π Complexes in benzidine rearrangement†

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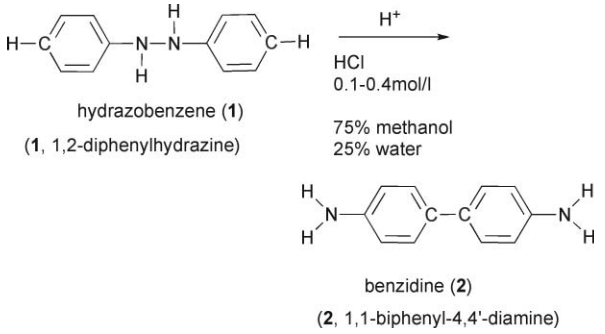
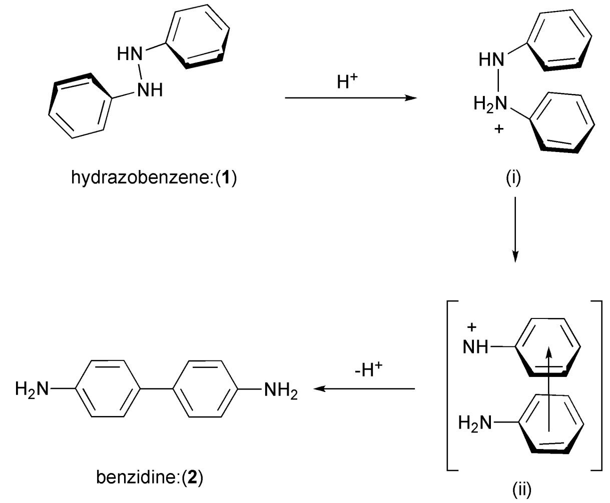
By the use of DFT calculations, the title rearrangement, Ph–NH–NH–Ph (**1**) → $H_2N–C_6H_4–C_6H_4–NH_2$ (**2**), was studied for the first time. Although it is a classical reaction (found in 1862), its mechanism is almost entirely unknown. There are three complexities associated with this mechanism. The first is the various rate orders for substituted hydrazobenzenes. The second is the product distribution. The third is the result of the kinetic isotope effect which is difficult to interpret. A reaction model, **1**, $(H_3O^+)_2$ and $(H_2O)_{10}$ was used to trace the reaction path. Two hydronium ions were included, because there are two nitrogen atoms in **1**. In the paths of the main reaction, **1**$(H^+)_2$ → **2**H^+ + H^+, transient intermediates were found. Through their conversion, the second product, diphenyline (**3**), was reached. For **1**H^+, only the Claisen shift path was found, and the π complex proposed by Dewar was not found. The absence is in accord with the kinetic result of Hammond and Shine. But the complex was revealed in the dimethoxyhydrazobenzene. Thus, while Dewar's π complex was ruled out in 1950, it has been revived by the present calculations.

I. Introduction

Scheme 1 shows the parent benzidine rearrangement. Apparently, it is a simple reaction where the N–N covalent bond in hydrazobenzene (**1**) is converted to the C–C bond in benzidine (**2**). It was found by Hofmann in 1862.[1] In spite of the apparent simplicity, the reaction has been assessed as having an "exceptional complexity".[2] In 1922, Jacobson surveyed the rearrangement extensively,[3] which promoted studies of the reaction mechanism. Particularly at the middle of the 20th century, controversies of the mechanism were like "battles" between Dewar on one hand and Banthorpe, Ingold and Hughes on the other.[4] Dewar's innovative postulate, "π complex" (ii) in Scheme 2,[5] was the source of the controversies.



Scheme 1 The parent benzidine rearrangement.



Scheme 2 Dewar's proposal of an intermediate (ii), "π complex".

In the scheme, a proton is attached to one nitrogen atom. Scission of the N–N bond leads to the π complex (ii). At that time, the postulate was very striking and called for the controversies. But, in 1950, Hammond and Shine reported that the rearrangement in Scheme 1 obeys not the second-order but the third- order rate equation in eqn (1).[6]

$$-d[\mathbf{1}]/dt = k[\mathbf{1}][H^+]^2 \qquad (1)$$

The result of the rate measurement indicates that the di-protonated form of the hydrazobenzene, **1**$(H^+)_2$, undergoes the rearrangement. Thus, the Dewar's postulate in Scheme 2 was ruled out. Since the first work in 1950, Shine continued his kinetic studies of the rearrangement and published 24 papers over 40 years.[6–29] His and related studies are reviewed briefly below.

The parent hydrazobenzene (**1**) gives not only benzidine (**2**, 70%) but also diphenyline (**3**, 30%).[30] A different product ratio (**2** 85% and **3** 15%) was reported by Shine and coworkers.[29] In contrast to the rate equation in eqn (1), *N*,*N*′-di(1-naphthyl)hydrazine (**8**) obeys the second-order equation (Scheme 3(a)).[26] As a more complex case, *N*,*N*′-di(2-methylphenyl)hydrazine (**13**) obeys the odd order equation (Scheme 3(b)).[31] The unclear order of rate

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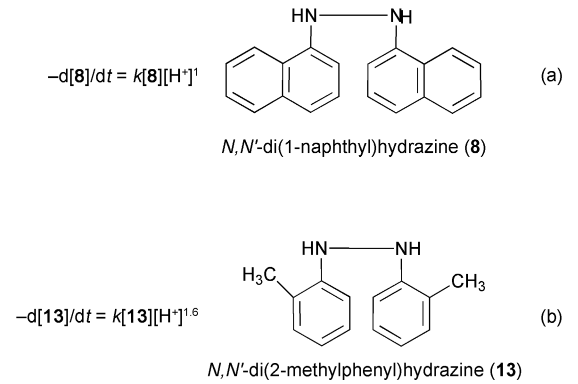
† Electronic supplementary information (ESI) available: Schemes S1–3; Fig. S1–12. See DOI: 10.1039/b909313c



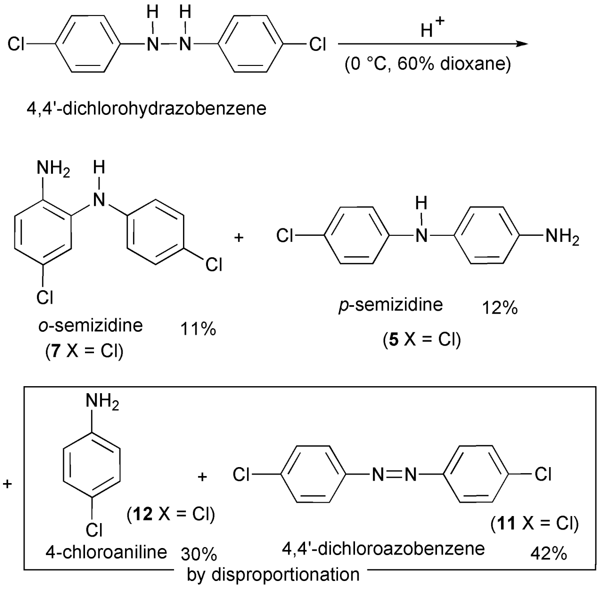
Scheme 3 Rate equations which depend on hydrazine substrates.

equations is the first reason of the complexity of benzidine rearrangement.

