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Reaction of methoxide ion with the *Z*- and *E*-isomers of *O*-methylbenzohydroximoyl cyanide. Theoretical calculations on the conformations of the tetrahedral intermediate

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ABSTRACT: Theoretical calculations (HF/6–31 + G*, MP2/6–31 + G*//HF/6–31 + G*, B3LYP/6–31 + G*//HF/6–31 + G*, HF-SCIPCM/6–31 + G*//HF/6–31 + G*, and B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G*) were carried out on the tetrahedral intermediate $RC(CN)(OCH_3)—NOCH_3^-$, where $R = C_6H_5$, $CH_2{=}CH$ or H, generated by nucleophilic attack of methoxide ion on (*Z*)- or (*E*)-*O*-methylhydroximoyl cyanide [$RC(CN){=}NOCH_3$]. These calculations indicate that the staggered conformation **4C**, which would lead to an *E*-substitution product, is approximately 7 (R = H) or 8 kcal mol^{-1} ($R = CH_2{=}CH$) less stable than conformation **4A**, which leads to a *Z*-substitution product. Furthermore, the lowest energy transition state leading to a *Z*-substitution product is approximately 5 kcal mol^{-1} lower in energy than the lowest energy transition state leading to an *E*-substitution product. These results provide an explanation for the experimental results reported recently that (*Z*)-*O*-methylbenzohydroximoyl cyanide gives only the less thermodynamically stable *Z*-substitution product under conditions where the purported tetrahedral intermediate should have a long enough lifetime to establish an equilibrium between all the staggered conformations. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: methoxide ion; *O*-methylbenzohydroximoyl cyanide isomers; tetrahedral intermediate; conformation; theoretical calculations

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Nucleophilic substitution reactions at the carbon–oxygen double bond are among the most important reactions in organic and biochemistry. The mechanisms of nucleophilic substitution at the carbon–oxygen double bond (acid chlorides, esters, amides, anhydrides, etc.) have received considerable attention,[1] but it has not been possible to study the stereochemistry of these reactions since the carbonyl group is not capable of geometric isomerism. Although the most common mechanism for nucleophilic acyl substitution is addition–elimination ($A_N + D_N$) with formation of a tetrahedral intermediate, other mechanisms including S_N1 ($D_N + A_N$) and S_N2 (A_ND_N) have been found to take place in some acid chlorides and esters (for some examples of S_N1 and S_N2 mechanisms in acid chlorides and esters, see Ref. 2).

We have been studying the mechanisms of nucleophilic substitution at the carbon–nitrogen double bond (imines). These mechanistic studies give insight into the chemistry of the carbon–nitrogen double bond and also the chemistry of the closely related carbon–oxygen double bond. Some time ago we were able to synthesize the first examples of thermally stable geometric isomers of an imine [hydroximoyl halides, $ArC(X){=}NOR$] in which a suitable leaving group (halide ion) is attached to the carbon–nitrogen double bond. Since that time we have reported on the mechanisms of solvolysis,[3a] alkoxide substitution,[3b] amine substitution,[3c] alkyl amide substitution[3c] and acid-catalyzed geometric isomerization[3d] of compounds containing the carbon–nitrogen double bond.

The substitution reactions of hydroximoyl halides with alkoxides, amines, or amide ions appear to be occurring by an addition–elimination mechanism. The most important experimental evidence for the addition–elimination mechanism in these reactions is the small element effect ($k_{Br}/k_{Cl} < 12$). Although these reactions

