Determination of Adiabatic Ionization Potentials and Electron Affinities of Energetic Molecules with the Gaussian-4 Method

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Abstract

Adiabatic ionization potentials (IP_{ad}) and electron affinities (EA_{ad}) are determined with the Gaussian-4 (G4) method for the energetic molecules PETN, RDX, β - δ -HMX, CL-17, TNB, TNT, CL-14, DADNE, TNA, and TATB. The IP_{ad} and EA_{ad} values are in the range of 8.43-11.73 and 0.74-2.86 eV, respectively. Variations are due to substitutional effects of electron withdrawing and donating functional groups. Enthalpies of formation are also determined for several of these molecules to augment the list of recently reported G4 values. The calculated IP_{ad} and EA_{ad} provide quantitative assessment of such molecular properties as chemical hardness, molecular electronegativity, and “intrinsic” molecular physical hardness.

The exposure of energetic materials such as explosives and propellants to electromagnetic radiation represents an unwelcome stimulus that could lead to undesirable, if not catastrophic, events. When gamma radiation of various penetrating energies is impinged upon energetic solids, three possible outcomes are expected: photoelectron effect, Compton scattering, or pair production, which may induce chemical and/or mechanical changes in the pristine material. [1] Be it ultraviolet light or gamma rays, induced chemical and mechanical changes in these solids lead to degradation of their structural, physical, and chemical integrities. Irradiated thin layers of the explosive HMX with γ rays in evacuated tubes at liquid nitrogen temperature showed significant enhanced sensitivity to impact, with frequent spontaneous explosions occurring at higher radiation doses. [2] Chemical changes in the insensitive explosive TATB due to both UV light and gamma irradiation showed a significant decrease in the onset of reaction exotherm. [3-5] While electron ejection from the irradiated material is one of the possible outcomes, that many of the organic energetic molecules do contain electron acceptor functional groups such as $-\text{NO}_2$ may also result in electron capturing by the same material. For the purpose of rapid explosive detection, [6] studies using mass spectroscopic methods that included laser photon ionization [7] and dissociative negative ions spectroscopy [8-10] have been conducted to identify and probe unique fragments. Computational studies of activation barriers to dissociation of both negative and positively charged explosive molecules have also been reported. [11-13] The accurate determination of ionization potentials (IPs) and electron affinities (EAs) is thus important in quantifying the susceptibility of energetic materials to radiation effects. Interesting observations or concepts correlating explosive shock and impact sensitivities with

chemical hardness or electronic band gaps can then be assessed based on such determinations. [14, 15]

Although many of the energetic solids and liquids have low vapor pressure, they are still amenable to molecular beam experiments. [16, 17] The dearth of experimental determinations of IPs and EAs of these materials, however, entice the effort to perform computational studies using the most accurate of quantum chemical methods. To facilitate comparison with any future experimental results, the adiabatic values of IPs and EAs must be determined. [18] From a theoretical perspective that assumes the Born-Oppenheimer approximation, the adiabatic valence ionization potential (IP_{ad}) and electron affinity (EA_{ad}) for a molecular species are defined as:

$$\begin{aligned} IP_{ad} &= [E_e (\text{optimized cation}) + \text{ZPE (cation)}] - \\ &\quad [E_e (\text{optimized neutral}) + \text{ZPE (neutral)}] \\ EA_{ad} &= [E_e (\text{optimized neutral}) + \text{ZPE (neutral)}] - \\ &\quad [E_e (\text{optimized anion}) + \text{ZPE (anion)}] \end{aligned} \quad (1),$$

where E_e is the electronic energy, and ZPE is the molecular zero-point vibrational energy. Thus, the calculations of IP_{ad} and EA_{ad} require the optimization of the neutral, cation, anion structures, and the associated frequency calculations of these structures. Due to their computational complexity, the use of highly-accurate electronic structure methods such as coupled cluster with single, double, and perturbative triple (CCSD(T)) has been restricted to calculating vertical IPs and EAs values of relatively small to moderate size molecules. [19, 20] To obtain such values, only the neutral species is optimized followed by a one-point energy calculation at the same resulting equilibrium geometry for the ion of interest. Although computationally intensive for large-size molecules, composite quantum mechanical approaches are providing an alternative to the calculation of such

properties as heat of formation, IPs and EAs with a purported achievement of the “chemical” accuracy limit. [21-24]

