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Investigation on the Stability of Multisubstituted Arylpentazoles and the Influence on the Generation of Pentazolate Anion

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A series of mono-, di- and tri-substituted arylpentazoles were obtained via different synthetic routes. The effects of the number and position of the substituents on the arylpentazoles stability have been investigated at different temperatures. Investigators used electrospray ionization tandem mass spectrometry to infer the decomposition pathway of arylpentazoles. The article examines the relationship between the arylpentazole stability and the relative intensity of the generated pentazolate anion.

Keywords: arylpentazole, pentazolate anion, polynitrogen compounds, synthesis

INTRODUCTION

Polynitrogen compounds have always attracted extensive attentions as candidates for high-energy density materials(HEDMs) (Chavez and Gilardi 2009; Ghule et al. 2013; Geiger, Haas, and Grinstein 2014). The reports on the synthesis of N_5^+ ion and its salts have greatly inspired the effort to isolate the pentazolate anion (N_5^-) from arylpentazoles (Nguyen 2003; Christe 2007), which are hitherto known to be the most stable compounds containing the cyclic pentazole moiety. In 2002, Vij et al. 2002 showed that the N_5^- could be produced and detected by the electrospray ionization mass spectrometry (Vij et al. 2002). This new discovery indicates a bright future for the experimental polynitrogen chemistry, holding a great promise for the bulk synthesis of N_5^- salts (Butler, Stephens, and Burke 2003; Schroer et al. 2005). However, owing to the highly endothermic temperatures of formation, aryl-pentazoles are apt to decompose into arylazides and dinitrogen. Thus, they generally must be kept at temperatures lower than –35 °C (Huisgen and Ugi 1957; Ugi and Huisgen 1958; Wallis and Dunitz 1983). Until now, there have been only indirect proofs for the presence of N_5^- (Butler et al. 2008; Ek et al. 2013; Geiger et al. 2013), which makes it challenging for experimental chemists to synthesize and isolate N_5^- and its salts.

As the most important precursor of N_5^-, the synthesis of arylpentazoles are being actively studied in the field of HEDMs (Geiger et al. 2014). Most recent research reports on arylpenta-zoles have focused on the synthesis of various monosubstituted arylpentazoles rather than on multisubstituted arylpentazoles (Ek et al. 2013). In this article, we report the synthesis of a series

of arylpentazoles substituted with 1, 2, or 3 electron-donating group(s) at the para-, meta-, or ortho-position(s) (Scheme 1). By observing their behavior in the generation of N_5^- we aim to reveal the effects of the number and position of the substituents on the stability and decomposition pathway of the arylpentazole. Besides, the tandem mass spectrometry is used to generate and detect the pentazolate ion; the relationship between the arylpentazole stability and the relative intensity of generated N_5^- is also discussed.

EXPERIMENTAL

Materials and Methods

All reagents and solvents used were of analytical grade. MS/MS (ESI) mass spectra were recorded on a Finnigan TSQ Quantum ultra-AM mass spectrometer (Thermo Fisher Scientific, Waltham, MA USA). The samples were dissolved in a 1:10 mixture of pyridine and acetonitrile, and infused via a syringe pump at 10 μL/min^{-1}. The instrument was run in the negative ion mode with the Capillary voltage at –4000 V and the dissociation potential (source CID) at –20 V. In the MS/MS mode, the quadrupole mass analyzer was set to pass the parent ion at unit mass resolution. Ar was used as the collision gas. ^{1}H NMR was recorded on a Bruker 500 MHz spectrometers (Billerica, MA, USA) with tetramethylsilane (TMS) as an internal standard.

