

multilayers built by the different methods suggests that the structure of the layers is independent of the preparation technique chosen. But, without additional investigations including such of other spacer lipid systems, the result should not be overestimated.

Conclusions

The spacer concept, that means the partial decoupling of the motions of the polymer backbone and the orientable, anisotropic side groups, proved to be useful for polymerizable lipids. The main problem of biomembrane models, that the stability achieved by polymerization will exclude the important mobility of the membrane, can thus be overcome. Polymeric model membranes of lipids with hydrophilic spacers still show the desired fluid phases. Moreover, the flexibility of polymerized lipids is sufficient to make possible monolayer spreading and vesicle formation of polymerized lipids. These unique properties offer wide possibilities in biomimetic systems. For example, proteins or enzymes can be incorporated in liposomes efficiently now, which before suffered either from poor stability in case of monomeric lipids or from

reduced fluid phases and damage by the polymerization process in case of polymerized vesicles. The multilayer systems, which are of special technical interest, also profit by the spacer concept. Distortions caused by the polymerization process are minimized, and thus the high quality of the layers is preserved. Furthermore, the flexibility of the polymeric lipids due to the spacer group allows one to build up multilayers from polymeric monolayers. Thus, potential distortions of the lipids created by the polyreaction are avoided, and the scope of polyreactions suited to polymerize amphiphiles is enlarged considerably.

Registry No. 1, 96326-70-4; 1 (alcohol), 96326-75-9; 2, 96326-71-5; 2 (alcohol), 96326-76-0; 3, 96326-72-6; 3 (alcohol), 96326-78-2; 4, 96326-73-7; 4 (phosphoric acid dichloride), 74123-29-8; 4 (dialcohol phosphate), 96326-79-3; 4 (hydrolysis product), 96326-80-6; [2,3-bis-(hexadecanoyloxy)propyl]dimethylamine, 96326-74-8; triethyleneglycol monoiodohydrin, 62573-16-4; methacrylic acid, 79-41-4; *N,N*-dioctadecylsuccinamide, 37519-63-4; tetraethyleneglycol, 112-60-7; 1,2-*O*-dihexadecylglycerol, 6076-35-3; 2,3-bis(hexadecyloxy)propyl succinate, 96326-77-1; phosphorus oxychloride, 10025-87-3.

Stereoelectronic Effect in Anionic 1,1-Addition to Isocyanides. An ab Initio Study of the H⁻ + HNC System

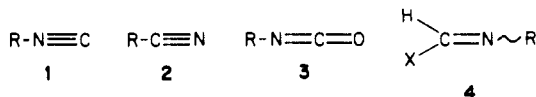
Minh Tho Nguyen,^{††} Anthony F. Hegarty,^{*†} Michel Sana,^{§±} and Georges Leroy^{*§}

Contribution from the Department of Chemistry, University College, Belfield Dublin 4, Ireland, and the Laboratoire de Chimie Quantique, Université Catholique de Louvain, B-1348-Louvain-la-Neuve, Belgium. Received December 3, 1984

Abstract: The stereochemistry of 1,1-addition to isocyanides initiated by nucleophilic attack has been modeled by using ab initio methods. The linear HNC molecule is surprisingly easily deformed: 3.9 kcal mol⁻¹ is sufficient to produce a bending of 30°. Addition of H⁻ to the carbon of HNC gives an energy surface in which a distinct valley favoring the *Z* (or *cis*) anion appears early in the reaction. The *Z* anion, then formed [HNCH]⁻, is, however, less stable by about 6.7 kcal mol⁻¹ than the *E* form. The energy barrier for *Z*-*E* interconversion of the anion is, however, high (38.2 kcal mol⁻¹ using MP4SDQ/6-31+G**//HF/4-31G) so that the *Z* form, although less stable, should be the kinetic product following rapid protonation of the carbanion. The favored route for *Z*-*E* interconversion of [HNCH]⁻ is by nitrogen inversion rather than inversion at the carbanionic center. The stereospecificity of the addition is consistent with the concerted electronic movement in the same direction about the isonitrile as the nucleophile approaches carbon.

Although isocyanides **1** were first discovered by Lieke in 1859,¹ this class of compounds has received relatively little attention by comparison with isomeric cyanides **2** or their close chemical parents isocyanates **3**.

