Theor Chim Acta (1993) 85: 127–136

**Theoretica Chimica Acta**

# Some applications of local density functional theory to the calculation of reaction energetics

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Received September 24, 1991/Accepted April 15, 1992

**Summary.** We report the results of a local density functional investigation of the energetics of some isomerization reactions, involving the conversions of several unsaturated systems to highly strained molecules related to triprismane and tetrahedrane. The program DMol was used at the DNP level to compute the activation barriers and total energy changes associated with these processes. We also show, for more than 70 first- and second-row atoms and molecules, that the errors (non-local corrections) in their energies correlate very well with the number of electrons, within isonuclear series. This should provide a useful empirical means for improving dissociation energies obtained within the local approximation.

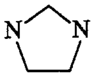
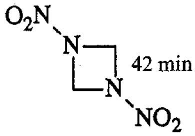
**Key words:** Reaction energetics – Local density functional theory – Isomerization reactions – Dissociation energies

## 1 Introduction and background

The important conceptual advances that have taken place in density functional theory (DFT) in recent years, reviewed in depth by Parr and Yang [1] and by Kryachko and Ludeña [2], have been paralleled by software development that has led to greatly increased use of DFT for atomic and molecular calculations [3–5]. Most of these applications involve solving the Kohn–Sham equations [6], and make use of a local density approximation (LDA), in which the exchange-correlation functional is approximated by a formula derived for a uniform (i.e. constant density) electron gas. Several such formulas have been proposed and investigated [1, 2, 5, 7]. Density functional theory is frequently described as a first-principles approach, even in a local density approximation, because it does not contain any empirical parameters [8], and it does take account of electronic correlation.

From a computational standpoint, the important advantage of a DFT-LDA approach, compared to *ab initio* methods, is the great reduction in CPU time and disk space requirements. This can be seen from the comparisons presented in Table 1, which indicates our experience using the program DMol at the DNP level, which corresponds roughly to a double-zeta plus polarization basis set.

**Table 1.** Comparison of computer disk space and cpu time requirements for single point calculations[a,b]

| Molecule | HF/6-31G* | | MP2/6-31G* | | MP4/6-31G* | | DFT-LDA/DNP | |
|---|---|---|---|---|---|---|---|---|
| | Time | Space | Time | Space | Time | Space | Time | Space |
| HF | 2 sec | 15 M | 3 sec | 15 M | 4 sec | 20 M | 0.2 sec | 20 K |
| HC≡CH | 5 sec | 22 M | 7 sec | 22 M | 11 sec | 70 M | 1 sec | 100 K |
|  | 4 min | 120 M | 5 min | 1 G | 15 min | 2 G | 0.5 min | 10 M |
|  | 42 min | 160 M | 300 min | 3 G | 1560 min | 8 G | 5 min | 50 M |

[a] These computer disk space cpu time requirements are for calculations carried out on a CRAY Y-MP8/864

[b] The disk space units are defined as follows: 1 K = $2^{10}$ bytes = 1024 bytes; 1 M = $2^{10}$ K; 1 G = $2^{10}$ M

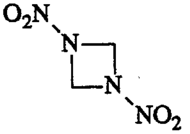
(DMol has been described and analyzed in detail by Delley [9].) Thus, with DFT-LDA techniques it is feasible to treat much larger systems than with *ab initio*. For example, we have computed the energies of a host-guest interaction between benzene and a cyclophane molecule containing 36 carbon atoms (a total of 270 electrons) [10], as well as a cluster of 22 Pd atoms (1012 electrons) [11].

