sulfuric acid in ethanol. Ethyl cyclohexaneacetate (**34**, R = C_6H_{11}) was thus obtained in an unoptimized yield of 63%. Compared to the multistep Arndt–Eistert procedure,[18] this homologation was effected in a single reaction, without use of hazardous diazomethane. This method also offers the option of utilizing the intermediate alkynolate anion (**33**) for transformations other than simple ester formation. Little is known of the reactions of such alkynolates[5] which should have a rich chemistry of their own (e.g., the β-lactone formation already cited). Further studies of this rearrangement reaction and the utility of the alkynolate anions produced are under way.

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Syn and Anti Transition States in the Addition of Ammonia to Cyanoacetylene. Formation of a Stable Zwitterionic Intermediate†

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Recent interest in the theory of nucleophilic additions[1] prompts us to report calculations on the addition of ammonia to cyanoacetylene, a process which has a nonzero activation barrier and also gives stable zwitterionic intermediates, in contrast to calculated gas-phase additions of nucleophiles to carbonyls.[1]

Ab initio (4-31G) calculations on the addition of a model nucleophile, hydride, to acetylene,[2] give a single transition state in which the acetylene moiety is bent in an anti fashion. Since the barrier to inversion of a vinyl anion is sufficiently high (37 kcal/mol by 4-31G)[2] to preclude rapid inversion, protonation in solution will occur faster than inversion. Anti addition is predicted for nucleophilic additions to unactivated acetylenes,[2] and this is observed experimentally.[3] However, the additions of nucleophiles to activated acetylenes give variable stereochemical results.[3] In polar or proton-donating solvents, anti stereochemistry is frequently observed, while in nonpolar aprotic solvents, syn addition often occurs (Figure 1). Some examples of kinetically controlled stereochemistries (at 25 °C) are given in Table I.[4-7] This variable

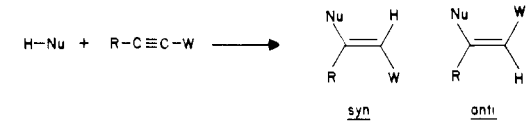

Figure 1. Definition of stereochemistries of nucleophilic additions to acetylenes.

syn and anti addition stereochemistry could arise from three possible mechanisms: (1) electron-withdrawing substituents could cause the formation of two separate transition states, resulting in formation of both syn and anti anionic or zwitterionic intermediates and syn and anti products; (2) a single stereochemistry of attack could be preferred, but syn and anti intermediates could equilibrate;[3,5] (3) linear vinyl intermediates could form,[3,6] with the product stereochemistry determined by the preferential site of protonation.[3]

We have found strong evidence for the first of these mechanisms by ab initio calculations[8] on the addition of a typical nucleophile, ammonia, to an activated acetylene, cyanoacetylene. Figure 2 and Tables II and III summarize the results of these calculations. Transition states were found with the STO-3G basis set and were identified by determining that each possessed only one negative force constant, which corresponds to the reaction coordinate. Single point calculations were then carried out on the stationary points on the surface by using the 4-31G basis set. Two distinct transition states are found, one corresponding to syn bending of the acetylene and the other to anti. As for acetylene, the anti bent transition state is preferred, a manifestation of the easier trans-bending mode of acetylenes.[2] When addition is accompanied, or followed, by rapid protonation, anti addition is preferred.

Two zwitterionic intermediates are shallow energy minima at the STO-3G level. The anti zwitterion is no longer predicted to be an intermediate at the 4-31G level, but we believe that this is an artifact of use of STO-3G geometries without reoptimization. The anti-bent zwitterion is higher in energy than the syn-bent zwitterion. Equilibration of these two zwitterions should lead to a greater percentage of the syn zwitterion and ultimately to syn addition product. These calculations, which are appropriate for the gas phase, indicate that there is no intramolecular mechanism of inversion but that dissociation and recombination should occur readily.

In solution, the various zwitterionic species should be highly stabilized with respect to the neutrals. A crude estimate of the influence of solvation on the relative energies of the various species calculated here was made from the calculated dipole moments and the Kirkwood equation.[9] The results for two solvents are given in Table III. Even with solvation estimates, calculated activation energies are too high, since values are of the order of 5–10 kcal/mol for such reactions in solution.[3] Anti addition is still favored, although less so in the nonpolar solvent than in the polar solvent. The stability of the zwitterions is greatly increased, and the barrier to inversion is now comparable to the barrier for reversion to reactants. Because of its smaller size, the anti zwitterion becomes slightly more stable than the syn in highly polar solvents, which may account for the greater proportion of anti product formed under these conditions.

