had been treated with decolorizing charcoal.[51] The extracts were cross-extracted with hexane to remove any residual hydrocarbons or chlorinated hydrocarbons from the sulfonyl chlorides and the sulfur dioxide was allowed to boil off. The monosulfonyl chlorides were extracted from the polysulfonyl chlorides with pentane, at −25° in the case of the bicyclooctane products, at room temperature in the case of the adamantane. The pentane was distilled off to leave viscous oils. No physical properties were determined in the case of the bicyclooctane product; in the case of adamantane they were $n^{20}{}_D$ 1.5412, $d^{20}{}_4$ 1.3070, M_D 55.78 (calcd 55.46).

Since attempts to separate the mixture of isomeric monosulfonyl chlorides were unsuccessful, these mixtures were used in the kinetic studies.

Derivatization of the Sulfonyl Chlorides.—The residue from thermal decomposition of the *sym*-bicyclooctanesulfonyl chlorides was treated with liquid ammonia to yield the same sulfonamide from the known secondary sulfonyl fluoride, mp 132–133°.[15]

The mixture of adamantanesulfonyl chlorides, in chloroform and freed of polysulfonyl chlorides, was treated with liquid ammonia to give a sulfonamide, mp 208.5–209.5°, believed to be the secondary isomer.

Anal. Calcd. for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51; S, 14.89. Found: C, 55.64; H, 7.88; N, 6.54; S, 14.92.

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(51) This treatment evidently removes some impurities in commercial grade sulfur dioxide and results in lighter colored, more stable sulfonyl chlorides.[9]

Group Electronegativity and Polar Substituent Constants

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The relationship between polar substituent constants (σ^*) and group electronegativity values calculated by the method of electronegativity equalization has been examined. It is found that the best correlation is between σ^* and the charge (δ) induced on the carbethoxy group as calculated from group electronegativity. If one assumes partial (instead of complete) equalization of electronegativity, the correlation is improved. Using 80% equalization, the relation ($\sigma^* = -12.84\delta + 3.54$; $r = 0.97$) is obtained for 47 organic groups. The use of partial equalization also obviates the difficulties in isomeric group electronegativities previously encountered.

The recently developed concepts of orbital electronegativity[1–3] and electronegativity equalization[2,4–6] have permitted facile calculation of electronegativities for σ-[2,7] and π-bonded[8] groups. However, two problems have confronted the use of group electronegativities: (1) the relatively simple procedures previously suggested yield, contrary to chemical intuition, identical values for all isomers of a group (assuming identical valence states); (2) the more inclusive and important question may be asked concerning the general validity and usefulness of the method. Group electronegativities calculated by Jaffé and co-workers[2] have been shown to correlate with various physical and chemical properties[9] and these same methods have proven useful in discussing charge distribution and nmr coupling constants.[10] However, no widespread comparison of the many available group values with experimental data has yet been made. The principal reason for this is that most of the empirically derived group electronegativities are restricted to a limited number of groups, often determined and applicable only under special circumstances. It is the purpose of the present investigation to examine the relation between calculated group values and empirical data and thereby establish confidence limits in using the former. In addition, it was found that methods developed in the present study obviate objections based on isomeric group electronegativities.

Polar Substituent Constants.—Although electronegativity has proven to be very useful to the inorganic chemist in explaining various phenomena,[11] it has been of limited usefulness to the organic chemist. Some attempts have been made to set up electronegativity scales for organic groups, but they have not been particularly successful. In contrast, data for a large number or reactions have been interpreted successfully in terms of the *polar substituent constant*, σ^*, and related parameters.[12] These parameters should reflect the charge distribution in a molecule (or more accurately, in an activated complex) under consideration and thus be related to the electronegativity of the substituent groups. Jaffé[2] plotted the electronegativities of halomethyl groups *vs.* their σ^* values and found reasonably good agreement if chlorine, bromine, and iodine were assumed to be hybridized to contain some *s* character.

