accord. A new experimental approach to the reaction kinetics in the gas phase could therefore eliminate any lingering doubts about the validity of those data and could substantiate the concept of a major solvation effect for the reaction in solution.
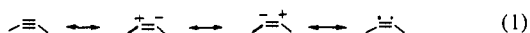
Effect of Bending on the Reactivity of Alkynes: A Semiempirical Study

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Abstract: The effect of cis bending on the reactivity of alkynes is studied with the semiempirical MNDOC and MNDO methods. The cycloaddition of ethylene to linear and bent acetylene and to benzyne and the addition of water (weak nucleophile) and hydroxide ion (strong nucleophile) to linear and bent acetylene were chosen as model reactions. It was found that only about 20% of the strain energy in the bent alkyne contributes to a direct reduction of the activation barrier for the cycloaddition reaction whereas almost 90% of that strain energy is released in the transition state for nucleophilic additions. The forbidden cycloaddition reaction is very sensitive to electron correlation but the addition of nucleophiles appears to be well described by RHF calculations. The biradicaloid intermediate predicted for the 2 + 2 cycloaddition reaction by limited CI method is highly polarizable and transforms into a closed-shell zwitterion upon interaction with a dipole. Extensive electron correlation treatment (TC-BWEN) removes the biradical as a defined intermediate and changes the reaction surface into a flat plateau supporting Hoffmann's twixtyl model. The effect of alkyne bending on the selectivity of addition reactions is discussed.

The reactivity of cyclic alkynes has puzzled organic chemists since the first report on the generation of benzyne by Wittig in 1942.[1] Despite much speculation on the nature of such reactive intermediates no definite proof emphasizing either the closed shell, the zwitterionic, or the biradicaloid structure has been presented.

 (1)

In several studies the effect of ring size on the reactivity of cyclic alkynes has been examined.[1-6] Cyclooctyne was found to be the smallest isolable unsubstituted cycloalkyne.[3] The most intensively investigated cycloalkyne is benzyne, the chemistry of which has been reviewed.[2,7] Although there is no experimental evidence for the existence of the smaller cyclopropyne[8] and cyclobutyne,[9] convincing evidence for the existence of cyclopentyne,[3,10] cyclohexyne,[3] and cycloheptyne[3] has been presented. The tentative assignment of a C≡C strech frequency at 1930 cm^{-1} obtained for acenaphthyne, a cyclopentyne derivative, indicates a considerable loss of bond strength for the bent triple bond.[11]

Table I. Effect of Various Calculational Levels on Energy and Geometry of 90° Deformed Acetylene in the MNDO Approximation

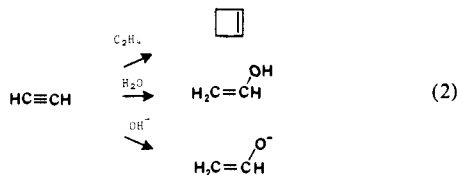| calculational level	C–C bond, Å	heat of formation, kcal/mol
closed shell	1.302	241.1
2 × 2 CI on c.s. geometry^a	1.302	218.5
2 × 2 CI optimized	1.372	217.4
3 × 3 CI optimized	1.357	218.8
triplet	1.360	212.2

^{a} c.s. = closed shell.

Competition reactions have shown that smaller cycloalkynes react faster.[3] Force-field calculations predict a strain energy increase of 21 kcal/mol accompanied by a change in angle bending from 172° to 150° at the alkyne position from cyclodecyne to cycloheptyne.[5] As expected, the ring size determines the degree of bending at the alkyne linkages which correlates with the reactivity. The effect of bending on the electronic structure of alkynes has been studied by ab initio calculations. The investigations show that the LUMO energy drops faster than the HOMO energy rises which explains the increased reactivity of benzyne and other cycloalkynes toward nucleophiles.[12] Although zwitterionic resonance structures have often been postulated to explain the chemistry of bent alkynes,[2] no convincing evidence for these "ylide" structures has been reported. Stereochemical studies of benzyne–olefin cycloadditions support the formation of biradical intermediates in 2 + 2 reactions with olefins.[13]

In the present study we address the question of how much of the strain energy resulting from alkyne bending is directly

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Effect of Bending on the Reactivity of Alkynes

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transformed into reactivity (decrease of activation barrier). Attention is paid to the importance of biradical or zwitterionic intermediates in the reactions of bent alkynes. Among the many reactions which demonstrate the increased reactivity of cyclic alkynes, the forbidden 2 + 2 cycloaddition reactions and the reactions with nucleophiles appear to be most sensitive to the degree of alkyne bending. As model reactions were chosen the hypothetical addition of ethylene, water, and hydroxide ion to linear and bent acetylene.

$$HC\equiv CH \quad \begin{matrix} \xrightarrow{C_2H_4} & \square \\ \xrightarrow{H_2O} & H_2C=CH \overset{OH}{\diagup} \\ \xrightarrow{OH^-} & H_2C=CH \overset{O^-}{\diagup} \end{matrix} \qquad (2)$$

Method

The subject of this theoretical study is the effect of alkyne bending on the energy surface of addition reactions. The selection of a suitable method for this study is critical. Thermally forbidden 2 + 2 dimerization reactions are generally believed to be stepwise processes which proceed through biradical or zwitterionic intermediates as indicated below.

$$\begin{matrix} = & \xrightarrow{} & \langle \cdot \\ \cdot & ? & \xrightarrow{} & \square \\ = & \xrightarrow{} & \langle + \end{matrix} \qquad (3)$$
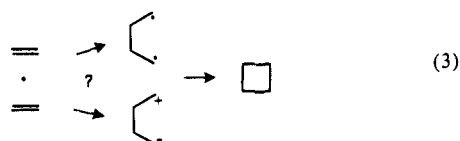
Forbidden reactions have the general feature of HOMO–LUMO degeneracy near the transition state. Since these two orbitals are usually of different symmetry, they must have considerable effect on the molecular geometry. Geometry optimization on the closed-shell SCF level will therefore result in a structure dictated by the HOMO whereas geometry optimization of the biradical state may overestimate the effect of the LUMO. Configuration interaction (CI) will give the wave function enough flexibility to adopt a structure where electron pairing and biradical character can be combined and additional information on the electronic nature of the ground state is provided.

The considerations above are supported by the results of various calculational levels of 90° cis deformed acetylene, summarized in Table I. Most drastic is the effect of CI on the C–C bond length which changes from 1.302 (closed shell) to 1.372 Å with 2 × 2 and 1.357 Å with biradical CI. When single-point CI is applied on the closed-shell optimized structure, the energy obtained is only 1.5 kcal/mol higher than the CI optimized energy, indicating that the molecular geometry of the reactive species may be more sensitive to electron correlation than the total energy.

