timate pathway for proton transfer.

The binding of Zn^{2+} distorts both the geometry and electronic structure of the directly ligated ImH very substantially. The energy of this polarized ImH is 4.9 eV higher than the optimized asymptotic ImH molecule. The NSE of the H bond is the resultant of large ionic and polarization effects, but it is difficult to assign weights to them because the direct ligation and polarization energy is much larger then the NSE and the calculations required to isolate the effects are not possible with present codes.

(e) $(ZnOH)^+(ImH)_2$. The perturbing effect of multiply charged cations will be ameliorated by other ligands attached to the cation. The $(ZnOH)^+$ molecule is intended to model such a case. As in the case of the Zn^{2+} perturbation, the maximum NSE for this perturber (14.6 kcal/mol) occurs for a reduced N1–NC distance of 5.495 bohr. Binding of the cation strengthens the H bond and tends to *reduce* the distance between the monomer fragments. In this case the ion-pair species is almost as bound as the neutral species. Using the ion-pair geometries, the excitation energy for proton transfer is only 3 kcal. Again, a substantial barrier, between 10–15 kcal, is obtained.

The $(ZnOH)^+$ fragment tends to withdraw electrons from the HA atom in the dimer comparably to the proton. The Zn^{2+} perturbation is calculated to be the largest as expected, but the loss of electron population at HA for the $ZnOH^+$ perturbation is 80% of the loss due to Zn^{2+} at the same N1–NC distance.

IV. Conclusion

The imidazole dimer H bond is significantly strengthened in all cases by the presence of cationic perturbers. Because of the aromatic character of the imidazole substantial population shifts are observed at atoms on the other side of the ring. The perturbation is even transmitted through the ring in a fashion to promote a positively cooperative effect on H-bonding energies and

distances for a chain of imidazoles. In all the singly charged species there is a substantial barrier to proton transfer and a double well is evident in all cases where the N1–NC distance is frozen at the value for the unperturbed dimer.

The double well has been sought in other hydrogen-bonded systems without success.[8,9] It is possible that stabilization of the ion-pair conformation results from the polarization of the fragments which is better described by the flexible CEP bases. The data for calculated polarizabilities for the larger aromatic bases are incomplete with regard to basis set dependence, and this will be investigated. The calculations with the Zn^{2+} perturber provide another clue to the origin of the double well. As the N1–NC distance is decreased, the barrier height decreases substantially. Qualitatively, this removal of the barrier can be seen as resulting from the overlap of two energy curves, due to the proton removal in the N1–H1 bond and proton binding in the H1–NC bond, crossing at lower energies as the N1–NC distance is shortened. In polymeric stabilized species the hydrogen bonds are shorter than they are for the dimer and a lower barrier would be expected.

The proton and $ZnOH^+$ perturbers resulted in a substantial reduction in the N1–NC distance. Such cationic perturbations could have significant biochemical consequences if they are not ameliorated by solvent effects. Cations mostly interact with the bases through their H_2O ligands, but there are reports of direct binding of, for example, a $(H_2O)_5 Mg^{2+}$ to a base in an oligomer of DNA.[20]

(20) A. H.-J. Wang, G. J. Quigley, F. J. Kolpak, G. van der Marel, J. H. van Boom, and A. Rich, *Science* **211**, 171 (1980).

Calculation of Group Electronegativity

John Mullay

Contribution from Atlas Powder Company, Atlas Research and Development Laboratory, Tamaqua, Pennsylvania 18252. Received May 24, 1985

Abstract: A simple relation is presented to calculate orbital electronegativity, viz., $\chi_{A,i} = \chi_{A,i}^0 (1 + 0.5\Sigma_{j \neq i}\delta_{A,j} + 1.5\delta_{A,i})$ (where A is the atom being considered, i is the bonding orbital on A that is being considered, $\chi_{A,i}^0$ is the orbital electronegativity of the neutral A atom, $\delta_{A,i}$ is the charge on A in orbital i, and the summation is over all bonds to A except i). This equation is a simple modification of a relation presented in an earlier paper. The $\delta_{A,i}$ are calculated assuming charge conservation and electronegativity equalization within each bond in the group. If A is the central atom of the group G (e.g., A is C in CH_3) and i is the orbital to be bonded then $\chi_G = \chi_{A,i}$ ($\delta_{A,i} = 0$). It is shown that this formalism leads to group electronegativity values that reproduce empirical trends more faithfully than methods using total electronegativity equalization and at least as well as other methods developed specifically to treat substituent effects.