General Synthesis of Arylpentazole

These compounds were prepared according to the procedure of Butler, Stephens, and Burke (2003) and Alisi et al., (2012) with minor modifications. Substituted aniline (5 mmol) was dissolved in water (2 mL) or THF (2 mL), cooled in an alcohol low-temperature bath to –5 °C, slightly acidified with conc. HCl (9 mmol). The aqueous solution of sodium nitrite (0.36 g, 5.2 mmol) was added dropwise and stirred for 0.5 h at the same temperature. Then, a cold mixture solution of methanol (6 mL) and petroleum ether (PE, 12 mL) was added and the reaction solution cooled to –40 °C. A cold aqueous solution of sodium azide (5.2 mmol) was slowly added while stirring, resulting in the formation of the suspension. The solid was collected at low temperature, washed with –40 °C methanol, and dried in vacuum at –30 °C to produce a grey solid (15% to 35% yield).

4-hydroxyphenylpentazole (**1**). ^{1}H NMR (CD$_3$OD): 7.89 (2H, d, J = 9.5), 7.79 (2H, d, J = 9.5); ESI-MS/MS (*m/z*, 10 eV), 162.04 [M-H]$^-$, 134.03, 106.06, 78.14;

2-methyl-4-hydroxyphenylpentazole (**2**). ^{1}H NMR (CD$_3$OD): 7.85 (2H, d, J = 8.0), 7.03 (2H, d, J = 8.0), 2.31 (3H, s); ESI-MS/MS (*m/z*, 10 eV), 176.03 [M-H]$^-$, 148.03, 120.05, 92.08;

3-methyl-4-hydroxyphenylpentazole (**3**). ^{1}H NMR (CD$_3$OD): 7.85 (1H, s), 7.78 (1H, s), 7.00 (1H, s), 2.31 (3H, s); ESI-MS/MS (*m/z*, 10 eV), 175.98 [M-H]$^-$, 147.99, 120.01, 92.06;

3,5-di-methyl-4-hydroxyphenylpentazole (**4**). ^{1}H NMR (CD$_3$OD): 7.65 (2H, s), 2.29 (6H, s); ESI-MS/MS (*m/z*, 10 eV), 190.05 [M-H]$^-$, 162.02, 134.04, 106.07;

3,5-di-tert-butyl-4-hydroxyphenylpentazole (**5**). ^{1}H NMR (CD$_3$OD): 7.60 (2H, s), 1.86 (18H, s); ESI-MS/MS (*m/z*, 10 eV), 274.16 [M-H]$^-$, 218.07, 161.07, 146.06;

2,6-di-methyl-4-hydroxyphenylpentazole (**6**). ESI-MS/MS (*m/z*, 10 eV), 190.00 [M-H]$^-$, 163.00, 134.02, 106.31.
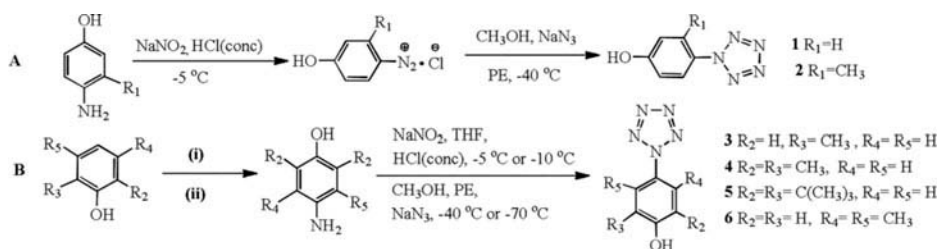
RESULTS AND DISCUSSION

