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Theoretical Study of the Barrier to Nitrogen Inversion in *N*-Cyano- and *N*-Diazoformimine. Mechanism of the Schmidt Reaction

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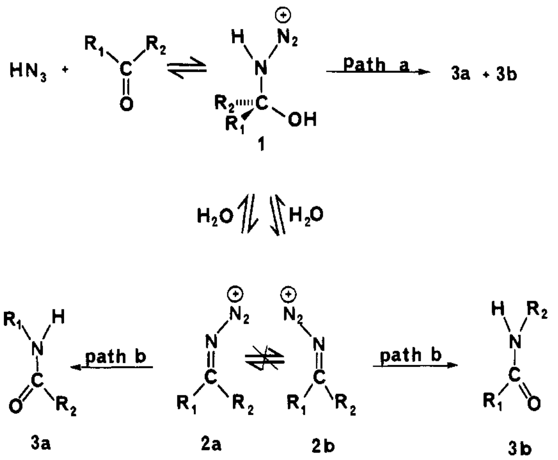
A theoretical investigation of the barriers to nitrogen inversion in *N*-cyano- and *N*-diazoformimine is described. The inversion process, or lateral shift mechanism, for topomerization of the *N*-cyano imine was calculated (6-31G) to be 14.5 kcal/mol while nitrogen inversion in the *N*-diazo imine was 28.2 kcal/mol. These observations mitigate against the involvement of rapidly isomerizing iminodiazonium ions in the Schmidt reaction with ketones. A theoretical analysis of the orbital interactions involved in inversion at imino nitrogen is presented.

The Beckman and Schmidt reactions are related 1,2-rearrangements that possess the common feature of a developing positive charge on nitrogen during the course of a concerted 1,2-migration.[1a] The Beckmann and the Schmidt reactions on ketones both appear to involve nitrilium ion intermediates.[1b] However, the rate-limiting step of the latter reaction still remains a subject of controversy.[2,3] It has been suggested that the acid-catalyzed reaction of hydrazoic acid with ketones may proceed by two principal pathways.[1a,4] The first of these involves the concerted "pinacol type" rearrangement of the tetrahedral intermediate **1** with concomitant loss of nitrogen (path a). The second pathway given in Scheme I requires dehydration of the α-hydroxyhydrazidium ion **1**, affording the two isomeric iminodiazonium ions **2a** and **2b** (path b).

Scheme I



There appears to be little question that phenyl ketones rearrange through the intermediacy of iminodiazonium ions.[1a,c] Convincing evidence that geometrical isomerism of cations **2a** and **2b** is slower than irreversible rearrangement to amides **3a** and **3b** has also been reported.[1c] A series of para-substituted benzophenones afforded ratios of products very close to unity regardless of the electronic properties of the substituent. Furthermore, these product ratios are very close to those from the Beckman rearrangement of the equilibrated oximes, where there is also no discernible steric hindrance at the migration origin. With hindered ketones, however, the intermediate iminodiazonium ions prefer a configuration where steric interactions with the diazo nitrogens are minimized, and the product ratios reflect this stereochemistry.[1a] It is therefore assumed, by analogy to the configurationally stable oximes used in the Beckman rearrangement, that the group trans to the departing nitrogen molecule will migrate.

In a recent study on the mechanism of the Schmidt reaction, the competitive migration of cyclopropyl vs. alkyl groups gave ratios of amides that were markedly influenced by the concentration and type of acid in the reaction medium.[4] One explanation offered in support of these data was that the intermediate iminodiazonium ions **2a** and **2b** were rapidly isomerizing. A similar suggestion has been made in a related study on the hydrolysis of vinyl azides.[5] A second pathway for interconverting stereoisomers **2a** and **2b** is the reversible addition of H_2O[6] to afford **1**, which can dehydrate to form the thermodynamic isomer. Since it has previously been assumed that amides arising from unsymmetrical ketones rearrange via nonequilibrating cations (**2a** and **2b**),[1] we felt that a realistic estimate of the barrier to nitrogen inversion in an iminodiazonium cation would be of vital importance in furthering our understanding of the mechanism of this reaction. We now report ab initio calculations which suggest that the barriers to interconversion via nitrogen inversion or rotation are high enough to preclude rapid isomerization of these cations at room temperature.

Results and Discussion

At present, highly reactive cationic intermediates such as **2a** and **2b** are not amenable to direct study. Therefore, we sought a related compound where the barrier to nitrogen inversion had been measured experimentally. An NMR study[7] on isomerization of a series of *N*-cyano imines (X = CH_3, SCH_3, OCH_3, and $NDCH_3$ and Y = CN) provided an excellent structural analogy with the triply bonded diazo cations **2**. In general, substitution by a heteroatom X at the imino carbon or by multiply bonded groups Y at nitrogen lowers the barrier to *Z–E* isomerization in imines **4**.[8,9] The experimental barrier to to-

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(1) (a) Smith, P. A. S. In "Molecular Rearrangements"; de Mayo, P., Ed.; Wiley: New York, 1963; Chapter 8. (b) Fodor, G.; Nagubandi, S. *Tetrahedron* **1980**, *36*, 1279. (c) Smith, P. A. S.; Horwtiz, J. P. *J. Am. Chem. Soc.* **1950**, *72*, 3718. Smith, P. A. S. Antoniades, E. P. *Tetrahedron* **1960**, *9*, 210.

