

charge. This is associated with an increase in the double bond character in the latter bond at the expense of the former. Less expected is the N-N-N bending in the carbenium by 12° , showing some resemblance to butadiene in its S-trans conformation. An additional contribution to the observed in-plane bending of the N_3 array comes most probably from electrostatic repulsion between the neighboring hydrogen and the terminal nitrogen atom. These two atoms are positively charged (0.31 and 0.12 charge unit respectively) and the electrostatic repulsion between them amounts to $0.12 \cdot 0.31 \cdot 300 / 3.3 = 3.7$ kcal/mol.⁸ The presence of electrostatic interactions in the system is also evident from comparison of the two H-C-N angles in 2. The difference between these two angles is affected even to a larger extent by the repulsion from the central nitrogen atom.

Using the energies of the species in equation 1, it was found that the methyl cation stabilization energy of the azido group is 65.6 kcal/mol. This stabilization energy is compared in Figure 1 with that of other substituents whose methyl cation stabilization energies were calculated by Hopkinson and Lien⁹ using the same basis set.

The location of the azido group between OH and NH_2 , which are the known to be the best groups to stabilize an α carbenium ion in solution, is remarkable. Although crossover can and most probably will occur upon moving from the gas phase to solution due to the high polarizability of the azido group (which is more important in the gas phase),¹⁰ this result is unanticipated.

Finally, we have calculated the transition state for the decomposition of the azidocarbenium and confirmed its identity by force constant analysis. Its geometrical parameters are given in scheme 1. From its energy (-201.99999 au) and that of 2, one obtains an activation energy of 4.6 kcal/mol for its decomposition into N_2 and $H_2C=N^+$. This low activation barrier is highly surprising since, in spite of the general instability of azides, their derivatives have rather high activation energies for the expulsion of N_2 . These could be in the range of 30 to 45 kcal/mol for Me, Et and similar azido derivatives.¹¹ This difference of an order of magnitude in activation energy between for example methyl azide and 2, most probably stems from the difference in the N-N bonding in the two species. In the former, one of the resonance structures (see above) has a double bond character between these two atoms, whereas in 2 the lone pair on N_1 is delocalised onto the carbenium center and accordingly does not strengthen the N-N bond. This is evident from the comparison of C-N and N-N bond

lengths in 1 and 2 (scheme 1). Thus, it can be anticipated that higher stability of azidocarbenium with respect to a split of N_2 can be achieved by substituting the hydrogens in 2 by carbenium stabilizing groups, such as MeO, thereby enabling observations of azidocarbenium derivatives in solution.

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