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Group Electronegativities, Inductive and Mesomeric Parameters from Semiempirical Quantum Chemical Computations

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Summary. Electronegativities, inductive parameters, and mesomeric dipole moments have been computed for different substituents X in CH_3X, XCH_2COOH, n-$C_5H_{11}X$, C_6H_5X, 4-X-$C_6H_4NH_2$, 4-X-$C_6H_4NO_2$, 2,6-di-X-C_5H_3N, and 2,6-di-X-$C_5H_3N^+CH_3$. The applicability of several semiempirical quantum chemical method to such calculations is demonstrated, and the dependence of the heuristic quantities on the nature of the substituents X is reported.

Keywords. Electronegativity; Inductive parameter; Mesomeric dipole moment; Semiempirical quantum chemical estimation.

Gruppenelektronegativitäten, induktive und mesomere Parameter aus semiempirischen quantenchemischen Berechnungen

Zusammenfassung. Elektronegativitäten, induktive Parameter und mesomere und mesomere Dipolmomente wurden für verschiedene Substituenten X in CH_3X, XCH_2COOH, n-$C_5H_{11}X$, C_6H_5X, 4-X-$C_6H_4NH_2$, 4-X-$C_6H_4NO_2$, 2,6-di-X-C_5H_3N und 2,6-di-X-$C_5H_3N^+CH_3$ berechnet. Die Anwendbarkeit einiger semiempirischer quantenchemischer Methoden auf solche Problemstellungen wird gezeigt, und die Abhängigkeit der berechneten Größen von den Eigenschaften der Substituenten X wird diskutiert.

Introduction

The electronegativities (EN) of atomic groups as well as their inductive and mesomeric effects expressed in terms of parameters following the linear free energy relationships principle [1–6] are extremely important for the description of the physicochemical properties of substances and molecules (spectra, ionization potentials, dipole moments, polarographic, and other characteristics), the investigation of reactivity, catalysis, extraction, solvation, and protolytic equilibria, and for establishing chemical, electrochemical, spectroscopic, and other properties. The substituents absolute EN offers a unique opportunity for a uniform approach to the two fundamental chemical problems, namely reaction barriers and molecular

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design [7, 8]. In the context of EN analysis, regioselectivity and ambivalency (*i.e.* nucleophilic-electrophilic dichotomy [7–12]) can be explained as well as chemical bonding, attracting forces, and the properties of molecules and crystals [13]. Owing to the EN concept, chemistry fits readily into the general theory of systems [13].

The aim of the present work is to elucidate the possibility of semiempirical quantum chemical estimation of electronegativities, inductive, and mesomeric characteristics of the atomic groups X in CH_3X, XCH_2COOH, n-$C_5H_{11}X$, C_6H_5X, 4-X-$C_6H_4NH_2$, 4-X-$C_6H_4NO_2$, pyridines 2,6-di-X-C_5H_3N, and N-methylpyridinium cations 2,6-di-X-$C_5H_3N^+CH_3$.

Methods

The calculations of the electronic structure of the compounds using the SCF MO LCAO CNDO/2 [14], INDO [15], and MINDO [16] methods were carried out using the programs of the VIKING [17] and GEOMO [18] packages for fixed spatial parameters selected on the basis of data from structural investigations [19, 20]. The MNDO [21] and AM1 [22] calculations were performed using the MOPAC software package [23, 24] with complete geometry optimization (*Broyden-Fletcher-Goldfarb-Shanno* function minimizer [25, 26]) involving *Thiel*'s fast minimization algorithm [26]. The preliminary optimization was realized by the MMX method [27] with the software of the PCMODEL package [27]. The maximal gradient condition was set to 0.02 kcal/mol/Å.

The regression analysis was performed with a confidence coefficient of 0.95.

