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ANOMERIC EFFECT AND RADICAL STABILITY

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Summary : The anomeric effect is shown to play an important role in the stabilization of β-disubstituted radicals.

Primary radicals are normally expected to be less stable than secondary radicals (1). In the course of our ab initio study of fluorine atom addition on substituted ethylenes (2), it was found however that $NH_2CHF\dot{C}H_2$ 1 is more stable than the secondary isomer $NH_2\dot{C}H\ CH_2F$ 2 although the latter should be furthermore stabilized by a (small) capto-dative effect (3).

The ab initio calculations were performed with the Monstergauss program (4) using the split-valence 3-21 G basis set (5) at the U H F level.

A preliminary conformational analysis was performed on 1 and 2 and on the non-fluorinated parent radicals $NH_2CH_2\dot{C}H_2$ 3 and $NH_2\dot{C}HCH_3$ 4. First, rotation about the C-C bond indicated that in the preferred conformations the singly occupied orbital is *anti* relative to a C-H bond and *gauche* relative to the C-N and/or the C-F bond (s) : Fig.1

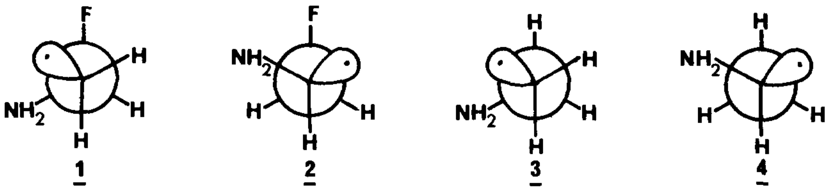


Fig 1

This is very similar to what was previously found for ethyl (6) and β-fluoro ethyl radicals (7). The conformational preference is rather small and the other staggered conformations are less than 2 kcal above 1-4. In addition the energy difference is strongly dependant on the basis set as it is discussed in (7).

Then rotation about the C-N bond was made on 1 and 3 and the results are shown in Fig.2. The geometries of the absolute minima 1a and 3a and of the maxima of lowest energy 1b and 3b were then fully optimized using a gradient method (8) so as the geometries of 2 and 4. The results are reported in Fig.3. We have also checked that rotation about the C-N bond in the other conformers of 1 does not give a conformation more stable than 1a.

For the β-fluororadical 1 the absolute minimum 1a corresponds to a conformation in which the lone pair of nitrogen is *anti* relative to the C-F bond and the maxima correspond to

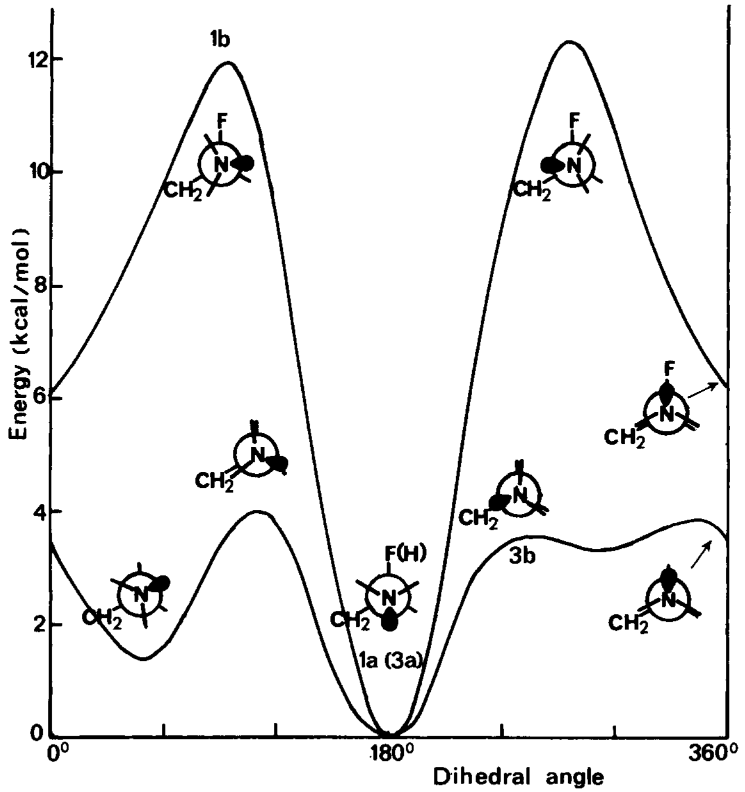


Fig.2 Rotation curves of $FNH_2CH\dot{C}H_2$ 1 and $NH_2CH_2\dot{C}H_2$ 3 about the C-N bond

conformations in which the lone pair is perpendicular to the C-F bond. For the parent radical 3, the minima correspond to staggered conformations and the maxima to eclipsed conformations.