(2) (a) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Rinehart, and Winston: New York, 1959; p 624. (b) Banthorpe, D. V. "The Chemistry of the Azido Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1971; p 405. (c) Liler, M. "Reaction Mechanisms in Sulfuric Acid"; Academic Press: New York, 1971; p 303. (d) Lowry, T. H.; Richardson, K. S. "Mechanisms and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 323. (e) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 1006.

(3) Vogler, E. A.; Hayes, J. M. *J. Org. Chem.* **1979**, *44*, 3682.

(4) Fikes, L. E.; Shechter, H. *J. Org. Chem.* **1979**, *44*, 741. Fikes, L. E.; Shechter, H. *Tetrahedron Lett.* **1976**, 2525.

(5) Hassner, A.; Ferdinandi, E. S.; Isbister, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 1672.

(6) Prager, R. H.; Tippett, J. M.; Ward, A. D. *Aust. J. Chem.* **1978**, *31*, 1989.

(7) McCarty, C. G.; Wieland, D. M. *Tetrahedron Lett.* **1969**, 1787.

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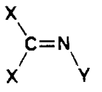

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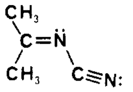

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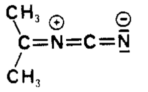


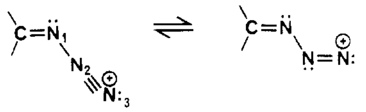
6

pomerization in N-cyano imine **5** is 18.9 kcal/mol with a coalescence temperature of 85 °C in acetone solvent. This barrier is lower than the corresponding N-phenyl compound[7] presumably because the transition state for inversion, **6**, is more highly stabilized by electron delocalization. Significantly, Mulliken charges show that the cyano group is polarized toward the cyano nitrogen, while the diazo group local dipole is directed toward the substituted nitrogen as in resonance structure **7a**.[10] The

$$-\overset{\oplus}{N}\equiv N: \longleftrightarrow -\ddot{N}=\overset{\oplus}{N}:$$

7 7a

electron deficiency at nitrogen makes the diazo group a powerful σ withdrawing group, but the direction of π-electron polarization has an important mechanistic implication. If resonance structure **7a** is an important contributor to the structure of the diazo group, then this substituent should be less effective than a cyano group in lowering the barrier to nitrogen inversion. Localizing an unshared pair of electrons on N_2 in **8** will result in lone pair–lone pair repulsion and cause a deviation from linearity in the diazo portion of the molecule as in **8a**. We



8 8a

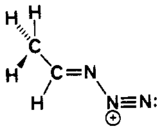
chose N-cyano- and N-diazoformimines **9** and **12** as our model compounds to test this hypothesis and to provide a basis for comparison of experiment with theory.

The calculations were performed with the Gaussian 70 series of programs.[11] The geometries of all structures were first optimized by employing an STO-3G basis set, and then more reliable energy differences were calculated with those parameters by using a 6-31G basis set. Several selected geometries were also fully optimized with the 6-31G basis where indicated.

Thermal isomerization of Z–E isomers may be attained by torsion about the C=N double bond, by inversion at imino nitrogen, or by an intermediate mechanism that has both torsional and inversional components.[12a] There is now a general consensus that Z–E isomerism of simple imines is an inversional process.[8] In a recent ab initio MO study we presented theoretical arguments that totally excluded any torsional contribution to the Z–E isomerism of methanimine.[12b] The present case is no exception, and 90° rotation about the C=N double bond in **9** affords **11** as a maximum that is 49.6 kcal/mol (6-31G) above the ground state. However, the inversion process, or lateral shift mechanism, had a calculated barrier of only 14.48 kcal/mol with full geometry optimization of transition state **10** at the 6-31G level of approximation.[13] The calculated inversion barrier on model compound **9** (14.5 kcal/mol) is in good agreement with the experimentally observed barrier (18.9 kcal/mol) on the dimethyl analogue **5**. The STO-3G basis set barrier is higher (27.2 kcal/mol) as anticipated on the basis of earlier work.[12b] The bond angles and distances for these structures are given in Table I.

Our calculations on the rotational and inversion barriers for the comparable N-diazoformimine (**12**) are given in Table II.[13] The transition state **13** for inversion is calculated to be 28.17 kcal/mol (6-31G) higher in energy than the ground state **12** while the barrier to rotation is 61.92 kcal/mol (6-31G). These data are consistent with the above suggestion that the diazo moiety $^{+}N\equiv N:$, although a π-electron acceptor,[10] is not nearly as efficient as a cyano group in stabilizing **13**, the linear delocalized transition state for inversion. Our agreement with experiment in the model cyano compound **9** gives us a confidence that the barrier to topomerization in a comparable diazo cation is clearly too high to allow rapid interconversion at room temperature.

We next examined the effect of alkyl substitution on the imino carbon by calculating the inversion barrier for iminodiazonium ions **15** and **16**. The inversion barrier in the methyl-substituted cation **15** was found to be 53.75 kcal/mol (STO-3G, full minimization) which does not differ from that calculated in the parent compound **12** (Table III). The calculated energy difference between the Z and E isomers of **15** is only 0.28 kcal/mol. It is also significant that the bisected cyclopropyl cation **16** exhibited a decrease in inversion barrier of only 1 kcal/mol ($\Delta G^{\ddagger}$ = 52.7 kcal/mol)[14] relative to **12**.