Results and Discussion

As an objective criterion for the overall electron acceptor ability and EN of the substituents X in CH_3X, XCH_2COOH, n-$C_5H_{11}X$, C_6H_5X, 4-X-$C_6H_4NH_2$, 4-X-$C_6H_4NO_2$, $C_5H_3NX_2$, and $C_5H_3N^+CH_3X_2$ we refer to the sum of charges on atoms in the fragments CH_3, CH_2COOH, C_5H_{11}, C_6H_5, $C_6H_4NH_2$, $C_6H_4NO_2$, C_5H_3N, and $C_5H_3N^+CH_3$. For the saturated systems CH_3X, XCH_2COOH, and n-$C_5H_{11}X$, the value outlined is a characteristic of the EN effect of X. Upon examination of molecules of the HX type, *Marriott*, *Reynolds et al.* have used the analogous index within the framework of the 6–31 G*//4–31 G [28] and 6–31 G*//6–31 G* [28, 29] approaches. Comparative analysis of the electron acceptor properties of different groups using such an integral index is sufficiently correct, since the substituents action range changes negligibly and irregularly within a series of compounds [30].

The EN effect of atomic groups is known to proceed over not more than 3 chemical bonds [5, 30]. The mesomeric effect decays more slowly: it is transferred through 3 alternating double bonds, even if vacant orbitals or negatively charged atoms do not take part in conjugation [4]. Obviously, for this reason the authors of Ref. [31] state that the charge on the *para*-carbon atom of the ring (q_{para}) may serve as a measure of pπ-conjugation in aromatic molecules. In principle, this value may also reflect $\pi\pi$-conjugation, *i.e.* describe the mesomeric properties of both n- and π-donor groups.

We have found 90 linear correlations of the EN values (obtained by different methods and scored on different scales) and the inductive parameter ι of atomic groups calculated by Eq. (1) [32] where Z^* is the effective charge of the valent shell and n^* is the effective principal quantum number, with the sum of charges on

Table 1. Electronegativities (χ) as a function of the sum of the atomic charges of fragments R in RX and RX_2 (Σ) according to $\chi = B \cdot \Sigma + A$

X	R	Method	Way of evaluation	Ref.	B	A	Correlation coefficient
H, CH_3, NH_2, OH, F	CH_3	CNDO/2	[a]	[36]	7.98±2.33	2.50±0.23	0.9876
H, CH_3, NH_2, OH, F	CH_2COOH	CNDO/2	[a]	[36]	7.32±2.01	2.71±0.18	0.9890
H, CH_3, NH_2, OH, F	$C_6H_4NO_2$	CNDO/2	[b]	[36]	7.78±2.35	2.67±0.24	0.9868
H, CH_3, NH_2, OH, F	CH_3	INDO	[b]	[36]	7.31±2.69	2.47±0.33	0.9806
H, CH_3, F	CH_3	CNDO/2	[c]	[39]	8.06±2.05	2.36±0.23	0.9998
H, CH_3, F	CH_2COOH	CNDO/2	[c]	[39]	7.39±0.71	2.58±0.08	1.000
H, CH_3, F	C_5H_{11}	CNDO/2	[c]	[39]	7.76±0.11	2.23±0.01	1.000
H, CH_3, F	CH_3	MINDO	[c]	[39]	4.90±0.54	2.33±0.10	1.000
CH_3, C_6H_5, CN, OH	C_5H_3N	CNDO/2	[d]	[41]	8.52±1.68	1.58±0.20	0.9979
H, CH_3, OH, F	C_5H_{11}	AM1	[e]	[36]	7.75±1.74	2.56±0.20	0.9973
NH_2, OH, OCH_3, F	CH_3	CNDO/2	[e]	[42]	6.05±1.36	2.82±0.17	0.9973
NH_2, OH, OCH_3, F	CH_2COOH	CNDO/2	[e]	[42]	5.63±0.91	2.97±0.10	0.9986
NH_2, OH, F	CH_3	INDO	[e]	[42]	4.92±0.70	2.81±0.11	0.9999
NH_2, OH, F	C_6H_5	INDO	[e]	[42]	4.80±0.71	2.83±0.11	0.9999
H, NH_2, OH, F	C_6H_5	MINDO	[e]	[42]	6.89±1.93	2.04±0.37	0.9958
CH_3, OH, F	C_5H_{11}	MINDO	[f]	[36]	9.41±2.32	2.19±0.38	0.9998
CH_3, NH_2, OH	CH_3	CNDO/2	[g]	[44]	11.96±2.46	2.29±0.16	0.9999
CH_3, NH_2, OH	C_5H_3N	CNDO/2	[g]	[44]	6.30±0.68	2.27±0.09	1.000
CH_3, NH_2, OH	CH_3	INDO	[g]	[44]	9.53±0.58	2.27±0.05	1.000
CH_3, NH_2, OH	CH_3	CNDO/2	[h]	[44]	14.74±2.26	1.94±0.15	0.9999
CH_3, NH_2, OH	CH_2COOH	CNDO/2	[h]	[44]	13.11±1.83	2.34±0.10	0.9999
CH_3, NH_2, OH	CH_3	INDO	[h]	[44]	11.50±2.61	1.94±0.22	0.9998
CH_3, NH_2, OH	CH_3	CNDO/2	i	[44]	14.48±2.97	2.32±0.19	0.9999
CH_3, NH_2, OH	C_5H_3N	CNDO/2	i	[44]	7.63±0.83	2.30±0.10	1.000
CH_3, NH_2, OH	$C_5H_3N^+CH_3$	CNDO/2	i	[44]	11.74±0.41	2.29±0.03	1.000
CH_3, NH_2, OH	CH_3	INDO	i	[44]	11.30±1.48	2.32±0.12	0.9999
CH_3, NH_2, $N(CH_3)_2$,	CH_3	CNDO/2	j	[45, 46]	8.34±1.24	2.55±0.09	0.9967