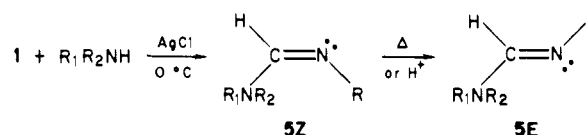
The rearrangement of **1** to **2** and the consequent preparative difficulties in obtaining pure and stable isocyanides was often considered as the main reason for this lack of interest. A ren-



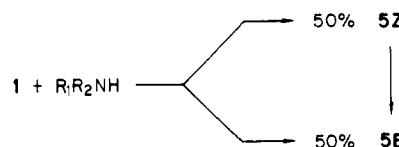
naissance of isocyanides has, however, occurred during the past 2 decades. Efficient and general synthetic routes for the laboratory preparation of isocyanides are now available, and these materials are shown to undergo a variety of reactions.^{2a}

In recent years, isocyanides attracted interest as complexing agents for transition-metal compounds,³ as synthons for a wide range of heterocycles through cycloaddition of their α -metalated

Scheme I



Scheme II



derivatives,⁴ or particularly as potential reagents for antibiotic synthesis via four-component condensations.⁵

Because of the presence of monocoordinated carbon atoms, 1,1-addition reactions of isocyanides to hydrogenated compounds (HX)

^{††} University College, Dublin.

[§] Université Catholique de Louvain

[†] On leave of absence from the Department of Chemistry, University of Leuven, B-3030-Heverlee, Belgium.

[±] Chercheur qualifié du Fonds National Belge de la Recherche Scientifique.

(1) Lieke, W. *Justus Liebigs Ann. Chem.* **1859**, 112, 316.

(2) Ugi, I. "Isonitrile Chemistry"; Academic Press, New York, 1971; (a) Chapter 2; (b) Chapter 4.

(3) Manning, A. R. *Coord. Chem. Rev.* **1983**, 51, 41.

(4) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1977**, 16, 339.

(5) Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 810.

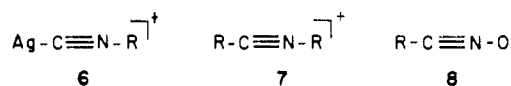
to form the substituted imines **4** constitute the first step in most of their chemical transformations.^{2b}

Experimental results on the stereochemistry of the addition of isocyanides to secondary amines can be summarized as follows. (a) In the absence of solvent and with AgCl as catalyst, the addition proceeded at temperatures < 0 °C to give a single *Z* isomer, **5Z**, stereospecifically⁶ (Scheme I). (b) In aqueous solution and without catalyst, the reaction is initiated by nucleophilic attack by, for example, an amine on the isocyanide. Under these conditions, the addition is not stereospecific. Both isomers **5E** and **5Z** were formed in approximately the same ratio⁷ (Scheme II).

In both cases, the *Z* isomers **5Z** were thermodynamically less stable. On heating above room temperature or in the presence of acids, **5Z** were converted rapidly and completely to **5E**.

The stereospecificity of the reaction in Scheme I can be understood by considering the possible coordination of isocyanides to Ag⁺ ion to give a pseudo-nitrilium ion **6**.

Nitrilium ion **7**, like nitrile oxides **8**, are well-known to form invariably *Z* isomers in the first step of nucleophilic attack.^{8,9} For



the reactions in Scheme II, the situation is less clear, but it can be emphasized that neutral substrates are involved as reactants. Overall, the stereochemistry of 1,1-addition to isocyanides appears to be greatly dependent upon the nature of nucleophiles and the reaction medium.

In this work, we wish to provide some answers to the question as to whether the addition of anionic nucleophiles to isocyanides is stereospecific or not. For this purpose, we have carried out a theoretical study on the simplest system with hydrogen isocyanide (isocyanic acid) and hydride ion as reactants:



The subsequent protonation of the anion formed is expected to be a fast step in aqueous solvent mixtures.

Details of Calculations. The molecular geometries of points on the energy surface HCNH⁻ have been optimized by the force method with analytical gradient as implemented in the GAUSSIAN 80 program¹⁰ by using the split-valence 4-31G basis set.¹¹ This basis set was found to reproduce reasonably experimental geometries of anions.¹² A set of diffuse s and p functions should be added (at least) to the basis set in order to improve the thermodynamic data.¹³ We have then recalculated single-point energies of some stationary points with the 6-31+G** (6-31G plus a set of diffuse functions s and p for C and N plus a set of polarization functions p for H and d for C and N),¹⁴ making use of their optimized 4-31G geometries. The electron correlation effect has also been taken into account via Møller-Plesset perturbation theory to second, third, and fourth order¹⁵ (with 6-31+G** basis set).