Since the exact $E[\rho]$ functional is not known and the local density approximation is being invoked, it is necessary to evaluate the effectiveness of DFT-LDA in computing various atomic and molecular properties, as measured against both *ab initio* and experimentally-determined values. Furthermore, since several LDA approaches have been developed, differing in such factors as the representation of the exchange-correlation functional and numerical vs. analytical basis sets, their respective capabilities and limitations must also be assessed. Many comparative studies have been carried out and reviewed [1–5]. The findings, overall, are encouraging. For ground-state properties, DFT-LDA results are generally at least as good as Hartree–Fock, and often are competitive with those obtained by post-Hartree–Fock methods (e.g. Møller–Plesset and configuration interaction). For instance, several studies have found DFT-LDA geometries to be comparable to MP/HF or MCSCF in quality [5, 8, 12, 13]. Calculated dipole moments and polarizabilities are in good agreement with measured values [14]. For a group of six isodesmic reactions, $\Delta E$ was reproduced to within 2 kcal/mol [15]. On the other hand, DFT-LDA approaches significantly overestimate dissociation energies, by as much as 50% [5, 8, 13, 16–20]. This appears to be due largely to the use of the local density approximation [5, 17, 18]. We shall return to this problem later.

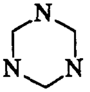
A common view is that "... density functional theory is primarily a ground-state theory." [22] There have accordingly been relatively few investigations of DFT-LDA as a means for studying transition states and activation barriers. One of the first was by Fan and Ziegler [23], who obtained good results for the activation barriers, transition state geometries, and vibrational frequencies associated with two symmetry-allowed isomerization reactions.

We have used a DFT-LDA approach (DMol [9]) to compute the activation energies for a number of reactions (both symmetry-allowed and -forbidden), including (a) a group of seven isomerizations of small molecules (two first-row atoms) [21], and (b) ring dissociations of four heterocycles, **I**–**IV** [20, 21, 24].

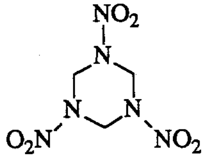
**I**



**II**



**III**



**IV**

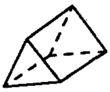
In these studies, we used *ab initio* Hartree–Fock optimized structures for the reactants, products and transition states, and calculated their DFT-LDA energies by single-point runs with the DMol program at the DN or DNP level [9]. This procedure was followed because DMol did not, at that time have adequate geometry optimization capabilities.

The results obtained for reactions of both type (a) and (b) were very satisfactory, in good agreement with the available experimental data [20, 21, 24]. In all instances except the dissociation of **IV**, we also compared the DFT-LDA activation barriers to those obtained with single-point MP/6-31G* calculations, still using the Hartree–Fock structures. A general tendency that we observed was for the magnitudes of the barriers to decrease as the *ab initio* computational level improved from Hartree–Fock to MP2/, MP3/ and MP4/6-31G*. Our DFT-LDA values were usually somewhat lower than the MP4/6-31G*.

The success of these DFT-LDA activation barrier calculations has encouraged us to continue to apply the procedure described above, and we shall present some new results in the next section. With regard to the total energy change, $\Delta E$, those for the isomerization reactions appear to be quite reasonable, judging by the corresponding MP4/6-31G** values, but they are again greatly exaggerated for the dissociations of **I**–**IV**. In this context, however, it is relevant to report that we did obtain accurate DFT-LDA estimates of the dissociation energy of the C–H bond in acetylene [25]. Presumably the errors in the computed energies of $H{-}C{\equiv}C{-}H$ and $H{-}C{\equiv}C\cdot$ are sufficiently similar that they cancel in calculating $\Delta E$.

## 2 Energetics of isomerizations to highly-strained systems

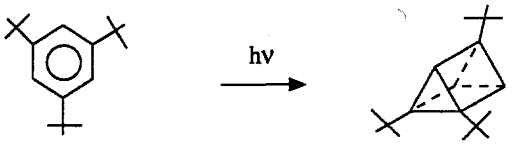
A number of instances are known of unsaturated molecules, including aromatics, undergoing isomerizations to derivatives or analogues of highly-strained trismane, **V** [26–33]; such processes are often photolytically induced.



