PAIR INTERACTIONS OF ATOMS AND PROPERTIES OF X-SUBSTITUTED METHANES AND THEIR RADICALS

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Abstract

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PAIR INTERACTIONS OF ATOMS AND PROPERTIES OF X-SUBSTITUTED METHANES AND THEIR RADICALS

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Let us consider X-substituted methanes with the general formula $\mathrm{CH}_{k X} l$, where X is some monovalent substituent consisting of an atom or group of atoms ($\mathrm{X} = \mathrm{Cl}, \mathrm{Br}, \mathrm{CH}_3, \ldots$); k is the number of H atoms; l is the number of X substituents in the molecule ($k = 4 - l,\ l = 0, 1, 2, 3, 4$). Denote by $E_{\mathrm{CH}_{k X} l}$ the energies (heats of formation from free atoms) of the molecules $\mathrm{CH}_{k X} l$. Further denote by ξ_{CH} and ξ_{CX} the energies of pair interactions of directly bonded C and H atoms and of C and X atoms* respectively, and by $\eta_{\mathrm{HH}}, \eta_{\mathrm{HX}}$, and η_{XX} the energies of pair interactions, respectively, of H and H atoms, H and X atoms, and X and X atoms separated by one C atom in the chain of the molecule $\mathrm{CH}_{k X} l$. Then, assuming the possibility of representing the energy of the molecule as the sum of the energies of pair interactions of atoms, and considering each pair interaction of a given type (for example, η_{HX}) to be the same in all molecules, for the energies of molecules of X-substituted methanes we shall have

$$E_{\mathrm{CH}_{k X} l} = k \xi_{\mathrm{CH}} + l \xi_{\mathrm{CX}} + \frac{k(k-1)}{2} \eta_{\mathrm{HH}} + k l \eta_{\mathrm{HX}} + \frac{l(l-1)}{2} \eta_{\mathrm{XX}}. \qquad (1)$$

Or, taking into account that $k = 4 - l$, further expanding the parentheses and collecting the terms free of indices, the terms in front of the index l, and the terms in front of the index l^2:

$$E_{\mathrm{CH}_{4-l} X_l} = (4 \xi_{\mathrm{CH}} + 6 \eta_{\mathrm{HH}}) + \left(-\xi_{\mathrm{CH}} + \xi_{\mathrm{CX}} - \frac{7}{2} \eta_{\mathrm{HH}} + 4 \eta_{\mathrm{HX}} - \frac{1}{2} \eta_{\mathrm{XX}}\right) l +$$

$$+ \left(\frac{1}{2} \eta_{\mathrm{HH}} - \eta_{\mathrm{HX}} + \frac{1}{2} \eta_{\mathrm{XX}}\right) l^2, \qquad (2)$$

i.e.,

$$E_{\mathrm{CH}_{4-l} X_l} = a_0 + a_1 l + a_2 l^2 \quad (l = 0, 1, 2, 3, 4), \qquad (3)$$

where

$$
\begin{aligned}
a_0 &= 4\xi_{\mathrm{CH}} + 6\eta_{\mathrm{HH}}, \\
a_1 &= -\xi_{\mathrm{CH}} + \xi_{\mathrm{CX}} - \frac{7}{2}\eta_{\mathrm{HH}} + 4\eta_{\mathrm{HX}} - \frac{1}{2}\eta_{\mathrm{XX}}, \\
a_2 &= \frac{1}{2}\eta_{\mathrm{HH}} - \eta_{\mathrm{HX}} + \frac{1}{2}\eta_{\mathrm{XX}}.
\end{aligned}
\tag{4}
$$

We have obtained formula (3) for calculating the energy of molecules of X-substituted methanes in the form of a linear combination of three constants a_0, a_1, a_2. This formula can also be used for calculating other properties of molecules. Indeed, assuming the possibility of representing some physicochemical property of a molecule as the sum of partial properties attributable to pair interactions of atoms, and considering the pair interactions of a given type to remain unchanged on passing from one molecule to another, we first obtain an expression of the form (1), whence through (2) we readily arrive at (3). The form of formula (3) was established by Bernstein (^{1}), and it has been used by a number of authors ($^{2-4}$) to calculate the properties of various substituted methanes. We tested this formula by calculating the energies of molecules of X-substituted methanes for the case $\mathrm{X} = \mathrm{Cl}, \mathrm{Br}, \mathrm{CH}_3$, as well as the heats of formation from the elemen-

* For brevity we shall speak of X as an atom, although it may also denote a group of atoms.

