ELECTRON IMPACT MASS SPECTRA OF SOME 2'-, 3'-, AND 4'-SUBSTITUTED THIOPHENE-2- AND 3-CARBOXANILIDES‡

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Abstract- The electron impact mass spectra (EI/MS) of 2- and 3-carboxanilides are dominated by the peak due to the corresponding thenoyl cations formed by cleavage of the C-N amide bond. This reaction is not affected by the polar effect of the substituents present in the phenyl ring. Most of the 2'-substituted derivatives undergo a cyclisation reaction with ejection of the substituent. In addition, for 2'-methyl and 2'-ethyl derivatives of both series of thiophene anilides a cryptic "ortho"-effect was suggested as responsible of the charge retention in the aniline moiety.

INTRODUCTION

The kinetics of base[1a] and acid[1b] hydrolyses, protonation equilibria,[2] ^{13}C-nmr spectra[3a] as well as the electronic and ir spectra[3b] of substituted thiophene-2- and 3-carboxanilides have been the object of recent investigations. The mass spectra of a limited number of 3'- and 4'-substituted thiophene-2- and 3-carboxanilides[3c, 4] have also been recorded, however similar determinations on the corresponding 2'-substituted derivatives have not yet been reported.

It is well known that the electron impact mass spectra (EI/MS) of ortho-substituted compounds frequently differ significantly from those of their meta- and para-analogues, owing to the interaction of ortho-substituents which can afford to unexpected reactions.[5]

Important differences were in fact observed in the EI/MS of 5- and 3-substituted thiophene-

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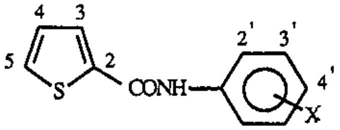
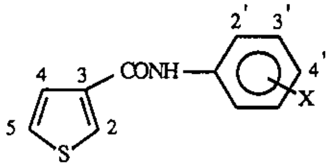
2-carboxamides[6] as well as in the EI/MS of 3- and 4(or 5)-substituted 2-thiophenecarboxylic acids.[7] Hence, the availability of a large number of thiophene-2- and 3-carboxanilides of the following structures



(compounds 1-26 as in Table 1)



(compounds 27-52 as in Table 2)

which include some fifteen 2'-substituted compounds, prompted us to examine their EI/MS with the aim of more firmly establish their preferential fragmentation pathways, the effect of the substituents in these reactions and, particularly, the "ortho"-effects in 2'-substituted derivatives.

EXPERIMENTAL

The compounds under investigation were prepared by the following general procedure: two equivalents of appropriate o-, m-, and p-substituted anilines in toluene were dropped into a stirred solution of the corresponding thiophenecarboxyl chloride.‡ The crude anilides were worked up and purified to constant melting point by recrystallization from suitable solvents. The acyl chlorides were obtained by refluxing the corresponding thiophenecarboxylic acids with an excess of thionyl chloride for one hour. The excess of thionyl chloride was removed under reduced pressure.

The 2- and 3-thiophenecarboxylic acids and the anilines were commercial products (Aldrich, Fluka or Carlo Erba).

Some of the anilides used in this work (**1**, **4**, **10**, **14**);[8] (**2**, **5**, **15**, **23**, **24**);[9] (**27**, **49**);[1b] (**28**, **30**, **31**, **36**, **41**, **50**)[10] were already known.

Anilides **3**, **6**, **7**, **8**, **9**, **11**, **12**, **13**, **16**, **17**, **18**, **19**, **20**, **21**, **22**, **25**, **26**, **29** **32**, **33**, **34**, **35**, **37**, **38**, **39**, **42**, **43**, **44**, **45**, **46**, **47**, **48**, **51**, **52**, **53**, **54**, and **55** have never been prepared before and their characteristics are reported in Table 3. All new compounds gave satisfactory CHNS elemental analyses (see Table 3).

The mass spectra were recorded on a "VG 70 70E" mass spectrometer. Ions were generated in the built-in electron ionization of 70 eV, and at a total emission current of about 18 m A. The

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‡ Occasionally triethylamine was used instead of the excess of aniline.