Group electronegativity is a concept which has proven quite useful in chemistry and especially in organic chemistry. Lately there has been a significant amount of work done that deals with the evaluation and use of group electronegativity.[1-6] A method

(1) Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842.
(2) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111.
(3) Marriot, S.; Reynolds, W. F.; Taft, R. W.; Topsom, D. *J. Org. Chem.* **1984**, *49*, 959.
(4) Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101.
(5) (a) Inamoto, N.; Masuda, S. *Tetrahedron Lett.* **1977**, 3287. (b) Inamoto, N.; Masuda, S.; Tori, K.; Yoshimura, Y. *Ibid.* **1978**, 4547. (c) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003, 1007.
(6) (a) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. (b) Huheey, J. E. *Ibid.* **1966**, *70*, 2086.

was introduced in a recent paper[1] (herein called paper 1) that can be used to calculate both atomic and group electronegativity in a simple manner. The method requires only a screened nuclear charge obtained from modified Slater's rules, an effective principal quantum number and a value for fractional p character in the atomic orbital being considered. It was shown to effectively reproduce prevous results for the entire periodic table as well as treat charge effects in molecules and groups.

However, it had deficiencies, viz., it could not differentiate between isomeric groups (e.g., CH_2CH_2F and $CHFCH_3$), it could not easily handle multiple bonds, and as will be seen below it tends to overestimate the effect of other atoms or groups attached to the central atom of the group (e.g., the effects of the H atoms on C in CH_3). The present paper describes a simple modification

of this method which resolves all three issues. It is shown that this scheme produces electronegativity values that correlate very well with several currently used methods.[2-5] In addition to being able to reproduce trends in electronegativity simply, the present method also retains the ability to calculate atomic charge easily. It is also shown that these latter values follow trends that conform with chemical experience.

Comparisons are also made between several other calculational schemes and empirical data. It is shown that the present method is superior to other methods that rely on total electronegativity equalization.

Calculational Scheme

In paper 1 (eq 22 and 32) it was shown that the electronegativity of orbital i on atom A in a molecule or group can be given by

$$\chi_{A,i}(\delta_{A,i}) = \chi_{A,i}^0(1 + 1.5 \sum_{j \neq i} \delta_{A,j} + 1.5\delta_{A,i}) \qquad (1)$$

in which $\chi_{A,i}^0$ is the atomic electronegativity of orbital i on A, $\delta_{A,i}$ is the charge in orbital i, and the $\delta_{A,j}$ are the charges on the other bonded orbitals on A. Note that if $\delta_{A,i} = 0$ and A is the central atom of a group G (e.g., if A is C in CH_3) then eq 1 gives the group electronegativity of G.

In order to resolve the issues mentioned above it has been found necessary only to change the coefficient of the $\sum \delta_{A,j}$ term (i.e., the 1.5). Through comparison with the available data and with the aid of simple geometrical considerations (given in the Appendix) it was found that a more reasonable value for this term is 0.5. With this change eq 1 becomes

$$\chi_{A,i}(\delta_{A,i}) = \chi_{A,i}^0(1 + 0.5 \sum_{j \neq i} \delta_{A,j} + 1.5\delta_{A,i}) \qquad (2)$$

This equation becomes useful when combined with δ values obtained from the bond electronegativity equalization and bond charge conservation principles presented in paper 1. These can be stated as follows. For any molecule (M) or group (G) there are two constraints on each bond in M or G, i.e., for bond i between atoms A and B

$$\chi_{A,i}^0(1 + 0.5 \sum_{j \neq i} \delta_{A,j} + 1.5\delta_{A,i}) = \chi_{B,i}^0(1 + 0.5 \sum_{l \neq i} \delta_{B,l} + 1.5\delta_{B,i}) \qquad (3)$$

$$\delta_{A,i} + \delta_{B,i} = 0 \qquad (4)$$

where the charges have been explicitly expressed in terms of A or B for clarity. Equation 3 is the electronegativity equalization principle and eq 4 is the charge conservation principle. Note that there are two unknowns per bond (i.e., $\delta_{A,i}$ and $\delta_{B,i}$) and two equations. Thus each orbital charge is specified. Since the atomic charge is just the sum of the orbital charges, each atomic charge is also specified.

