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RELATIONS BETWEEN TORSIONAL FREQUENCY AND IONIZATION POTENTIAL IN HALOPROPANES AND ALLYL HALIDES

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ABSTRACT

It is shown that linear relation $\tau = k + m\Lambda$ exists between the fractional torsional torsional frequency $\tau[\tau = (\nu_P - \nu_X)/\nu_P$; where P represents n-propane or propene, respectively, and $X = P$, F, Cl, Br and I] and the fractional ionization potential $\Lambda[\Lambda = (\Lambda_P^* - \Lambda_X^*)/\Lambda_P^*]$ for the same structural groups of normal and iso-halogenated propanes and allyl halides.

INTRODUCTION

Earlier Lielmezs and Morgan[1] and Lielmezs and Hagan[2] have shown that a relation may be found by plotting the potential barrier to internal rotation in the case of ethyl halides, and the torsional frequency for 1-fluoro-2-haloethanes and allyl halides against the first ionization potential of the substituent halogen atoms. Noting the strong change of the ionic character of the C–X (X = F, Cl, Br, I) bond when the halogen atoms are substituted in the given structural series; these observations[1,2] led to the support of Pauling's[3] assertion that the potential barriers are not inherently the property of the axial bond itself (compare with Wilson[4]) but result rather 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. This, then seemed to indicate that the change in the nature of the hybrid character of the bond orbitals introduced by the first ionization potential shift of the substituent X-atoms (X = F, Cl, Br, I); if considered to reflect the change of the interaction energy of the adjacent hybrid bonds (Pauling's approach[3]), becomes the primary cause while the nature of the axial bond (Wilson's statement[4]) appears to become a secondary effect in the overall assessment of the origin of potential barrier to the internal rotation.

EXPERIMENTAL

The presented findings of this work while reaffirming this observation additionally yield useful empirical correlation between the torsional frequency and the

TABLE 1

SUMMARY OF DATA USED

Compound	*Ionization potential*			*Torsional frequency*[a]			$\tau = \frac{\nu_P - \nu_X}{\nu_P}$	$\Lambda = \frac{\Lambda_P^* - \Lambda_X^*}{\Lambda_P^*}$
	eV	*cal mol⁻¹ × 10⁵*	*Ref.*	*cm⁻¹*	*cal mol⁻¹*	*Ref.*		
n-Propane	11.07	2.55296	5	215[b]	614.71	6	0	0
skew-1-Fluoropropane				139[c]	397.41	7	0.35349	
skew-1-Chloropropane	10.87	2.49531	5	132[c]	377.40	7	0.38605	0.2258
skew-1-Bromopropane	10.18	2.34772	5	127[c]	363.11	7	0.40930	0.08039
skew-1-Iodopropane	9.26	2.13554	5	120[c,d]	343.10		0.44186	0.16350
i-Butane	10.57	2.43765	5	256[e]	731.93	8	0	0
2-Fluoropropane								
2-Chloropropane	10.78	2.48608	5	259[f]	740.51	9	−0.20465	0.026197
							(−0.01172)[g]	(−0.01987)[g]
2-Bromopropane	10.075	2.32350	5	256[f]	731.93	9	−0.19069	0.08980
							(0.00000)[g]	(0.4683)[g]
2-Iodopropane	9.17	2.11479	5	251[f]	717.63	9	−0.16743[g]	0.17163[g]
							(0.01954)	(0.13245)
Propene	9.73	2.24393	10	188	537.51	11	0	0
cis-3-Fluoropropene	17.15[h]	3.95513	12	163	466.03	13	0.13298	−0.76259
cis-3-Chloropropene	11.21[h]	2.58525	12	124	354.53	13	0.34042	−0.15211
cis-3-Bromopropene	10.43[h]	2.40537	12	119	340.23	13	0.36703	−0.07195
cis-3-Iodopropene	9.30[h]	2.14477	12	107	305.92	13	0.43086	0.04419

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[a] All torsional frequency values are given for the gaseous state unless stated otherwise. [b] This torsional frequency is taken as an average frequency between the in and out of phase torsion of the methyl group in liquid state. This is comparable with the torsional frequency treatment of 2-halopropanes (see footnote [f], this Table; also ref. 9). [c] This is skeletal torsion. [d] To retain the selfconsistency among the torsional frequency assignment for *skew*-1-halopropanes, value of 120 cm⁻¹ is used. The value of 127 cm⁻¹ as suggested by Radcliffe and Wood[7] is thought to be too high. [e] This is E–torsional mode. [f] This frequency value represents an average between in and out of phase values[9]. [g] These listed τ and Λ values for 2-halopropanes refer to isobutane (CH_3 as the reference state instead of n-propane). In this case one hydrogen atom is exchanged for one CH_3-group. [h] These are lone pair orbital (substituent is halogen atom) ionization potential values[12].

