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An MO Approach to the Interpretation of Organic Mass Spectra. I. Relative Bond Energy of the Molecule Ion by the Extended Hückel Method

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A method of comparing the relative bond energies is applied to the interpretation of the simple cleavage and the McLafferty rearrangement reactions in organic mass spectrometry. A qualitative correlation between the relative bond energy and the charge density at the highest occupied orbital is found. The behavior of the highest occupied and some lower vacant orbitals is discussed.

In the molecular orbital approaches to the interpretation of organic mass spectra, many papers have appeared[1-6] discussing only the relationship between the scission probability and the charge density at the highest occupied (HO) orbital of the molecule ion. Some[2,3,6] of these studies explain well the experimental data. However, some explanation is needed for the correlation between the bond energy and the charge distribution at the HO orbital, since apparently the bond energy is governed not only by the electron(s) of the HO orbital, but by all the electrons included. Besides, it has been shown that σ-π interactions play a significant role in the organic reactions.[7,8] The characteristic allylic cleavage and the McLafferty rearrangement reactions give evidence of direct and/or spacial σ-π interactions in the fragmentation processes of the electron-impact state. Some authors[9,10] have pointed out the significance of the excitation of electrons to some vacant orbitals.

Our object is to solve those problems by using a simple expression for the correlation between the electronic state and the bond energies, including all the valence electrons. In this paper we will adopt the extended Hückel (EH) MO theory,[11] which has the simplest form as an MO for valence electrons.

Method

The bond energies may vary according to the electronic state. Though the electronic state for the molecule ion remains an unsolved problem,[9,10] for the sake of simplification, we will consider the states in which a single electron occupies the HO orbital and will consider that only one electron is excited in a vacant orbital from the HO orbital. (The extension to multi-excited states may be straightforward.)

The total energy (E^j) is expressed by using the LCAO wave functions to give the Coulomb (H_{pp}) and the exchange (B^j_{AB}) terms. If the unpaired electron occupies the jth orbital, E^j is calculated by means of the following equations:

$$E^j = \sum_p \Big[\sum_i^{occ-1} 2(C_p{}^i)^2 + (C_p{}^j)^2\Big] H_{pp} + \sum_{\mathrm{A>B}} B^j_{\mathrm{AB}} \tag{1}$$

$$B^j_{\mathrm{AB}} = \sum_p^{\mathrm{onA}} \sum_q^{\mathrm{onB}} K(H_{pp}, H_{qq}) \Big(4 \sum_i^{occ-1} C_p{}^i C_q{}^i + 2C_p{}^j C_q{}^j\Big) \qquad (\mathrm{A} \neq \mathrm{B}) \tag{2}$$

where H_{pp} is the Coulomb integral and where $C_p{}^i$ is the coefficient for the atomic orbital (ϕ_p) of the ith wave function. *occ* is the number of the occupied orbitals in the ground state of the molecule. $\sum_p^{\mathrm{onA}}$ indicates the summation on the atom, A. $K(H_{pp}, H_{qq})$ represents the function which gives the approximate exchange integral; *e.g.*, in the present calculation, we adopted the Wolfsberg-Helmholtz's approximation,[12] $0.5K(H_{pp}+H_{qq})S_{pq}$, where S_{pq} is the overlap integral between ϕ_p and ϕ_q and where the value of K is 1.75, according to Hoffmann's result.[11]

The exchange term (B^j_{AB}) is considered to express the relative bond energy[13] between two atoms, A and B. The Coulomb integrals are usually approximated by the negative values of the valence-state ionization potentials (VSIP) in terms of eV. Therefore, B^j_{AB} has the unit of eV, where a negative value indicates a bonding character and a positive value, an antibonding character.

A neglect of the explicit consideration of electron-electron repulsions causes, in some cases, an inversion of the orbitals which may play an important role in the chemical reaction.[14,15] The iterative extended Hückel (IEH) method for the self-consistent charge distribution has been reported[14-18] to improve the

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[1] N. D. Coggeshall, *J. Chem. Phys.*, **30**, 593 (1959).

[2] K. Fueki and K. Hirota, *Nippon Kagaku Zasshi*, **81**, 212 (1960).

