Theoretical Studies on Phenyl Group Migration of Protonated 1,2-Diphenyl Hydrazines

Chan Kyung Kim,* In Young Lee, Chang Kon Kim, and Ikchoon Lee

Department of Chemistry, Inha University, Inchon 402-751, Korea
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Phenyl group migration within protonated 1,2-diphenyl hydrazines has been studied theoretically using the semi-empirical AM1 method. This reaction proceeds through a 3-memberedcyclic transition state and requires high activation energy. In the reactant, there was no resonance stabilization for the moving Z-ring, however, resonance stabilization between two nitrogen atoms and the Z-ring was achieved at the transition state. The Hammett ρ_Z values are large due to the direct involvement of the Z-ring in the reaction, and the development of a negative charge on the reaction center gives them a positive value. In the case of the non-moving ring, ρ_Y values are small and negative owing to the smaller positive charge increase in the reaction center. The cross-interaction constant, ρ_{YZ}, was obtained from the activation enthalpies, using the multiple linear regression method, and the interaction between two substituents, Y and Z, is examined.

Introduction

Phenyl group migration reactions have been studied in carbanionic,[1] radical[2] and carbocationic[3] systems experimentally. The 1,2-shift passes through a half-migrated structure, (I), which can be classified as a transition state (TS) or perhaps an intermediate depending on the reaction systems.

(I)
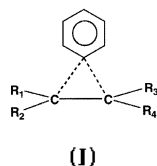
Theoretical studies also have been carried out on anionic[4] (Scheme 1), neutral[5] (Scheme 2) and protonated[6] (Scheme 3) systems. In these reactions, cross-interaction constant,[7] ρ_{YZ} has been determined using Eq. (1),[7a] where Y and Z refer to the substituent on the non-moving and moving phenyl rings,

Scheme 1

Scheme 2

Scheme 3
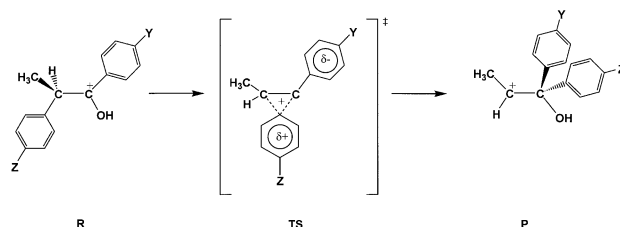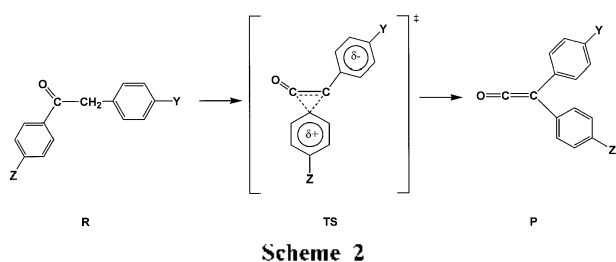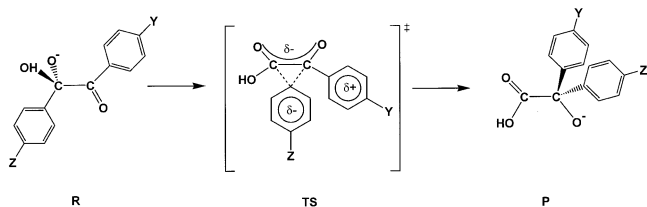
respectively, and their interaction has been discussed.

$$\log(k_{YZ}/k_{HH}) = \rho_Y \sigma_Y - \rho_Z \sigma_Z + \rho_{YZ} \sigma_Y \sigma_Z \qquad (1)$$

The cross-interaction constant, ρ_{YZ}, can be determined using Eq. (2),[7a] and the magnitude of ρ_{YZ} is the result of the change in the intensity of interaction on going from the reactant (I°_{YZ}) to the TS ($I^{\ne}_{YZ}$), Eq. (3).[7b]

$$\rho_{YZ} = \partial\rho_Y/\partial\sigma_Z = \partial\rho_Z/\partial\sigma_Y \qquad (2)$$

$$\rho_{YZ} \propto \Delta I^{\ne}_{YZ} \; (-I^{\ne}_{YZ} - I^\circ_{YZ}) \qquad (3)$$