Two examples of the use of these equations will be presented for clarification. Consider the group CH_3. Since the hybridization used by the C and H respectively are sp^3 and s, $\chi_C^0 = 2.47$ and $\chi_H^0 = 2.08^1$ (note that specific reference to an orbital has been suppressed). The fact that there are three CH bonds would indicate three sets of equations like (3) and (4) to be solved. However, since all three bonds are equivalent there are only two independent equations, i.e.

$$2.47(1 + 0.5(2)\delta_C + 1.5\delta_C) = 2.08(1 + 1.5\delta_H) \qquad (5)$$

$$\delta_C + \delta_H = 0 \qquad (6)$$

remember that the δ_C and δ_H are orbital charges. Equations 5 and 6 are easily solved to give $\delta_C = -0.042$. Thus the electronegativity of CH_3 is given by

$$\chi_{CH_3} = 2.47(1 - 0.5(3)(0.042)) = 2.32 \qquad (7)$$

Consider also a group with multiple bonds, i.e., CCH. In this case the C atom uses sp and p orbitals in the σ and π bonds, respectively. For these cases $\chi_{C\sigma}^0 = 3.17$ and $\chi_{C\pi}^0 = 1.78$. Again $\chi_H^0 = 2.08$. This group has four bonds, i.e., 1 CC σ, two CC π,

Table I. Electronegativities of Isomeric Groups

group	χ_G	δ^a	$\chi_{G(Huheey)}^b$
$CFHCH_2CH_2CH_3$	2.585	0.093	2.528
$CH_2CFHCH_2CH_3$	2.381	-0.072	2.421
$CH_2CH_2CFHCH_3$	2.354	-0.094	2.381
$CH_2CH_2CH_2CH_2F$	2.351	-0.096	2.364
$CH_2CH_2CH_2CH_3$	2.350	-0.097	2.347

^{a} Charge on carbon atom to be bonded. ^{b} Data from ref 6.

Table II. C Atom Charges in *n*-Octyl Fluoride

atom^a	Jolly and Perry^b	present study
C_1	0.08876	0.042
C_2	-0.02595	-0.079
C_3	-0.03300	-0.094
C_4	-0.03344	-0.096
C_5	-0.03347	-0.097
C_6	-0.03351	-0.097
C_7	-0.03427	-0.100
C_8	-0.04655	-0.123

$^a C_1$ is bonded directly to the F atom. ^{b} Reference 7.

and one CH σ. However, since the two π bonds are equivalent there are only three sets of equations of the type (3) and (4). If for brevity we combine (3) and (4) for each bond we get the following three equations

$$2.69(1 + 0.5(2)\delta_\pi + 1.5\delta_\sigma) = 2.69(1 - 0.5(2)\delta_\pi + 0.5\delta_{CH} - 1.5\delta_\sigma) \qquad (8)$$

$$1.78(1 + 0.5\delta_\sigma + 0.5\delta_\pi + 1.5\delta_\pi) = 1.78(1 - 0.5\delta_\sigma - 0.5\delta_\pi + 0.5\delta_{CH} - 1.5\delta_\pi) \qquad (9)$$

$$2.69(1 - 0.5(2)\delta_\pi - 0.5\delta_\sigma + 1.5\delta_{CH}) = 2.08(1 - 1.5\delta_{CH}) \qquad (10)$$

solving these equations gives $\delta_\pi = -0.015$, $\delta_\sigma = -0.015$, $\delta_{CH} = -0.147$. This in turn gives $\delta_{C(1)} = -0.044$, $\delta_{C(2)} = -0.102$, $\delta_H = 0.147$ in which C(1) is the atom with one unbonded orbital. The electronegativity is given by