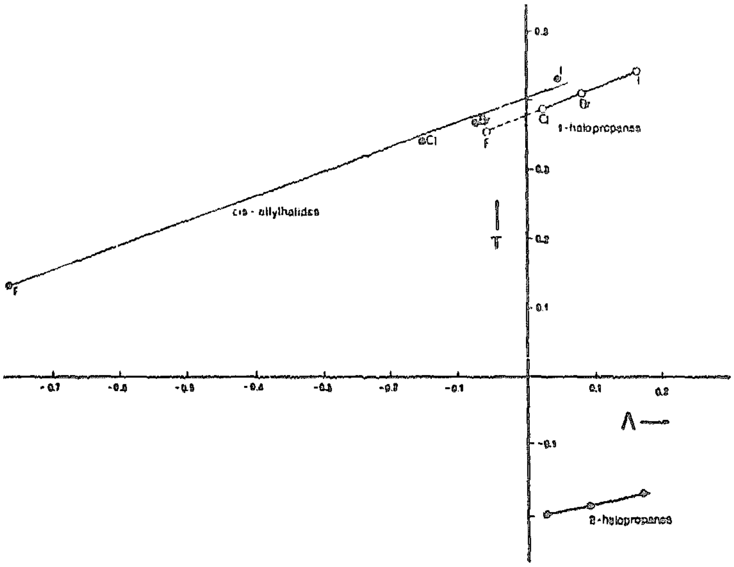

Fig. 1. τ–Λ relation (eqn (3)). Dashed line (— — —) indicates the predicted τ–Λ coordinates for *skew*-1-fluoropropane.

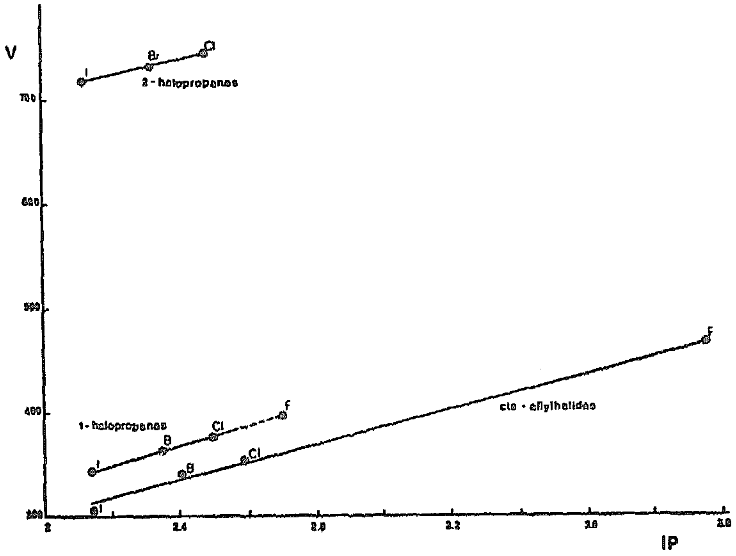

Fig. 2. Direct relation between the torsional frequency, ν in cal mol^{-1} and the molecular ionization potential, I.P. in calmol$^{-1} \times 10^5$. Dashed line (— — —) yield the predicted ν and I.P. values for *skew*-1-fluoropropane.

molecular ionization potential for the same structural groups of normal and isohalogenated propanes and allyl halides (Table 1, Figs. 1 and 2 and eqn (3)).