In the case of the neutral carbene system (Scheme 2), the reactant was stabilized by the vicinal n–σ* overlap. Large structural change and the development of opposite charges on the two rings at the TS resulted in a large cross-interaction constant ($\rho_{YZ} = -0.53$).[5] This is quite similar to the benzilic case ($\rho_{YZ} = -0.48$)[4] though there is no stable interaction in the initial state. On the other hand, a negligible constant ($\rho_{YZ} = 0.03$) was observed in the protonated ketone system which is due to the larger interactions both in the reactant and TS.[6]

Group migrations within heteroatom centers have been studied experimentally. While nitrogen is a neighbor of the carbon atom, they have different physical and chemical properties. In this sense, hydrazine could be thought of as an analogue of ethane, which is used as a skeleton of numerous phenyl group rearrangements. Indeed, substituted hydrazines have been employed in the intramolecular 1,2-[8] as well as

1,4-[9] and 1,5-[10] rearrangement of alkyl, phenyl and organo-silyl[11] groups. In this study, phenyl group migration within substituted hydrazine is investigated theoretically in order to study the substituent effects quantitatively.

Calculation

Since the reaction system considered in this study contained two phenyl rings, the semi-empirical AM1 method[12] was employed to conserve computer time. Mopac 6.0 package[13] was used throughout this work.

All stable structures, including reactant (R) and product (P), were minimized using the energy gradient method. Transition states were located using the TS option starting from the highest energy point determined previously using the usual reaction coordinate method.[14] Frequency calculations were performed to confirm all positive frequencies for local minima and one negative frequency for the TS.[15] An intrinsic reaction coordinate (IRC) calculation[16] was performed to verify the smooth connection between the TS and local minima on both sides of the potential energy surface.

Results and Discussion

Phenyl group migration within protonated 1,2-diphenyl hydrazine is a concerted mechanism that proceeds through a transition state irrespective of substituents, and the TS has a three-membered bridged shape. The reaction pathway is depicted in Scheme 4. The Z-ring refers to a ring migrating from N_1 to N_2 and the Y-ring to a non-migrating ring. The substituent of each ring was varied from electron donating to electron withdrawing, i.e., Y and Z=NH_2, OCH_3, CH_3, H, Cl, CN.

The AM1-optimized structures of the reactant, TS and
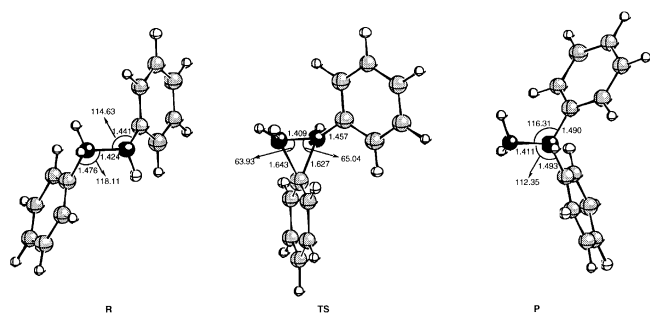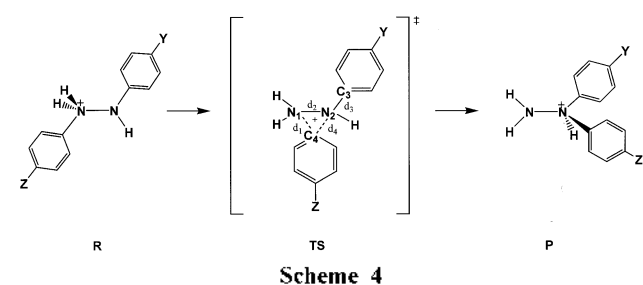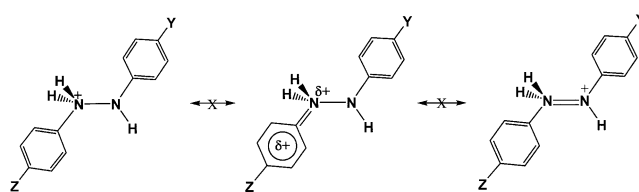

Scheme 4

Figure 1. AM1 optimized structures of reactant (R), TS, and product (P) (Y=Z=H).

Scheme 5

product for the case of Y=Z=H are described in Figure 1.

