Conformational Control in Substituted Allyl Radicals
by Nonbonded Attraction

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Allyl Radicals, INDO Calculations

Experimental investigations on the conformation equilibria 1 ↔ 2 of at C1 substituted allyl radicals are limited to X = alkyl. With increasing bulk of X(CH3 < Et < t-Bu) the less steric hindered anti-conformation 2 is preferred.

In the following communication we present theoretical evidence that in the case of X = F, CF3 the more steric hindered 1 should be more stable than 2, due to the mixing of dipolaric contributions into the ground state, as it has been previously recognized in halogen substituted allyl radicals.

According to the preceding canonical structures, charge separation in the 1,4-dipolaric structure of the anti-conformation is stronger than in the syn-conformation: hence the latter should be more stable. Model calculations within the INDO approximation for X = CH3, F and CF3 indeed confirm this point. Relative energies (in kcal per mole) for the cations and radicals are reported in Fig. 1.

For X = CH3 the energy difference for the different conformations 3 to 8 are in qualitative accord with the pioneering conclusions reached by BANK et al. and by HOFFMANN and OLOFSON. In the case of X = F, CF3 the INDO calculations suggest for the radicals a strong energy preference of 1 over 2. Since our calculations are not optimized and semi-empirical SCF-methods are open to criticism regarding their numerical accuracy, the energy differences between 1 and 2 may be overestimated. However the importance of dipolaric contributions to the ground state of 1 and 2 is supported by π-bond orders and π-charge densities, here reported for 7 and 8.

The preference of the more steric hindered syn-conformation 1 over the anti-conformation 2 for X = F, CF3 may also be considered as important for X = Cl, Br. However it is difficult to assess the importance of dipolaric contributions for the conformation control of these substituents, because...
the steric hindrance, which favours 2 over 1, increases in the opposite order.

Our predictions, which must await experimental verification are related to the anomeric effect, the preference for an axial over an equatorial position in C₁-electronegative substituted pyranose ring compounds. Experimental studies on the equilibrium $1 \rightleftharpoons 2$ for $X = Cl$ are under investigation.

4 a J. A. Popple and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, Inc., New York, N. Y. 1971; standard geometries have been used according to this reference;
5 b Previous theoretical studies on halogen substituted allyl systems have been reported. L. D. Kispert, C. U. Pittmann (Jr.), D. L. Allison, T. B. Patterson (Jr.), C. W. Gilbert (Jr.), C. F. Hains, and J. Prather, J. Amer. Chem. Soc. 94, 5979 [1972].
8 Both theoretical interpretations of the unusual stability of the syn-conformation of 1-methyl-allyl anion are related to each other, since molecular orbitals can be transformed to valence bond orbitals. C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. 35, 457 [1963].