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THE INFLUENCE OF ELECTRON-WITHDRAWING SUBSTITUENTS ON THE GEOMETRIES AND BARRIERS TO INVERSION OF VINYL ANIONS

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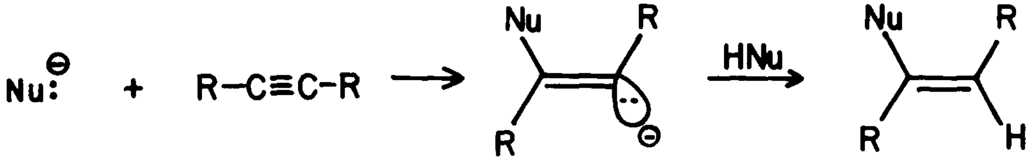
Dedicated to Professor Rolf Huisgen on the occasion of his sixtieth birthday.

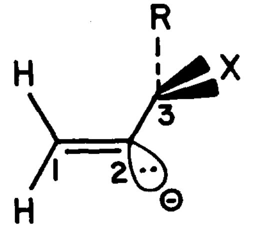
Abstract: Whereas *ab initio* calculations predict that the vinyl anion is bent and has a high barrier to inversion, substitution of cyano, methoxycarbonyl, and formyl substituents at C-1 lower this barrier. Nevertheless, the first two substituents produce significantly bent anions, while the bent and linear 1-formylvinyl anions are essentially isoenergetic.

We recently reported a computed transition state for the reaction of acetylene with hydride, a model for a potent nucleophile.[2] For this reaction, there is a single transition state involving *anti*-bending of the acetylene moiety. This result explains the observed *anti*-stereoselectivity of nucleophilic additions of potent nucleophiles to relatively unactivated (alkyl or aryl) acetylenes.[3] The anions formed by attack of nucleophiles on such acetylenes have sufficiently high barriers to linearization to preclude inversion before protonation to give the final product, as indicated below:



However, numerous studies of nucleophilic additions to activated acetylenes indicate that either *syn* or *anti* stereoselectivity may be observed in particular cases, or low stereoselectivity may be observed.[3] These results imply that either (1) both *syn* and *anti* anions are formed and these anions readily interconvert, or (2) these species give linear anions, which can be protonated from either side.[4] There is experimental evidence that 1-cyanovinyl anions are bent in solution.[5]

In order to acquire theoretical evidence about whether bent, 1, or linear, 2, species were more stable for vinyl anions substituted by electron-withdrawing groups, we have carried out partial geometry optimizations with ab initio HF calculations using the STO-3G basis set, as well as single-point energy calculations with the 4-31G basis set.[6] In order to estimate barriers for inversion of bent anions, calculations were also performed on a species with linearity enforced at the anionic carbon.



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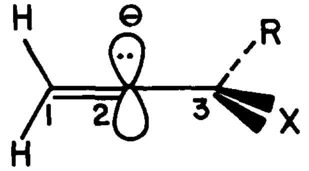

2

RC=X	Bent Anion					Linear Anion			E(linear)-E(bent) (kcal/mol)	
	E(STO-3G) au	r_{12}	r_{23}	r_{3x}	θ°	r_{12}	r_{23}	r_{3x}	STO-3G	4-31G
-H	-76.23303	1.33			105	1.26			+50.4	+36.6
-CN	-166.85860	1.33	1.48	1.16	111	1.28	1.31	1.19	+17.9	+10.3
	-166.85874[a]	1.33	1.48	1.16	111	1.29	1.31	1.19	+16.7	+9.4
$-CO_2Me$	-299.94541	1.32	1.51	1.24	115	1.28	1.36	1.28	+12.1	+5.0
-CHO	-187.49878	1.32	1.48	1.24	119	1.28	1.36	1.28	+7.7	-5.7

(a) Fully optimized

The heavy atom bond lengths and angles were optimized by STO-3G, using the same H_2C fragment geometry present in vinyl anion. The methoxy group in the ester was held constant at standard values. For the cyano compound, a full geometry optimization gives a slightly lower energy, but a similar barrier to inversion, so that we feel that full geometry optimization will not change the overall conclusions.

Although the very large barrier calculated for the vinyl anion is drastically lowered by electron-withdrawing substituents, the bent species are still favored for all three substituted anions at the STO-3G level. The split-valence 4-31G calculation predicts that the 1-formylvinyl anion is linear. Assessments of the degree of accuracy expected for these different types of computations can be made by considerations of the performance of these calculations on simpler systems. The barrier to inversion of the methyl anion is calculated to be 24.0 kcal/mol by STO-3G//STO-3G, while this drops to 7.6 kcal/mol at the 4-31G//STO-3G level.[7] The 4-31G//4-31G barrier is 8 kcal/mol.[8] Experimental estimates of this quantity center around 5.0 kcal/

mol, so that STO-3G calculations grossly overestimate such barriers while the 4-31G calculations will be relatively accurate. Whereas the 4-31G//STO-3G barrier to inversion of the vinyl anion is 36.6 kcal/mol, indirect experimental estimates are 25-35 kcal/mol.[9] The experimental barriers are likely to be slightly lower than the 4-31G barriers. Thus, the vinyl anion and the 1-CN and 1-CO_2Me are predicted to be bent with barriers of 30, 10, and 5 kcal/mol, while the formyl species prefers a linear shape, with rather low out-of-plane bending force constants.

The geometrical differences between the bent and linear anions, and the barriers to rotation about the C-C(O) in the formyl anion bond indicate that the bent anions are stabilized primarily by inductive effects and "dipole-stabilization",[10] while these factors plus conjugation are important for the linear species. In the bent anion, rotation of the formyl group by 90° to form the anti-planar species requires only 4.7 kcal/mol (STO-3G, or 6.4 kcal/mol by 4-31G), and rotation to the syn takes 9.7 (STO-3G, or 13.9 kcal/mol by 4-31G). Thus, in the bent species, there is little conjugation of the lone-pair orbital with the carbonyl group. In the linear species, rotation of the formyl group by 90° requires an enormous 45.1 kcal/mol (STO-3G, or 50.2 kcal/mol by 4-31G). Thus, maintenance of the bent geometries for these species is a result of the several mechanisms by which electron-withdrawing groups stabilize anions; the high s character of the lone-pair orbital of the bent species makes the parent vinyl anion strongly bent. This effect, plus the ability of electron-withdrawing groups to stabilize anions inductively and by electrostatic ("dipole-stabilization") effects, causes the cyano and methoxycarbonyl substituted species to remain bent. Only the powerful conjugative-stabilizer, formyl, completely linearizes the vinyl anion. The bent species may also be expected to be stabilized preferentially by solvation, since there is more charge localization in the bent anions than in the linear.

Thus, we conclude that cyano- and ester-substituted vinyl anions formed by attack of charged nucleophiles on activated acetylenes are bent, but have only very low barriers to inversion. These species can rapidly interconvert in solution, accounting for the low or variable stereochemistry of nucleophilic additions to activated acetylenes.

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1. (a) On leave from the University of Pavia, Italy; (b) Address correspondence to the Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.

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