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# A VIOLATION OF THE CHEMICAL NON-CROSSING RULE

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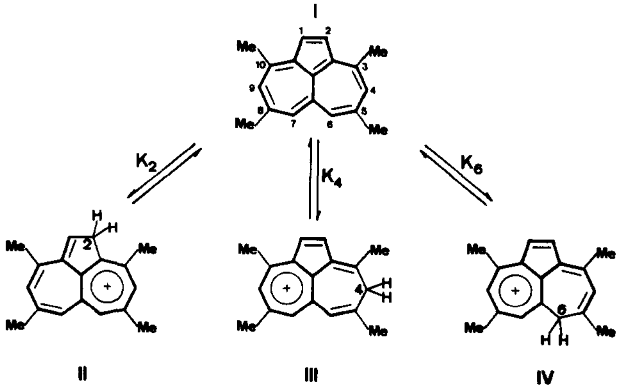
We wish to report that protonation of 3,5,8,10 - tetramethylaceheptylene[1] (I) in trifluoroaceticacid (TFAA) at -15°C. leads in a kinetically controlled step to the conjugate acid II, the solution of which is dark blue.



At room temperature its colour changes to red as the thermodynamically more stable conjugate acid III (or IV) is formed.

Fig. 1 shows the electronic spectra of these two species and the spectra which would be expected from PPP-calculations[2] for the cations II, III and IV. The agreement between experimental and theoretical values is satisfactory, particularly for the relative positions of the long wavelength absorptions of II and of III (or IV). However, a distinction between structure III and IV for the thermodynamically most stable cation on the basis of these calculations is not possible since the calculated spectra for both are quite similar.

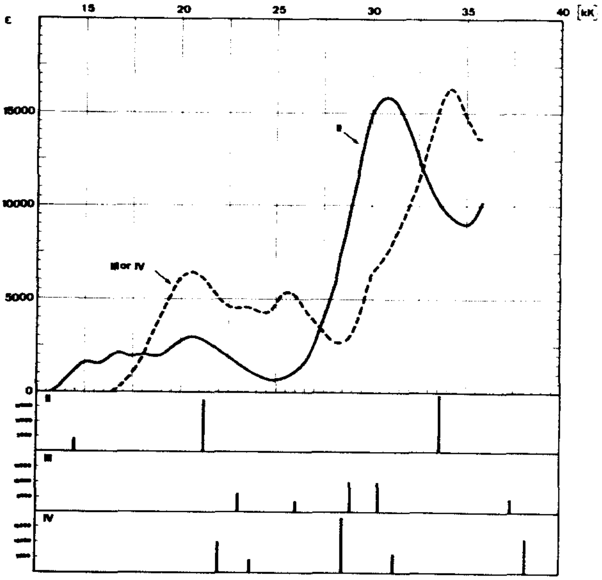


Fig. 1

The NMR spectrum of I in TFAA (reference TMS, room temperature) exhibits an AB-system at 7.53 ppm and 8.2o ppm. (integral 1H+1H), the coupling constant being 0.9 cps. This rules out structure II for the thermodynamically most stable cation. The methylengroup signal (integral 2H) appears at 4.06 ppm. Again, a destinction between III and IV on the basis of the NMR spectrum is not possible. Determination of the rate of hydrogen-deuterium exchange in deutero-TFAA at -15°C. shows clearly that substitution in position 1,2 is faster than in 4,6,7 and 9. (From NMR, amount exchanged after 14 minutes: pos. 1,2 : 50% ; pos. 4,9 : 9% ; pos. 6,7 : 2%).

Summarizing these results we find:

a) H/D-exchange (kinetic control):

1,2 faster than 4,9 faster than 6,7.

b) Stability of conjugate acid (thermodynamic control):

III (4,9) and/or IV (6,7) more stable than II (1,2)

These experimental facts can be rationalised only if the free energy profiles for the processes I→II and I→III (or IV) cross once (or an odd number of times) in the region of the reaction coordinate between the transition states and the products. (Fig. 2)

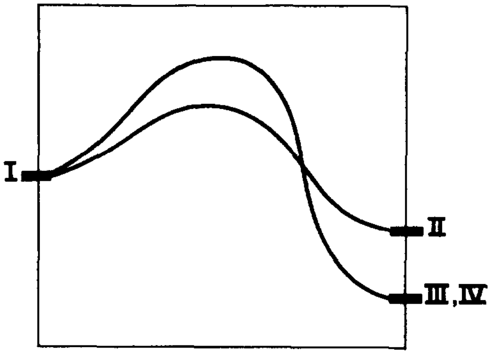


Fig. 2

R.D. Brown[3] has pointed out that such crossings might in fact occur for non-alternant hydrocarbons[4] if the two sequences of relative reactivity predicted from electron densities[4] $q_\mu$ and localisation energies[4] $L^+_\mu$ differ. This is never the case in alternant systems[4] in which the so called "chemical non crossing rule" is strictly observed.[3]

HMO-calculations for I yield the following values for $q_\mu$ and $L^+_\mu$:

$q_{1,2} = 1{,}125$ $L^+_{6,7} = 1{,}875$
$q_{6,7} = 1{,}092$ $L^+_{4,9} = 1{,}995$
$q_{4,9} = 1{,}088$ $L^+_{1,2} = 2{,}014$

(Similar results are obtained for the unsubstituted parent hydrocarbon aceheptylene, see ref. 5). If the relative heights of the transition states in the reaction profile are those predicted under the assumption that protonation of I is charge controlled, then the theoretical treatment is in agreement with the experimental results.

3,5,8,10-tetramethylaceheptylene (I) is (to our knowledge) the first example of a hydrocarbon for which the breakdown of the chemical non-crossing rule has been observed, in full agreement with the theoretical predictions of R.D. Brown.[3]

A full account of these investigations including results obtained from substitution reactions on I will be the subject of a full paper.[6]

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