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A New Method to Evaluate the Stability of the Covalent Compound: By the Charges on the Common Atom or Group

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A new method of comparing and analyzing the electrostatic potential (ESP) charges of the common atom or group to evaluate and compare the stabilities of covalent compounds was introduced. That is, covalent compounds will become more stable when the electron acceptors accept adequate electrons and possess adequate negative charges, and the electron donors donate adequate electrons and possess adequate positive charges accordingly. All calculations were performed by density functional theory (DFT) and the general gradient approximation (GGA) method with the Beck-LYP hybrid functional and the DNP basis set in Acceryls' code Dmol^3. Calculation results verified the method considering the molecular structure is well applied in the covalent molecule systems of hydrides, oxides, alkyl radicals, and nitro compounds. Furthermore, the method has good operability, for the charges can be easily obtained by simple calculation.

1. Introduction and Methodology

Usually, geometry structure, including bond length, bond angle, and dihedral angle, and electron structure such as bond order (BO), bond population, orbital composition and characteristic (for example, the phase and energy level of the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO), and orbital stabilizing energy (orbital interaction) can be used to evaluate the strength of a covalent bond and further the stability of a covalent compound. Also, the atomic positions in the periodic table can tell us the chemical characteristics of the compounds containing the corresponding atoms and help us to compare the molecular stabilities of one group. In this paper, a new method of calculating and comparing the charges of the common atoms or groups to evaluate and compare the stabilities of the covalent compounds is introduced.

In covalent compounds, different atoms or groups have different abilities to attract or offer electrons, i.e., some atoms or groups are electron acceptors, and others are electron donors. Atoms or groups should be charged once the compounds are formed. The common (same) atoms or groups in different compounds possess different quantities of the charges, due to the different chemical or bonding environments in the different compounds. So we can explore the chemical environment, including the molecular stability, by the charge quantity of the atom or group. Covalent compounds will become more stable when the electron-attracting atoms or groups accept adequate electrons and the electron-offering atoms or groups donate adequate electrons. Accordingly, the electron acceptors possess adequate negative charges and the electron donors possess adequate positive charges. Atomic charges are defined quantities, not physical observables. There exist some defined atomic charges currently, such as Mulliken charges,[1] electrostatic potential (ESP) charges,[2−5] Hirshfeld charges, natural charges, charges derivated from charge equilibration methods (QEq), and other charges. The charges of a group are charge algebraic summation of all atoms on the group. By comparing the charges of the common atoms or the common groups, we can compare the stabilities of the covalent compounds of the same group, for example, the hydrogen atoms in hydrides, the oxygen atoms in covalent oxides, and the nitro groups in nitro compounds, etc. We used ESP-derived charges as the indicators of stabilities and calculated them according to the following equations.[2]

$$\sigma^2(q_\alpha) = \frac{1}{N}\sum_i w_i\left[V(r_i) - \sum_\alpha \frac{q_\alpha}{r_{i\alpha}}\right]^2 \qquad (1)$$

In eq 1, where w_i is the integration weight at point i, $V(r_i)$ is the Coulomb potential at point i, and q_α is the fitted charge on atom α. The total molecular charge is conserved, using a Lagrange multiplier. The grid points i in eq 1 are selected based on the following criteria:

$$\alpha{:}r_{i\alpha} \le R_\alpha^{\text{ext}},\ \wedge\alpha{:}r_{i\alpha} \ge R_\alpha^{\text{int}} \qquad (2)$$

where R_α^{int} and R_α^{ext} are the internal and external radii of the atomic α shells and depend on the atom type. To make the results less sensitive to the selection of the grid, the concept of a layer border was introduced. The weights w_i change smoothly across the border layer, as evident from the following formula:

$$w_i = \left[\prod_\alpha w_{i\alpha}^{\text{int}}\right]\left[1 - \prod_\alpha (1 - w_{i\alpha}^{\text{ext}})\right] \qquad (3)$$

where $w_{i\alpha}^{\text{int}}$ and $w_{i\alpha}^{\text{ext}}$ are the partial weights calculated with