In the present work it was found that, if the electronegativity, a, of a group is plotted *vs.* its polar substituent constant, there is a tendency for a linear relationship to hold, but the fit is not very close ($r = 0.84$). One should expect that since σ^* is a reaction parameter, it should be a function of the charge induced at the reaction site rather than of the inherent electronegativity *per se*. The charge distribution in molecules is a function of both the inherent electronegativity, a, and the charge coefficient, b.[7] However, when the partial charge, δ, is plotted *vs.* σ^*, it is found that the preciseness of fit worsens ($r = 0.30$). This rather surprising result indicates that, in general, the values of b are somewhat less accurate than the values of a. Inspection of those groups which seem to deviate most from a linear relationship with σ^* indicates that they are the higher alkyl groups with calculated low values of b (predicted to be better donators than they really are) or Ω-substituted-nitro- and -fluoroalkyl

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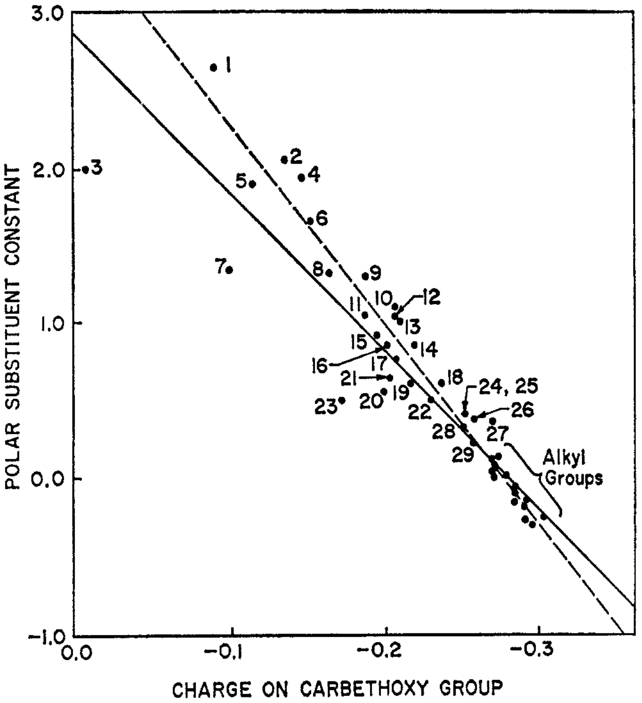

Figure 1.—Polar substituent constants plotted *vs.* charges on carbethoxy groups as calculated from group electronegativities. Solid line is based on all 50 points and is described by $\sigma^* = -10.49\delta + 2.93$. Dashed line is based on best 47 points and is described by $\sigma^* = -12.84\delta + 3.54$.

groups with high calculated values of a (predicted to be better acceptors than they actually are). Both of these difficulties, as well as that of isomeric identity of electronegativity result from the hypothesis of electronegativity equalization. Pritchard[13] has pointed out that complete equalization of electronegativity will not take place because of other energy terms such as overlap, and Klopman[14] has introduced the term *molecular electronegativity* to represent the difference between the equalization of atomic (*i.e.*, orbital electronegativities) and the situation which actually obtains. Therefore, in the following discussion, an additional parameter, p, has been introduced to represent the per cent equalization of orbital electronegativity upon formation of a covalent bond.

Methods.—Electronegativities were calculated by previously described methods.[7,8] Hybridization values were determined by bond angles[15] of typical compounds when available. In the case of the halogens, the following amounts of s character were used in the hybridization in line with the suggestions of Hinze, Whitehead, and Jaffé:[2] F, 0%; Cl, 18%; Br, 23%; I, 25%. All σ^* values were taken directly from Table XII of Taft[12] except for that of the methoxymethyl group, +0.64.[16]

The charge induced on a carbethoxy group, by the group R was calculated by the equation

$$\delta = p\left(\frac{a'_{\mathrm{COOEt}} - a'_{\mathrm{R}}}{b'_{\mathrm{COOEt}^+} + b'_{\mathrm{R}}}\right) \qquad (1)$$

For the case where $p = 1.00$ (equalization is complete) eq 1 reduces to eq 3 of Jaffe[2] and eq 39 of Huheey.[7]

The parameters a' and b' correspond to the a and b of orbital or group electronegativity[7] except that they have been corrected for incomplete equalization of electronegativity as follows.

