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Semi-empirical Expression for Diagonal Torsional Force Constants in Halogenated Propanes and Ethanes

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A very simple formula for the diagonal elements within the torsional part of the valence force field in halogenated propanes and ethanes has been proposed. It has been shown, that to a good approximation, the torsional force constant of an ethane-like fragment may be expressed as a sum of six contributions, corresponding to the second order derivatives of the six *gauche* energy interactions.

If the Y,Z atoms of an ethane-like fragment Y′YY″C-CZ′ZZ″ are in nearly staggered positions, then the torsion-angle dependent part of the potential energy (V) is approximately equal to the sum of six Y...Z *gauche* interactions. (Each one of the *gauche* energy terms includes atom-atom interactions as well as bond-bond interactions.)

The torsional force constant ($F\phi(C-C)=\partial^2V/\partial\phi^2$) is also expected to be equal to a sum of six contributions, corresponding to the second-order derivatives of the six *gauche* energy terms.

If we consider a propane derivative $R_1-YCY'-R_3$, with Y(Y′) equal to H or X (halogen) and R(CH_3, CH_2X, CHX_2, CX_3), we need *five* different partial force constants (F^*_{HH}, F^*_{CH}, F^*_{XH}, F^*_{XX}, F^*_{CX}) in order to express the total diagonal force constant ($F\phi$).

$$F\phi=N_{HH}\ \ F^*_{HH}+N_{CH}\ \ F_{CH}^*+N_{XH}\ \ F^*_{XH}+N_{XX}\ \ F^*_{XX}+N_{CX}\ \ F^*_{CX}$$

N is the number of *gauche* interactions of the types indicated ($\sum N=6$).

The formula of an ethane derivative R_1-R_2 (R: CH_3, CH_2X, CHX_2, CX_3) has only *three* different terms ($N_{CH}=N_{CX}=0$).

For $H_3C-CHX-CH_3$ the formula would be $F\phi(C_1-C_2)=F\phi(C_2-C_3)=2F^*_{HH}+2F^*_{CH}+2F^*_{XH}$, and for XH_2C-CH_2X we get $F\phi$(*anti*) $=2F^*_{HH}+4F^*_{XH}$ and $F\phi$ (*gauche*) $=3F^*_{HH}+2F^*_{XH}+F^*_{XX}$.

The F^* values may be adjusted in order to reproduce the "experimental" force constants of several molecules. Depending on the number and types of molecules included one will get different sets of F^* values. The set of F^* values presented here reproduce the experimental force constants of 16 related molecules. The average deviation is *ca.* 10 %, as shown in Table 1. The estimated error limits for most of the experimental values in Table 1 are *larger than* 10 %.

In adjusting the F^* values, halogenated (X) propanes with parallel C–X bonds on the same side of the CCC skeleton were not included.

The F^* values are: 0.013(HH), 0.017(CH), 0.032(ClH), 0.100(ClCl), and 0.110(CCl) in units of mdyn Å (rad)$^{-2}$. The halogenes F, Br, and I may be included in this list. However, the amount of experimental information at present is not as abundant as for chlorinated hydrocarbons. (Useful values for F^*_{CBr} and F^*_{BrBr} are 0.130 and 0.160, respectively, with $F^*_{BrH}\simeq F^*_{ClH}$). The list of partial force constants could be extended in order to include molecules containing different kinds of halogenes. (F^*_{ClBr}, F^*_{ClF}, F^*_{BrF} *etc.*)

Certain limitations of the present model are known for some heavily chlorinated propanes. In the two molecules (X=Cl), $X_2HC-CX_2-CHX_2$(*P6*) and $X_3C-CX_2-CX_3$ (*P8*), the experimental values of the diagonal torsional force constants are 0.86 and 0.36 mdyn Å

Table 1. Diagonal torsional force constants (F_ϕ) for chlorinated ethanes and propanes. $F_\phi(\text{calc.}) = 0.013\,N_{\text{HH}} + 0.017\,N_{\text{CH}} + 0.032\,N_{\text{XH}} + 0.100\,N_{\text{XX}} + 0.110\,N_{\text{CX}}$, in mdyn Å (rad)$^{-2}$.