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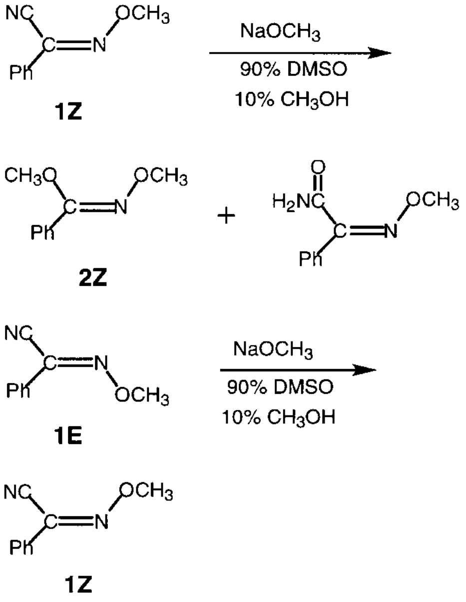
involve tetrahedral intermediates which could undergo stereomutation by rotation around a carbon–nitrogen single bond, the reactions are stereospecific: (*Z*)-chloride + nucleophile → *Z*-substitution product; (*E*)-chloride + nucleophile → *E*-substitution product (major) + *Z*-substitution product (minor). We have attempted to explain these results in terms of stereoelectronic control[4] in the breakdown of the tetrahedral intermediates. This intriguing aspect of these reactions led us to investigate nucleophilic substitution reactions on imines that contain a poor leaving group (cyanide ion). With a poor leaving group it was anticipated that the tetrahedral intermediate would have a long enough lifetime that stereomutation of the intermediate would take place.

Ta-Shma and Rappoport[5] investigated nucleophilic substitution on imidoyl cyanides [ArC(CN)=NAr′] with amines and alkoxides. They suggested that these substitution reactions proceed by an addition–elimination mechanism with the elimination step being the rate-determining step ($A_N + D_{N\#}$). The stereochemistry of the imidoyl cyanide reactions could not be determined since the *Z*-and *E*-isomers of these compounds and their substitution products are not known.

We recently published on the mechanism of methoxide ion substitution in (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl cyanides (**1Z** and **1E**).[6] The reaction of the (*Z*)-hydroximoyl cyanide with methoxide ion [in 9:1 dimethyl sulfoxide (DMSO)–methanol] gave a 1:1 mixture of methyl (*Z*)-*O*-methylbenzohydroximate (**2Z**) and the *O*-methyloxime of α-ketophenylacetamide. It was found that the (*E*)-hydroximoyl cyanide underwent methoxide ion-catalyzed isomerization to the *Z*-isomer faster than it reacted by nucleophilic substitution:

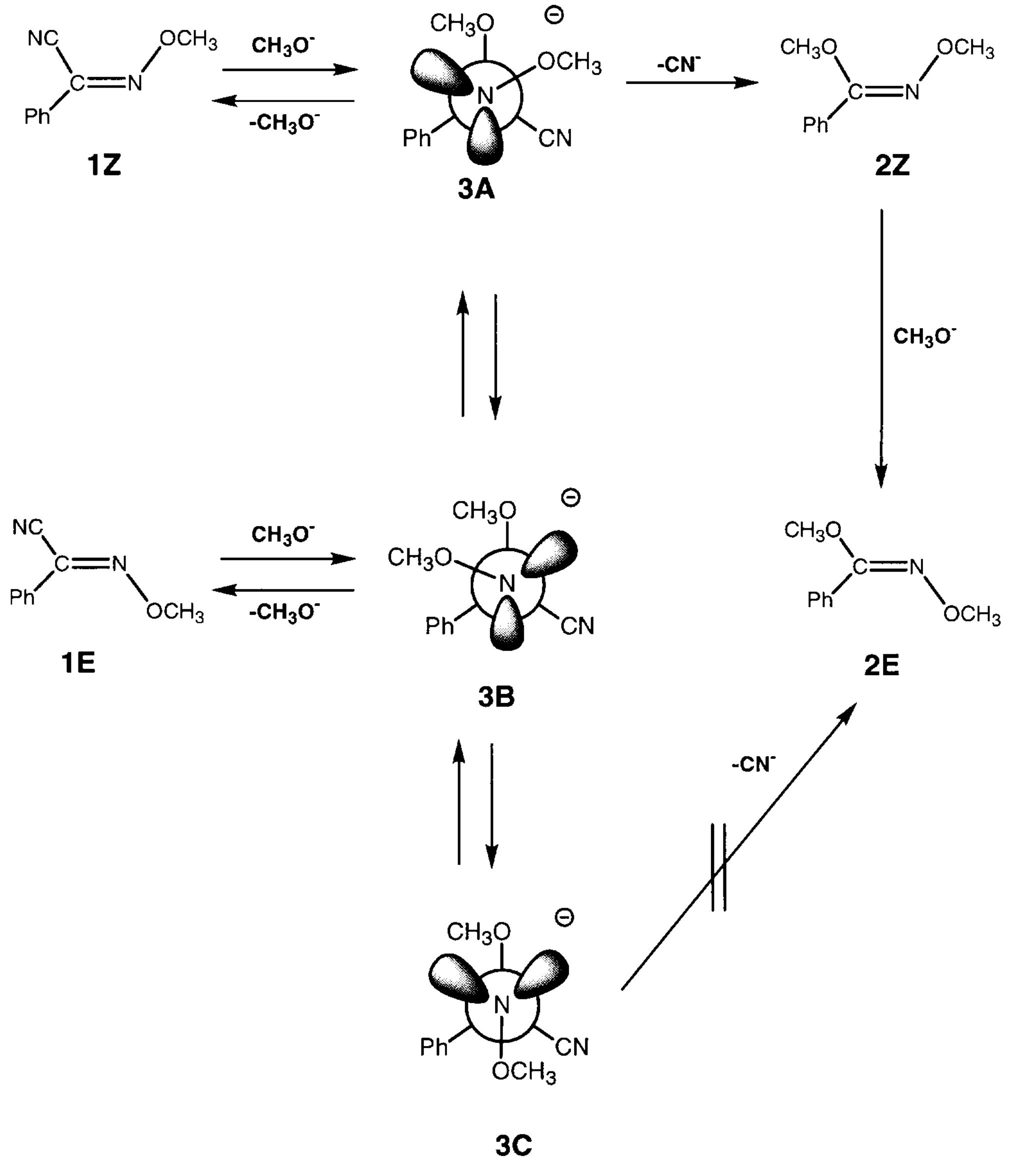


Both substitution and isomerization follow second-order kinetics (first order in methoxide ion and first order in the hydroximoyl cyanide). The possiblity of isomerization occurring by methoxide ion attack on the imine nitrogen was ruled out since there was no evidence for alkoxide exchange in the methoxide ion-catalyzed isomerization of the *N*-ethoxy cyanide [$PhC(CN)C{=}NOCH_2CH_3$]. These observations were interpreted in terms of an addition–elimination mechanism in which the rate-determining step is elimination of cyanide ion ($A_N + D_{N\#}$, Scheme 1).

Although the $A_N + D_{N\#}$ mechanism is a reasonable interpretation of our observations, there is a serious matter left unresolved. Since loss of the nucleofuge in this mechanism is rate determining, it seems reasonable to assume that all conformations of the tetrahedral intermediate should be accessible during the reaction of the (*Z*)-hydroximoyl cyanide with methoxide ion (see Scheme 1). Of the three staggered conformations (**3A**–**3C**), only **3A** and **3C** have the p-orbitals on carbon and nitrogen aligned properly for formation of the carbon–nitrogen π-bond, i.e. there is not a p-orbital *anti* to the leaving group (cyanide ion) in **3B**. Since only the *Z*-substitution product (**2Z**) was initially produced in this reaction, it would appear that only conformation **3A** is leading to product. It is difficult to rationalize why the *E*-substitution product (**2E**) is not formed from conformation **3C** under conditions where one would expect all staggered conformations to co-exist. What is even more difficult to explain is the fact that the (*Z*)-hydroximate is the kinetic product of the reaction, i.e. the *Z*-substitution (**2Z**) product slowly isomerizes to the thermodynamically more stable (*E*)-hydroximate (**2E**). Hence it cannot be argued that the rate of reaction from conformation **3A** is greater than from **3C** because of a difference in stability of the incipient double bond in the transition state for the reaction **3A** → **2Z** as compared with **3C** → **2E**.

In an attempt to resolve this problem, we carried out molecular orbital calculations (AM1) on the tetrahedral intermediate that would be formed in this reaction by methoxide attack at the carbon–nitrogen double bond. Using the AM1 method[7] the energy of the tetrahedral intermediate was calculated as a function of rotation around the carbon–nitrogen single bond axis. These calculations show that the staggered conformations at a torsional angle corresponding approximately to conformations **3A** and **3B** in Scheme 1 represent minima in potential energy. The other staggered confromation, which corresponds approximately to conformation **3C,** is much higher in energy with a conformational relative energy $5.6\,\mathrm{kcal\,mol^{-1}}$ ($1\,\mathrm{kcal} = 4.184\,\mathrm{kJ}$) higher than conformation **3A**. The AM1 calculations showed **3B** to be $1.2\,\mathrm{kcal\,mol^{-1}}$ higher in energy than **3A**.