Table 1 (*continued*)

X	*R*	Method	Way of evaluation	Ref.	*B*	*A*	Correlation coefficient
OH, OCH_3							
CH_3, NH_2, $N(CH_3)_2$, OH, OCH_3	CH_2COOH	CNDO/2	j	[45, 46]	7.48±1.52	2.79±0.08	0.9939
CH_3, NH_2, OH	C_5H_3N	CNDO/2	k	[47]	6.30±0.68	2.27±0.09	1.0000
CH_3, NH_2, OH	CH_3	INDO	k	[47]	9.33±1.23	2.30±0.10	0.9999
CH_3, NH_2, OH	CH_3	INDO	l	[48]	9.10±1.83	2.64±0.12	0.9999
CH_3, $CH=CH_2$, CCH, COOH, CN, NH_2, OH	CH_3	CNDO/2	m	[50]	8.48±1.66	2.44±0.09	0.9858
CH_3, $CH=CH_2$, CCH, COOH, CN, NH_2, OH	CH_2COOH	CNDO/2	m	[50]	7.54±1.25	2.68±0.05	0.9898
H, CH_3, CN, OH, F	CH_3	AM1	n	[51]	9.24±1.28	2.67±0.26	0.9769
H, CH_3, OH, F	C_5H_{11}	AM1	n	[51]	11.21±2.67	2.76±0.31	0.9970
H, CH_3, F	C_5H_{11}	CNDO/2	o	[53, 54]	8.54±1.70	2.16±0.21	0.9999
NH_2, OH, F	CH_3	CNDO/2	p	[55]	7.38±2.08	2.94±0.27	0.9998
CH_3, NH_2, OH, F	CH_2COOH	CNDO/2	p	[55]	7.53±2.10	3.04±0.21	0.9958
NH_2, OH, F	CH_3	INDO	p	[55]	6.04±0.20	2.92±0.03	1.000
NH_2, OH, F	C_6H_5	INDO	p	[55]	5.89±1.52	2.93±0.24	0.9998
CH_3, OH, F	C_6H_5	AM1	p	[55]	22.72±5.64	2.90±0.24	0.9998
H, CH_3, OH, F	C_5H_{11}	AM1	q	[36]	8.28±1.28	2.51±0.51	0.9987
H, CH_3, OH, F	C_5H_{11}	AM1	r	[28, 29]	2.11±0.42	0.153±0.048	0.9979
H, CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, OC_6H_5, NO	CH_3	CNDO/2	s	[57, 58]	9.98±2.08	2.54±0.13	0.9493
H, CH_3, $CH=CH_2$, CCH,	CH_2COOH	CNDO/2	s	[57, 58]	9.43±1.92	2.82±0.09	0.9513

CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, OC_6H_5, NO							
H, CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, OC_6H_5, NO	C_6H_5	CNDO/2	[s]	[57, 58]	9.78±2.48	2.48±0.17	0.9277
CH_3, $CH=CH_2$, CCH, CN, NH_2, OH, NO	$C_6H_4NH_2$	CNDO/2	[s]	[57, 58]	9.22±2.63	2.27±0.09	0.9705
CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3	CH_3	CNDO/2	[t]	[59, 60]	14.78±2.50	2.49±0.14	0.9758
CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3	CH_2COOH	CNDO/2	[t]	[59, 60]	13.47±2.25	2.90±0.09	0.9764
CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3	C_6H_5	CNDO/2	[t]	[59, 60]	14.14±3.57	2.44±0.22	0.9482
CH_3, $CH=CH_2$, CCH CHO, COOH, CN, NH_2, OH	$C_6H_4NH_2$	CNDO/2	[t]	[59, 60]	15.16±3.06	2.21±0.20	0.9801
CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, OH	C_5H_3N	CNDO/2	[t]	[59, 60]	7.55±1.64	2.46±0.17	0.9771
CH_3, $CH=CH_2$, CCH, CHO, $COCH_3$, COOH, CN, NH_2, OH, NO, NO_2, F	CH_3	MINDO	[u]	[61]	14.91±3.25	8.97±0.53	0.9552
CH_3, $CH=CH_2$, CCH, CHO, COOH, CN, NH_2, OH, NO, NO_2, F	C_6H_5	MINDO	[u]	[61]	15.92±3.63	9.04±0.57	0.9572

Table 1 (*continued*)

X	*R*	Method	Way of evaluation	Ref.	*B*	*A*	Correlation coefficient
H, CH_3, CH=CH_2, CCH, CHO, $COCH_3$, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, NO	CH_2COOH	CNDO/2	[v]	[61]	268.43±67.91 90.20±22.81	17.55±2.81 5.69±0.94	0.9344[aa] 0.9344[bb]
CH_3, COOH, OH, NO_2, F	C_5H_{11}	MINDO	[w]	[58}	1.16±0.25	0.151±0.049	0.9930
CH_3, CHO, COOH, CN, NH_2, OH, NO_2, F	C_6H_5	MINDO	[w]	[58]	1.23±0.13	0.133±0.022	0.9944
CH_3, COOH, OH, NO_2, F	C_5H_{11}	MINDO	[x]	[58]	1.20±0.04	0.150±0.008	0.9998
CH_3, CHO, COOH, CN, NH_2, OH, NO_2, F	C_6H_5	MINDO	[x]	[58]	1.27±0.16	0.130±0.027	0.9922
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, OH, OCH_3, NO, NO_2, F	CH_3	CNDO/2	[y]	[63]	26.96±6.69 9.08±2.24	7.26±0.58 2.23±0.19	0.9366[aa] 0.9371[bb]
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, OH, OCH_3, NO, NO_2, F	CH_2COOH	CNDO/2	[y]	[63]	25.00±6.07 8.42±2.03	8.00±0.45 2.48±0.14	0.9391[aa] 0.9396[bb]
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, OH, NO, NO_2, F	CH_3	INDO	[y]	[63]	21.56±5.49 7.26±1.84	7.17±0.58 2.20±0.19	0.9404[aa] 0.9407[bb]
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, OH, NO, NO_2, F	CH_3	MINDO	[y]	[63]	14.65±2.72 4.93±0.92	7.09±0.44 2.18±0.15	0.9969[aa] 0.9664[bb]
H, CH_3, COOH, OH, NO_2, F	C_5H_{11}	MINDO	[y]	[63]	17.63±0.90 5.94±0.31	6.87±0.16 2.10±0.06	0.9993[aa] 0.9993[bb]
H, CH_3, CH=CH_2, CCH,	C_6H_5	INDO	[y]	[63]	20.06±5.58	7.16±0.63	0.9301[aa]

