Rel. int.	8	3	1	1	4	2	3	1	5
m/e	111	113	115	116	117	118	119	120	125
Rel. int.	6	2	5	5	6	4	3	8	1
m/e	127.5	128	129	137	138	139	140	151	152
Rel. int.	4	1	1	7	4	3	1	5	3
m/e	153	164	165	191	192	193	219	220	227
Rel int.	2	1	1	1	1	1	1	1	2



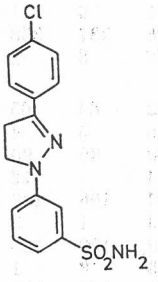
9

m/e	253	254	255	256	257	258	271	272	273
Rel. int.	2	3	20	5	7	1	16	3	6
m/e	303	332	333	334	335	336	337	338	
Rel. int.	2	4	6	100	22	39	8	2	
m/e	27	39	50	51	52	59	62	63	64
Rel. int.	1	4	3	3	1	4	1	8	3
m/e	65	74	75	76	77	78	89	90	91
Rel. int.	2	1	5	5	5	2	4	9	5
m/e	92	101	102	103	104	106	111	113	115
Rel. int.	2	1	3	3	3	1	5	2	6
m/e	116	117	118	119	120	121	125	132	135
Rel. int.	5	6	4	2	2	1	1	6	3
m/e	137	138	139	140	141.5	142	142.5	143	149
Rel. int.	5	3	2	1	15	3	6	1	5
m/e	151	152	153	157	158	162	163	164	165
Rel. int.	6	1	2	4	1	1	1	1	1
m/e	254	255	256	257	279	281	283	284	285
Rel. int.	1	3	2	1	1	1	21	4	7
m/e	286	312	313	314	315	316	317		
Rel. int.	2	4	10	100	23	34	8		



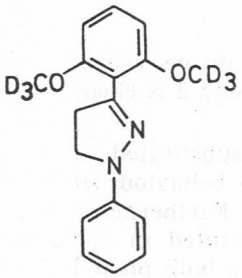
10

m/e	39	50	51	52	62	63	64	65	74
Rel. int.	4	3	4	2	1	9	8	3	1
m/e	75	76	77	78	79	80	89	90	91
Rel. int.	8	6	4	2	2	4	4	10	6
m/e	93	96	101	102	103	104	105	106	107
Rel. int.	2	1	1	4	2	4	2	6	1
m/e	111	113	114	115	116	117	118	119	120
Rel. int.	7	2	1	6	6	5	2	3	6
m/e	125	127.5	135.5	136	137	138	139	140	151
Rel. int.	1	2	2	1	6	4	3	1	7
m/e	152	153	156	164	165	168	191	192	193
Rel. int.	2	2	1	2	1	1	1	1	1
m/e	218	219	227	253	254	255	256	257	270
Rel. int.	1	1	1	2	3	11	3	4	2
m/e	271	272	273	300	302	333	334	335	336
Rel. int.	11	2	3	1	1	5	9	100	20
m/e	337	338	339						
Rel. int.	39	7	2						



11

m/e	27	38	39	41	50	51	52	62	63
Relt. int.	2	1	7	1	4	5	2	1	11
m/e	64	65	74	75	76	77	78	79	80
Rel. int.	7	4	1	9	5	5	3	4	2
m/e	89	90	91	92	101	102	104	105	106
Rel. int.	4	12	11	4	2	4	1	4	2
m/e	107	111	113	114	115	116	117	118	119
Rel. int.	1	7	3	1	7	9	6	3	2
m/e	120	125	127.5	137	138	139	140	151	152
Rel. int.	1	2	2	7	4	3	2	9	2
m/e	153	156	164	165	167.5	168	168.5	170	183
Rel. int.	3	2	1	2	4	1	2	3	1
m/e	191	192	218	219	227	243	153	254	255
Rel. int.	1	1	2	1	2	1	5	3	4
m/e	256	257	300	333	334	335	336	337	338
Rel. int.	1	1	1	10	7	100	20	37	8
m/e	339								
Rel. int.	2								