The reactant has a positive charge on N_1, which could not be stabilized by resonance interaction with either the neighboring Z-ring or the N_2 atom due to the saturation of valence allowed for the nitrogen atom (see Scheme 5). AM1 bond lengths and group charges are summarized in Tables 1 and 2, respectively. Table 1 shows that the bond lengths N_1-C_4, N_1-N_2, and N_2-C_3 of the reactants do not change much. Consistency of the bond lengths is also reflected in the group charge distribution. Therefore, the reactant might be considered to have constant geometrical characteristics irrespective of the substituents.

Since the moving ring forms a three-membered cyclic structure at the TS, the d_2 bond (Δd_2^-) was shortened invariably by ca. 0.02 Å compared with that of the reactant. However, the largest change occurs in the d_4 bond and, especially, a slightly shorter d_4 compared with d_1 implies a later TS. In the TS, charge dispersion was possible because the Z-ring could make resonance interaction with N_1 and N_2 atoms, and, as a result, the charge of the NH_2 group decreased and the charge of the NH and Z-ring increased slightly (see Table 2). The reorganization of NH_2 and Z-ring group charges was more pronounced as the substituent became more electron donating. However, negligible charge change was observed in the Y-ring, which suggests no resonance interaction with N_1, N_2 and the Z-ring. This is also supported by the constant increase in d_3 ($\Delta d_3^- \cong$ ca. 0.02 Å) on going from the reactant to the TS. In the product, the two phenyl rings are bonded to a common atom, N_2, and have skewed conformation.

AM1 heats of formation are summarized in Table 3. Heats of formation of the reactant, TS and product are denoted $\Delta H_f(R)$, $\Delta H_f(TS)$ and $\Delta H_f(P)$, respectively and activation enthalpy and endothermicity $\Delta H^\ddagger$ and ΔH^o, respectively.

All reactions are endothermic ($\Delta H^o = 7.8$-9.7 kcal mol^{-1}) because the phenyl group migration results in the sterically crowded product, requiring a higher activation enthalpy ($\Delta H^\ddagger = 57.6$-64.9 kcal mol^{-1}). These activation enthalpies are much higher than those reported for the protonated ketone system ($\Delta H^\ddagger = 36.5$-47.5 kcal mol^{-1}).[6]

Let us first examine the Z-substituent effect on reactivity. The activation energy decreases as the substituent becomes more electron withdrawing (64.3 kcal mol^{-1} for Z=NH_2, Y=H vs. 58.0 kcal mol^{-1} for Z=CN, Y=H). This could arise from two opposing effects, that is, (1) destabilization of the positively charged reactant by a more electron withdrawing substituent, (2) stabilization of TS by resonance interaction with the Z-ring and two nitrogen centers. Trends in the activation enthalpies were in line with those of the endothermicities summarized in Table 3. As the substituent became more

Table 1. AM1 optimized bond lengths of reactant (R) and changes in bond lengths. $\Delta d^{\ddagger}$. and Δd° in Å

