The Stability of Arylpentazoles

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The stability of phenylpentazole along with para-substituted and ortho,para-substituted arylpentazoles have been studied using high-level density functional theory (DFT). The decomposition of arylpentazoles to N_2 and the corresponding azide is a first-order reaction, where the breaking of the N1−N2 bond is concomitant with cleavage of the N3−N4 bond. Calculations confirm that the stability of arylpentazoles increases with electron-donating groups and decreases with electron-withdrawing groups, in the para position, as found in experiments. The stabilizing effect of the electron-donating groups is shown to be due to a resonance interaction with the electron-withdrawing pentazole ring. Addition of solvation effects, using the polarizable continuum model to simulate the polar solvent methanol, increases the stability of arylpentazoles. This is due to a more polar ground state than transition state. The calculated free energies of activation for the arylpentazoles agree well with experimental results. From the calculations, the electron-withdrawing effect of the pentazole group is found to be similar to that of cyanide (−CN). Some new arylpentazoles with hydroxyl groups in the ortho position are proposed. These are predicted to be more stable than all previously synthesized neutral arylpentazoles.

I. Introduction

Early studies of arylpentazoles (**1**, Figure 1) were performed by Huisgen and Ugi in the late 1950s.[1−3] The arylpentazoles were prepared by adding an aqueous solution of azide to a mixture of aryldiazonium chloride, aqueous methanol, and petroleum ether at −40 to −20 °C with stirring.[2] The pure arylpentazole crystallizes from the two-phase reaction mixture.

Phenylpentazole, a colorless crystalline substance, is stable at temperatures below −20 °C but decomposes violently at room temperature. In further investigations, Huisgen and Ugi showed that electron-donating substituents in the para position of the benzene ring stabilize the pentazole system.[3] For example, [4-(dimethylamino)phenyl]pentazole can be kept for a few hours at room temperature in solid form. They also found that the stability of phenylpentazole in solution generally increases with the dielectric constant of the solvent, indicating that the transition state is less polar than the ground state.[4] The most stable arylpentazole synthesized to date is the (4-oxophenyl)pentazole anion with an experimentally determined free energy of activation of 21.0 kcal/mol in methanol.[3] The mechanism of decomposition of arylpentazoles have been addressed in two relative recent NMR studies by Butler and co-workers.[5,6] On the basis of NMR measurements and theoretical calculations they concluded that the arylpentazoles decompose through a concomitant breaking of the N1−N2 and N3−N4 bond in the transition state. This is today the accepted picture of the decomposition of arylpentazoles (see Figure 2).

In recent years there has been an increased interest in **1**, mainly due to the use of polynitrogen compounds as candidates for high-energy-density materials (HEDMs). In 1999 the novel v-shaped N_5^+ ion was synthesized, the first new stable all-nitrogen compound in more than 100 years.[7] Christe and co-workers have since reported the preparation and isolation of several N_5^+ salts.[8,9] This recent breakthrough has prompted much effort in isolating N_5^- from arylpentazoles. Calculations have shown that *cyclo*-N_5^- (D_{5h}) (**2**) is the most stable isomer of N_5^- toward fragmentation to N_3^- and N_2, with a barrier of around 27 kcal/mol in the gas phase.[10] Ugi and co-workers were the first to try to isolate **2** from arylpentazoles, through ozonization of [4-(dimethylamino)phenyl]pentazole and reduction of phenylpentazole with sodium in NH_3 (l); neither scheme was successful.[2] The ozonization route has since been revisited by Radziszewski and co-workers.[11] In a recent study by the authors of the present article a route similar to that used for amination of halobenzenes is suggested as a possible way to isolate **2** from **1** in solution.[12] The detection of **2** in mass

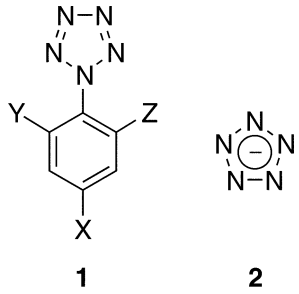

Figure 1. Arylpentazole (**1**) and the pentazole anion (**2**).

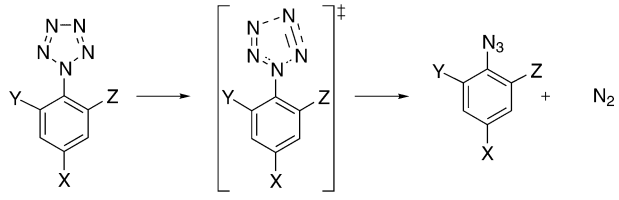

Figure 2. Decomposition of arylpentazoles.

