MASS SPECTRA OF DITRIAZOLYLS AND BIS-sym-TRIAZOLOPYRIDAZINES

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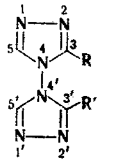
The mass spectra of ditriazolyl and its 3- and 3'-substituted derivatives (R, R' = CH_3, C_6H_5, and C_6H_4Cl) were investigated. It is shown that the ditriazolyl molecule is characterized by exceptionally large selectivity and resistance to electron impact; this constitutes evidence for the high degree of conjugation between the triazole rings. Deformation of the ditriazolyl molecule when bulky substituents are introduced in the 3 and 3' positions leads to a decrease in the resistance to electron impact. The ratio of the intensities of the peaks in the spectra shows that, despite the considerable twisting of the triazole rings along the 4N—4'N bond, cleavage of the latter is less favorable than cleavage of the bonds in the triazole rings. The incorporation of an additional double bond between the triazole rings in bis-5-triazolo[4,3-b,4',3'-f]pyridazine derivatives leads to a relative increase in the selectivity and stability of the molecular ion and to a change in the character of the fragmentation. The fragmentation is realized in practice via two principal pathways. In addition to the intense $[CNR']^+$ ion peak that is peculiar to the spectra of substituted ditriazolyls, one observes a peak of a pyridazine cation radical (m/e 78), the formation of which is more favorable than fragmentation with cleavage of the bonds between the triazole rings.

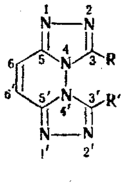
Considerable conjugation between the two six-n,π-electron systems of triazole rings may occur in di-4,4-(1,2,4-triazolyls) and bis-sym-triazolo[4,3-b,3',4'-f]pyridazines. The degree of this conjugation should depend to a large extent on the deformation of the molecule as a consequence of various types of steric hindrance.

It seemed of interest to study the peculiarities of the mass spectra of this group of compounds and, in particular, to examine the effect of the introduction of bulky substituents that distort the planar structure of the molecule because of steric repulsions on the fragmentation of the compounds [1-4].

We investigated the mass spectra of the following substituted 4,4'-ditriazolyls and bis-sym-triazolo[4,3-b,3'4'-f]pyridazines:



I–IV



V–IX

I R=R'=H; II R=CH_3, R'=C_6H_5; III R=CH_3, R'=C_6H_4Cl-*p*; IV R=R'=C_6H_5; V R=H, R'=C_6H_5; VI R=CH_3, R'=C_6H_5; VII R=CH_3, R'=C_6H_4Cl-*p*; VIII R=R'=C_6H_5; IX R=R'=CH_3

The mass numbers of the observed ions and the relative intensities of their peaks are presented in Table 1.

It follows from an examination of the data obtained that the stability with respect to electron impact of the molecular ion of the unsubstituted ditriazolyl (I) has a high

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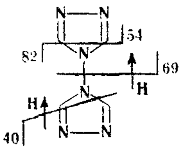
TABLE 1. Mass Spectra of I-IX