Finally, the molecular electrostatic potentials (mep) were calculated by means of the DENPOT program¹⁶ by employing the 4-31G basis set.

- (6) Hegarty, A. F.; Chandler, A. *Tetrahedron Lett.* **1980**, 21, 885.
 (7) Hegarty, A. F.; Cunningham, I., unpublished results.
 (8) Hegarty, A. F. *Acc. Chem. Res.* **1980**, 13, 448.
 (9) Nguyen, M. T.; Sana, M.; Leroy, G.; Dignam, K. J.; Hegarty, A. F. *J. Am. Chem. Soc.* **1980**, 102, 573.
 (10) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Defrees, D. J.; Topiol, H. B.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, 138, 406.
 (11) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, 54, 724.
 (12) Radom, L. *Mod. Theor. Chem.* **1977**, 4, 333.
 (13) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, 103, 5609.
 (14) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, 80, 3265.
 (15) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 4244.
 (16) Peeters, D.; Sana, M. *QCPE Bull.* **1978**, 11, 360.

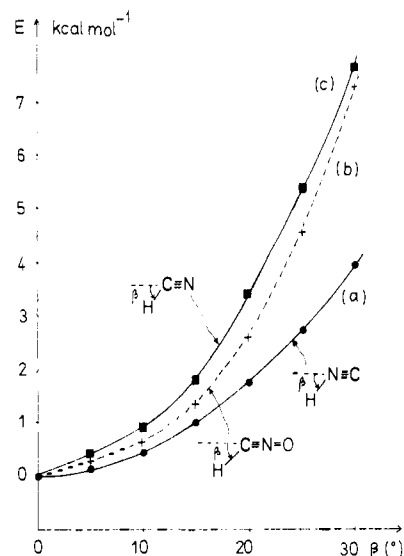


Figure 1. Potential curves relevant to the bending modes in (a) HNC, (b) HCN, and (c) HCN in HCNO. For each value of β angles, other parameters were optimized. Energies calculated with 4-31G basis set.

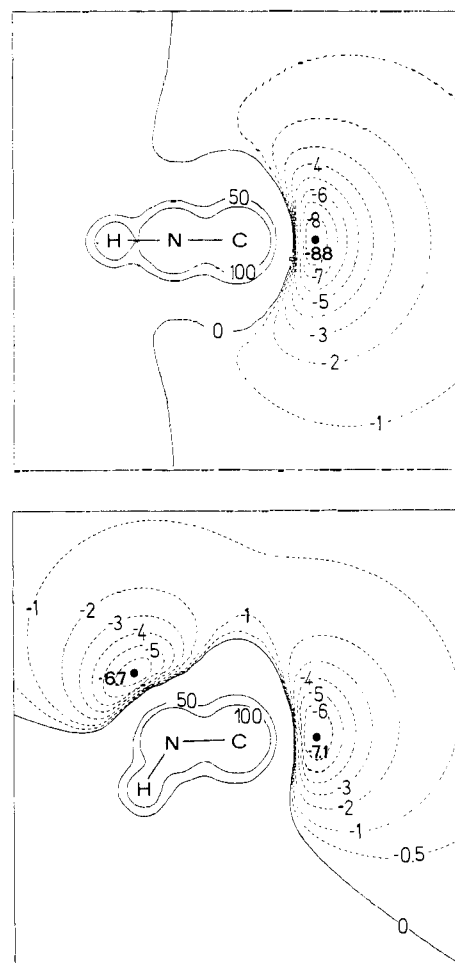


Figure 2. Molecular electrostatic potential maps (4-31G) of (a) linear HNC and (b) bent HNC with HNC = 120°. Isocontours and potential minima values are given in 10⁻² au.