$$\chi_{CCH} = 2.69(1 + 3(0.5)0.102) = 3.10 \qquad (11)$$

Note two things regarding these calculations. First, they easily account for the multiple bonds between the two carbon atoms. Of course this scheme would work just as easily if the bent bond formalism were used. Second, the two carbon atoms are no longer equivalent with respect to charge. This property allows isomers to be distinguished. This difference arises because the difference in coefficients in eq 2 and 3 hinder complete transmission of charge along the molecule. Thus C(2) is able to attract a greater share of electrons from the H atom in the bond but does not transfer all of the charge to C(1). This characteristic allows for a resolution of both the isomer problem and also the difficulty in overestimating the effects of bonded atoms or groups. Whether attached groups are accounted for properly can be seen from the group electronegativity comparisons in Tables III and IV.

Note also that complete electronegativity equalization is not achieved throughout the group. This is because relation 3 holds only for the atoms involved in an individual bond. This partial equalization allows for the ability to handle multiple bonds and also for the differences in charge on C(1) and C(2).

Results and Discussion

Table I presents results that illustrate the effectiveness of the present formulation in treating different isomers. It can be seen that the charge on the C atom to be bonded follows the normally accepted trend. It is also clear from the results that electronegativity trends are as expected.

Table II compares atomic charge results obtained from the present scheme to values derived from an empirical method which was calibrated with core binding energies.[7] Again it can be seen that inductive effects are handled in a reasonable manner.

(7) Jolly, W. L.; Perry, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442.

Table III. Correlation of Calculated Group Electronegativity and "Mutually Consistent" Values

group	Wells[a]	Huheey[b]	Sanderson[c]	Bratsch[d]	paper 1	Marriot[e]	ι[f]	present study
CH_3	2.3	2.27	2.33	2.23	2.17	0.17	2.14	2.32
$CHCH_2$	(3.0)	2.41	2.34		2.29	0.17	2.34	2.56
CCH	(3.3)	2.90	2.40		2.70	0.28	2.52	3.10
CN	3.3	3.84	2.68	2.77	3.69	0.31	2.61	3.46
CO_2H	(2.85)	3.52	2.85	2.80	3.09	0.18	2.36	3.15
CF_3	3.35	3.46	3.45	3.49	3.46	0.17	2.47	3.10
NH_2	3.35	2.61	2.48	2.42	2.39	0.33	2.47	3.15
NMe_2	(3.0)	2.40	2.39		2.26	0.34	2.48	3.24
NO_2	3.4	4.83	3.28	3.30	4.23	0.40	2.75	4.08
OH	3.7	3.51	2.80	2.68	2.85	0.43	2.79	3.97
OCH_3	(3.7)	2.68	2.51	2.44	2.42	0.44	2.82	4.03
SiH_3	(2.2)	2.21	2.18	2.12	2.04	-0.13	1.79	1.97
SH	(2.8)	2.32	2.47	2.37	2.27	0.12	2.17	2.42
corr coef		0.53	0.49	0.52	0.48	0.85	0.94	0.89

[a] Reference 2. [b] Reference 6. [c] Reference 15 and relation $\chi = (0.21S + 0.77)^2$ where S is the geometric mean of Sanderson's stability ratios for the atoms in the group. [d] Reference 4. [e] Reference 3. [f] Reference 5.
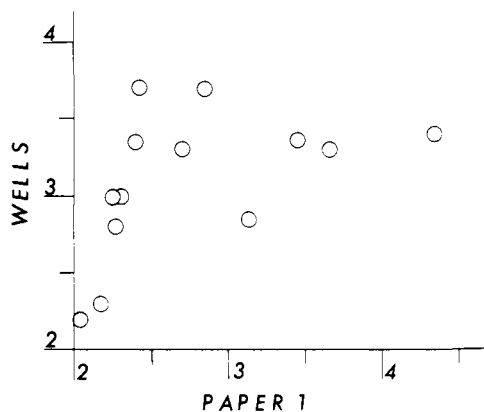

Figure 1. Wells electronegativity values vs. those calculated from paper 1 plus the Huheey method.