If we introduce the following set of dimensionless coordinates:

$$\tau = \frac{\nu_P - \nu_X}{\nu_P} \tag{1}$$

and

$$\Lambda = \frac{\Lambda_P^* - \Lambda_X^*}{\Lambda_P^*} \tag{2}$$

where: ν is the torsional frequency, cal mol^{-1};

Λ is the molecular ionization potential cal $\text{mol}^{-1} \times 10^5$;

P refers to n-propane or propene, depending on the used reference state;

X = F, Cl, Br, I; the substituent halogen atoms in the given hydrocarbon series;

then it is possible to write a linear relation between τ and Λ; i.e.

$$\tau = k + m\Lambda \tag{3}$$

such that k and m are characteristic constants (intercept and slope) for each of the given halogenated hydrocarbon series.

Using the data as found in Tables 1 and 2* and Figs. 1 and 2**; the constant k and m values were determined as follows***—for *skew*-1-halopropanes: $k = 0.3770$; $m = 0.4020$; for 2-halopropanes: $k = 0.2104$; $m = 0.2195$; and for *cis*-3-halopropenes: $k = 0.4018$; $m = 0.3566$. Although only up to 4 data point pairs (Table 1) were used; and the so presented relations (eqn (3)) would appear to be weak correlations; nevertheless for each of the obtained lines the correlation coefficient§ was $r = 1.0000$.

Figures 1 and 2 were obtained using the data listed in Table 1. Figure 1 shows that the already introduced dimensionless coordinates (eqns (1) and (2)); the fractional frequency τ and the fractional molecular ionization potential Λ, when referred to n-propane (for *skew*-1-halopropane and 2-halopropane series) and propene (for allyl halides) as the reference states, correlate into a linear relation (eqn (3)).

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*See also refs. 5–16.

**As Fig. 2 indicates similar relations (eqn (3)) could be established directly between the torsional frequency and the ionization potential. However, we preferred to use the dimensionless form (eqns (1) and (2)) of the involved parameters referring to "parent" compounds.

***If we choose for 2-halopropanes iso-butane (instead of n-propane) as the "parent" compound, then the used experimental data (Table 1, Fig. 3) yield: $k = -0.0082$; $m = 0.1757$; $r = 1.0000$.

§The correlation coefficient r is defined as:

$$r = \frac{\sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{n} (X_i - \bar{X})^2 \sum (Y_i - \bar{Y})^2}}; \text{ where } \bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} \text{ and } \bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n}$$

In terms of the fractional coordinates chosen with respect to "parent" molecule (n-propane and propene) with known configurational and spectral properties; this change of torsional frequency value versus the corresponding change of the molecular ionization potential may be either positive or negative (Table 1, Fig. 1) depending on the initial molecular structure and the nature of the compound bonding of the chosen "parent" molecule. This is brought out for the case of 2-halopropanes when n-propane and iso-butane have been chosen as two possible "parent" molecules* (Table 1, Fig. 3). Within each of the given structural series (*skew*-1-halopropanes, 2-halopropanes, allyl halides) as expected[5,10,12] the ionization potential decreases with the increasing size of substituent halogen atom ($X = F$, Cl, Br, I). This lowering of the ionization potential of the molecule as the halogen atom substituents pass from fluoride to iodide (Tables 1 and 2) is associated with a simultaneous decrease of the respective torsional frequency values**.

This correlating aspect of the substituent halogen atoms additional to Fig. 1 is found in Fig. 2 where torsional frequency is plotted against the corresponding ionization potential. Considering that the molecular ionization potential describes the energy relations characteristic of the configurational and spectral property changes of the molecule, the above observation endorses the previously made statement that the primary cause of the internal rotation is found in the interaction energy of the adjacent hybrid bonds[3]. Then the nature of the axial bond[4] becomes a secondary effect alone not sufficient to explain the origin of the barrier to the internal rotation. Therefore a systematic classification of molecular ionization potential sets is needed to assess the particular behavior of torsional frequencies within any compound series.

DISCUSSION

As seen from the photoelectron spectroscopy[5,10,12,17–20] the theoretical analysis of the photoelectron spectra yields very accurate information regarding the energy relations of the specific molecular orbitals and the vibrational structure found in the energy bands. Indeed the variations of ionization potential for any distinct energy level can be correlated along the structurally related compound series[5,10,12,18,19]. Analyzing the data displayed in Table 2, we already noted that the adiabatic ionization potential did decrease slowly with the increased chain-length. The same trend is also observed in mono-olefins. In this case the ionization potential of the olefinic π-electron

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*Comparing the structures of these "parent" molecules (Fig. 3) we see that either the H-atom (in case of n-propane) or CH_3-group (for iso-butane) can be substituted to form the issuing 2-halopropane series. Of course, this changes the initial reference torsional frequency and ionization potential values (Tables 1 and 2) which in turn yield alternate relations on the τ–A diagram (Table 1, Fig. 1).