Results and Discussion

Deformation of HNC. The bending of the HNC angle is the only mode of nuclear deformation of hydrogen isocyanide. As seen in Figure 1, the bending in HNC is much easier than that of the HCN angle and that of the HCN angle in fulminic acid (HCNO). The opening of the β angle (Figure 1) by 30° requires 3.9, 7.3, and 7.6 kcal/mol for HNC, HCNO, and HCN, re-

Table I. Total and Relative Energies of Systems Considered at Different Levels of Calculations

system ^a	4-31G	6-31+G**	MP2/6-31+G**	MP3/6-31+G**	MP4SDQ ^b /6-31+G**
Total Energies, au					
H ⁻	-0.422 44	-0.422 44	-0.435 39	-0.437 57	-0.438 10
HNC, 9	-92.716 78	-92.865 24	-93.141 38	-93.148 27	-93.154 57
HNCH ⁻ , 10	-93.186 74	-93.371 13	-93.683 60	-93.694 79	-93.701 31
11	-93.192 31	-93.381 43	-93.694 60	-93.705 44	-93.711 85
12	-93.094 47	-93.288 26	-93.609 29	-93.617 54	-93.624 31
13	-93.130 45	-93.310 16	-93.623 91	-93.633 53	-93.640 40
Relative Energies, kcal/mol					
(H ⁻ + HNC)	0.0	0.0	0.0	0.0	0.0
10	-29.8	-52.3	-67.0	-68.3	-68.1
11	-33.3	-58.8	-73.9	-75.0	-74.8
12	28.1	-0.4	-20.4	-19.9	-19.8
13	5.5	-14.1	-29.6	-29.9	-29.9
$\Delta E(10-11)$	3.5	6.5	6.9	6.7	6.7
$\Delta E^{\ddagger}(13-10)$	35.3	38.2	37.4	38.4	38.2

^aUsing the 4-31G optimized geometries given in Figure 3. ^bMøller-Plesset fourth-order perturbation theory including single, double, and quadruple substitutions.

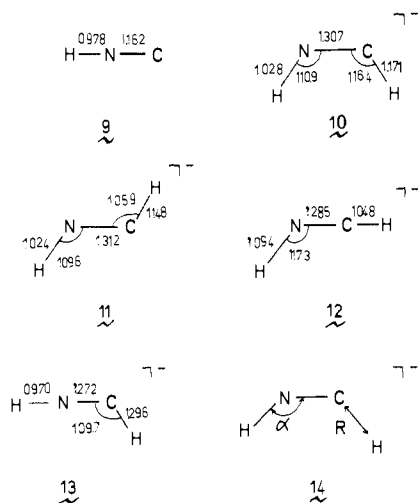


Figure 3. Optimized 4-31G geometries of some particular points on the HCNH⁻ energy surface. **14** defines the internal coordinates R and α .

spectively (at 4-31G level). This is consistent with the observation of a lower vibrational frequency for the bending mode of HNC (490 cm^{-1} ¹⁷ instead of 727 cm^{-1} for that of HCN¹⁸).

Within the values of $0 \leq \beta \leq 30^\circ$, the potential functions of the bending modes can be expressed as follows: HNC, $\Delta E = \beta(0.580\beta^2 + 13.982\beta + 0.064)$; HCN, $\Delta E = \beta(-1.972\beta^2 + 28.947\beta - 0.063)$; HCNO, $\Delta E = \beta(50.0\beta^2 - 4.541\beta + 2.880)$, where $\Delta E = E(\beta) - E(0)$ is in kilocalories/mole and β is in radian.

Figure 2 shows the maps of molecular electrostatic potential calculated with the 4-31G basis set for both linear and bent ($\beta = 60^\circ$) HNC. It is worth noting that as the isocyanide bends, a second potential minimum, less deep but still important (-42.0 kcal/mol), appears around the nitrogen atom.

In other words, accompanying the nuclear deformation of HNC, an electron pair of the $C\equiv N$ triple bond is displaced to form the lone pair of the nitrogen atom. On the other hand, the potential minimum relevant to the terminal carbon lone pair remains almost unchanged in both position and magnitude during the bending of the HNC angle.

