Structural Chemistry
https://doi.org/10.1007/s11224-020-01567-z

ORIGINAL RESEARCH

Generation and trapping of non-aromatic cycloimines via diazotization/dediazotization of N-amino cyclic amines: theoretical and experimental results

Minita Ojha[1] · Raj K. Bansal[1]

Received: 7 May 2020 / Accepted: 12 June 2020

Abstract
A theoretical investigation of the model diazotization/dediazotization of N-aminopiperidine and N-aminomorpholine at the DFT (B3LYP/6-31+G(d)) level indicated that the corresponding cycloimines can be generated transiently, which can be trapped with dimethyl acetylenedicarboxylate (DMAD) to form a 1,4-dipole followed by cycloaddition of the latter with a second molecule of DMAD to give the corresponding pyrido-annelated products. All steps have low activation free energy barriers and are thermodynamically favoured. Based on the theoretical results, we carried out successfully diazotization of N-amino cyclic amines, namely N-aminopiperidine, 4-aminomorpholine and 1-amino-4-methylpiperazine with *tert.*-butyl nitrite followed by dediazotization to generate transiently the corresponding cycloimines, which could be trapped with dimethyl acetylenedicarboxylate. to afford new annelated pyridine derivatives, namely tetramethyl *9H*-5,6,7,8-tetrahydroquinolizine-1,2,3,4-tetracarboxylate, tetramethyl 5,6,8,9-tetrahydropyrido[2,1-c][1,4]oxazine-1,2,3,4-tetracarboxylate and tetramethyl *9H*-5,6,7,8-tetrahydro-7-methylpyrido[1,2-a]pyrazine-1,2,3,4-tetracarboxylate which were duly characterized.

Keywords 1,4-Dipoles · Annelated pyridines · Tetramethyl *9H*-5,6,7,8-tetrahydroquinolizine-1,2,3,4-tetracarboxylate · Tetramethyl 5,6,8,9-tetrahydropyrido[2,1-c][1,4]oxazine-1,2,3,4-tetracarboxylate · Tetramethyl *9H*-5,6,7,8-tetrahydro-7-methylpyrido[1,2-a]pyrazine-1,2,3,4-tetracarboxylate · DFT calculations

Introduction

Diels and Alder [1] in 1932 reported the formation of an unstable red product from the reaction of pyridine with dimethyl acetylenedicarboxylate (DMAD), whose correct structure as tetramethyl *4H*-quinolizine-1,2,3,4-tetracarboxylate **(3)** could be assigned almost three decades later by Acheson and co-workers [2–4]. However, Huisgen and co-workers [5, 6] for the first time postulated it as an example of 1,4-dipolar cycloaddition reaction wherein a 1,4-dipole **(1)** was generated in situ from the reaction of pyridine with DMAD which subsequently reacted with a second molecule of DMAD acting as dipolarophile to afford the final product **(3)** (Scheme 1) [5, 6].

Furthermore, it was pointed out that in contrast to 1,3-dipoles, 1,4-dipoles are not isolable and are produced in situ from the reaction of a nucleophilic substrate (a = b) with an electrophilic reagent (c = d) followed by the reaction with the dipolarophile e = f (Scheme 2) [5, 6].

Imine (a>C=N-) is such a nucleophilic component which has been frequently used for generating 1,4-dipoles that subsequently undergo 1,4-dipolar cycloaddition to afford a variety of N-heterocyclic products. Nair and co-workers [7] have reviewed these reactions in a systematic manner. A close look at the types of imines employed for producing 1,4-dipoles reveals that they belong either to the acyclic category [8, 9] or the aromatic N-heterocycles, such as pyridines [10, 11], isoquinoline [12–15], quinoline [16–18], benzothiazoles [19–22] and other similar systems [23, 24]. However, we could not find a report about the use of non-aromatic cycloimines, possibly due to their non-availability commercially.

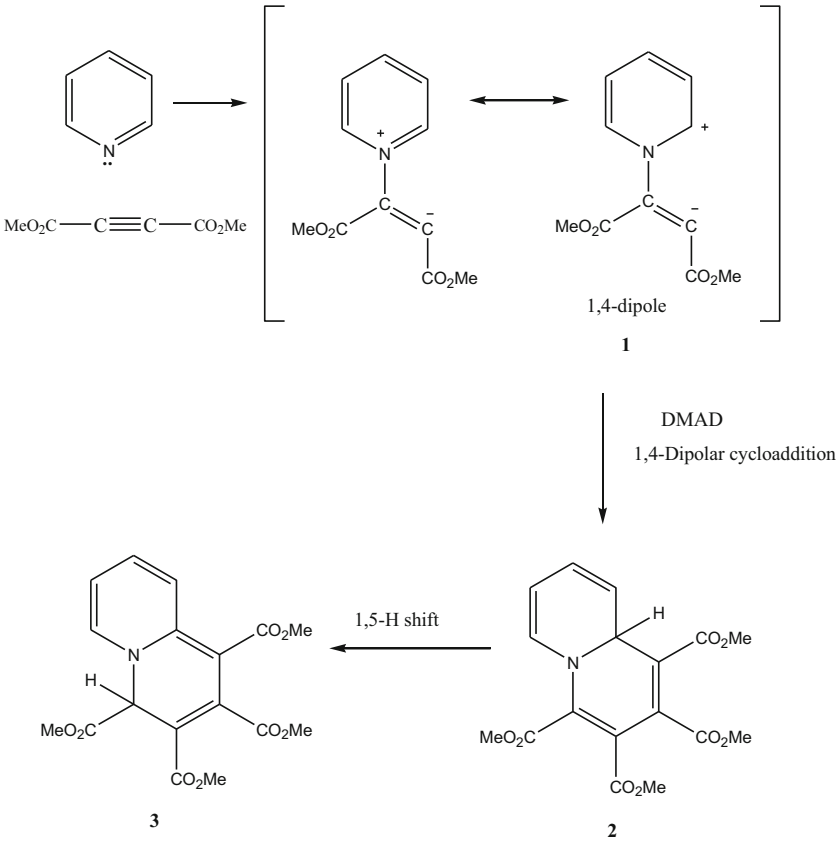
Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11224-020-01567-z) contains supplementary material, which is available to authorized users.