The dipole moment changes calculated here are quite similar to those deduced for zwitterions formed in enol ether–tetracyanoethylene reactions on the basis of solvent polarity changes.[10] Similar solvent polarity rate effects have been measured for additions of secondary amines to acetylenic esters.[11]

† Dedicated to Professor Rolf Huisgen on the occasion of his 60th birthday.
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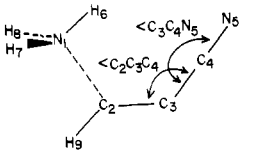
Table I. Examples of Stereochemistries of Nucleophilic Additions to Activated Acetylenes

nucleophile	acetylene	solvent	% syn addition	% anti addition	ref
MeOH	NC–C≡C–CN	MeOH	78	22	4
t-BuOH	NC–C≡C–CN	0.01% N-Me-morpholine; *t*-BuOH	100		4
t-BuNH$_2$	HC≡C–CO$_2$Me	PhH	70	30	4
aziridine	HC≡C–CO$_2$Me	DMF	97	3	6
aziridine	HC≡C–CO$_2$Me	MeOH	47	53	6
aziridine	HC≡C–CO$_2$Me	EtSH	24	76	6
p-MePhSNa	HC≡C–SO$_2$Tol	MeOH		100	7
p-MePhSNa	HC≡C–COMe	MeOH	18	82	7

Table II. Geometries and Energies of Stationary Points on the NH$_3$ + HC≡CCN Surface



	species				
	NH$_3$ + HC≡CCN	syn TS	anti TS	syn ZI	anti ZI
		Distances, Å			
N_1C_2	∞	1.774	1.747	1.566	1.614
C_2C_3	1.175	1.239	1.260	1.310	1.301
C_3C_4	1.409	1.398	1.418	1.455	1.452
C_4N_5	1.159	1.163	1.162	1.160	1.161
C_2H_9	1.065	1.079	1.078	1.080	1.078
N_1H_6	1.032	1.033	1.034	1.038	1.037
N_1H_7=N_1H_8	1.032	1.034	1.034	1.038	1.037
		Angles, deg			
$N_1C_2C_3$		113.3	121.3	112.4	122.9
$C_2C_3C_4$	180.0	217.7	131.0	244.7	117.9
$C_3C_4N_5$	180.0	182.8	177.7	174.7	182.4
$C_3C_2H_9$	180.0	149.5	138.9	140.7	132.4
$H_6N_1C_2$	114.3	106.5	108.8	104.7	108.6
$H_{8(7)}N_1C_2$	114.3	113.3	112.9	108.3	107.3
E(STO-3G//STO-3G), a.u.	−221.86624	−221.81253	−221.81625	−221.81990	−221.81733
E(4-31G//STO-3G), a.u.	−224.40018	−224.35213	−224.35286	−224.35800	−224.35172

Table III. Summary of Calculations and Estimates of Energetics (kcal/mol) in Solution

species	E_{rel}(STO-3G)	E_{rel}(4-31G)	μ(4-31G), D	r,[a] Å	E_{rel}(4-31G) PhH[b]	E_{rel}(4-31G) MeOH[c]
reactants	≡0	≡0			≡0	≡0
NH$_3$			2.42	3.73		
HC≡CCN			4.14	3.74		
syn TS	33.8	30.2	10.02	4.22	27.2	24.1
syn ZI	29.1	26.5	10.20	4.10	23.0	19.2
anti TS	31.5	30.4	9.05	3.30	24.3	17.8
anti ZI	30.7	29.1	9.24	3.46	23.8	18.0
inversion TS[d]	40.2	33.9	10.90	3.95	29.0	23.7

[a] See ref 9. [b] $E_{rel}(4\text{-}31G) - \Delta(\mu^2/r^3)[(\epsilon - 1)/(2\epsilon + 1)]$, with $\epsilon = 2.27$. [c] Same as footnote *b*, with $\epsilon = 32.6$. [d] N_1C_2 fixed at 1.60 Å, $\angle C_2C_3C_4$ fixed at 180°.

The syn zwitterion appears ideally suited for intramolecular proton transfer. However, our preliminary calculations indicate that there is a rather high barrier (>5 kcal/mol) to intramolecular proton transfer, which must necessarily arise from the highly nonlinear nature of this proton transfer and the enforced large separation of N and C atoms. Proton transfers involve a close approach of the heavy atoms between which the proton is being transferred, followed by a low-energy proton movement or tunneling.[12] Large atomic groupings (e.g., PhSe) can be transferred intramolecularly,[13] but a more likely mechanism for proton transfer in the present case involves intervention of a solvent molecule which simultaneously deprotonates the nitrogen and delivers a proton to the anionic center.[14] Indeed, third-order kinetics are observed in some cases,[15] particularly in nonpolar solvents. Our calculations on the syn zwitterion plus an additional ammonia molecule indicate that a "termolecular" proton transfer to form *trans*-1-amino-2-cyanoacetylene occurs without activation.[16]

We believe that these calculations, tempered by qualitative considerations about the effect of solvation, give a reasonable picture of the course of nucleophilic additions to activated acetylenes in solution. Anti bending of the acetylene is favored, giving the "anti" zwitterion as kinetically preferred product. If this species is rapidly protonated, or is highly stabilized by polar solvents, then anti addition is favored overall. If, however, pro-