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spectrometry experiments[13−15] has been reported, and the possible detection of zinc−pentazolate salt in solution has also been presented.[16] The common feature of all these studies on isolating **2** is that the parent pentazole is an arylpentazole, which warrants an investigation on the stability of this interesting group of molecules.

II. Methods and Procedure

Stationary points, transition states, and minima were fully optimized at the B3LYP/6-31+G* level. The stationary points have further been characterized by vibrational frequency analysis at the same level of theory. Single point calculations were performed at the B3LYP/6-311+G(2df,2p) level to obtain accurate energies. Solvent effects were estimated by the polarizable continuum model (PCM);[17,18] single point calculations were performed at the PCM-B3LYP/6-31+G* level, utilizing the Bondi[19] van der Waals radii with standard scaling factors for the cavity generation and the dielectric constant of methanol. The PCM method has been used extensively to analyze solvent effects on thermochemistry and chemical reactivity. Although the method lacks a discrete description of the solvent, it has been shown that it performs reasonably well also when hydrogen bonds can be formed between the solvent and solute. Successful examples from the literature include the calculation of absolute solvation energies, conformational equilibria for solutes with and without internal hydrogen bonds, and reaction energetics.[17,18,20−23] The calculations of optimized geometries, vibrational frequencies, gas-phase energies, and solvation have been performed with the Gaussian 98 suite of programs.[24]

To analyze the effect of electron-withdrawing and electron-donating para substituents on arylpentazole, the electrostatic potential, $V(\mathbf{r})$, on the molecular surface was calculated for the ground state and transition state structures of three different arylpentazoles. The potential was evaluated at the B3LYP/6-31+G* level of theory and the molecular surface was defined according to Bader et al.,[25] by the 0.001 au contour of the electron density. The electrostatic potential is in contrast to most other molecular descriptors, such as atomic charges, a real physical property that is rigorously defined and can be evaluated experimentally as well as theoretically.[26−28] The electrostatic potential has been used extensively to analyze chemical reactivity and molecular interaction tendencies. It has been shown to be particularly useful for the analysis of substituent effects in aromatic systems.[29,30] A locally developed code (hs95) was used for the electrostatic potential calculations.

III. Results and Discussion

The energy barriers ($\Delta E^{\ddagger}$, Table 1) for decomposition of the para-substituted arylpentazoles follow the trend found by Huisgen and Ugi.[3] The most stable of the para-substituted arylpentazoles is (4-oxyphenyl)pentazole anion, with an energy barrier of 24.0 kcal/mol. The least stable para-substituted arylpentazole is (4-nitrophenyl)pentazole with an energy barrier of 18.6 kcal/mol. The stability of **1** is increased with electron-donating groups in the para position, following how strong the electron-donating effect is, and decreases with electron-withdrawing groups. When zero-point and thermal corrections are added to the energy barriers, they are lowered by approximately 2 kcal/mol. After addition of entropy corrections to obtain free energies, they are decreased further by ∼1 kcal/mol. The overall order of stability of the para-substituted arylpentazoles is not significantly altered by the added corrections.

TABLE 1: Energy Barriers toward Decomposition for the Arylpentazoles, All Values in kcal/mol[a]

X	Y	Z	$\Delta E^{\ddagger}$	$\Delta H_g^{\ddagger\circ}$	$\Delta G_g^{\ddagger\circ}$	$\Delta G_{sol}^{\ddagger\circ}$	$\Delta G_{exp}^{\ddagger\circ}$ [b]	σ_p^+ [c]
NO_2	H	H	18.6	16.4	15.2	17.9	18.7	0.79
HSO_3	H	H	18.8	16.7	15.4	18.3		
CN	H	H	19.0	16.8	15.5	18.5		0.66
N_5	H	H	19.1	16.9	15.3	18.4		
CF_3	H	H	19.3	17.2	15.8	18.9		0.61
Cl	H	H	20.1	17.9	16.4	19.5	19.6	0.11
H	H	H	20.2	18.0	16.5	19.5	19.8	0
CH_3	H	H	20.7	18.5	17.7	20.8	20.0	−0.31
OH	H	H	20.9	18.7	17.7	20.8	20.3	−0.92
NH_2	H	H	21.3	19.0	18.1	21.1		−1.30
$N(CH_3)_2$	H	H	21.5	19.2	18.3	21.3	20.7	−1.70
SO_3^-	H	H	22.6	20.3	19.6	20.9		0.35[d]
O^-	H	H	24.0	21.4	20.8	22.0	21.0	−2.30
NH_2	OH	H	22.6	20.2	19.0	20.1		
NH_2	OH	OH	23.9	21.2	19.1	18.6		
NH_2	O^-	H	19.9	17.7	17.3	19.5		
NH_2	CH_3	H	19.6	17.4	16.3	19.1		