✉ Raj K. Bansal
bansal56@gmail.com

[1] Department of Chemistry, The IIS University, Jaipur 302020, India

Published online: 27 June 2020

Scheme 1 Generation of 1,4-dipole and its subsequent 1,4-dipolar cycloaddition with DMAD



On looking in the literature, we found that unsubstituted 2,3,4,5-tetrahydropyridine (also named as Δ^1-piperideine) is unstable and changes into its trimer immediately [25]. The methods for synthesizing substituted 2,3,4,5-tetrahydropyridine are cumbersome and involve multiple steps [26].

We recently reported generation of the nitrenium ion in situ from diazotization/dediazotization of 4-amino-1,2,4-triazole-5-thione followed by loss of nitrogen, which subsequently underwent tandem S-S coupling, 1,2-proton migration and reduction to afford a disulfide [27]. It has been reported earlier that the nitrenium ion may get stabilized through 1,2-alkyl or hydride shift to generate an imine [28–30]. With this background, we perceived that initially produced nitrenium ion from diazotization/dediazotization of 2-unsubstituted N-amino cyclic amine might get stabilized through a 1,2-prototropic shift to generate cycloiminium ion, which in the presence of a base would change into cycloimine. First, we investigated the veracity of this hypothesis theoretically and then guided by the theoretical results, studied reactions of three N-amino cyclic amines; the results are presented here.

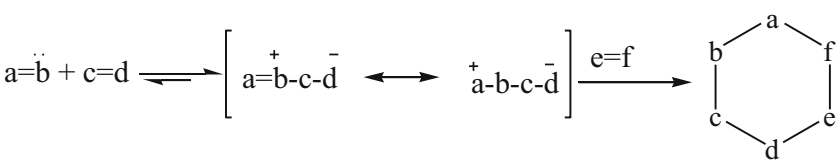
Computational details

Gaussian 016 suite of programs was used for all calculations [31].

Geometries of the reactants, transition structures, intermediates and the product involved in the model reaction were optimized in the gas phase at the B3LYP/6-31+G(d) level of theory. Frequency calculations were done at the same level to characterize the energy minimum or the first saddle point in the presence of no imaginary and only one imaginary frequency, respectively.

The intrinsic reaction coordinate (IRC) calculations [32, 33] starting from the transition structure were carried out at the same theory level to confirm its relation to the respective reactants and the intermediate/product. The total enthalpy was

Scheme 2 Formation of 1,4-dipole and its subsequent 1,4-dipolar cycloaddition



calculated by adding thermal corrections to the sum of the electronic and thermal enthalpy. The free energy ΔG at a temperature of 298.15 K was calculated as follows:

$\Delta G = \Delta H – T\Delta S$

$\Delta H =$ relative enthalpy

$\Delta S =$ relative entropy

$T = 298.15$ K

Experimental details

General

1-Aminopiperidine, 4-aminomorpholine, 1-amino-4-methylpiperazine and *t*-butyl nitrite were purchased from Sigma Aldrich and were used as such. Solvents were freshly dried and distilled.

IR spectra were recorded on a Brucker or Perkin-Elmer spectrometer in KBr pellet. NMR spectra were recorded in $CDCl_3$ on a Jeol- 400-MHz spectrometer, ^1H NMR at a frequency of 399.78 MHz using TMS as the internal reference. The C, H, N elemental analyses were done on a FLASH Ea 1112 series CHN analyser.