15

m/e	27	39	41	42	43	44	50	51	52
Rel. int.	1	3	2	1	1	1	1	7	2
m/e	53	55	63	64	65	66	67	76	77
Rel. int.	1	1	3	5	5	1	1	2	17
m/e	78	79	80	81	89	90	91	92	93
Relt. int.	3	2	1	1	1	2	18	3	3
m/e	94	95	103	104	105	106	107	108	109
Rel. int.	2	2	1	5	4	2	3	1	1
m/e	117	117.5	118	119	120	121	123	124	132
Rel. int.	2	3	3	3	2	2	10	1	3
m/e	133	134	135	135.5	136	137	138	144	144.5
Rel. int.	1	1	12	2	1	1	1	6	1
m/e	147	148	149	151	152	157	164	165	166
Rel. int.	2	1	1	1	1	1	2	3	1
m/e	167	168	169	170	180	181	183	184	195
Rel. int.	1	1	2	1	2	1	3	3	1
m/e	223	224	235	237	242	252	253	269	270
Rel. int.	2	1	1	1	1	6	2	1	3
m/e	286	287	288	289	300				
Rel. int.	10	36	100	19	3				

DISCUSSION

In order to study the effect of phenyl ring substitution in 1,3-diphenyl-2--pyrazoline on the electron impact, we paid attention to the effect of:

i) monosubstitution of one or both phenyl rings,

ii) polysubstitution of one or both phenyl rings.

All compounds exhibit a very pronounced molecular ion (base peak) and the stabilitiy of this species can be explained by the unusually low ionization energy of 1,3-diphenyl-2-pyrazoline as found by molecular photoelectron spectroscopy (< 7 eV)[3].

The compounds investigated follow the general fragmentation scheme given for the unsubstituted 1,3-diphenyl-2-pyrazoline[1]. Fragmentation reactions commonly involved (e. g. the formation of ions with *m/e* 64, 77, 91, 103, 104, 105, 115, 117, 118 and their analogues) can easily be recognized by examination of their mass spectra (see figure 1). For some fragment ions containing only one of the phenyl rings two forms, i. e. the unsubstituted one and the one bearing substituents, usually appear in the spectrum, but their relative abundances may greatly differ.

1,3-Diphenyl-2-pyrazolines Monosubstituted in the Phenyl Rings

According to their characteristcs, the mass spectra of 1,3-diphenyl-2-pyrazolines monosubstituted in one or both phenyl rings can be divided into three groups[2]:

1. 1,3-diphenyl-2-pyrazolines, having the substituent relatively tightly bound, fragment from the molecular ion in the same manner as the unsubstituted compound. Examples from ref. 2 are e. g. F, Cl, Br, CF_3, CN, CH_3 as *para* substituents.

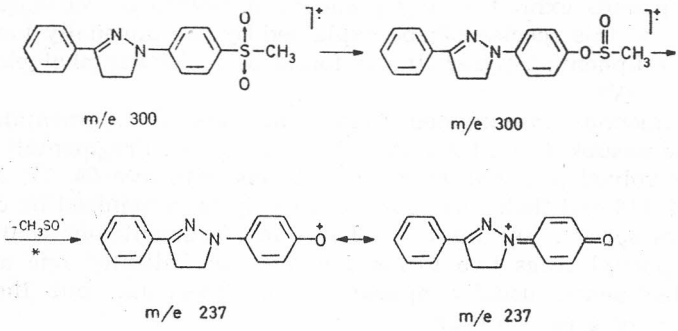
2. 1,3-diphenyl-2-pyrazolines of this group readily lose their substituents or parts of substituents and are fragmented further from the (M-substituent)$^+$ ion in the same way as the parent compound. Examples from ref. 2 are e. g. $COCH_3$ and I as *para* substituents, as well as OCH_3 and NO_2 in *para* position of 1-phenyl and 3-phenyl, respectively.

3. 1,3-diphenyl-2-pyrazolines which show new types of fragmentation and involve the substituent in the possible rearrangement reactions prior to fragmentation (OCH_3 in *para* position of 3-phenyl and NO_2 in *ortho* and *para* position of 1-phenyl).

Although the differences between groups 1 and 2 are not always sharp, the inclusion of compounds *1*—*5* with complex substituents in group 2 is clear. By contrast, the $N(CH_3)_2$ compound (*6*) belongs to group 1.