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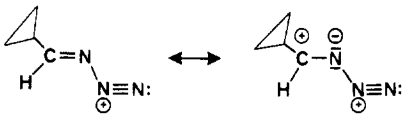

16 16a

Although alkyl substituents on carbon do not influence the inversion barrier, examination of resonance structure **16a** suggests that the rotational barrier about the carbon–nitrogen double bond should be reduced. In the bisected conformation the Walsh orbital on the cyclopropane can effectively stabilize the developing positive charge in **16a** by the well-established cyclopropylcarbinyl delocalization.[16] We estimated the geometry of the transition state for isomerization via rotation and calculated (STO-3G) a barrier of ~45 kcal/mol. Although rotation is lower than inversion by ~8 kcal/mol, one would still not anticipate rapid isomerization between the syn and anti diazo cations of **16**. These observations mitigate against the involvement of isomerizing iminodiazonium ions in the Schmidt reaction with alkyl cyclopropyl ketones.[4]

The thermodynamic stability of N-diazoformimine (**12**) relative to its spontaneous dissociation to N_2 and $CH_2=N^{+}$

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(8) (a) Kalinowski, H.-O.; Kessler, H. *Top. in Stereochem.* **1973**, *7*, 295. (b) Lehn, J.-M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311.

(9) For example, when X = CH_3 and $N(CH_3)_2$ in **4**, the experimental (NMR) barrier to topomerization was 20.3 and 12.1 kcal/mol, respectively (Y = C_6H_5).[7] When Y = $CH_2C_6H_5$ and C_6H_5, the barriers were >23.0 and 20.3 kcal/mol, respectively (X = CH_3).

(10) Ballard, M. J.; Bouma, W. J.; Radom, L.; Vincent, M. A. *Aust. J. Chem.* **1979**, *32*, 1401.

(11) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. QCEP Program No. 236, University of Indiana, Bloomington, IN, 1973.

(12) (a) Raban, M. *Chem. Commun.* **1970**, 1415. Raban, M.; Carlson, E. *J. Am. Chem. Soc.* **1971**, *93*, 685. (b) Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.*, **1981**, *103*, 3275.

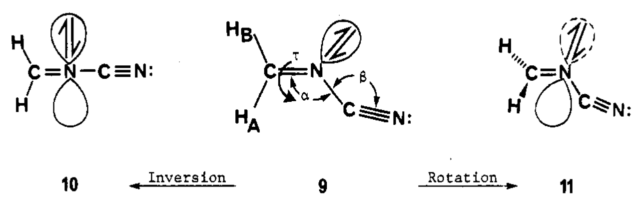
(13) Five points along the inversion surface and four on the rotational surface were fully optimized by STO-3G. The 6-31G calculations utilized the STO-3G geometry with the exception of the minimal structure and the transition state for inversion which were fully optimized at the 6-31G level.

(14) The STO-3G calculations were done by using the geometry of structure **15** after replacing the methyl group with a cyclopropyl ring. The geometry of the cyclopropyl ring was that reported by Hehre.[15]

(15) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5918.

(16) For a recent discussion with pertinent earlier references see: Bach, R. D.; Blanchette, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 46.

Table I. Geometry Optimization of *N*-Cyanoformimines



Geometry Minimized by STO-3G

	bond angles, deg					E_{rel}, kcal/mol	
structure	α	β	τ	H_A—C=N	H_B—C=N	STO-3G	6-31G[a]
10 (Inv_{max})[b]	180.00	180.00	0.0	122.46	122.46	27.22	12.65
9a	160.00	174.89	0.0	124.38	120.17	22.32	9.38
9b	140.00	172.37	0.0	125.52	118.17	10.33	2.15
9c	110.00	177.11	0.0	125.32	117.93	0.75	2.61
9 (E_{min})	115.38	175.65	0.0	125.67	117.67	0.00	0.0
9d	115.38	176.13	30.0	125.16	118.38	11.00	9.22
9e	115.38	177.98	60.0	124.77	120.05	39.87	32.67
11 (Rot_{max})[c]	115.38	180.70	90.0	123.09	123.09	62.48	49.62

	bond lengths, Å					E_{tot}, au	
structure	C=N	N—C	C≡N	H_A—C	H_B—C	STO-3G	6-31G[a]
10 (Inv_{max})	1.2417	1.3086	1.1694	1.0992	1.0992	−183.323 26	−185.624 80
9 (E_{min})	1.2823	1.4161	1.1589	1.0923	1.0910	−183.366 64	−185.644 96
11 (Rot_{max})	1.2998	1.3641	1.1622	1.1074	1.1074	−183.267 07	−185.565 88

Geometry Minimized by 6-31G

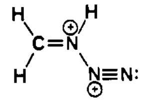
	bond angles, deg					
structure	α	β	τ	H_A—C=N	H_B—C=N	E_{rel}, kcal/mol
10	180.00	180.00	0.0	121.74	121.74	14.48
9	123.32	174.87	0.0	124.00	117.86	0.0

	bond lengths, Å					
structure	C=N	N—C	C≡N	H_A—C	H_B—C	E_{tot}, au
10	1.2392	1.2735	1.1595	1.0801	1.0801	−185.627 15
9	1.2679	1.3505	1.1486	1.0761	1.0702	−185.650 22

[a] 6-31G energy calculated by using STO-3G fully minimized structures. [b] Structures **9a–c** are fully minimized points on the pathway to inversion. [c] Structures **9d** and **9e** are fully minimized points on the pathway to rotation.