···tures, molar refractions, diamagnetic susceptibilities, entropies for the case $X = \mathrm{Cl}$. Agreement with experiment was good throughout.

Next, in the molecule $\mathrm{CH}_{kX}l$, let us first break the C—H bond

$$\mathrm{CH}_{kX}l \to \dot{\mathrm{C}}\mathrm{H}_{k-1}X_l + \mathrm{H},$$

and then the C—X bond

$$\mathrm{CH}_{kX}l \to \dot{\mathrm{C}}\mathrm{H}_{kX_{l-1}} + \mathrm{X}.$$

Let $E_{\dot{\mathrm{C}}\mathrm{H}_{k-1}X_l}$ and $E_{\dot{\mathrm{C}}\mathrm{H}_{kX_{l-1}}}$ denote the energies (heats of formation from free atoms) of the radicals $\dot{\mathrm{C}}\mathrm{H}_{k-1}X_l$ and $\dot{\mathrm{C}}\mathrm{H}_{kX_{l-1}}$, respectively, and let $\tilde{\xi}_{\mathrm{CH}}$, $\tilde{\xi}_{\mathrm{CX}}$ denote the energies of pair interactions of directly bonded atoms C and H, and atoms C and X, respectively; let $\tilde{\eta}_{\mathrm{HH}}$, $\tilde{\eta}_{\mathrm{HX}}$, $\tilde{\eta}_{\mathrm{XX}}$ denote the energies of pair interactions of atoms H and H, atoms H and X, and atoms X and X, respectively, separated by one carbon atom in the chain of these radicals. Assuming that the energies of radicals can be represented as the sum of the energies of pair interactions of atoms, and considering each pair interaction of a given kind (for example $\tilde{\eta}_{\mathrm{HX}}$) to be the same in all radicals, for the energies of the radicals $\dot{\mathrm{C}}\mathrm{H}_{k-1}X_l$ and $\dot{\mathrm{C}}\mathrm{H}_{kX_{l-1}}$, respectively, we find

$$E_{\dot{\mathrm{C}}\mathrm{H}_{k-1}X_l} = (k-1)\tilde{\xi}_{\mathrm{CH}} + l\tilde{\xi}_{\mathrm{CX}} + \frac{(k-1)(k-2)}{2}\tilde{\eta}_{\mathrm{HH}} + (k-1)l\tilde{\eta}_{\mathrm{HX}} + \frac{l(l-1)}{2}\tilde{\eta}_{\mathrm{XX}}; \tag{5}$$

$$E_{\dot{\mathrm{C}}\mathrm{H}_{k}X_{l-1}} = k\tilde{\xi}_{\mathrm{CH}} + (l-1)\tilde{\xi}_{\mathrm{CX}} + \frac{k(k-1)}{2}\tilde{\eta}_{\mathrm{HH}} + k(l-1)\tilde{\eta}_{\mathrm{HX}} + \frac{(l-1)(l-2)}{2}\tilde{\eta}_{\mathrm{XX}}. \tag{6}$$

Or, taking into account that $k = 4 - l$, expanding the parentheses and collecting the terms free of indices, the terms before the index l, and the terms before the index l^2:

$$E_{\dot{\mathrm{C}}\mathrm{H}_{3-l}X_l} = \tilde{a}_0 + \tilde{a}_1 l + \tilde{a}_2 l^2 \quad (l = 0, 1, 2, 3); \tag{7}$$

$$E_{\dot{\mathrm{C}}\mathrm{H}_{4-l}X_{l-1}} = \tilde{\tilde{a}}_0 + \tilde{\tilde{a}}_1 l + \tilde{\tilde{a}}_2 l^2 \quad (l = 1, 2, 3, 4), \tag{8}$$

