

## 241. Nucleophilic Addition to a Triple Bond; Preliminary *ab initio* Study

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### Summary

Preliminary *ab initio* calculations (minimal basis set STO-3 G) suggest that the preferred direction of approach of a nucleophilic centre towards a CC triple bond makes an obtuse angle ( $\sim 120^\circ$ ) with this bond. The stereoelectronic requirements for nucleophilic addition to triple bonds and to ketones are thus rather similar.

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Experimental evidence [1] and theoretical calculations [2] suggest that in nucleophilic addition to ketones, the  $\text{Nu} \cdots \text{C}=\text{O}$  approach angle  $\alpha$  (see **1**) is close to the corresponding angle in the tetrahedral addition product. Although this kind of correspondence cannot be expected to be valid in all cases it may serve as a rough and ready rule for the preliminary delineation of reaction paths in general. In connection with the formation of cyclic structures by nucleophilic addition to multiple bonds it has been suggested [3] that the  $\text{Nu} \cdots \text{C}=\text{C}$  approach direction for olefines is similar to that for a ketone (**1**), but that the approach direction for acetylenes is as in **2**. We have investigated the approach of a nucleophile to acetylene by *ab initio* calculations with a minimal basis set (STO-3 G) [4] without geometrical optimization of the acetylene (standard bond lengths were used [5]:  $\text{CC}=1.2 \text{ \AA}$ ,  $\text{CH}=1.06 \text{ \AA}$ ). Several obvious objections can be levelled at this procedure but it does have the advantages of simplicity and economy and at least provides a convenient starting point for further discussion. In the case of addition to ketones the approach direction found by this procedure [6] is practically the same as that obtained by far more elaborate calculations using an extended basis set and full geometrical optimization [2].

For the system  $\text{H}^- + \text{HC}\equiv\text{CH}$  with  $\text{H}^- \cdots \text{C}$  distances of  $1.5 \text{ \AA}$  and  $2.0 \text{ \AA}$  our calculations lead to an optimal approach angle  $\alpha$  between  $110^\circ$  and  $120^\circ$  (see *Table 1*). At distances greater than  $2.3 \text{ \AA}$   $\text{H}^-$  approaches along the axis of the acetylene<sup>3)</sup>. As a test of the quality of our basis set the geometry of the

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<sup>3)</sup> Preliminary calculations show the existence of two valleys on the potential surface, one leading to nucleophilic addition ( $\alpha \sim 120^\circ$ ), the other to proton abstraction ( $\alpha = 180^\circ$ ).

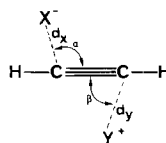


Table 1. Values of geometrical parameters

X	Y	$d_X$	$a$	$d_Y$	$\beta$
H		2.00 Å	118.4°		
H		1.50	109.5		
F		1.68	110.0		
F	Na <sup>a)</sup>			2.40 Å	76.0°
F	Na	1.56	108.4	2.15	87.8
F	Na <sup>a)</sup>	1.49	66.2	2.15	73.8

a)  $C_{2v}$  symmetry

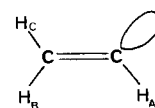


Table 2. Geometry of vinyl anion obtained from various calculations

C(1)-C(2)	C(2)-H <sub>A</sub>	C(1)-H <sub>B</sub>	C(1)-H <sub>C</sub>	C(2)H(1)H <sub>C</sub>	C(2)C(1)H <sub>B</sub>	C(1)C(2)H <sub>A</sub>	Ref. Basis set
1.331 Å	1.126 Å	1.093 Å	1.089 Å	123.7°	127.4°	105.5°	STO-3G a)
1.367	1.112	1.097	1.087	121.4	125.8	109.9	Double zeta [7]
1.340	1.086	1.086	1.086	120.0	120.0	108.7	Triple zeta [8a]
1.356	1.198	1.154	1.128	124.5	130.7	107.4	STO-4G [8b]
1.367	1.114	1.076	1.076	124.1	124.2	110.6	SS [8b]
1.351	1.110	1.076	1.076	124.1	124.2	108.0	SS + d [8b]

a) This work.

'final product'  $H_2C=CH^-$  was optimized and compared (Table 2) with results of previous calculations [7] [8]<sup>4)</sup>. In agreement with our rule the  $H_B-C=C$  angle is not too far from  $a$ . Dykstra *et al.* [7] have determined the reaction path for addition of  $H^-$  to  $HC\equiv CH$  using an extended basis set and allowing for complete relaxation of the geometry of the system. Their approach angle is about  $126^\circ$  for  $H^- \cdots C$  distances between 1.3 and 2 Å. We regard the agreement between the results of the two sets of calculations as a vindication of the utility of our simple-minded procedure.

Results with the system  $F^- + HC\equiv CH$  (no 'final product' optimization) are similar to those obtained with  $H^-$  as nucleophile (Table 1).

The correlation diagram obtained from *Extended Hückel* calculations<sup>5)</sup> for the transformation 4-5 suggests that the instability of 2 with respect to 1 can be associated with the behaviour of the occupied MO 6; the antibonding interaction a

4) In view of the current interest in stereoelectronic effects [9] it is noteworthy that the CH bond of the methylene group *trans* to the lone pair is slightly longer than the CH bond *cis* to the lone pair.