Y	Z	$d_1(R)$	$d_2(R)$	$d_3(R)$	$d_4(R)$	$\Delta d_1^{\ddagger\,a}$	$\Delta d_4^{\ddagger\,a}$	Δd_1^{ob}	Δd_2^{ob}	Δd_3^{ob}	Δd_4^{ob}
NH₂	NH₂	1.468	1.432	1.434	2.491	0.174	-0.864	0.940	-0.018	0.048	-1.005
	OCH₃	1.471	1.433	1.433	2.496	0.169	-0.871	0.936	-0.019	0.049	-1.007
	CH₃	1.474	1.434	1.432	2.498	0.163	-0.875	0.934	-0.021	0.050	-1.006
	H	1.475	1.434	1.431	2.499	0.161	-0.877	0.933	-0.021	0.051	-1.006
	Cl	1.474	1.435	1.431	2.500	0.158	-0.883	0.932	-0.022	0.050	-1.008
	CN	1.475	1.436	1.431	2.502	0.152	-0.890	0.932	-0.022	0.050	-1.009
OCH₃	NH₂	1.469	1.428	1.438	2.487	0.176	-0.858	0.939	-0.014	0.048	-1.005
	OCH₃	1.472	1.428	1.437	2.491	0.170	-0.863	0.937	-0.015	0.048	-1.002
	CH₃	1.474	1.429	1.437	2.493	0.167	-0.867	0.935	-0.017	0.052	-1.005
	H	1.475	1.429	1.437	2.495	0.165	-0.870	0.935	-0.017	0.052	-1.005
	Cl	1.474	1.429	1.437	2.495	0.162	-0.875	0.934	-0.016	0.048	-1.003
	CN	1.476	1.430	1.436	2.497	0.155	-0.882	0.932	-0.017	0.049	-1.004
CH₃	NH₂	1.469	1.426	1.440	2.484	0.177	-0.853	0.939	-0.013	0.052	-1.002
	OCH₃	1.472	1.426	1.440	2.488	0.171	-0.858	0.937	-0.014	0.048	-0.999
	CH₃	1.475	1.426	1.440	2.490	0.167	-0.862	0.936	-0.014	0.049	-0.999
	H	1.476	1.426	1.440	2.491	0.165	-0.864	0.935	-0.015	0.049	-0.998
	Cl	1.475	1.426	1.440	2.491	0.166	-0.868	0.934	-0.014	0.048	-0.999
	CN	1.476	1.427	1.439	2.493	0.160	-0.875	0.932	-0.015	0.049	-1.000
H	NH₂	1.469	1.424	1.442	2.483	0.178	-0.852	0.942	-0.011	0.047	-0.998
	OCH₃	1.472	1.424	1.441	2.486	0.172	-0.855	0.938	-0.012	0.049	-0.997
	CH₃	1.475	1.424	1.441	2.488	0.169	-0.860	0.936	-0.013	0.050	-0.999
	H	1.476	1.424	1.441	2.490	0.167	-0.863	0.936	-0.013	0.049	-0.997
	Cl	1.475	1.425	1.441	2.490	0.163	-0.866	0.935	-0.013	0.049	-0.998
	CN	1.477	1.425	1.441	2.492	0.156	-0.873	0.932	-0.014	0.049	-0.999
Cl	NH₂	1.469	1.424	1.441	2.483	0.180	-0.853	0.937	-0.011	0.051	-1.002
	OCH₃	1.472	1.424	1.441	2.487	0.175	-0.857	0.936	-0.011	0.051	-1.001
	CH₃	1.475	1.424	1.441	2.489	0.171	-0.861	0.934	-0.012	0.051	-1.000
	H	1.476	1.425	1.440	2.490	0.169	-0.863	0.934	-0.013	0.052	-0.998
	Cl	1.475	1.425	1.440	2.490	0.166	-0.867	0.935	-0.014	0.049	-0.999
	CN	1.476	1.425	1.440	2.492	0.160	-0.873	0.934	-0.014	0.049	-0.999
CN	NH₂	1.469	1.423	1.442	2.480	0.183	-0.849	0.938	-0.009	0.051	-0.999
	OCH₃	1.473	1.423	1.442	2.484	0.177	-0.853	0.935	-0.010	0.051	-0.999
	CH₃	1.475	1.422	1.442	2.486	0.174	-0.857	0.933	-0.012	0.051	-0.998
	H	1.477	1.423	1.442	2.488	0.171	-0.859	0.932	-0.012	0.051	-0.998
	Cl	1.476	1.423	1.442	2.488	0.164	-0.864	0.934	-0.012	0.051	-0.999
	CN	1.477	1.423	1.441	2.490	0.162	-0.870	0.934	-0.012	0.050	-0.997

$^a\Delta d^{\ddagger} = d(TS) - d(R)$. $^b\Delta d^\circ = d(P) - d(R)$

electron withdrawing, endothermicity as well as the activation enthalpy decreases, causing the TS to become more reactant-like according to the Hammond postulate.[17] This can be seen from the $\Delta d_1^{\ddagger}$ bond length change (0.178 Å for Z=NH₂, Y=H *vs.* 0.156 Å for Z=CN, Y=H).

For Y-ring case, activation energy increases as the substituent becomes more electron withdrawing due to the destabilization of the TS (59.4 kcal mol⁻¹ for Y=NH₂, Z=H *vs.* 60.4 kcal mol⁻¹ for Y=CN, Z=H), and this is well described by the $\Delta d_1^{\ddagger}$ change (0.161 Å for Y=NH₂, Z=H *vs.* 0.171 Å for Y=CN, Z=H). However, the effect of the Y was weaker than the effect of the Z (*vide infra*).