Addition $H^- + HNC$. Figure 3 displays the optimized 4-31G geometries of HNC **9** and some stationary points on the HNCH⁻ energy surface including the Z form **10**, the E form **11**, and two transition structures **12** and **13**. The $Z-E$ isomerization of **10** to **11** can occur either by C inversion via **12** or by N inversion via **13** (see ref 28). The total and relative energies calculated at different levels of theory employing the optimal 4-31G geometries are recorded in Table I. Structure **14** (Figure 3) defines the two internal parameters R and α which have been selected as inde-

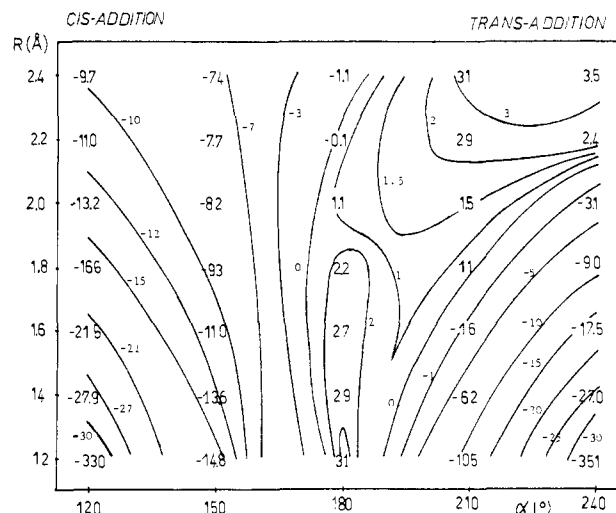


Figure 4. Energy map for the addition of H^- to HNC. See **14** in Fig. 3 for the definition of R and α coordinates. Isocountour values are given in kcal/mol. Zero-energy level is the $H^- + HNC$ system.

pendent variables. For each couple of fixed (R and α) values, the remaining parameters were optimized. The two-dimensional energy surface for the addition of H^- to HNC with respect to R and α is presented in Figure 4.

From these calculated results, the following points are noteworthy. (a) Inclusion of both diffuse and polarization functions (6-31+G**) and electron correlation effects in the calculations stabilizes appreciably all forms of the HCNH⁻ anion with respect to the isolated molecules ($H^- + HNC$). Nevertheless, the relative energies of the anions are similar at all levels of calculation.

(b) The Z form **10** is calculated to be higher in energy than the E form **11**. The 6-31+G** basis set tends to favor the E form, but the correlation energy has nearly no effect on the energy difference. Our best value (MP4/6-31+G**) provides a cis-trans energy separation of 6.7 kcal/mol which is close to that of 6-7 kcal/mol previously reported for the diimide ($HN=NH$) at CI/DZP level.^{19,20}

(c) The most favored pathway for the $Z-E$ interconversion between **10** and **11** is N inversion via **13**. The C inversion via **12** requires a relatively higher energy barrier ($\sim 10\text{ kcal/mol}$) than that for N inversion. On the other hand, we found that the $Z-E$ interconversion via rotation can be excluded.

The energy barrier of 38.2 kcal/mol (MP4/6-31+G**) to N inversion of **10** lies in between those of diimide ($HN=NH$, 55 kcal/mol at CI/DZP^{19,20}) and methylenimine ($H_2C=NH$, 33.5

(17) Creswell, R. A.; Robiette, A. G. *Mol. Phys.* **1978**, *36*, 869.

(18) Strey, G.; Mill, I. M. *Mol. Phys.* **1973**, *26*, 1973.

(19) Parsons, C. A.; Dykstra, C. E. *J. Chem. Phys.* **1979**, *71*, 3025.

(20) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77.

Table II. Net Charges and Overlap Populations of **9**, **10**, and **11** (with 6-31+G** Basis Set)

	9	10	11
Net Charge			
C	0.089	-0.423	-0.436
N	-0.454	-0.662	-0.725
H(C)		-0.088	-0.042
H(N)	0.365	0.173	0.203
Overlap Populations			
C-N ^(a)	0.786	0.320	0.385
C-H		0.322	0.342
N-H	0.320	0.296	0.216

^aThe overlap population of C=N in methylenimine is 0.560.

kcal/mol at MP4/6-31G**²¹). Like the case in the latter, the correlation effect does not modify the height of the barrier to inversion. Figure 3 shows that the carbon-nitrogen bond lengths in anions **10** and **11** (~ 1.31 Å) are longer than those of the N=N bond (1.25 Å at 4-31G) in diimide and the C=N bond (1.26 Å at 4-31G) in methylenimine. That could confer to the former a partial double bond character (see overlap populations collected in Table II) and consequently does increase the barrier to inversion. Nevertheless, it seems that this less-than-double-bond character is not strong enough to allow a preference for the rotation mechanism such as is the case in several anions or cations.^{21,22} Indeed, the difference between both barriers to inversion of **10** and of methylenimine is only ~ 5 kcal/mol. Thus, we keep in mind that the conversion of the Z form **10** to E form **11** of the HNCH⁻ anion is a rather difficult process.