Compound	Mass spectra of I-IX; m/e values (relative intensities of the ion peaks in percent of the maximum peak)
I	40 (16,9), 41 (7,1), 42 (4,4), 43 (3,4), 44 (1,6), 45 (2,8), 52 (2), 53 (6,4), 54 (18), 55 (2,5), 56 (1,4), 57 (2,1), 69 (3), 74 (1,1), 75 (1), 76 (1), 81 (1,8), 82 (1,6), 85 (1), 103 (4,6), 104 (1), 109 (1,7), 136 (100), 137 (6,2)
II	40 (10,2), 41 (41), 42 (23), 50 (16,7), 51 (15,4), 52 (9), 53 (5,1), 54 (11,5), 62 (9), 63 (32), 76 (25,6), 77 (13,4), 103 (100), 104 (37), 129 (5,1), 130 (16,7), 144 (6,4), 145 (10,2), 157 (12,8), 171 (3,9), 226 (97,5), 227 (15,4)
III	40 (25), 41 (50), 42 (33,3), 44 (25), 54 (10), 55 (4,2), 56 (4), 57 (4), 63 (4), 77 (4,1), 78 (2,5), 79 (1,7), 83 (5), 85 (1,7), 86 (1,8), 87 (1,6), 88 (1,7), 89 (1,9), 91 (5), 95 (2,5), 96 (2,6), 97 (1,7), 101 (1,8), 102 (25), 103 (4,2), 111 (2,5), 123 (33,3), 124 (2,5), 125 (10,8), 136 (8.3), 137 (83,3), 138 (33,3), 139 (29,5), 140 (12,5), 150 (3,3), 151 (2,5), 152 (4,2), 163 (3,3), 164 (8,3), 178 (2,5), 179 (8,3), 191 (2,5), 260 (100), 261 (12,5), 262 (29,2), 263 (4,2)
IV	39 (2,3), 52 (5,4), 62 (7,7), 63 (30,4), 64 (3,6), 75 (4,5), 76 (21,4), 77 (11,8), 89 (37,7), 90 (4,5), 102 (4,1), 103 (100), 104 (40,5), 116 (5), 117 (2,7), 118 (2,3), 129 (3,6), 130 (9,1), 145 (4,1), 157 (11,4), 232 (2,3), 288 (30,4), 289 (6.8)
V	50 (13,8), 51 (17,5), 52 (8,8), 63 (6,2), 76 (18,1), 77 (15,6), 78 (25), 103 (100), 104 (10), 236 (75), 237 (12)
VI	40 (3,3), 41 (6,3), 42 (19,2), 43 (3,2), 49 (1,3), 50 (13,5), 51 (1,5), 52 (6,7), 53 (1,6), 55 (9,6), 56 (2,9), 62 (2), 63 (5,3), 64 (3,2), 65 (1,4), 66 (1,2), 76 (17,3), 77 (13,5), 78 (21), 89 (1,3), 103 (100), 104 (10,5), 119 (1), 125 (1,9), 250 (86,5), 251 (15,4)
VII	40 (11,1), 41 (6,7), 42 (35,6), 43 (8,8), 44 (13), 50 (6,6), 51 (6,5), 52 (2,2), 55 (4,4), 56 (4,3), 57 (4,5), 63 (1), 64 (1,1), 65 (2,2), 66 (1,3), 67 (1,4), 75 (2,2), 76 (2,1), 77 (4,4), 78 (35,6), 79 (4,4), 91 (1,3), 92 (2,1), 93 (1,4), 102 (17,8), 103 (2,2), 111 (2,1), 119 (4,4), 120 (1,3), 121 (1,2), 137 (100), 138 (11,1), 139 (31), 140 (4,4), 150 (1.3), 151 (1,3), 152 (2,2), 185 (2,3), 186 (2,2), 187 (2,2), 188 (2,1), 284 (82,2), 285 (13,3), 286 (26,7), 287 (4,4).
VIII	43 (1), 45 (1,3), 50 (6.5), 51 (8), 52 (2,6), 62 (1,4), 63 (4.8), 64 (1,3), 76 (14), 77 (10), 78 (1,6), 89 (1,2), 102 (1,1), 103 (100), 104 (9,1), 126 (1,3), 152 (1), 156 (2), 206 (1,3), 207 (1,3), 283 (2,2), 284 (2,9), 312 (43.5), 313 (11,3)
IX	40 (7,3), 41 (5,9), 42 (36.7), 43 (6,5), 44 (6,5), 50 (6,5), 51 (4,4), 52 (2,9), 53 (1), 54 (1), 55 (1,4), 56 (1,4), 57 (2,9), 60 (2,8), 64 (1,4), 65 (3), 66 (1,5), 67 (1,4), 68 (1,5), 69 (1,5), 77 (3), 78 (33,8), 79 (2,9), 91 (1,3), 119 (3), 188 (100), 189 (5,3)

value (W_M = 55.3%).* The most intense peak in the spectrum of I belongs to the molecular ion. It is known that aromatic systems are, as a rule, characterized mass spectrally by high W_M values and intense molecular-ion peaks.