Synthesis of Arylpentazoles

As illustrated in Scheme 1 (Pathway A), the preparation of 4-hydroxyphenylpentazole (**1**) and 2-methyl-4-hydroxyphenylpentazole (**2**) was according to literature methods (Butler, Stephens, and Burke 2003). This synthetic route was a two-step reaction starting from an arylamine, which was diazotized to give a diazocompound and then followed by addition of an azide ion yielding the arylpentazole. In Pathway B, two independent routes were used to synthesize required arylamines by nitrosation of phenols. 3-Methyl-4-hydroxyphenylpentazole (**3**), 3,5-di-methyl-4-hydroxyphenylpentazole (**4**) and 3,5-di-tert- butyl-4-hydroxyphenylpentazole (**5**) were prepared from the corresponding commercially available phenols by diazotization and followed by reduction of the resulting diazocompounds with $Na_2S_2O_4$ to give the known aminophenols (Alisi et al. 2012). When the latter reacted with $NaNO_2$ and NaN_3, the *p*-aminophenol derivatives **3** and **4** were obtained (Scheme 1Finally, 2,6-di-methyl-4-hydroxyphenylpentazole (**6**) was prepared via a four-step reaction. 4-Amino-3,5-di-methylphenol was successfully prepared from the nitrosation of 3,5-dimethylphenol followed by reduction with $Na_2S_2O_4$ (Uma, Lee, and Kang 2005). To our surprise, diazotization of the amino group followed by treatment of the diazonium salt solution with sodium azide at –40 °C was unable to give compound **6**. When the reaction was carried out at –70 °C for 30 min, the products were analyzed by MS spectroscopy and only trace amounts of compound **6** was detected, but it was difficult to isolate the neat solid.
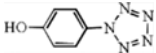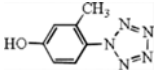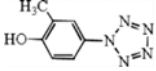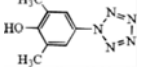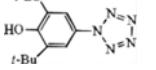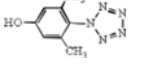
The Stability of Arylpentazoles

In order to elaborate the effects of the position of electron-donating substituents on the arylpentazoles stability, the mass spectrometry was employed to detect compounds **1-6** at different temperatures of –70 °C, –30 °C, –20 °C, and –10 °C, respectively. As shown in Table 1, the results demonstrated that all compounds could be stored for a long time at –70 °C and exist over 1 month at –30 °C except compound **6**. At about –20 °C, compound **3** showed the best stability ($\geq$ 20 days). However, the compound **1** could exist no more than 10 days, while the compound **2** was almost completely decomposed within 3 days. When the temperature reached –10 °C, compounds **1** and **2** disappeared after 6 h. Furthermore, the stability of pentazoles was also dependent on the number of substituents on

SCHEME 1 synthesis of a series of arylpentazoles. (**i**) p-aminobenzene sulfonic acid, Na_2CO_3, $NaNO_2$, NaOH, $Na_2S_2O_4$, HCl(conc), this method for synthesis of corresponding arylamines of compounds **3-5**; (**ii**) $NaNO_2$, H_2SO_4 (conc), 10% NaOH, $Na_2S_2O_4$, this method for the synthesis of corresponding arylamines of **6**.

TABLE 1
The existent days or hours of arylpentazoles at different temperature

Compounds	Structure	Temperature			
		−70 °C (day)	−30 °C (day)	−20 °C (day)	−10 °C (hour)
1		Long-term storage	≥30	≤10	2 ~ 6
2		Long-term storage	≥30	≤3	0 ~ 1
3		Long-term storage	≥30	≥20	5 ~ 10
4		Long-term storage	≥60	≥30	8 ~ 12
5		Long-term storage	≥60	≥30	≥12
6		<2	Inexistence	Inexistence	Inexistence