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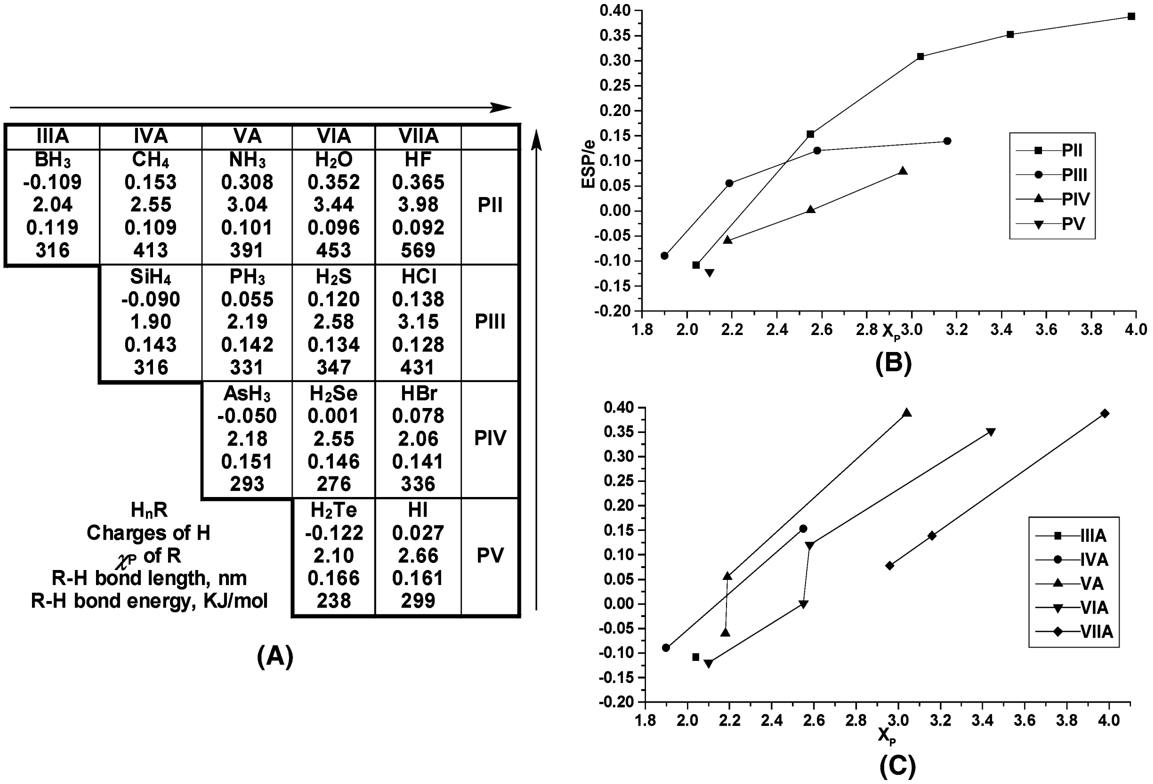


IIIA	IVA	VA	VIA	VIIA	
BH_3 -0.109 2.04 0.119 316	CH_4 0.153 2.55 0.109 413	NH_3 0.308 3.04 0.101 391	H_2O 0.352 3.44 0.096 453	HF 0.365 3.98 0.092 569	PII
	SiH_4 -0.090 1.90 0.143 316	PH_3 0.055 2.19 0.142 331	H_2S 0.120 2.58 0.134 347	HCl 0.138 3.15 0.128 431	PIII
		AsH_3 -0.050 2.18 0.151 293	H_2Se 0.001 2.55 0.146 276	HBr 0.078 2.06 0.141 336	PIV
H_nR Charges of H χ_P of R R-H bond length, nm R-H bond energy, KJ/mol			H_2Te -0.122 2.10 0.166 238	HI 0.027 2.66 0.161 299	PV

Figure 1. (A) The ESP charges of hydrogen atoms, Pauling electronegativities (χ_P) of non-hydrogen atoms (R), bond lengths, and bond energies in hydrides. The arrows point to the increase of molecular stability (bond length decreases and bond energy increases). Monotonic relationships between χ_P and ESP charges of hydrogen atoms in the same rows (B) or in the same columns (C). The bond lengths, bond energies and χ_P were cited from ref 8.