CHO, COOH, CN, NH_2, OH, NO, NO_2, F					6.76±1.86	2.20±0.19	0.9311[bb]
H, CH_3, CH=CH_2, CCH,	C_6H_5	MINDO	[y]	[63]	16.82±2.15	6.88±0.32	0.9839[aa]
CHO, COOH, CN, NH_2, OH, NO, NO_2, F					5.66±0.72	2.11±0.11	0.9839[bb]

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[a] Based on number of electrons and covalent or ionic radii [33–35]; [b] based on estimated effective nuclear potentials and covalent radii [37, 38]; [c] from ν_{CO} in R^1R^2CO; [d] according to *Pauling* [40] from dissociation energies of *R*-H, *R*-*R*, and H-H; [e] according to *Pauling* [40]; [f] *via* mean effective potentials of valence electrons [43]; [g] according to *Hinze*'s method from valence angles; [h] according to *Hinze*'s method for fluorides; [i] according to *Hinze*'s method for hydrides; [j] by iterative method for saturated structures; [k] under the assumption that χ is equal for all bonds; [l] from thermochemical data; [m] from the modified *Gordy* relation [49]; [n] using a summary system based on thermochemical data; [o] by *Hinze*'s method [52] for $CH_2 = CHX$ based on NMR data; [p] based on screening constants for orbital energies obtained from *Dirac*'s relativistic equation using X-ray spectroscopic data for the calculation of effective nuclear charges for the valence atoms; [q] from the nonempirical electrostatic model [56]; [r] *ab initio* calculation based on electron density distribution; [s] according to *Gordy* [49] taking into account neighbouring effects; [t] χ of bonding orbital calculated via χ of electroneutral atoms and orbital charge contribution; [u] *ab initio* calculation of χ_G applying the principle of electronegativity equalization within the framework of *Mulliken* population analysis; [v] *ab initio* calculation of χ_{G^0} applying the principal of electronegativity equalization within the framework of *Mulliken* population analysis; [w] 4–31 G *ab initio* calculation of hydrogen atomic charges $1 - q_H$ in H*X*; [x] 6–31G *ab initio* calculation of hydrogen atomic charges $1 - q_H$ in H*X*; [y] calculation of χ from *Bader*'s theory of molecular structure [62] in terms of the analysis of topological electron distribution properties; [aa] according to *Mulliken*; [bb] according to *Pauling*

Table 2. Inductive parameter (ι, [64]) as a function of the sums of the atomic charges of fragments R in RX (Σ) according to $\iota = B \cdot \Sigma + A$

X	R	Method	B	A	Correlation coefficient
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, OC_6H_5, F	CH_3	CNDO/2	5.16±0.84	2.23±0.07	0.9682
	CH_2COOH	CNDO/2	4.78±0.78	2.37±0.05	0.9679
	C_6H_5	CNDO/2	4.96±1.14	2.20±0.09	0.9398
H, CH_3, COOH, OH, F	C_5H_{11}	CNDO/2	5.14±1.48	2.05±0.17	0.9880
H, CH_3, CH=CH_2, CCH, CHO, COOH, CN, NH_2, OH, F	$C_6H_4NH_2$	CNDO/2	5.07±1.33	2.13±0.12	0.9519
	CH_3	INDO	4.08±1.12	2.21±0.11	0.9477
	C_6H_5	INDO	4.13±1.19	2.20±0.11	0.9431

Table 3. Mesomeric dipole moments (μ_m, [1]) as a function of the charges in *para* positions of the aromatic rings of 4-YC_6H_4X (q_{para}) as obtained from CNDO/2 calculations according to $\mu_m = B \cdot q_{para} + A$