Because of the HOMO–LUMO degeneracy close to the transition state, the limited configuration interaction treatment should be sufficient to cover the gross effect of electron correlation on molecular geometries during the reaction path. However, we cannot estimate the effect of higher order correlation on the total energy. Although application of limited CI should already result in a greatly improved wave function and geometry, it cannot account for special electron correlation effects on the reaction path of the forbidden reaction due to higher state contributions.[14] A complete CI treatment on the various stationary points of the reaction paths is desirable to estimate the limited and higher order electron correlation effects on the reaction. Such an investigation is still prohibitively expensive on any "ab initio" level. We therefore chose the semiempirical MNDOC program developed by Thiel.[15]

MNDO has been parametrized to reproduce experimental bond lengths and energies of organic molecules by closed-shell RHF calculations.[16] This implies that the major inherent error of RHF calculations, the electron correlation, has been accounted for by the parametrization. The approach appears to work well for closed-shell molecules and allowed processes. For the reaction of the acetylenes with water and hydroxide ion in this study, the MNDO method proved to be sufficient. Problems arise in cases of orbital degeneracy or HOMO–LUMO crossing where the closed-shell wave function is principally insufficient.[17] For example, in the calculation of homolytic bond cleavage reactions, the closed-shell
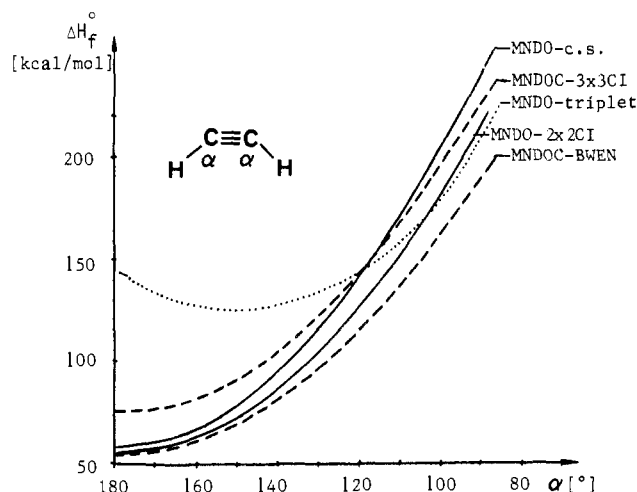

Figure 1. Effect of symmetrical in-plane cis bending of acetylene on the energy calculated at various levels.

approach breaks down in spite of the parametrization: a separation of the hydrogen atoms in H_2 to 5 Å results in an energy of 259 kcal/mol by closed-shell MNDO; 2 × 2 CI reduces this energy readily to the expected 100 kcal/mol. Although in bond homolysis as well as in forbidden processes the application of limited CI in MNDO results in a drastic improvement of the description of changes in the wave function during the reaction, it also leads to an overestimation of correlation effects which enter the calculation twice, first through the parametrization and second through the CI treatment. The extent of overestimation of correlation effects in any particular case is impossible to predict, which makes this approach unreliable for the application to the study of reactions where bond formation or cleavage occurs.

Thiel has reparametrized MNDO to reproduce experimental energies after a correction of the SCF energy by a perturbational CI treatment, several of which are available in the program (BWEN, RSMP, BWMP, RSEN).[15] The BWEN[18] approach provides the best approximation to the exact MNDOC correlation energy, which means that the total energy corrected by the BWEN treatment is the one that should be comparable with experimental data. An inherent error in perturbational CI treatments (second-order perturbation) is overestimation of the stabilization in cases of degenerate electronic states (degenerate HOMO–LUMO set). For such cases the program allows a two-configurational SCF treatment with BWEN corrections on both configurations (TC-BWEN).

For the above reasons the MNDOC program package seemed to be ideal for the investigation of forbidden reactions, since it allows the study of the effects of various levels of electron correlation on the total energy, geometry, and charge separation at points of interest on the reaction path. Since HOMO–LUMO crossing is a dominant feature of thermal 2 + 2 reactions, we have used the TC-BWEN method exclusively in this investigation. Geometries were completely optimized on the 3 × 3 CI level for each point along the reaction path chosen for the formation of the C–C bond of interest. Stationary points were confirmed by gradient optimizations with MNDO on the 2 × 2 CI level.[19]

Results and Discussion

The effect of cis bending on the energy of acetylene calculated by various methods is illustrated in Figure 1. It shows that the energy increases rapidly with deformation angles larger than 20°. This compares well with the fact that cyclooctyne with a C≡C—C angle of 159°[20] is still isolable. Force-field calculations (MM2)[5] on cyclooctyne predict a strain energy increase of 8 kcal/mol relative to cyclooctane and a heat of hydrogenation of 72 kcal/mol in good agreement with the experimental value of 69 kcal/mol.[21] This strain energy of 8 kcal/mol is quite close to the energy increase for acetylene bending by 20° which is calculated to 9.7

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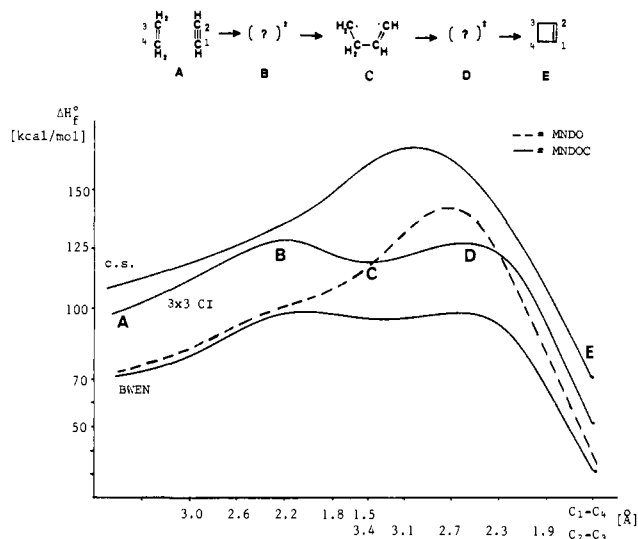(17) Staemmler, V. *Theor. Chim. Acta* **1977**, *47*, 89.

(18) BWEN stands for Brillon–Wagner–Epstein–Nesbet which characterizes the combination of methods used for the calculation of the correlation energy by second-order perturbation treatment. For more detailed information consult ref 13.
(19) Calculated with the MOPAC program, J. J. Stewart, QCPE No. 455, which is a very convenient program package based on the MNDO method; Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1976**, *98*, 4899.
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Figure 2. Reaction path for the formation of cyclobutene from acetylene and ethylene on various calculational levels of MNDOC.

kcal/mol on the closed-shell level and 8.4 kcal/mol with BWEN (see Figure 1). Such good agreement of the semiempirical model calculations with the force-field results and experimental data supports the use of bent acetylene as a valid model for cyclic alkynes.

Electron correlation becomes important with increasing deformation as seen on the increasing separation of the MNDO closed-shell (c.s.) and 2 × 2 CI curve with larger angles (Figure 1). The two parallel curves for 3 × 3 CI (MNDOC) and BWEN prove that limited configuration interaction is sufficient to cover the dominant effect of angle bending relative to the linear ground-state molecule. All higher correlation contributions appear to affect ground and transition states by equal amounts. As expected from the non-vanishing exchange integrals, singlet biradical states are unimportant for the ground-state description of bent alkynes (documented by the lack of biradical coefficients for the ground state in the 3 × 3 CI matrix). The effect of trans bending, although of interest, has not been investigated in this study since it is not related to the electronic changes of cyclic alkynes.