in the absence of alkyl (hydrogen) migration to afford a nitrilium ion is relevant to the overall mechanism of this reaction. With the minimal STO-3G basis set, which is not always reliable for nonisodesmic comparisons,[17] the dissociation is endothermic by 36.4 kcal/mol, and with a 6-13G basis set ΔH = 124.5 kcal/mol.[18] Similar results were calculated for loss of nitrogen from the methyl-substituted cation **15** where formation of N_2 and CH_3CHN^+ is calculated (STO-3G) to be endothermic by 19.3 kcal/mol.[18] Values of this magnitude suggest that once the diazocation is formed, it must either rearrange with loss of nitrogen or revert to the tetrahedral intermediate **1**. This suggestion is particularly plausible in concentrated H_2SO_4 where the rate of reaction is typically maximized and provides one explanation for the change in amide product ratios with cyclopropyl ketones[4] (Scheme I).

In concentrated sulfuric acid, a strong dehydrating medium, the likelihood of hydrating the iminodiazonium ion **2** with water to give a tetrahedral intermediate is reduced. This raises the intriguing possibility which we have not seen in the literature that **2** may equilibrate not through reversible hydration (Scheme I) but rather by the analogous addition of H_2SO_4 to the C=N double bond. We have also examined the effect of protonation of the iminodiazonium cation on the ease of *Z–E* isomerization, in view of the fact that these reactions typically proceed better in concentrated H_2SO_4 than at 50% acid strength. The rotational barrier of the dication **17** was calculated to be 53.3 kcal/mol (STO-3G) which tends to preclude this mode of *Z–E* equilibration under the conditions of the Schmidt reaction. Protonation of **2** would therefore have a retarding influence on syn–anti topomerization by thwarting the inversion pathway.



17

There are several aspects of the calculated geometries and charge distributions that are worthy of note. At the beginning of this paper we alluded to the possibility that a significant contribution from resonance structure **8a** would render the diazo portion of the molecule nonlinear. Indeed, we see that the N-N-N bond angle β in **12** is 160.0° (Table II) and that the calculated charges on the azide moiety (=N_1—N_2≡N_3) are +0.10, +0.09 and +0.28, respectively. The change in hybridization at N_2 (sp → sp^2) not only reduces the N_2–N_3 bond order but also makes the *terminal nitrogen* bear the highest positive charge. The increased localization of electron density at N_2 also man-

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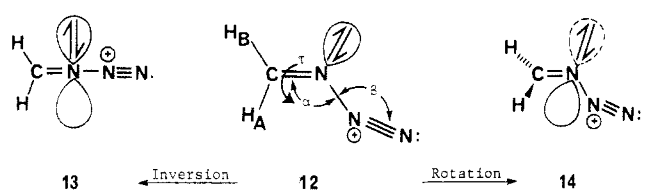
[17] (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Chem. Soc. A* **1971**, 2299. (c) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339.

[18] The calculated total energies for N_2 and CH_2N^+ are −107.500 64 and −91.890 56 (STO-3G), and −108.868 01 and −92.818 22 (6-31G) au, respectively. The total energy for CH_3CHN^+ is −130.524 57 au.

Table II. Geometry Optimization of *N*-Diazoformimines



Geometry Minimized by STO-3G

	bond angles, deg					E_{rel}, kcal/mol	
structure	α	β	τ	H_A—C=N	H_B—C=N	STO-3G	6-31G[a]
13 (Inv_{max})[b]	180.00	180.00	0.0	120.40	120.40	53.79	30.18
12a	160.00	169.37	0.0	122.44	117.22	46.91	20.94
12b	140.00	158.83	0.0	126.67	112.66	26.69	14.82
12c	120.00	157.30	0.0	127.76	111.19	4.62	2.64
12 (E_{min})	107.87	163.11	0.0	127.71	112.32	0.0	0.0
12d	107.87	162.40	30.0	127.59	112.77	12.09	11.27
12e	107.87	164.31	60.0	125.95	116.23	47.73	44.07
14 (Rot_{max})[c]	107.87	168.64	90.0	121.43	121.43	72.06	61.92

	bond lengths, Å					E_{tot}, au	
structure	C=N	N—N	N≡N	H_A—C	H_B—C	STO-3G	6-31G[a]
13 (Inv_{max})	1.2684	1.2513	1.1703	1.1095	1.1095	−199.363 43	−201.820 10
12 (E_{min})	1.3075	1.6072	1.1417	1.1004	1.1048	−199.449 15	−201.868 20
14 (Rot_{max})	1.4183	1.3434	1.1545	1.1206	1.1206	−199.334 31	−201.769 53

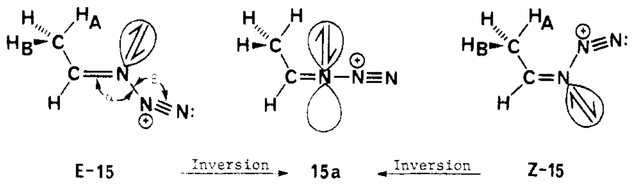
Geometry Minimized by 6-31G

	bond angles, deg					
structure	α	β	τ	H_A—C=N	H_B—C=N	E_{rel}, kcal/mol
13	180.00	180.00	0.0	120.20	120.20	28.17
12	110.15	160.01	0.0	127.38	112.22	0.0

	bond lengths, Å					
structure	C=N	N—N	N≡N	H_A—C	H_B—C	E_{tot}, au
13	1.2545	1.2020	1.1079	1.0770	1.0770	−201.835 71
12	1.2679	1.6072	1.0863	1.0704	1.0775	−201.880 60

[a] 6-31G energy calculated by using STO-3G fully minimized structures. [b] Structures **12a–c** are fully minimized points on the pathway to inversion. [c] Structures **12d** and **12e** are fully minimized points on the pathway to rotation.