The second complexity is in product distributions in Scheme 4.[4a] X-Substituted hydrazobenzenes give *p*-semidine (**5**) and *o*-semidine (**7**). Hydrazonapthalene (*N*,*N*′-di(1-naphthyl)hydrazine **8**, Scheme 3(a)) gives **9** in Scheme 4(d). Disproportionation of $(\mathbf{10})_2$ leads to **11** and **12** in Scheme 4(e). For X = Cl, those four products are generated (Scheme 5).[28]

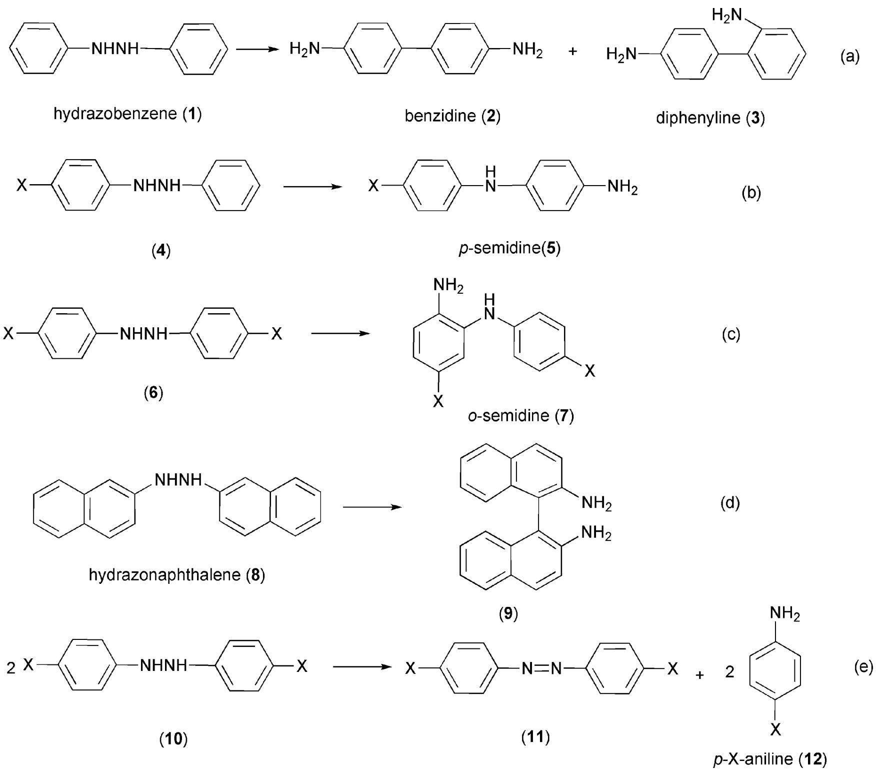
The most typical benzidine rearrangement is attained by the 2,2′-dimethoxyhydrazobenzene (**14**) substrate (Scheme 6).[25] 3,3-Dimethoxybenzidine (**15**) was afforded exclusively with the second-order rate equation, *i.e.*, $-\mathrm{d}[\mathbf{14}]/\mathrm{dt} = k[\mathbf{14}][\mathrm{H}^+]$.

The third complexity is in the kinetic isotope effect (KIE). Representative KIE data and their discussions[22] are exhibited in Scheme 7. From the hydrazobenzene (**1**), benzidine (**2**) was found to be afforded concertedly and diphenyline (**3**) to be afforded in a stepwise route. It is strange that the two products are derived from the different mechanisms.

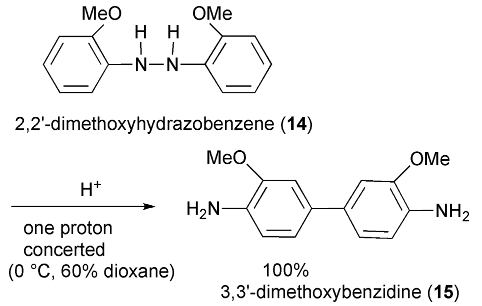


Scheme 5 Rearrangement products of 4,4′-dichlorohydrazobenzene.

Although Shine was extensively engaged in kinetic study of benzidine rearrangement, still the mechanism, with it's three complexities, remained hidden. "Despite many studies conducted over 100 years, there remain many problems which should be solved."[32] In March's textbook,[33] the rearrangement is explained concisely and the formation of **3** (2,4′-diaminobiphenyl) is noted to have an unclear mechanism. Although Shine ruled out the Dewar's



Scheme 4 Distributions of rearrangement products.



Scheme 6 Rearrangement of 2,2′-dimethoxyhydrazobenzene.

π complex theory kinetically, he seemed to be in favor of the theory (the title of his review,[4a] "Reflections of the π-complex theory…").

In this work, the rearrangement was investigated by means of DFT calculations. Surprisingly, there have been no computational studies on benzidine rearrangement. It is a prime question whether the Dewar's π complex is really invalid or is involved in the rearrangement. Hydrogen bonds concerned with the rearrangement were considered explicitly to describe proton relays.

II. Calculation method

The geometries were determined by density functional theory calculations. The B3LYP method[34] was used for geometry optimizations. B3LYP seems to be a suitable method, because it includes the electron correlation effect to some extent. RB3LYP/6-31G* and B3LYP/6-311+G** geometry optimizations and subsequent vibrational analyses were conducted. Energies were refined by single point calculations of B3LYP/6-311+G** SCRF=(PCM, solvent = water)[35] on the B3LYP/6-311+G** geometries.

Transition states (TSs) were characterized by vibrational analyses, which checked whether the obtained geometries have single imaginary frequencies ($\nu^{\ddagger}$s). From TSs, reaction paths were traced by the IRC (intrinsic reaction coordinate) method[36] to obtain the energy-minimum geometries. The Gibbs free energy was estimated by the use of the equations of molecular thermodynamics. That is, the free energy was calculated by the 6-311+G** SCRF=PCM electronic energy, the Cartesian coordinates of the optimized B3LYP/6-311+G** geometries and the harmonic frequencies. Biradical characters of the transient π-complex intermediates were evaluated by CISD/6-31G* single-point calculations.

The B3LYP method sometimes affords problems involving middle range interactions like aromatic–aromatic stacking.[37] In order to check them, MPWBIK/6-31G* calculations[38] were also carried out on key π complexes.