Diazotization and reaction with DMAD: general procedure

To a solution of N-amino cyclic amine (4 mmol; 1-aminopiperidine 400 mg, 430 μL; 4-aminomorpholine 409 mg, 386 μL; 1-amino-4-methylpiperazine 461 mg, 481 μL) in acetonitrile (5 mL), taken in a 25 mL Round Bottom (RB) flask and cooled to − 5 °C, was added *t*-butyl nitrite (4.8 mmol, 494 mg, 570 μL) under a nitrogen atmosphere with continuous stirring. After the addition was complete, stirring was continued for another half an hour maintaining the temperature at − 5 °C to 0 °C. Thereafter, a solution of DMAD (8 mmol, 1136 mg, 980 μL) in acetonitrile (2 mL) was added dropwise with continuous stirring and allowing the reaction mixture to warm up to r.t. (~ 25 °C). Progress of the reaction was monitored by TLC; it was complete after ca. 11–16 h. The reaction mixture was concentrated and a few drops of diethyl ether were added and kept in refrigerator. A coloured solid settled down, which was separated and dried under vacuum. In the case of the reaction with 1-aminopiperidine and 1-amino-4-methylpiperazine, it was chromatographed over a column of silica gel, eluent: EtOAc/$CHCl_3$, 0.2:9.8 *v*/v % and MeOH/$CHCl_3$, 0.1:9.9, v/v% respectively. The elute was concentrated and left in refrigerator whereupon a pale yellow crystalline solid deposited, which was separated and dried under vacuum.

Results and discussion

Theoretical results

We computed the following model sequence of reactions starting from the piperidinediazonium ion generated from the reaction of 1-aminopiperidine with *t*-butyl nitrite [34–37], the reagent actually used for diazotization as described later, at the DFT (B3LYP/6-31+G(d)) level (Fig. 1).

Optimized geometries

The B3LYP/6-31+G(d) optimized geometries of the transition structures **TS1a-6a** are given in Fig. 2. The Cartesian coordinates of the optimized geometries of other species are given in the Supplementary Material.

Although it has been possible to locate the transition structure **TS2a** involved in 1,2-prototropic shift in the nitrenium ion **5a** to produce iminium ion **6a**, the former was not found to be a global minimum as it had one imaginary frequency at − 48.6 cm^{-1}. On computing IRC calculations of **TS2a** in the reverse direction, a ring contracted species **12a** was obtained as the global minimum. As **TS2a** could be located successfully, it seems probable that nitrenium ion **5a** is generated transiently, which changes rapidly into thermodynamically more stable iminium ion **6a** before it can rearrange to **12a** through ring contraction. The latter change, i.e. change of **5a** to **12a** is expected to be a higher energy path as it involves cleavage of the C–C bond in contrast to the C–H cleavage during the change of **5a** to **6a** (Fig. 3).

Energetics

The thermodynamic data of different species are given in Table 1**.**

Dediazotization of piperidinediazonium ion **4a** to generate the nitrenium ion **5a** has expectedly a small activation free energy barrier of 11.07 kcal mol^{-1} only. As discussed earlier, the nitrenium ion **5a** undergoes preferentially a 1,2-prototropic shift to produce the iminium ion **6a**. Such 1,2-prototropic shifts in the nitrenium ions have been reported earlier [28–30]. It may be noted that conversion of **5a** into **6a** is exergonic ($\Delta G° = -63.62$ kcal mol^{-1}) and hence is expected to occur spontaneously. In the presence of a strong base ($^{-}O^{t}Bu$) produced during diazotization with $^{t}BuONO$ [34–37], iminium ion **6a** undergoes deprotonation to generate imine, i.e. 2,3,4,5-tetrahydropyridine **7a.** The latter reacts subsequently with DMAD to produce 1,4-dipole **8a**. The reaction has low activation enthalpy barrier ($\Delta H^{\#} = 12.05$ kcal mol^{-1}), but as it is accompanied by a decrease in entropy, the activation free energy $\Delta G^{\#}$ is raised to 24.50 kcal mol^{-1}. The formation of the 1,4-dipole **8a** is endergonic ($\Delta G° =$ 21.47 kcal mol^{-1}), and hence, this step is expected to be slow.