where

$$\begin{aligned}
\tilde{a}_0 &= 3\tilde{\xi}_{\mathrm{CH}} + 3\tilde{\eta}_{\mathrm{HH}},\\
\tilde{a}_1 &= -\tilde{\xi}_{\mathrm{CH}} + \tilde{\xi}_{\mathrm{CH}} + \frac{5}{2}\tilde{\eta}_{\mathrm{HH}} + 3\tilde{\eta}_{\mathrm{HX}} - \frac{1}{2}\tilde{\eta}_{\mathrm{XX}},\\
\tilde{a}_2 &= \frac{1}{2}\tilde{\eta}_{\mathrm{HH}} - \tilde{\eta}_{\mathrm{HX}} + \frac{1}{2}\tilde{\eta}_{\mathrm{XX}},\\
\tilde{\tilde{a}}_0 &= 4\tilde{\xi}_{\mathrm{CH}} - \tilde{\xi}_{\mathrm{CX}} + 6\tilde{\eta}_{\mathrm{HH}} - 4\tilde{\eta}_{\mathrm{HX}} + \tilde{\eta}_{\mathrm{XX}},\\
\tilde{\tilde{a}}_1 &= -\tilde{\xi}_{\mathrm{CH}} + \tilde{\xi}_{\mathrm{CX}} - \frac{7}{2}\tilde{\eta}_{\mathrm{HH}} + 5\tilde{\eta}_{\mathrm{HX}} - \frac{3}{2}\tilde{\eta}_{\mathrm{XX}},\\
\tilde{\tilde{a}}_2 &= \frac{1}{2}\tilde{\eta}_{\mathrm{HH}} - \tilde{\eta}_{\mathrm{HX}} + \frac{1}{2}\tilde{\eta}_{\mathrm{XX}}.
\end{aligned} \tag{9}$$

We have obtained formulas (7) and (8) for calculating the energies of radicals of X-substituted methanes in the form of linear combinations of three constants. These formulas can also be used for calculating other properties of radicals.

Let us now take the differences, first between (3) and (7), and then between (3) and (8). These differences will give the rupture energies of the C—H and C—X bonds, respectively, in X-substituted methanes. But let us first note that, evidently,

$$\eta_{\mathrm{HX}} \simeq \frac{\eta_{\mathrm{HH}} + \eta_{\mathrm{XX}}}{2}, \qquad \tilde{\eta}_{\mathrm{HX}} \simeq \frac{\tilde{\eta}_{\mathrm{HH}} + \tilde{\eta}_{\mathrm{XX}}}{2}. \tag{10}$$

Consequently, the constants a_2, $\tilde{a}_2$, $\tilde{\tilde{a}}_2$ are small quantities. The differences $a_2 - \tilde{a}_2$, $a_2 - \tilde{\tilde{a}}_2$ will, generally speaking, evidently also be small quantities. In subtrac-

substitution of (7) into (3) and (8) into (3), respectively, we obtain

$$D_l^{\mathrm{C-H}} = d_0' + d_1' l \quad (l = 0, 1, 2, 3); \tag{11}$$

$$D_l^{\mathrm{C-X}} = d_0'' + d_1'' l \quad (l = 1, 2, 3, 4), \tag{12}$$

where

$$\begin{aligned}
d_0' &= a_0 - \tilde{a}_0 = 4\xi_{\mathrm{CH}} - 3\tilde{\xi}_{\mathrm{CH}} + 6\eta_{\mathrm{HH}} - 3\tilde{\eta}_{\mathrm{HH}}, \\
d_1' &= a_1 - \tilde{a}_1 = -\xi_{\mathrm{CH}} + \tilde{\xi}_{\mathrm{CH}} - \xi_{\mathrm{CX}} + \tilde{\xi}_{\mathrm{CX}} + \tfrac{7}{2}\eta_{\mathrm{HH}} - \tfrac{5}{2}\tilde{\eta}_{\mathrm{HH}} \\
&\quad + 4\eta_{\mathrm{HX}} - 3\tilde{\eta}_{\mathrm{HX}} - \tfrac{1}{2}\eta_{\mathrm{XX}} + \tfrac{1}{2}\tilde{\eta}_{\mathrm{XX}}, \\
d_0'' &= a_0 - \tilde{a}_0 = 4\tilde{\xi}_{\mathrm{CH}} - 4\xi_{\mathrm{CH}} + \tilde{\xi}_{\mathrm{CX}} + 6\eta_{\mathrm{HH}} - 6\tilde{\eta}_{\mathrm{HH}} + 4\eta_{\mathrm{HX}} - \tilde{\eta}_{\mathrm{XX}}, \\
d_1'' &= a_1 - \tilde{a}_1 = -\xi_{\mathrm{CH}} + \tilde{\xi}_{\mathrm{CH}} - \xi_{\mathrm{CX}} + \tilde{\xi}_{\mathrm{CX}} - \tfrac{7}{2}\eta_{\mathrm{HH}} + \tfrac{7}{2}\tilde{\eta}_{\mathrm{HH}} \\
&\quad + 4\eta_{\mathrm{HX}} - 5\tilde{\eta}_{\mathrm{HX}} - \tfrac{1}{2}\eta_{\mathrm{XX}} + \tfrac{3}{2}\tilde{\eta}_{\mathrm{XX}}.
\end{aligned} \tag{13}$$