the benzene ring. Comparing the stability of compounds **3, 4, 5**, and **6**, it can be found that compound **4** bearing with two methyl groups in the **meta-position** exhibited more stable than compound **3**. Compound **6** where the two methyl groups locate in the ortho-position showed the worst stability, such as the synthesis of compound **6** needed to −70 °C. Compound **5** showed the best stability and does not completely decompose within 12 h at −10 °C. Based on the above results, it can be concluded that the stability of the compound improved with the increasing number of the substituents in meta/para-position, and the stability decreased when a donating substituent or two substituents are added in the ortho-position. To further explore the importance of resonance for the stability of arylpentazoles, we need to emphasze the mechanism of the pentazole formation. According to Butler et al. 1998, the formation of the five-membered nitrogen ring does not proceed via a concerted cycloaddition (see Fig. 1) and pentazenes were considered to be important intermediates in the reaction of aryl diazonium cations with sodium azide. If the azide was added to a cis fashion, in relation to the aryl ring, ring-closure to the pentazole cannot occur (Ek et al. 2013). Indeed, the MS was used to analyze the synthesis process of compound **1**, and the hydrogen chloride coordinated to 4-hydroxyphenylpentazene as a ligand appeared at a peak of 198 (see Fig. 1). Because the complex was unstable, the peak m/z 198 decayed along with the formation of another peak at m/z 170. Therefore, if we want to achieve the N_5 ring, the pentazenes must first isomerize into a trans-configuration to allow cyclization, which could occur via rotation around the N-N single bond. When the substituents were in the ortho-position of arylpentazoles, it would be of no benefit to the rotation. Moreover, compounds **2** and **6** with methyl group in the ortho-position would be expected to increase the stability. But due to electrostatic and steric repulsion, the aryl and pentazole rings are not coplanar in the ground states of these molecules. Thus, no through-resonance has to be broken for the molecules to decompose (Carlqvist, Ostmark, and Brinck 2004).
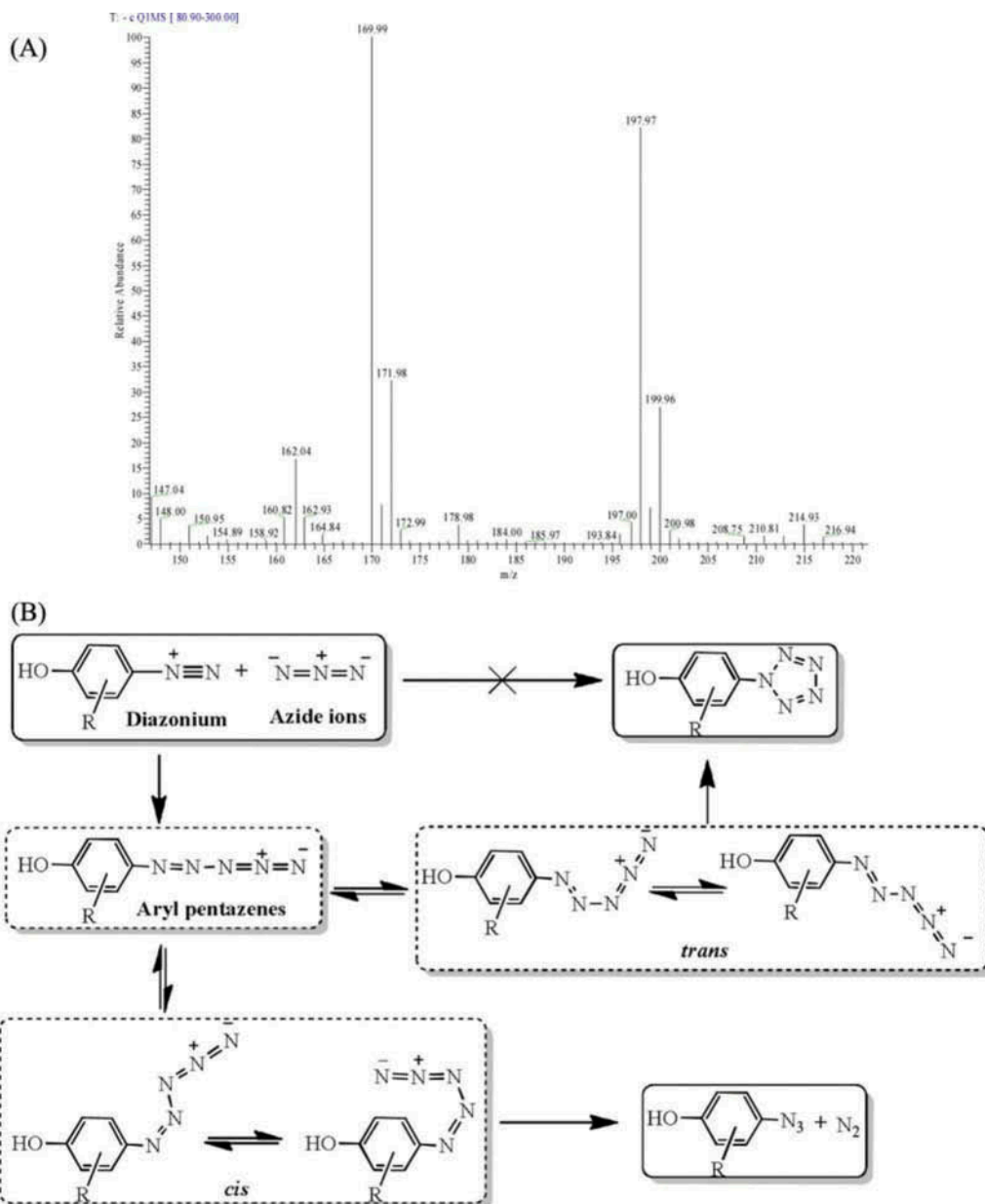
FIGURE 1 MS spectroscopy of the synthesis process of 1 and Mechanism of the pentazole formation.