X	Y	B	A	Correlation coefficient
CH_3, $COCH_3$, CN, NH_2, NO_2, F	NH_2	−36.30±8.38	4.97±1.15	−0.9865
	NO_2	−33.95±7.02	1.01±0.24	−0.9891

atoms of the corresponding molecular fragments as well as of mesomeric dipole moment (μ_m) of substituents X (presenting a vector difference of group moments for benzene and methane derivatives, and for irregular groups the difference component assigned to the C–X bond direction [1]) with the q_{para} values (Tables 1–3).

$$\iota = (Z^* + 1)/n^* \tag{1}$$

Given the mentioned dependences, the drawbacks of the CNDO/2 approach do not restrict its applicability for the EN values estimation. Besides, the CNDO/2 method enables one to obtain correct data on the electron density distribution in C, H, N, O, F, and Cl containing molecules [14, 17, 30, 65, 66]. The above scheme is parameterized favourably for the study of the inductive effect [66, 67]. Criticism of the method in the context of the analysis of the electrostatic component of the conformational enthalpy change calculated from the point charge interaction model [69] is not conclusive because of the inadequate simulation. Numerous data of ^{13}C NMR, NQR, photoelectron spectroscopy, *ab initio* calculations, *etc*. justify the results of calculations by the CNDO/2 method [65, 66]. The results of CNDO/2 and *ab initio* calculations of electronic effects are in accordance with each other [70].

Conclusion

The linear dependences obtained provide an evidence for the correctness of the series of electron acceptor and electron donor properties of various substituents in organic molecules [30]. The possibility of a simple estimation of electronegativity, inductive and mesomeric parameters of atomic groups by means of the semiempirical methods of quantum chemistry (including that on the CNDO/2 level) using the correlations of the values mentioned with the indices of the electronic structure of the molecules has been demonstrated. Commonly used constants following from the free energies linearity principle possess a number of limitations (multiplicity of sets, ambiguous interpretation, *etc.*). The quantities evaluated in the present work (EN, ι μ_m) overcome the aforesaid drawbacks to a significant extent, because they are expressed *via* values of clear physical meaning: Σ, q_{para} Z^*, n^*, group moments.

Addendum

During the manuscript consideration, some new correlations of the $X = B \cdot \Sigma + A$ type appeared, the effective X values of bonded atoms being determined on the basis of the principle of electronegativity equalization with absolute X of free atoms according to *Mulliken*, taking into account both charge and hybridization effects and using screening constants [71]. The MINDO/3 [72] calculations were performed with the GEOMO package at fixed molecular geometries.

X	*R*	Method	*B*	*A*	Correlation coefficient
CH_3, $CH{=}CH_2$, NH_2, OH, F	CH_3	CNDO/2	3.95±1.15	2.41±0.11	0.9877
CH_3, $CH{=}CH_2$, NH_2, OH, F	CH_2COOH	CNDO/2	3.60±0.98	2.52±0.09	0.9892
CH_3, $CH{=}CH_2$, NH_2, OH, F	C_6H_5	CNDO/2	3.72±1.31	2.42±0.14	0.9821
CH_3, $CH{=}CH_2$, NH_2, OH, F	$C_6H_4NH_2$	CNDO/2	3.84±1.25	2.38±0.14	0.9847
CH_3, $CH{=}CH_2$, NH_2, OH, F	C_6H_5	INDO	3.18±0.95	2.41±0.12	0.9871
CH_3, $CH{=}CH_2$, NH_2, OH, F	C_6H_5	MINDO/3	2.23±0.80	2.43±0.14	0.9815

A correlation of the same kind applies for the EN values obtained from a relative hydrogen scale (recalculated *Gordy's* scale) [73].