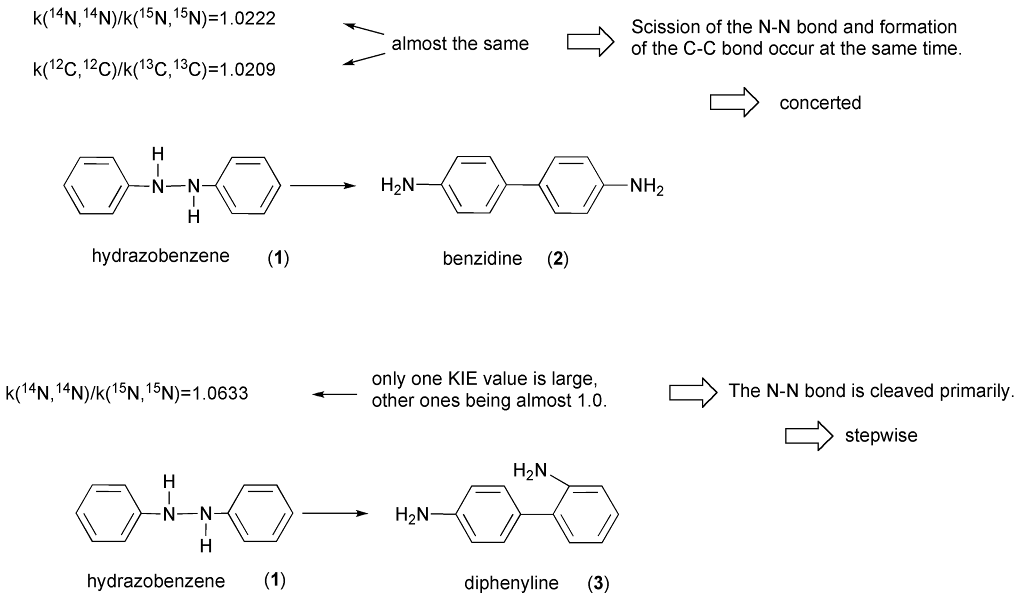
All the calculations were carried out using the *GAUSSIAN 03*[39] program package at Research Center for Computational Science, Okazaki, Japan.

III. Calculated results and discussions

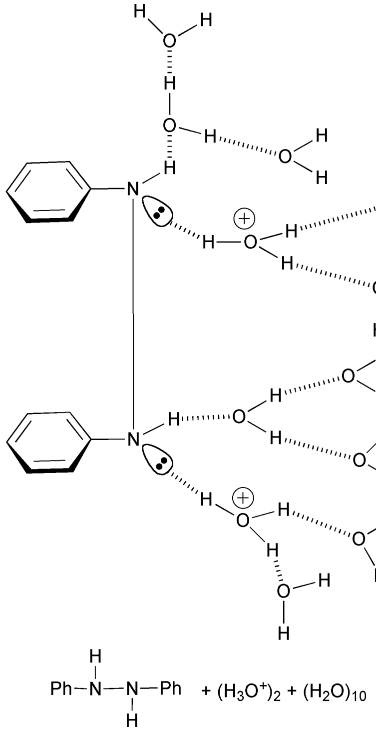
Rearrangement of the parent substrate to benzidine in the di-protonated form

Scheme 8 shows the reaction model to trace the reaction path. In accordance with eqn (1), two hydronium ions, $(H_3O^+)_2$, are included. Even without information of eqn (1), the two are needed, because the two nitrogen lone-pair electrons attract protons strongly (*cf.* proton affinities, 166.3 kcal mol^{-1} (H_2O) << 203.6 kcal mol^{-1} (NH_3), 1 kcal = 4.184 kJ). Ten water molecules are added to the model so as to simulate hydrogen bonds around them.

First, the main path, *i.e.*, **1** → **2**, was investigated. It is shown in Scheme 9 and Fig. S1 in the ESI.† "Precursor" means the hydrazobenzene reactant where one proton is attached to one nitrogen. The nitrogen site has a large proton affinity (224.4 kcal mol^{-1} by RB3LYP/6-311+G** electronic and zero-point energies), and the initial geometry of **1** + $(H_3O^+)_2$ + $(H_2O)_{10}$ is converted to that of **1**H$^+$ + $(H_3O^+)_1$ + $(H_2O)_{10}$ by many attempts. Therefore, the "precursor" geometry was taken to be the starting one. The second proton is moved to the second nitrogen at TS1. The di-protonated substrate, **1**$(H^+)_2$, was formed ("Int1"). At Int1, the N–N distance is large (= 1.5557 Å compared to 1.45 Å of the



Scheme 7 Different kinetic isotope effects lead to different products.[22]

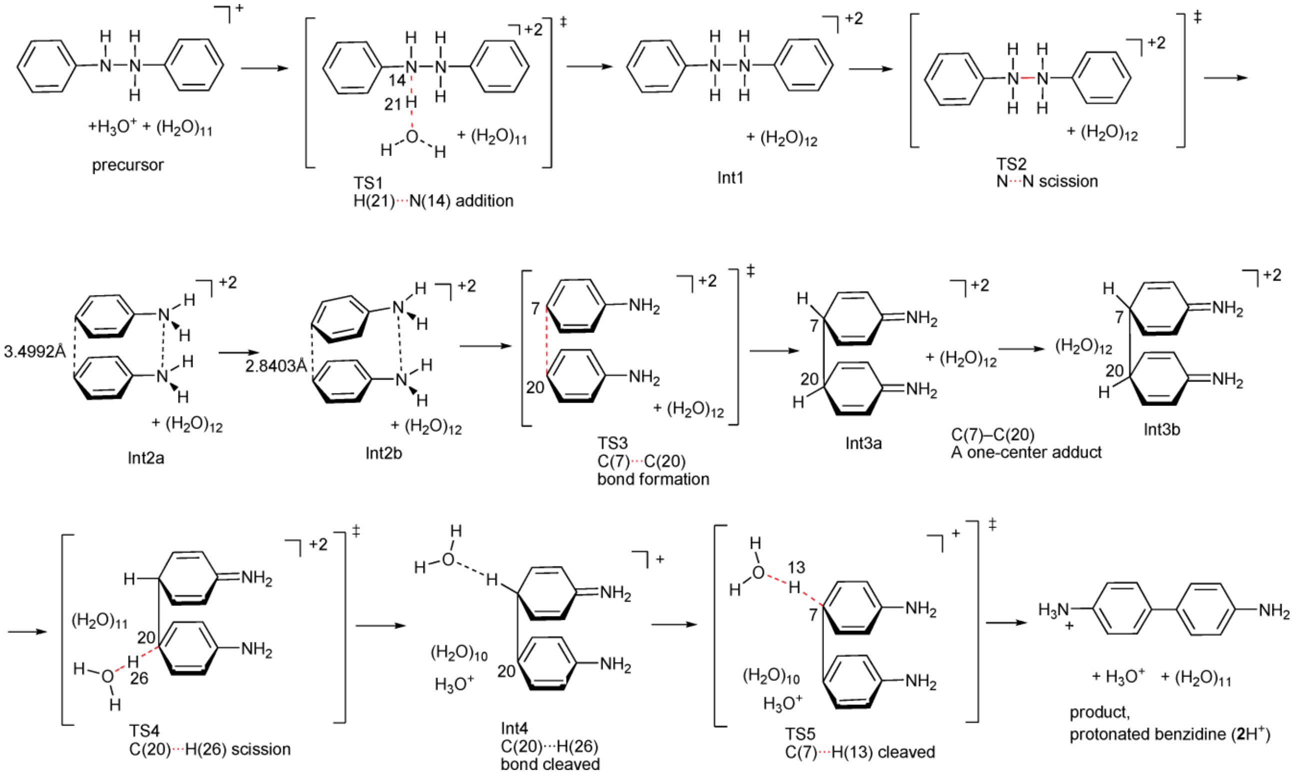


Scheme 8 A reaction scheme adopted in this work.