Table III. Geometry Optimization of *N*-Diazoacetimines



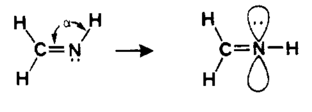
Geometry Minimized by STO-3G

	bond angles, deg							E_{rel},
structure	α	β	H—C=N	C—C=N	H_A—C—C	H_B—C—C	H_A—C—H_B	kcal/mol
(*E*)-**15**	107.76	162.67	124.51	115.38	110.55	108.16	110.49	0.0
15a	180.00	180.00	117.64	123.07	110.73	108.85	110.17	53.75
(*Z*)-**15**	108.94	160.10	107.87	132.82	111.35	108.12	110.36	0.28

	bond lengths, Å							
structure	C=N	N—N	N≡N	H—C	C—C	H_A—C	H_B—C	E_{tot}, au
(*E*)-**15**	1.315	1.622	1.141	1.101	1.526	1.088	1.091	−238.055 91
15a	1.275	1.248	1.170	1.111	1.528	1.087	1.091	−237.970 25
(*Z*)-**15**	1.311	1.626	1.141	1.107	1.520	1.087	1.092	−238.055 47

ifests itself in an increased barrier to inversion relative to the cyano analogue **9**. As expected the N–C–N bond angle in the *N*-cyano imine **9** is more nearly linear at 174.9°.

The origin of the inversion barriers and those factors that influence the relative barrier heights remain to be discussed. Before we attempted to explain the differences in the magnitude of the barriers of the cyano and diazo-substituted imines, we deemed it advisable to first analyze the inversion process in the simplest imine, methanimine (**18**).



18 **19**

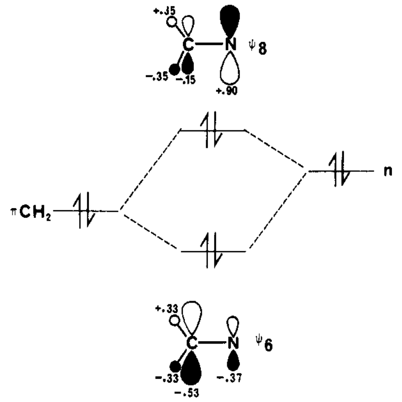


Figure 1. Energy diagram and orbital coefficients illustrating the interaction of the π_{CH_2} orbital of methylene with a lone-pair orbital of the nitrogen in the transition state (**19**) for nitrogen inversion.

The transition state to nitrogen inversion (**19**) is 25.2 kcal/mol above the ground state **18** (6-31G).[12b] This increase in energy upon inversion is due to a first approximation to the promotion of an electron pair from an sp^2 orbital to a p orbital on nitrogen attendant upon a change in C–N–H bond angle from $\alpha = 115.7°$ to 180°. The lone pair on nitrogen (n) in both the ground and transition states is strongly mixed with a π_{CH_2} orbital[19] of the methylene group as illustrated in Figure 1. It is interesting to note that, as expected, the lower lying MO is comprised mainly of the CH_2 group, whereas the higher MO is principally (~82%) the nonbonding electron pair on nitrogen. The bonding combination (ψ_5) in the ground state also contains a small amount of σ_{C-N}. During the inversion process both the HOMO orbital ψ_8, which is the higher lying ($\pi_{CH_2} - n$) combination, and $\psi_6(\pi_{CH_2} + n)$ are elevated in energy by 42.9 and 36.6 kcal/mol, respectively. The energy of the π orbital of the carbon–nitrogen double bond (ψ_7) remains virtually unchanged while ψ_6, a σ HNCH orbital in **18**, correlates with ψ_5 in the transition state and is decreased in energy by 53.3 kcal/mol. In this relatively simple model compound the inversion barrier of 25.2 kcal/mol may be largely attributed to the relative increase in energy (26.2 kcal) of the occupied frontier molecular orbitals upon inversion. Thus, the orbitals responsible for the inversion barrier are both orthogonal to the π system of the carbon–nitrogen double bond. We emphasize that *both* of these filled orbitals, the bonding and antibonding π combinations of the lone pair on nitrogen, increased in energy on going to transition state **19** (Figure 1). In the absence of such orbital interactions the electron pair on nitrogen would occupy a pure p orbital in the transition state which would obviously result in a higher barrier to inversion. The net destabilizing effect of the four-electron interaction is compensated for by an energy decrease in lower lying orbitals.

It has been established experimentally that the influence of substituents on imino nitrogen stereomutation has a parallel trend in pyramidal nitrogen inversion in amines. Electron-releasing substituents such as alkoxy raise the barrier, and electron-withdrawing groups like the acyl moiety facilitate nitrogen inversion. This may be qualitatively attributed to electron repulsion of the adjacent lone pairs in the former example and resonance delocalization of the occupied nitrogen p orbital in the transition state in the latter.[8] It has been generally accepted that the π orbials of the substituent Y on nitrogen lower the barrier by increasing the conjugation in the transition states for inversion, **10a**. We sought to corroborate this suggestion by an analysis similar to that used above in methanimine (**18**).