Table 1

Significant peaks of the mass spectra of thiophene-2-carboxyanilides

Compound		$M^{+\cdot}$		*a*	*b*	*c*	*a'* or *d*		*e*
	X	m/z	(I%)	m/z 111	m/z 83	m/z 39	m/z	(I%)	m/z 202
1	4'-OMe	233	(68)	(100)	(3.0)	(7.0)	122	(5.0)	/
2	3'-OMe	233	(94)	(100)	(4.0)	(4.7)	122	(3.0)	/
3	2'-OMe	233	(53)	(100)	(5.0)	(6.0)	122	(1.1)	(3.0)
4	4'-Me	217	(45)	(100)	(3.6)	(4.4)	106	(2.2)	/
5	3'-Me	217	(41)	(100)	(3.6)	(7.7)	106	(0.5)	/
6	2'-Me	217	(44)	(100)	(5.0)	(8.1)	106	(8.1)	(2.3)
7	4'-Et	231	(36)	(100)	(21)	(4.4)	120	(0.4)	/
8	3'-Et	231	(51)	(100)	(4.0)	(5.0)	120	(0.7)	/
9	2'-Et	231	(40)	(100)	(7.4)	(9.8)	120	(52)	(1.2)
10	H	203	(49)	(100)	(4.0)	(13)	92		/
11	4'-F	221	(50)	(100)	(5.6)	(8.6)	110		/
12	3'-F	221	(29)	(100)	(9.0)	(24)	110		/
13	2'-F	221	(41)	(100)	(7.0)	(10)	110		/
14	4'-Cl	237	(38)	(100)	(5.0)	(11)	126		/
		239	(14)				128		
15	3'-Cl	237	(43)	(100)	(5.0)	(10)	126		/
		239	(15)				128		
16	2'-Cl	237	(17)	(100)	(6.5)	(13)	126		(44)
		239	(6.1)				128		
17	4'-Br	281	(19)	(100)	(4.8)	(10)	170		/
		283	(17)				172		
18	3'-Br	281	(29)	(100)	(4.8)	(6.8)	170		/
		283	(29)				172		
19	2'-Br	281	(9.4)	(100)	(6.4)	(11)	170		(48)
		283	(9.4)				172		
20	4'-I	329	(100)	(96)	(6.2)	(7.0)	218		/
21	3'-I	329	(100)	(100)	(4.9)	(7.0)	218		/
22	2'-I	329	(21)	(100)	(6.8)	(11)	218		(70)
23	4'-NO_2	248	(26)	(100)	(14)	(13)	137		/
24	3'-NO_2	248	(43)	(100)	(9.0)	(6.0)	137		/
25	2'-NO_2	248	(10)	(100)	(14)	(14)	137		(5.6)
26	2',6'-diMe	231	(72)	(100)	(4.6)	(11)	120	(65)	216 (1.8)

Table 2

Significant peaks of the mass spectra of thiophene-3-carboxyanilides

Compound		$M^{+\cdot}$		*a*	*b*	*c*	*a'* or *d*		*e*
	X	m/z	(I%)	m/z 111	m/z 83	m/z 39	m/z	(I%)	m/z 202
27	4'-OMe	233	(28)	(100)	(14)	(3.1)	122	(2.8)	/
28	3'-OMe	233	(56)	(100)	(13)	(4.4)	122	(0.7)	/
29	2'-OMe	233	(39)	(100)	(12)	(16)	122	(1.0)	(2.2)
30	4'-Me	217	(49)	(100)	(20)	(4.3)	106	(2.9)	/
31	3'-Me	217	(29)	(100)	(7.0)	(6.3)	106	(1.1)	/
32	2'-Me	217	(46)	(100)	(12)	(11)	106	(5.5)	(0.5)
33	4'-Et	231	(36)	(100)	(16)	(10)	120	(2.0)	/
34	3'-Et	231	(33)	(100)	(10)	(12)	120	(0.8)	/
35	2'-Et	231	(35)	(100)	(12)	(20)	120	(37)	(1.3)
36	H	203	(37)	(100)	(20)	(13)	92		/
37	4'-F	221	(48)	(100)	(12)	(9.0)	110		/
38	3'-F	221	(61)	(100)	(14)	(8.3)	110		/
39	2'-F	221	(52)	(100)	(12)	(8.4)	110		/
40	4'-Cl	237	(41)	(100)	(32)	(27)	126		/
		239	(15)				128		
41	3'-Cl	237	(35)	(100)	(78)	(11)	126		/
		239	(14)				128		
42	2'-Cl	237	(17)	(100)	(85)	(12)	126		(33)
		239	(6.1)				128		
43	4'-Br	281	(25)	(100)	(12)	(8.9)	170		/
		283	(28)				172		
44	3'-Br	281	(28)	(100)	(21)	(24)	170		/
		283	(28)				172		
45	2'-Br	281	(9.6)	(100)	(12)	(12)	170		(51)
		283	(11)				172		
46	4'-I	329	(72)	(100)	(9.5)	(6.6)	218		/
47	3'-I	329	(100)	(92)	(10)	(3.1)	218		/
48	2'-I	329	(17)	(100)	(17)	(17)	218		(88)
49	4'-NO_2	248	(26)	(100)	(10)	(8.1)	137		/
50	3'-NO_2	248	(20)	(100)	(11)	(5.9)	137		/
51	2'-NO_2	248	(17)	(100)	(13)	(14)	137		(12)
52	2',6'-diMe	231	(51)	(100)	(13)	(14)	120	(20)	216 (1.4)