[3] K. Hirota and Y. Niwa, *J. Phys. Chem.*, **72**, 5 (1968).

[4] J. C. Lorquet, *Mol. Phys.*, **9**, 101 (1965).

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[7] S. L. Altmann, *Proc. Roy. Soc. Ser.*, *A*, **210**, 327 (1952).

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[9] R. C. Dougherty, *ibid.*, **90**, 5780 (1968).

[10] R. A. W. Jonstone and S. D. Ward, *J. Chem. Soc.*, *C*, **1968**, 1805.

[11] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[12] M. Wolfsberg and L. Helmholtz, *ibid.*, **20**, 837 (1952).

[13] K. Shimizu, K. Miyamichi, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **90**, 1206 (1969).

[14] T. Yonezawa, K. Shimizu, H. Morimoto, and H. Kato, *ibid.*, **90**, 1196 (1969).

[15] O. Yamamoto, H. Kato, and T. Yonezawa, *ibid.*, **91**, 23 (1970).

[16] L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965).

[17] D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966).

[18] R. Rein, N. Fukuda, H. Win, and G. A. Clarke, *ibid.*, **45**, 4743 (1966).

faults of the original EH method. Besides, the converged Coulomb integrals which are obtained from the calculation of the IEH method for small molecules are shown[14] to be successfully applicable, as parameters, to large molecules. This enables self-consistent calculations for such large molecules as steroids by medium-sized computers.

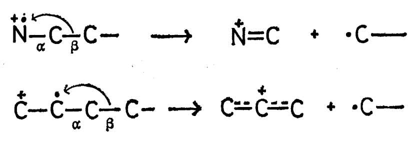
The iteration was carried out according to the following equation:

$$H_{rr}(n+1) = H_{rr}(0) - (Z_X - M_X(n))(I_{pr} - A_r) \qquad (3)$$

Here, $H_{rr}(n+1)$ is the Coulomb integral at the $(n+1)$-th turn. X indicates the atom to which the atomic orbital (ψ_r) belongs, Z_X is the number of the valence electrons, and $M_X(n)$ is the atomic population of the nth turn. A_r is the electron affinity of ψ_r.

Results and Discussion

Energetic Consideration on Simple Cleavage. It has been established[19] that, under electron-impact, amines and unsaturated hydrocarbons go mainly through the paths which are shown by a "fishhook" as below:



For convenience, we call this type of simple cleavage "β-bond cleavage." It has been reported[6] for alkylamines that there is a quantitative correlation between the scission probability and the charge density at the HO orbital of the molecule ion. Our first purpose is to find out the relationship between the relative bond energy and such a charge density. If we can determine this relationship for these simple compounds, it can probably be adapted to discussions of the fragmentation mechanisms of their derivatives.

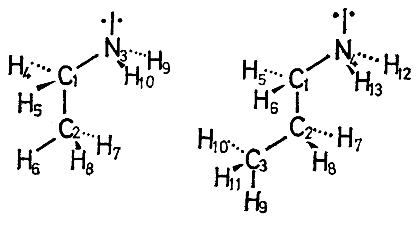
The relative bond energies of ethylamine, n-propylamine (by the IEH method), and 1-butene (by the EH method) are calculated. The input parameters are as follows:

Atom	H	C		N	
ψ	1s	2s	2p	2s	2p
$H_{rr}(0)=-I_{pr}$(eV)[20]	−13.60	−21.43	−11.42	−27.50	−14.49
A_r(eV)[20]	0.75	9.26	0.58	13.79	1.58

and the bond lengths are, C–H 1.09, N–H 1.02, C=C 1.35, =C–C 1.50, C–C 1.54, and C–N 1.50 (in Ångstroms).