Addition of Ethylene to Linear and Bent Acetylene. To obtain information about the effect of bending in cyclic alkynes on the potential energy surface of cycloaddition reactions with olefins, the cycloaddition reactions of ethylene with relaxed acetylene is compared to that of ethylene with cis-bent acetylene. A CCH bond angle of 120° was chosen to mimic more strained alkynes like benzyne, cyclohexyne, and cyclopentyne.

The addition of acetylene to ethylene is expected to follow a reaction path similar to the dimerization of ethylene which may be reduced to the question of the existence of tetramethylene as a defined gauche intermediate.[22] Although there is much indirect evidence for such an intermediate,[23] it has defied experimental detection, and its existence as a defined intermediate presents an unresolved controversy in quantum mechanical calculations. Hoffmann predicted from EHT calculations in 1970 the presence of a flat plateau on the potential energy surface where the molecule may be spending relatively long times exploring the plateau and thus becoming indistinguishable from a true intermediate (twixtyl model).[24] With MINDO/3–CI calculations, Dewar and Kirschner in 1974[25] predicted the existence of the gauche tetramethylene as a "ridge" on the hypersurface.[25] Segal characterized the gauche intermediate with 15-configuration STO-3G calculations as a defined intermediate,[26] but he was later contradicted

Table II. ΔH_f° of Stationary Points for the Reaction of Ethylene with Acetylene as Calculated by MNDOC (kcal/mol)

level	A	B	C1	D	E	C5	C6
3 × 3 CI	102.0	128.2	122.1	126.0	51.6	144	156
TC-BWEN	70.7	96.1	95.2	96.6	29.1	114	120

Chart I. Stationary Points on the Reaction Path for the Formation of Cyclobutene from Acetylene and Ethylene (obtained with MNDOC-3 × 3 CI)
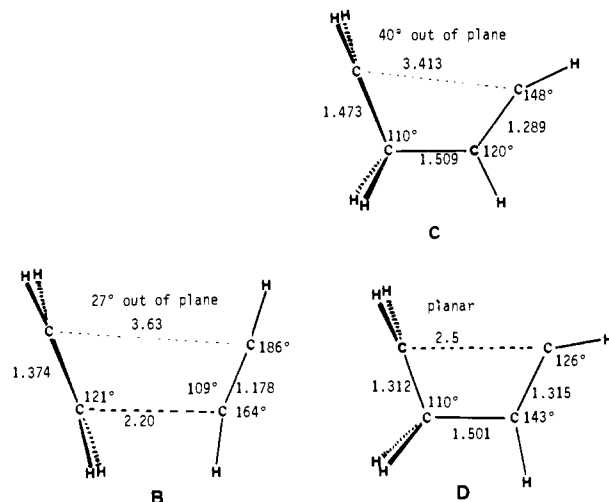
by Doubleday, McIver, and Page, who showed that the gauche minimum is an artifact of the STO-3G basis set.[27] The most sophisticated calculations reported by Doubleday et al.[28] clearly support the twixtyl model.
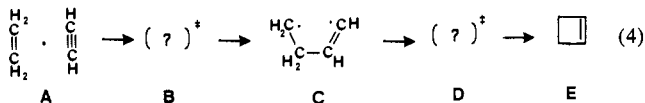

$$(4)$$

Figure 2 summarizes our results for the lowest energy reaction path. We have chosen the first C–C bond formation as the initial reaction path. With complete geometry optimization on the 3 × 3 CI level the first transition state B was detected at a C_1–C_4 distance of 2.2 Å, the intermediate C at C_1–C_4 = 1.5 Å and C_2–C_3 = 3.4 Å. Complete geometry optimization without any restriction confirmed the existence of C as a true intermediate on the 3 × 3 CI level. At this point, the reaction path is continued by the formation of the C_2–C_3 bond. After a second transition state D at about 2.4 Å, the energy drops and the final product, cyclobutene (E), is formed. The structures of the intermediate C and the transition states[29] B and D are outlined in Chart I; Table II contains calculational details. To confirm the transition-state nature of the two structures, B and D, we applied a gradient optimization with MNDO–2 × 2 CI; the force constant matrix in both cases showed only one negative eigenvalue (the structures obtained were practically identical with the MNDOC-3 × 3 CI reaction path structures outline in Chart I).

The activation barrier of 25.4 kcal/mol predicted for the addition of ethylene to acetylene by MNDOC–TC-BWEN appears quite small. Although we calculated it as a model reaction, the question about the accuracy of the calculated activation barrier and the experimental feasibility of the reaction itself remains to be addressed. To our knowledge the formation of cyclobutene from acetylene and ethylene is not known and the predicted barrier cannot be judged readily. Since pure acetylene is well-known for

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(27) Doubleday, C.; McIver, J.; Page, M. *J. Chem. Phys.* **1982**, *104*, 3768.

(28) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447.

(29) Due to the flat surface the transition states where not exactly located and the structures presented represent the highest point on the reaction coordinate calculated (step size 0.05 Å).

its explosive nature even at room temperature, the low activation barrier calculated for ethylene addition may be more of an indication about the activation barrier for an uncontrollable polymerization reaction under liquid-phase conditions and thus not unreasonable. A related reaction, the well-known dimerization of ethylene to cyclobutane, must therefore serve for a calibration of the method. The activation barrier for this reaction is calculated by MNDOC (BWEN) to be 39 kcal/mol[30] which is in better agreement with the experimental value of 43 kcal/mol than the 50.5 kcal/mol predicted by MCSCF ab initio calculations based on a 3-21G basis set.[28] From this comparison we have to conclude that the low activation barrier predicted for the ethylene addition to acetylene is correct and the reaction should be realizable under controlled conditions.

The stereochemistry of the cycloaddition reaction was examined by calculating the rotational dependence around the newly forming C–C bond in the first transition state (B) and in the intermediate (C). No rotational selectivity appears at the transition state for the first bond formation where the gauche, 90°, and the 180° trans conformations are calculated to be isoenergetic within 0.5 kcal/mol.