In this work, the IP_{ad} and EA_{ad} for the set of ten energetic molecules listed in Figure 1 are calculated using the Gaussian-4 (G4) composite method as implemented in Gaussian 09 program. [22, 25] In addition to containing some of the most commonly known explosive molecules of interest, such as PETN, HMX, RDX, TATB, and TNT, the list contains a variety of energetic structures with various effects. These include aromatic rings (as in TATB, TNT, TNB, and TNA), electron donor and acceptor functional groups ($-NH_2$ and $-NO_2$, respectively), N-substituted rings (as in HMX, and RDX), furoxan rings (CL-14 and CL-17), and absence of ring structures altogether (PETN and DADNE). The sequence of *ab initio* calculations performed within the G4 method to obtain the total energy of a given molecular species at the MP4 and CCSD(T) level, in particular, represented a significant computational challenge that dedicated runs on a specialty computer platform with 500 GB of physical memory distributed among 32 CPUs had to be performed for over a period of 25 days for the 29 atoms PETN anion specie alone. Finally, enthalpies at $T=298.15\text{ K}$ (H_{298}) are also reported, which allow for the determination of enthalpies of formations $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ at 0 and 298.15 K for several species, thus expanding the list of recently reported ΔH_f^0 values of energetic molecules. [26]

Table I reports the results of the calculated zero-point-corrected total electronic energies, $E_0 = E_e + \text{ZPE}$, the corresponding zero-point vibrational energies (*ZPE*), the enthalpies at $T=298.15\text{ K}$ (H_{298}) of the neutrals, cations, and anions species, and the resulting IP_{ad} and EA_{ad} as defined in equation (1). All species yielded equilibrium

structures with positive vibrational frequencies of all the modes at the B3LYP/6-31G (2df, p) level performed within the G4 method. As shown in Table I, all neutral species have larger ZPEs than their cations or anions, the largest being 4.2 kcal/mol difference between the neutral and anion of HMX in its δ conformation (discussed below), and 4.1 kcal/mol difference between the same species in PETN. All cations yielded a relatively larger ZPEs than their corresponding anions with the exception of TNT.

IP_{ad} values range from 8.43 to 11.73 eV, and EA_{ad} from 0.74 to 2.86 eV. The IP_{ad} values are similar to other organic molecules, typically ~8-11 eV. [20] Variations in the IP_{ad} values are due to interplay between the presence of the strong electron withdrawing $-NO_2$ group in all of the structures, which destabilizes the cations and leads to larger IP_{ad} values, and the presence of strongly ($-NH_2$, $-NR_2$) and weakly (alkyl: $-CH_3$, phenyl: $-C_6H_5$) electron donating groups. Both CL-17 and CL-14 contain similar ring structures and the datively-bonded, N-oxide group ($-N \rightarrow O^+$). The IP_{ad} of CL-17 at 9.19 eV is higher than CL-14's (8.43 eV), due to the presence of one more electron withdrawing $-NO_2$ replacing the electron donating $-NH_2$, the only difference between the two molecules. Balancing effects between strongly donating and strongly withdrawing groups is also manifested for the lowest IP_{ad} values among all the molecules, that of CL-14, TATB (8.56 eV), and DADNE (8.92 eV). The three (two) $-NO_2$ withdrawing groups are counterbalanced by the three (two) $-NH_2$ donating groups in TATB (DADNE), leading to similarly "low" IP_{ad} values. The lower IP_{ad} for TATB than that of DADNE's could perhaps be explained due to the presence of the weakly electron donating phenyl group ($-C_6H_5$) in TATB. Increasing the number of electron donating substituents groups of various strengths in the phenyl ring leads to lower IP_{ad} values. This is evident in the

series of structures TNB (11.00) > TNT (10.54) > TNA (9.33) > TATB (8.56) eV. The addition of H₂C-N-NO₂ to RDX to transform it into HMX, and containing both strong electron donating (-NCH₂) and withdrawing (-NO₂) groups, produces only a relatively lower IP_{ad} value, 10.09 and 9.73 eV, respectively.