normal average N–N single bond). However, the bond is not cleaved. The scission TS was sought and was obtained as TS2, where the N···N distance is 1.9026 Å. After TS2, the second intermediate, Int2a, was reached, where two aniline–dication moieties are separated. A π complex was obtained. The distance between two *para* carbon atoms is 3.4992 Å, which is similar to that (= 3.4 Å) in the graphite layer. When the distance is shortened slightly, an isomer, Int2b, was found. From Int2b, the C···C forming TS, TS3, and the subsequent adduct Int3a were obtained. In Int3a, the water aggregate is near two amino groups. The aggregate is converted to the opposite (*para*) region to simulate the deprotonation path. The conversion is needed in the model with the limited number of water molecules. Then, an isomer, Int3b, was reached. The intermediate Int3a or Int3b, *i.e.*, di-C-protonated benzidine was observed as a stable species in super acid solution at −78 °C.[40] It is reasonable that deprotonation from the intermediate is difficult under the very acidic condition and it is trapped spectroscopically. From Int3b, deprotonation processes, Int3b → TS4 → Int4 → TS5, lead to the product, the protonated benzidine (**2**H$^+$). The concerted path, $\mathbf{1}(\mathrm{H}^+)_2 \rightarrow \mathbf{2}(\mathrm{H}^+)_2$, was suggested kinetically[22] which is a [5,5] sigmatropic rearrangement. However, it was not obtained computationally. Int2a is absent in gas phase (Fig. S2 in the ESI†).

Rearrangement of the parent substrate to other products in the di-protonated form

In Fig. S1,† Int2a has a geometry of the nearly parallel aniline planes and is the unstable (transient) intermediate. Its mobility gives a different intermediate to Int2b, Int5, *via* slight slide movement (Fig. 1). In Int5, two intermolecular distances, C(6)···C(16) = 2.8614 Å and C(2)···N(21) = 2.9231 Å, are small. Shortening them would lead to products other than the benzidine (**1**). Scheme 10 and Fig. S3† exhibit geometric changes starting



Scheme 9 Reaction paths of [**1**H$^+$ + H$_3$O$^+$(H$_2$O)$_{11}$] → [**2**H$^+$ + H$_3$O$^+$(H$_2$O)$_{11}$]. Geometries of precursor, TSs, intermediates and product are shown in Fig. S1 in the ESI.†

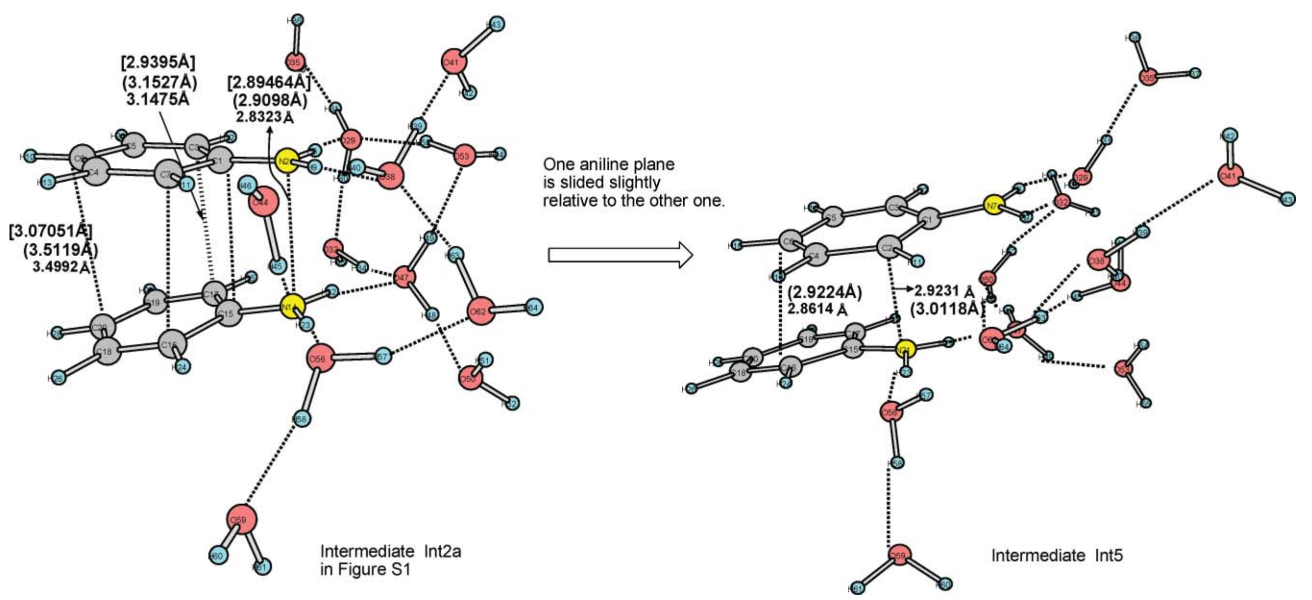
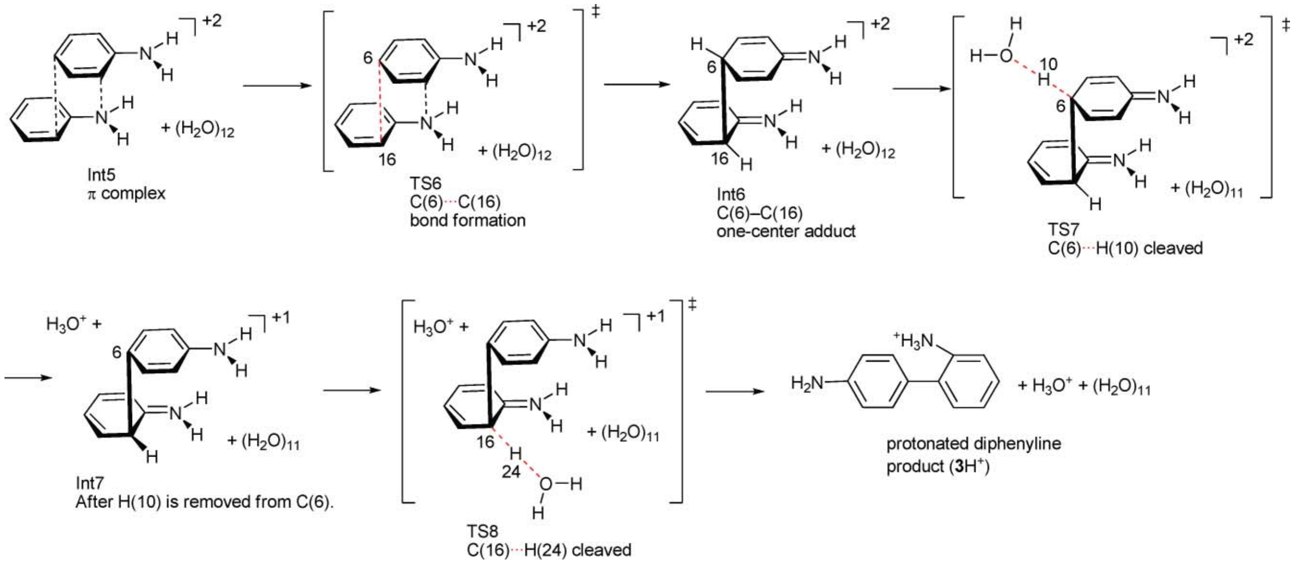