5) Program ICON Version 8. We are grateful to Dr. Peter Hofmann for a CDC adapted copy of this program. Coulombic integrals and orbital exponents are standard for C and H (C:  $H_{2s} = -21.4$  eV,  $H_{2p} = -11.4$  eV,  $\zeta = 1.625$ , H:  $H_{1s} = -13.6$  eV,  $\zeta = 1.3$ ). For F the coulombic integrals were modified to simulate an anion:  $H_{2s} = -20.0$  eV,  $H_{2p} = -10.0$  eV,  $\zeta = 2.425$ .

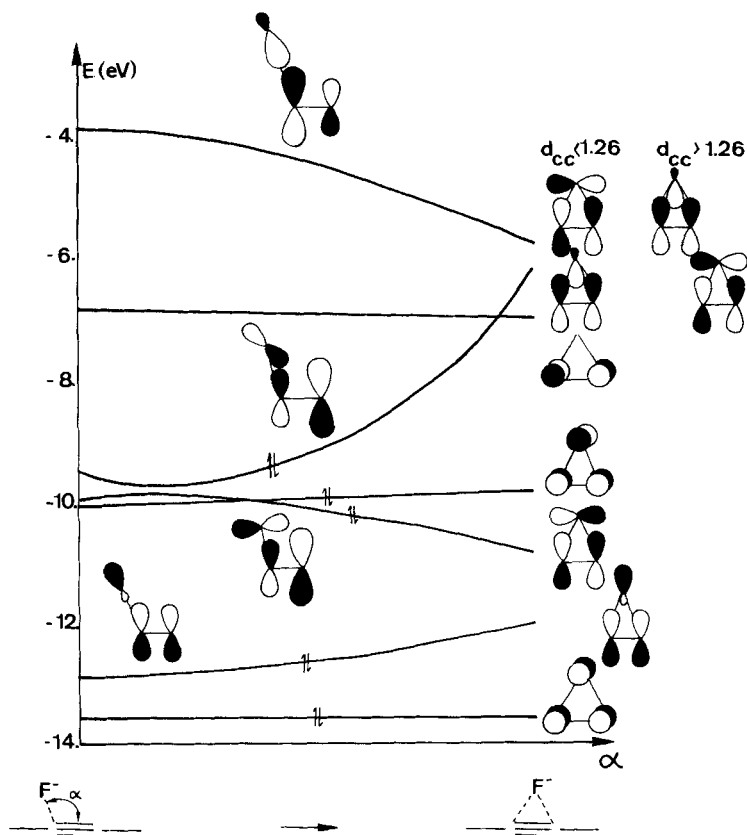
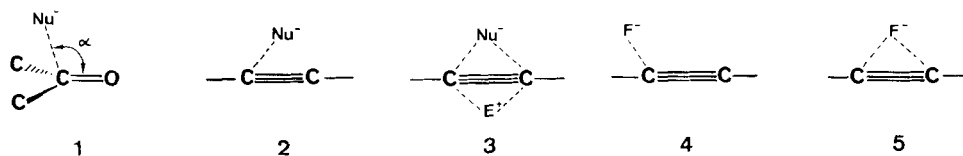


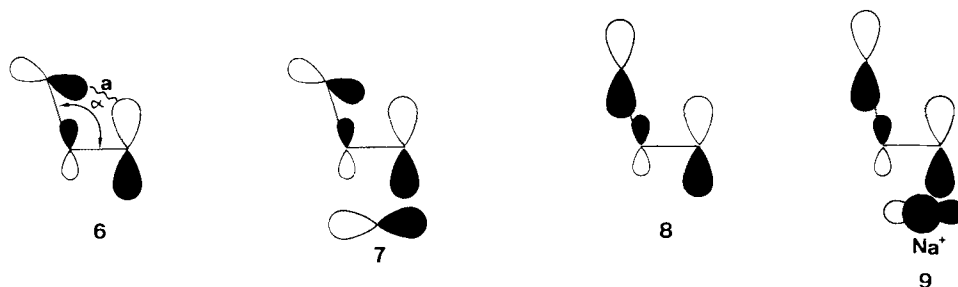
Fig. Extended Hückel correlation diagram for the transformation 4-5



increases as  $\alpha$  decreases. In the presence of an external cation or other electrophilic centre, this interaction may be offset by combination of MO 6 with an appropriate vacant orbital (e.g. 7)<sup>6)</sup>.

The proton is a poor candidate for the cation in question (the 1s orbital is of wrong symmetry and the 2p orbitals are high in energy). Calculations were made with  $\text{Na}^+$  as external cation. In the absence of an anion the most stable position for  $\text{Na}^+$  is found to be symmetrical with respect to the acetylene (see Table 1), in agreement with frontier orbital arguments. When both ions were placed at their

<sup>6)</sup> Correlation diagrams were constructed for C,C-bond lengths of 1.20 and 1.34 Å,  $\alpha$  being the only variable. The main features are the same, apart from the inversion of the two highest orbitals depicted on Figure 1.



previously optimized positions,  $F^-$  moved 0.12 Å towards the closer C-atom and  $\alpha$  was hardly changed; the cation  $Na^+$  was displaced by 0.52 Å from the symmetrical position towards the other C-atom. This displacement can be understood from the properties of the HOMO of the 'supermolecule'  $F^- \cdots HC \equiv CH$  (**8**); since the coefficient on C(2) is larger than on C(1) [11] the best position of the cation is closer to the latter (**9**). The symmetrical structure **3** was found to be unstable.

We consider that these calculations indicate the essential similarity between stereoelectronic requirements for nucleophilic addition to double and triple bonds.

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