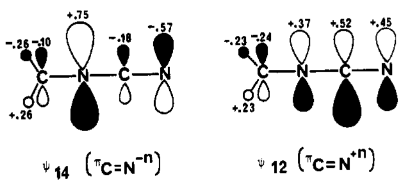


Figure 2. Frontier molecular orbitals of the transition state **10** for nitrogen inversion in *N*-cyanoformimine.

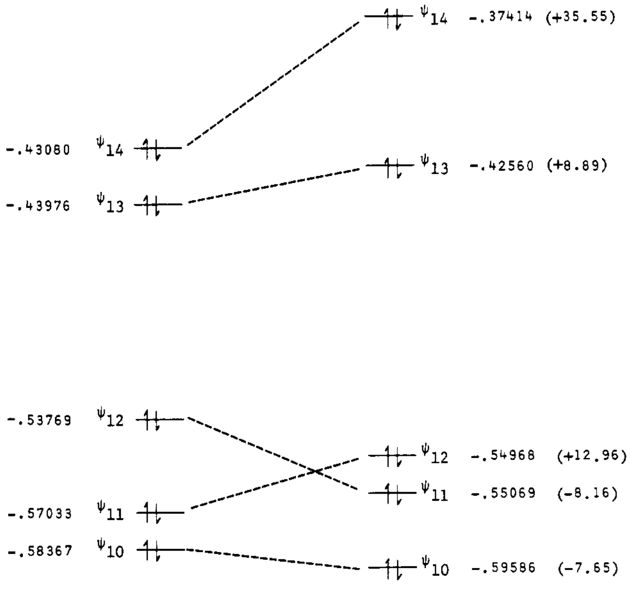
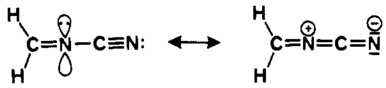


Figure 3. 6-31G calculated occupied frontier orbital energies (au) for *N*-cyano compound **9** and the net change in orbital energies (kcal/mol) in the transition state for nitrogen inversion, **10** (given in parentheses).



10 **10a**

In methanimine the transition state for inversion **19** involves a lone pair on nitrogen interacting with an adjacent filled methylene fragment. With the *N*-cyano imine **10**, the lone pair on nitrogen may also be stabilized by resonance delocalization with the parallel π orbitals of the adjacent cyano group. As illustrated in Figure 2, the pertinent occupied frontier MO's are principally a lone pair on nitrogen combined in a bonding (ψ_{11}) and antibonding (ψ_{14}) manner with a $\pi_{C=N}$ orbital. Both orbitals contain a small component of a π_{CH_2} orbital mixed in an out-of-phase manner. The π_{CH_2} is mixed in ψ_9 in a bonding manner (no nodes), and this orbital is principally composed of the π_{CH2} fragment.

The HOMO (ψ_{14}) in the ground-state structure **9** is elevated in energy 35.55 kcal/mol (STO-3G) while the lower lying MO (ψ_{11}) also containing the nitrogen lone pair increased in energy by only 12.96 kcal/mol (ψ_{12}, Figure 3). These molecular orbitals are a manifestation of the clas-

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[19] The π-type CH_2 group orbital is orthogonal to the carbon–nitrogen π bond and is constructed from an atomic 2p orbital on carbon and the two 1s orbitals on hydrogen which are mixed in a bonding manner. For a discussion see: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; p 6.

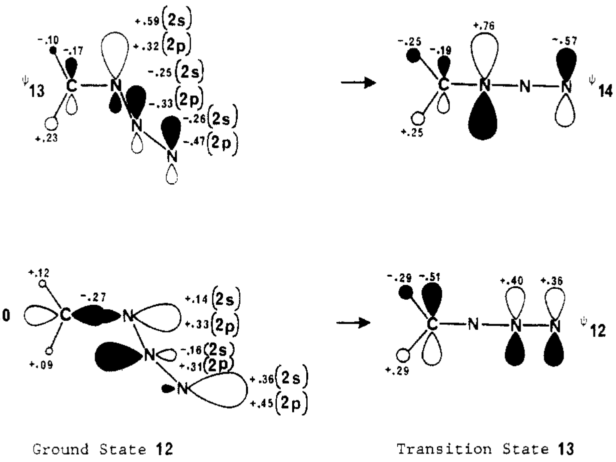

Figure 4. Frontier molecular orbitals in *N*-diazoformimine.

sical "allylic anion" resonance interaction, and as a result these orbital fragments have the approximate phase properties of ψ_2 and ψ_1 of an allyl system, perturbed somewhat by the π_{CH_2} group. Again we emphasize that these orbitals are orthogonal to the C=N π bond of the imine.