Fig. 1 Two isomeric π complexes in the stacked form, Int2a and Int5. RB3LYP/6-31G* and RB3LYP/6-311+G** distances are shown without and with parentheses, respectively. In square brackets, MPWB1K/6-31G* distances are shown. The geometry of Int5 is converted to that of Int6 in Fig. S3-2† with MPWBIK/6-31G*.



Scheme 10 Reaction paths of Int5 → [$3H^+$ + $H_3O^+(H_2O)_{11}$]. Each geometry is shown in Fig. S3.†

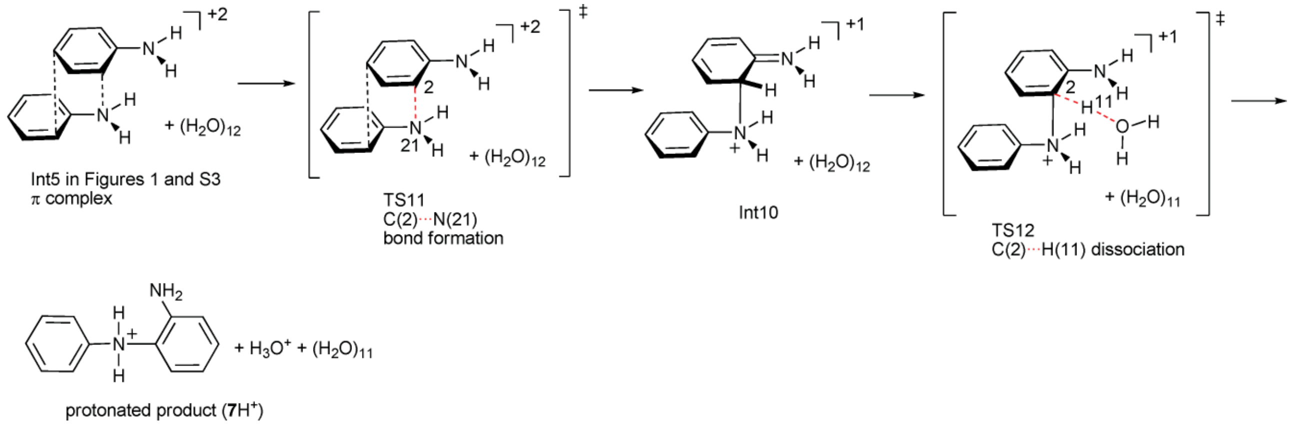
from Int5, where the distance of C(6) ··· C(16) is shortened. In the Fig., the path, Int5 → TS6 → Int6 → TS7 → Int7 → TS8 → $\mathbf{3}H^+$, is shown.

Scheme 11 and Fig. S4† show those with the shortened C(2) ··· N(21) distance. The path, Int5 → TS11 → Int10 → TS12 → $\mathbf{7}H^+$(X = H), was obtained. From the di-protonated hydrazobenzene ($\mathbf{1}H_2^{+2}$), the straightforward route is brought about by a "seesaw" motion, $\mathbf{1}H_2^{+2} \rightarrow \mathbf{2}H_2^{+2}$ in Fig. S1.† During the motion a, bypass, Int2a → Int5, may be present where there are no covalent bonds between aniline moieties. The intermediate Int5 has two reaction channels (to $\mathbf{3}H^+$ and to $\mathbf{7}H^+$(X = H)).

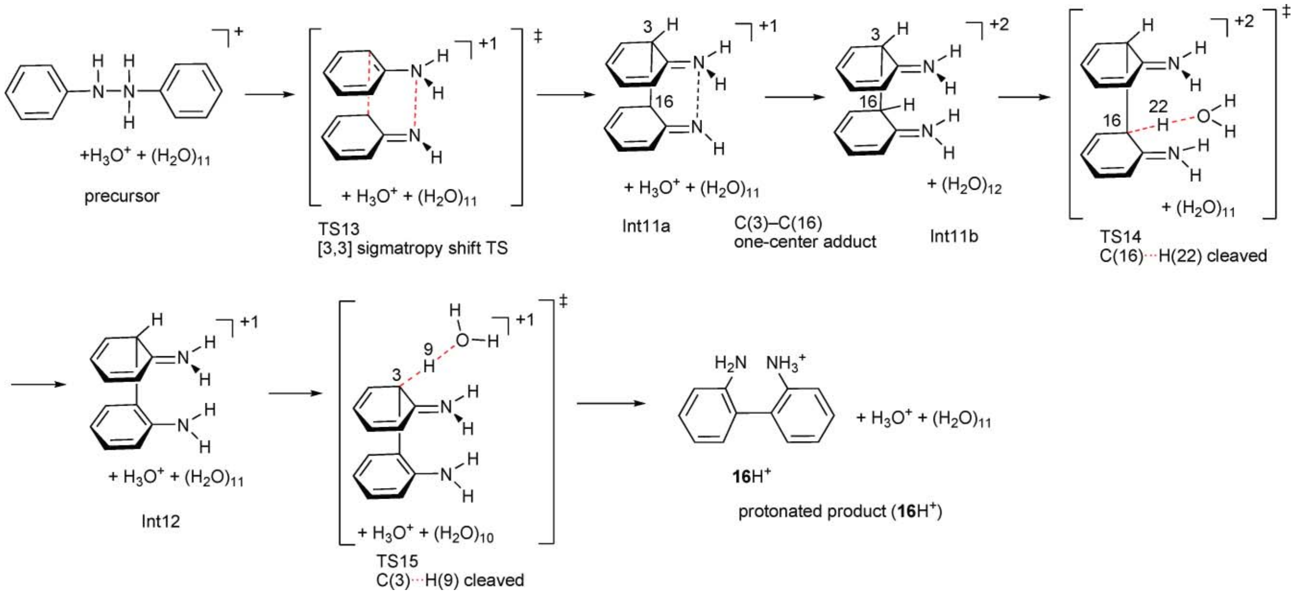
Another route leading to *p*-semidine (**5** X = H) was sought. However, its precursor π complex could not be found after many attempts of Scheme S1 and Fig. S6 and S7 in the ESI.† Thus, the parent hydrazobenzene (**1**) in the di-protonated form was computed to give benzidine (**2**), diphenyline (**3**) and *o*-semidine (**7** X = H). However, experimentally **7** (X = H) was not obtained, which will be discussed energetically.