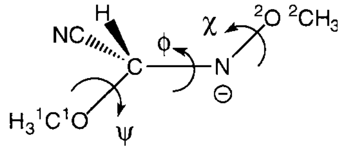
It is disconcerting that conformation **3C** is predicted by AM1 to be so much more unstable than the other staggered conformations. This would suggest that there is a major destabilizing interaction in conformation **3C**. To explore this surface in more detail, we performed a series of *ab initio* molecular orbital calculations on the stable conformations of **4**. This compound is a model of the



k (E-cyanide → Z-cyanide) = 8.66 x $10^{-3}M^{-1}s^{-1}$
k (hydroximate formation) = 3.50 x $10^{-4}M^{-1}s^{-1}$
k (Z-hydroximate → E-hydroximate) = 1.59 x $10^{-5}M^{-1}s^{-1}$

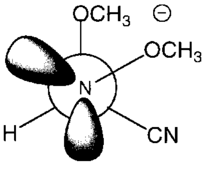
Scheme 1

tetrahedral intermediate formed from methoxide attack on **1Z** and **1E**, but with the phenyl ring replaced by a hydrogen for the sake of computational expediency.

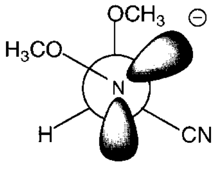

4

Ab initio calculations were performed, using the Gaussian 94 series of programs,[8] on all staggered conformations of **4** transition states leading to the formation of both *Z* and *E* products, as well as the rotational barriers for interconverting tetrahedral intermediate conformers **4A**, **4B** and **4C**. Geometries were fully optimized at the Hartree–Fock (HF) level of theory, using the 6–31 + G(*) basis set.[9] Single-point energy calculations using both the Møller–Plesset (MP2) and hybrid density functional (B3LYP) levels of theory[10] were completed to help account for electron correlation effects. To help account for solvent polarity effects, single-point energy calculations were performed using the self-consistent iterative polarizable continuum method (SCIPCM) of Tomasi and co-workers,[11] with a dielectric value of 47.0, which should be similar to that for DMSO which was used in the experimental work on these reactions. These single-point energy calculations did not involve a reoptimization of the geometry. Complete vibrational frequency analysis was completed at the HF level of theory using the HF fully optimized geometries. All reactants, products and intermediates (**4A**, **4B**, **4C**) had all positive eigenvalues of the second derivative matrix (Hessian), indicating all structures were true equilibrium minima. On the other hand, all transition states for either elimination to products or reactants, or rotational transition states, had exactly one negative frequency, corresponding to motion along the appropriate reaction coordinate.

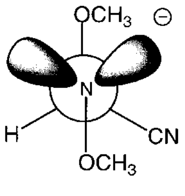
In **4** there are three independent internal rotors (ϕ, ψ, χ) leading to 27 possible stable staggered conformations. As in the AM1 simulations, there are three possible staggered conformations around the central C—N bond (ϕ), leading to conformations **4A**, **4B** and **4C**, in analogy to conformations **3A**, **3B** and **3C**, from the AM1 study. Newman projections for these conformations are shown below, looking down the central C—N bond.



4A



4B



4C

For each of **4A, 4B** and **4C**, there are nine possible stable conformations corresponding to rotation around the ^{1}C—^{1}O—C-N (ψ) and C—N—^{2}O—^{2}C (χ) bonds (see previous structure for definitions of atoms and bonds). Although optimized geometries for all 27 possible stable conformations were attempted, only 10 stable minima were located. Four of these corresponded to structures of the **4A** type (labeled **4A-1, 4A-2, 4A-3**, and **4A-4**, three of the **4B** type (labeled **4B-1, 4B-2** and **4B-3**) and three of the **4C** orientation (**4C-1, 4C-2, 4C-3**). Table 1 shows the calculated ϕ, ψ and χ dihedral angles for the optimized geometries. Table 2 gives a summary of calculated relative energies at the various levels of theory employed here. These energies are relative to the calculated energy for the most stable intermediate (**4A-2**). These calculations clearly show that at all levels of theory the lowest energy conformations of **4A** and **4B** are very similar, and significantly lower in energy than the corresponding **4C** conformations. Table 3 summarizes the relative energies of the most stable conformations of **4A, 4B** and **4C**.

