Chemical pathways for the polymerization of enines

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AM1 calculations are reported for enines with aromatic substituents. It was found that the position of the unsaturated bonds in each molecule may account for the reactivity of each isomer via different polymerization pathways. The resonant structure of the charged form of one of the molecules allowed speculation about the observed inhibition of the polymerization reaction.

(Keywords: polymerization; enines; aromatic substituent)

INTRODUCTION

Enines are important molecules in the intermediate steps in organic synthesis[1] and have been the subject of several studies, which focus on their laboratory preparation[2]. The existence of unsaturated bonds suggests that enines will readily undergo polymerization and the large electron delocalization leads to the possibility that they may be electrically conducting. The aim of this paper is to explore the possible pathways via which polymerization can occur and to analyse the theoretical behaviour of some typical species of this group. Some characteristics of the possible resulting polymers are also discussed.

METHODOLOGY

The theoretical results were obtained by the AM1 method[3] using MOPAC software[4] with total optimization of geometry based on the BFGS algorithm. Standard parameters were used and geometries were obtained using the MMX method[5].

RESULTS AND DISCUSSION

The isomeric species (I and II) shown in *Figure 1* were considered. Calculations were carried out on the neutral, charged and free radical species of both isomers in order to find the most stable form, and thus find the most probable reaction pathway.

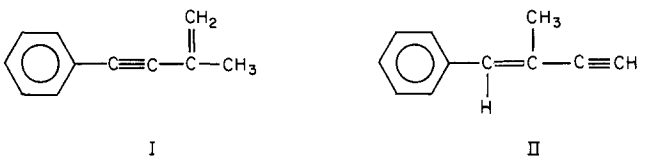
There is little information available on the polymerization of this kind of compound but it is well established that a double bond is more active than a triple bond in anionic or free radical pathways. The greater energy of the triple bond represents an inhibition of the availability of electrons for nucleophilic attack. Therefore the positions of the double and triple bonds are fundamental when considering the reaction pathway.

Small but important differences in the stability of the isomers were found. *Table 1* show the results obtained for both species and their active forms (charged and free radical).

The mean values of charges and overlap population are shown in *Figure 2* for the neutral molecules and in *Figure 3* for the charged versions; the results for the free radical are almost identical to those for the charged case. Isomer II has two conformational isomers; calculations were carried out for both, and the results are presented later.

Comparing *Figure 2* with *Figure 3* it can be seen that the delocalization of electrons changes from neutral to charged. The effect is so strong that the aromaticity of the ring is broken and a highly delocalized system with a negative charge density at the ends is generated (*Figure 4*).

It is useful to analyse the distribution of charge in each case. Molecule I shows an almost uniform value for the overlap population on the ring bonds in the neutral case. The bond between the ring and the lateral chain seems to be a single bond. Both unsaturated bonds remain localized and there is no large charge density (*Figure 2*).



I II

Figure 1 Enines with aromatic ring substituents

Table 1 Energetic results

Species	ΔH_f (kJ mol^{-1})	ΔU (eV)
I	344.1209	−1543.4786
Ic[a]	407.3441	−1542.8234
II	358.1718	−1543.3330[b]
IIc[a]	410.3966	−1542.7918

[a]c indicates active species (charged or free radical)
[b]Results of the more stable conformational isomer (*cis*)