Consider a diatomic group AB. The electronegativity of this group (χ_{AB}) is the electronegativity of B as perturbed by A. If the group is uncharged

$$\delta_{\mathrm{B}} = p\left(\frac{a_{\mathrm{A}} - a_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}}\right) \qquad (2)$$

$$\chi_{\mathrm{B}} = pb_{\mathrm{B}}\left(\frac{a_{\mathrm{A}} - a_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}}\right) + a_{\mathrm{B}} \qquad (3)$$

$$\chi_{\mathrm{B}} = \frac{pa_{\mathrm{A}}b_{\mathrm{B}} - pa_{\mathrm{B}}b_{\mathrm{B}} + a_{\mathrm{B}}\,b_{\mathrm{A}} + a_{\mathrm{B}}b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}} \qquad (4)$$

This will then be the electronegativity of the neutral group, a'_{AB}.

$$\chi_{\mathrm{B}} = \chi_{\mathrm{AB}} = \frac{pa_{\mathrm{A}}b_{\mathrm{B}} + a_{\mathrm{B}}b_{\mathrm{A}} + (1 - p)a_{\mathrm{B}}b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}} = a'_{\mathrm{AB}} \qquad (5)$$

Comparison of eq 5 with 26 (ref 7) reveals that a'_{AB} is a weighted average of the *bond electronegativity*[2] of group AB and the *orbital electronegativity* of the linking atom B.

If the total charge on the group is +1, the amount of charge which can be transferred to A is

$$\delta_{\mathrm{A}} = p\left(\frac{a_{\mathrm{B}} - a_{\mathrm{A}} + b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}}\right) \qquad (6)$$

and that which remains on B is

$$\delta_{\mathrm{A}} + \delta_{\mathrm{B}} = +1 \qquad (7)$$

$$\delta_{\mathrm{B}} = 1 - \left(\frac{a_{\mathrm{B}} - a_{\mathrm{A}} + b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}}\right)p = \qquad (8)$$

$$\chi_{\mathrm{B}} = a_{\mathrm{B}} + b_{\mathrm{B}} - pb_{\mathrm{B}}\left(\frac{a_{\mathrm{B}} - a_{\mathrm{A}} + b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}}\right) \qquad (9)$$

$$\chi_{\mathrm{B}} = \frac{(1 - p)a_{\mathrm{B}}b_{\mathrm{B}} + pa_{\mathrm{A}}b_{\mathrm{B}} + a_{\mathrm{B}}b_{A} + b_{\mathrm{A}}b_{\mathrm{B}} + (1 - p)b_{\mathrm{B}}^2}{b_{\mathrm{A}} + b_{\mathrm{B}}} \qquad (10)$$

which differs from eq 5 by

$$\frac{(1 - p)b_{\mathrm{B}}^2 + b_{\mathrm{A}}b_{\mathrm{B}}}{b_{\mathrm{A}} + b_{\mathrm{B}}} = b'_{\mathrm{AB}} \qquad (11)$$

or eq 11 may be written

$$\chi_{\mathrm{B}} = \chi_{\mathrm{AB}} = a'_{\mathrm{AB}} + b'_{\mathrm{AB}}\,\delta_{\mathrm{AB}} \qquad (12)$$

The relation between a and a' and b and b' for a diatomic group linked through B is

$$a'_{\mathrm{AB}} = pa_{\mathrm{AB}} + (1 - p)a_{\mathrm{B}} \qquad (13)$$

$$b'_{\mathrm{AB}} = b_{\mathrm{AB}} + (1 - p)\frac{b_{\mathrm{B}}^2}{b_{\mathrm{A}} + b_{\mathrm{B}}} \qquad (14)$$

For the more general case of linking atom W surrounded by substituent atoms X, Y, Z, ..., the relation for a' remains the same

$$a'_{\mathrm{WXYZ}\ldots} = pa_{\mathrm{WXYZ}\ldots} + (1 - p)a_{\mathrm{W}} \qquad (15)$$

and the relation for b' becomes

$$b'_{\mathrm{WXYZ}\ldots} = b_{\mathrm{WXYZ}\ldots} + (1 - p)\frac{b^2_{\mathrm{W}}}{b_{\mathrm{W}} + b_{\mathrm{XYZ}\ldots}} \qquad (16)$$

where the terms $b_{\mathrm{WXYZ}\ldots}$ and $b_{\mathrm{XYZ}\ldots}$ may be obtained from the appropriate eq (26, 30, 36) of ref 7.

