

## A THEORETICAL STUDY OF SUBSTITUTED ALLYL ANIONS

A. ATKINSON, A. C. HOPKINSON and E. LEE-RUFF

Department of Chemistry, York University, Downsview, Ontario, Canada

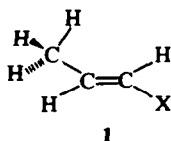
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**Abstract**—CNDO/2 calculations have been used to optimise the geometry of the allyl anion. Electron-withdrawing substituents are found to decrease the proton affinities of allylic anion, with the *trans*-substituted anion being the more stable. However when the only substituent on the anion is an alkyl group then the *cis* anion is the more stable. The calculated proton affinities of several monosubstituted allyl anions and the electron densities of the methyl hydrogens in the hydrocarbons are both found to correlate with the Hammett substituent constants.

Recent NMR studies have shown that diphenylallyl carbanions form stable ion pairs with alkali metal ions in ether solutions.<sup>1-3</sup> In general, phenyl substitution increases the stability of anions,<sup>4,5</sup> but allyl anions containing only alkyl groups are postulated as intermediates in the base-catalysed polymerisation of olefins<sup>6</sup> and of dienes,<sup>7</sup> and the parent ion has also been observed directly by NMR.<sup>8</sup> The early studies on allyl anion-alkali metal complexes indicated that these had covalent structures,<sup>9,10</sup> but more recently it has been shown that in polar solvents, they exist as ion pairs.<sup>5,11</sup>

Allylic anions are postulated as intermediates in the base-catalysed isomerisation of olefins.<sup>12-15</sup> Detailed kinetic work on the isomerisation of pent-1-ene and but-1-ene led to the general conclusion that *cis*-allylic anions containing only alkyl substituents are more stable than their *trans*-isomers.<sup>15,16</sup> In order to assess the effect of other types of substituents on the relative stabilities of allylic anions we have performed SCF-MO calculations using the CNDO/2 method on nine isomeric pairs of anions.

**Computational details.** The CNDO/2<sup>17</sup> program was used on an IBM 370-155 computer. Initially a series of calculations were performed on the *trans*-substituted propenes (1), where X = H, CH<sub>3</sub>, CH<sub>2</sub>=CH, F, Cl, NO<sub>2</sub>, CF<sub>3</sub>, OH and OCH<sub>3</sub>. Average



values were taken for all bond lengths,<sup>18</sup> all bond angles involving C atoms were assumed to be either tetrahedral or trigonal, and the Me group was assumed to be in the eclipsed\* conformation. A

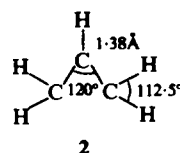
\*Defined relative to C=C bond.

subsequent optimisation of the geometry of *trans*-but-2-ene showed that these initial assumptions were essentially correct. The COH and COC angles of the enols were assumed to be tetrahedral, and conformational studies showed that both substituents lie in the same plane as the remainder of the C atoms, agreeing with *ab initio* calculations on CH<sub>2</sub>CHOH.<sup>19,20</sup> The ONO angle of the nitro group was assumed to be 129°, and was also found to lie in the molecular plane.

The geometry of the allyl anion was optimised and then taken as standard for the other anions. The geometries of the substituents, with the exception of the ethylenic group, were taken to be the same as in the parent hydrocarbon. The geometry of the allyl anion having a double bond as substituent, i.e. the pentadienyl anion, was optimised separately. Finally, conformational studies on the enols showed that, in contrast to the hydrocarbons, the hydrogen and Me groups on the O atoms were out of the plane of the anion, with a dihedral angle of 90°.

### RESULTS AND DISCUSSION

In the initial calculations the geometry of the allyl anion was optimised with respect to the computed total energy. The order of the optimisation was (i) C—C bond length, (ii) HCH, (iii) CCC and (iv) the out-of-plane angle of the terminal C atoms. The optimum values given in structure 2 are similar to those in a previous theoretical study.<sup>21</sup>

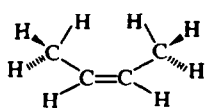


The C—H bond length was taken to be 1.08 Å. The terminal methylene groups were found to be

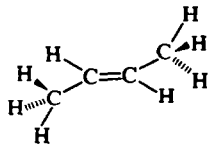
planar, in contrast with the results from a previous *ab initio* study,<sup>22</sup> in which only a partial geometry optimisation was carried out. This does not necessarily imply disagreement between the two types of calculations, since the previous workers only examined trigonal and tetrahedral geometries for the terminal methylene groups, and the CNDO/2 calculations also show that of these two the tetrahedral geometry is preferred.