**Careful scrutiny of data found in Table 2 reveal that for instance, for n-paraffins the adiabatic ionization potential values decrease with increasing chain-length (increased molecular size). On the other hand, these data also reveal that as the ionization potential values decrease; the available torsional frequency values as shown separately for solid and gas states (torsional frequency values overlap for n-butane) decrease.

TABLE 2

IONIZATION POTENTIALS[a] AND TORSIONAL FREQUENCIES[b] OF SOME MOLECULES

Compound	*Ionization potential (eV)*	*Ref.*	*Torsional frequency (cm⁻¹)*	*Ref.*	*Compound*	*Ionization potential (eV)*	*Ref.*	*Torsional frequency (cm⁻¹)*	*Ref.*
Methane	12.98	5			Methyliodide	9.54	5		
Ethane	11.65	5	289	14	Ethyliodide	9.33	5		
Propane	11.07	5	215[c]	6	i-Iodopropane	9.26	5	120[d]	9
n-Butane	10.63	5	197(254)[e]	15(16)	2-Iodopropane	9.17	5	251	
i-Butane	10.57	5	256	8	i-Iodobutane	9.21	5		
n-Pentane	10.32	5	(240)[e]	(16)	i-Iodopentane	9.19	5		
n-Hexane	10.18	5	(240)[e]	(16)	F_2	15.7	5		
n-Heptane	10.08	5	(240)[e,f]	(16)	Ethene	10.52	10		
Cl_2	11.48	5			Propene	9.73	10	188	11
Methylchloride	11.28	5			1-Butene	9.58	10		
Dichloromethane	11.35	5			1-Pentene	9.50	10		
Trichloromethane	11.42	5			2-Methylpropene	9.23	10		
Tetrachloromethane	11.47	5			2-Butene (*cis*)	9.13	10		
Ethylchloride	10.98	5	251.5	14	2-Butene (*trans*)	9.13	10		
1,2-Dichloroethane	11.12	5	288	14	Vinylchloride	9.995	5		
1-Chloropropane	10.82	5	132	7	Vinylbromide	9.80	5		
2-Chloropropane	10.78	5	259	9	1-Bromopropene	9.30	5		

TABLE 2 (*continued*)

Compound	*Ionization potential (eV)*	*Ref.*	*Torsional frequency (cm⁻¹)*	*Ref.*	*Compound*	*Ionization potential (eV)*	*Ref.*	*Torsional frequency (cm⁻¹)*	*Ref.*
1-Chlorobutane	10.65	5			$CH_3CF{=}CH_2$			191	11
1-Chlorobutane	10.65	5			CH_3CCl_3			305	11
Br_2	10.55	5			CH_3CH_2F			243	14
Methylbromide	10.53	5			CH_3CHF_2			222	14
Dibromomethane	10.49	5			CH_3CF_3			234	14
Tribromomethane	10.51	5			$CFCl_3$	11.77	5		
Ethylbromide	10.29	5			CF_2Cl_2	12.31	5		
1-Bromopropane	10.18	5	127	7	CF_3Cl	12.91	5		
1-Bromopropane	10.075	5	256	9					
1-Bromobutane	10.13	5							
1-Bromopentane	10.10	5							
I_2	9.28	5							