Mass Spectrometric Analysis and Decomposition Pathway

Although the attempts to prepare either the parent HN_5 molecule or N_5^- have so far been unsuccessful, it has been reported in the literature that N_5^- can be produced and detected by mass spectrometry (Ostmark et al. 2003). In our pursuit of the N_5^-, we have applied the electrospray ionization tandem mass spectrometry (ESI-MS/MS) to detect the decomposition pathway of compound **4** in CH_3CN/CH_3OH (10:1) by variable collision energy. As shown in Figure 2, compound **4** has a prominent base peak at m/z 190 that can be dissociated in two ways, depending on the collision energy. At low collision energy of 10 eV, the m/z 190 ion underwent stepwise N_2, N_2, and CO loss, giving rise to intense peaks with m/z values of 162, 134, and 106, respectively. The loss of the first N_2 molecule was assigned to the opening of the pentazole ring and produced the 2,6-di-methyl-4-azidophenolate ion. The second N_2 loss occurred from the azido group and generated the deprotonated quinine-imide. This ion then underwent CO extrusion giving a $[C_7H_8N]^-$ ion. At high-energy collision (76 eV), the m/z 190 ion gave a very different fragmentation pattern. The specific peaks at m/z 70 and 42 appeared. The m/z 70 peak can only be due to N_5^- and the m/z 42 peak was attributed to the azide anion. These results clearly demonstrated that the use of high energy allowed the C-N bond to be cleanly cleaved, then the
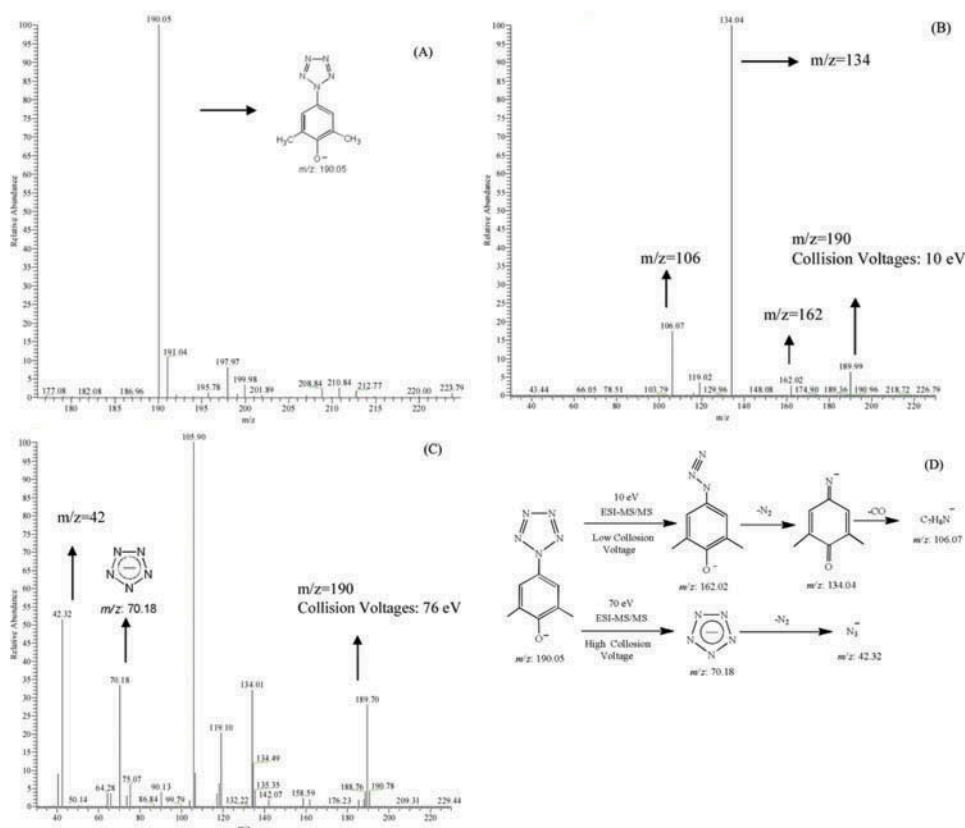