X	*R*	Method	*B*	*A*	Correlation coefficient
CH_3, $CH{=}CH_2$, CCH, CHO, COOH	CH_3	CNDO/2	12.69±2.61	1.16±0.07	0.9938

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References

[1] Pal'm VA (1974) An Introduction to Theoretical Organic Chemistry. Vysshaya Shkola, Moscow (in Russian)

[2] Chapman NB, Shorter J (eds) (1978) Correlation Analysis in Chemistry: Recent Advances. Plenum Press, New York London

[3] Shorter J (1983) Correlation Analysis of Organic Reactivity with Particular Reference to Multiple Regression. Wiley, New York

[4] Dneprovskii AS, Temnikova TI (1991) Theoretical Bases of Organic Chemistry. Khimiya, Leningrad (in Russian)

[5] Topsom RD (1983) Accounts Chem Res **16**: 292

[6] Hansch C, Leo A, Taft RW (1991) Chem Rev **91**: 165

[7] Volovik SV, Staninets VI, Zefirov NS (1992) Doklady Akad Nauk (Russia) **326**: 282

[8] Volovik SV, Staninets VI, Zefirov NS (1993) Doklady Akad Nauk (Russia) **330**: 321

[9] Volovik SV (1988) Teoret i Experim Khimiya **24**(3): 274

[10] Volovik SV, Dyadyusha GG, Staninets VI (1988) In: Pokhodenko VD (ed) Regioselectivity and Reactivity of Free Radicals in Addition and Aromatic Substitution Processes. Naukova Dumka, Kiev (in Russian)

[11] Volovik SV, Staninets VI, Zefirov NS (1990) Teoret i Experim Khimiya **26**(4): 413

[12] Volovik SV, Staninets VI, Zefirov NS (1991) Doklady Akad Nauk (Russia) **320**: 368

[13] Urusov VS (1994) Zhurn Strukt Khimii **35**(1): 111

[14] Pople JA, Segal GA (1966) J Chem Phys **44**: 3289

[15] Pople JA, Beverigde DL, Dobosh PA (1967) J Chem Phys **47**: 2026

[16] Baird NC, Dewar MJS (1969) J Phys Chem **50**: 1262

[17] Shchembelov GA, Ustynyuk YA, Mamaev VM, Ishchenko SY, Gloriozov IP, Luzhkov VB, Orlov VV, Simkin VY, Pupyshev VI, Burmistrov VN (1980) In: Ustynyuk YA (ed) Quantum Chemical Methods of Molecules Calculation. Khimiya, Moscow (in Russian)

[18] Rinaldi D (1977) Comput Chem **1**: 102

[19] Gordon AJ, Ford RA (1972) The Chemist's Companion. A Handbook of Practical Data, Techniques, and References. Wiley, New York London Sydney Toronto

[20] Kitaigorodskii AI, Zorkii PM, Bel'skii VK, Structure of Organic and Elementoorganic Molecules: Bibliographic Guide. (1929–1979) In: Porai-Koshits MA (ed) (1984) Nauka, Moscow (in Russian)

[21] Dewar MJS, Thiel W (1977) J Amer Chem Soc **99**: 4899

[22] Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) J Amer Chem Soc **107**: 3902

[23] Stewart JJP (1983) MOPAC, A Semi-Empirical Molecular Orbital Program, QCPE, Program N 455

[24] Clark T (1985) A Handbook of Computational Chemistry. A Practical Guide to Chemical Structure and Energy. Wiley, New York Chichester Brisbane Toronto Singapore

[25] Dennis JE, Schnabel RB (1983) Numerical Methods for Unconstrained Optimization and Nonlinear Equations. Prentice-Hall, Englewood Cliffs, New Jersey

[26] Thiel W (1988) J Mol Struct Theochem **163**: 415

[27] Burkert U, Allinger NL (1982) Molecular Mechanics, ACS Monograph 177, American Chemical Society, Washington, DC

[28] Reynolds WF, Taft RW, Marriott S, Topsom RD (1982) Tetrahedron Lett **23**: 1055

[29] Marriott S, Reynolds WF, Taft RW, Topsom RD (1984) J Org Chem **49**: 959

[30] Pankratov AN (1995) Indian J Chem **34B**: 689

[31] Berestova SS, Terekhova MI, Bondarenko NA, Bogachev YS, Petrov ES, Tsvetkov EN, Shatenshtein AI (1982) Zhurn Obshch Khimii **52**: 513