The Hammett equation[18] was used to correlate the equilibrium (or rate) constant with the electronic property of the substituents in a reaction series and could be written as Eq. (5) when the entropy change is negligible in the series. σ^1

values[19] were used in the case of the Z-substituent to get a better correlation for strongly delocalized TS. The cross-interaction constant, ρ_{YZ}, was calculated using the multiple linear regression. Simple Hammett ρ_Y, ρ_Z^1 and cross-interaction ρ_{YZ} values are summarized in Table 4. Although negative ρ_Y values were observed in the Y-ring owing to the

$$\Delta H^{\ddagger}/(-2.3RT) = \rho\sigma \qquad (5)$$

positive charge development at the TS, their magnitude is quite small due to the smaller change in the activation enthalpies. However, ρ_Z^1 values were positive and large because the Z-ring was transferred to the neighboring nitrogen atom, N₂, and the activation energy depended in large measure on the substituents. As the Y-substituent becomes more electron donating, the electron density of the Z-ring

Table 2. Formal group charges of reactant and changes in formal charges. $\Delta q^{\neq}$, and Δq° in electronic charge unit

Y	Z	Reactant				$\Delta q^{\neq \, a}$				$\Delta q^{\circ \, b}$			
		NH₂	NH	Y-ring	Z-ring	NH₂	NH	Y-ring	Z-ring	NH₂	NH	Y-ring	Z-ring
NH₂	NH₂	0.59	0.07	0.16	0.18	-0.31	0.15	0.02	0.13	-0.45	0.38	0.03	0.04
	OCH₃	0.58	0.08	0.17	0.17	-0.29	0.15	0.03	0.12	-0.44	0.37	0.02	0.05
	CH₃	0.58	0.08	0.17	0.17	-0.28	0.15	0.03	0.11	-0.43	0.36	0.02	0.05
	H	0.57	0.08	0.18	0.17	-0.28	0.15	0.03	0.10	-0.42	0.36	0.02	0.05
	Cl	0.58	0.08	0.18	0.16	-0.27	0.15	0.03	0.10	-0.42	0.36	0.02	0.05
	CN	0.57	0.09	0.19	0.16	-0.26	0.15	0.03	0.08	-0.43	0.35	0.02	0.05
OCH₃	NH₂	0.60	0.06	0.15	0.19	-0.31	0.15	0.02	0.14	-0.46	0.39	0.04	0.03
	OCH₃	0.60	0.07	0.16	0.18	-0.30	0.14	0.03	0.13	-0.45	0.37	0.03	0.04
	CH₃	0.59	0.07	0.16	0.18	-0.29	0.14	0.03	0.11	-0.44	0.36	0.03	0.04
	H	0.59	0.07	0.16	0.18	-0.28	0.14	0.03	0.11	-0.43	0.36	0.03	0.05
	Cl	0.59	0.07	0.17	0.17	-0.28	0.15	0.03	0.10	-0.43	0.36	0.03	0.05
	CN	0.59	0.08	0.17	0.17	-0.27	0.15	0.04	0.09	-0.43	0.36	0.02	0.05
CH₃	NH₂	0.61	0.06	0.15	0.19	-0.32	0.15	0.02	0.14	-0.46	0.39	0.04	0.04
	OCH₃	0.60	0.06	0.15	0.18	-0.30	0.14	0.03	0.13	-0.45	0.38	0.04	0.04
	CH₃	0.60	0.06	0.16	0.18	-0.29	0.14	0.03	0.12	-0.44	0.37	0.03	0.04
	H	0.60	0.07	0.16	0.18	-0.29	0.14	0.03	0.11	-0.44	0.36	0.03	0.04
	Cl	0.60	0.07	0.16	0.18	-0.39	0.14	0.03	0.10	-0.44	0.36	0.03	0.04
	CN	0.60	0.07	0.17	0.17	-0.38	0.15	0.04	0.09	-0.43	0.36	0.03	0.05
H	NH₂	0.61	0.05	0.14	0.20	-0.32	0.15	0.03	0.15	-0.46	0.39	0.04	0.04
	OCH₃	0.61	0.06	0.15	0.19	-0.30	0.14	0.03	0.13	-0.45	0.38	0.04	0.04
	CH₃	0.60	0.06	0.15	0.19	-0.29	0.14	0.03	0.12	-0.44	0.37	0.03	0.04
	H	0.60	0.06	0.16	0.18	-0.29	0.14	0.03	0.11	-0.44	0.36	0.03	0.04
	Cl	0.60	0.06	0.16	0.18	-0.29	0.15	0.03	0.11	-0.44	0.37	0.03	0.04
	CN	0.60	0.07	0.16	0.17	-0.28	0.15	0.04	0.09	-0.44	0.36	0.03	0.05
Cl	NH₂	0.61	0.05	0.14	0.20	-0.32	0.15	0.02	0.15	-0.46	0.39	0.04	0.04
	OCH₃	0.61	0.06	0.14	0.19	-0.30	0.14	0.03	0.13	-0.45	0.38	0.04	0.04
	CH₃	0.60	0.06	0.15	0.19	-0.29	0.14	0.03	0.12	-0.44	0.37	0.03	0.04
	H	0.60	0.07	0.15	0.19	-0.29	0.14	0.03	0.12	-0.44	0.36	0.03	0.04
	Cl	0.60	0.07	0.15	0.18	-0.29	0.15	0.03	0.11	-0.44	0.37	0.03	0.04
	CN	0.60	0.07	0.16	0.17	-0.28	0.15	0.04	0.09	-0.44	0.36	0.03	0.05
CN	NH₂	0.62	0.05	0.13	0.20	-0.32	0.15	0.02	0.15	-0.47	0.39	0.04	0.04
	OCH₃	0.61	0.06	0.14	0.19	-0.31	0.14	0.03	0.14	-0.45	0.38	0.04	0.04
	CH₃	0.61	0.06	0.14	0.19	-0.30	0.14	0.03	0.12	-0.44	0.37	0.04	0.04
	H	0.61	0.06	0.14	0.19	-0.29	0.14	0.03	0.12	-0.44	0.37	0.03	0.04
	Cl	0.61	0.06	0.14	0.19	-0.29	0.14	0.03	0.11	-0.44	0.37	0.03	0.04
	CN	0.61	0.07	0.15	0.18	-0.28	0.15	0.04	0.10	-0.44	0.36	0.03	0.04

