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The Stability of Substituted Benzylpentazoles

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Abstract: Pentazoles have been received increasing attentions in recent several decades. The most stable pentazole synthesized so far only exists for several hours at 0 ºC in methanol. Some *para*-substituted benzylpentazoles were explored in this study. The results elucidated that (4-oxobenzyl)pentazole anion is more stable than (4-oxophenyl)pentazole anion in either gas phase or methanol, while most of benzylpentazoles desiged are approximately ten-to-hundred times more stable than (4-oxophenyl)pentazole anion in methanol.

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Pentazoles have been received increasing attentions in recent several decades, because of their potential application in forming energetic allogenic nitrogen. They were first successfully prepared by Huisgen and Ugi at -40 ºC in the late 1950s by adding an aqueous solution [1-3]. Nguyen et al [4] estimated that pentazole ion (N_5^-) has an energy barrier of at least 19.0 kcal/mol to decompose to stable N_3^- and N_2. Glukhovtsev et al [5] and Benin et al [6] have predicted that pentazole anion (N_5^-) has a half-life time ($t_{1/2}$) of 2.3 days, while $t_{1/2}$ is only about 10 min for HN_5 in methanol at 0 ºC. Those studies suggested that the half-life time of N_5^- is long enough to isolate. Unfortunately, pentazole ion can only be detected in spectrum

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although many experimental efforts were made [7-16]. Both experimental [1-3] and theoretical [17] studies showed that (4-oxophenyl)pentazole anion is the most stable pentazole species known so far. Despite this, it only exists for several hours at 0 ºC in methanol [6].

Whether a pentazole derivative is capable to possess a half-life time of days or longer, it would contribute to its deposit and consequent dealing. Design and synthesize some long-lived pentazole derivatives are desirable. This study would explore some benzylpentazoles (**Figure 1**) at the B3LYP/6-311+G(2df,2p)//6-31+G(d) and PCM-B3LYP/6-31+G(d)//6-31+G(d) levels[18].

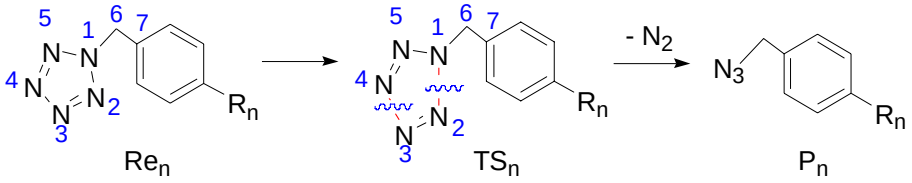

Figure 1: Degradation of benzylpentazoles (R_n = $-O^-$,$-N(CH_3)_2$, $-NHCH_3$, $-NH_2$, $-OCH_3$, -OH, $-CH_3$, and -H (n = 2-9)).

The compound, (4-oxophenyl)pentazole anion was also investigated for comparison and avoiding computational system errors in this study. Benzylpentazoles **2**-**9** are some pentazole derivatives with electron-donating groups of $-O^-$, $-N(CH_3)_2$, $-NH(CH_3)$, $-NH_2$, $-OCH_3$, -OH, $-CH_3$, and -H in the *para* position of the benzene ring respectively. Among five N-N bonds of pentazole ring, the N2-N3 bond is the shortest while the N3-N4 bond is the longest for benzylpentazoles **2**-**9**. The differences between the longest and shortest bond lengths were calculated to be 0.038, 0.044, 0.044, 0.044, 0.045, 0.045, 0.045, and 0.046 Å for benzylpentazoles **2**-**9**, respectively. Among eight benzylpentazoles, (4-oxobenzyl)pentazole anion possesses the largest electronic delocalization in the pentazole ring. However, the bond length difference between the longest and shortest ones was calculated to be 0.021 Å in (4-oxophenyl)pentazole. This allowed us to propose that the electronic delocalization effect of the pentazole ring in benzylpentazoles is less than that in (4-oxobenyl)pentazole anion. Meanwhile, the N1-C6 bonds calculated are 1.514, 1.479, 1.479, 1.478, 1.476, 1.475, 1.474, and 1.504 Å in benzylpentazoles **2**-**9**, respectively, larger than the C-N bond (1.411 Å) of (4-oxobenyl)pentazole. This implies that the introduction of the methylene group makes the electronic overlap between the pentazole ring and the benzyl group less and loosens the C-N bond strength.

Benzylpentazoles **2**-**9** release N_2 through synchronous breakage of two N-N bonds readily (**Figure 1**). In transition states TS_2-TS_9, the N2-N3 bonds calculated are 1.173 Å, close to the experimental value (1.098 Å) of the N≡N bond length in nitrogen molecule; the N1-N5 distances calculated range from 1.276 to 1.291 Å, slightly larger than the experimental value (1.216 Å) of the N=N bond length of CH_3N_3, while the distances of N4-N5 were calculated to