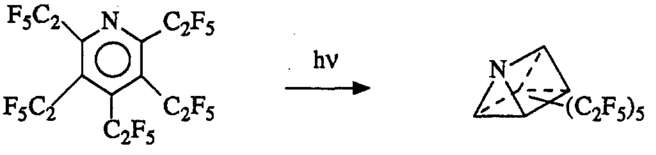
**V**

**VI**

Examples are shown as Eqs. (1) [27] and (2) [29]:



(1)



(2)

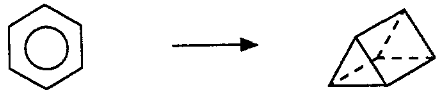
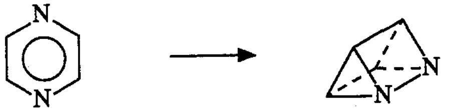
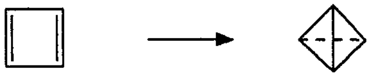
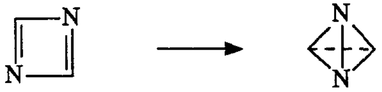
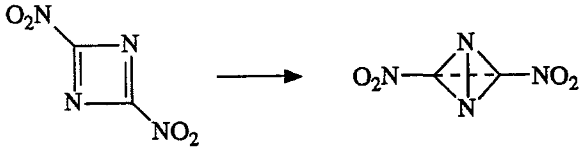
Since highly-strained molecules, especially in the form of their nitro derivatives, are of interest as energetic materials, we have made some preliminary investigations of the energetics associated with several such isomerizations. Two types of reactions were studied: (a) conversions of benzene-like systems to the corresponding triprismanes, and (b) conversions of butadiene-like systems (including a dinitro derivative) to tetrahedrane (VI) and analogues. All geometries (reactants, transition states and products) were optimized at the *ab initio* Hartree–Fock 3-21G level [34], and were verified as corresponding to local minima or transition states by vibrational frequency calculations. The program DMol was then used to compute DFT-LDA/DNP energies for these structures.

The results are in Table 2. These are all endothermic processes, and the transition states were accordingly expected to resemble the products (Hammond's postulate [35]). This was indeed what we found; they were boat-type structures for the conversions to triprismanes, and tetrahedron-like for the others. Since the wavelength used for some of the known photolytic conversions was 254 nm [27, 28], which translates to about 100 kcal/mol, the magnitudes of the activation energies in Table 2 suggest that several of these isomerizations may be attainable. It must be recognized, however, that we have not investigated the entire potential surfaces; thus there may exist other preferred paths or competing reactions. (For more extensive discussions of the cyclobutadiene/tetrahedrane rearrangement, see Refs. [36] and [37].)

## 3 Dissociation energies

As was mentioned in Sect. 1, DFT-LDA approaches tend to overestimate dissociation energies [5, 8, 13, 16–20]. This problem does not extend to total energy changes in general, since good $\Delta E$ values are obtained for isomerization processes [21] and for isodesmic reactions [15]. The error seems to arise when the reactants and products differ considerably in molecular size, as in dissociations; it comes about because of inconsistencies in how well the local density approximation treats exchange and correlation in the fragments of a system compared to the whole [5]. Much effort has been devoted to the development of useful non-local exchange/correlation functionals, and it has led to important advances [1, 2, 38–42]. These do however increase the complexity of the calculations, and the demands upon computer resources. An option that has been used

**Table 2.** Calculated DFT-LDA/DNP reaction and activation energies[a]

| Isomerization process | $\Delta E$ (kcal/mol) | Activation energy (kcal/mol) |
|---|---|---|
|  | 104 | 182 |
|  | 103 | 283 |
|  | 121 | 159 |
|  | 11 | 79 |
|  | 17 | 58 |
|  | 32 | 86 |

[a] Energies were computed using a DFT-LDA approach with the DNP basis set, using structures optimized at the HF/3-21G level

quite successfully is to add non-local corrections to DFT-LDA energies [4, 5, 17, 43, 44]. There has also been some interest in less rigorous means of improving DFT-LDA dissociation energies. Thus, Becke obtained good diatomic bond energies by correcting separately the correlation and exchange contributions to DFT-LDA energies, using empirically-determined parameters in the latter term [17].