Molecule (X = Cl)	F_ϕ-value		Conformation	Ref.
	exp.	calc.		
$X_3C-CX_2-CHX_2$(G)	0.54[a]	0.50[a]	G: C_1 symmetry	12
$X_2HC-CX_2-CH_3$(A)	0.41[b]	0.48	A: C_s symmetry	11
X_3C-CHX_2	0.44[c]	0.46		9
$X_2HC-CHX-CHX_2$	0.43[a]	0.35[a]	GG(ag)	10
X_3C-CH_2X	0.31[d]	0.33[d]		9
$X_3C-CH_2-CHX_2$(G)	0.32[a]	0.30[a]	G:C_1 symmetry	8
$XH_2C-CHX-CH_2X$	0.24[e]	0.23[e]	mixture[e]	7
XH_2C-CH_2X(G)	0.25	0.19	G: *gauche*	4
$XH_2C-CH_2-CH_2X$	0.17[f]	0.18[f]	mixture[f]	6
$H_3C-CX_2-CH_3$	0.13	0.16		5
XH_2C-CH_2X(A)	0.17	0.15	A: anti	4
X_2HC-CH_3	0.14	0.15		3
$H_3C-CHX-CH_3$	0.13	0.12		2
XH_2C-CH_3	0.12	0.12		1
$H_3C-CH_2-CH_3$	0.078	0.086		1
H_3C-CH_3	0.077	0.078		1

[a] Average of $F_\phi(C_1-C_2)$ and $F_\phi(C_2-C_3)$. [b] Estimated from $V^0 = 12.9$ kcal/mol and $F_\phi = \frac{9}{2} V_0$. [c] Estimated from $V_0 = 14.2$ kcal/mol. [d] Estimated from $V_0 = 10.0$ kcal/mol. [e] Weighted average of $F_\phi(C_1-C_2$ and $F_\phi(C_2-C_3)$ for three conformers: 69 % *GG*(*ag*), 26 % *AG*(*ga*), and 5 % *AG*(*gg*). [f] Weighted average of $F_\phi(C_1-C_2)$ and $F_\phi(C_2-C_3)$ for three conformers: 73 % *GG*, 24 % *AG* and 3 % *AA*.

(rad)$^{-2}$, respectively, as determined by electron-diffraction works.[13,14] Although the experimental estimates are quite uncertain (*ca.* 30 %), the values calculated by the present formula, 0.46 (*P6*) and 0.62 (*P8*), are significantly different from the experimental ones. A rather small value of F_ϕ for *P8* was expected. The stable conformer of *P8* has C_{2v} symmetry [14] corresponding to parallel (1:3) X···X interactions on both sides of the CCC skeleton. The most stable conformer (*GG*) of *P6* has C_2 symmetry [13] without parallel (1:3) X···X interactions. Therefore the experimental estimates, $F_\phi(P6)$ $F_\phi(P8)$, are reasonable. It is, however, surprising that the calculated F_ϕ values for $X_3C-CH_2-CHX_2$ and $X_3C-CX_2-CHX_2$ agree (Table 1) with the experimental ones. The most stable conformer of both molecules possesses one parallel (1:3) X···X interaction.

The limitations pointed out here should be kept in mind. However, for halogenated propanes and related molecules, the most stable conformers usually do *not* possess parallel (1:3) X···X interactions. It is therefore suggested that the simple formula for F_ϕ is a useful approximation for molecules of the type Y′YY″C−CZZ′R with Y,Z = H or X (halogen) and R = H,X, $-CH_3$, $-CH_2X$, $-CHX_2$, or $-CX_3$.

In order to calculate vibrational frequencies, mean amplitudes of vibration, and related quantities for propanes, the torsional interaction force constant ($F_{\phi\phi'} = \partial^2 V/\partial\phi\partial\phi'$) ought to be included in the force field. However, reliable mean amplitudes of vibration may usually be calculated assuming $F_{\phi\phi'} = 0$. (See Refs. 6−8, 10, 12−14). Moreover, the $F_{\phi\phi'}$ values for most halogenated propanes are probably much smaller than the diagonal term (F_ϕ). But a conformer possessing parallel (1:3) X···X interactions may have a $F_{\phi\phi'}$, value which is in magnitude comparable to the F_ϕ value, and most probably negative.[12,14]

Conformational differences in torsional force constants may be estimated from the simple formula suggested here. For the chlorinated propanes shown in Table 2 the experimental values of the torsional force constants were not available. The calculated values for the heavily chlorinated compounds in Table 2 may deviate as much as 20−30 % from the experimental value, but the *average* deviation of all F_ϕ values is expected to be *ca.* 10 %.