Since **4B** cannot lead to product formation and **4C** is significantly destabilized, it follows logically that all product should arise from conformation **4A**. Detailed inspection of electron density–electrostatic potential contour diagrams (not shown) reveals a possible explanation as to why conformation **C** is significantly destabilized relative to the **A** and **B** conformations. This diagram clearly shows enhanced electron–electron repulsion between the two lone pairs of electrons on nitrogen and the ^{1}O lone pairs for conformation **C**, while such interactions are reduced in either the **A** or **B** conformations. We believe that this increased electron–electron repulsion, present only in conformation **C**, is why all product formation occurs from conformation **A**.

Table 1. Summary of optimized [HF/6–31 + G(d)] dihedral angles ° for stable conformations of 4 and 4-vinyl

Conformation	ϕ	ψ	χ
4A-1	77.2	−44.7	131.7
4A-2	68.9	164.1	137.8
4A-3	69.9	164.5	−112.7
4A-4	64.1	40.4	136.6
4A-vinyl	63.3	33.7	133.8
4B-1	−74.0	−35.9	−149.0
4B-2	−78.0	162.5	117.4
4B-3	−89.3	50.6	−133.3
4B-vinyl	−64.4	−34.8	−164.5
4C-1	−167.4	−45.9	−136.9
4C-2	−169.6	163.0	−136.4
4C-3	−158.0	58.6	−132.1
4C-vinyl	−174.0	44.7	−130.5

To investigate further the kinetics of this system, for each stable conformation of the type **4A, 4B** or **4C**, we probed the potential energy hypersurface to locate the lowest energy transition state leading to either the reactants, the *Z*-substitution product (from **4A**) or the *E*-substitution product (from **4C**). From Table 2, one can clearly see that at the best level of theory (B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G* + ZPVE) the lowest energy transition state for elimination of cyanide (**4A-4-elim-Z**) to form the *Z*-product is approximately 3 kcal mol^{-1} lower in energy than the corresponding lowest energy transition state for elimination of cyanide to from the *E*-product (**4C-1-elim-E**), 4.6 versus 7.5 kcal mol^{-1}. Furthermore, the lowest energy path connecting the **4A** conformations to the **4C** conformations has a calculated rotational energy barrier of 9.7 kcal mol^{-1} (**4A-1-rot-C1** at B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G*), which is significantly higher than the barrier for eliminating cyanide to form the Z-product (4.6 kcal mol^{-1}).

These calculations agree remarkably well with the experimentally observed results, and help us to understand what is occurring in solution. From Table 2 we can see that the overall reaction is predicted to be exothermic by about 22 kcal mol^{-1}, in keeping with the well known solution stabilities of cyanide relative to methoxide, thus providing the driving force for the reaction to occur. Formation of the most stable **4A** intermediate (**4A-2**) is

Table 2. Calculated relative energies (with respect to 4A-2) (kcal mol^{-1})[a]