Although the gauche intermediate, which is the precursor for formation of the final ring, is calculated to be out of plane deformed by 40° (see Chart I), no considerable barrier for rotation around the newly formed bond could be detected. The minimum conformation of the intermediate is the twisted conformation C2 (90°); its energy of 92.1 kcal/mol is about 2.6 kcal/mol lower than that of the gauche minimum C1 (activation barrier 0.2 kcal/mol). The trans intermediate C3 is, with 92.6 kcal/mol, only slightly higher in energy than the C2 conformation.
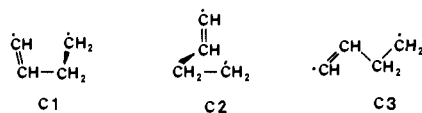
The only process competing with a stereospecific addition is the rotation around the terminal CH_2 bond. This rotation has an activation barrier of 4.5 kcal/mol relative to C3 and is calculated to be less favorable than the ring closure by about 1 kcal/mol. That this is the right order of magnitude is shown by a comparison with experimental data, where a quite general 4:1 sterospecifity for 2 + 2 cycloaddition reactions with benzyne points to a free energy increase of about 0.5 kcal/mol for the nonstereospecific addition of olefins.[13]

The CI matrix of the 3 × 3 CI calculation for the unsymmetrical gauche intermediate C1 shows an unusual composition for the ground state: 42% S_0, 32% S_1, and 26% S_2, indicating the presence of three almost degenerate singlet states. This result is also supported by the TC-BWEN calculation where an unusual 57% of the total correlation energy originates from the two-configurational CI and only 43% is due to higher order correlation energy. Since no special charge distribution is calculated, the intermediate is best described as a biradicaloid. This predicts that the required HOMO–LUMO crossing on the reaction path can be localized at the intermediate structure.

How polarizable are biradicaloids? The flexible wave function of the shallow intermediate may be susceptible to dipole interactions. This hypothesis is tested with MNDO–2 × 2 CI calculations where a dipole is induced by the addition of a positive and a negative charge, separated by 7 Å at a distance of 3.5 Å from the terminal carbon atoms in C1. This dipole was found to induce a charge separation of 0.93 e between the two terminal groups of the molecule (compared to a charge separation of less than 0.2 e in the absence of the dipole). In addition the wave function in the presence of the dipole changes from biradicaloid to zwitterionic (C4, closed shell, 100% S_0!). MNDO thus predicts a strong effect of the local environment on the nature of the twixtyl intermeidate which is predicted to be a biradicaloid in the gas phase (or an unpolar solvent) and a zwitterion in a polar solvent. The effect

(30) Lebrilla, C. B.; Maier, W. F., unpublished results.

Table III. $\Delta H_f°$ of Stationary Points Calculated for the Reaction of Ethylene with Cis-Bent Acetylene (kcal/mol)

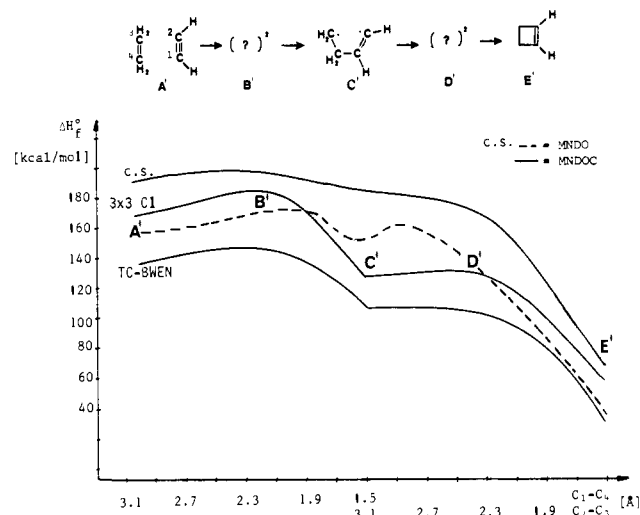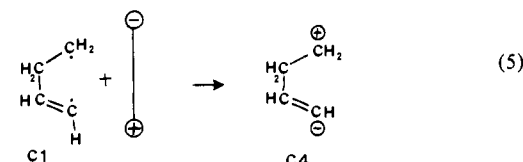| level	A′	B′	C1′	D′	E′	C5′	C6′
3 × 3 CI	166.0	187.5	129.2	133.6	60.3	211	217
TC-BWEN	132.7	147.2	108.4	106.9	37.5	171	168

Figure 3. Reaction path for the formation of cyclobutene from bent acetylene and ethylene on various calculational levels.

of the same dipole on acetylene itself is with a charge separation of 0.6 e clearly lower compared to the change from C1 to C4.

(5)

Scheme II shows that the reaction path on the 3 × 3 CI level is characterized by the formation of a reactive intermediate C. The application of TC-BWEN reduces the activation barriers and predicts a flat plateau instead of the defined intermediate. Such qualitative agreement with the 20 configurational 3-21G ab inito calculations of Doubleday and McIver[27] on tetramethylene demonstrates the strength of this semiempirical MNDOC approach.

For the purpose of demonstration we include the closed-shell MNDO surface in Figure 2 as derived by single-point calculations on the 3 × 3 CI structures and also the optimized closed-shell MNDO surface. The lack of a plateau or intermediate on this surface could be confirmed by a reoptimization of the intermediate on the closed-shell level which led directly to the starting materials. The shape as well as the high activation barrier illustrates once more the deficiency of single-configuration calculations in "forbidden" reactions.

The above reaction path was calculated to serve as a reference path for the reaction with the bent acetylene. To model the effect of angle bending on the reactivity of alkynes, the reaction path for the cycloaddition of acetylene to ethylene was repeated with a cis-deformed acetylene (both CCH angles fixed in plane at 120°).

(6)
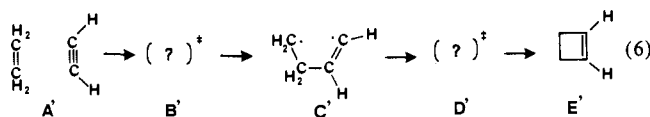
The results are illustrated in Figure 3 and Table III. The reaction proceeds through a distinct first transition state B′ to a shallow reactive intermediate C′ followed by the next transition state D′ which leads to the final product E′. The structures calculated for the stationary points A′–E′ are very similar to the structures in Chart I. The major differences are the hydrogen atoms in the alkyne fragment which are fixed to the 120° cis

conformation. Comparison of Figure 3 with Figure 2 reveals the dominant effect of angle bending on the reaction path of the 2 + 2 cycloaddition reaction. Although the activation barrier for the first bond formation is reduced, the effect is much larger for the second transition state. The limited CI calculations predict a low activation barrier for the second transition state, and therefore the path is dominated by the first transition state which clearly represents the rate-determining step. TC-BWEN, however, changes the intermediate and second transition state into a flat plateau. This shorter plateau (relative to the relaxed acetylene path) together with the thermal energy gained after the first transition state points to a decreasing lifetime for the twixtyl intermediate with increasing bending deformation of the alkyne.

Contrary to the relaxed acetylene reaction, the desired gauche conformation is calculated to be more favorable during the first transition state B' by 0.7 kcal/mol relative to the trans conformation which favors the correct preorientation for the desired ring closure. Even the intermediate C' in its trans conformation is calculated to be only 0.8 kcal/mol lower in energy than the gauche conformation which points to a more facile ring closure in cyclic alkynes relative to straight-chain alkynes. The isomerization around the terminal CH_2 group is also facilitated and has a calculated activation barrier of only 2.4 kcal/mol. However, the small energy differences calculated, although clearly in the right direction, are not significant (considering the calculational level) and point to a sensitive reaction type where entropic factors, solvent, or steric effects may dominate the stereochemical results.