Table 2. Diagonal torsional force constants (F_ϕ) predicted for chlorinated propanes ($X=Cl$). (Conformers possessing parallel $C-X$ bonds on the same side of the CCC skeleton were not included.) $F_\phi = 0.013N_{HH} + 0.017N_{CH} + 0.032N_{XH} + 0.100N_{XX} + 0.110N_{CX}$

Propane $(C_1-C_2-C_3)$	Conformation	F_ϕ in mdyn Å (rad)$^{-2}$ (C_1-C_2)	 (C_2-C_3)
$XH_2C-CH_2-CH_3$	$XC-C-C$	0.14	0.086
	$\overset{X}{C}-C-C$	0.20	0.086
$XH_2C-CHX-CH_3$	$XC-\overset{X}{C}-C$	0.21	0.12
	$\overset{X}{C}-\overset{X}{C}-C$	0.27	0.12
	$\underset{X}{C}-\overset{X}{C}-C$	0.24	0.12
$X_2HC-CH_2-CH_3$	$\overset{X}{\underset{X}{C}}-C-C$	0.31	0.086
	$X\underset{X}{C}-C-C$	0.24	0.086
$X_3C-CH_2-CH_3$	$X\overset{X}{\underset{X}{C}}-C-C$	0.35	0.086
$X_2HC-CH_2-CH_2X$	$X\underset{X}{C}-C-\overset{X}{C}$	0.24	0.20
	$\overset{X}{\underset{X}{C}}-C-CX$	0.31	0.14
	$X\overset{X}{C}-C-CX$	0.24	0.14
$X_2C-CHX-CH_3$	$X\underset{X}{C}-\overset{X}{C}-C$	0.32	0.12
	$X\overset{X}{C}-\overset{X}{C}-C$	0.37	0.12
	$\overset{X}{\underset{X}{C}}-\overset{X}{C}-C$	0.40	0.12
$XH_2C-CX_2-CH_3$	$XC-\overset{X}{\underset{X}{C}}-C$	0.30	0.16
	$\underset{X}{C}-\overset{X}{\underset{X}{C}}-C$	0.32	0.16
$X_3C-CHX-CH_3$	$X\overset{X}{\underset{X}{C}}-\overset{X}{C}-C$	0.48	0.12

Table 2. Continued.

$X_2HC-CHX-CH_2X$	X X C−C−CX X	0.40	0.21
	X XC−C−CX X	0.32	0.21
	X X XC−C−C X	0.32	0.27
	X X XC−C−CX	0.37	0.21
	X X XC−C−C X	0.37	0.24
$XH_2C-CX_2-CH_2X$	X XC−C−CX X	0.30	0.30
	X X C−C−C X X	0.32	0.32
	X X XC−C−C X	0.30	0.32
$X_2HC-CH_2-CHX_2$	X XC−C−CX X	0.24	0.24
$X_3C-CH_2-CH_2X$	X XC−C−CX X	0.35	0.14
$X_3C-CX_2-CH_3$	X X XC−C−C X X	0.62	0.16
$X_2HC-CX_2-CH_2X$	X X C−C−CX X X	0.48	0.30
	X XC−C−CX X X	0.46	0.30
	X X XC−C−C X X	0.46	0.32
$X_3C-CHX-CH_2X$	X XC−C−CX X X	0.48	0.21
$X_3C-CX_2-CH_2X$	X X XC−C−CX X X	0.62	0.30

Using the partial force constants F^*_{BrH} (0.032), F^*_{CBr}(0.130), F^*_{BrBr}(0.160), and the values of F^*_{HH} and F^*_{CH} already given, the F_ϕ values for brominated ethanes and propanes may be estimated, but with less confidence than for the chlorinated compounds.

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