$^{a}\Delta q^{\neq} = q(TS) - q(R)$. $^{b}\Delta q^{\circ} = q(P) - q(R)$.

increases and does the ρ_Z' value ($\rho_Z' = 2.37$ for Y=NH₂ vs. $\rho_Z' = 2.32$ for Y=CN). Note that the cross-interaction constant, ρ_{YZ}, is quite small (-0.04) in this reaction. This is not unusual considering the geometrical characteristics. In the reactant, no resonance interaction exists between the Y- and Z-ring (smaller l_{YZ}°) and at the same time no mutual interaction exists between the two rings in the TS (smaller $l_{YZ}^{\neq}$), which results in a cross-interaction constant (see Eq. (3)) that is nearly zero. A similar trend was observed in the phenyl group rearrangement of the protonated ketone system[6] (Scheme 3). The origin of a small cross-interaction constant, however, is quite different. In the latter reaction, difference between two strong interactions of two rings in the reactant as well as in the TS results in a smaller ρ_{YZ} value (0.03).

In order to further examine the tendencies reported above, the Swain-Lupton dual substituent equation.[20] Eq. (6), was applied. The results are summarized in Table 5. The F and R in Eq. (6) refer to the field and the resonance constant.

$$-\Delta H^{\neq} /2.3RT = fF - rR \qquad (6)$$

respectively, and r and f are the susceptibility of each effect. Table 5 shows that the r/f values of the Z-ring are always greater than 2, whereas those of the Y-ring are always less than 1. This means that the resonance and field effects are greatly increased in the Z-ring and Y-ring, respectively, which is in line with the conclusions drawn from the Hammett constants (ρ_Y, ρ_Z) and the cross-interaction constant.