FIGURE 2 ESI-MS/MS fragmentation of 4 at low and high collision energy and its decomposition pathway.

N_5^- was formed. The fragments of the m/z 70 to 42 were due to the loss of dinitrogen, which was agreed well with the theoretically predicted decomposition pathway of N_5^- (Vij et al. 2002).

N_5^- Release and Comparsion

Theory calculations suggested that the cleavage energy of the C-N bond is more than those of the N-N, N=N bonds in arylpentazole. In order to obtain the N_5^-, the high energy energy (55 eV) was employed to cut off the C-N bond in mass spectrometric detection. All prepared arylpentazoles except compound **6**, have been used to cleave the C-N bond to generate N_5^- under the same circumstances including concentration, energy collision, flow rate etc. Figure 3 shows the MS/MS spectra of arylpentazoles (Fig. 3, A, B, C, D, F) and
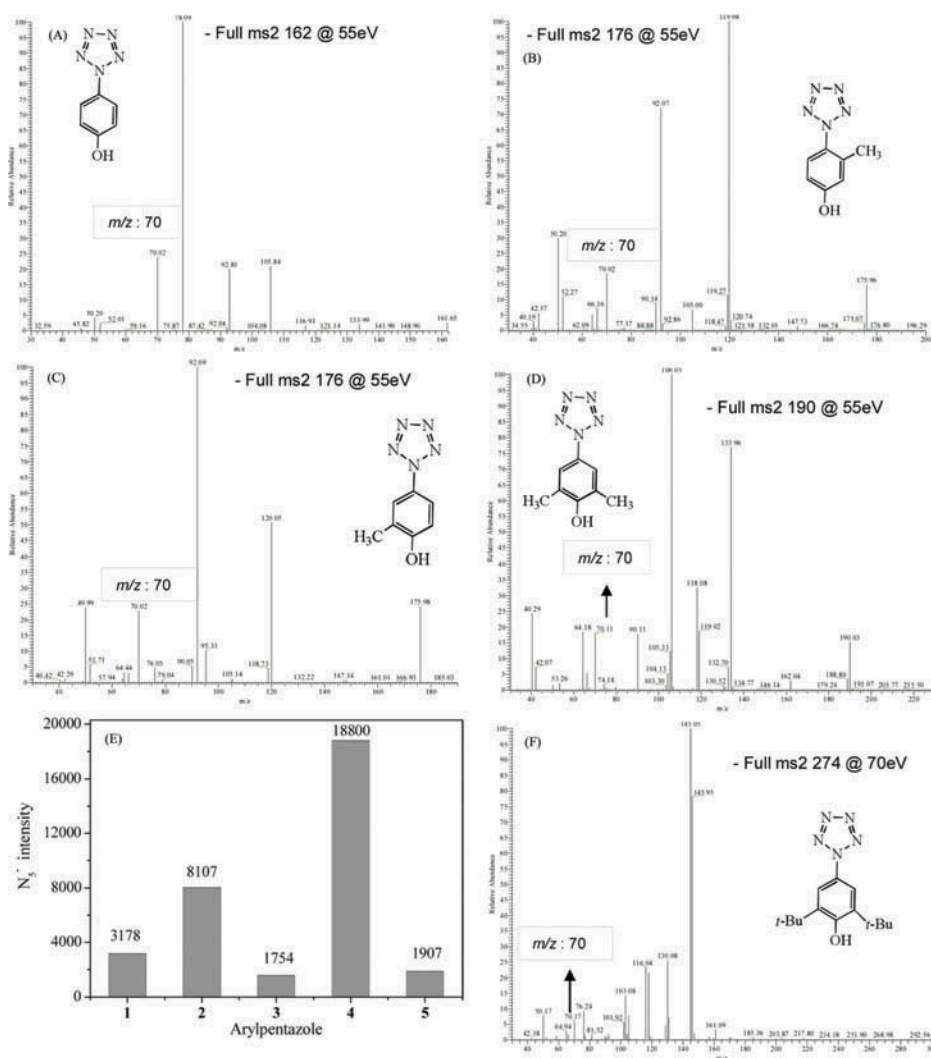

FIGURE 3 ESI-MS/MS fragmentation of compounds 1~5 and the N_5^- intensity observed in mass spectrometric experiments.

the relationship between the relative intensity of generated N_5^- and the arylpentazole stability (Fig. 3 E). It can be found that compound **3** has excellent stability, but with less N_5^- intensity than compounds **1** and **2**. Especially, compound **5** needs to use a high collision energy of 70 eV to generate N_5^- (Fig. 3, F). At high energy collision of 55 eV, the N_5^- was decomposed firstly into azide. The results