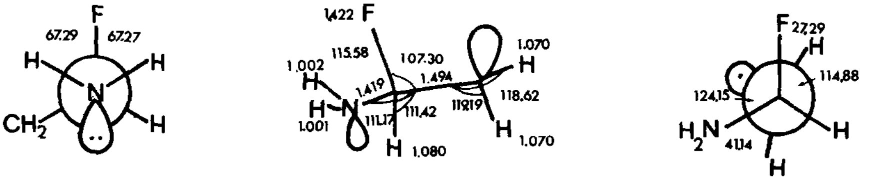
One can deduce from Fig.3 that

i) The primary radical 1 is more stable than its secondary isomer 2 by 4.3 kcal/mol whereas the parent radical 3 is less stable than 4 by 8.3 kcal/mol.

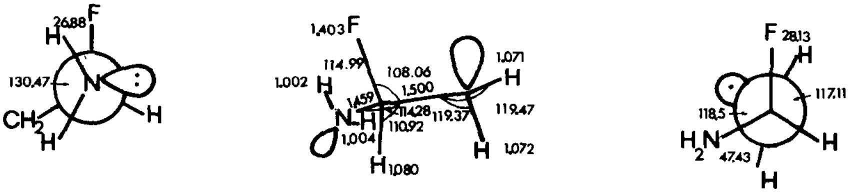
ii) The C-F bond is much longer in 1a than in 1b (1.422 versus 1.403). This shortening is accompanied by an important lengthening of the C-N bond (from 1.419 to 1.459).

iii) The rotation barrier about the C-N bond is 9.3 kcal/mol for 1 and only 2.6 kcal/mol for 3 (9).

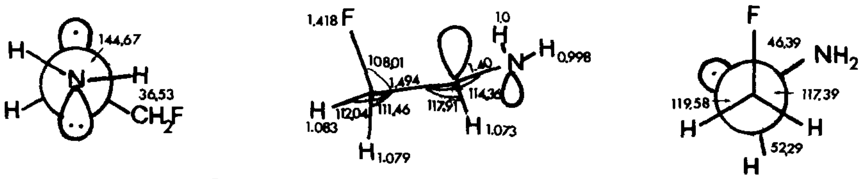
All these results, as also the anti position of the nitrogen lone pair relative to the C-F bond, are in agreement with an important anomeric effect (10) in 1.



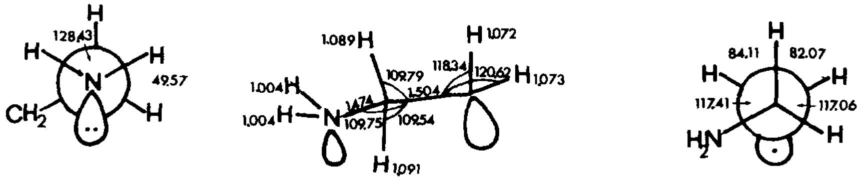
1a E = -231.20972



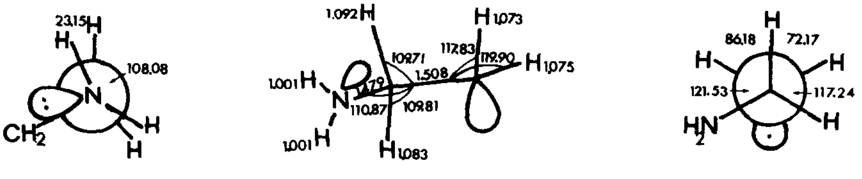
1b E = - 231.19498



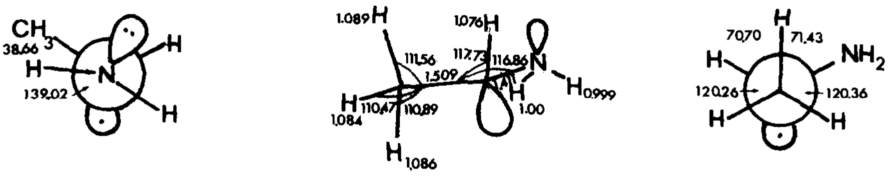
2 E = -231.20291



3a E = -132.87272



3b E = -132.86863



4 E = -132.88598

Fig.3 Distances in Å, angles in degrees. Energies in a.u (1 a.u = 627.5 kcal/mol)

The extrastabilization induced by this effect on the intrinsic stability (1b) of radical 1 can be estimated by the enthalpy ΔH = 15.6 kcal/mol of the following reaction (12) :

$$NH_2CHF\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow FCH_2\dot{C}H_2 + NH_2CH_2\dot{C}H_2$$

By comparison the extrastabilization induced by "captodative effect" in radical 2 is only 2.96 kcal/mol following the reaction :

$$FCH_2\dot{C}HNH_2 + CH_3\dot{C}H_2 \longrightarrow FCH_2\dot{C}H_2 + NH_2\dot{C}HCH_3$$

Therefore the anomeric effect seems to be of the same order of magnitude as the greatest calculated captodative effect (11) and thus appears to play an important role in the stabilization of radicals.

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