respect to all ESP centers in the system:

$$w_{i\alpha}^{\text{int}} = -\frac{1}{4}\rho^3 + \frac{3}{4}\rho + \frac{1}{2}$$

$$\rho = \min[\max[-1,(r_{i\alpha} - R_{i\alpha}^{\text{int}})/\Delta R],1] \tag{4}$$

$$w_{i\alpha}^{\text{ext}} = \frac{1}{4}\rho^3 - \frac{3}{4}\rho + \frac{1}{2}$$

$$\rho = \min[\max[-1,(r_{i\alpha} - R_{i\alpha}^{\text{ext}})/\Delta R],1] \tag{5}$$

where ΔR is the "diffusion" width of the layer border. Thus, the w_i change smoothly from 0 to 1 in the region $R_\alpha^{\text{int}} - \Delta R$, $R_\alpha^{\text{int}} + \Delta R$, and from 1 to 0 across the external radii $R_\alpha^{\text{ext}} - \Delta R$, $R_\alpha^{\text{ext}} + \Delta R$. The final set of linear equations is solved via the Gauss elimination technique to determine the point charges.

All calculations were performed by density functional theory (DFT) and the general gradient approximation (GGA) method with the Beck-LYP hybrid functional and the DNP (double-numeric-quality basis with polarization functions) basis set in Acceryls' code Dmol^3.[6] At the same time, bond length, bond energy, dissociation energy, dissociation temperature and decomposition percentage at a specified temperature, and the index of impact sensitivity of explosive, the height H_{50}, from where a given weight falling upon the compound gives a 50% probability of initiating explosion, were used to assess the molecular stabilities. Additionally, the data not explained in this paper were cited from ref 7.

2. Results and Discussion

2.1. Hydrides. Hydrides are a kind of important and simple (only the single bond between the hydrogen atom and the non-hydrogen atom, R–H) covalent compound, and hydrogen atoms are the common atoms in them. In Figure 1A, from left to right in the same row (the same period), or from the bottom to the top in the same column (the same main group), the ESP charges of hydrogen atom, the non-metallicity or electronegativity (χ_P) of non-hydrogen atom, and the bond energy increase, while the bond length decreases, i.e., the stability of the hydride increases. Certainly, this regular change of molecular stability can be seen from the decomposition percentage at 1273 K of hydrogen halides (in Table 1). Figure 1 shows that the ESP charges of the hydrogen atoms are very consistent with the χ_P of the non-hydrogen atoms. That is to say, the larger χ_P the non-hydrogen atom has, the more positive charges the hydrogen atom possesses in the corresponding hydride. The figure also indicates that there are monotonic relationships between χ_P and ESP charges in the same rows or in the same columns. Because the χ_P of hydrogen is 2.20, more than that of boron (B), silicon (Si), arsenic (As), and tellurium (Te), the hydrogen atoms are electron acceptors and have negative charges in these relevant hydrides. They are usually unstable, for their hydrogen atoms are neither electron donors nor effective electron acceptors (too few negative charges). In other hydrides, the non-hydrogen atoms have more χ_P and stronger non-metallicities than hydrogen atoms. So, the hydrogen atoms are electron donors and possess positive charges. The compounds become more stable when they offer more electrons and have more positive charges. Therefore, ESP charges of the hydrogen atoms can be used to compare the molecular stabilities of different covalent hydrides, the same

TABLE 1: Decomposition Percentage (%) of Hydrogen Halides (HX) at 1273 K

HX	HF	HCl	HBr	HI
%	negligible	0.0014	0.5	33

Figure 2. The ESP charges of oxygen atoms in O_3 and SO_2, and their thermal stabilities.