Rearrangement of the parent substrate to the other product in the mono-protonated form

So far, rearrangements in the di-protonated reactant ($\mathbf{1}H_2^{+2}$) have been investigated. It is a question whether the mono-protonated substrate ($\mathbf{1}H^+$) really has no reactivity of any rearrangements. A reaction, Claisen shift,[41] was found. The route is shown in Scheme 12 and Fig. S5.† The precursor is the same as that in Fig. S1.† A [3,3] sigmatropic shift is TS13, where scission of



Scheme 11 Reaction paths of Int5 → [$7H^+ + H_3O^+(H_2O)_{11}$]. Each geometry is shown in Fig. S4.†



Scheme 12 Reaction paths of [$\mathbf{1}H^+ + H_3O^+(H_2O)_{11}$] → [$\mathbf{16}H^+ + H_3O^+(H_2O)_{11}$]. Each geometry is shown in Fig. S5.†

N(2)···N(14) and formation of C(16)······C(3) occur at the same time. After TS13, changes of Int11a,b → TS14 → Int12 → TS15 → $\mathbf{16}H^+$ were calculated. The route does not contain π complexes. The product $\mathbf{16}H^+$ was not obtained experimentally,[4a] while hydrazonaphthalene (**8**) gives this kind of product (**9**) (Schemes 3(a) and 4). Scheme S2 and Fig. S8 in the ESI† explain the effect of the naphthyl ring on the reactivity.

Changes of Gibbs free energies

Fig. 2 shows energy changes along the paths in Fig. S1, S3, S4 and S5.† The one-proton process has a rate-determining step, TS 13 (Claisen shift) with a significantly large $\Delta G^{\ddagger}$ value (= +20.55 kcal mol^{-1}). This process is ruled out, which is consistent with eqn (1). From Int1 with two protons, $Ph–NH_2–NH_2–Ph^{+2}$, the transient (unstable) intermediate, Int2a, is formed. One isomerization, Int2a → Int2b, leads eventually to the protonated benzidine ($\mathbf{2}H^+$). Energy changes along Int2a → → → $\mathbf{2}H^+$ are most favorable both kinetically and thermodynamically. The other isomerization, Int2a → Int5, eventually gives both the protonated diphenyline ($\mathbf{3}H^+$) and the protonated *o*-semidine ($\mathbf{7}H^+$ X = H). However, the route toward $\mathbf{7}H^+$ has a rate-determining step, TS11, with a somewhat large $\Delta G^{\ddagger}$ value (= +10.27 kcal mol^{-1}). More unfavorably, the product $\mathbf{7}H^+$ is much more unstable than $\mathbf{2}H^+$ and $\mathbf{3}H^+$. Thus, the preference for benzidine formation followed by that of diphenyline formation has been shown by the energy diagram of Fig. 2.

Discovery of the Dewar's π complex and substituent effects

Scheme 6 has shown the rearrangement with exclusive benzidine formation from the mono-protonated substrate, 2,2′-dimethoxyhydrazobenzene ($\mathbf{14}H^+$).[25] The involvement of Dewar's π complex is expected. In fact, the complex was found (Fig. 3, right side)! Two methoxy groups attached to the hydrazobenzene skeleton give a clear donor–acceptor complex. The complex may even be present in the gas phase (Fig. S9†). When the two MeO groups are replaced by two hydrogens, the geometry of the π complex disappeared and that of the precursor was recovered (Fig. S10†). For the mono-protonated parent substrate, $\mathbf{2}H^+$, Dewar's π complex is absent.

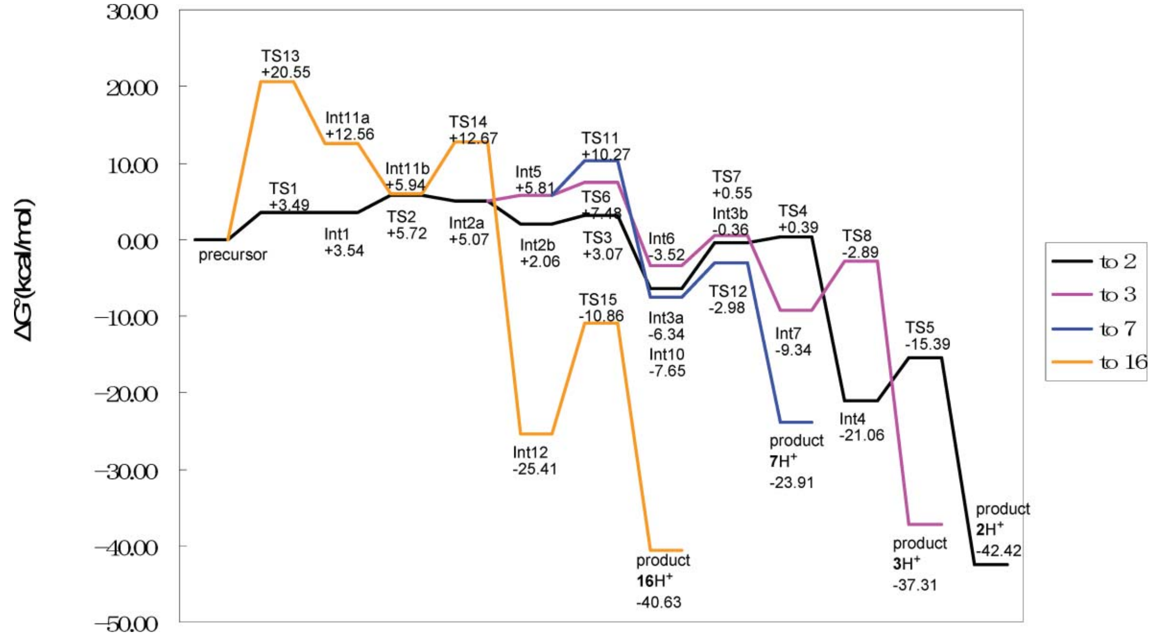


Fig. 2 ΔG° changes ($T = 298.15$ K and $P =$ atm) of reactions in Scheme 9 (Fig. S1), Scheme 10 (Fig. S3), Scheme 11 (Fig. S4) and Scheme 12 (Fig. S5)† which were calculated by RB3LYP/6-311+G** SCRF=(PCM, solvent = water)//RB3LYP/6-311+G**.