The remaining orbitals in Figure 3 are not as drastically altered upon nitrogen inversion since they are all orthogonal to the orbital bearing the nitrogen "lone pair". Thus, ψ_{10}, ψ_{13}, and ψ_{15} (the LUMO in 10) are the π molecular orbitals of the conjugated C=N—C=N diene system and hence have the same nodal properties as the linear combination of π orbitals, ψ_1, ψ_2, and ψ_3, in butadiene. The σ bonding in this system embodies ψ_{12} which also contains a lone pair on the terminal nitrogen. The fluctuations in the total energy of the molecule upon inversion closely follow those of its HOMO level. Thus, in the transition state ψ_{10} and ψ_{13} are the occupied "symmetric and antisymmetric" π molecular orbitals of the conjugated C=N—C=N system, and ψ_{11} is a σ orbital with a "lone pair" directed along the σ axis. The LUMO in 10 is the π MO of the linear π system containing two nodes. On balance, we can attribute a large share of the inversion barrier to the 35.55 kcal/mol increase in energy of the HOMO orbital (ψ_{14}) that contains the lone pair on nitrogen. The relative change in energy of the "butadiene-like" π orbitals has only a modest influence on the inversion barrier.

The composition and symmetry of the frontier molecular orbitals in *N*-diazoformimine (**12**) closely resemble those of *N*-cyanoformimine (**9**). However, there are minor changes in the order of the respective energy levels. The HOMO ψ_{14} in the ground state of **12** is the π molecular orbital of $C=N_1—N_2=N$, i.e., the linear combination of four p orbitals with one node between N_1 and N_2. This orbital increases in energy by 21.01 kcal/mol, affording ψ_{13} in the transition state **13**. The "culprit orbital" that contributes most significantly to the inversion barrier is the next to the highest MO (NHOMO), ψ_{13}. As shown in Figure 4, this orbital is the higher lying occupied combination of the "lone pair" and a nitrogen–nitrogen double bond and therefore resembles the nonbonding ψ_2 in a typical allyl anion. The bonding combination, ψ_{10} in **12**, is the other in-phase combination containing the imine nitrogen "lone pair". Both of these orbitals are seen (Figure 5) to increase upon inversion at nitrogen by 79.57 and 20.24 kcal/mol (6-31G), respectively. In the transition state (**13**) we see that ψ_{14} has a minor contribution from the "π-type" CH_2 fragment[19] mixed in an out-of-phase manner while ψ_{12} arises in part from a lower lying σ_{CH_2}-type orbital. Both ψ_{12}, a σ orbital, and ψ_{11}, a C=N—C=N π orbital (no nodes), decrease in energy. Again we see that the relatively high inversion barrier reflects the trend in the highest MO containing the nitrogen "lone pair".

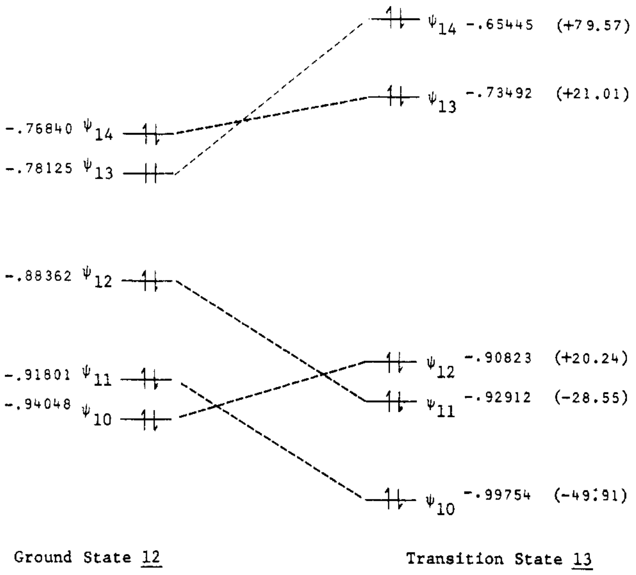

Figure 5. 6-31G calculated occupied frontier orbital energies (au) for *N*-diazoformimine (**12**) and the net change in orbital energies (kcal/mol) in the transition state for nitrogen inversion, **13** (given in parentheses).

The overall similarity between the C≡N: and $^+N≡N$: groups in attempting to stabilize the transition state for inversion is striking. The 6-31G calculated barriers for nitrogen inversion in compounds **9**, **18**, and **12** are 14.5, 25.2, and 28.2 kcal/mol, respectively. In each case, a frontier molecular orbital containing the nitrogen lone pair is seen to rise in energy by 35.6, 42.9, and 79.6 kcal/mol, respectively.[20] These data provide a clear indication that the inversion barrier is not simply the result of the elevation of an electron pair in a sp^2 orbital on nitrogen but rather the rise in energy of one or more molecular orbitals which contain this electron pair. The simple resonance picture that illustrates the stabilization of the transition state for imine nitrogen inversion **10a** is clearly illustrated by the orbitals given in Figures 2 and 4. The cyano group is capable of extending the conjugation in the transition state and hence lowering the barrier in **9** relative to our model methanimine (**18**). The cyano group, however, is not as effective as a carbonyl in extending conjugation, and calculations suggest that $^-CH_2CN$ is actually pyramidal, albeit with a low carbon inversion barrier of 0.1 kcal/mol.[21] In contrast, the *N*-diazo compound **12** has the lone pair highly localized on the *imine nitrogen* (ψ_{14}, Figure 4) which results in a higher activation energy for inversion than that for **18**. For the sake of comparison we include a calculated (6-31G) barrier for oxime inversion on **20**[22] which is 59.1 kcal/mol.[23] This compound demonstrates the adverse effects of lone-pair repulsion on the barrier to nitrogen inversion in imines.

In summary, the mechanism of the Schmidt reaction on ketones appears to involve rearrangement of nonisomer-

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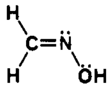
[20] The energies of the STO-3G molecular orbitals (45.0, 54.7, and 77.0 kcal/mol) show a similar trend.