Various methods for obtaining group electronegativity and inductive substituent parameters are compared in Table III. The first set of values presented in the table (Wells) was obtained from a survey of various experimental methods of obtaining electronegativity values.[2] It represents about the best currently available from experimental correlations. Note that the values in parentheses are much more uncertain than the others. Since these values represent about half of the groups in the table, a good correlation with this total set of values may not be desirable for guaging the merit of a potential calcualtional scheme on an absolute basis. However, relative fits with these data should give valid comparisons. The particular groups used were chosen to allow the maximum number of recent schemes to be compared on an equal basis. For this purpose a correlation coefficient was calculated for each method as compared to the mutually consistent values.

It can be seen that three of the methods give relatively poor correlations (i.e., Huheey, Bratsch, and paper 1). Figure 1 presents a plot of the data derived from paper 1 using the method for treating multiple bonds as given by Huheey[6] vs. the Wells data. All of these schemes are based on complete equalization of the electronegativities of all of the atoms in the molecule. Apparently in all cases the effects of the atoms attached to the central atom are overestimated. Note, for example, the results for NH_2 and NO_2.

As shown in the Appendix, the scheme in paper 1 is based on implicit assumptions which cause an overestimation of attached atom effects. Huheey's method is very similar to the one given in paper 1. In addition, the equation used to calculate the Bratsch values (eq 2 in ref 4) is exactly the same as that used in paper 1 (eq 43). In fact the two schemes differ only in the coefficient of the electron repulsion term (Bratsch uses 1.0 instead of 1.5). All three methods then would be expected to have the same problem of overestimation of repulsion effects. This of course would explain the poor correlation in all three cases.

Table IV. Comparison of ι, Marriot Scale, and Present Results

group	ι[a]	Marriot[b]	present results
CH_2Me	2.15	0.16	2.35
$CHMe_2$	2.15	0.15	2.38
CMe_3	2.16	0.16	2.41
CH_2NH_2	2.18	(0.15)	2.42
CH_2OH	2.22	(0.17)	2.50
CH_2F	2.24	(0.18)	2.55
CH_2CN	2.20	(0.23)	2.48
CHO	2.39	0.14	2.89
$COMe$	2.39	0.14	2.93
CO_2Me	2.37	0.19	3.16
$CONH_2$	2.30	0.14	3.06
$NHMe$	2.50	0.34	3.19
$NHCHO$	2.50	0.39	3.30
$NHNH_2$	2.50	0.34	3.34
NCO	2.83	0.42	4.20
$OCOMe$	2.80	0.46	4.18
F	3.10	0.52	4.73
SMe	2.16	0.10	2.46
corr coef[c]		0.932	0.975

[a] Reference 5. [b] Reference 3. [c] Calculated with results from both Tables III and IV.

The other three methods correlate much better with Wells' data. The Marriot scale[3] involves an interesting purely theoretical approach to obtaining electronegativities for groups. The actual values used are the atomic electron population on the H atom in HG compounds (where G is the group being considered). These were obtained from ab initio calculations using a Mulliken population analysis. The method of course has the drawback of requiring the necessary theoretical results. It can be seen that both the present formulation as well as the ι values give a better fit with the empirical data. In addition, both of these latter methods involve much less calculational effort and expense.

The ι scale represents the best correlation.[5] This scale has been developed by using extensive correlations with NMR data for a wide variety of chemical groups. As with Wells its strong empirical base makes it well suited for use as a reference set. The high degree of correlation between the two sets is not unexpected. The scale has been modeled on a method developed by Gordy[8] and Wilmhurst[9] and adapted by Inamoto and co-workers to reproduce substituent group effects.[5] The present method, while not correlating as well as ι with this set of data, does perform better than the other methods. In addition it is simple to use and since it gives explicit atomic charges is more versatile than the Inamoto method.