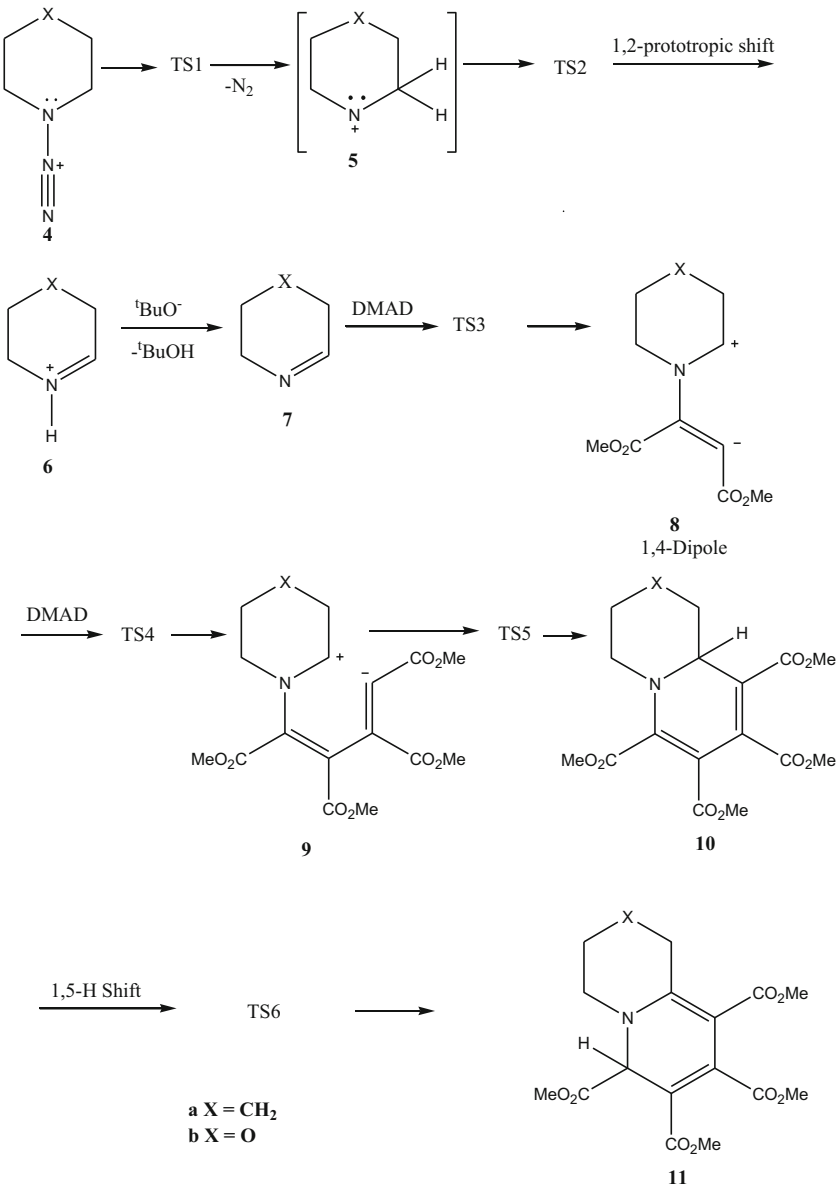


Fig. 1 Model sequence of reactions computed at the B3LYP/6-31+G(d) level

The next step involves a reaction between 1,4-dipole **8a** and the second molecule of DMAD. Here, another question comes into picture, i.e. whether it follows a concerted mechanism like 1,3-dipolar cycloaddition reactions [38] or a stepwise mechanism. Huisgen et al. for the first time predicted the possibility of stepwise mechanism for these reactions [6]. Recently, a stepwise mechanism was established on the basis of a theoretical investigation of 1,4-dipolar cycloaddition between propa-1,2-diene and imines catalysed by PBu_3 [39]. Our results also support a stepwise mechanism on two counts: firstly, all attempts to locate a concerted transition structure on the PES failed, and secondly, in the HOMO of the 1,4-dipole **8a** (reproduced in Fig. 4), coefficient of the *p*-orbital at the C2 atom is almost negligible, whereas at the β-carbon atom, it is quite large. Thus, it can be perceived judiciously that 1,4-dipole **8a** reacts with a second molecule of DMAD to produce zwitterion **9a.** This step is found to be barrier-less in terms of activation enthalpy ($\Delta H^{\#} = -3.33$ kcal mol^{-1}). Activation free energy value ($\Delta G^{\#} = 10.06$ kcal mol^{-1}) for this step is also small. Intramolecular cyclization of **9a** to afford **10a** is also barrier-less in terms of activation enthalpy ($\Delta H^{\#} = -0.27$ kcal mol^{-1}), with a small activation free energy ($\Delta G^{\#} = 5.05$ kcal mol^{-1}). Furthermore, it may be noted that cyclization of **9a** to **10a** is an exergonic process with a standard free energy $\Delta G°$ value of −53.49 kcal mol^{-1}.

As regards the 1,5-prototropic shift, our theoretical as well as experimental (^{1}H NMR discussed later) results indicate that in contrast to the reaction of pyridine with DMAD wherein initially formed product undergoes 1,5-protoropic shift to afford the final product, tetramethyl *4H*-quinolizine-1,2,3,4-tetracarboxylate **(3)** [2–4], no such shift occurs in the present