The geometry of the allylic fragments of the remainder of the anions was taken to be that in 2. The validity of this assumption was tested by carrying out an optimisation of the C—C bond lengths on the least ideal of the substituted allyl anions, the pentadienyl anion. Only the most stable "w" shaped ion<sup>11</sup> was considered, and all bond lengths were found to be the same, 1.38 Å, as in the parent allyl anion. Also bond angle optimisations in the butenyl anions gave C—C—CH<sub>3</sub> angles of 124.7°, compared with the estimated value of 123.75° taken from the optimised geometry for the allyl anion. This excellent agreement between the estimated and optimised geometries for the only two other anions whose geometries were independently varied, suggests that the allyl anion is a good model for the monosubstituted anions.

The geometries of *cis*- and *trans*-but-2-ene have been optimised by *ab initio* molecular orbital calculations.<sup>23</sup> In order to further verify that CNDO/2 calculations provide meaningful results on these small unsaturated hydrocarbons we repeated the same optimisation. The CNDO/2 calculations gave optimum C—C—C angles of 129° and 126° for the *cis*- and *trans*-isomers respectively, compared with *ab initio* values of 128° and 124.5°. Also, as in Radom and Pople's work,<sup>23</sup> the Me groups were found to prefer the eclipsed-eclipsed conformation (3) at the optimum C—C—C bond angles, but with the ideal angle of 120°, the staggered-staggered conformation was the most stable. For the *trans*-but-2-ene the eclipsed-eclipsed conformation (4) was the preferred one at all C—C—C angles.



3



4

The conformations of the Me groups in both the *cis*- and *trans*-butenyl anions were calculated in the same way as for the hydrocarbons, and both were found to be eclipsed.

Penta-1,3-diene, in addition to *cis-trans* isomerism about one of the double bonds, may also be *cis* or *trans* about the formally single bond between C atoms 2 and 3. A rotational study showed that the *s-trans* conformation is the preferred one.

Table 1. Energy difference (kcal/mole) between *cis* and *trans*-anions

Substituent	
F	<i>trans</i> by 2.11
Cl	<i>trans</i> by 3.14
CF <sub>3</sub>	<i>trans</i> by 1.41
NO <sub>2</sub>	<i>trans</i> by 5.29
CH <sub>2</sub> =CH	<i>trans</i> by 0.55
CH <sub>3</sub>	<i>cis</i> by 0.36
HO	<i>trans</i> by 0.35
CH <sub>3</sub> O	<i>trans</i> by 0.55

The computed energy differences between the carbanions for a given substituent (Table 1) are quite large (and therefore can be treated with considerable confidence) with the most electron-withdrawing substituent, the nitro group, having the largest difference (5.29 kcal/mole) and favouring the *trans* anion. The Me substituted anion is the only one for which the *cis* anion is the more stable, and even in this case the energy difference is small. Although this particular difference is too small to be reliable it is interesting to note that the base-catalysed conversion of but-1-ene into but-2-ene forms the *cis*-isomer much faster than the *trans*- and that the usual explanation given is that this *cis*-allylic anion is the thermodynamically more stable one due to favourable internal dipole-dipole interactions.<sup>12,16</sup> Electron-donating substituents appear to have little effect on the relative stabilities of a pair of anions whereas electron-withdrawing groups, which remove part of the negative charge from the "allyl part" of the anion, prefer to have the substituent in the *trans* position, thereby distributing the negative charge over a larger volume than would be possible in the *cis* anion.

If the unstable allyl anion is considered to be close to the transition state in the ionisation process,<sup>24</sup> then the difference in the proton affinities should give a guide to the effect of substituents on the base-catalysed reactivities of the hydrocarbons. The parent hydrocarbons were assumed to have the ideal trigonal bond angles and the subsequent optimisation of the geometry of *trans*-but-2-ene shows that this leads to an underestimation of the proton affinity of this molecule by 2.3 kcal/mole. However the proton affinities listed in Table 2 vary over a range of 57 kcal/mole and discrepancies caused by using slightly incorrect geometries will not seriously change the order of the computed proton affinities. Two values are recorded for the proton affinity of the pentadienyl anion, one for the symmetric ion and the other for an ion containing a double bond.