TABLE 2: ESP Charges of Oxygen Atoms (Q_O, e) and Decomposition Temperature (T_D, K) of Oxide R_2O

R_2O	OF_2	Cl_2O	Br_2O	I_2O	H_2O
Q_O, e	0.081	−0.168	−0.233	−0.279	−0.704
T_D, K	523	293	303	273−623	exists stably at 1273 K

TABLE 3: Homolytic Reactions of Alkanes and Their Reaction Heat Cited from Ref 9

homolytic reaction	heat of reaction
$CH_4 \rightarrow CH_3 + H$	$\Delta H = 435$ kJ/mol
$C_2H_6 \rightarrow C_2H_5 + H$	$\Delta H = 410$ kJ/mol
$C_3H_8 \rightarrow Me_2CH + H$	$\Delta H = 397$ kJ/mol
$Me_3CH \rightarrow Me_3C + H$	$\Delta H = 381$ kJ/mol

as χ_P of the non-hydrogen atoms, bond length, bond energy, and decomposition percentage at a specified temperature.

2.2. Covalent Oxides. Covalent oxides are another kind of important compound, and the oxygen atom is the common atom in them. In above hydrides, all the hydrogen atoms bond with non-hydrogen atoms by single bonds, i.e., they have the same bond type, the single bond. Generally, comparing with hydrides, oxides are more complicated, due to the multi bonding manners of oxygen atoms. To compare the stabilities of covalent oxides, we classed the oxides according to their bond types (single, double, triple, or resonant) and compared their stabilities by charge analyses.

O_3 and SO_2 (in Figure 2) have the same bonding characteristic (two σ bonds and one Π_3^4 bond). In these two molecules, the common atom is oxygen atom and an electron acceptor. O_3 is less stable than SO_2, due to the rapid decomposition of O_3 at 437 K and the stable existence of SO_2 at the same temperature. The negative charges of the common atom in O_3 (the termination oxygen atom) are less than those in SO_2. This verified that the more negative charges the electron acceptor possesses, the more stable the molecule becomes. OF_2, ClO_2, BrO_2, IO_2, and H_2O (in Table 2) are of another bond type (one σ bond between O and R, O−R). In this kind of oxide, oxygen atoms are the common atoms, but not all are electron acceptors. That is to say, the oxygen atom in OF_2 is an electron donor. From this viewpoint, OF_2 should not belong to the group of ClO_2, BrO_2, IO_2, and H_2O but instead to the group of HF. For OF_2 and HF, we can use the rule to compare their stabilities. Fluorine atoms are common atoms and electron acceptors in these two molecules. Their negative charge quantities (0.081e and 0.388e, respectively) can explain that OF_2 decomposes at 523 K and HF exists very stably 1273 K. As to ClO_2, BrO_2, IO_2, and H_2O, the rule can also work well to explain and compare their stabilities: the common atom and electron acceptor, oxygen atom, possesses the more negative charge, and the corresponding oxide has the higher composition temperature and the higher stability (in Table 2).

As mentioned above, it is difficult to compare stabilities of oxides, owing to multi and complicated bonding manners of the oxygen atoms. But when some covalent oxides are in the same group (the same bonding characteristic), we can compare their stabilities by the rule.

2.3. Alkyl Radicals. The stabilities of the alkyl radicals have well been researched.[9] It can be seen from Table 3 that their stabilities decrease as $Me_3C > Me_2CH > C_2H_5 > CH_3$. The stabilities of the corresponding C−H bonds in the parent molecules (alkanes) increase in the same order. Because the χ_P of hydrogen (2.04) is less than that of carbon (2.55), the hydrogen atoms are the electron donors in alkanes. According to the rule, the more positive charges the hydrogen atom possesses, the more stable the corresponding C−H bonds become. Commonly, the strength of the weakest bond determines the molecular stability. So we can use the least positive charges or the most negative charges on the hydrogen atom of one type (such as primary hydrogen atom, secondary hydrogen atom, and tertiary hydrogen atom) to evaluate the strength of the C−H bond of the corresponding type. Either in four isolated molecules (methane, ethane, propane, and 2-methypropane in Figure 3) or in one molecule (2-methybutane), the charges on the hydrogen atoms show a good relationship between the charges and the strengths of C−H bonds and the stabilities of the corresponding radicals. Further, the more positive charges the hydrogen atom possesses, the stronger the C−H bond is and the less stable the corresponding radical is. Because methane has the most positive hydrogen atom charges, its C−H bond is the strongest and it has the most heat of homlytic reaction; methyl radical is the least stable. Secondary and tertiary hydrogen atoms possess fewer positive charges, even negative charges, so they can be more easily dissociated from the parent molecules, have lower heat of homlytic reaction, and the corresponding radicals are more stable.