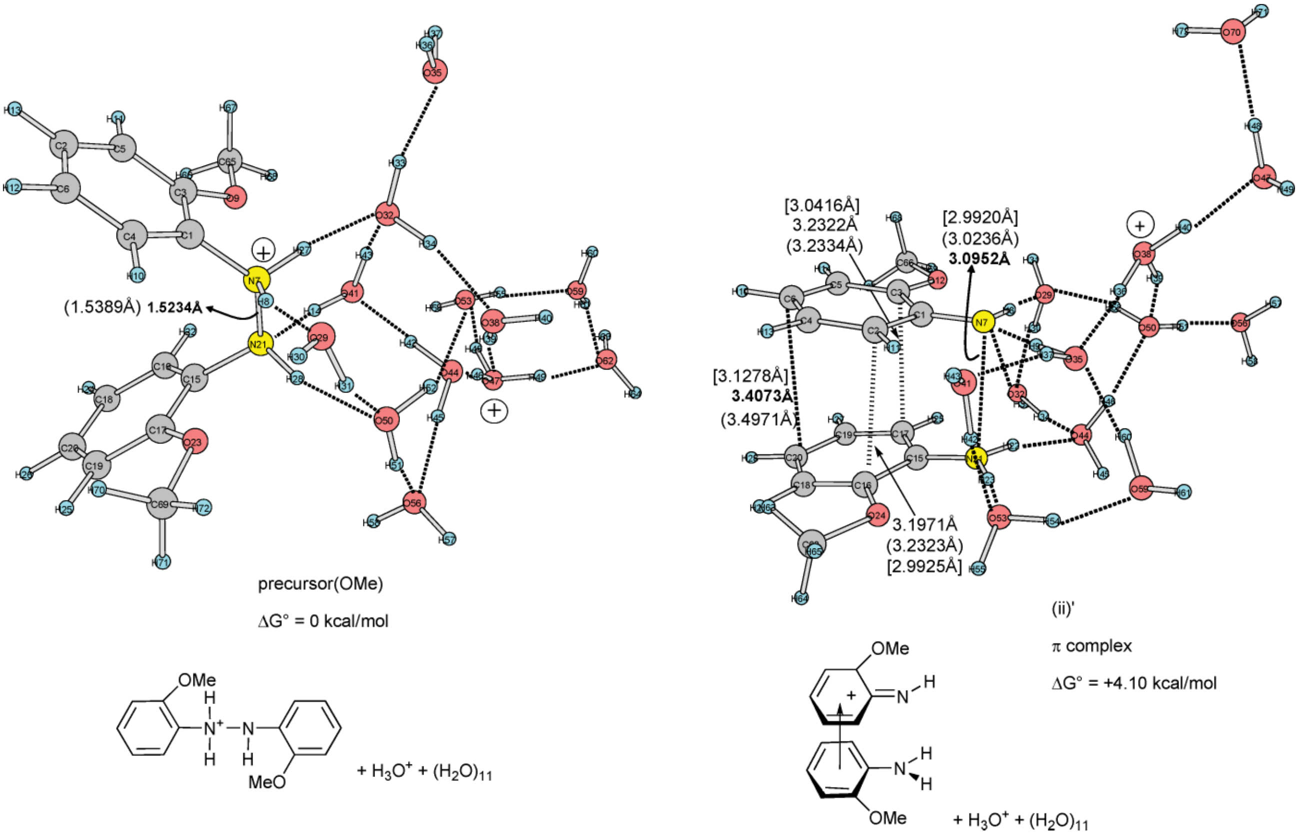
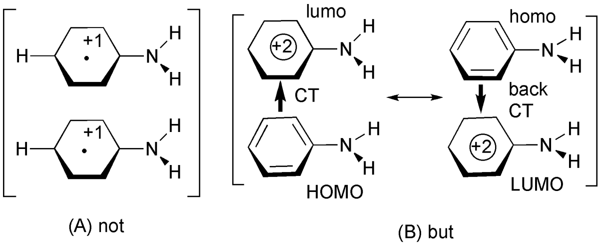


Fig. 3 Geometries of the protonated 2,2′-dimethoxyhydrazobenzene (**14**) and the π complex in the mono-protonated form. The notation, (ii)′, means Dewar's π complex (ii) in Scheme 2 for the dimethoxy substituted substrate. RB3LYP/6-31G* and RB3LYP/6-311+G** distances are shown without and with parentheses, respectively. In square brackets, MPWB1K/6-31G* distances are shown.

Scheme 5 has shown that **11** and **12** were obtained as the main products for X = Cl.[28] Fig. S11 in the ESI† shows the path. The first intermediate, Int13a, in an interacting system between the π complex $(Cl–C_6H_4-NH_2)_2^{+2}$ and a neutral substrate, 4,4′-dichlorohydrozobenzene. While the di-cation character is delocalized in the π complex, the isomerization of Int13a → Int13b gives 4-chloroaniline and 4-chloroaniline^{+2}. The di-cation moiety is coordinated in the stack configuration to the neutral substrate. The coordination causes a proton movement at TS16 and results in formation of products, **12**H^+ X = Cl, **11**H^+ X = Cl and 4-chloroaniline. Thus, the disproportionation is initiated by two hydrogen bonds where chlorine substituents enhance their formation.

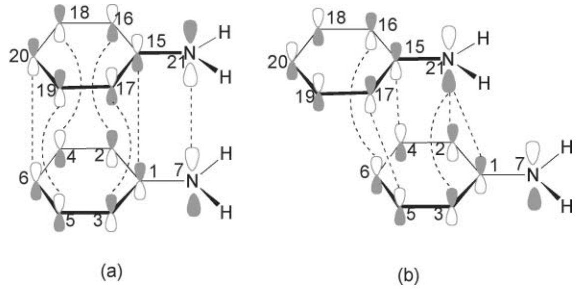
IV. Frontier orbital interactions involved in π complexes

It is of mechanistic interest to examine the source for stabilizing π complexes. Except for twelve water molecules, the complex, Int2a in Fig. 1, is the aniline dimer dication $(Ph-NH_2)_2^{+2}$. Scheme 13 shows two types of cation assignment, (A) and (B).



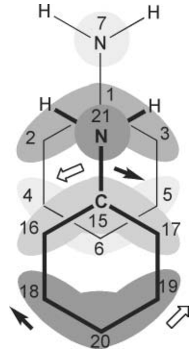
Scheme 13 Interactions for formation of the di-cation π complexes. CT is the charge transfer.

Historically, radical species of (A) were sought by ESR spectroscopy but were not detected.[32] Single-point CISD/6-31G* calculations were made to judge electronic structures of the π complexes. For the dimer geometries of Int2a and Int5a without $(H_2O)_{12}$, the largest CI coefficients are 0.037 and 0.035 of HOMO → LUMO double excitation, respectively. These small values indicate that complexes of $(aniline)_2^{+2}$ do not involve the biradical character in (A). Thus, the mutual (HOMO → lumo and homo → LUMO) charge transfers (CTs) should work to stabilize them. They are shown in Scheme 14.