The maximum intensities of the ion peaks that are the products of fragmentation of the molecular ion of I (m/e† 40 and 54) do not exceed 18%. Such behavior under electron impact indicates that the ditriazolyl molecule (I) actually has a high degree of conjugation between the rings and in this respect can be compared with diphenyl; the W_M value of the ditriazolyl exceeds that of diphenyl (36.1% [5]). In contrast to the fragmentation of diphenyl, in which one observes cleavage of the bond between the phenyl rings in the $[M - H]^+$ ion, intense peaks corresponding to cleavage of the N–N bond between the triazole rings are absent in the spectrum of I, and this constitutes evidence for the relative stability of this bond. The intensity of the ion at 69, to which a triazole cation structure can be assigned, amounts to only 3%. The cleavage of the bonds in the triazole rings to give fragments at 40, 54, and 82, as shown in Scheme 1, is the preferred process:

Scheme 1



It has been demonstrated in [4] that the introduction of bulky substituents in the 3 and 3' positions leads to considerable turning of the triazole rings about the 4N–4'N ring because of the resulting steric hindrance. The decrease in the conjugation between the rings because of their deviation from a single plane is reflected in the sharp decrease in

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*Here $W_M = I_M/\Sigma_{40}I$, where I_M is the sum of the intensities of the isotope peaks of the molecular ion, and Σ_{40} is the sum of the intensities of all of the peaks in the spectrum up to m/e 40 inclusive.

†Here and subsequently, the numbers in the text and schemes are the ion mass-to-charge ratios.

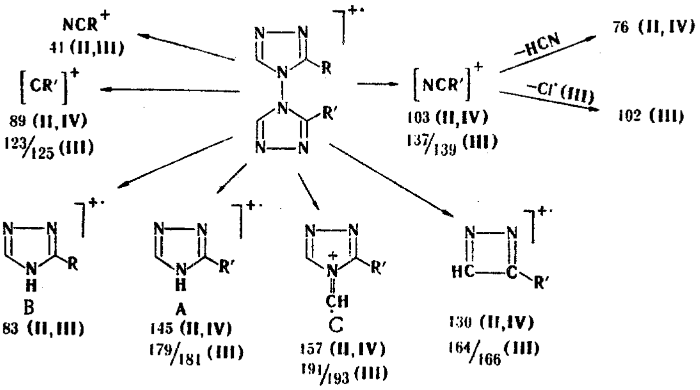
TABLE 2. Stabilities with Respect to Electron Impact (W_M) and Fragmentation Selectivities ($S_{1/2}$) for I-IX

	Compound								
	I	II	III	IV	V	VI	VII	VIII	IX
W_M	55,3	19,9	23,0	10,1	28,9	29,5	25,4	25,4	39,9
$S_{1/2}$	1	4	4	4	2	2	2	2	2

the stability of the molecular ion in the spectra of II-IV as compared with I. The fragmentation selectivity ($S_{1/2}$)* also changes from unity to four (Table 2).

The most intense peaks in the spectra of II-IV correspond to $[NCR]^+$ and $[NCR']^+$ fragments and to the products of their subsequent fragmentation. Ion peaks that are formed by cleavage of other bonds in the triazole ring, as shown in Scheme 2, are also observed along with these peaks in the spectra.

Scheme 2



The appearance of ion peaks A and B in the spectra of II-IV is due to cleavage of the 4N—4'N bond and is in agreement with the assumption of a decrease in the conjugation between the triazole rings. The formation of ion C is probably due to rearrangement processes that accompany this cleavage. However, it should be noted that, despite the effect of the considerable twisting of the triazole rings about the 4N—4'N bond, the cleavage of the latter during fragmentation remains less favorable than cleavage of the bonds in the triazole ring. This is attested to by the fact that the overall relative intensity of the A, B, and C ion peaks is considerably less than the intensity of the NCR^+, $[NCR']^+$, and $[CR']^+$ ion peaks (Table 1). At the same time, the large difference in the relative intensity of the $C_6H_5CN^+$ and $C_6H_5^+$ ion peaks in the spectra of II-IV indicates that, despite the deformation of the molecule in phenyl-substituted ditriazolyls (according to the data in [4], the phenyl group is situated at an angle on the order of 30° relative to the plane of the triazole ring), conjugation of the phenyl group with the C=N bond in the triazole ring is retained in the molecule.