In Tables 1, 2, and 3, we set the conformation of the amines so that the lone pair is *trans* (Conformation *A*), perpendicular (Conformation *B*), and *cis* (Conformation *C*) to the β bond respectively. For each electronic state of the electron-impact ion, the difference in energy from its closed-shell ground state (which is referred to as the normal state), that is, $B^j_{AB} - B^{normal}_{AB}$, is listed. In all the conformations, the

Table 1. The electronic state of molecule ions and relative bond energies (eV) of amines (Conformation *A*)



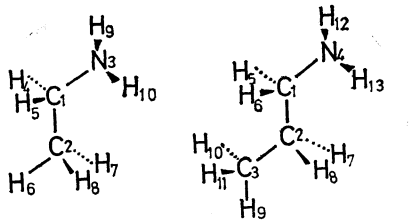
Ethylamine

Bond	normal state	$j=10$ (HO)	$j=11$ (LV)	$j=12$
C_1–C_2	−17.23	0.75	1.88	19.55
C_1–N_3	−15.70	−0.80	15.87	−1.12
C_1–H_4	−21.18	0.05	0.23	1.62
C_2–H_6	−19.82	0.02	0.33	0.29
C_2–H_7	−19.79	0.01	0.05	1.38
N_3–H_9	−20.27	−0.01	0.71	0.34

n-Propylamine

Bond	normal state	$j=13$ (HO)	$j=14$ (LV)	$j=15$
C_1–C_2	−18.07	0.87	1.11	14.49
C_1–N_4	−15.63	−0.85	13.08	−0.29
C_1–H_5	−21.14	0.05	0.19	1.32
C_2–C_3	−16.38	0.06	2.07	4.40
C_2–H_7	−20.57	0.00	0.08	0.32
C_3–H_9	−19.88	0.05	0.11	1.73
C_3–H_{10}	−19.87	0.01	0.06	0.01
N_4–H_{12}	−20.28	0.00	0.55	0.51

Table 2. The electronic state of molecule ions and relative bond energies (eV) of amines (Conformation *B*)



Ethylamine

Bond	normal state	$j=10$ (HO)	$j=11$ (LV)	$j=12$
C_1–C_2	−17.15	−0.06	0.94	12.59
C_1–N_3	−15.93	−0.76	14.00	−2.72
C_1–H_4	−21.12	0.37	0.99	2.17
C_1–H_5	−21.24	0.44	0.87	2.57
C_2–H_6	−19.82	0.02	0.37	0.14
C_2–H_7	−19.81	0.04	0.08	0.87
C_2–H_8	−19.79	0.01	0.03	1.86
N_3–H_9	−19.14	−0.02	0.93	0.88
N_3–H_{10}	−19.17	−0.03	0.86	3.41

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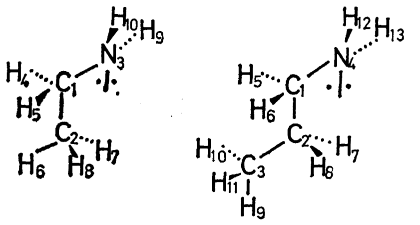
[19] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Fransisco, California.

[20] H. O. Pritchard and H. A. Skinner, *Trans. Faraday Soc.*, **49**, 1254 (1953).

n-Propylamine

Bond	normal state	$j=13$ (HO)	$j=14$ (LV)	$j=15$
C_1–C_2	−17.99	−0.03	−0.08	11.69
C_1–N_4	−15.87	−0.75	13.06	1.63
C_1–H_5	−21.07	0.36	0.91	2.38
C_1–H_6	−21.19	0.43	0.85	2.40
C_2–C_3	−16.39	0.02	2.17	0.59
C_2–H_7	−20.59	0.01	0.03	0.44
C_2–H_8	−20.57	0.01	0.07	1.25
C_3–H_9	−19.88	0.00	0.02	1.05
C_3–H_{10}	−19.87	0.01	0.05	0.05
C_3–H_{11}	−19.87	0.00	0.06	0.10
N_4–H_{12}	−19.13	−0.03	0.68	0.26
N_4–H_{13}	−19.19	−0.02	0.64	3.24

TABLE 3. THE ELECTRONIC STATE OF MOLECULE IONS AND RELATIVE BOND ENERGIES (eV) OF AMINES (CONFORMATION *C*)