[a] Energies of TS relative **1**, evaluated at the B3LYP/6-311+G(2df,2p) level of theory. Geometries optimized at the B3LYP/6-31+G* level of theory with thermal corrections to the energy calculated at the same level. Definitions of the energetics: $\Delta E^{\ddagger}$ = classical energy. $\Delta H_g^{\ddagger\circ} = \Delta E^{\ddagger} + \Delta\Delta H_g$, where $\Delta\Delta H_g$ is the enthalpy correction. $\Delta G_g^{\ddagger\circ} = \Delta E^{\ddagger} + \Delta\Delta G_g$, where $\Delta\Delta G_g$ is the free energy correction. $\Delta\Delta H_g$ and $\Delta\Delta G_g$ are calculated at 273.15 K and 1 atm. $\Delta G_{sol}^{\ddagger\circ} = \Delta G_g^{\ddagger\circ} + \Delta\Delta G_{sol}$, PCM solvation free energy correction. [b] $\Delta G_{exp}^{\ddagger\circ}$, experimental values are estimated from reaction rates in methanol at 273.15 K.[3] [c] σ_p^+ values from ref 31. [d] σ_p for SO_3^- from ref 31.

The increased stability of phenylpentazole in polar solvents, found by Ugi and co-workers,[4] is reproduced by our solvent model and holds for all para-substituted arylpentazoles, showing that the transition state is indeed less polar than the ground state. This is easy to understand, a strong electron-withdrawing substituent (the pentazole, see discussion below) is transformed to a less electron-withdrawing azide group. Although our calculated free energies of activation in methanol agrees well with experiments, the substituent effect is nearly twice as large in the calculations. This discrepancy is most likely due to problems with our description of the solvent. Although the PCM method is known to reproduce the effects of hydrogen bonding solvents relatively well, it cannot be expected to fully account for specific interactions between the solute and solvent.[20−22]

The free energy of activation for an arylpentazole with *cyclo*-N_5 as para substituent shows the strong electron-withdrawing effect of the pentazole ring. On the basis of their similar free energy of activation, the electron-withdrawing effect can be estimated to be of the same size as cyanide (−CN); it has previously been reported that the pentazole ring has the same inductive electron-withdrawing effect as $-NO_2$.[5,32] The free energy of activation for the degradation of para-substituted arylpentazoles correlates better with σ_p^+ than with σ_p, indicating that resonance donation is important for the stability. The linear correlation coefficients, (R^2), are 0.91 and 0.85, respectively (Figure 3).

When the transition state structures for the different para-substituted arylpentazoles are analyzed, one interesting fact becomes evident. For phenylpentazole and all arylpentazoles with electron-donating groups the pentazole ring is rotated out of the plane of the phenyl ring, whereas for those with electron-withdrawing groups, with the exception of (4-chlorophenyl)-pentazole, the rings are in the same plane (see Figure 4). Benin and co-workers found a similar relationship between the rotational angle and the character of the substituent in their analysis of a more limited set of substituted arylpentazoles.[11] It

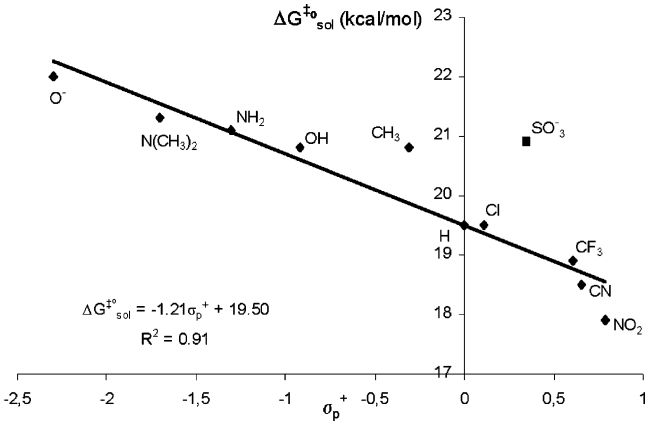

Figure 3. Calculated free energy relationship for the decomposition of para-substituted arylpentazoles.