Scheme 14 The orbital overlaps to give CT and back-CT interactions. Orbital shapes of HOMO (and homo) of aniline and LUMO (and lumo) of aniline dication are similar. Scheme 14(b) shows the second orbital overlap to support the slided configuration, where signs of orbital lobes of the upper aniline plane are switched.

Scheme 14(b) shows the MO overlap in the slided geometry, which has C_s symmetry by the gas-phase geometry optimization. The C_s symmetry may be distorted (rotated) slightly to reach the geometry of Int5 *via* the in-phase overlap region (Scheme 15). The CT interaction involved in the monoprotonated π complex of 2,2′-dimethoxyhydrazobenzene of Fig. 3 is illustrated in Scheme S3.† Two monoprotonated π complexes of 2-methoxyhydrazobenzene are also found and shown in Fig. S12.†

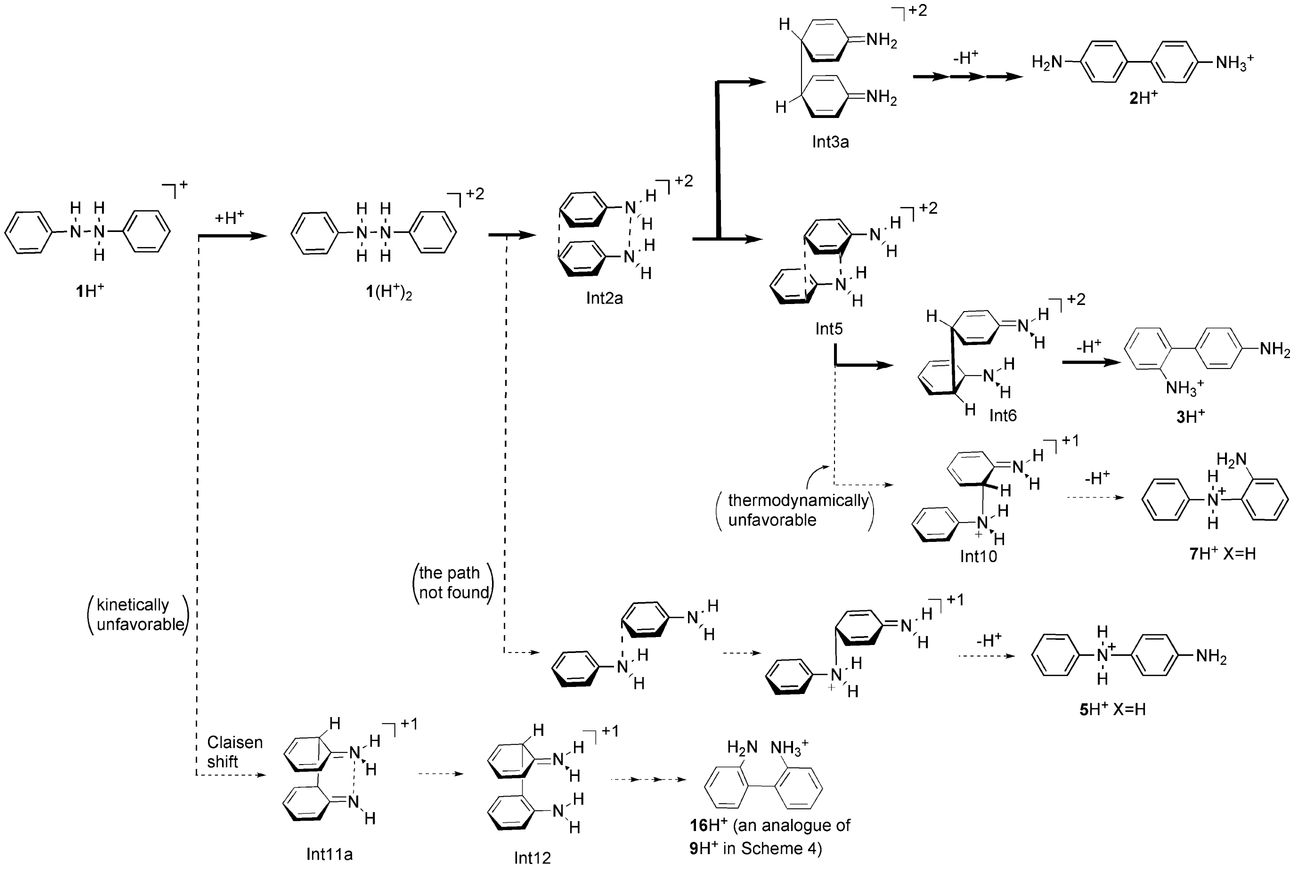


Scheme 15 The C_s-symmetry geometry supported by the second orbital overlap may be distorted in the in-phase region to reach the geometry of Int5 with either N(21)—C(3) and C(17)—C(6) or N(21)—C(2) and C(16)—C(6) vertical interactions.

V. Concluding remarks

In this work, benzidine rearrangement has been investigated theoretically. The reaction has three mechanistic problems, various rate orders, product distributions and inexplicable KIE results. By the use of the H_2O containing models, elementary processes have been unveiled for the first time. The main route, **1** → **2** in the di-protonated form, was found to be "nearly concerted"; the energies become lowered almost monotonically in spite of various intermediates. A bypass, Int2a → Int5, may give the second product **3**. Energy changes towards **3** are also likely, while TS6 has an appreciable energy, $\Delta G^{\ddagger} = +7.48$ kcal mol^{-1}. The third product **7** is also possible kinetically but unlikely thermodynamically. The π complexes (Int2a and Int5) come from mutual charge transfer interactions. A channel of the Claisen shift has been found in the mono-protonated form. However, its activation energy is too large to coexist with benzidine rearrangement. Naphthyl rings are needed to cause the Claisen shift. Scheme 16 shows a summary of the present study. Dewar's π complex for the parent hydrazobenzene was also ruled out in the present calculations, but it has been found for the dimethoxy substituted substrate. The H_2O containing reaction models are found to be needed to the trace routes of the rearrangement.

In the Introduction, three complexities in the mechanism were raised. The first complexity, the unclear order of rate equations, may be interpreted in terms of competition of mono- and di-protonated reactions. In the mono-protonated reaction, either the Claisen shift or formation of the Dewar's π complex is brought about. In the di-protonated reaction, a stepwise path starts from π complexes of aniline (and its derivative) di-cation. The second complexity comes from the same source as that for the first one: for both mono- and di-protonated hydrazobenzenes there are various



Scheme 16 Calculated results for the parent hydrazobenzene (**1**).

reaction channels. The third complexity in KIE would arise from the slight difference in energy-barrier height of the reaction paths for **2**H⁺ and **3**H⁺ shown in Fig. 2.

Acknowledgements

This work is dedicated to Professor Henry J. Shine for his long career and great achievements in benzidine rearrangement.

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