Table 3

Physical properties[a] and data of microanalysis of 2- and 3-thiophenecarboxanilides

Compound		m p °C	Cristallization solvent	λ_{max} nm water	Elemental Analysis Required(%) (Found)			
					C	H	N	S
3	2'-OMe	87	methanol	280.0	61.8 (62.0)	4.8 (4.8)	6.0 (6.1)	13.7 (13.8)
6	2'-Me	132	methanol	275.0	66.3 (66.4)	5.1 (5.2)	6.5 (6.5)	14.8 (14.9)
7	4'-Et	145-146	methanol	282.5	67.5 (67.7)	5.7 (5.8)	6.1 (6.1)	13.9 (14.1)
8	3'-Et	113	methanol	283.0	67.5 (67.7)	5.7 (5.7)	6.1 (6.2)	13.9 (14.0)
9	2'-Et	144-145	methanol	273.0	67.5 (67.6)	5.7 (5.7)	6.1 (6.1)	13.9 (14.1)
11	4'-F	124	methanol	280.0	59.7 (59.7)	3.6 (3.6)	6.3 (6.4)	14.5 (14.6)
12	3'-F	111-112	water/methanol	285.0	59.7 (59.8)	3.6 (3.6)	6.3 (6.3)	14.5 (14.7)
13	2'-F	108-110	toluene	277.5	59.7 (59.7)	3.6 (3.6)	6.3 (6.3)	14.5 (14.5)
16	2'-Cl	123	methanol	276.5	55.6 (55.7)	3.4 (3.4)	5.9 (5.9)	13.5 (13.5)
17	4'-Br	192-193	dioxane	280.0	46.8 (46.9)	2.9 (2.9)	5.0 (5.1)	11.4 (11.4)
18	3'-Br	150-151	methanol	280.0	46.8 (46.8)	2.9 (2.9)	5.0 (5.0)	11.4 (11.5)
19	2'-Br	116-117	water/methanol	275.0	46.8 (46.9)	2.9 (2.9)	5.0 (5.0)	11.4 (11.5)
20	4'-I	210	dioxane	287.0	40.1 (40.2)	2.4 (2.4)	4.3 (4.3)	9.7 (9.8)
21	3'-I	151-152	methanol	283.0	40.1 (40.2)	2.4 (2.4)	4.3 (4.4)	9.7 (9.7)
22	2'-I	91	methanol	273.0	40.1 (40.1)	2.4 (2.4)	4.3 (4.3)	9.7 (9.8)
25	2'-NO_2	82-83	methanol	263.0	53.2 (53.3)	3.2 (3.2)	11.3 (11.5)	12.9 (13.1)
26	2',6'-diMe	168-169	methanol	300.0	67.5 (67.7)	5.7 (5.8)	6.1 (6.2)	13.9 (14.0)
29	2'-OMe	78-79	methanol	248.0	61.8 (62.0)	4.8 (4.9)	6.0 (6.1)	13.7 (13.8)
32	2'-Me	150-152	water/dioxane	247.0	66.3 (66.5)	5.1 (5.2)	6.5 (6.6)	14.8 (14.9)
33	4'-Et	141-142	methanol	263.0	67.5 (67.7)	5.7 (5.8)	6.1 (6.2)	13.9 (13.9)
34	3'-Et	103-105	methanol	260.0	67.5 (67.6)	5.7 (5.7)	6.1 (6.1)	13.9 (14.0)
35	2'-Et	160	methanol	245.0	67.5 (67.5)	5.7 (5.7)	6.1 (6.1)	13.9 (13.9)
37	4'-F	165-166	methanol/dioxane	255.0	59.7 (59.8)	3.6 (3.6)	6.3 (6.3)	14.5 (14.6)
38	3'-F	121	benzene	260.0	59.7 (59.7)	3.6 (3.6)	6.3 (6.4)	14.5 (14.7)
39	2'-F	98-100	water/methanol	250.0	59.7 (59.8)	3.6 (3.6)	6.3 (6.4)	14.5 (14.5)
42	2'-Cl	122-123	methanol	248.5	55.6 (55.6)	3.4 (3.4)	5.9 (6.0)	13.5 (13.6)
43	4'-Br	203	water/dioxane	275.0	46.8 (46.8)	2.9 (2.9)	5.0 (5.0)	11.4 (11.5)
44	3'-Br	143	methanol	260.0	46.8 (46.9)	2.9 (2.9)	5.0 (5.0)	11.4 (11.4)
45	2'-Br	118-120	methanol	248.0	46.8 (46.9)	2.9 (2.9)	5.0 (5.1)	11.4 (11.4)
46	4'-I	219	dioxane	278.0	40.1 (40.1)	2.4 (2.4)	4.3 (4.3)	9.7 (9.8)
47	3'-I	144-145	methanol	260.0	40.1 (40.2)	2.4 (2.4)	4.3 (4.3)	9.7 (9.7)
48	2'-I	110-111	methanol	245.0	40.1 (40.2)	2.4 (2.4)	4.3 (4.4)	9.7 (9.7)
51	2'-NO_2	82-83	methanol	252.0	53.2 (53.3)	3.2 (3.2)	11.3 (11.4)	12.9 (13.0)
52	2',6'-diMe	218-219	water/methanol	245.0	67.5 (67.7)	5.7 (5.7)	6.1 (6.2)	13.9 (14.0)