Steric effects also play a role in producing different IP_{ad} and EA_{ad} values. Solid HMX exhibits three crystal polymorphs at ambient pressure, two of the important ones involved in its energy release process are β and δ phases. [27, 28] Figure 2 shows the molecular conformations of these two phases: the chair (β) and boat (δ) forms. The chair structure has a slightly higher IP_{ad} (9.73 eV) than the boat (9.58 eV), indicating equal energy for the highest occupied molecular orbital (HOMO) in the two conformations. The chair form, however, produces almost double the value of EA_{ad} (1.86 eV) than the boat (0.98 eV), which indicates a significant energy increase in lowest unoccupied molecular orbital (LUMO) for the δ structure. An interesting interfacial property related to organic photovoltaics might be noted here, if this trend were to also persist in the solid state, whereby an electron transfer process occurs from the LUMO of δ -donor to that of the β -acceptor polymorph. [29] For comparison, a recent DFT study of δ -HMX reported IP_{ad} of 10.10 (9.24) eV and EA_{ad} of 1.42 (1.67) eV using the functionals M06 (and PBE) and the 6-31+G(2df,p) basis set. [13] At the MP2/6-311++G(2d,p) level of theory, EA_{ad} of 1.35 eV for β -HMX was reported. [9] Both studies report significantly different EA_{ad} values than obtained here with the current G4 method.

It would be expected that molecules with the most electron withdrawing groups to have the largest EA_{ad} values, indicative of high stabilization of their anions. This is not universal, however, among the reported EA_{ad} values in Table I due to other factors such

as steric effects and bond conjugations. CL-14 has one less $-\text{NO}_2$ group, and thus shows a lower EA_{ad} value of 2.32 eV than CL-17, which has the largest EA_{ad} of all structures at 2.86 eV. Similarly, β -HMX has one more $-\text{NO}_2$ group, yielding a larger EA_{ad} at 1.86 eV than RDX at 1.04 eV, while steric effects reduce the value of δ -HMX as noted above. TNA, TNB, TNT, and TATB all have three $-\text{NO}_2$ groups, with somewhat similar EA_{ad} values at 2.33, 2.17, 2.02, and 1.73 eV, respectively, the difference being for inclusion of various electron donating groups. The most pronounced exception is exhibited in PETN, which interestingly yields both the largest IP_{ad} (11.73 eV) and the lowest EA_{ad} (0.74 eV) of all molecules, indicative of a lower propensity to undergo an electron ejection or acceptance process. Finally, it should be noted that using the room-temperature enthalpies values that are also reported in Table I instead of the total energies will only change the calculated IP_{ad} and EA_{ad} values negligibly, at the most by 0.04 eV in the case of EA_{ad} of β -HMX.

Recently, the enthalpies of formation $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ at 0 and 298.15 K, respectively, were determined for several energetic molecules, including some considered in this study (among others): PETN, RDX, β -HMX, TNT, DADNE, and TATB, using the G2, G3, G4, and ccCA-PS3 composite methods. [26] Following the same computational approach in that study, the computed enthalpies of neutral species δ -HMX, CL-17, TNB, CL-14, and TNA reported in Table I are used to calculate the atomization energies, and are combined with JANAF values for the atomic ΔH_f^0 and for the standard state of the elements, $[H^0(298\text{ K}) - H^0(0\text{ K})]_{ST}$, [30, 31] to determine $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ of these species, and are reported in Table II. Of note, the reported $\Delta H_f^0(298\text{ K}) = 55.5\text{ kcal/mol}$ of δ -HMX is only slightly higher than