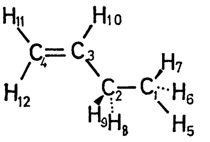
Ethylamine

Bond	normal state	$j=10$ (HO)	$j=11$ (LV)	$j=12$
C_1–C_2	−17.04	0.63	3.06	17.64
C_1–N_3	−15.35	−0.83	13.56	1.81
C_1–H_4	−21.28	0.07	0.11	2.15
C_2–H_6	−19.81	−0.02	0.28	0.04
C_2–H_7	−19.80	−0.01	−0.03	1.24
N_3–H_9	−20.29	0.01	0.69	−0.07

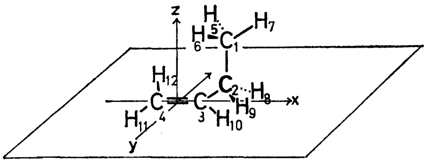
n-Propylamine

Bond	normal state	$j=13$ (HO)	$j=14$ (LV)	$j=15$
C_1–C_2	−17.90	0.73	2.13	13.44
C_1–N_4	−15.30	−0.90	11.75	3.37
C_1–H_5	−21.22	0.06	0.09	1.39
C_2–C_3	−16.38	0.01	1.96	4.91
C_2–H_7	−20.58	−0.01	−0.02	0.12
C_3–H_9	−19.88	0.02	0.05	1.90
C_3–H_{10}	−19.87	0.00	0.02	0.00
N_4–H_{12}	−20.29	0.01	0.53	0.02

TABLE 4. THE ELECTRONIC STATE OF MOLECULE ION AND RELATIVE BOND ENERGIES (eV) OF 1-BUTENE



Conformation *D*



Conformation *E*

Conformation *D*

Bond	normal state	$j=12$ (HO)	$j=13$ (LV)	$j=14$
C_1–C_2	−17.71	−0.34	−0.69	18.09
C_1–H_5	−19.92	0.00	0.00	0.66
C_1–H_6	−20.01	0.26	0.52	1.43
C_2–C_3	−20.39	−1.25	−1.89	−2.74
C_2–H_8	−20.08	1.21	2.22	2.99
C_3–C_4	−32.50	3.34	14.13	6.97
C_3–H_{10}	−21.05	0.00	0.00	0.88
C_4–H_{11}	−20.37	0.00	0.00	0.05
C_4–H_{12}	−20.32	0.00	0.00	0.07

Conformation *E*

Bond	normal state	$j=12$ (HO)	$j=13$ (LV)	$j=14$
C_1–C_2	−17.26	1.33	2.51	18.23
C_1–H_5	−19.97	0.08	0.15	0.91
C_1–H_6	−19.92	−0.02	−0.08	0.34
C_1–H_7	−19.94	0.16	0.33	1.64
C_2–C_3	−20.30	−0.66	−0.96	4.10
C_2–H_8	−20.42	0.24	0.47	0.44
C_2–H_9	−20.31	0.00	−0.06	0.19
C_3–C_4	−32.58	3.24	13.89	5.72
C_3–H_{10}	−20.97	0.02	0.04	0.82
C_4–H_{11}	−20.31	0.06	0.12	0.40
C_4–H_{12}	−20.37	0.09	0.19	1.18

relative bond energies of the C–C bonds are lower than those of C–N in the closed-shell ground state. These are qualitatively in the same inclination as the experimental values. (They are not directly comparable to the experimental values, since the energies of the electronic and internuclear interaction among all non-bonding atoms are not taken into account in determining the relative bond energy.) On the other hand, in the *A* and *C* conformations, the removal of one electron from the HO orbital ($j=10$ and 13 respectively for ethylamine and *n*-propylamine) causes the energy of the β C–C bond to be higher than that in the closed-shell ground state, while the α C–N bond is strengthened. In the *B* conformation, however, this inclination is not clearly observed. Instead, the β C–H bond is weakened. It should be pointed out that the β C–H bond *trans* to the lone pair is more weakened than that of *cis*. These results indicate that the conformation of the nitrogen atom plays an important role in the strength of the β bond. This will be discussed in the next section.