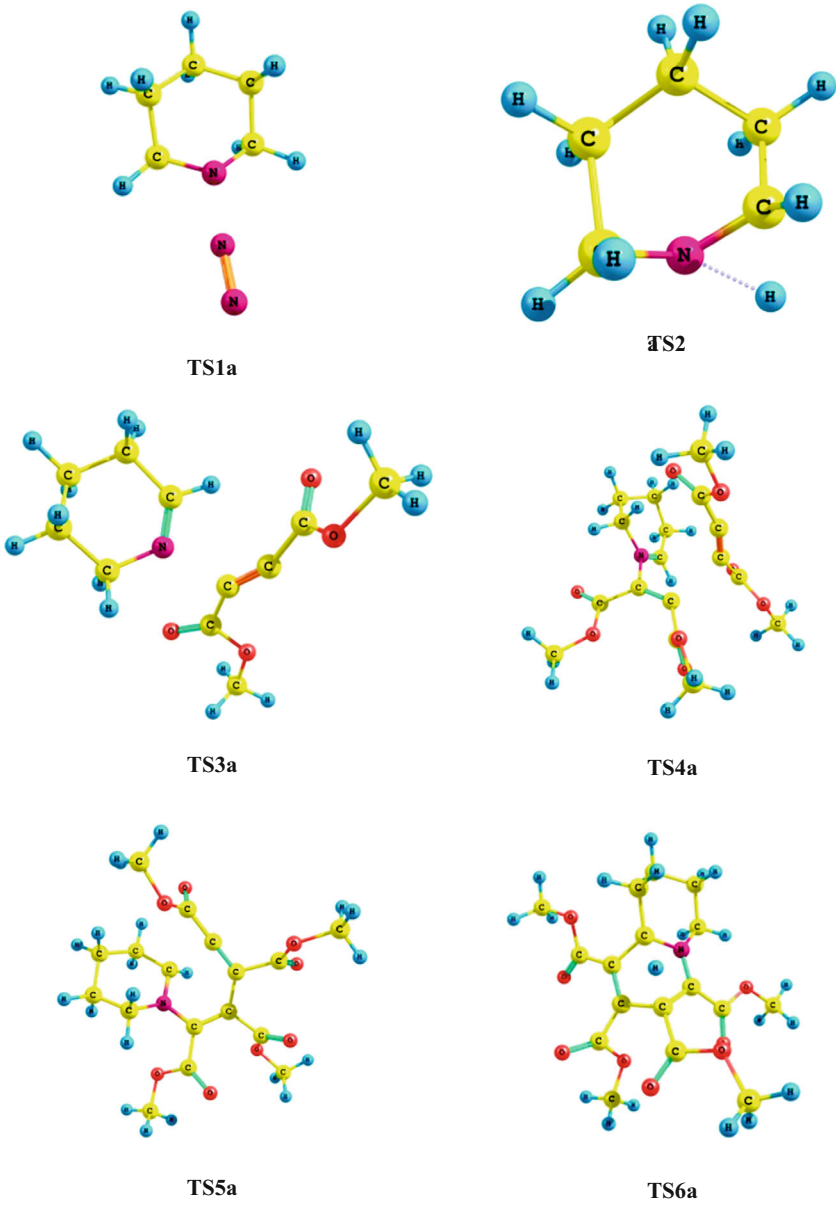


Fig. 2 Geometries of the transition structures TS1a-6a optimized at the B3LYP/6-31+G(d) level

case. A high activation free energy barrier ($\Delta G^{\#}$ = 42.06 kcal mol^{-1}) for the 1,5-protoropic shift in **10a** to give **11a** makes it improbable. In fact, induction of the extended conjugation in tetramethyl *4H*-quinolizine-1,2,3,4-tetracarboxylate **(3)** resulting from 1,5-protoropic shift in the initially formed adduct of pyridine with DMAD (**2**) appears to be the driving force. However, this kind of driving force is missing in the present case. It is supported by the standard free energy ($\Delta G°$) values in the two cases calculated at the B3LYP/6-31+G(d) level (Scheme 3).

It may be noted from Table 1 that activation energies of different steps in the reaction sequence of piperidiniumdiazonium ion (**4a**) are almost parallel to those of morpholiniumdiazonium ion (**4b**), which indicates that a CH_2/O exchange in the piperidine ring at 4-position does not affect course of the reaction.

Experimental results

Traditionally, nitrous acid ($NaNO_2$+HCl) is used for diazotization of the primary amines. However, this reagent suffers from several disadvantages: acidic conditions, poor functional group tolerance and formation of undesirable side products. In recent years, alkyl nitrites, particularly *t*-butyl nitrite and amyl nitrite, have emerged as the reagents of choice for diazotization as these reagents can be used under neutral conditions also [34–37]. In view of this, particularly when N-

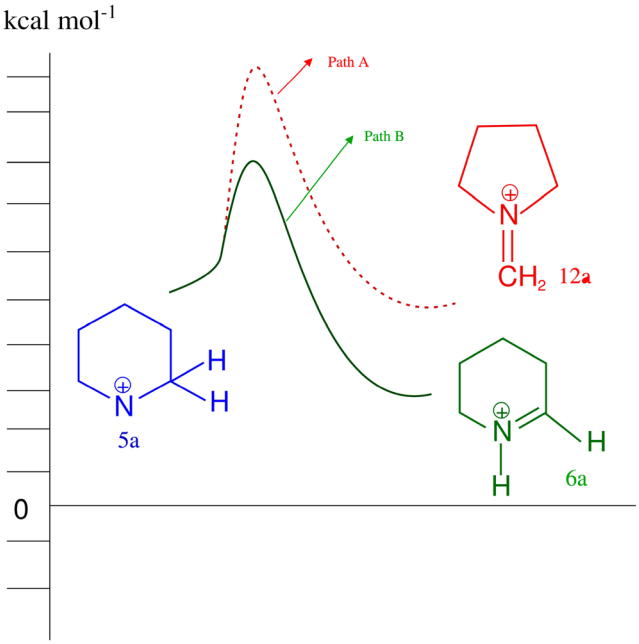


Fig. 3 Comparative energy paths for the ring contraction (path A) and isomerization to iminium ion (path B) of the nitrenium ion **5a**