indicated that the electron-donating substituents (di-tertiary-butyl groups) in the meta/para-position of the benzene ring can stabilize the pentazole system. However, it is worth mentioning that compound **4** releases the superior intensity levels of N_5^- (Fig. 3, D, F), which is almost six times bigger than compound **1**. Therefore, based on the arylpentazole stability and cleavage of the C-N bond, it is concluded that compound **4** is a candidate for obtaining the N_5^- or its salts.

CONCLUSION

A series of multisubstituted arylpentazoles were prepared and characterized. Comparisons between 4-hydroxyphenylpentazole and multisubstituted arylpentazole showed that the stability of the arylpentazole increases with electron-donating substitutes in the meta/para-position and decreases with the substitutes in the ortho-position. The order of stability of these compounds is as follows: 3,5-di-tert-butyl-4-hydroxyphenylpentazole>3,5-di-methyl-4-hydroxyphenylpentazole>3-methyl-4-hydroxyphenylpentazole>4-hydroxyphenylpentazole>2-methyl-4-hydroxyphenyl-pentazole>2,6-di-methyl-4-hydroxyphenylpentazole. Furthermore, the tandem mass spectrometry was applied to analyze the multisubstituted arylpentazoles, which demonstrated that the C-N bond could be cleaved while leaving the pentazole ring intact. The 3,5-di-methyl-4-hydroxyphenylpentazole showed the best property to produce N_5^-.

FUNDING

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