Very recently, we have computed optimized DMol/DNP geometries and total energies for more than 70 first- and second-row atoms and molecules [13, 45]. The errors in these DFT-LDA total energies were determined by taking the highly accurate GAUSSIAN 1 values as the standard [46, 47]. All of these energies are presented in Table 3. Figures 1–4 extend our earlier findings for the first-row systems [13], and show that the errors, which can be interpreted as the non-local corrections to the LDA energies, tend to increase as there are more electrons and fewer nuclei. Within each isoelectronic group, the errors diminish as the number of nuclei increases (e.g. see Fig. 5); this may be at least partially due to the accompanying expansion of the basis set.

Particularly striking in Figs. 2–4 are the excellent linear correlations between the errors and the numbers of electrons within each isonuclear series of molecules. Four of these have correlation coefficients of 1.00, and the fifth would

**Table 3.** Comparison of GAUSSIAN 1 energies with those obtained by the DMol/DNP method[a]

| System | GAUSSIAN 1 (G1)[b] | DMol/DNP[c] | Error DMol/DNP-G1 |
|---|---|---|---|
| H | −0.5000 | −0.46620 | 0.0338 |
| $H_2$ | −1.1745 | −1.14200 | 0.0325 |
| Li | −7.4322 | −7.34014 | 0.0921 |
| Be | −14.6234 | −14.45456 | 0.1688 |
| B | −24.6028 | −24.34881 | 0.2540 |
| C | −37.7846 | −37.43458 | 0.3500 |
| N | −54.5178 | −53.99894 | 0.5189 |
| O | −74.9820 | −74.46842 | 0.5136 |
| F | −99.6327 | −99.10258 | 0.5301 |
| LiH | −8.0252 | −7.92719 | 0.0980 |
| BeH | −15.1996 | −15.03489 | 0.1647 |
| CH | −38.4184 | −38.10464 | 0.3138 |
| $CH_2\ (^3B_1)$ | −39.0835 | −38.77782 | 0.3057 |
| $CH_2\ (^1A_1)$ | −39.0731 | −38.75353 | 0.3196 |
| $CH_3$ | −39.7702 | −39.45561 | 0.3146 |
| $CH_4$ | −40.4504 | −40.13144 | 0.3190 |
| NH | −55.1479 | −54.77757 | 0.3703 |
| $NH_2$ | −55.8045 | −55.43089 | 0.3736 |
| $NH_3$ | −56.4878 | −56.11389 | 0.3739 |
| OH | −75.6503 | −75.20806 | 0.4422 |
| $OH_2$ | −76.3489 | −75.91036 | 0.4385 |
| HF | −100.3560 | −99.84698 | 0.5090 |
| $Li_2$ | −14.9077 | −14.73669 | 0.1710 |
| LiF | −107.2922 | −106.71220 | 0.5800 |
| HCCH | −77.2123 | −76.63767 | 0.5746 |
| $H_2CCH_2$ | −78.4629 | −77.87526 | 0.5876 |
| $H_3CCH_3$ | −79.6978 | −79.09471 | 0.6031 |
| CN | −92.5874 | −91.96111 | 0.6263 |
| HCN | −93.3015 | −92.66381 | 0.6377 |
| CO | −113.1822 | −112.47516 | 0.7070 |
| HCO | −113.7103 | −113.01295 | 0.6974 |
| $H_2CO$ | −114.3634 | −113.65398 | 0.7094 |
| $H_3COH$ | −115.5800 | −114.85887 | 0.7211 |
| $N_2$ | −109.3993 | −108.69423 | 0.7051 |
| $H_2NNH_2$ | −111.7271 | −111.01742 | 0.7096 |
| NO | −129.7436 | −128.97961 | 0.7640 |
| $O_2$ | −150.1520 | −149.29846 | 0.8535 |
| HOOH | −151.3891 | −150.54921 | 0.8399 |
| $F_2$ | −199.3277 | −198.35316 | 0.9746 |
| $CO_2$ | −188.3725 | −187.28343 | 1.0890 |
| Na | −161.8462 | −161.4324 | 0.4138 |
| Mg | −199.6461 | −199.1369 | 0.5092 |
| Al | −241.9317 | −241.3019 | 0.6298 |
| Si | −288.9338 | −288.1486 | 0.7852 |
| P | −340.8180 | −339.8432 | 0.9748 |
| S | −397.6549 | −396.8634 | 0.7915 |
| Cl | −459.6767 | −458.6425 | 1.0342 |
| SiH | −289.5507 | −288.8250 | 0.7257 |
| $SiH_2\ (^1A_1)$ | −290.1792 | −289.4409 | 0.7383 |
| $SiH_2\ (^3B_1)$ | −290.1418 | −289.4132 | 0.7286 |
| $SiH_3$ | −290.7936 | −290.0434 | 0.7502 |