Though it is well known that the Hückel method is not well adapted to the study of excited states, the general behavior of the excited molecule ion is considered to be significant. In all conformations, the excitation to the lowest vacant (LV) orbital weakens the α C–N bond. Usually, however, the *M*-NH_2 peaks are not intensely observed in alkylamines. It should also be pointed out that the positive charge remains not on the fragment of NH_2 but on the alkyl site, judging from Stevenson's rule.[21] That is, the

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[21] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

TABLE 5. COEFFICIENTS OF HO AND SOME LV ORBITALS OF ETHYLAMINE

Conformation	Wave function	C$_1$ 2s	C$_1$ 2p_x	C$_1$ 2p_y	C$_1$ 2p_z	C$_2$ 2s	C$_2$ 2p_x	C$_2$ 2p_y	C$_2$ 2p_z
A	$j=10$(HO)	−0.003	−0.030	−0.180	0.000	0.070	0.058	0.235	0.000
	$j=11$(LV)	0.144	0.910	0.421	0.000	0.050	0.070	0.249	0.000
	$j=12$	−0.174	−0.364	0.969	0.000	0.094	−0.094	1.018	0.000
B	$j=10$(HO)	0.027	0.090	0.041	−0.163	−0.006	−0.030	−0.041	0.028
	$j=11$(LV)	0.130	0.883	0.474	0.044	0.049	0.050	0.321	0.030
	$j=12$	−0.140	−0.388	0.820	0.020	0.070	−0.121	0.881	−0.075
C	$j=10$(HO)	0.035	0.099	−0.131	0.000	0.062	0.016	0.177	0.000
	$j=11$(LV)	0.137	0.849	0.541	0.000	0.052	0.030	0.391	0.000
	$j=12$	−0.186	−0.547	0.895	0.000	0.098	−0.105	0.962	0.000

Conformation	Wave function	N$_3$ 2s	N$_3$ 2p_x	N$_3$ 2p_y	N$_3$ 2p_z	Hydrogens H$_4$	Hydrogens H$_5$
A	$j=10$(HO)	0.156	0.013	0.939	0.000	−0.048	−0.048
	$j=11$(LV)	−0.143	0.934	0.060	0.000	0.146	0.146
	$j=12$	−0.072	−0.140	−0.097	0.000	−0.371	−0.371
B	$j=10$(HO)	−0.186	−0.341	−0.118	0.868	0.119	−0.182
	$j=11$(LV)	−0.163	0.858	0.290	0.254	0.165	0.078
	$j=12$	0.002	−0.296	0.271	−0.070	−0.344	−0.350
C	$j=10$(HO)	−0.167	−0.556	0.766	0.000	−0.102	−0.102
	$j=11$(LV)	−0.127	0.772	0.466	0.000	0.088	0.088
	$j=12$	0.121	−0.191	−0.224	0.000	−0.407	−0.407

ionization potential (I_p) of NH_2 might almost be equal to that of the 2p orbital of the nitrogen atom in the valence state.[22] The I_p's of alkyl radicals are considered to be lower than that of the 2p orbital of the carbon atom because of hyperconjugation (*e.g.*, 8.64, 8.35, 7.93, and 7.42 eV for *n*-, *iso*-, *sec*-, and *t*-butyl radicals respectively.[23] The I_p's of the 2p orbitals of nitrogen and carbon atoms have been shown[20] to be 14.49 and 11.42 respectively. Therefore, the positive charge is located predominantly on the fragment of the alkyl group.

This consideration raises a question concerning the role of the electronic excitation. As for higher excitation, it is significant that excitation to the second level (LV+1; $j=12$ and 15 respectively for ethylamine and *n*-propylamine) makes the β bond sharply antibonding. Thus, interestingly, electronic excitation to a vacant orbital makes a certain bond extraordinarily loose. Similar results are obtained for 1-butene. In this case, π electrons play a role similar to that of the lone pair in amines. On calculations, two kinds of conformations were chosen. Conformation *D* shows that all the carbon atoms are on the x-y plane, while Conformation *E* shows only the bond of C_1–C_2 as perpendicular to the x-y plane (Table 4).