[a] All compounds are colorless except compounds (**25**) and (**51**) that are yellow.

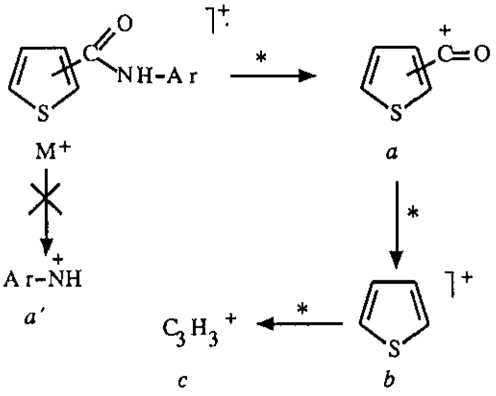
accelerating voltage was 6 kV. The ionization chamber temperature was about 180°C. All compounds were heated at 100-180°C under reduced pressure (10^{-6} torr).

RESULTS AND DISCUSSION

The significant peaks in the EI/MS of compounds (**1-26**) and (**27-52**) are reported in Tables 1 and 2, respectively.

General features

The molecular ions of the compound under investigation (**1-52**) are always abundant [from 10 (**25**) up to 100% (**20**, **21**, **47**) of the base peak] and the main fragmentation route involves simple fission leading to cleavage of the C-N amide bond as previously observed.[3c, 4] This pathway is responsible for the formation of the ion at m/z 111 (ion *a* in Scheme 1) which constitutes the most abundant fragment ion representing (except for **20** and **47**)[‡] the base peak of all the examined compounds.



Common fragmentations of thiophene-2- and 3-carboxanilides.

Scheme 1

As previously reported[3c, 4] the ion *a*, according to its thenoyl cation structure, decays as shown in Scheme 1, giving rise to ions *b* (m/z 83) and *c* (m/z 39). A comparison of the relative intensities of ions *b* reported in Tables 1 and 2 shows that the 3-thenoyl cations fragment more extensively than the corresponding 2-thenoyl cations.