[21] Mezey, P. G.; Robb, M. A.; Yates, K.; Csizmadia, I. G. *Theor. Chim. Acta* **1978**, *49*, 277.

[22] The minimized geometry was taken from: Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie Mellon Quantum Chemistry Archive", Carnegie Mellon University: Pittsburgh, PA, 1980.

[23] Bach, R. D.; Wolber, G. J. *J. Org. Chem.*, in press.



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izing iminodiazonium ions **2a** and **2b**. Any equilibration of these two ions, as in the hydrolysis of vinyl azides, must involve reversible addition of water (or sulfuric acid) to yield a tetrahedral intermediate. If the rate of this equilibration is slow, compared to the rate of rearrangement, then the ratio of products formed will depend on steric effects, whereas if the rate of equilibration is fast, the product will depend on the migratory aptitude and charge-stabilizing ability of the groups R_1 and R_2. Direct rearrangement of the tetrahedral intermediate 1 may occur if dehydration is unfavorable due to steric or other reasons. This study not only has resolved an important question concerning the mechanism of the Schmidt reaction but also has heightened our knowledge of the effect of the direction of polarization of multiple bonds attached to imino nitrogen on the inversion barrier to isomerism of imines.

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Registry No. 9, 43730-26-3; **12**, 79827-95-5; (*E*)-**15**, 79827-96-6; (*Z*)-**15**, 79827-97-7.

Theoretical Analysis of the Barrier to Nitrogen Inversion in *N*-Fluoroformimine and Formaldoxime

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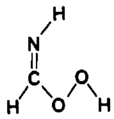
The barriers to nitrogen inversion in *N*-fluoroformimine and formaldoxime have been computed to be 77.4 and 59.5 kcal/mol, respectively, by employing a 6-31G basis set with full geometry optimization. A theoretical analysis of the origin of these barriers suggests that an "allyl type" MO containing the nitrogen lone pair is largely responsible for the increase in total energy in the transition state for planar nitrogen inversion.

In principle, inversion at planar nitrogen in imines may occur by rotation about the C═N double bond or by an in-plane lateral shift mechanism.[1] There is now a consensus of opinion that favors the latter process in most compounds. However, in specific cases heteroatom substitutents at the imino carbon may sufficiently perturb the C═N π system to lower the barrier to rotation, and a combined inversion–rotation mechanism may ensue.[2] In contrast, when the substitutent at imino nitrogen is a heteroatom bearing a lone pair of electrons (O, N, halogen), the inversion barrier usually increases. For example, the barrier to inversion in oximes is typically above 23 kcal/mol and isolation of epimers becomes feasible.[2]

A number of theoretical studies on the mechanism of syn–anti isomerism of oximes[3-5] agree that an inversion mechanism is lower in activation energy than a rotational process. Computed inversion barriers of 23.0 (Hückel),[5] 37.5 (CNDO),[4] 35.8 (FSGO),[3] and 50.6 (ab initio)[4] kcal/mol have been reported for formaldoxime (1). The origin of the increase in energy of the linear transition 1a has been attributed to the σ-electron-withdrawing effect of the electronegative substitutent and to the electron repulsion between the nitrogen lone-pair and the nonbonding electrons on heteroatom substitutents.[1,4] The transfer of electrons from a relatively diffuse 2s orbital to a more directed higher energy p orbital upon rehybridization ($sp^2 \rightarrow p$) at nitrogen also contributes to the barrier.[1a]

Our interest in nitrogen inversion stems from a theoretical study of syn–anti isomerism in peroxyformimidic acid (2). We demonstrated a pure inversion mechanism with no detectable torsional component to the *Z*–*E* isomerization pathway despite the heteroatom substitutent at carbon.[6] However, both the inversion and rotational barriers were diminished by the electronic influence of the lone pair on oxygen.



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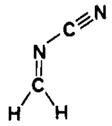

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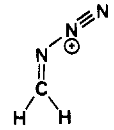

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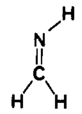

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In our related studies on the inversion barriers in *N*-cyano- and *N*-diazoformimine (3 and 4),[7] we found that a comparison between the frontier molecular orbitals in 3 and 4 to those in the simplest model substrate, methylenimine (5), provided us with considerable insight into the origin of the inversion barrier. With *N*-cyanoformimine (3), we observed good agreement between our computed barrier (14.5 kcal/mol) and the experimental barrier on the corresponding dimethyl analogue (18.9 kcal/mol)[8] when an extended 6-31G basis set was used. We now

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[1] (1) For excellent reviews on this topic see: (a) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311. (b) Kalinowski, H.-O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.

[2] (2) (a) Raban, M. *Chem. Commun.* **1970**, 1415. (b) Raban, M.; Carlson, E. *J. Am. Chem. Soc.* **1971**, *93*, 685.

[3] (3) Hwang, W. F.; Kuska, H. A. J. *J. Phys. Chem.* **1978**, *82*, 2126.

[4] (4) Liotard, D.; Dargelos, A.; Chaillet, M. *Theor. Chim. Acta* **1973**, *31*, 325.

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[7] (7) Bach, R. D.; Wolber, G. J., preceding paper in this issue.

[8] (8) McCarty, C. G.; Wieland, D. M. *Tetrahedron Lett.* **1969**, 1787.

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