Table 3. Heat of formation of reactant (R), TS, product (P) and activation ($\Delta H^{\neq}$) and reaction (ΔH^0) enthalpies

Y	Z	$\Delta H_f(R)$	$\Delta H_f(TS)$	$\Delta H_f(P)$	$\Delta H^{\neq}$	ΔH^0
NH₂	NH₂	225.02	288.94	233.55	63.92	8.53
	OCH₃	192.42	254.31	200.58	61.89	8.16
	CH₃	223.17	283.26	231.36	60.09	8.19
	H	232.02	291.42	240.12	59.40	8.10
	Cl	227.55	286.69	235.50	59.14	7.95
	CN	269.66	327.21	277.41	57.55	7.75
OCH₃	NH₂	191.83	255.96	200.58	64.13	8.75
	OCH₃	159.42	221.51	167.97	62.09	8.55
	CH₃	190.23	250.52	198.69	60.29	8.46
	H	199.16	258.74	207.58	59.58	8.42
	Cl	194.76	254.12	203.07	59.36	8.31
	CN	237.01	294.82	245.13	57.81	8.12
CH₃	NH₂	222.56	286.72	231.36	64.16	8.80
	OCH₃	190.23	252.31	198.69	62.08	8.46
	CH₃	221.06	281.38	229.50	60.32	8.44
	H	230.02	289.62	238.35	59.60	8.33
	Cl	225.65	285.03	233.86	59.38	8.21
	CN	267.95	325.80	275.96	57.85	8.01
H	NH₂	231.16	295.46	240.12	64.30	9.05
	OCH₃	198.88	261.11	207.58	62.23	8.70
	CH₃	229.74	290.20	238.35	60.46	8.61
	H	238.72	298.46	247.28	59.74	8.56
	Cl	234.38	293.91	242.83	59.53	8.45
	CN	276.73	334.74	284.98	58.01	8.25
Cl	NH₂	226.21	290.82	235.50	64.61	9.29
	OCH₃	194.00	256.54	203.07	62.54	9.07
	CH₃	224.89	285.66	233.86	60.77	8.97
	H	233.89	293.94	242.83	60.05	8.94
	Cl	229.58	289.43	238.54	59.85	8.96
	CN	271.97	330.33	280.74	58.36	8.77
CN	NH₂	267.75	332.67	277.41	64.92	9.66
	OCH₃	235.67	298.54	245.13	62.87	9.46
	CH₃	266.60	327.68	275.96	61.08	9.36
	H	275.66	336.02	284.98	60.36	9.32
	Cl	271.39	331.58	280.74	60.19	9.35
	CN	313.88	372.59	323.14	58.71	9.26

Table 4. Simple Hammett ρ values and cross-interaction constants. ρ_{YZ}

Y or Z	NH₂	OCH₃	CH₃	H	Cl	CN	
$\rho_Y^{a,b}$	-0.59	-0.57	-0.58	-0.56	-0.61	-0.67	$\rho_{YZ}= -0.038$
$\rho_Z^{b,c}$	2.37	2.36	2.35	2.34	2.33	2.32	(r=0.99)

$^a\sigma$ values are used. ^{b}all correlation coefficients are better than 0.98. $^c\sigma/\sigma^-$ values are used.

Conclusion

Phenyl group rearrangement of protonated 1,2-diphenyl hydrazines is a one-step reaction that proceeds through a three-membered bridged TS. This reaction is endothermic, producing sterically crowded product and thus requires a relatively higher activation energy. A more electron withdraw-

Table 5. Dual substituent parameter analysis

		f	r	r/f	r⁰
Z-ring	Y=NH₂	0.59	1.31	2.22	0.988
	Y=OCH₃	0.55	1.30	2.36	0.987
	Y=CH₃	0.55	1.30	2.36	0.986
	Y=H	0.54	1.30	2.41	0.986
	Y=Cl	0.52	1.29	2.48	0.985
	Y=CN	0.49	1.29	2.63	0.985
		f	r	r/f	r⁰
Y-ring	Z=NH₂	-0.39	-0.17	0.44	0.998
	Z=OCH₃	-0.41	-0.16	0.39	0.996
	Z=CH₃	-0.39	-0.17	0.44	0.998
	Z=H	-0.39	-0.16	0.41	0.996
	Z=Cl	-0.41	-0.17	0.41	0.998
	Z=CN	-0.44	-0.20	0.45	0.999

^{0}correlation coefficient.

ing Z and a more electron donating Y lower the activation barrier.

The ρ_Y values are small because the Y-ring does not participate in the reaction directly, but the ρ_Z^+ values are large because the Z-ring is involved in the reaction. The absence of resonance interaction between the rings in the reactant and the TS owing to the saturation of nitrogen valence in both states, results in a small cross-interaction constant. This was confirmed by the results obtained from the dual substituent equation.

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