When calculating the adjusted (*i.e.*, $p \pm 1$) electronegativity of a group composed of a central atom W surrounded by atoms X, Y, ..., and groups G,H..., the parameters a_{W}, b_{W}, a_{X}, b_{X}, a'_{G}, b'_{G}, etc., are employed.

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TABLE I

	Group	a	b	a'	b'	δ_{COOEt}	σ^*
1.	Cl_3C	10.44	2.87	9.96	5.05	−0.088	2.65
2.	F_2CH	9.55	3.73	9.24	5.64	−0.134	2.05
3.	$CH_3OC(O)$	9.38	2.94	11.20	5.70	−0.004	2.00
4.	Cl_2CH	9.51	2.98	9.20	5.12	−0.144	1.94
5.	$(CH_3)_3N^+CH_2$	8.43	0.82	9.74	4.36	−0.112	1.90
6.	$CH_3C(O)$	8.61	2.30	9.09	5.26	−0.150	1.65
7.	$C_6H_5C{\equiv}C$	8.38	1.03	9.71	6.02	−0.098	1.35
8.	$CH_3S(O_2)CH_2$	9.11	1.35	9.12	4.36	−0.162	1.32
9.	$NCCH_2$	9.42	2.87	8.68	4.97	−0.186	1.30
10.	FCH_2	8.39	3.46	8.31	5.42	−0.205	1.10
11.	$HOC(O)CH_2$	9.51	2.04	8.73	4.70	−0.186	1.05
12.	$ClCH_2$	8.48	3.11	8.38	5.14	−0.205	1.05
13.	$BrCH_2$	8.48	2.92	8.38	4.99	−0.208	1.00
14.	ICH_2	8.33	2.81	8.28	4.90	−0.218	0.85
15.	CF_3CH_2	9.23	2.09	8.52	5.23	−0.193	0.92
16.	$C_6H_5OCH_2$	8.28	0.90	8.80	4.76	−0.199	0.85
17.	$C_6H_5C(OH)H$	8.34	0.90	8.58	4.30	−0.206	0.765
18.	$CH_3C(O)CH_2$	8.16	1.65	8.14	4.55	−0.236	0.60
19.	C_6H_5	8.03	1.21	8.43	4.43	−0.215	0.60
20.	$HOCH_2$	8.77	2.74	8.54	4.85	−0.198	0.555
21.	CH_3OCH_2	8.14	1.68	8.50	4.79	−0.202	0.64
22.	$O_2NCH_2CH_2$	9.77	1.49	8.25	4.48	−0.229	0.50
23.	H	7.18	12.85	7.18	12.85	−0.171	0.49
24.	$C_6H_5CH{=}CH$	8.01	0.89	8.21	3.70	−0.251	0.41
25.	$(C_6H_5)_2CH$	7.99	0.56	8.16	3.97	−0.249	0.405
26.	$ClCH_2CH_2$	8.04	1.81	7.88	4.53	−0.257	0.285
27.	$CH_3CH{=}CH$	7.66	1.64	7.96	3.88	−0.269	0.360
28.	$CF_3CH_2CH_2$	8.64	1.40	7.94	4.55	−0.251	0.32
29.	$C_6H_5CH_2$	7.90	0.94	7.93	4.41	−0.256	0.215
30.	$CH_3CH{=}CHCH_2$	7.91	0.74	7.76	4.28	−0.273	0.13
31.	$CF_3CH_2CH_2CH_2$	8.34	1.06	7.74	4.43	−0.270	0.12
32.	$C_6H_5C(CH_3)H$	7.82	0.78	7.90	4.06	−0.268	0.11
33.	$C_6H_5CH_2CH_2$	7.81	0.78	7.74	4.40	−0.271	0.08
34.	$C_6H_5C(C_2H_5)H$	7.76	0.66	7.91	3.98	−0.269	0.04
35.	$C_6H_5CH_2CH_2CH_2$	7.75	0.48	7.66	4.40	−0.278	0.02
36.	CH_3	7.37	3.24	7.50	5.25	−0.268	0.00
37.	$c\text{-}C_6H_{11}CH_2$	7.43	0.62	7.62	4.30	−0.284	−0.06
38.	C_2H_5	7.40	1.85	7.56	4.46	−0.284	−0.10
39.	$n\text{-}C_3H_7$	7.41	1.30	7.59	4.42	−0.282	−0.115
40.	$i\text{-}C_4H_9$	7.42	1.00	7.61	4.35	−0.283	−0.125
41.	$n\text{-}C_4H_9$	7.42	1.00	7.60	4.41	−0.282	−0.130
42.	$c\text{-}C_6H_{11}$	7.43	0.72	7.63	3.96	−0.293	−0.150
43.	$(CH_3)_3CCH_2$	7.42	0.81	7.63	4.28	−0.283	−0.165
44.	$i\text{-}C_3H_7$	7.41	1.30	7.60	4.15	−0.290	−0.190
45.	$c\text{-}C_5H_9$	7.43	0.87	7.63	3.96	−0.293	−0.200
46.	$sec\text{-}C_4H_9$	7.42	1.00	7.63	4.06	−0.290	−0.210
47.	$(C_2H_5)_2CH$	7.42	0.81	7.64	3.98	−0.291	−0.225
48.	$(CH_3)_3SiCH_2$	7.56	0.78	7.54	3.93	−0.302	−0.260
49.	$(CH_3)_3C(CH_3)CH$	7.42	0.68	7.66	4.01	−0.289	−0.280
50.	$t\text{-}C_4H_9$	7.42	1.00	7.63	3.88	−0.295	−0.300