**Table 3** (continued)

| System | GAUSSIAN 1 (G1)[b] | DMol/DNP[c] | Error DMol/DNP-G1 |
|---|---|---|---|
| $SiH_4$ | −291.4487 | −290.6885 | 0.7602 |
| PH | −341.4326 | −340.6124 | 0.8201 |
| $PH_2$ | −342.0603 | −341.2337 | 0.8266 |
| $PH_3$ | −342.6999 | −341.8653 | 0.8346 |
| SH | −398.2914 | −397.3706 | 0.9208 |
| $SH_2$ | −398.9425 | −398.0182 | 0.9243 |
| HCl | −460.3445 | −459.3235 | 1.0210 |
| $Na_2$ | −323.7244 | −322.9243 | 0.8001 |
| $Si_2$ | −577.9871 | −576.5814 | 1.4057 |
| $P_2$ | −681.8227 | −680.2164 | 1.6064 |
| $S_2$ | −795.4683 | −793.6754 | 1.7929 |
| $Cl_2$ | −919.4471 | −917.4376 | 2.0095 |
| NaCl | −621.6820 | −620.2641 | 1.4179 |
| SiO | −364.2218 | −363.0954 | 1.1264 |
| SC | −435.7155 | −434.5253 | 1.1902 |
| SO | −472.8312 | −471.5221 | 1.3091 |
| PO | −416.0241 | −414.8063 | 1.2178 |
| ClO | −534.7574 | −533.3489 | 1.4086 |
| ClF | −559.4085 | −577.9165 | 1.4920 |
| $Si_2H_6$ | −581.7161 | −580.2334 | 1.4826 |
| $CH_3SH$ | −438.1896 | −436.9796 | 1.2100 |
| $CH_3Cl$ | −499.5884 | −498.2847 | 1.3036 |
| HOCl | −535.4205 | −534.0056 | 1.4148 |
| $SO_2$ | −548.0191 | −546.3061 | 1.7130 |

[a] All values are in hartrees (1 hartree = 27.21 eV)

[b] Taken from Ref. [46]

[c] The first forty DMol/DNP energies were reported in Ref. [13]; the latter are for molecules containing only first-row atoms.

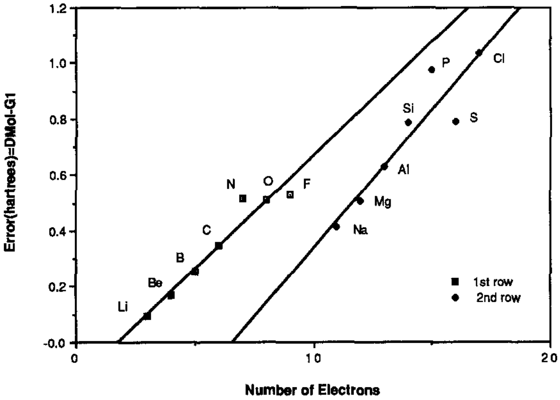


**Fig. 1.** Plot of DMol/DNP error versus number of electrons for first- and second-row atoms. The correlation coefficients are 0.97 and 0.93, respectively.