Nevertheless, the results are in qualitative agreement with the observed increase in stereoselectivity for cyclic alkynes. The reaction of benzyne with alkenes proceeds with 70–80% stereoselectivity[13] whereas the more strained cyclopentyne is reported to undergo 2 + 2 cycloaddition reactions with complete retention of stereochemistry.[10b] The reduced activation barrier for the first C–C bond formation followed by the facile ring closure predicted for bent alkynes also explains the increasing tendency of cyclic alkynes to undergo 2 + 2 cycloaddition reactions with conjugated dienes. Whereas benzyne reacts with 2,3-dimethylbutadiene to give a 50/50 mixture of 2 + 2 and 4 + 2 cycloaddition products,[31] cyclopentyne is reported to undergo exclusive 2 + 2 addition with butadiene.[10b]

For the bending of acetylene to 120° an energy increase of 63 kcal/mol is calculated (see Figure 1). The activation barrier for the 2 + 2 cycloaddition of bent relative to linear acetylene drops from 25.4 to 14.5 kcal/mol, indicating that only about 11 kcal/mol of the 63 kcal/mol of strain energy contribute directly to a reduction of the activation barrier. Most of the strain energy in the bent alkyne is released *after* the first transition state where the twixtyl plateau ($\Delta H°_f$ = 108 kcal/mol) is only 13 kcal/mol higher than in the unstrained alkyne reaction. Inspection of the geometries of the intermediate and second transition state (Chart I) illustrate this effect, since the vinyl hydrogen in the intermediate and the transition state is perfectly preoriented in the cis-deformed alkyne.

An interesting side reaction frequently encountered during our search on the reaction path was a facile conversion of the biradicaloid twixtyl C or C' into cyclopropylcarbene. The reverse of this reaction (as pointed out by one of the referees) has been observed already in the generation of acetylene from a cyclopropylcarbene precursor.[32]

$$H_2C\cdot \quad \cdot C{-}H$$
$$H_2C{-}C \longrightarrow \triangleright\!\!\!<\!\!{C{-}H}$$
$$\qquad\qquad H \qquad\qquad H$$
$$c,c' \tag{7}$$
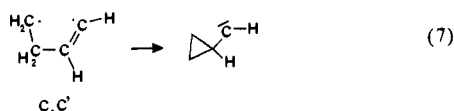
So far the calculations have shown that electron correlation has a pronounced effect on the geometries and energies of stationary points of the stepwise reaction path of this 2 + 2 cycloaddition reaction. This raises the question on the importance of concerted
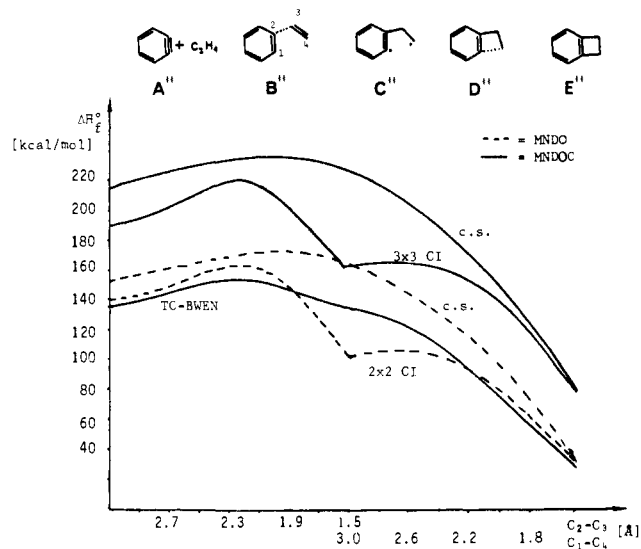

Figure 4. Reaction path for the formation of benzocyclobutane from benzyne and ethylene on various calculational levels.

pathways where the effect of electron correlation cannot readily be predicted. We have therefore calculated the reaction path for the "forbidden" planar (C5) and the "allowed" twisted (C6) concerted reaction for the addition of ethylene to acetylene. It has to be pointed out that the allowed and forbidden terminology here is based on the RHF picture of electrocyclic reactions as popularized by the Woodward–Hoffmann rules.[33]

$$\tag{8}$$
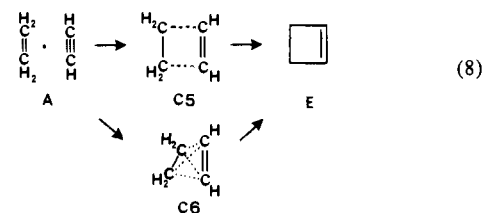
The results of the concerted path calculations are summarized in Tables II and III. During the path calculation the reaction system is forced to have identical C–C distances for both newly formed bonds. The transition state is located at a C–C distance of 2.2 Å for the planar C5 and 2.4 Å for the perpendicular transition state C6. The activation barrier on the 3 × 3 CI level, 51 kcal/mol for the planar and 45 kcal/mol for the orthogonal transition state, is considerably higher than the more reasonable barrier calculated for the stepwise process. It was surprising to note that the BWEN treatment inverts the order of the concerted transition states, favoring the formally "forbidden" planar transition state over the "allowed" twisted transition state by 3 kcal/mol. This result points to the irrelevance of the terms in reactions where RHF calculations and their approximations are inadequate. However, the gap between the concerted and the stepwise processes even increases at the BWEN level to 21 kcal/mol in favor of the stepwise reaction. The lack of contribution of the biradical state in the limited CI calculation also excludes a biradical mechanism for the concerted dimerization.

Addition of Ethylene to Benzyne. The above study has been restricted to the most simple model cases of linear and bent acetylene. To estimate its relevance for cyclic alkynes a comparison with the reaction path calculated for benzyne and ethylene is valuable. The calculations are summarized in Figure 4 and Table IV. All geometry parameters except those of the four hydrogen atoms on the benzyne fragment were completely optimized with limited CI. Comparison with Figure 3 reveals a similar reaction path as the path calculated for the bent acetylene. The presence of the defined intermediate followed by a consid-

(31) Wittig, G.; Dürr, H. *Liebigs Ann. Chem.* **1964**, *672*, 55.
(32) Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 3118.

(33) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970.

Table IV. $\Delta H_f°$ of Stationary Points Calculated for the Reaction of Ethylene with Benzene (kcal/mol)

level	A″	B″	C″	D″	E″	CS″
MNDO c.s.	153.7	174.1	(166.0)	142.4	38.3	202.7
MNDO–2 × 2 CI	140.1	161.6	102.2	103.2	33.9	191.3
MNDOC–3 × 3 CI	191.4	220.4	161.9	163.8	91.7	246.4
MNDOC–BWEN	136.4	155.6	(131.8)	122.3	37.7	189.8

*Single point calculation on 2 × 2 CI geometry. ᵇSingle point calculation on 3 × 3 CI geometry.