Results and Discussion

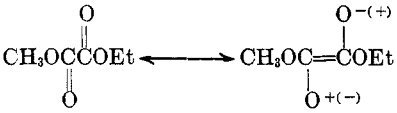
It was found that an equalization coeffiicent (p) of 80% improved the values of group electronegativities. A comparison of values of a, b, a', and b' for 50 organic groups having known values of σ^* is given in Table I. In each case, a' reflects the increased influence of the linking atom in the group. Values of b' are always greater than corresponding values of b, and the larger the group, the greater the disparity. When the induced charge on a carbethoxy group, δ, is plotted *vs.* the σ^* value of each group, the correlation is improved ($r = 0.93$) over that based on values of a and b (Figure 1). In addition, it will be seen that if three substituents, hydrogen, phenylethynyl, and carbomethoxy, are omitted the correlation improves considerably. The remaining 47 points determine a straight line described

$$\sigma^* = -12.84\delta + 3.54 \quad (r = 0.97) \qquad (17)$$

This equation makes it possible to predict σ^* values for untested groups. The standard deviation of predicted values is 0.20 or slightly less. In comparison, 26 groups which have been determined experimentally by two or more methods have median deviations of 0.01–0.07.[12]

In view of the diversity of hybridizations (te, tr, and di) of the carbon atoms, and the variation in electronegativity of atoms involved (C, N, O, F, Si, S, Cl, Br, I), the correlation is surprisingly good. Of the substituents which are seriously in error, hydrogen probably deviates because it is the only atomic substituent present. As such it may be more sensitive to the inaccuracies resulting from the approximations used. Resonance is probably responsible for the deviation of the phenylethynyl and carbomethoxy group. The present calculations are based solely on the σ system and ignore contributions from polarization of the π system. The result of such polarization is that phenylethynyl behaves more like phenyl (low electronegativity of sp^2 carbon) of which it is a vinylog and less like acetylene (higher electronegativity of sp carbon).