2.4. Nitro Compounds. Nitro compounds are also a group of important compounds, applied especially in the field of explosives. Today, nitro compounds are still the main and most important explosives containing C, H, N, and O. So it is interesting and meaningful to investigate the stabilities of nitro compounds as high-energy materials. Different from the above hydrides and oxides, the common part of the nitro compounds is not an atom, but a group, the nitro group. To verify that there is a relationship between molecular stability and nitro group charges, we calculated the C-nitro bond lengths and nitro group charges of nitrobenzene and nitroanilines (right in Figure 4) and related the nitro group charges with C-nitro bond lengths, which are used to measure the strength of C-nitro bond and the stabilities of the compounds (for the compounds of the same group). The calculation results showed there is an approximate linear correlation between the nitro group charges and C-nitro

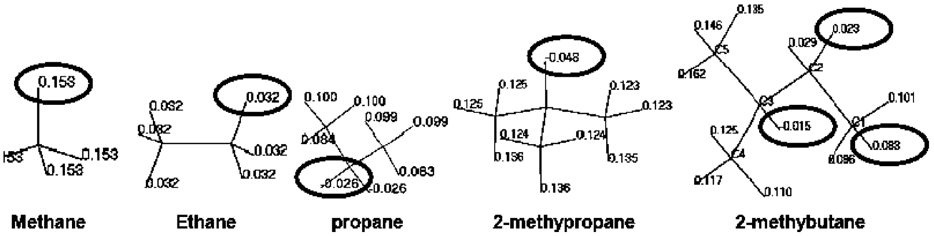


Figure 3. The ESP charges of hydrogen atom in alkanes. The hydrogen atom indicated in a circle has the least positive charge or the most negative charge for a particular type of hydrogen atom.

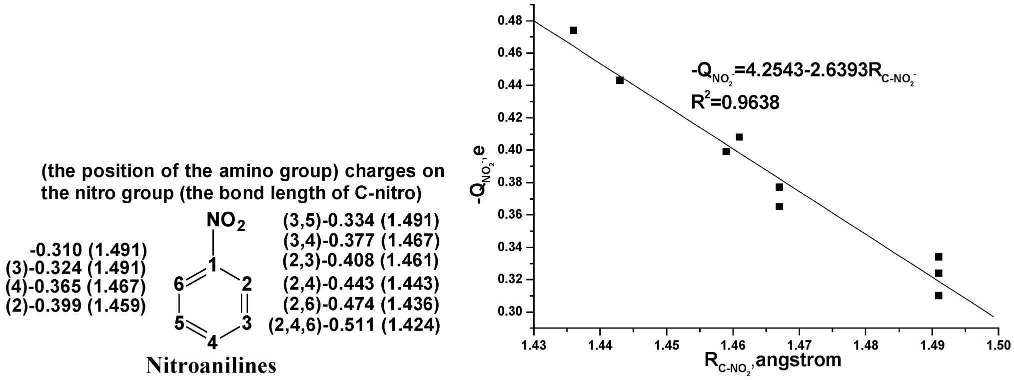


Figure 4. Dependence of the C-nitro bond lengths and the charges on the nitro group in nitroanilines.