Chart II. Stationary Point Structures on the Reaction Path for the Formation of Benzocyclobutane from Benzyne and Ethylene (obtained with MNDO 2 × 2 CI)
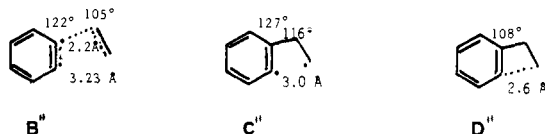
erable activation barrier on the closed-shell MNDO path for the benzyne reaction is the major difference on the reaction path of the bent acetylene relative to that of benzyne (compare Figures 3 and 4).


$$\tag{9}$$
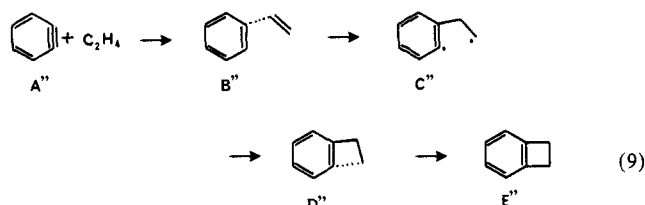
The defined intermediate C″, predicted by the 3 × 3 CI level with MNDOC, disappears with the application of the extensive correlation treatment TC-BWEN. Contrary to the bent acetylene case, the twixtyl-type intermediate, most pronounced in the relaxed acetylene reaction (see Figure 2), has virtually disappeared on the benzyne path (Figure 4). This change in reaction path goes hand in hand with the increase of exothermicity (41.6, 95.2, and 98.7 kcal/mol for linear and bent acetylene and benzyne, respectively). The activation barrier calculated for the reaction of benzyne, 19.2 kcal/mol, is similar to that of the model bent acetylene (14.5 kcal/mol). Even the structures of the stationary points on the benzyne reaction path are very similar to the structures calculated for the acetylene model (compare Charts I and II).

Most impressive in Figure 4 is the similar curve shape of the MNDOC–TC-BWEN and the closed-shell MNDO path which seem to suggest that the parametrized closed-shell approach is as good as the more sophisticated correlation methods. The scheme, however, is misleading since it only documents the lowest energy path calculated and does not show the problems encountered with the change in electron configuration in the closed-shell path in the region of intermediate C. Nevertheless, the similarity of the BWEN and MNDO curves also serves as an impressive documentation of the effectiveness of Dewar's parametrization approach in the MNDO method.

The similarity between the results obtained for the reaction of benzyne and those of bent acetylene confirms that bent acetylene is a suitable model for the study of the effect of bending on the reactivity of cyclic alkynes. No indication for special electronic effects due to the aromatic conjugation or the true cyclic structure in benzyne relative to the bent acetylene model was obtained.

For completeness the reaction path for planar symmetrical attack of the ethylene was also calculated. The results (activation barrier 53.4 kcal/mol) were similar to those calculated for bent acetylene (38.4 kcal/mol), excluding the symmetrical path as an important alternative for such reactions.

The calculations presented have shown that semiempirical methods with proper treatment of electron correlation give a consistent and meaningful picture of "forbidden" electrocyclic
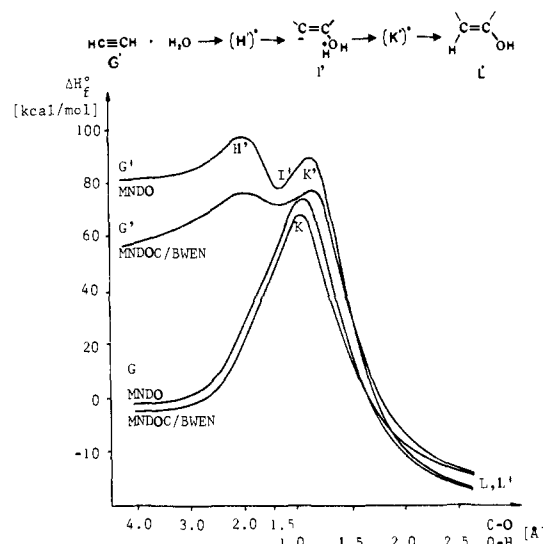
Figure 5. Reaction paths for the addition of water to bent and relaxed acetylene calculated by MNDO and MNDOC/BWEN.

Table V. $\Delta H_f°$ for the Stationary Points Calculated for the Addition of Water to Bent and Linear Acetylene

level	G	K	L	G′	H′	I′	K′	L′
MNDO	–3.6	75.4	–34.4	81.2	97.5	78.0	89.4	–34.3
MNDOC	–5.8	70.5	–28.9	56.5	77.2	73.0	79.4	–28.7

reactions. Limited CI seems to overestimate the stability of the biradical intermediate. Inclusion of the total correlation energy by the TC-BWEN method favors the presence of a "twixtyl" species rather than a defined intermediate structure. The close analogy of the nature of the 1-butene-1,4-biradical intermediate with the tetramethylene as a flat energy plateau rather than a defined structure predicts that 1,4-biradicals are elusive species.

Nucleophilic Addition. Nucleophilic addition to alkynes are well-studied reactions.[34] For example, vinyl ethers are formed by the reaction of alkynes with alkoxides in alcohol.[35] Bent alkynes, however, are found to exhibit a special reactivity for nucleophiles. Acenaphthyne is trapped by water to form acenaphenone.[11] Benzyne reacts with alcohols[36] to give ethers and with water to give phenol.[37] Reaction of substituted benzynes with alcohols and water is more para selective than addition of the stronger nucleophiles hydroxide and alkoxide which result in para/meta ratios of about 1.0.[38] On the basis of ab initio calculations, this increased electrophilicity of bent alkynes has been attributed to the lower LUMO energy calculated.[12] If this hypothesis is valid, a marked effect on the activation barrier of nucleophile addition by alkyne bending has to be expected. We have therefore calculated the addition of water and of hydroxide to linear and bent acetylene as model reactions for the reaction of cycloalkynes with nucleophiles.

$$\tag{10}$$
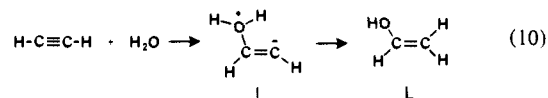
After verifying that the reaction path for the addition of acetylene to water is not sensitive to electron correlation, the

(34) Dickstein, J. I.; Miller, S. I. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; J. Wiley & Sons: New York, 1978.
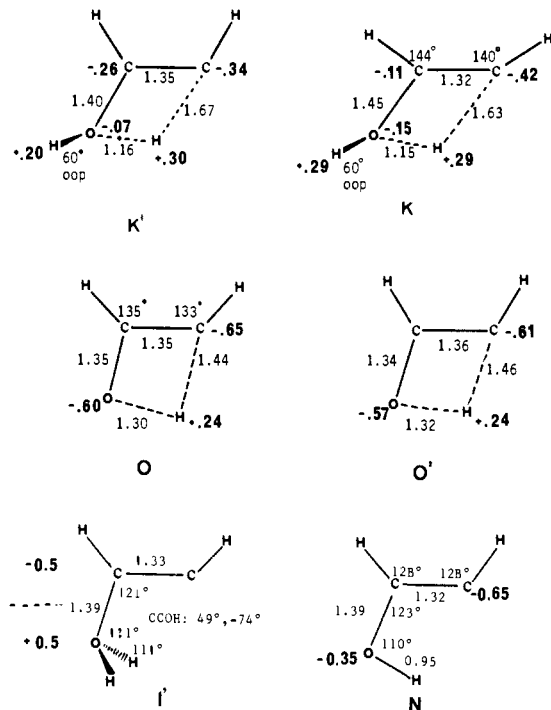
(35) Miller, S. I.; Tanaka, R. In "Selective Organic Transformations"; Thyagarajan, B. S., D.; Wiley-Interscience: New York, 1970; Vol. Winterfeldt *Newer Methods Preparative Org. Chem.* **1971**, *6*, 243.