We have obtained formulas (11) and (12) for calculating the energies of rupture of, respectively, C–H bonds and C–X bonds in X-substituted methanes in the form of linear combinations of two constants. We checked these formulas by calculating the rupture energies of C–H and C–X bonds for the case $X = \mathrm{Cl}, \mathrm{Br}, \mathrm{CH}_3$. The agreement with experiment proved to be quite good. We note that formulas (11) and (12) are obtained from (3), (7), and (8) also if all pair interactions of a given type in molecules and radicals (for example, η_{HX} and $\tilde{\eta}_{\mathrm{HX}}$) are assumed to be approximately equal.

Let us note that the method described is readily extendable to XY- and XYZ-substituted methanes. For XY-substituted methane, formula (1) takes the form

$$\begin{aligned}
E_{\mathrm{CH}_{4-l-m}X_lY^m} &= (4-l-m)\xi_{\mathrm{CH}} + l\xi_{\mathrm{CX}} + m\xi_{\mathrm{CY}} + \frac{(4-l-m)(3-l-m)}{2}\eta_{\mathrm{HH}} \\
&\quad + (4-l-m)l\eta_{\mathrm{HX}} + (4-l-m)m\eta_{\mathrm{HY}} + \frac{l(l-1)}{2}\eta_{\mathrm{XX}} + lm\eta_{\mathrm{XY}} + \frac{m(m-1)}{2}\eta_{\mathrm{YY}}
\end{aligned} \tag{14}$$

or

$$E_{\mathrm{CH}_{4-l-m}X_lY^m} = a_0 + a_1 l + a_2 l^2 + b_1 m + b_2 m^2 + f(lm), \tag{15}$$

where $a_0,\ a_1,\ a_2$ have the same form as in (4), and

$$\begin{aligned} b_1 &= -\xi_{\mathrm{CH}} + \xi_{\mathrm{CY}} - \tfrac{7}{2}\eta_{\mathrm{HH}} + 4\eta_{\mathrm{HY}} - \tfrac{1}{2}\eta_{\mathrm{YY}}, \\ b_2 &= \tfrac{1}{2}\eta_{\mathrm{HH}} - \eta_{\mathrm{HY}} + \tfrac{1}{2}\eta_{\mathrm{YY}}, \\ f &= \eta_{\mathrm{HH}} - \eta_{\mathrm{HX}} - \eta_{\mathrm{HY}} + \eta_{\mathrm{XY}}. \end{aligned} \tag{16}$$

For calculating the energies of XY-substituted methane molecules, we have obtained formula (15) with 6 constants—the quantities $a_0, a_1, a_2, b_1, b_2, f$. For XYZ-substituted methane,

$$\begin{aligned} E_{\mathrm{CH}_{4-l-m-n}X_{lY_{mZ}}n} = {} & (4-l-m-n)\xi_{\mathrm{CH}} + l\xi_{\mathrm{CX}} + m\xi_{\mathrm{CY}} + n\xi_{\mathrm{CZ}} \\ & + \frac{(4-l-m-n)(3-l-m-n)}{2}\eta_{\mathrm{HH}} + (4-l-m-n)l\eta_{\mathrm{HX}} \\ & + (4-l-m-n)m\eta_{\mathrm{YH}} + (4-l-m-n)n\eta_{\mathrm{HZ}} + \frac{l(l-1)}{2}\eta_{\mathrm{XX}} \\ & + lm\eta_{\mathrm{XY}} + ln\eta_{\mathrm{XZ}} + \frac{m(m-1)}{2}\eta_{\mathrm{YZ}} + \frac{n(n-1)}{2}\eta_{\mathrm{ZZ}} \end{aligned} \tag{17}$$

or

$$E_{\mathrm{CH}_{4-l-m-n}X_{lY_{mZ}}n} = a_0 + a_1 l + a_2 l^2 + b_1 m + b_2 m^2 + c_1 n + c_2 n^2 + f(lm) + g(ln) + h(mn), \tag{18}$$