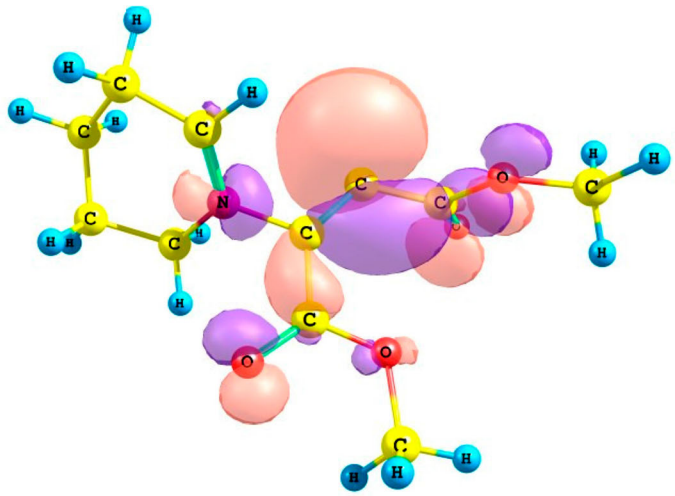
aminomorpholine was to be diazotized, we preferred the use of the commercially available *t*-butyl nitrite. Thus, successive diazotization of N-aminocyclic amines **13a-c** with *t*-butyl nitrite, warming up to r.t. and reaction with DMAD (2 equiv.) afforded the products **15a-c** (Scheme 4).

The compounds **15a-c** are pale yellow crystalline solids soluble in common organic solvents, such as dichloromethane, chloroform and ethyl acetate. The structures could be established on the basis of elemental analysis and spectral studies. For example in the case of tetramethyl *9H*-5,6,7,8-tetrahydroquinolizine-1,2,3,4-tetracarboxylate (**15a**), strong absorption bands at 1727 cm^{-1} (C=O str.) and 1207 cm^{-1} (C(O)-O str.) in the IR spectrum confirm the presence of the ester groups. In the ^{1}H NMR spectrum, a triplet at δ 4.55 ppm ($^3J_{HH}$ = 6.0 Hz) can be assigned to the methylene protons at the C5 atom. As discussed earlier, in contrast to tetramethyl *9H*-quinolizine-1,2,3,4-tetracarboxylate, 1,5-prototropic shift does not occur in the present case. It is confirmed by the presence of a triplet at δ 3.94 ($^3J_{HH}$ = 6.0 Hz), which partially overlaps with the signals resulting from the OC$\underline{H_3}$ protons of the ester groups, due to the C(9)$\underline{H}$ proton. The methoxy protons give a singlet at δ 3.91. The methylene protons at the C6

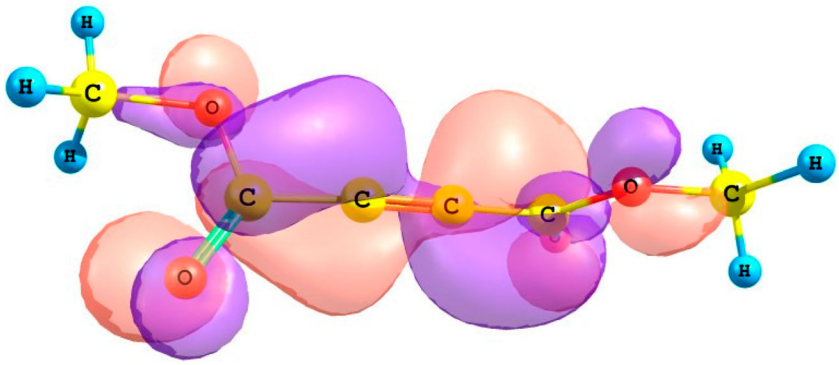
Table 1 Thermodynamic data of different species computed in the gas phase at the B3LYP/6-31+G(d) level

Species	Total enthalpy (a.u.)	Entropy cal mol^{-1} K^{-1}	Activation enthalpy $\Delta H^{\#}$ (kcal mol^{-1})	Activation entropy $\Delta S^{\#}$ (Cal mol^{-1} K^{-1})	Activation free energy $\Delta G^{\#}$ (kcal mol^{-1})	Standard enthalpy ΔH° (kcal mol^{-1})	Standard free energy ΔG° (kcal mol^{-1})
4a	−360.156120	85.125	–	–	–	–	–
TS1a	−360.138234	85.643	11.22	0.518	11.07	–	–
N_2	−109.511987	45.785	–	–	–	–	–
5a	−250.659797	72.973		–	–	−9.83	−19.86
TS2a	−250.600114	72.741	37.45	−0.232	37.52	–	–
6a	−250.760643	74.103	–	–	–	−63.28	−63.62
7a	−250.414332	73.613	–	–	–	–	–
DMAD	−532.845835	106.451	–	–	–	–	–
TS3a	−783.240969	138.303	12.05	−41.761	24.50	–	–
8a	−783.247940	133.789	–	–	–	7.67	21.47
TS4a	−1316.099082	195.346	−3.33	−44.894	10.06	–	–
9a	−1316.136575	192.653	–	–	–	−26.86	−12.67
TS5a	−1316.137007	174.810	−0.27	−17.843	5.05	–	–
10a	−1316.227218	181.314	–	–	–	−56.88	−53.49
TS6a	−1316.160681	180.281	41.75	−1.033	42.06	–	–
11a	−1316.230835	181.161	–	–	–	−2.27	−2.23
4b	−396.085933	83.954	–	–	–	–	–
TS1b	−396.071478	84.305	9.07	0.352	8.96	–	–
5b	−286.605475	72.072	–	–	–	−19.78	−29.89
TS2b	−286.528880	71.599	48.06	−0.472	–	–	–
6b	−286.687511	72.898	–	–	–	−51.48	−51.73
7b	−286.354153	72.567	–	–	–	–	–
TS3b	−819.178840	136.105	13.27	−42.913	26.06	–	–
8b	−819.184526	132.482	–	–	–	9.70	23.57
TS4b	−1352.033905	193.236	−2.22	−45.697	11.40	–	–
9b	−1352.071598	189.595	–	–	–	−25.88	−11.17
TS5b[a]	–	–	–	–	–	–	–
10b	−1352.167850	181.924	–	–	–	−60.40	−58.11
TS6b	−1352.096794	179.066	44.59	−2.858	45.44	–	–
11b	−1352.186189	180.786	–	–	–	−11.51	−11.17