Resonance in methyl ethyl oxalate should tend to reduce the reactivity of the carbonyl carbon and therefore



$$\mathrm{CH_3O}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{C}}}}}\mathrm{COEt} \longleftrightarrow \mathrm{CH_3OC}{=}\overset{\mathrm{O}^{-(+)}}{\underset{\mathrm{O}^{+(-)}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{OEt}$$

reduce the experimentally determined value σ^*. Effects extraneous to the σ system (π delocalization, hydrogen bonding, hyperconjugation) may cause deviations which may be anticipated by inspection of the molecular structures involved.

In addition, all of the calculations involved here will be somewhat in error to the extent that the ground states of the esters upon which the calculations are based differ from the transition state involved in the reaction.

Methylene Dilution Factor.—It has been found[12] that the ratio of σ^* values of two groups R and RCH$_2$ is often about 2.8. It is possible to estimate this ratio by using the calculated group electronegativities of R and RCH$_2$. We have

$$\chi_{\mathrm{R}} = a'_{\mathrm{R}} + b'_{\mathrm{R}}\,\delta_{\mathrm{R}} \tag{18}$$

and

$$\chi_{\mathrm{CH_2}} = 7.44 + 4.33\delta_{\mathrm{CH_2}} \tag{19}$$

which yields

$$a'_{\mathrm{RCH_2}} = 0.8\left(\frac{7.44\,b'_{\mathrm{R}} + 4.33\,a'_{\mathrm{R}}}{4.33 + b'_{\mathrm{R}}}\right) + 1.60 \tag{20}$$

$$b'_{\mathrm{RCH_2}} = \frac{4.33\,b'_{\mathrm{R}}}{4.33 + b'_{\mathrm{R}}} + \frac{77123 + 17825b'_{\mathrm{R}}}{29075 + 8907b'_{\mathrm{R}}} \tag{21}$$

If we let $b'_{\mathrm{R}} = 5.2$ (the average of b' values listed in Table I) we obtain

$$a'_{\mathrm{RCH_2}} = 4.85 + 0.363a'_{\mathrm{R}} \tag{22}$$

$$b'_{\mathrm{RCH_2}} = 4.54 \tag{23}$$

Using eq 1 and 15–17, the charges R and RCH$_2$ induced on the carbethoxy group can be calculated

$$\sigma^*_{\mathrm{R}} = 0.95a'_{\mathrm{R}} - 7.04 \tag{24}$$

$$\sigma^*_{\mathrm{RCH_2}} = 0.37a'_{\mathrm{R}} - 2.83 \tag{25}$$

and σ^* estimated (eq 24, 25); the ratios of these

$$K = \sigma^*_{\mathrm{R}}/\sigma^*_{\mathrm{RCH_2}} \tag{26}$$

may be evaluated from various values of a'_{R}. The results are listed in Table II. For highly electronegative groups, R, the value of k approaches 2.8. As the electronegativity of R approaches that of the methylene group, the predicted value of k increases. Equation 26 becomes meaningless at electronegativity values <8.0 (just as the 2.8 rule is meaningless when discussing the σ^* values of methyl and ethyl groups).

TABLE II

a'_{R}	$\sigma^*_{\mathrm{RCH_2}}$
11.0	2.82
10.0	2.92
9.0	3.17
8.0	5.14

Isomerism and Electronegativity.—If electronegativity is assumed to be complete (p = 1.00), isomeric groups have identical calculated electronegativity values. This difficulty is overcome if partial equalization is allowed. For example, using p = 0.8, the calculated electronegativities of monofluorobutyl groups decrease as the fluorine atom is moved further from the point of attachment until the electronegativity of 4-fluorobutyl group is little different from that of the n-butyl group (Table III).

TABLE III

	a'	b'
1-Fluorobutyl	8.14	4.48
2-Fluorobutyl	7.82	4.42
3-Fluorobutyl	7.70	4.41
4-Fluorobutyl	7.65	4.41
Butyl	7.60	4.41

Conclusions

The results of the present study are of interest from two points of view. First, they offer a method of predicting σ^* fairly accurately in the absence of experimental data. Secondly, by correlating the large body of experimental data represented by σ^* values, they strengthen the argument that orbital electronegativity and electronegativity equalization provide a useful approach to the problem of charge distribution in molecules.