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Relation between Torsional Frequency and Ionization Potential of Substituent Atoms in 1-Fluoro-2-Haloethanes and Allyl Halides

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The potential barrier to internal rotation of 1-fluoro-2-haloethanes and allyl halides is plotted against the ionization potential of substituend atoms.

Lielmezs and Morgan [1] showed that a relation can be found by plotting the potential barrier to internal rotation of ethyl halides against the ionization energy of the substituent halogen atom. The present availability of 1-fluoro-2-haloethane [2, 3] and allyl halide [4] torsional frequency data (Table), has prompted us to reasses this previously established relation. If the torsional frequency of the axial bond found in these compound series, is plotted against the ionization potential of substituent atoms (Fig. 1), smooth curve (1-fluoro-2-haloethanes) and a linear relation (allyl halides) result. Fig. 1 thus generally confirms the already presented [1] behaviour of the restricted rotational barrier and the ionization potential of the substituent halogen atoms in ethyl halides. On the other hand, if we note the strong change of the ionic character of the C–X (X = F, Cl, Br, I) bond enforced by the changes in electronegativities upon substitution of the halogen atoms in the given series, the proposed relations (Fig. 1) seem indirectly to support Pauling's

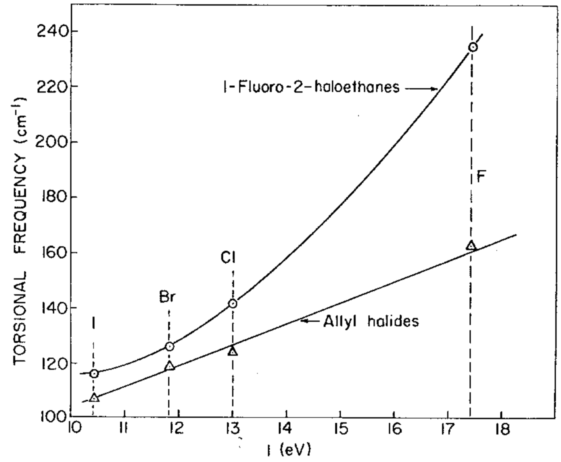

Fig. 1. Pronounced relation between the torsional frequency and the ionization potential of substituent atoms

[5] assertion that the potential barriers are not inherently the property of the axial bond itself (compare with Wilson, Ref. [6]) but rather result from the exchange interactions of electrons involved in the other bonds of the attached atoms as determined by the overlap between the parts of the adjacent bond orbitals that extend from each of these atoms towards the other. That is, the change in the nature of the hybrid character of the bond orbitals (C–X bond, $X = F$, Cl, Br, I) introduced by the first ionization potential shift (recall that first ionization potential is related to the electronegativity) of the substituent X-atoms, if considered to reflect the change of the interaction energy of the adjacent hybrid bonds (Pauling's statement), becomes the primary cause while the nature of the axial bond (Wilson's statement) becomes a secondary effect in interpreting the origin of potential barrier to the internal rotation.

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Table. *Summary of data*

Compound	Torsional frequency (cm^{-1})	Ionization energy substituent atom (Ref. [7]) (eV)
$C_2H_4F_2$	235 (Ref. [2])	17.42
C_2H_4FCl	142 (Ref. [3])	13.01
C_2H_4FBr	126 (Ref. [3])	11.84
C_2H_4FI	116 (Ref. [3])	10.44
C_3H_5F	163 (Ref. [4])	17.42
C_3H_5Cl	124 (Ref. [4])	13.01
C_3H_5Br	119 (Ref. [4])	11.84
C_3H_5I	107 (Ref. [4])	10.44

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