Characteristics of the HO and Some LV Orbitals. As has already been shown, the bond energy of β C–C varies according to the conformation of the nitrogen atom. This indicates that the lone pair which occupies the HO orbital of amine plays an important role in determining the strength of the β bond. In Table 5, the coefficients of the HO and some lower vacant orbitals are listed. In the *A* and *C* conformations, the electron of the HO orbital is predominantly distributed on the 2p_y atomic orbitals of N_3, C_1, and C_2. The sign of the coefficient for N_3 is positive, and that for C_1 is negative. The π-overlap integral ($S_{\pi\pi}$) between these atomic orbitals has a positive value (Fig. 1-a). Therefore, the HO orbital has an antibonding effect on the C_1–N_3 bond, since the interaction energy (e^j_{pq}) between atomic orbitals, ϕ_p and ϕ_q, given by singly-occupied jth orbital is expressed by Eq. (4), where H_{pp} is negative:

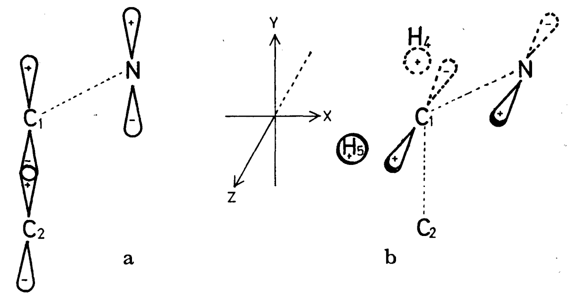

Fig. 1. Coordinate-dependent atomic orbitals of ethylamine.

$$e^j_{pq} = C_p{}^jC_q{}^jK(H_{pp}+H_{qq})S_{pq} \qquad (4)$$

The sign of the coefficient for the 2p_y of C_2 is positive, while the σ-overlap integral ($S_{\sigma\sigma}$) between the 2p_y atomic orbitals of C_1 and C_2 is negative. Hence, the HO orbital is bonding in this bond. On the other hand, in the *B* conformation it is shown in Fig. 1-b and Table 5 that the HO orbital is antibonding in N_3–C_1, while it is bonding in both the C_1–H_4 and

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[22] The configurations of those radicals are assumed to be sp^2.

[23] F. P. Lossing and J. B. de Sousa, *J. Amer. Chem. Soc.*, **81**, 281 (1959).

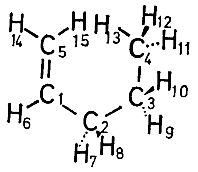
C_1–H_5 bonds. Likewise, it will be shown below that the LV and LV+1 orbitals are sharply antibonding in the C_1–N_3 and C_1–C_2 bonds respectively.

From the above considerations, it can be understood that the removal of one electron from the HO orbital makes the α C–N bond stronger (because the HO orbital is antibonding on this bond), while the β bond especially *trans* to the lone pair of the nitrogen atom becomes weaker. The behavior of the HO orbitals in other homologous amines is found to be analogous to that of ethylamine.

It may be evident that the positive charge is not distributed on the position where the HO orbital is antibonding, but where the HO orbital is bonding. We now recognize a correlation between the bond scission and the net positive-charge density. It is, however, not observed that the bond energy of the α C–N is lower than that of β C–C. The actual difference in energy becomes almost zero. There are two probable reasons for this. One might be the rough application of the MO theory, in which the molecule ions are calculated on the basis of the parameters for the closed-shell ground state. The electron distribution of the HO orbital is concentrated on the nitrogen atom under the electron-impact state; the values of the Coulomb integrals for the atomic orbitals belonging to the nitrogn atom should be lowered compared to those in the normal state. The other is that there may be other factors that regulate the reaction path, *e.g.*, the stability of the ions produced.

The McLafferty Rearrangement Reaction. Boer *et al.*[24] have already treated the McLafferty rearrangement reaction on 2-pentanone by means of Mulliken's population analysis. The following results, therefore, may serve to reconfirm the reaction processes proposed by them.

It has been established[25–26] that the γ-hydrogen atom is transferred in the rearrangement. Hence, it can be expected that, as the molecule ion takes a conformation favorable for the rearrangement, the bonding interaction between γ-hydrogen and the hydrogen-accepting atoms increases, while that between γ-hydrogen and the hydrogen-leaving atoms decreases.