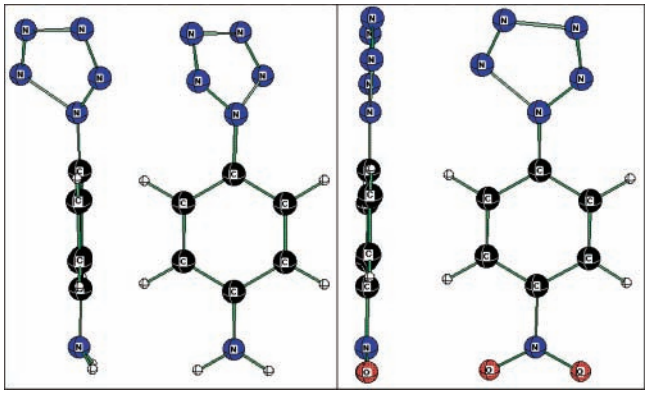

Figure 4. Transition state structures for (4-aminophenyl)pentazole (left) and (4-nitrophenyl)pentazole (right).

should be noted that the product of the reaction, the aryl azide, in all cases has the azide group coplanar with the phenyl ring. Thus, on the basis of the geometries of reactants and products, a transition state with the two rings coplanar would have been expected for all arylpentazoles. The observed rotation of the rings in the transition states of the arylpentazoles with electron-donating groups suggests that there is a significant resonance stabilization in these molecules that has to be broken to facilitate the decomposition. Substituted pentazoles where the substituent is not an aryl group are generally less stable than arylpentazoles,[33] and for these "non-aryl" pentazoles the stability seems to be mainly determined by the capacity of the substituent for inductive donation. For example, we have computed the activation energies of HN_5 and FN_5 to be 0.40 and 5.4 kcal/mol, respectively, lower than the activation energy of phenylpentazole. In the transition state of the arylpentazoles with electron-donating substituents the resonance interaction between aryl ring and the pentazole ring is decreased due to the rotation and the activation energy is thereby lowered. However, there is trade off between the gain in energy from lowering the resonance and the cost in energy for the rotation. Thus, the degree of distortion from coplanarity in transition state reflects both the strength of the resonance interaction and the barrier toward rotation. The fact that the transition state of (4-chlorophenyl)pentazole is nonplanar strengthens our line of reasoning; although the halogen has an inductive electron-withdrawing effect due to its electronegativity, it is a resonance donor.

If the hypothesis that for arylpentazoles with resonance donors in the para position the coplanarity of the rings has to be broken before decomposition holds, one would expect that the introduction of internal hydrogen bonds between the phenyl and pentazole ring that hinders the rotation should increase the stability. The disubstituted arylpentazole, (2-hydroxy-4-aminophenyl)pentazole, has an internal hydrogen bond from the hydroxyl group to N2 of the pentazole ring. In the transition state structure the two rings are no longer coplanar and the energy barrier ($\Delta E^{\ddagger}$) is 22.6 kcal/mol. The stability is increased by 1.3 kcal/mol compared to (4-aminophenyl)pentazole. The increase in stability can be attributed to the internal hydrogen bond, which makes it harder to rotate the pentazole ring out of plane of the phenyl ring and thereby reduce the resonance interaction. After introduction of a second internal hydrogen bond [(2,6-dihydroxy-4-aminophenyl)pentazole] the energy barrier ($\Delta E^{\ddagger}$) becomes 23.9 kcal/mol; the increase in stability is doubled. After addition of free energy corrections the increase in stability is only 0.6 and 0.7 kcal/mol for the mono- and dihydroxy compounds, respectively. However, there are reasons to believe that the calculated free energy corrections are misleading and that the compounds with internal hydrogen bonds are more stable than indicated by the calculations. The internal rotation barriers for the hydroxyl groups are significantly reduced in the transition states due to the breaking of the internal hydrogen bonds, and it is known that by treating such internal rotations as harmonic vibrations their contributions to the internal entropy are overestimated.[34] However, even without considering this effect, (2,6-dihydroxy-4-aminophenyl)pentazole is the most stable uncharged arylpentazole in the gas phase in this study. The stability of this compound is significantly reduced after consideration of solvent effects. The reason for this is that the two polar hydrogens are free to interact with the solvent in the transition state structure. To further explore the importance of resonance for the stability of arylpentazoles, the activation energies for two other disubstituted arylpentazoles were calculated. Both (2-oxy-4-aminophenyl)pentazole and (2-methyl-4-aminophenyl)pentazole have a lower energy barrier, 19.9 and 19.6 kcal/mol, respectively, than (4-aminophenyl)pentazole. The two electron-donating groups 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.