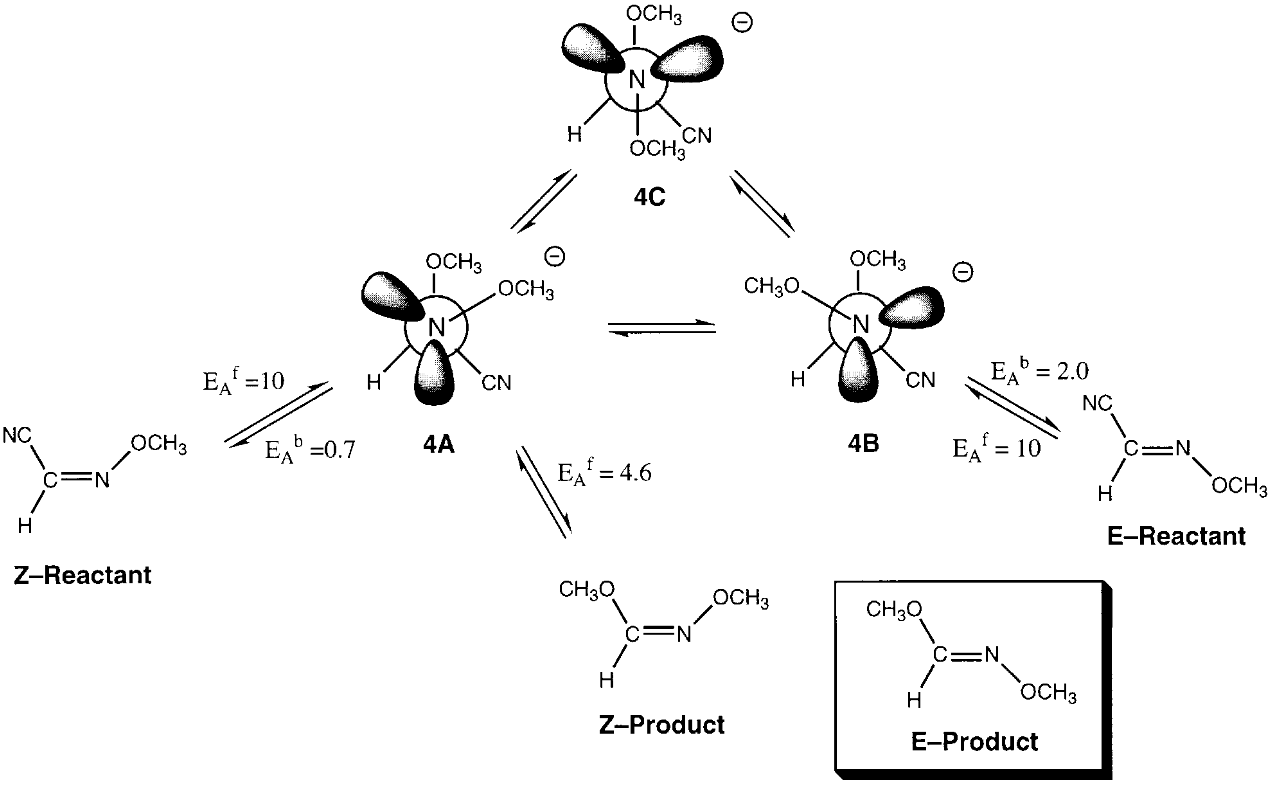
	HF + ZPVE[b]	HF (scrf) + ZPVE	B3LYP//HF + ZPVE	MP2//HF + ZPVE	B3LYP (scrf) //HF + ZVPE
Reactants					
4Z + methoxide	24.8	3.0	21.9	28.2	1.4
Intermediates					
4A1	0.7	2.5	0.2	−0.1	1.1
4A2	0.0	0.0	0.0	0.0	0.0
4A3	4.2	0.9	2.6	3.7	0.3
4A4	4.0	0.2	3.0	3.5	0.1
4B1	0.2	1.0	−0.4	0.4	−0.4
4B2	3.3	0.6	2.1	3.2	0.9
4B3	1.6	2.3	0.7	1.2	1.0
4C1	5.1	6.5	7.4	8.4	7.4
4C2	8.9	5.4	10.8	12.5	7.9
4C3	5.2	5.4	6.8	8.5	6.9
Transition states					
4A1 (elim-SM)	12.3	11.7	0.6	2.4	0.7
4A1 (elim-Z)	8.9	9.1	7.3	9.8	7.4
4A2 (elim-Z)	10.5	9.8	9.1	11.8	9.4
4A3 (elim-Z)	9.8	6.8	7.5	10.4	4.8
4A4 (elim-Z)	10.7	6.4	8.7	12.0	4.6
4A1 (rot-4B1)	9.8	13.6	9.9	10.9	9.7
4A2 (rot-4B2)	12.4	10.7	12.6	13.7	11.9
4C1 (elim-E)	7.1	7.6	7.1	10.0	7.5
4C2 (elim-E)	10.8	7.8	9.9	13.4	7.7
4C3 (elim-E)	11.0	13.1	9.7	13.6	8.5
Products					
Z + cyanide	−12.9	−29.9	−4.2	0.8	−20.8

[a] All calculations used the 6–31 + G* basis set.
[b] All ZPVEs were scaled by 0.9.