Results of a more extensive correlation between ι and both the Marriott and the present scheme are given in Table IV. The data base available is limited by the Marriott scale. The values used to obtain the correlation coefficients given in Table IV are con-

(8) Gordy, W. *Phys. Rev.* **1946**, *69*, 604.
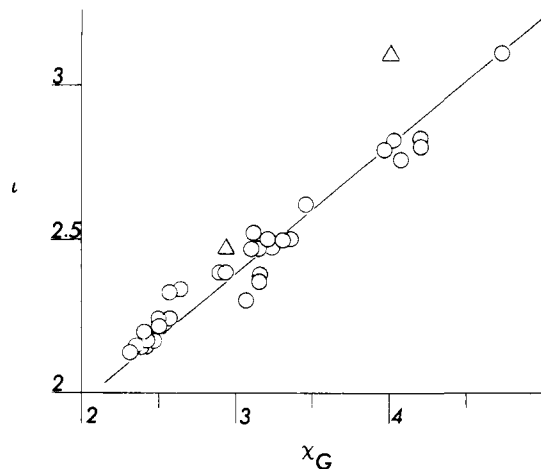(9) Wilmhurst, J. K. *J. Chem. Phys.* **1957**, *27*, 1129.

Figure 2. ι vs. χ_G (from eq 2). Triangular points are for pure p orbitals on the F atom.
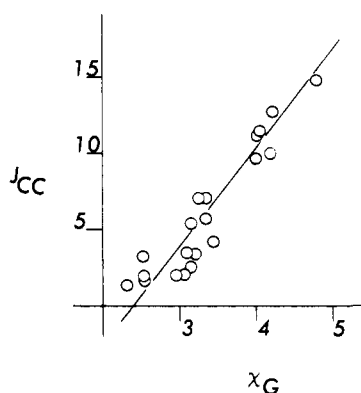

Figure 3. χ_G (from eq 2) vs. J_{CC} for monosubstituted benzenes.

tained in both Tables III and IV. Note that the revised Marriott values were used for this correlation. It can be seen that there is a high degree of correlation in both cases. The present method, however, comes out better. The relation between ι and present values is also shown in Figure 2 and given by the following equation

$$\iota = 2.42\chi_G - 2.77 \tag{12}$$

Note that the χ_G values given in Table IV for F-containing groups used 10% s character for the F bonding orbital. Figure 2 also presents data for these groups with 0% s as is normally assumed. It can be seen that this would lead to a much poorer relationship. Thus it appears likely that F uses some s hybridization in these groups. This result is consistent with other work.[10,11]

Figure 3 presents the relationship between present electronegativity values from Tables III and IV for groups containing first-row elements as central atoms and NMR coupling constants $^1J_{CC}$ (ortho-ipso) for monosubstituted benzenes from ref 3. Again it can be seen that the correlation is good. This relationship has a correlation coefficient of 0.94 and is given by the following equation

$$J_{CC} = 6.45\chi_G - 15.42 \tag{13}$$

It can be seen from these comparisons that the scheme presented here is able to reproduce group electronegativity values much better than the one presented in paper 1 and at least as well as currently accepted methods.

(10) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.
(11) Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219.

Summary

The general method derived in paper 1 for calculating atomic and group electronegativity is modified to yield more reasonable group electronegativity values. In contrast to the previous method the present scheme allows the calculation of groups with multiple bonds in a natural manner. Further it resolves the problem of distinguishing between the electronegativity of isomers. The main relationship is eq 2 with the present modification being the adjustment of the coefficient of the summation term to 0.5 instead of the former 1.5 value. Both bond electronegativity equalization and charge conservation principles are retained in the present paper (eq 3 and 4). It is shown that results obtained with this method correlate well with accepted electronegativity values and with NMR data.

Appendix

The use of the coefficient 1.5 for the $(\sum_{j \neq i}\delta_{A,j})$ term in eq 1 involves at least two major assumptions, viz.:

(1) Electron transfer in each bond j is complete. This means that electrons withdrawn from atom A in bond j are completely removed to infinity or electrons accepted by A in j are brought from infinity. This, of course, is incorrect since the electrons go to or come from the atom bonded to A.

(2) The repulsions between electrons in orbital i and those in orbital j are the same as those for electrons in i. This is also incorrect since electron pairs in different bonds tend to distribute themselves so as to minimize repulsions whereas electrons within an orbital are on the average closer together.[12,13] Since in the present scheme the charge coefficients of the j-bonded orbitals represent this interorbital repulsion, it should be less than the 1.5 value used for the intraorbital repulsion.