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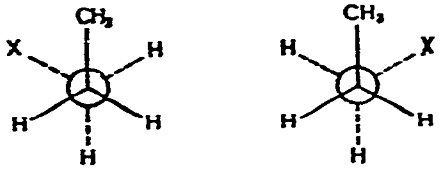
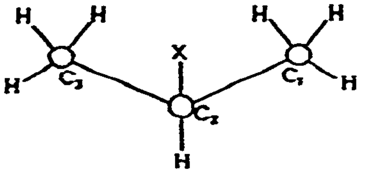
[a] The listed ionization potentials if not otherwise stated, are adiabatic ionization potentials. [b] Torsional frequencies, if not otherwise stated, are given for the gaseous state. [c] Compare with Table 1, footnote [b]. [d] Estimated, this work; compare also with Table 1, footnotes [c,d]. [e] These are solid state methyl end-group torsional frequencies obtained by means of neutron inelastic scattering[16]. Although the last 3 values are given as constant (240 cm⁻¹), it is felt that they should slowly decrease as the chain-length increases, and that therefore this constancy should be subject to further experimental scrutiny. [f] Since we did not have available ionization potential value for n-octane, we did not list this compound in the Table. However, the solid state methyl and group torsional frequency assignment has been made[16] as 237 cm⁻¹. This once more asserts (footnote [e]) that torsional frequencies should decrease with increased paraffin chain-length the same way as the value of the corresponding ionization potential decreases.

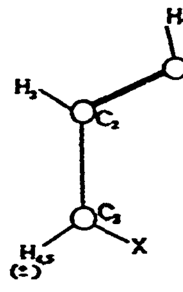
decreases as the size of the molecule increases. In the case of alkyl halides the behavioral pattern of data series seems to be consistent with the suggestions made by Mulliken[21] that the most loosely bound electron for this type of compound series is one of the non-bonding np-orbitals localized in the halogen atom. As shown by Watanabe et al.[5] the variations of ionization potential follow this reasoning (see Table 2); for instance, if Cl is exchanged with the H-atom in CH_4, the ionization potential will decrease from 12.98 to 11.28 eV. The difference in ionization potentials between Cl_2 and CH_3Cl is 0.2 eV, yet the ionization potential value of CCl_4 is about the same as that of Cl_2 indicating that the non-bonding electron of the Cl-atom in Cl_4 is similar to that of Cl_2. Hence, any further substitution of Cl-atoms in CH_3Cl will increase the ionization potential value up to that of CCl_4. Similar ionization potential decrease[5] is found in dichloroethane and dichloropropane relative to ethyl chloride and chloropropane with subsequent increase in ionization potential if we substitute additional Cl-atoms. The same can be also said of other halogenated (F, Br, I) hydrocarbons[5,10,18]. Clearly, the ionization potential values and the configurational and spectral properties of the "parent" molecular framework are affected by the substituent atom. In view of the presented data (Tables 1 and 2; Figs. 1–3) the



(a) 1-halopropanes : 2 equivalent skew forms



(b) 2-halopropanes



(c) cis-1-halopropenes

(± indicates that H-atom lies above and below central plane of the molecule)

Fig. 3. Molecular configurations (not to scale) of 1-halopropanes, 2-halopropanes and *cis*-1-halopropenes.

question arises: do indeed the torsional frequencies (structural and spectral property) follow the same sequential pattern of changes as displayed by the variations found in ionization potential values upon introduction of substituent atoms in the framework of the "parent" molecule. This query in principle could be answered by the many currently used molecular orbital calculation methods used to study the behavior of configurational and spectral characteristics of molecules[5,10,12,17–21].

Indeed, if we compare the magnitudes of energies involved (torsional frequency as compared to the energy of the ionization potential), it may well be conceived that the torsional frequency changes, characterizing the variation of the energy found in the rotational barrier to the internal rotation, may form a measure of regularly occurring second-order energy perturbations when taken with respect to the distribution of exchange energy of delocalized electrons found over the molecule and given as the ionization potential.

Indirectly these behavioral patterns may be observed through the study of the established empirical relations between the torsional frequencies and molecular ionization potentials (for instance τ–Λ diagrams, this work) along the structurally similar molecules. When smooth connections of this type can be established confidence in the used torsional frequency and the photoelectron spectra (ionization potential) data is increased and further relations between geometric and energetic parameters describing the internal rotational barrier may be deduced.

In this work we listed τ–Λ (or torsional frequency–ionization potential) relations for *skew*-1-halopropanes, 2-halopropanes and *cis*-3-halopropenes.

Earlier we have indicated similar relations for alkyl halides and 1-fluoro-2-haloethanes[1,2]. Systematic availability of photoelectron spectral data and molecular ionization potentials are needed to study further the behavior of internal rotational barrier.

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