The fragmentation of the 1,3-diphenyl-2-pyrazolines monosubstituted in both phenyl rings can easily be rationalized on the basis of the behaviour of corresponding compounds monosubstituted in one phenyl ring. Furthermore, the comparison of mass spectra of two compounds monosubstituted in one phenyl ring with the corresponding compound monosubstituted in both phenyl rings indicates that neither the stability of the molecular ion nor the intensities of analogous ions are changed significantly which implies the nonexistence (or unimportance) of synergistic substituent effects.

The characteristic phenyl migration from sulfur to oxygen in the mass spectra of sulfones[4] is also apparent in the mass spectra of compounds *1*, *2*, *7* and *8* containing the SO_2CH_3 substitutent in the *para* position of phenyl. Hence, these compounds not only eliminate CH_3 from their molecular ion (to give $(M - CH_3)^+$ which decomposes by expulsion of O), but also lose CH_3SO in a one-step process (scheme 1).



Scheme 1

1,3-Diphenyl-2-pyrazolines Polysubstituted in the Phenyl Rings

In contrast to the 1,3-diphenyl-2-pyrazolines monosubstituted in one or both phenyl rings, the mass spectra of doubly and triply substituted compounds were not examined in our previous work[2]. Thus, the mass spectra of the six dimethoxy *(12—17)*, two trimethoxy *(20—21)* and one trimethyl substituted compound *(22)*, all substituted in the 3-phenyl ring, as well as the two isomers *(18—19)*, each bearing two methoxy and two methyl groups in 3-phenyl and 1-phenyl positions, respectively, were investigated in more detail.

Examination of these spectra shows that the polymethoxy substituted 1,3-diphenyl-2-pyrazolines, similarly to the monomethoxy compounds reported in ref. 2, undergo two characteristic primary fragmentation reactions, namely, loss of H and CH_3. A very important secondary fragmentation process is the elimination of CO from the $(M—CH_3)^+$ ions.

The abundance of the $(M—H)^+$ ion in the mass spectra of dimethoxy and trimethoxy substituted compounds varies from 1 to 39% (table II), depending on the position and number of the substituents. For comparison, in the mass spectra of 1,3-diphenyl-2-pyrazolines substituted by a methoxy group in the 3-phenyl ring, $(M—H)^+$ ions of 36, 25 and 16% relative intensities were found for the *ortho*, *meta* and *para* isomers, respectively.

TABLE II

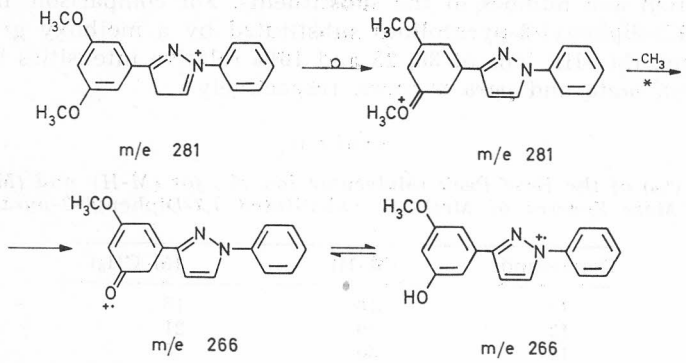
Percentages (%) of the Base Peak (Molecular Ion M^+) for $(M-H)^+$ and $(M-CH_3)^+$ Ions in the Mass Spectra of Methoxy Substituted 1,3-Diphenyl-2-pyrazolines

Compound	$(M-H)^+$	$(M-CH_3)^+$
12	16	16
13	19	21
14	39	5
15	36	3 (CD_3)
16	4	17
17	16	—
20	26	7
21	1	50