Because the importance of resonance has been established, four of the para-substituted arylpentazoles in our study represent special cases. First is the previously discussed, (4-chlorophenyl)-pentazole, where the halogen is an electron-withdrawing group, but at the same time resonance-donating. The two effects nearly cancel out; (4-chlorophenyl)pentazole is predicted to be slightly less stable than phenylpentazole. In the transition state structure the pentazole ring is rotated out of the plane of the phenyl ring, indicating the need to break resonance to decompose. In the second case, (4-methylphenyl)pentazole, there is a slight increase in the free energy of activation compared to phenylpentazole, and in the third case, [4-(trifluoromethyl)phenyl]pentazole, there is a slight decrease in the free energy of activation. These results show that groups which cannot directly participate in resonance still affect the stability, although groups which can have a greater effect. The fourth and final special case in our study is the (4-sulfitophenyl)pentazole anion. The sulfite group is by its σ_p value predicted to be electron-withdrawing and should thus have a destabilizing effect. The opposite situation is predicted by our calculations, which show a transition state structure where the pentazole is rotated out of plane relative the phenyl ring and a free energy of activation of 19.6 kcal/mol in the gas phase. The results suggest that the sulfite group participates in the resonance

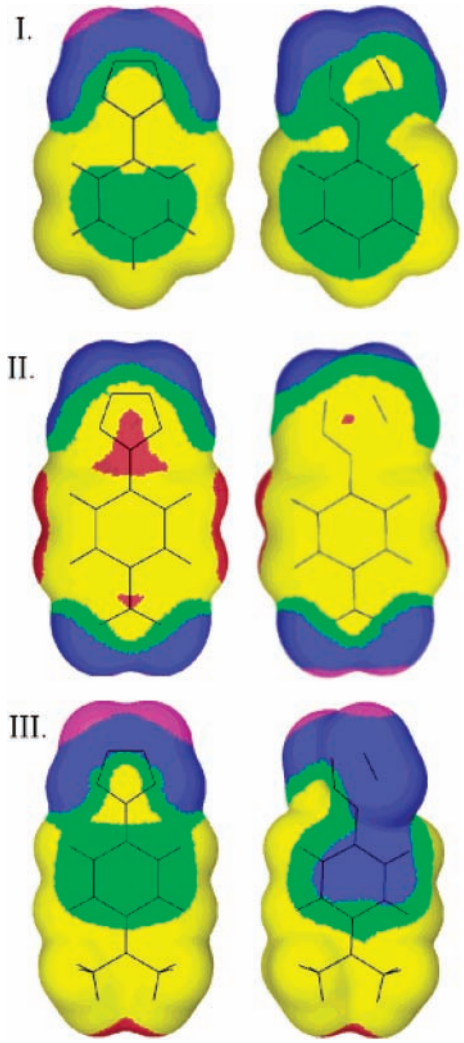

Figure 5. Calculated electrostatic potentials [$V(\mathbf{r})$] on the molecular surfaces for the ground state and transition state structures of (I) phenylpentazole, (II) (4-nitrophenyl)pentazole, and (III) [4-(dimethylamino)phenyl]pentazole. Color ranges in kcal/mol: red for $V(\mathbf{r}) > 25$; yellow for $5 < V(\mathbf{r}) < 25$; green for $-5 < V(\mathbf{r}) < 5$; blue for $-25 < V(\mathbf{r}) < -5$; purple for $V(\mathbf{r}) < -25$.

stabilization of the arylpentazole. We are not able to explain this phenomena, because the sulfite group is not considered to be a resonance-donor, but the results are supported by preliminary experimental results. Due to the discrepancy between the predicted and actual effect of the (4-sulfitophenyl)pentazole anion, it is omitted from the free energy relationship in Figure 3.