where a, a_1, a_2, b_1, b_2, f have the same form as in (4) and (16), and

$$\begin{aligned} c_1 &= -\xi_{\mathrm{CH}} + \xi_{\mathrm{CZ}} - \frac{7}{2}\eta_{\mathrm{HH}} + 4\eta_{\mathrm{HZ}} - \frac{1}{2}\eta_{\mathrm{ZZ}}, \\ c_2 &= \frac{1}{2}\eta_{\mathrm{HH}} - \eta_{\mathrm{HZ}} + \frac{1}{2}\eta_{\mathrm{ZZ}}, \\ g &= \eta_{\mathrm{HH}} - \eta_{\mathrm{HX}} - \eta_{\mathrm{HZ}} + \eta_{\mathrm{XZ}}, \\ h &= \eta_{\mathrm{HH}} - \eta_{\mathrm{HY}} - \eta_{\mathrm{HZ}} - \eta_{\mathrm{YZ}}. \end{aligned} \tag{19}$$

For calculating the energies of molecules of XYZ-substituted methane, we obtain formula (18) with 10 constants—the quantities $a_0, a_1, a_2, b_1, b_2, c_1, c_2, f, g, h$, etc. Analogously, it can be shown that, for the energies of radicals of XY-substituted methane, formulas (7) and (8) become

$$E_{\dot{\mathrm{C}}\mathrm{H}_{3-l-m}X_{lY}m} = \tilde{a}_0 + \tilde{a}_1 l + \tilde{a}_2 l^2 + \tilde{b}_1 m + \tilde{b}_2 m^2 + \tilde{f}(lm),$$

$$E_{\dot{\mathrm{C}}\mathrm{H}_{4-l-m}X_{l-1}Y_m} = \tilde{\tilde{a}}_0 + \tilde{\tilde{a}}_1 l + \tilde{\tilde{a}}_2 l^2 + \tilde{\tilde{b}}_1 m + \tilde{\tilde{b}}_2 m^2 + \tilde{\tilde{f}}(lm), \tag{20}$$

$$E_{\dot{\mathrm{C}}\mathrm{H}_{4-l-m}X_{lY_{m-1}}} = \tilde{\tilde{\tilde{a}}}_0 + \tilde{\tilde{\tilde{a}}}_1 l + \tilde{\tilde{\tilde{a}}}_2 l^2 + \tilde{\tilde{\tilde{b}}}_1 m + \tilde{\tilde{\tilde{b}}}_2 m^2 + \tilde{\tilde{\tilde{f}}}(lm),$$

where $\tilde{a}_0, \tilde{a}_1, \ldots, \tilde{\tilde{\tilde{f}}}$ are certain constants.

For calculating the energies of radicals of XY-substituted methane, we obtain formulas with certain 6 constants, etc. Further, in an approximation analogous to (10), for the bond-dissociation energies in XY-substituted methane we obtain

$$D_{lm}^{\mathrm{C-H}} = d'_0 + d'_1 l + d'_2 m,$$

$$D_{lm}^{\mathrm{C-X}} = d''_0 + d''_1 l + d''_2 m, \tag{21}$$

$$D_{lm}^{\mathrm{C-Y}} = d'''_0 + d'''_1 l + d'''_2 m,$$

where $d'_0, d'_1, \ldots, d'''_1$ are certain constants. For calculating the bond-dissociation energies in XY-substituted methane, we obtain formulas with certain 3 constants, etc.

In conclusion, we note that the described method of approach to the study of the properties of molecules as functions of their structure is more general than for X-, XY-, and XYZ-substituted methanes. It was first given by Bernstein [1], and was developed in greater detail by us [5–7] using alkanes as an example. It is easy to see, in particular, that this approach can without particular difficulty be extended in general to compounds with a tetrahedral valence system with a general formula of the form

$$\mathrm{AB}_{4-l-m-n-\ldots-t}X_{lY_{mZ}}n \ldots W_t,$$

where $\mathrm{A} = \mathrm{C}, \mathrm{Si}, \mathrm{Ge}, \ldots;\quad \mathrm{B}, \mathrm{X}, \mathrm{Y}, \mathrm{Z}, \ldots, \mathrm{W} = \mathrm{H}, \mathrm{Cl}, \mathrm{Br}, \mathrm{CH}_3, \ldots.$

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Note: Figure translations are in progress. See original paper for figures.