[a] Could not be located



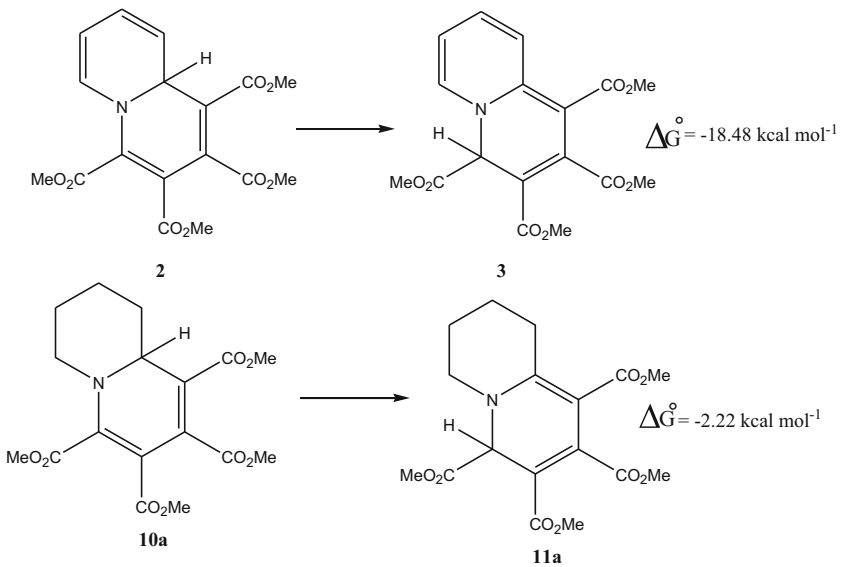
8a HOMO



DMAD LUMO

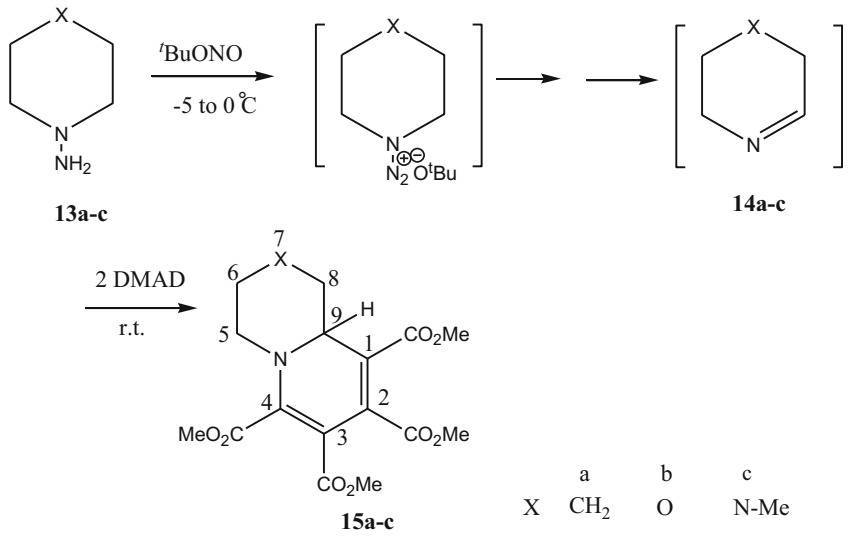
Fig. 4 Kohn-Sham Frontier Molecular Orbitals of 1,4-dipole **8a** and DMAD

and C8 carbon atoms give partially overlapping quintet and quartet at δ 1.93 ($^3J_{HH}$ = 6.0 Hz) and δ 1.89 ($^3J_{HH}$ = 6.0 Hz) respectively. The methylene protons at the C7 atom give a quintet at δ 1.77 ($^3J_{HH}$ = 5.6 Hz). The structure was unambiguously confirmed by recording a ^{1}H-^{13}C correlated 2D NMR spectrum (reproduced in the Supplementary Material).



