6. M. Isobe, N. Fukami, and T. Nishikava, *Heterocycles*, 1987, **25**, 521.
7. J. L. Charlton and M. M. Alaudin, *Tetrahedron*, 1987, **43**, 2873.
8. M. S. Miftakhov, I. N. Gaisina, and F. A. Valeev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2047 [*Russ. Chem. Bull.*, 1996, **45**, 1942 (Engl. Transl.)].
9. M. A. Zottola, R. Alonso, G. D. Vite, and B. Fraser-Reid, *J. Org. Chem.*, 1989, **54**, 6123.
10. G. J. Martin and M. L. Martin, *Progr. Nuc. Mag. Reson. Spect.*, 1972, **8**, 174.

Received June 10, 1996

Schemes of calculation of the properties of substituted ethylenes

Yu. G. Papulov,* M. G. Vinogradova, and I. G. Davydova

Tver' State University, 33 ul. Zhelyabova, 170000 Tver', Russian Federation.
Fax: 007 (082 2) 33 1274

Calculation schemes for estimation of the properties of X-substituted ethylenes based on the concept of atoms interacting in pairs are described. The equivalence of these schemes are shown, and the relations between their parameters are established.

Key words: schemes of additivity; interactions of atoms, substituted ethylenes.

Several schemes of calculation occur in the literature for X-substituted ethylenes (X = Cl, Me, ...), which present a certain property as the sum of properties (P) due to interactions of atoms in pairs, valence interactions (p_{CC_0}, p_{CH_0},...), nonvalence interactions of alternate atoms (p_{CH_1}, p_{HH_1},...), and nonvalence interactions of every third alternate atoms (p_{HH_2},...), taking into account their *cis*- (0) or *trans*- (π) positions:

1) Bernstein's scheme[1]

$$P_{CH_{2-l}X_f=CH_{2-l'}X_{f'}} = P_0 + x_a a + x_b b + x_c c + x_d d, \quad (1)$$

where

$$\left.\begin{aligned}
P_0 &= p_{CC_0} + 4p_{CH_0} + 4p_{CH_1} + 2p_{HH_1} + 2p^0_{HH_2} + \\
&\quad + 2p^{\pi}_{HH_2}, \\
a &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\
&\quad - p^0_{HH_2} - p^{\pi}_{HH_2} + p^0_{HX_2} - p^{\pi}_{HX_2}, \\
b &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HX_1} + p_{XX_1} - \\
&\quad - p^0_{HH_2} - p^{\pi}_{HH_2} + p^0_{HX_2} - p^{\pi}_{HX_2}, \\
c &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\
&\quad - p^0_{HH_2} - p^0_{HX_2} - p^{\pi}_{HX_2} + p^{\pi}_{XX_2}, \\
d &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\
&\quad - p^{\pi}_{HH_2} - p^0_{HX_2} + p^{\pi}_{HX_2} + p^0_{XX_2}
\end{aligned}\right\} \quad (2)$$

2) the scheme proposed in Ref. 2

$$P_{CH_{2-l}X_f=CH_{2-l'}X_{f'}} = \lambda_0 + (l + l')\lambda_1 + (l^2 + l^{2'})\lambda_2 + (ll')\lambda_3 \pm q^{HX}, \quad (3)$$

where

$$\left.\begin{aligned}
\lambda_0 &= p_{CC_0} + 4p_{CH_0} + 4p_{CH_1} + 2p_{HH_1} + 2p^0_{HH_2} + \\
&\quad + 2p^{\pi}_{HH_2}, \\
\lambda_1 &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - 3/2\, p_{HH_1} + \\
&\quad + 2p_{HX_1} - 1/2\, p_{XX_1} - p^0_{HH_2} - p^{\pi}_{HH_2} + p^0_{HX_2} + \\
&\quad + p^{\pi}_{HX_2}, \\
\lambda_2 &= 1/2\, p_{HH_1} - p_{HX_1} + 1/2\, p_{XX_1}, \\
\lambda_3 &= 1/2\,(p^0_{HH_2} + p^{\pi}_{HH_2} - 2p^0_{HX_2} - 2p^{\pi}_{HX_2} + p^0_{XX_2} + \\
&\quad + p^{\pi}_{XX_2}), \\
q^{HX} &= 1/2\,(p^0_{HH_2} - p^{\pi}_{HH_2} - 2p^0_{HX_2} + 2p^{\pi}_{HX_2} + \\
&\quad + p^0_{XX_2} - p^{\pi}_{XX_2}).
\end{aligned}\right\} \quad (4)$$

3) the scheme proposed by S. E. Tomberg[3]

$$P_{CH_{2-l}X_f=CH_{2-l'}X_{f'}} = \alpha_1[CH]_0 + \alpha_2[CX]_0 + \beta_1[HX]_1 + \beta_2[HX]^0_2 + \beta_3[HX]^{\pi}_2, \quad (5)$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2586—2587, October, 1996.
1066-5285/96/4510-2455 $15.00