The origin of hydrogen, which is lost by primary fragmentation from the molecular ion, was studied in a number of methoxy substituted aromatic compounds[5,6]. The deuterium labelling experiments showed that loss of a methoxy hydrogen was negligible for these compounds. In this study we are using the hexadeuterodimethoxy compound *(15)* and are thus able to distinguish between ring and methoxy hydrogens and indicate the loss of a pyrazoline ring hydrogen. As a matter of fact, the mass spectrum of compound *15*, which contains 95% d_6 molecules, showed a $(M-1)^+$ peak of 36% to be compared with 39% in the unlabelled compound *14* (table II). About 3% of hydrogen is lost from the methyl group as indicated by a corresponding enhancement of the $(M-2)^+$ ion (8% in *14*, 10% in *15*). This agrees with the primary fragmentation of the $(M—H)^+$ ions in the mass spectra of methoxy substituted 1,3-diphenyl-2-pyrazolines, as indicated by m. i. k. e. spectra. It also involves the loss of methyl and, hence, of untouched methoxy groups. However, it would be of interest to see what kind of interaction between the methoxy and pyrazoline methylene group is responsible for the high loss in the *ortho* substituted compounds *(14* and *20)*. The same interaction might be operative in the formation of the fragment ion *m/e* 121 $(C_7H_9N_2)^+$ in these compounds.

If the methoxy groups are *ortho* or *para* with respect to each other, more favourable fragmentations like CH_3 loss prevail over the hydrogen loss. This can be seen in the spectra of *13*, *16* and *21* (figure 1). In the case of *21* the $(M—H)^+$ ion is nearly absent. The importance of the CH_3 loss, provided that methoxy groups are *ortho* or *para* to each other, has been attributed to the stability of the resulting $(M—CH_3)^+$ ion, due to the formation of a quinoid structure. The low intensity of the $(M—CH_3)^+$ ion in *17* is ascribed to the inability of the two methoxy groups in *meta* position to form a quinoid structure. However, the loss of methyl from the $(M—H)^+$ ion in this compound

indicates possible rearrangements within the molecular ion stabilizing the resulting inon of *m/e* 266 (scheme 2).



Scheme 2

EXPERIMENTAL

The low-resolution mass spectra were obtained on a Varian CH-7 mass spectrometer, using an ionization current of 100 μA, an electron energy of 70 eV, and an ion accelerating voltage of 3 kV. The accurate mass measurements by the peak matching technique and the measurements of the metastable transitions using m. i. k. e. and i. k. e. spectra were determined with a CEC 21-220C double focusing mass spectrometer at 70 eV, 150 μA and 6 kV. All samples were introduced into the ion source (temperature 200 °C) on a direct insertion probe.

Substituted 1,3-diphenyl-2-pyrazolines were prepared by reaction of β-dimethylaminopropiophenone hydrochloride (Mannich base) or a correspondingly substituted β-dimethylaminopropiophenone hydrochloride with phenylhydrazine or correspondingly substituted phenylhydrazines[7]. Details on their characterization, purity and spectral data are given in Refs. 8—10. The Mannich base and corresponding compounds were synthesised by reaction of acetophenone with dimethylamin hydrochloride and paraformaldehyde[11]. 2,6-Dimethoxy-d_6-acetophenone was prepared by methylation of 2,6-dihydroxy-acetophenone with hexadeuterodimethylsulfate (Merck, 99% d_6) in sodium hydroxide solution[12]. It was characterized by mass spectrometry (97% d_6). The resulting hexadeuterated 1-phenyl-3-(2",6"-dimethoxy-d_6-phenyl)-2-pyrazoline *15* contained 95% d_6 molecules.

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SAŽETAK

Istraživanje fragmentacije supstituiranih 1,3-difenil-2-pirazolina

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Fragmentacija dvadeset i dva 1,3-difenil-2-pirazolina mono-, di- i trisupstituirana u jednom ili oba fenila, do koje dolazi nakon bombardiranja s elektronima, studirana je korištenjem spojeva obilježenih deuterijem, a uz pomoć spektrometrije masa visokog i niskog razlučivanja i spektroskopije kinetičkih energija iona. U radu se govori o utjecaju vrste supstituenta i položaja supstitucije na fragmentaciju.

Rezultati uspoređeni s podacima za nesupstituirani spoj pokazuju da se supstitucijom fenila u pravilu ne mijenja osnovna fragmentacija. Moguće nastajanje iona kinoidne strukture utječe na fragmentaciju spojeva supstituiranih s metoksi grupom.

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