Scheme 3 Standard free energies for the 1,5-prototropic shift in the annelated pyridine- and piperidine derivatives calculated at the B3LYP/6-31+G(d) level

Scheme 4 Generation and trapping of non-aromatic cycloimines with DMAD



Tetramethyl *9H*-5,6,7,8-tetrahydroquinolizine-1,2,3,4-tetracarboxylate **15a**: From 1-aminopiperidine and DMAD; Light yellow crystalline solid; mp 68–70 °C; yield 52%; [found; C, 55.61;H, 5.79;N, 3.80; $C_{17}H_{21}NO_8$ requires C, 55.58; H, 5.76; N, 3.81]; Rf (20%EtOAc/Chloroform) 0.81; νmax (KBr, ν cm^{-1}) 1727 (s, C=O str.), 1509 (s, C=C str.), 1207 (s, C(O)-O str.), and 1010 (s, C-N str.); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 4.55 (t, $^3J_{HH}$ = 6.0 Hz, 2H, C(5)$\underline{H_2}$) 3.94 (t, $^3J_{HH}$ = 6.0 Hz, 1H, C(9)$\underline{H}$), 3.91 (s, 12H, OC$\underline{H_3}$), 1.93 (quint., $^3J_{HH}$ = 6.0 Hz, 2H, C(6)$\underline{H_2}$), 1.89 (q., $^3J_{HH}$ = 6.0 Hz, 2H, C(8)$\underline{H_2}$),1.77 (quint., $^3J_{HH}$ = 5.6 Hz, 2H, C(7)$\underline{H_2}$).

Tetramethyl 5,6,8,9-tetrahydropyrido[2,1-c][1,4]oxazine-1,2,3,4-tetracarboxylate **15b:** From 4-aminomorpholine and DMAD; Yellow coloured crystalline solid; mp 83–85 °C; yield 50%; [found; C, 52.09;H, 5.22;N, 3.75; $C_{16}H_{19}NO_9$ requires C, 52.03; H, 5.19; N, 3.79]; Rf (20%EtOAc/Chloroform) 0.65; ν_{max} (KBr, ν cm^{-1}) 1700 (s, C=O str.), 1615 (s, C=C str.), 1279 (s, C(O)-O str.), 1213 (s, C(O)-O str.), and 1098 (w, C-N str.); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 4.70 (t, $^3J_{HH}$ = 5.2 Hz, 2H, C(5)$\underline{H_2}$), 3.97 (unresolved triplets, 4H, C(6)$\underline{H_2}$ and C(8)$\underline{H_2}$), 3.93, 3.92, 3.91, 3.90 (closely spaced singlets, 12H, four OC$\underline{H_3}$), 3.88 (t, $^3J_{HH}$ = 6.0 Hz, 1H, C(9)$\underline{H}$).

Tetramethyl *9H*-5,6,7,8-tetrahydro-7-methylpyrido[1,2-a]pyrazine-1,2,3,4-tetracarboxylate **15c:** From 1-amino-4-methylpiperazine and DMAD; brown coloured solid; mp 138–139 °C (decomposed); yield 53%; [found; C, 53.45; H, 5.86; N, 7.28; $C_{17}H_{22}N_2O_8$ requires C, 53.40; H, 5.80; N, 7.33]; Rf (4%MeOH/Chloroform) 0.49; ν_{max} (KBr, ν cm^{-1}) 1732 (s, C=O str.), 1624 (s, C=C str.), and 1216 (s, C(O)-O str.), 977 (w, C-N str.); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, J Hz): 4.54 (t, $^3J_{HH}$ = 6.0 Hz, 2H, C(5)$\underline{H_2}$), 3.99 (t, $^3J_{HH}$ = 4.8 Hz, 1H, C(9)$\underline{H}$), 3.94, 3.93, 3.91, 3.90 (s, 12H, 4 OC$\underline{H_3}$), 3.77 (s, 3H, N-C$\underline{H_3}$), 1.90 (t, $^3J_{HH}$ = 6.0 Hz, 2H, C(6)$\underline{H_2}$), 1.77 (d, $^3J_{HH}$ = 4.8 Hz, 2H, C(8)$\underline{H_2}$).

Conclusions

A model reaction computed at the DFT (B3LYP/6-31+G(d)) level indicated that the diazonium ion produced from diazotization of an N-amino cyclic amine undergoes dediazotization to generate the nitrenium ion with low activation free energy barrier. The nitrenium ion so produced undergoes 1,2-prototropic shift to form iminium ion. The latter loses a proton to generate cycloimine transiently, which reacts with DMAD to form a 1,4-dipole with low activation free energy barrier. The 1,4-dipole so formed reacts with a second molecule of DMAD to produce annelated pyridine derivatives, which are thermodynamically stable. The theoretical results could be verified experimentally when three N-amino cyclic amines, namely 1-aminopiperidine, 4-aminomorpholine and 1-amino-4-methylpiperazine were diazotized with *t*-butyl nitrite, and the cycloimines so generated could be trapped with DMAD to give *9H*-5,6,7,8-tetrahydroquinolizine derivatives.

Acknowledgements We acknowledge the support of the authorities of the IIS (deemed to be University), Jaipur (India) for providing research facilities. We thank the anonymous reviewer for giving valuable suggestions.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal studies This article does not contain any studies with human participants or animals performed by any of the authors.

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Author agreement All authors have read and approved to submit it to your journal. This paper has not been submitted elsewhere for consideration of publication.

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