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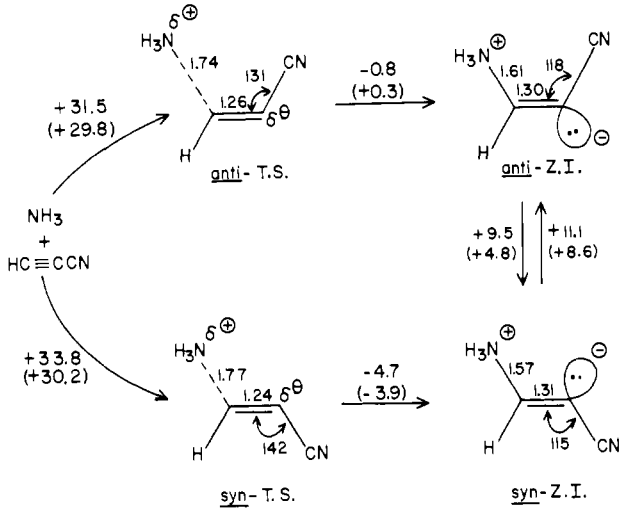

Figure 2. Geometrical parameters and relative energies (kcal/mol) of reactants, transitions states, and intermediates by STO-3G (4-31G).

tonation is slow compared to inversion, which will have a barrier of approximately 4 kcal/mol in solution, then the "syn" zwitterion will be formed. Subsequent protonation involving the intervention of solvent molecules will give the syn product preferentially. This corresponds to one of the mechanisms proposed earlier by Huisgen.[5]

This reaction contrasts to the water–formaldehyde reaction, where no stable zwitterion is found to be stable computationally.[1] We attribute this difference to the greater nucleophilicity and lower acidity of ammonia as compared to water and to the relatively high stability of the cyanovinyl anion. In the absence of the cyano group, ammonia adds to acetylene by the same mechanism as found for water plus formaldehyde.[16]

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Stabilization of the Monoanion of 1,8-Diaminonaphthalene by Intramolecular Hydrogen Bonding. A Novel Case of Amide Ion Homoconjugation in a Superbase Solution

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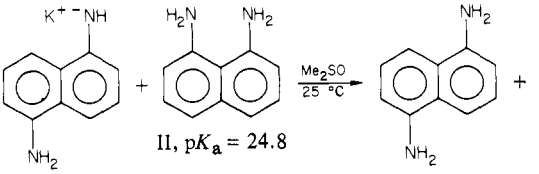
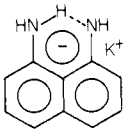
One of the most important means for stabilizing ammonium and oxonium cations in solution is through hydrogen bonding to basic nitrogen or oxygen sites in the solvent.[1] Likewise, oxyanions in hydroxylic solvents are strongly hydrogen bonded.[2,3] However, there is no evidence, of which we are aware, for significant stabilization by this means of nitroanions, such as amide ions. Thus, although alkoxy and phenoxy ions are strongly homoconjugated in Me_2SO by their conjugate acids (e.g., ROH—$^-$OR), there is no evidence for a similar stabilizing factor in the deprotonation of aniline bases.[4]



II, $pK_a = 24.8$

I, $pK_a = 29.2$

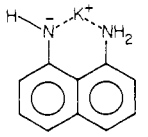


In the hope of discovering homoconjugate nitroanion stabilization, we chose to compare the deprotonation of 1,8-diaminonaphthalene (II) with its 1,5 isomer (I).

In the strongly basic medium K^+DMSYL^-/Me_2SO, I is less acidic than its peri isomer, 1,8-diaminonaphthalene (II), by *4.4* pK_a units. The thermodynamics of the exchange reaction are presented in Table I, providing dramatic evidence of a special proximity effect.

Although the unusual acidity of II might be considered at first sight to be obviously predictable in view of the high basicity of Proton Sponge [1,8-bis(dimethylamino)naphthalene], the driving forces for proton transfer in the two systems are quite different. As R. W. Alder et al.[5] have shown, Proton Sponge is a strong base primarily because of lone-pair repulsion in the neutral molecule which is relieved by protonation. Also, steric inhibition of resonance in neutral Proton Sponge prevents delocalization of the lone-pair electrons into the aromatic system. In fact, II is only 0.5 pK_a units more basic than I in aqueous media whereas Proton Sponge is more basic by 7.7 pK_a units.

We can visualize readily two reasonable explanations for the striking acidity difference between the isomers I and II: (a) the 1,8 nitroanion is stabilized by an internal hydrogen bond from the adjacent amino group, as shown in the above equation; (b) the 1,8 nitroanion from II forms a chelated ion pair (III) that is more stable than its 1,5 isomer which cannot chelate.



III

Evidence against the ion-pairing possibility is provided by titrations[6] with and without Kryptofix which indicate no measurable interaction of K^+ with anion II. Also the order of the gas-phase acidities,[7] which were determined in the complete absence of cations, rules out this possibility (Table I).

One might also suggest that neutral diamine II is relatively destabilized by lone-pair repulsions between the amine nitrogens as in the case of Proton Sponge but that seems unlikely to begin with since it would require that there should be less electron repulsion in the anion of II than in its initial neutral state. Certainly, sterically enforced electron repulsion in neutral Proton

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