[32] Inamoto N, Masuda S (1977) Tetrahedron Lett 3287

[33] Sanderson RT (1952) J Chem Educ **29**: 539

[34] Sanderson RT (1954) J Chem Educ **31**: 2

[35] Sanderson RT (1954) J Chem Educ **31**: 238

[36] Luo Yu-Ran, Benson SW (1990) J Phys Chem **94**: 914

[37] Allred AL, Rochow EG (1958) J Inorg Nuclear Chem **5**: 269

[38] Allred AL (1961) J Inorg Nuclear Chem **17**: 215

[39] Kagarise RE (1955) J Amer Chem Soc **77**: 1377

[40] Pauling L (1960) The Nature of the Chemical Bond. Cornell University Press, Ithaca New York

[41] Constantinides E (1964) Proc Chem Soc 290

[42] Cherkasov AR, Galkin VI, Zueva EM, Cherkasov RA (1996) Zhurn Obshch Khimii **66**: 411

[43] Gao Shou-Fil (1961) Acta Chim Sinica **27**: 190

[44] Hinze J, Whitehead MA, Jaffé HH (1963) J Amer Chem Soc **85**: 148

[45] Gallais F, Voigt D, Labarre J-F (1965) Compt Rend Acad Sci Paris **260**: 128

[46] Gallais F, Voigt D, Labarre J-F (1965) J Chim Phys et Phys-Chim Biol **62**: 761

[47] Huheey JE (1965) J Phys Chem **69**: 3284

[48] Yingst A (1965) J Chem Soc Chem Commun 480

[49] Gordy W (1946) Phys Rev **69**: 604

[50] Chandra S, Chandra S (1966) Tetrahedron **22**: 3403

[51] Batsanov SS (1969) Electronegativity of Elements and Chemical Bond. Press of Siberian Branch of USSR Academy of Sciences, Novosibirsk (in Russian)

[52] Hinze J, Jaffé HH (1962) J Amer Chem Soc **84**: 540

[53] Yalymova SV, Samitov YY (1970) Zhurn Organ Khimii **6**: 1945

[54] Samitov YY, Yalymova SV (1972) Zhurn Organ Khimii **8**: 441

[55] Mande C, Deshmukh P, Deshmukh P (1977) J Phys (B) Atom Mol Phys **10**: 2293

[56] Boyd RJ, Marcus GE (1981) J Chem Phys **75**: 5385

[57] Inamoto N, Masuda S (1982) Chemistry Letters 1003

[58] Inamoto N, Masuda S, Niwa J (1990) J Phys Org Chem **3**: 209

[59] Mullay J (1985) J Amer Chem Soc **107**: 7271

[60] Mullay J (1987) Structure and Bonding **66**: 1

[61] Datta D (1988) Proc Indian Acad Sci (Chem Sci) **100**: 549

[62] Bader RFW (1991) Chem Rev **91**: 893

[63] Hati S, Datta D (1992) J Comput Chem **13**: 912

[64] Inamoto N, Masuda S (1982) Chemistry Letters 1007

[65] Clark DT, Kilcast D (1971) J Chem Soc A 3286

[66] Politzer P, Whittenburg SL, Wärnheim T (1982) J Phys Chem **86**: 2609

[67] Gineityte VL, Shatkovskaya DB (1984) Zhurn Strukt Khimii **25**(5): 152

[68] Shatkovskaya DB, Gineityte VL (1988) Zhurn Strukt Khimii **29**(1): 21

[69] Stolow RD, Samal PW, Giants Th W (1981) J Amer Chem Soc **103**: 197

[70] Hehre WJ, Pople JA (1970) J Amer Chem Soc **92**: 2191

[71] Ferreira R (1963) Trans Faraday Soc **59**: 1064

[72] Bingham RC, Dewar MJS, Lo DH (1975) J Amer Chem Soc **97**: 1285

[73] Bykov GV (1960) Electronic Bond Charges in Organic Compounds, Russian Academy of Sciences Press, Moscow (in Russian)

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