$\Delta H_f^0(298\text{ K}) = 52.3\text{ kcal/mol}$ for β -HMX. [26] It should be noted that while ΔH_f^0 G4 computed values are consistently similar to those obtained from the G3 method, [32] they differ by as much as $\sim 8\text{ kcal/mol}$ for PETN from those obtained with the variant correlation consistent composite approach (ccCA-PS3). [24]

The calculated ionization potentials and electron affinities provide an opportunity for quantitative assessment of several important physical properties that are usually invoked in determining the propensity of a material to undergo chemical or physical changes, thus related to its reactivity and stability. Chemical hardness, [33] is defined as $\eta = (\text{IP} - \text{EA})/2$, and is a measure of the molecular HOMO-LUMO energy gap. The principle of maximum hardness postulates as a rule of “nature” for molecules to arrange themselves to be as hard as possible. [34] Electronegativity, a classical structural chemistry concept defined as $\chi = (\text{IP} + \text{EA})/2$, is directly related to the chemical potential, $\mu = -\chi$. [35] Both of these two quantities continue to be used extensively to make predictions about chemical behavior, as in the Q-*e* scheme. [36, 37] Furthermore, physical hardness is a measure of the resistance to change of the nuclear positions in a system, [38] and is related to the bulk modulus or compressibility of the material. [14] An “intrinsic” physical hardness of a molecule, with a molecular volume V_0 , can be defined as $\eta^* = \eta/V_0$, having the unit of pressure. For crystalline solids, it was shown that V_0/κ , where κ is the compressibility, correlates with experimentally measured crystal hardness. [39]

Since X-ray and neutron diffraction data are available for all of the energetic molecules considered in this work (with the exception of CL-17) as shown in Table III, the molecular volume can also be determined. From the reported IP and EA values in

Table I, the chemical hardness η , the electronegativity χ , and the intrinsic physical hardness η^* are determined and listed in Table III. Based on these values, the energetic molecules can be ordered in terms of decreasing η as PETN > RDX > TNB > TNT = δ -HMX > DADNE > β -HMX > TNA > TATB > CL-17 > CL-14, in terms of decreasing χ as TNB > TNT > PETN > CL-17 > β -HMX = TNA > RDX > C-14 > δ -HMX > TATB > DADNE, and in terms of decreasing η^* as DADNE > RDX > TNB > TNT = PETN > TNA > δ -HMX > TATB > β -HMX > CL-14.

Finally, many attempts have been made to establish a correlation between a certain molecular property and the sensitivity of energetic materials to either shock or impact. [40] These included, among many others, molecular electronegativities and HUMO-LUMO gap. [15, 41] The lack of experimental data for shock sensitivity for pure materials, and the lack of uniformity of conditions in impact tests make correlation studies problematic and non-universal to include all energetic materials. It may well be that such correlation only exists within a structurally related group of molecules. In this vein, we note that the reported η , χ , and η^* values in Table III for the homologous series TNB, TNT, TNA, and TATB show a uniform decrease in all of the three properties. The order of decreasing sensitivity based on available impact drop hammer tests for this series is TNB (71) > TNT (98) > TNA (121) > TATB (345). [15, 40]

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Figure Captions:

Figure 1. The 10 energetic molecules along with commonly used acronyms considered in the current study.

Figure 2. Molecular structures of the (a) β (chair), and the (b) δ (boat) conformations of HMX.

Table I. Total energies, enthalpies at T=298.15 K, and zero-point vibrational energies of neutrals, cations, anions, and the corresponding IP_{ad} and EA_{ad} .^a