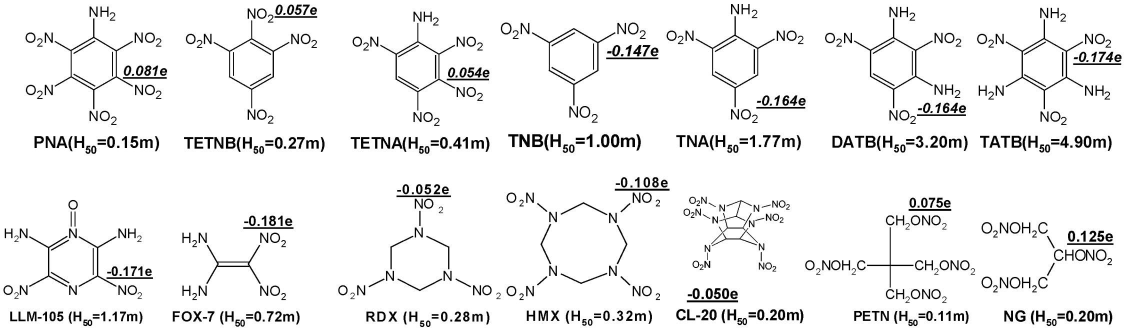


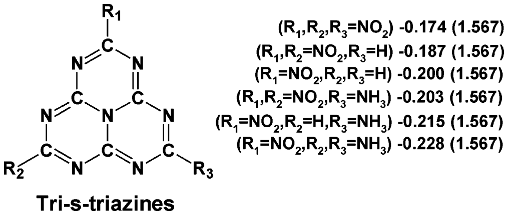
Figure 5. The ESP charges of nitro group in nitrobenzenes and their impact sensitivities (H_{50}).

bond length (left in Figure 4): the more negative nitro group charges, the shorter C-nitro bond length. This indicates that nitro group charges can be used to evaluate the stabilities of nitro compounds.

We have related the charges on the nitro group with the impact sensitivity (measured by the height H_{50}) of the explosive.[10] Data in Figure 5 show that nitro group charges can be regarded as a structural parameter to assess impact sensitivity. The compound will have high H_{50} when it has large negative nitro group charges. Additionally, from the viewpoint of nitro group charges, it can be tentatively concluded that The $C-NO_2$ compounds TATB, DATB, LLM-105, and FOX-7 are less sensitive (higher drop height values) than the $N-NO_2$ compounds RDX, HMX, and CL-20 and the $O-NO_2$ compounds PETN and NG. Certainly, the impact sensitivity depends on many factors besides nitro group charges, so there is no completely monotonic correlation between them. But it is notable of the rule of nitro group charges to evaluate the impact sensitivities of nitro explosives.

For polynitro aromatic compounds, it must be emphasized that the approach is competent only when the nitro groups cannot react with other substituents such as amino, hydroxy, alkyl, and sulfur groups. Many experimental evidences indicate that the nitro group primarily reacts with these substituents through its oxygen atom (C−N bond is conserved here) when polynitro aromatic compounds are heated or shocked.[11] So, the rule works well in polynitro aromatic compounds when the $C-NO_2$ rupture is the initial step of explosive decomposition.

By the way, the nitro group charges may be more sensitive than bond length. For instance, in tri-s-triazines (also called "Pauling ring"), when the substituents change from nitro to amino groups and hydrogen atoms, the nitro group charges change obviously, but the bond length of C-nitro keeps a constant, 1.567 angstrom. Apparently, the molecular stabilities cannot be evaluated by bond length, for there should be stability differences among these six molecules, C-nitro bond lengths are a constant. However, the nitro group charges are evidently different among them. So, it may be the advantage of the rule.



3. Conclusions

By comparing the stabilities of hydrides, covalent oxides, alkyl radicals, and nitro compounds, it can be found the charges of the common atom or group in one sort of covalent compounds can be used as a new method and a structural parameter to evaluate and compare the molecular stabilities, for they are derived from the molecular structures (this method can possibly used to other covalent systems). Also, they can be easily obtained by simple calculation, so this method has good operability. However, some points should be emphasized when using the rule. (1) The charges should be on the common atom or on the common group of the covalent compounds, for example, the hydrogen atoms in the hydrides or the nitro groups in the nitro compound. (2) The bond joining with the common atom or group should be of the same type, for example, the single, double, triple, or resonant. (3) The bond joining with the common atom or group should be the weakest in the molecule, for the strength of the weakest bond determines the molecular stability.

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