1-Pentene

The values of B^j_{AB} between those atoms when the distances between γ-H(H_{13}) and C_4 are 2.4 Å (Conformation *F*) and 1.7 Å (Conformation *G*) were calculated for 1-pentene; they are listed in Tables 6 and 7 respectively. On the *F* conformation, it is shown in all the electronic states of the molecule ion (j=15—17) that: (1) C_5 has a strong bonding interaction with H_{13} and (2) the relative bond energy between C_4 and H_{13} becomes quite small, indicating cleavage at this bond. This inclination becomes more apparent when the molecule ion takes the *G* conformation. The relative bond energy between C_2 and C_3, however, is not weakened by changing the conformation from *F* to *G*. As for the electronic gound state (j=15), those observed are quite analogous to Boer's results. It may be worth considering that the excited molecule ion has a similar reaction tendency.

TABLE 6. THE VALUES OF B^j_{AB} OF 1-PENTENE (CONFORMATION *F*)

A–B	normal state	j=15 (HO)	j=16 (LV)	j=17
C_1–C_2	−20.87	−0.95	1.58	−1.08
C_1–C_5	−32.56	3.05	13.41	6.20
C_1–H_6	−20.99	0.07	0.14	0.14
C_2–C_3	−16.47	0.79	1.42	9.23
C_2–H_7	−20.40	0.67	1.31	2.12
C_2–H_8	−20.43	0.01	−0.02	0.92
C_3–C_4	−17.93	−0.06	−0.17	9.57
C_3–H_9	−20.82	0.35	0.71	0.73
C_3–H_{10}	−20.80	0.35	0.70	0.76
C_4–H_{11}	−19.80	0.00	0.00	0.97
C_4–H_{12}	−20.06	0.02	0.00	0.31
C_4–H_{13}	−20.21	0.80	1.64	1.73
C_5–H_{14}	−20.38	0.00	0.00	0.00
C_5–H_{15}	−20.32	0.00	−0.01	0.05
C_5–H_{11}	−0.02	0.01	0.02	0.02
C_5–H_{12}	0.15	0.04	0.06	0.10
C_5–H_{13}	0.15	−0.46	−1.10	−0.89

TABLE 7. THE VALUES OF B^j_{AB} OF 1-PENTENE (CONFORMATION *G*)

A–B	normal state	j=15 (HO)	j=16 (LV)	j=17
C_1–C_2	−20.80	0.07	0.66	0.13
C_1–C_5	−32.88	0.75	8.59	1.49
C_1–H_6	−20.90	0.22	0.44	1.10
C_2–C_3	−16.68	−0.04	−0.22	0.00
C_2–H_7	−20.37	0.00	−0.06	1.19
C_2–H_8	−20.10	0.12	0.07	0.64
C_3–C_4	−18.56	−0.18	−0.15	6.42
C_3–H_9	−20.78	0.24	0.46	0.47
C_3–H_{10}	−20.73	0.00	−0.03	0.00
C_4–H_{11}	−19.57	0.33	0.65	1.42
C_4–H_{12}	−20.63	0.06	0.12	0.25
C_4–H_{13}	−19.16	3.72	7.15	7.64
C_5–H_{14}	−20.51	0.18	0.36	0.40
C_5–H_{15}	−20.17	3.05	6.00	6.52
C_5–H_{11}	0.06	0.12	0.20	0.30
C_5–H_{12}	0.70	−0.06	0.08	−0.08
C_5–H_{13}	1.33	−1.98	−3.61	−3.69

Conclusion

(1) There is a clear correlation between the bond energy and the charge density at the HO orbital of the molecule ion, which might support Hirota's assumption.[2,3,6] However, there also seem to be other

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factors that regulate the reaction path. (2) The conformation of the nitrogen atom plays an significant role in connection with the strength of the β-bond. The β bond *trans* to the lone pair is more weakened than that of *cis*. (3) Electronic excitation from the HO orbital to a vacant orbital makes a certain bond extraordinarily loose. (4) As for the simple β cleavage of amines, electronic excitation to a vacant orbital is in doubt. (5) A method of comparing the relative bond energies is useful in the interpretation of rearrangement reactions.

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