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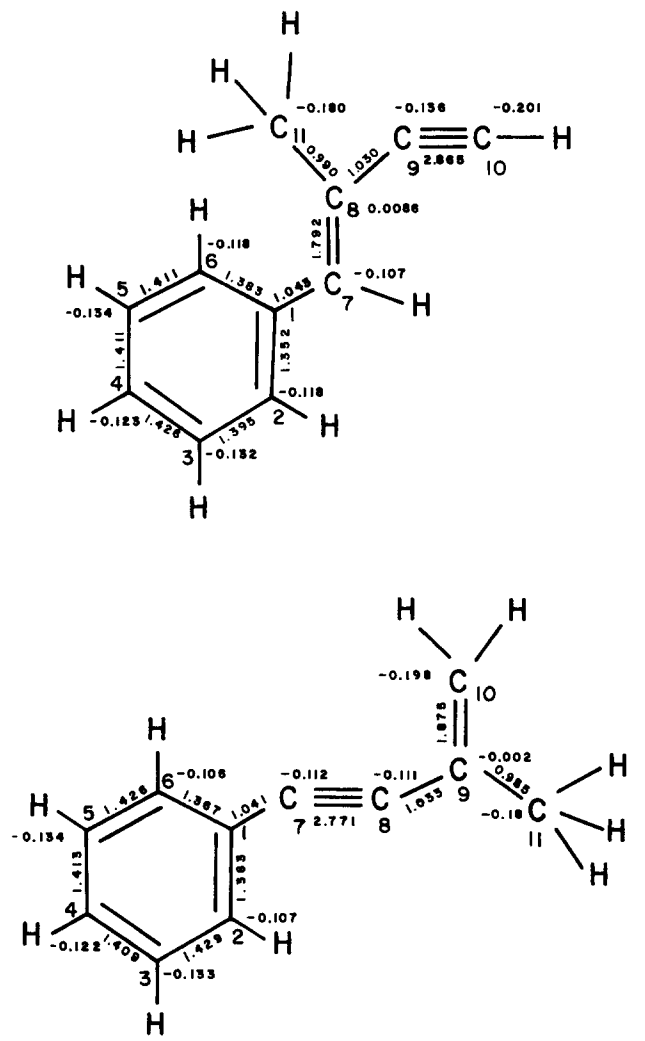

Figure 2 Charges and overlap populations for neutral molecules

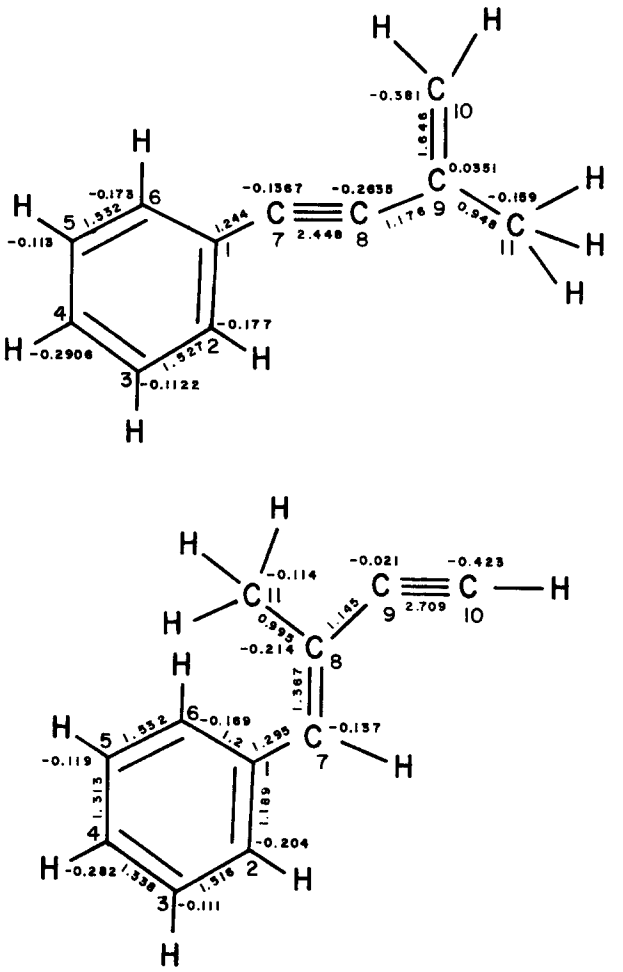

Figure 3 Charges and overlap populations for anionic molecules

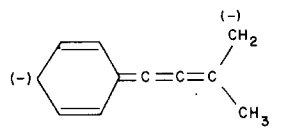

Figure 4 Delocalization on anionic molecule

Strong changes occur in the case of the anionic form (*Figure 3*), the overlap populations of the 1–6 and 1–2 bonds of the ring reduce almost to the single bond value, but the most important effect is the increase in the overlap populations of the 5–6 and 2–3 bonds of the ring, almost as if they were double bonds. The overlap population of the bond between the ring and the chain also increases and the unsaturated bonds delocalize.