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(37) Wittig, G.; Hoffmann, R. W. *Chem. Ber.* **1962**, *95*, 2718. Howe, R. J. *Chem. Soc. C* **1966**, 478.

(38) Bunnett, J. F.; Happer, D. A. R.; Patsch, M.; Pyun, C.; Takayama, H. *J. Am. Chem. Soc.* **1966**, *88*, 5250. Bottini, A. T.; Roberts, J. D. *J. Am. Chem. Soc.* **1957**, *79*, 1458.

Chart III. Transition and Intermediate Structures for the Addition of H_2O and OH^- to Linear and Bent Acetylene Calculated by MNDO (Bulk Numbers with Sign Indicate Charge Distributions)

Table VI. ΔH_f° of the Stationary Points Calculated for the Addition of OH^- to Linear and Bent Acetylene

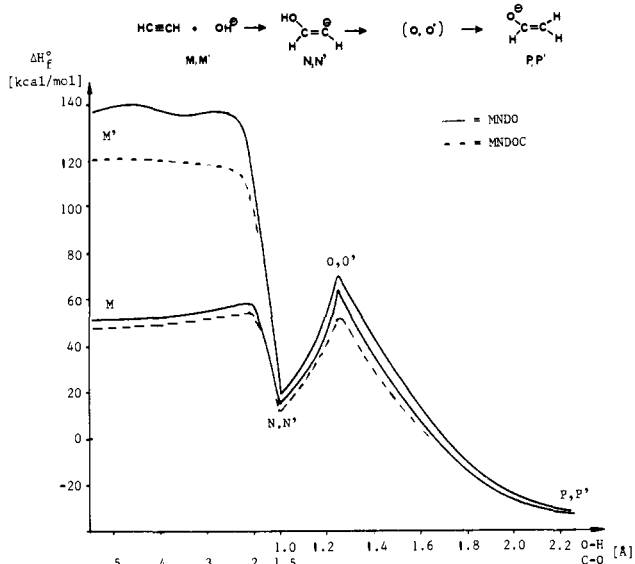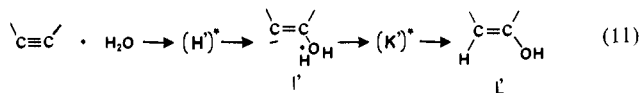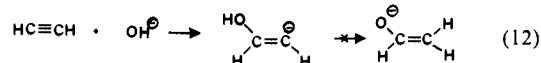| level	M	N	O	P	M'	N'	O'	P'
MNDO	51.5	15.0	65.3	−36.0	136.4	16.7	72.6	−35.2
MNDOC	57.3	10.3	56.4	−29.6	122.0	8.7	57.3	28.3

Figure 6. Reaction paths for the addition of HO^- to bent and relaxed acetylene calculated with MNDO and MNDOC/BWEN.

simpler closed-shell MNDO approach was applied.[19] Figure 5 and Table V show the reaction path as calculated by MNDO for the addition of acetylene to water. For demonstrational purposes we have combined the MNDO reaction path and the MNDOC/BWEN path (constructed from single-point calculations on 2 × 2 CI optimized geometries). Figure 5 does not exhibit any special electron correlation effects during the reaction path. The only area where correlation becomes important is with the bent alkyne itself as already discussed above.

According to MNDO, the addition of water to acetylene is an exothermic process (−30.8 kcal/mol with MNDO; −23.1 kcal/mol with MNDOC) with a single transition state and no intermediate. The activation barrier of 79.0 kcal/mol is close to the MNDOC value of 76.3 kcal/mol. The transition structure (K) (see scheme 8) shows that the acetylene adds directly to a lone pair at the oxygen atom, the migrating hydrogen atom is in the OCC plane, and the second hydrogen at the oxygen atom is oriented above the plane (dihedral angle 60°), preventing allylic conjugation. The structure is in complete agreement with an early transition state as expected from the exothermicity of the reaction. A considerable charge separation is predicted in the transition structure (see Chart III). The alkyne withdraws electron density from the lone pair of the water molecule and a considerable negative charge builds up at the β-carbon, facilitating the transfer of the proton from the oxygen atom.

Quite different is the behavior of the bent acetylene. The activation barrier for water addition drastically reduces to 5.5 kcal/mol by MNDO and 22.4 by MNDOC and a true intermediate I' is formed. The difference between the MNDO and MNDOC barrier reflects the difference in the isolated bent acetylene. The structure of this intermediate shows a large polarization of the molecule. The positive charge on the oxygen atom and the negative charge on the β-carbon indicate that in this intermediate the alkyne unit acts as electrophile (Lewis acid character) to form a complex with the water molecule where the oxygen atom exhibits oxonium ion character. This calculated behavior is in complete agreement with Houk's conclusion on the increased nucleophilicity due to the low-energy LUMO of bent alkynes.[12] MNDOC indicates a reduced stability of the intermediate I' relative to MNDO. After this first intermediate I' (which may be an artifact of the MNDO method) the reaction

path of the bent and the relaxed alkyne almost coincide as evident from Figure 5.

$$\underset{C}{\overset{\backslash}{C}}{\equiv}\overset{/}{C} \; + \; H_2O \longrightarrow (H')^* \longrightarrow \underset{\underset{H}{\overset{+}{O}}H}{\overset{\backslash}{C}{=}\overset{/}{C}} \longrightarrow (K')^* \longrightarrow \underset{H}{\overset{\backslash}{C}{=}\overset{/}{C}}{\overset{}{\searrow}_{OH}} \quad (11)$$
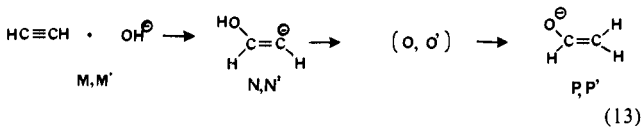$$\qquad\qquad\qquad\qquad\quad I' \qquad\qquad\qquad L'$$

The calculations predict that most of the strain energy required to bend the acetylene is directly released in the first transition state H'. The activation barrier for water addition to acetylene drops from 79 to 5.5 kcal/mol with the bent alkyne on closed-shell MNDO, predicting that over 80% of the strain inherent in the bent alkyne directly reduces the activation barrier. MNDOC predicts a 76% contribution of the 63-kcal/mol strain in the bent alkyne contributes to direct reduction of the activation barrier. The overall difference to the forbidden cycloaddition reaction is that most of the strain energy in cyclic alkynes is released in the transition state for polar addition reactions, indicating a strong preference of cyclic alkynes for polar addition over cycloaddition.