Table 3. Relative energies of the most stable conformations of 4A, 4B and 4C

	Relative energy (kcal mol)$^{-1}$		
	4A	**4B**	**4C**
HF/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	0.2	5.1
B3LYP/6–31 + G*//HF/6–31 + G* + ZPVE	0.4	0.0	7.8
MP2/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	0.5	8.5
B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G* + ZPVE	0.4	0.0	7.3

predicted to be exothermic at the B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G* level of theory by 1.4 kcal mol^{-1}, when considering only enthalpy of reaction. If we add in the calculated (HF/6–31 + G*//HF/6–31 + G*) change in entropy for this reaction ($\Delta S = -38.5$ eu), the overall free energy change at 300 K would be approximately 10 kcal mol^{-1} endothermic on going from reactants to **4A-2**. Since the activation barrier for elimination to the *Z*-product is 4.6 kcal mol^{-1} (negligible entropy effects) compared with the 0.7 kcal mol^{-1} barrier (at B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G*) for the elimination of methoxide ion to reform starting material, the second step of this reaction is rate determining, in excellent agreement with the conclusions reached experimentally. The ‘sluggishness’ of this reaction can also be explained by the very low activation barrier for the elimination of methoxide from **4A-2** to give back starting materials ($E_A = 0.7$ kcal mol^{-1}), thus causing **4A-2** to dissociate to starting material much more often than it goes on to eliminate cyanide to form product. The fact that only *Z*-product is formed in this reaction is readily understood now in terms of the calculated potential energy surface. After formation of **4A-2**, the complex can either revert to starting material (0.7 kcal mol^{-1} barrier), eliminate to give *Z*-product (4.6 kcal mol^{-1} barrier) or rotate to form **4C-1** (9.7 kcal mol^{-1} barrier), which then goes on to eliminate cyanide to form *E*-product. Clearly, the 5.1 kcal mol^{-1} lower barrier for eliminating cyanide to form the *Z*-product versus rotation followed by elimination from **4C-1** to give the *E*-product is more than enough free energy difference to account for 99.99% *Z*-product formation. The energy diagram in Scheme 2 summarizes these calculations.



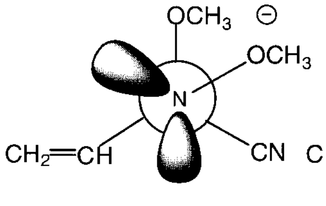
Scheme 2

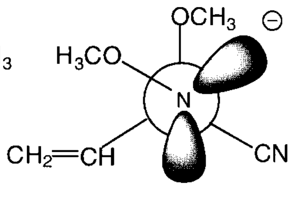
To address the question of whether or not our simplified model system (**4**), which had a hydrogen in place of the phenyl ring used experimentally, is sufficient to model accurately the possible steric and electronic effects of the larger 'real' system, we performed several calculations on the most stable conformations of **4A, 4B** and **4C**, this time using a vinyl substituent instead of hydrogen (or phenyl). The results were remarkably similar to those for our simple model system (**4-hydrogen**). The three general staggered conformations of the vinyl system (**4-vinyl**) are shown in Newman projections.

The relative energies of the most stable conformations of **4-vinyl** are summarized in Table 4 at several different levels of theory.

Tables 3 and 4 are very similar, that is, replacing the hydrogen by a vinyl group had very little effect on the overall relative energy difference between the **4A** conformations (which lead to *Z*-product) and the **4C** conformations (which lead to *E*-product). Therefore, even when the model system is increased to include the steric and electronic effects of the vinyl group, the calculations still conclude that conformation **4C** is much more unstable than conformation **4A**, and lead to the same conclusion as before: one should expect only *Z*-product formation, which is what is observed experimentally, even though the *E*-product is thermodynamically more stable (by 1 kcal mol^{-1} at B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G*).

The results obtained in the reaction of methoxide ion with hydroximoyl cyanides are in sharp contrast to the nucleophilic substitution reactions we have reported for the *Z*-and *E*-isomers of *O*-methylbenzohydroximoyl chlorides.[3b] Since the hydroximoyl chloride reactions are stereospecific it appears that the lifetimes of the tetrahedral intermediates are so short that conversion of conformation **B** to **A** (or **A** to **B**) does not compete with loss of the leaving group (chloride ion) from these conformations.