Linear relationships log Z/Z_0 ($Z = [a]_x/[M^{+\cdot}]_x$; $Z_0 = [a]_H/[M^{+\cdot}]_H$) vs σ and σ^+ Hammett substituent

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[‡] The abundances of the ion at m/z 111 for **20** and **47** are *96%* and *92% of the base peaks* represented by their molecular ions, respectively, as shown in Tables 1 and 2.

constants were previously found for 3'- and 4'-substituted thiophene-2- and 3-carboxanilides.[3c,4] The slopes, ρ (and ρ^+), and correlation coefficients, r, reported for the correlations with σ (and σ^+) values are, respectively:

thiophene-2-carboxanilides ($\rho = 0.64$, $r = 0.82$, $n = 10$), ($\rho^+ = 0.40$, $r = 0.72$, $n = 10$)
thiophene-3-carboxanilides ($\rho = 0.48$, $r = 0.97$, $n = 9$), ($\rho^+ = 0.35$, $r = 0.90$, $n = 9$)

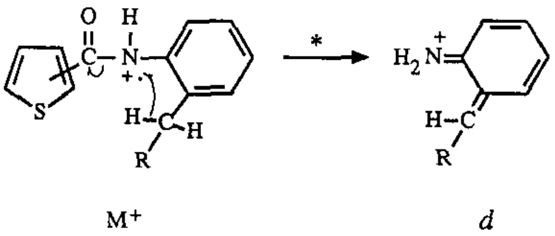
Interestingly the ρ value for thiophene-2-carboxanilides is very close to that reported[11] for p-toluanilides ($\rho = 0.6$), however the above correlations were admittedly poor. Treatment of our own values ($n = 17$ instead of 10 and $n = 17$ instead of 9 for 2- and 3-thiophene anilides respectively) in terms of the above ρ/σ correlations, dramatically decreases the correlation coefficients to $r < 0.3$. As a consequence to the above treatment of our data can hardly be attributed any mechanistic conclusion as to the polar effects of the substituents X on the fragmentation process $M^{+\cdot} \rightarrow a$ of Scheme 1.

Attempts to correlate other functions,[12] such as $\log [a]/[M_o](1\text{-}f)$ (where M_o represents the total number of molecular ions formed by the electron impact process and f the fraction of decomposing molecular ions) with σ or σ^+ also failed.

The scarce effect of the substituent X on particular spectral properties and reactivities of thiophenecarboxanilides, such as ^{13}C-nmr chemical shifts of the carbonyl-carbon atom[3a] and protonation constants in solution of strong acids (pK_{BH^+}) has already been noticed[2b] and is possibly a consequence of the internal conjugation of the carbamoyl group which strongly reduces that between this same group and the phenyl ring.[13] However it should be recalled that substituents influence ionic abundances in EI/MS in a complex fashion, as they can produce different effects on internal energy distributions, reaction rates, further fragmentations, degrees of freedom and so forth. Hence caution should be used in reaching conclusions based on the above type of correlations.[12]

Ortho effects

The fact that the complementary ion $[M\text{-}111]^+$ of (**1-52**) was generally not observed agrees with the Stevenson's rule[14] as the thenoyl radical should have an ionization energy lower than that of the anilyl radical. The small amounts of these ions observed in the EI/MS of methoxy and alkyl 3'- and 4'-substituted compounds of both series of anilides (0.4-5% of the base peak) could be explained by considering that these substituents significantly reduce the ionisation energies of the corresponding anilyl radicals. However this effect cannot justify the very abundant $[M\text{-}111]^+$ ions present in the EI/MS of 2'-methyl (**6, 32**) (8.1 and 5.5% of the base peak), 2',6'-dimethyl (**26, 52**) (65 and 20% of the base peak) and 2'-ethyl (**9, 35**) (52 and 37% of the base peak) derivatives. A possible explanation is that a competitive reaction occurs for these compounds involving an hydrogen migration from the "ortho"-alkyl group to the amide-nitrogen via a five membered transition state as depicted in Scheme 2.