(d) The addition of hydride ion to hydrogen isocyanide is moderately exothermic. As stated above, electron correlation effect acts in favor of the anionic adduct. At the MP4/6-31+G** level, the heat of reaction is calculated to be -74.8 kcal/mol (with respect to the Z form **10**). This value is rather large in comparison with the energy difference of 26 kcal/mol previously reported between the system H⁻ + H-C≡C-H and vinyl anion H₂C=CH⁻ (at SCEP/DZP level).²³

Like other anionic additions such as OH⁻ + CO₂,²⁴ OH⁻ + HCNO,²⁵ or OH⁻ + H₂C=C=NH,²¹ the addition of H⁻ to HNC occurs without activation energy. It is striking to note that Dykstra et al.²³ reported an activation energy of 16 kcal/mol (SCEP/DZP) for the addition of H⁻ to acetylene (HC≡CH). The energy barrier in the latter addition could probably be due to the difficulty in deforming the acetylene molecule and to the relative instability of the vinyl anion.

(e) Figure 4 shows that even at large values of the intermolecular distance R ($R \geq 2.0$ Å) when the H⁻ anion attacks the terminal carbon, the hydrogen isocyanide already becomes strongly bent (HNC $\sim 120^\circ$) and the supermolecule adopts the Z structure.

In this region of the energy surface, only the Z structure exists; the E structure is found to be repulsive. Around $R \sim 2.2$ Å, the E structure begins to form, but the Z structure is still more favored in energy and then remains so until $R \sim 1.4$ Å. Another important fact is that both forms are separated by an appreciable energy barrier (see Figure 4 along the path $R, \alpha = 180^\circ$).

Thus, there appears early in the energy surface a distinct valley which directly drives the supermolecule to the formation of the Z form **10**. Because of the sizeable energy barrier involved in the conversion of **10** to **11**, in aqueous solution **10** will be protonated in a subsequent step, leading hence to the kinetic formation of the (Z)-amine **5Z**. From these results it would be predicted that the addition of hydride ion to isocyanide is stereospecific since

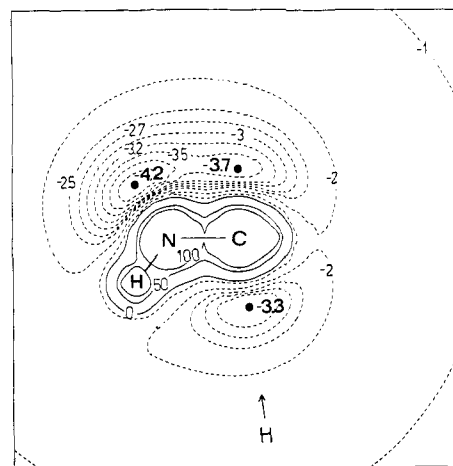
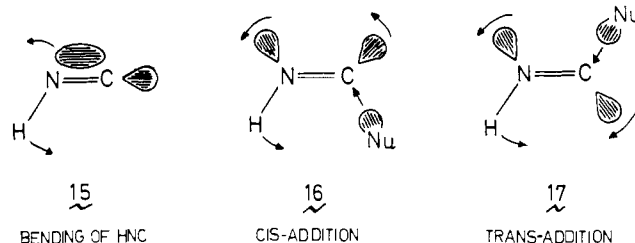


Figure 5. Molecular electrostatic potential map (4-31G) of the point ($R = 2.0$ Å, $\alpha = 125^\circ$). Isocontours and potential minima values are given in 10^{-2} au.

the interaction between reactants at large values of the intermolecular distance predominates and determines the stereospecific pathway of the addition. As a possible interpretation of this stereoelectronic effect, we consider the movement of the migrating electron pairs that are responsible for the formation of the adduct:



The creation of the nitrogen lone pair following the bending of HNC, as discussed above, can be described as **15**. The movement of the electron pairs involved in both cis-addition and trans-addition of the nucleophile to the terminal carbon of isocyanides can be pictured as **16** and **17**, respectively. We can see that in the cis-addition, when two reactants approach each other, all migrating electron pairs, namely the lone pair of the nucleophile, the lone pair of the terminal carbon, and the electron pair of the C≡N bond, move in the same sense (see **16**). On the contrary, in the trans-addition, two electron pairs of isocyanide are shown to migrate in opposite senses (see **17**).