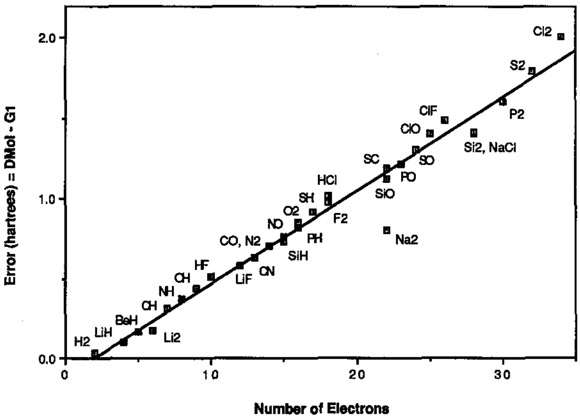


**Fig. 2.** Plot of DMol/DNP error versus number of electrons for systems with two atoms. The linear correlation coefficient is 0.99

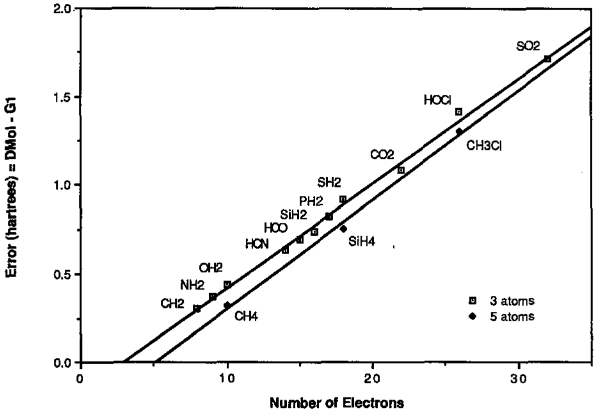


**Fig. 3.** Plot of DMol/DNP error versus number of electrons. Two lines are indicated, for systems with three and five atoms. The correlation coefficients are 1.00

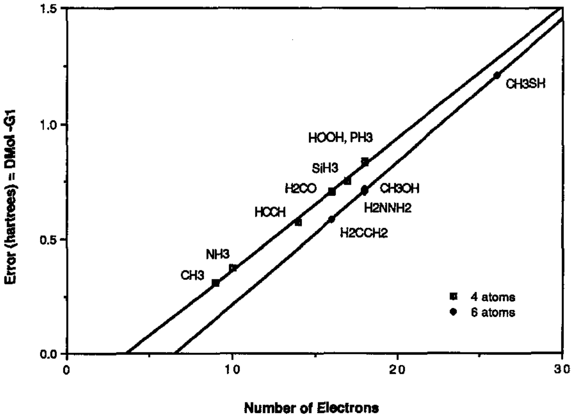


**Fig. 4.** Plot of DMol/DNP error versus number of electrons. Two lines are indicated, for systems with four and six atoms. The correlation coefficients are 1.00

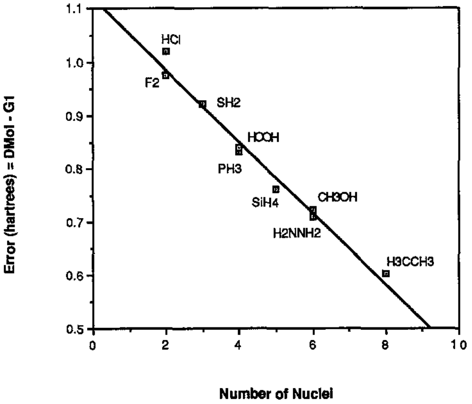


**Fig. 5.** Plot of DMol/DNP error versus number of nuclei for nine molecules with 18 electrons. The linear correlation coefficient is 0.99

also were it not for the deviation shown by $Na_2$. Some theoretical basis for such relationships can be found in earlier work [48]. It is gratifying that these encompass both first- and second-row systems. Figures 2–4 make it possible to obtain reasonable estimates of the non-local corrections to the DMol/DNP total energies of a large number of molecules (not limited to those in Table 3), suggesting that this approach provides a useful empirical means of obtaining dissociation energies.

## Conclusion

Our objective in this paper has been to present an overview of our applications of a DFT/LDA approach to the investigation of reaction energetics. We have summarized our earlier work, and also presented new results related to some isomerization processes as well as a promising empirical method for estimating the corrections needed to obtain reliable dissociation energies. We are continuing and expanding these types of studies.

*Acknowledgements.* We are grateful for the support of this work by the Office of Naval Research, through contract # N00014-91-J-4057, and by the Air Force Office of Scientific Research, through contract # AFOSR-88-0068. We also appreciate the computing facilities provided by the San Diego Supercomputer Center.

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