The electrostatic potential (EP) on the molecular surface for the ground state and transition state of phenylpentazole, (4-nitrophenyl)pentazole, and [4-(dimethylamino)phenyl]pentazole, demonstrates the effect of substituents (see Figure 5). From the EP of phenylpentazole, the previously discussed electron-withdrawing effect of the pentazole ring becomes evident. The pentazole ring clearly has most of the negative potential, drawing electrons from the phenyl ring. The EP of [4-(dimethylamino)phenyl]-pentazole shows an increase of negative potential over the two rings compared to phenylpentazole, demonstrating the electron-donating effect of the substituent. Finally, for (4-nitrophenyl)-pentazole, the pentazole and phenyl ring shows less negative potential, because the nitro group draws electrons away from the rings. The picture illustrates the importance of electron density in the ring system for the stability of the para-substituted arylpentazoles. A key feature of the transition states in Figure 5 is the disappearance of positive potential at N1 in the pentazole ring. This is in accordance with the positive ρ value for the decomposition of arylpentazoles.[3,6]

TABLE 2: Reaction Energies for Arylpentazoles, All Values in kcal/mol[a]

X	Y	Z	ΔE	ΔH°_g	ΔG°_g	ΔG°_{sol}
NO_2	H	H	−37.4	−39.6	−51.7	−49.9
HSO_3	H	H	−37.0	−39.2	−51.5	−48.1
CN	H	H	−36.9	−39.0	−51.2	−47.6
N_5	H	H	−36.8	−39.0	−51.2	−47.3
CF_3	H	H	−36.2	−38.6	−49.4	−45.6
Cl	H	H	−35.0	−37.4	−48.7	−44.9
H	H	H	−34.7	−36.9	−49.5	−45.6
CH_3	H	H	−33.8	−36.2	−47.3	−43.2
OH	H	H	−33.3	−35.6	−47.8	−43.7
NH_2	H	H	−32.4	−34.6	−46.8	−42.2
$N(CH_3)_2$	H	H	−31.8	−34.1	−45.6	−41.3
SO_3^-	H	H	−28.9	−31.4	−42.1	−44.1
O^-	H	H	−20.0	−22.7	−34.6	−37.9
NH_2	OH	H	−31.4	−33.6	−46.3	−43.4
NH_2	OH	OH	−25.8	−28.3	−42.1	−41.6
NH_2	O^-	H	−25.9	−28.2	−40.2	−39.6
NH_2	CH_3	H	−34.1	−36.3	−48.8	−44.2

[a] For definitions of energetics, see Table 1.

The reaction energies for the decomposition of arylpentazoles offer no surprises (see Table 2); all the arylpentazoles decompose in highly exothermic reactions, due to the formation of the highly stable N_2 molecule. When thermal effects and entropy are considered, it becomes clear that the reaction is practically irreversible.

Theoretical studies have reported that the most promising way to use the pentazole anion is to trap it in a metal complex.[16,35−41] Because arylpentazoles are likely to be the pentazole source for such complexes, the stability of arylpentazole in the presence of metal cations should be investigated. We are currently looking at the stability of arylpentazoles and **2** with a number of the different metal cations.

IV. Summary and Conclusions

The decomposition of 17 different arylpentazoles to N_2 and the corresponding azide has been studied. Comparisons between phenylpentazole and substituted arylpentazoles show that the stability of the arylpentazoles increases with electron-donating substituents and decreases with electron-withdrawing substituents, and the largest effects are observed when the substituent can directly participate in resonance donation. In the transition state structures of arylpentazoles with resonance-donating groups the two rings are not in the same plane, whereas in the transition state structure for those with electron-withdrawing groups the rings are coplanar. This is explained by a resonance interaction over the two rings. The pentazole ring is stabilized by resonance, and this resonance interaction is enhanced by resonance-donating substituents such as $-N(CH_3)_2$ and $-OH$. The pentazole ring has to rotate out of the plane of the phenyl ring to break the resonance and decompose. The stabilizing resonance effect was confirmed with calculations on disubstituted arylpentazoles. Addition of hydroxyl groups in the ortho position, forming internal hydrogen bonds with the pentazole and thus making it harder to break the resonance, increases the stability. When either a methyl group or an oxyanion is added in the ortho position, the stability decreases. In the ground state the pentazole ring is rotated out of the plane of the phenyl group due to electrostatic and steric repulsion, which results in a reduced resonance interaction that decreases the free energy of activation. The (2,6-dihydroxy-4-aminophenyl)pentazole is predicted to be

the most stable uncharged arylpentazole in the gas phase with a free energy of activation of 19.1 kcal/mol. The stability of the arylpentazoles increases in the polar solvent methanol, due to a more polar ground-state structure than transition structure. The electron-withdrawing effect of the pentazole moiety was explored by studying the decomposition of arylpentazole using the pentazole as a substituent, and it was found that its electron-withdrawing effect is similar to that of the cyanide substituent.

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