The picture **16** can in part be illustrated by the map of electrostatic potential as presented in Figure 5. In cis-addition, at $R \approx 2$ Å, the migration of the carbon lone pair is practically complete. A third potential minimum is created between C and H atoms to form the new bond. As in other additions,^{26,27} the motion of the electron pairs in the same sense as **16** can be regarded as the natural trend during a reaction, and accordingly this pathway is favored.

In contrast, the trans-addition **17** is not possible because at large R values, such an attack has to produce a breakdown in the motion of the electronic cloud of the isocyanide without any necessary compensation. Only a strong overlap between two reactants (later at $R \leq 2$ Å) might reduce the electronic disadvantage.

In previous work on the 1,3-dipolar cycloadditions,^{26,27} a similar consideration of the electronic movement has allowed us to rationalize reasonably both substituents effect and regiochemistry for a variety of dipoles and dipolarophiles.

(21) Nguyen, M. T.; Hegarty, A. F., unpublished results.
 (22) Veillard, A. In "Quantum Mechanics of Molecular Conformations"; Pullmann, B., Ed.; Wiley: New York, 1975; p 1.
 (23) Dykstra, C. E.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007.
 (24) Jönsson, B.; Karlström, G.; Wennerström, H. *J. Am. Chem. Soc.* **1978**, *100*, 1658.
 (25) Leroy, G.; Nguyen, M. T.; Sana, M.; Dignam, K. J.; Hegarty, A. F. *J. Am. Chem. Soc.* **1979**, *101*, 1988.

(26) Leroy, G.; Sana, M.; Burke, L. A.; Nguyen, M. T. "Quantum Theory of Chemical Reactions"; Daudel, R., et al., Eds.; Reidel: Holland, 1980; Vol. 1, p 91.

(27) Sana, M.; Leroy, G.; Dive, G.; Nguyen, M. T. *J. Mol. Struct. Theochem.* **1982**, *89*, 147.

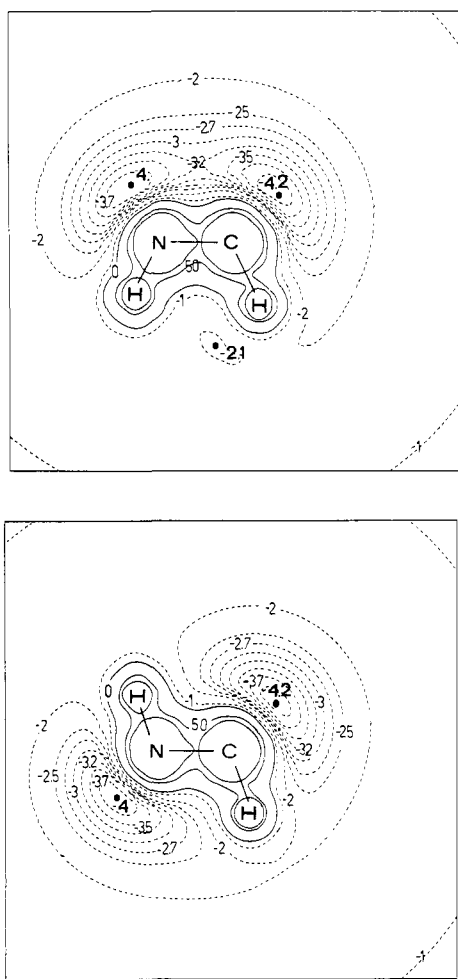


Figure 6. Molecular electrostatic potential map (4-31G) of (a) **10** and (b) **11**. Isocontours and potential minima values are given in 10^{-2} au.