R = H, Me

C-N Amide bond cleavage induced by hydrogen migration from "ortho"-alkyls.

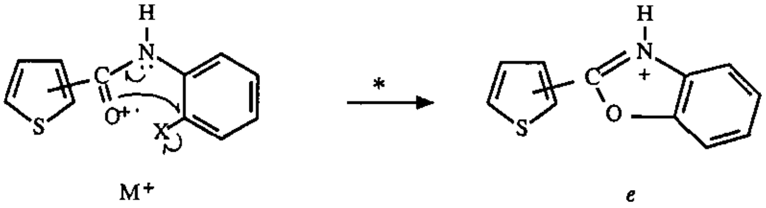
Scheme 2

The resulting *d* ion should be stabilized by its "ortho"-quinoide structure. This effect is clearly enhanced in compounds (**26**) and (**52**), as compared to compounds (**6**) and (**32**), respectively, by the presence of the two "ortho"-methyl groups. In this case the formation of the cation *d* is probably favoured by both the statistical factor and the electronic effect of the second methyl group. The occurrence of such a rearrangement process instead of the simple C-N amide bond cleavage is in agreement with the fact that intense peaks for the ions *d* were observed in the B/E linked scan spectra of the molecular ions of these compounds. The relatively higher abundance of the ion *d* in 2'-ethyl as compared to 2'-methyl substituted derivatives can be explained in terms of the electron repelling effect of the substituent R (Scheme 2).

A more general reaction of 2'-substituted derivatives involves loss of the "ortho"-substituent present in the phenyl ring. A peak at m/z 202 is in fact observed in the EI/MS of all of the 2'-substituted compounds of both series of anilides but the unsubstituted (**10** and **36**) and the fluoro-substituted (**13** and **39**) derivatives. Relative abundances of these peaks at m/z 202 appear to depend strongly upon the nature of the present "ortho"-substituent (see Tables 1 and 2). The loss of "ortho"-substituents in the form of radicals as a consequence of the formation of four, five or six membered rings is a relatively common process in mass spectrometry.[14] In particular the EI/MS of acetanilides evidenced such a fragmentation[15] that was interpreted assuming the formation of five membered rings bearing the carbonyl oxygen bonded to the phenyl group. The m/z 202 ion should have similarly the structure *e* as depicted in Scheme 3.

The occurrence of the above cyclization product in "ortho"-substituted benzene-,[‡] methane-[15] and 3-thiophenecarboxanilides discounts the possibility of a participation of the sulfur atom in the cyclization process of thiophene-2-carboxanilides.

[‡] The EI/MS of 2'-bromobenzanilide show a very abundant fragment ion analogous to *d* at m/z 196 (65%). The remaining significant fragments are: the benzoyl ion $[C_6H_5CO]^+$ m/z 105 (base peak); the molecular ions $M^{+\cdot}$ m/z 275 (9.3%) and m/z 277 (9.3%) and the phenyl ion $[C_6H_5]^+$ m/z 77 (4.6%).



X = OMe, Me, Et, Cl, Br, I, NO_2

Loss of "ortho"-substituents by ring closure reactions.

Scheme 3

The presence of intense metastable ions for this loss of 2'-substituents supports the rearrangement process of Scheme 3. It is in fact noticeable that the B/E linked scan spectra show that in both series of anilides the peak at m/z 202 constitutes the only one observed peak for the 2'-halogen (apart from fluoro) and 2'-nitro derivatives and the same peak at m/z 202 is the most intense peak for 2'-methoxy substituted compounds.

The extent of "ortho"-substituent loss, as manifested by relative abundances of the corresponding peaks in the EI/MS, is apparently related to the C-X bond energies. This behaviour closely parallels that observed in similar reactions of "ortho"-substituted thioureas.[16]

However the abundances of the m/z 202 peaks for both 2'-nitro-substituted compounds (**25** and **51**) seem anomalously low as compared, for example, to the corresponding 2'-chloro derivatives (**16** and **42**). Based on bond energies alone NO_2 radical should indeed be more extensively lost with respect to the Cl radical.[17,18]

This fact can probably be attributed to steric effects as well as to increased internal energy of the corresponding molecular ions which should enhance simple cleavage reactions as compared to rearrangement processes.

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