Tetrahedron Vol. 38, No. 16, pp. 2453 to 2454, 1982
Printed in Great Britain.

0040–4020/82/162453–02$03.00/0
Pergamon Press Ltd.

ERRATA

JAMES R. LARSON, N. D. EPIOTIS and SASON S. SHAIK: A simple theoretical approach to bond energies. *Tetrahedron* **37**, 1205 (1981).

The following corrections should be made:

p. 1206, eqn (8) should read:

$$Eb = \tfrac{1}{2}\{E(\psi^+) + E(DA) + \sqrt{[E(\psi^+) - E(DA)]^2 + 8h^2}\} - E(DA)_\infty + V_{nn}. \quad (8)$$

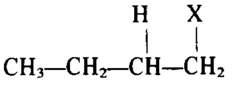
p. 1207, eqn (12) should read;

$$dE_b = \left\{\frac{4h}{\sqrt{(1 - A + C_2)^2 + 8h^2}}\right\} dh + \frac{1}{2}\left\{1 + \frac{(1 - A + C_2)}{\sqrt{(1 - A + C_2)^2 + 8h^2}}\right\} d(1 - A)$$

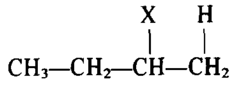
eqn (13) should read:

$$dE_b = \left\{\frac{2h}{\sqrt{(I_R - A_X + C_2)^2 + 4h^2}}\right\} dh + \frac{1}{2}\left\{1 + \frac{(I_R - A_X + C_2)}{\sqrt{(I_R - A_X + C_2)^2 + 4h^2}}\right\} d(I_R - A_X).$$

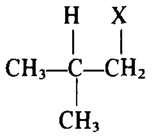
p. 1208, structures 5–8 should read:



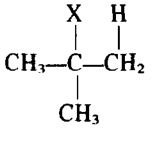
$CH_3—CH_2—\overset{\overset{H}{|}}{C}H—\overset{\overset{X}{|}}{C}H_2$ (5)



$CH_3—CH_2—\overset{\overset{X}{|}}{C}H—\overset{\overset{H}{|}}{C}H_2$ (6)



$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}—\overset{\overset{X}{|}}{C}H_2$ (7)



$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{X}{|}}{C}}—\overset{\overset{H}{|}}{C}H_2$ (8)

p. 1210, equation (17) should read

$$E_t = \frac{1}{2(1 - S_{12}^2)}\left\{H_{11} + H_{22} - 2H_{12}S_{12} + \sqrt{(H_{11} - H_{22})^2 + 4H_{11}H_{22}S_{12}^2 - 4H_{12}(H_{11} + H_{22})S_{12} + 4H_{12}^2}\right\} \quad (17)$$

eqn (22) should read

$$H_{12} = \frac{2}{1 + S_{RX}^2}\left\{\beta_{RX} + (\varepsilon_R + V_{ne})S_{RX} + \left\langle \phi_R\phi_R \left|\frac{1}{r_{12}}\right| \phi_X\phi_R \right\rangle\right\} \quad (22)$$

p. 1211, text should read:

A. These led to the following values:
$C_1 = +1eV$
$C_2 = -5eV$
$k = -0.95$ (i.e. $h = -8.44eV$. see eqn 5)

Using these values the bond energy we get is $|E_b| = 129.6$ kcal mole (eqn 9). These parameters were used to calculate C–H bond energies and we get the following results:[13]

CH_3–H	113 kcal mole ($h = -6.935$ eV)
C_2H_5–H	105 kcal mole ($h = -6.350$ eV)

Repeating this procedure and treating H_2 as a heteropolar bond (i.e. interacting only one ionic configuration with the covalent configuration) we get the following parameters

$C_1 \approx -5eV$
$C_2 \approx -2eV$
$k \approx -1.25.$

Using these parameters to calculate C–F bond energies we get:[13]

CH_3–F	116 kcal/mole ($h = -5{,}305$ eV)
C_2H_5–F	115 kcal/mole ($h = -4.835$ eV)
$(CH_3)_2CH$–F	109 kcal/mole ($h = -4{,}220$ eV)

We have used different parametrizations for h with the same result that the difference in C–F bond strengths is smaller than that of the corresponding C–H bonds (for discussion see text). Moreover, the C–F bonds are much less sensitive to the decrease of |h|.

We have tried these sets of parameters for all bond types. The numerical results are only fair, but most of the qualitative trends are reproduced. These parameters underestimate bonds with small overlap values (e.g., C–C) but overestimate bonds having high overlap values (e.g., Si–H). Thus, we have calculated the H_2 molecule using STO-3G integrals at various H-H separations. It turns out that while k varies just a little, C_1 and C_2 vary substantially and for overlaps ≤ 0.5 one should use $C_1 = -2eV$, $C_2 = -5eV$ in order to get reasonable numerical results. For example, using these values, one gets 83 kcal/mole for $H_3C–CH_3$. It is obvious therefore, that only two sets of parameters for *all* bond types are insufficient to reproduce the experimental bond energies. Quantitative predictions across the board would only be attainable by careful parametrization of C_1 and C_2.

Reference 13 should read:

[13] The overlap values were obtained using Slater Type orbitals and CNDO (open shell) coefficients for the ϕ_R and ϕ_X orbitals. Only central atom coefficients were used. All carbon and silicon radicals were taken to be tetrahedral. Chlorine and fluorine were taken unhybridized.