Scheme III

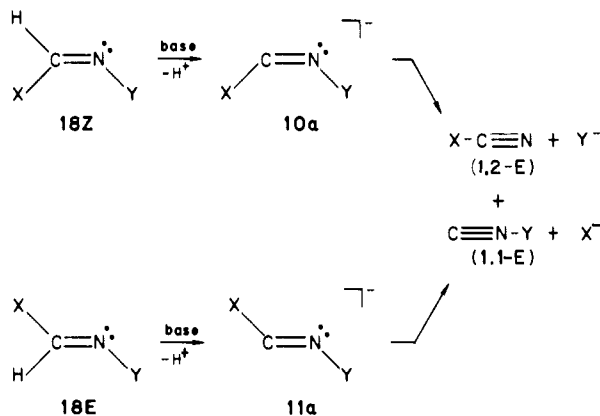


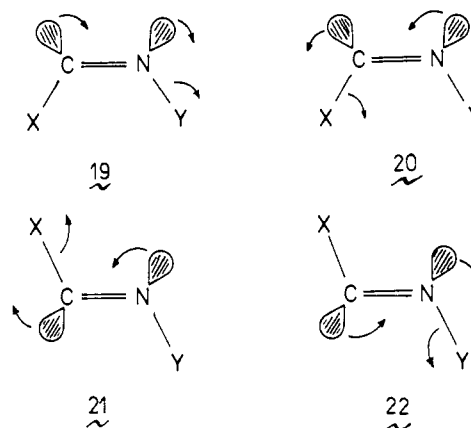
Figure 6 shows electrostatic potential maps of anions **10** and **11**. In both anions, the potential minima are found to be almost the same. For each form, the potential minimum around the carbon atom is slightly deeper (≈ 12 kcal/mol at 4-31G). This is somewhat different from the charge distributions according to

the Mulliken analysis given in Table II; this could be due to the basis set effect.

Nevertheless, the charge transfer from the hydride anion to the hydrogen isocyanide is mainly toward the carbon atom.

1,1- and 1,2-Elimination Reactions of Imines. This work provides us with an opportunity to comment on the 1,1- and 1,2-eliminations (reverse additions) of imines (Scheme III). For instance, both eliminations have the same structures **10** and **11** as possible intermediates (**18Z** and **18E**) after removing a proton by an appropriate base. From **10a** and **11a**, both 1,1- and 1,2-elimination could take place, accordingly to the nature of the leaving groups X^- and Y^- , to produce isocyanides and cyanides, respectively.

Using these ideas, we can describe the four following possible situations **19–22** and predict their relative reactivity in regard to stereolectronic effects:



- 19**, 1,2-trans-elimination, stereolectronically allowed;
20, 1,1-trans-elimination, stereolectronically allowed;
21, 1,1-cis-elimination, stereolectronically forbidden;
22, 1,2-cis-elimination, stereolectronically forbidden.

Conclusions. Nucleophilic addition to isocyanides by anions is predicted to be stereospecific, with high inversion barriers at both carbon and nitrogen for the intermediate formed. The reaction will be overall stereospecific only if it is truly stepwise with rapid proton transfer to carbon. Concerted protonation of carbon (perhaps through a chain of water or amine molecules) could therefore be responsible for the lack of stereospecificity observed in some cases.

Acknowledgment. M.T.N. and A.F.H. are indebted to the Department of Education (Irish Government) for financial support. Dr. Paul Brint is gratefully acknowledged for computer assistance. Conversations with Dr. R. A. More O'Ferrall were very helpful.

Registry No. HNC, 75-13-8; H^- , 12184-88-2; HCNH^- , 90623-30-6.

(28) During the calculation of the HCNH^- energy surface using the distinguished coordinate method (cf. **14** and Figure 4), the bond angles NCH of **12** and CNH of **13** were both constrained to be equal to 180° . In reality, both true saddle points adopt slightly *E*-bent configurations ($3\text{--}4^\circ$) with the following geometrical parameters (4-31G): **12a**, $\text{CN} = 1.290 \text{ \AA}$, $\text{CH} = 1.047 \text{ \AA}$, $\text{NH} = 1.085 \text{ \AA}$, $\text{HCN} = 177.0^\circ$, $\text{CNH} = 113.2^\circ$, $E = -93.09399 \text{ au}$; **13a**, $\text{CN} = 1.275 \text{ \AA}$, $\text{CH} = 1.281 \text{ \AA}$, $\text{NH} = 0.970 \text{ \AA}$, $\text{HCN} = 109.3^\circ$, $\text{CNH} = 176.1^\circ$, $E = -93.12991 \text{ au}$. The energies of **12a** and **13a** are thus found to be negligibly higher than those of **12** (0.29 kcal/mol) and **13** (0.32 kcal/mol), respectively (see Table I).