The approximation of using the *symmetric* pentadienyl anion for the transition states is suspect and, in an attempt to produce a more realistic model, the terminal "double bond" of the pen-

Table 2. Computed proton affinities (kcal/mole)

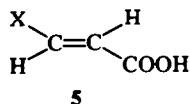
Substituent	
H	590.0
F	582.1
Cl	557.8
CF <sub>3</sub>	550.1
NO <sub>2</sub>	533.2
CH <sub>2</sub> =CH (a) symmetrical anion	561.8
(b) unsymmetrical anion	563.9
CH <sub>3</sub>	581.6
HO	590.8
CH <sub>3</sub> O	586.8

Table 3. Charge on hydrogen atoms of methyl groups of *trans* substituted propenes

Substituent	In-plane	Out-of-plane
H	+ 0.0060	+ 0.0085
F	+ 0.0043	+ 0.0109
Cl	+ 0.0114	+ 0.0186
CF <sub>3</sub>	+ 0.0144	+ 0.0225
NO <sub>2</sub>	+ 0.0174	+ 0.0288
CH <sub>2</sub> =CH	+ 0.0044	+ 0.0079
CH <sub>3</sub>	+ 0.0026	+ 0.0051
HO	- 0.0008	+ 0.0028
CH <sub>3</sub> O	- 0.0006	+ 0.0030

tadiene was retained, and the allyl anion geometry used for the remainder of the ion.

The  $pK_a$  values for the ionisation of *trans*-3-substituted acrylic acids (5) are linearly related to



the Hammett  $\sigma$  constants for *para*-substituents in benzoic acids.<sup>25</sup> Formation of allyl anions for *trans*-substituted propenes is a similar process and a plot of the computed proton affinities, assumed to approximate the  $pK_a$  values, against  $\sigma$  was constructed (Fig 1). This shows a general trend for the

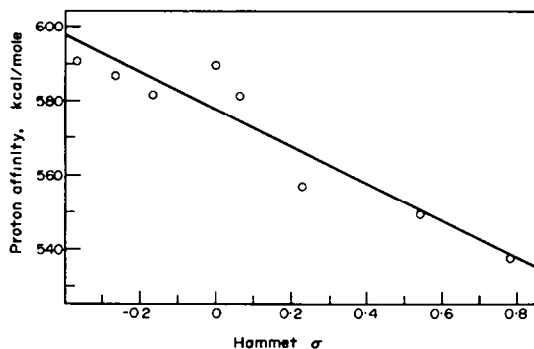


Fig 1. Plot of computed proton affinities against Hammett  $\sigma$  values.

proton affinity to decrease with ascending  $\sigma$  value, but there is appreciable scatter, possibly due to the inaccuracy of the CNDO method and solvation effects not included by use of the gas phase proton affinities.

An alternative method of assessing the relative acidities of the propenes, is to examine the charges on the H atoms of the Me group which loses the proton in the ionisation process, and these are recorded in Table 3. In every molecule the out-of-plane H atoms carry a slight positive charge and are

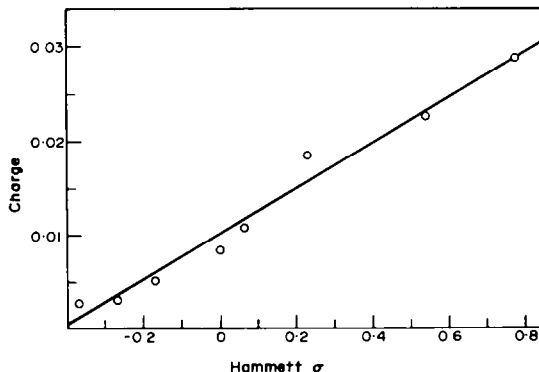


Fig 2. Plot of the computed charge on the out-of-plane hydrogen atom against Hammett  $\sigma$  values.

more acidic than the in-plane H atom. The substituent also has an appreciable effect on these H atoms, with the electron-withdrawing substituents causing higher positive charges. The use of trigonal geometry instead of a slightly larger C—C—C angle makes very little difference to the computed charge on the out-of-plane H atom (+ 0.0051 at 120° and + 0.0075 at 126°). A plot of the charge on the out-of-plane H atoms against the substituent constant  $\sigma$  (Fig 2) gives a better correlation than the one involving proton affinities.

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