Table 1. Parameters of calculated schemes for X-substituted ethylenes

Substituent of ethylene	scheme (1)					scheme (3)					scheme (5)				
	P_0	a	b	c	d	λ_0	λ_1	λ_2	λ_3	q^{HX}	$[CH]_0$	$[CX]_0$	$[HX]_1$	$[HX]^0_2$	$[HX]^\pi_2$
$CH_2=CH_2$	1	0	0	0	0	1	0	0	0	0	4	0	0	0	0
$CH_2=CHX$	1	1	0	0	0	1	1	1	0	0	3	1	1	1	1
$CH_2=CX_2$	1	1	1	0	0	1	2	4	0	0	2	2	0	2	2
cis-CHX=CHX	1	1	0	0	1	1	2	2	1	+1	2	2	2	0	2
trans-CHX=CHX	1	1	0	1	0	1	2	2	1	−1	2	2	2	2	0
$CHX=CX_2$	1	0	1	1	1	1	3	5	2	0	1	3	1	1	1
$CX_2=CX_2$	1	−2	2	2	2	1	4	8	4	0	0	4	0	0	0

where

$$\left.\begin{aligned}
[CH]_0 &= 1/4\, p_{CC_0} + p_{CH_0} + p_{CH_1} + 1/2\, p_{HH_1} + \\
&\quad + 1/2\, p^0_{HH_2} + 1/2\, p^\pi_{HH_2}, \\
[CX]_0 &= 1/4\, p_{CC_0} + p_{CX_0} + p_{CX_1} + 1/2\, p_{XX_1} + \\
&\quad + 1/2\, p^0_{XX_2} + 1/2\, p^\pi_{XX_2}, \\
[HX]_1 &= -1/2(p_{HH_1} - 2p_{HX_1} + p_{XX_1}), \\
[HX]^0_2 &= -1/2(p^0_{HH_2} - 2p^0_{HX_2} + p^0_{XX_2}), \\
[HX]^\pi_2 &= -1/2(p^\pi_{HH_2} - 2p^\pi_{HX_2} + p^\pi_{XX_2}).
\end{aligned}\right\} \qquad (6)$$

The values of P_0, a, b, c, and d in scheme (1), λ_0, λ_1, λ_2, λ_3, and q^{HX} in scheme (3), and $[CH]_0$, $[CX]_0$, $[HX]_1$, $[HX]^0_2$, and $[HX]^\pi_2$ in scheme (5) appear as parameters expressed, according to (2), (4), and (6), in terms of valence and nonvalence atomic interactions. The factors preceding the parameters in schemes (1), (3), and (5) are the number of these parameters in the molecule (Table 1).

Schemes (1), (3), and (5), each containing five independent parameters, are equivalent, and it is not difficult to establish links between the parameters. For example:

$$\left.\begin{aligned}
\lambda_0 &= P_0 = 4[CH]_0, \\
\lambda_1 &= 1/2(3a - b) = -[CH]_0 + [CX]_0 + 2[HX]_1 + \\
&\quad + [HX]^0_2 + [HX]^\pi_2, \\
\lambda_2 &= 1/2(b - a) = -[HX]_1, \\
\lambda_3 &= 1/2(c + d - 2a) = -[HX]^0_2 - [HX]^\pi_2, \\
q^{HX} &= 1/2(-c + d) = -[HX]^0_2 + [HX]^0_2;
\end{aligned}\right\} \qquad (7)$$

as well as

$$\left.\begin{aligned}
&P_0 = \lambda_0,\ a = \lambda_1 + \lambda_2,\ b = \lambda_1 + 3\lambda_2, \\
&c = \lambda_1 + \lambda_2 + \lambda_3 - q^{HX},\ d = \lambda_1 + \lambda_2 + \lambda_3 + q^{HX}
\end{aligned}\right\} \qquad (8)$$

and similarly in other cases.

A method for construction of schemes of additivity was described previously (see Ref. 4 and 5) based on the solution of the matrix equation $\mathbf{D} \cdot \Lambda = \mathbf{C}$, where $\mathbf{C}$ is the coefficient matrix of the initial scheme of expansion of property P in terms of intramolecular interactions, $\mathbf{D}$ is the coefficient matrix of the final scheme, and Λ is the matrix of interaction numbers, through which the parameters of the working scheme are expressed. Using this procedure allows obtaining schemes (1), (3), and (5) linked by (7) and (8) as well as other schemes (see Ref. 5).

This work was performed with financial support from the Russian Foundation for Basic Research (Project No. 96-03-32384).

References

1. H. J. Bernstein, *J. Chem. Phys.*, 1952, **20**, 263, 1328.
2. Yu. G. Papulov, *Zh. Fiz. Khim.*, 1963, **37**, 648 [*Russ. J. Phys. Chem.*, 1963, **37** (Engl. Transl.)].
3. S. E. Tomberg, *Raboty po fizicheskoi khimii* [*Works in Physical Chemistry*], GIPKh, Leningrad, 1983, 18 pp. (in Russian).
4. Yu. G. Papulov and T. G. Shaporova, *Svoistva veshchestv i stroenie molecul* [*Properties of Substances and Molecular Structure*], KGU, Kalinin, 1982, 3 (in Russian).
5. V. M. Smolyakov, M. M. Kanovich, T. Yu. Papulova, and A. N. Leshina, *Svoistva veshchestv i stroenie molecul* [*Properties of Substances and Molecular Structure*], KGU, Kalinin, 1984, 98, 126 (in Russian).

Received June 27, 1996