There are large charge densities; the most important are those on C10 at the end of the olefin and on C4 at the end of the ring. It should also be mentioned that there is another large charge density on the end of the triple bond. This analysis yields the structure shown in *Figure 4*.

Analysis of molecule II results in a similar behaviour with both neutral and anionic forms but now the largest charge density of all the situations considered in this study is found; this is the charge on C10 at the end of the triple bond, which suggests that this would be an important reactive centre. Again a strong charge is found on the end of the ring and the aromaticity is destroyed.

This last result indicates that a good candidate has been found as a reactive species for an anionic polymerization pathway but the possibility of inhibition of the polymerization exists because of the rupture of aromaticity and the presence of a strong charge on the ring. The anionic molecule can also react by electrophilic substitution on the ring and this prevents an increase in the molecular weight of the polymer. The design of any synthetic process must take this into consideration.

A description has been given of how the two species can react by an anionic pathway to yield polymers. From a theoretical point of view they should react to form different products, since one reacts through its olefinic portion and the other through its acetylenic portion.

When a strong base, such as alkyl anion, attacks molecule I, molecular addition takes place at C10 and an anion is formed at C9. This leads to a certain degree of resonance stabilization in the triple bond, and this extends to the aromatic ring. In the case of molecule II, the addition of base at C10 results in the formation of a carbanion at C9 which conjugates with the double bond C7–C8 and with the aromatic ring. These reactions are shown in *Figure 5*.

Compound II has two conformational isomers (*cis* and *trans*). The particular geometry would change the structure of the formed polymer, and it is therefore important to determine which is the most stable isomer. *Table 2* shows the energetic results for both species.

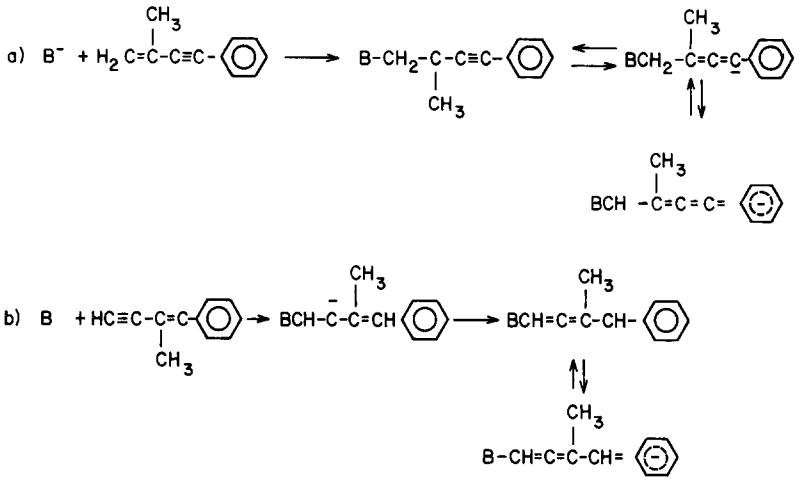

Figure 5 Nucleophilic attacks on compounds I and II

Table 2 Energetic results

Species	ΔH_f (kJ mol^{-1})	ΔU (eV)
cis-II	358.1698	−1543.333
trans-II	361.2510	−1543.301

The proportions of *trans* and *cis* isomers are 28.76% and 71.24%, respectively, as indicated by Boltzmann populations. It can be concluded that the *cis* isomer is the most stable, in agreement with calculations carried out on similar systems[6], and it must therefore be expected to dominate in a polymerization reaction. Experimental studies are currently in progress and the results will be reported in due course.

CONCLUSIONS

Calculations have been performed to show a possible reason for the inhibition of chain growth in the polymerization of enines. The best explanation is the large electron delocalization that arises when a reactive species (free radical or ion) is formed. This delocalization favours other reaction pathways.

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