The first assumption can be made more reasonable quite easily. This can be done simply by taking an average of the case representing complete transfer and that representing no transfer. In order to do this eq 1 must be expanded to its full form

$$\chi_{A,i} =$$
$$B_A(i) + A_A/2 - N_M A_A - \sum_{j \neq i} A_A(1 - \delta_{A,j}) - A_A(1 - \delta_{A,i}) \tag{14}$$

where $B_A(i)$ is the attraction of the core of A for an electron in i, A_A is the electron repulsion term, N_M is the number of unbonded electrons, and the summation is over all bonded orbitals aside from i. For each orbital j there is an $A_A(1 - \delta_{A,j})$ term. Since A_A is the repulsion term, complete removal implies A_A goes to 0. Likewise, the no-transfer situation implies that A_A goes to A_A, i.e., no change. The average of these two situations is simply the case in which removal of an electron from atom A is expressed as A_A going to $A_A/2$. With both electrons on A the repulsion remains $2A_A$. However, with both removed it now becomes A_A (i.e., $2(A_A/2)$). Thus the repulsion term becomes $A_A(1.5 - 0.5\delta_{A,j})$.

Reduced electron transfer can be accounted for by using a factor $K < 1$ in the repulsion term, i.e., $KA_A(1.5 - 0.5\delta_{A,j})$. K can be chosen in a number of ways. An obvious one in this case would be to fit calculated group electronegativity data to an accepted scale. However, K would then be dependent on the scale chosen. Since this is not a well-resolved issue at present it will not be used in the present paper. A value will be chosen in a manner which keeps the scheme simple while at the same time keeping K in a reasonable range.

To do this the electrons in the bonding orbital will be considered points on a sphere[14] with repulsion being inversely related to distance between the points. K would be largest for the most repulsion and smallest for the least. The least repulsion would be for electrons in two sp hybrid orbitals in which the points would be on opposite sides of the sphere. In this case the distance between the electrons in the two orbitals would be $2r$ where r is the radius of the sphere. Since the angle between bonds is not usually $<90°$,

(12) Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295.
(13) Coulson, C. A. "Physical Chemistry"; Eyring, H., D. Henderson, D., Jost, W., Eds.; Academic Press: New York, 1970; Vol. 5, pp 287–367.
(14) Bartell, L. S.; Barshod, Y. Z. *J. Am. Chem. Soc.* **1984**, *106*, 7700.

this case would represent the largest value for K. In this case the distance would be $2^{1/2}r$. Thus interelectron distance would vary between $2^{1/2}r$ and $2r$. If repulsion within an orbital is inversely proportional to r, i.e., $A_A \propto 1/r$, then approximate limits for K are $0.71 \geq K \geq 0.5$ (i.e., $1/2^{1/2} \geq K \geq 1/2$).

The value $K = 0.67$ falls within these bounds and when substituted into the repulsion term gives $A_A(1 - 0.33\delta_{A,j})$. This yields

eq 2 when combined with (14) and the relations of paper 1. The good correlation with other schemes and the simplicity of (2) suggest that the value is reasonable. Further correlations will be necessary to verify this estimate.

(15) Sanderson, R. T. "Chemical Bonds and Bond Energy", 2nd ed.; Academic Press: New York, 1976; p 41.

SINDO1 Study of Photochemical Reaction Mechanisms of Diazirines

Peter L. Müller-Remmers and Karl Jug*

Contribution from Theoretische Chemie, Universität Hannover, 3000 Hannover 1, Federal Republic of Germany. Received June 1, 1984

Abstract: The photochemical reaction mechanisms of diazirine, 3,3-dimethyldiazirine, and 3-formyldiazirine were studied with the semiempirical MO method SINDO1. The properties of equilibria amd transition states as well as diradical and zwitterionic intermediates were calculated on configuration interaction (CI) potential surfaces. It is shown that the substituents have a decisive influence on the relative energy of the singlet and triplet surfaces to the ground state. Therefore, localized excitations can initiate reactions which lead primarily either to carbenes or to diazomethanes. A classification of the photochemical reaction mechanisms of diazirines is discussed. Good agreement is obtained with available experimental results.