The introduction of an additional double bond between the triazole rings in 3,3-disubstituted bis-sym-triazolo[4,3-b,3',4'-f]pyridazines (V-IX) evidently increases the planar character of the ditriazolyl system and leads to an increase in the conjugation between the triazole rings.

This shows up in the mass spectra as an increase by a factor, on the average, of 1.5-2 in the stability with respect to electron impact in the case of 3- and 3'-substituted bis-triazolopyridazines as compared with the corresponding ditriazolyl derivatives (Table 2). The stability is especially high in the case of dimethyl derivative IX, the steric hindrance in which is evidently the least in the series of compounds under consideration. As the size of the substituents in the 3 and 3' positions increases, the stability of the molecule decreases; this is evidently due to an increase in the degree of deformation of the molecule. The results of x-ray diffraction analysis [2, 3] have shown that this deformation is realized in the form of twisting of the pyridazine ring, a change in the bending angles of the

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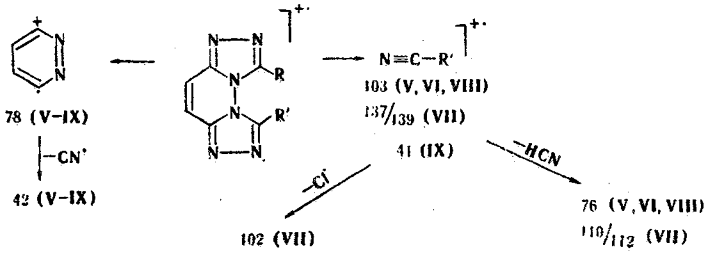
*Fragmentation selectivity $S_{1/2}$ is defined as the number of most intense peaks in the mass spectrum, the overall intensity of which is 50% of the total ion current [6].

triazole rings (4'N4N3C, 4N4'N3C, 4'N3'CR', and 4N3CR) to different sides of the plane of the six-membered pyridazine ring, etc.

The introduction of a second bond between the triazole rings changes the character of the mass spectra of V-IX. Upon the whole, the fragmentation differs with respect to greater selectivity and is realized in a practical sense via two principal pathways (Scheme 3).

Scheme 3



The $[CNR']^+$ ion, which is formed as in the case of II-IV by cleavage of the 4'N—3'C and 1'N—2'N bonds, has the highest intensity in the spectra of V-IX.

A characteristic peak at 78, which is absent in the spectra of the ditriazolyl derivatives (II-IV), also appears in the spectra. The formation of this ion, to which a pyridazine cation-radical structure should be assigned, can be explained by cleavage of the 1N—2N, 1'N—2'N, 4N—5C, and 4'N—5'C single bonds with subsequent ring closing and by cleavage of the 3C—4N, 3'C—4'N, 1N—5C, and 1'N—5C bonds. The formation of this fragment, which has an aromatic structure, is apparently more favorable than cleavage of the 4N—4'N and 6C—6'C bonds between the triazole rings. As a consequence of this, ion peaks associated with this sort of cleavage are absent in the spectra of V-IX.

Thus the mass spectra of the investigated substituted ditriazolyls and bis-sym-triazolopyridazines reflect the change in the degree of conjugation between the triazole rings through the 4N—4'N bond. The introduction of bulky substituents in the 3 and 3' positions of the triazole rings, which deform the molecule, leads to a decrease in the stability of the molecular ion with respect to electron impact and to characteristic changes in the mass-spectrometric fragmentation.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 mass spectrometer equipped for direct introduction of the samples into the source. The ionizing voltage was 50 V, and the temperature of the ionization chamber was 125°C.

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