4A-vinyl


4B-vinyl

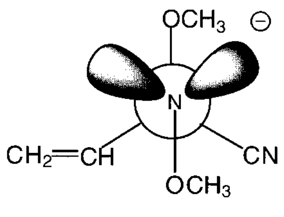

4C-vinyl

Table 4. Relative energies of the most stable conformations of 4-vinyl

	Relative energy (kcal mol)$^{-1}$		
	4A-vinyl	**4B-vinyl**	**4C-vinyl**
HF/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	1.9	6.4
B3LYP/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	1.8	7.8
MP2/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	1.7	8.0
B3LYP-SCIPCM/6–31 + G*//HF/6–31 + G* + ZPVE	0.0	2.5	8.0

We anticipate that theoretical calculations will be a useful tool in assisting us in explaining the stereochemistry and kinetics of nucleophilic substitution reactions at the carbon–nitrogen double bond. We are currently investigating the possibility of finding a system where the electron–electron repulsion on conformation **C** is diminished to the point that it competes favorably with conformation **A** in producing product.

Acknowledgements

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REFERENCES

1. (a) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., pp. 710–723. Harper and Row, New York (1987); (b) J. March, *Advanced Organic Chemistry*, 3rd ed., pp. 290–295. Wiley-Interscience, New York (1985).
2. (a) D. N. Kevill and M. J. D'Souza, *J. Org. Chem.* **63**, 2120–2124 (1998); (b) T. W. Bentley, G. Llewellyn and J. A. McAlister, *J. Org. Chem.* **61**, 7927–7932 (1996); (c) M. J. Colthurst and A. Williams, *J. Chem. Soc., Perkin Trans.* **2**, 1493–1497 (1997).
3. (a) J. E. Johnson, E. C. Reisgo and I. Jano, *J. Org. Chem.* **33**, 1583–1592 (1996); (b) J. E. Johnson, A. Ghafouripour, M. Arfan, S. L. Todd and D. A. Sitz, *J. Org. Chem.*, **50**, 3348–3355 (1985); (c) J. E. Johnson, S. M. Dutson, D. D. Dolliver, S. L. Todd and M. R. Hotema, *J. Phys. Org. Chem.* **8**, 344–350 (1995); (d) J. E. Johnson, N. M. Silk and M. Arfan, *J. Org. Chem.* **47**, 1958–1961 (1982).
4. (a) P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry*. Pergamon Press, Elmford, NY (1983); (b) M. L. Sinnott, *Adv. Phys. Org. Chem.* **24**, 113–204 (1988).
5. R. Ta-Shma and Z. Rappoport, *J. Chem. Soc., Perkin Trans. 2*, 659–667 (1977).
6. J. E. Johnson, S. L. Todd, J. L. Gardner, T. M. Gardner, P. Buck, A. Ghafouripour and W. Zimmerman, *J. Phys. Org. Chem.* **7**, 352–358 (1994).
7. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902–3912 (1985).
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, Stewart M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94, Revision D.3.* Gaussian, Pittsburgh, PA (1996).
9. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople., *Ab Initio Molecular Orbital Theory*. Wiley– Interscience, New York (1986), and references cited therein.
10. (a) W. Kohn, A. D. Becke and R. G. Parr, *J. Phys. Chem.* **100**, 12974–12979 (1996); (b) R. G. Parr and W. Yang., *Density Functional Theory of Atoms and Molecules*. Oxford University Press, New York (1989); (c) R. M. Dreizler and E. K. V. Gross, *Density Functional Theory*. Springer, Berlin (1990); (d) A. D. Becke, *Phys. Rev.* A **38**, 3098–3105 (1988); (e) C. Lee, W. Yang and R. G. Parr, *Phys. Rev.* **B 37**, 785–790 (1988).
11. (a). J. B. Forseman, T. A. Keith, K. B. Wiberg, J. Snoonian and M. J. Frisch, *J. Phys. Chem.* **100**, 16098–16102 (1996). (b). J. Tomasi, R. Bonaccorsi, R. Cammi, F. J. O. Valle, *J. Mol. Struct. (Thermochem.)* **234**, 401–402 (1991).