Molecule	Neutral	ZPE	Cation	ZPE	Anion	ZPE	IP_{ad}	EA_{ad}
PETN	-1316.029668 -1316.007883	116.9	-1315.598643 -1315.576353	113.2	-1316.056912 -1316.034064	112.8	11.73	0.74
RDX	-897.090086 -897.076480	88.3	-896.719150 -896.705288	85.4	-897.128410 -897.114203	85.1	10.09	1.04
β -HMX	-1196.123877 -1196.105446	118.5	-1195.766410 -1195.747271	115.9	-1196.192291 -1196.172422	114.8	9.73	1.86
δ -HMX	-1196.118704 -1196.100225	118.1	-1195.766662 -1195.747832	115.7	-1196.154822 -1196.135120	113.9	9.58	0.98
CL-17	-1159.300858 -1159.284074	74.5	-1158.962982 -1158.945645	73.4	-1159.405835 -1159.388604	72.7	9.19	2.86
TNB	-845.452747 -845.439756	66.6	-845.048403 -845.034806	64.3	-845.532528 -845.519272	64.0	11.00	2.17
TNT	-884.729931 -884.715348	83.7	-884.342577 -884.327125	81.3	-884.804287 -884.789419	81.4	10.54	2.02
CL-14	-1010.216397 -1010.201490	84.1	-1009.906614 -1009.891273	83.5	-1010.301832 -1010.286734	81.4	8.43	2.32
DADNE	-598.105038 -598.094765	57.0	-597.777253 -597.766717	56.6	-598.141867 -598.131592	54.5	8.92	1.00
TNA	-900.793644 -900.779725	77.5	-900.450603 -900.437271	76.1	-900.879298 -900.865287	75.5	9.33	2.33
TATB	-1011.469035 -1011.453214	98.3	-1011.154618 -1011.138287	97.7	-1011.532596 -1011.516369	95.6	8.56	1.73

^a Enthalpies values are below the total energies E_0 , where $E_0 = E_e + \text{ZPE}$, both are in unit of Hartree. ZPE values are in kcal/mol. IP_{ad} and EA_{ad} are eV.

Table II. Enthalpies of formation $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ at 0 and 298.15 K.^a

Molecule	$\Delta H_f^0(0\text{ K})$	$\Delta H_f^0(298\text{ K})$
δ -HMX	69.6	55.5
CL-17	82.1	74.5
TNB	15.4	9.7
CL-14	65.0	56.3
TNA	12.8	5.6

^a Units are in kcal/mol.

Table III. Experimental crystal cells and molecular volumes, chemical hardness, electronegativity, and intrinsic molecular physical hardness. ^a

Compound	Cell Volume	V_0	η	χ	η^*
PETN	589.50 ^b	294.75	5.5	6.2	2.99
RDX	1633.86 ^c	204.23	4.5	5.6	3.57
β -HMX	517.16 ^d	259.70	3.9	5.8	2.44
δ -HMX	1676.27 ^{d1}	279.38	4.3	5.3	2.47
CL-17	NA	NA	3.2	6.0	
TNB	3377.73 ^e	211.10	4.4	6.6	3.34
TNT	1823.60 ^f	227.95	4.3	6.3	2.99
CL-14	432.00 ^g	216.00	3.1	5.4	2.26
DADNE	515.90 ^h	128.98	4.0	5.0	4.91
TNA	854.43 ⁱ	213.61	3.5	5.8	2.63
TATB	442.49 ^j	221.24	3.4	5.1	2.46

^a Cell and molecular volumes are in $\text{\AA}^3$. η and χ in eV. η^* in GPa.

^b Ref. [42], ^c Ref. [43], ^d Ref. [44], ^{d1} Ref. [28], ^e Ref. [45], ^f Ref. [46], ^g Ref. [47], ^h Ref. [48], ⁱ Ref. [49], ^j Ref. [50]

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[3-Nitrooxy-2,2-bis
(nitrooxymethyl)propyl] nitrate
PETN

5,7-diamino-4,6-dinitrobenzofuroxan
CL-14

Octahydro-1,3,5,7-tetranitro-
1,3,5,7-tetraazacyclooctane
HMX

7-amino-4,5,6-trinitrobenzofuroxan
CL-17

1,3,5-triamino-2,4,6-trinitrobenzene
TATB

2,4,6--trinitrotoluene
2,4,6-TNT

Hexahydro-1,3,5-trinitro-
1,3,5-s-triazine
RDX

1,3,5-trinitrobenzene
TNB

1,1-diamino-2,2-dinitro-ethylene
DADNE

2,4,6-trinitroaniline
TNA

δ -HMX