1. Introduction

The discovery of the diazirines[1,2] in 1960/61 concluded the discussion about the open or cyclic structure of diazo compounds.[3] The interest in the research in this field of heterocycles is undiminished even today.[4,5] There are still controversies about the photolytic and thermolytic reaction mechanisms of diazirines.[4,6,7] It is known that the cyclic compounds are experimentally more easily accessible and thermodynamically more stable that their linear isomers.
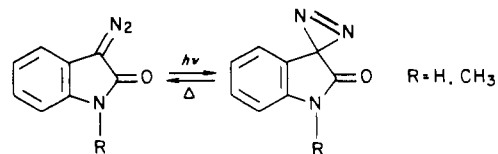
The difficulties with the interpretation of reaction pathways may be discussed in a few examples. Amrich and Bell[8] obtained 20% diazomethane in the photolysis of diazirine in the gas phase. In the photolysis of diazirine in a $^{15}N_2$ matrix, Moore and Pimentel[9] found diazomethane, which originates from the reaction of methylene with the $^{15}N_2$ matrix, as secondary product. Frey[10] concludes that the diazomethane generated in the gas phase must appear through intersystem crossing (ISC) in its first triplet state.

3-Chloro-3-methoxydiazirine[11] and 3,3-dimethyldiazirine[12] decompose thermally in first-order reactions into nitrogen and the corresponding carbenes and their conversion products. It is not clear whether the ring bonds are cleaved in a synchronous or sequential homolytic or heterolytic fashion and whether transition states or intermediates have diradical or zwitterionic character.

High preexponential factors would suggest acyclic diradical transition states. It is an open question why linear diazo compounds are not found as products.

Schmitz[3] states that the diazirine is destabilized by an α-keto group compared to the alkyl-substituted compound. Thus α-ketopentamethylenediazirine loses nitrogen already at 40 °C whereas pentamethylenediazirine requires 160 °C for the analogous reaction. Liu[4] postulates very generally ionic transition states for the decomposition of diazirines.

An interesting, but mechanistically not clarified topic is the chemistry of α-diazoamides. They are representatives of those linear diazo compounds which are known to lead photolytically to a moderate yield of ring closure. Voigt and Meier[13] report in this context an interesting equilibrium in the photochromic system

3-diazo-2-oxoindoline/2-oxospiro[diazirine-3,3'-indoline]. The linear diazo compound can be converted to the cyclic form by irradiation, and the latter thermally reverts to the former after a short time.

Theoretical investigations of diazirines are scarce. Among them are studies on the vertical excitation energies of diazirine, diazomethane,[14-18] and 3,3-difluorodiazirine.[15,16] Hoffmann[18] examined the photochemical behavior of diazirine with the extended Hückel method. Later Devaquet[17] studied the same molecule by

(1) S. R. Paulsen, *Angew. Chem.* **72**, 781 (1960).
(2) E. Schmitz and R. Ohme, *Chem. Ber.*, **94**, 2166 (1961).
(3) E. Schmitz, *Angew. Chem.*, **76**, 197 (1964).
(4) M. T. H. Liu, *Chem. Soc. Rev.*, **11**, 127 (1982).
(5) D. P. Cox, R. A. Moss, and J. T. Terpinski, *J. Am. Chem. Soc.*, **105**, 6513 (1983).
(6) W. Kirmse, "Carbene Chemistry", Vol. I, 2nd ed., Academic Press, New York and London, 1971.
(7) M. Nastasi and J. Streith in "Rearrangements in Ground and Excited States", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980.
(8) M. J. Amrich and J. A. Bell, *J. Am. Chem. Soc.*, **86**, 292 (1964).
(9) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **41**, 3504 (1964).
(10) M. H. Frey, *Adv. Photochem.*, **4**, 225 (1966).
(11) N. P. Smith and I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 213 (1979).
(12) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc. III*, 3865 (1962).

(13) E. Voigt and H. Meier, *Chem. Ber.*, **108**, 3326 (1975).
(14) S. P. Walch and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 5319 (1975).
(15) M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *J. Chem. Phys.*, **51**, 45 (1969).
(16) K. Vasuvedan and W. E. Kammer, *Chem. Phys.*, **15**, 103 (1978).
(17) B. Bigot, R. Ponec, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100**, 6575 (1978).
(18) R. Hoffmann, *Tetrahedron*, **22**, 539 (1966).