Alkyne bending therefore directly affects the reaction with weak nucleophiles. The reaction is predicted to show considerable solvent effects due to the polarization during the transition state.

$$HC{\equiv}CH \; + \; OH^\ominus \longrightarrow \underset{H}{\overset{HO}{\searrow}}C{=}\overset{\ominus}{C}\underset{H}{\nearrow} \; {\longrightarrow}{\hspace{-0.3em}\rightarrow} \; \underset{H}{\overset{O^\ominus}{\searrow}}C{=}C\underset{H}{\overset{H}{\nearrow}} \quad (12)$$

The addition of the strong nucleophile OH^- to acetylene is outlined in Figure 6 and Table VI. there is a barrier of only 10 kcal/mol for the addition to the relaxed acetylene, but no barrier is detected with the bent acetylene. Both form an almost identical adduct, which indicates that all of the strain in the bent alkynes is already released at that point. The rearrangement to the more stable enolate shows a surprisingly high barrier for both alkynes. The structures of intermediate N and transition states O and O' are outlined in Chart III.

$$HC{\equiv}CH \; + \; OH^\ominus \longrightarrow \underset{H}{\overset{HO}{\searrow}}C{=}\overset{\ominus}{C}\underset{H}{\nearrow} \; \longrightarrow \; (O, O') \; \longrightarrow \; \underset{H}{\overset{O^\ominus}{\searrow}}C{=}C\underset{H}{\overset{H}{\nearrow}}$$
$$\qquad\qquad M, M' \qquad\qquad\quad N, N' \qquad\qquad\qquad\qquad\qquad P, P'$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (13)$$

The thermal energy gain by the anion addition to the bent alkyne provides enough excess energy to allow the rearrangement, whereas in the case of the relaxed alkyne decomposition to the starting material is more favorable. The transition state for addition is located very early at an O–C distance of 3.0 Å with the bent alkyne and much later at 2.0 Å with the relaxed alkyne. Alkyne bending therefore not only eliminates the activation barrier but also increases the probability for the addition of strong nucleophiles. The stability of the intermediates N and N′ indicates that intermolecular protonation by hydrogen abstraction from solvent molecules is more likely than the unfavorable intramolecular 1,3-hydrogen shift.

The overall conclusion of this study is that cis bending of alkynes, as in cyclic alkynes, most effectively reduces the activation barrier for nucleophilic addition. Considerable charge separation in the transition structure for water addition predicts a strong solvent effect for such reactions. The absence of any activation barrier for the addition of hydroxide ions explains the lack of selectivity found in the reaction of benzyne with strong nucleophiles.[34–38] In contrast to the nucleophilic addition, the electrocyclic addition of olefins to alkynes is only partly affected by cis bending of the alkyne unit. With bent alkynes the formation of the first C–C bond becomes the rate-determining step, and the ring-closure

reaction to the cyclobutyl ring is greatly accelerated relative to linear alkynes. This explains very nicely the tendency of cyclic alkynes to undergo 2 + 2 cycloaddition reactions at all (compared to the pronounced polymerization behavior of linear alkynes); it also accounts for the increase in stereospecifity of 2 + 2 cycloaddition reactions of cyclic alkynes observed with decreasing ring size. Electron correlation is not important for the nucleophilic addition reactions but essential for a reasonable description of the forbidden cycloaddition. The flexible wave function of the biradicaloid twixtyl in the 2 + 2 cycloaddition reaction makes the nature of this intermediate extremely environment dependent. In polar solvents the intermediate may have a zwitterionic nature, but in unpolar solvents or in the gas phase the ground state is predicted to be biradicaloid. We also think that MNDOC represents a very valuable extension of the MNDO method which greatly expands the applicability of this semiempirical approach.

Ionization of *N*-Arylsulfonyloxy Amines: The Nitrenium Ion Question[1]

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Contribution from the Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003. Received August 23, 1984. Revised Manuscript Received April 4, 1985

Abstract: The solvolyses of the *p*-nitrobenzenesulfonoxy derivatives of 2-methyl-2-octylamine, (**7**), 1-methylcyclohexylamine, (**8**), and 4,7,7-trimethyl-2-azabicycloheptane (**10**) and the *m*-(trifluoromethyl)benzenesulfonoxy derivative of dibenzylamine, (**9**) gave high yields of carbon-to-nitrogen rearrangement products. No parent amines were produced, even in the presence of heavy-atom solvents. The results, when compared to data from the literature, suggest that competing reaction pathways lead to rearranged or hydrogen abstraction products in the solvolysis of compounds with leaving groups attached to nitrogen.

Reaction intermediates involving positively charged, electron-deficient nitrogen atoms, nitrenium ions, have been a subject of considerable interest and some controversy.[2] Nitrenium ions are divalent nitrogen cations, which are isoelectronic with carbenes, and can exist in either a singlet, **1**, or triplet, **2**, spin state. Central
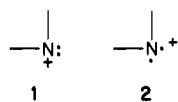
to the debate is the question of the spin state of nitrenium ions produced solvolytically in solution from compounds having leaving groups attached to nitrogen. While spin conservation requires that the first-formed ion is a singlet, the triplet state is the ground state,[3] and intersystem crossing to the triplet state has been used to explain some of the products of solvolysis.

Specifically, the formation of parent amine, **6**, from the solvolysis of chloramine, **3**, has been interpreted as evidence for the

Scheme I
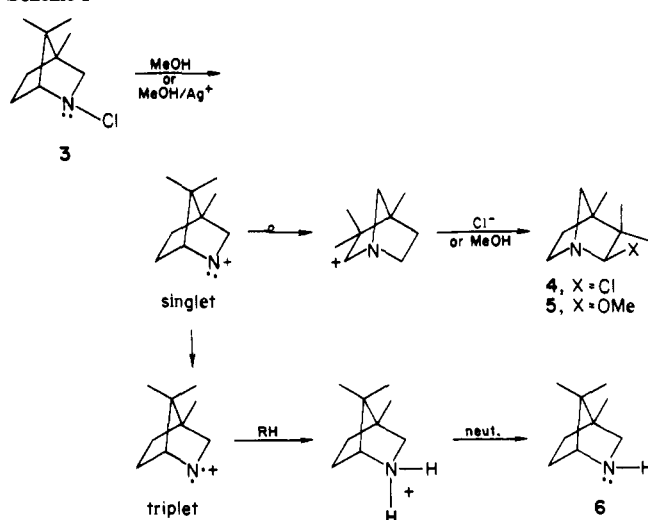
formation of a discrete nitrenium ion, which underwent intersystem crossing to the triplet. The triplet, being a 1,1 diradical, abstracted hydrogen from the solvent to give an ammonium salt and, upon neutralization, the parent amine, (Scheme I). Chloramine, **3**, is a well studied, but not unique, example of this behavior.[4] Of

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(1) Taken in part from the Ph.D. Thesis of A.K. submitted to the Graduate School of New Mexico State University, December 1983.

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