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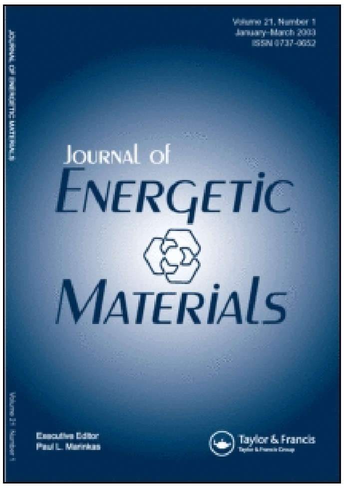

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A DFT Study on Nitro Derivatives of Pyridine

Lemi Türker[a]; Selçuk Gümüş[a]; Taner Atalar[a]
[a] Department of Chemistry, Middle East Technical University, Ankara, Turkey

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A DFT Study on Nitro Derivatives of Pyridine

LEMİ TÜRKER, SELÇUK GÜMÜŞ, and
TANER ATALAR

Department of Chemistry, Middle East Technical
University, Ankara, Turkey

The heat of formation values of all possible nitro derivatives of pyridine have been calculated by the application of various density functional theory (DFT) methods by a proper isodesmic reaction. The heat of formation data trends in series are found to be independent of the selected DFT method, although some differences have been observed in value. Total energies and nucleus-independent chemical shift (NICS(0)) values have also been calculated in order to jugde the aromatic stabilities for the nitropyridine derivatives. Moreover, a novel topological (Türker-Gümüş, TG) index has been defined for modeling the detonation properties of the explosives.

Keywords: heat of formation, isodesmic reaction, NICS, nitropyridines, topological index

Introduction

The pyridine ring system occurs in the structures of many natural products, pharmaceutical and agrochemical compounds, and other commercial substances. A wide range of synthetic

Address correspondence to Lemi Türker, Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey. E-mail: lturker@metu.edu.tr

methods has, therefore, been developed, both for construction of the pyridine ring and for its substitution [1]. However, with common nitrating systems, nitration of pyridine and its simple C-alkyl derivatives at a ring carbon atom generally results in a very low yield of nitropyridine and is of little synthetic value [2]. Unfortunately, one of the most important classes of aromatic substitution reactions, electrophilic aromatic substitution, takes place with great difficulty and only under forcing conditions [3], due to the electron-deficient character of the pyridine ring. Thus, many simple nitropyridines, which are synthetic precursors of potential pharmaceutical and agrochemical importance [1,4–8], are not available by conventional direct nitration of the parent pyridine. Katritzky et al. [9] and Bakke [1] have reported the synthesis of β-nitro (3-nitro) pyridine.

The search for new potential high-energy density materials (HEDMs) is ongoing [10–16]. Good high-energy materials possess high density, have a fast velocity of detonation, and are energetically unstable with respect to their reaction products. They are also expected to have relatively high positive heat of formation (HOF) values. In the literature, there are a few studies (either experimental or theoretical) considering nitro pyridines as explosives [17–19]. With the idea that nitro derivatives of pyridine can be candidates for HEDMs, we have performed a theorectical analysis on all possible nitro derivatives of pyridine. The HOF values of all the systems obtained by several computational methods (B3LYP, B3P86, B3PW91, and BH and HLYP) have been reported.

Method of Calculation

Computations were performed via the Gaussian 03 package program [20]. The geometry optimizations of all the structures have been performed by the application of density functional theory (DFT) calculations with various exchange correlation functions (B3LYP, B3P86, B3PW91, and BH and HLYP) and basis sets (6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), and cc-pvdz).

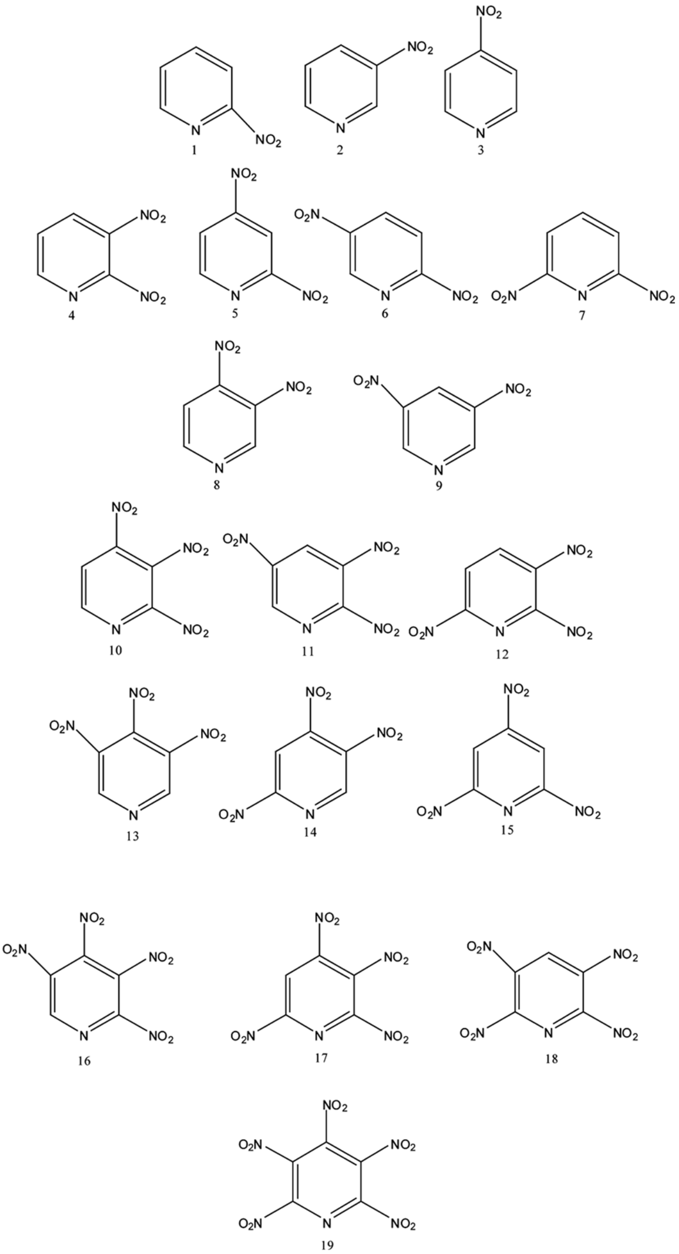


Figure 1. Structures of the considered species.

Various isodesmic reaction schemes were selected for the calculation of the heats of formation of all possible mono through penta nitropyridines (see Fig. 1 for the structures).

Nucleus-independent chemical shift calculations at the center of the rings (NICS(0)) were performed on all the molecules using the gauge-invariant atomic orbital (GIAO) approach [21] at the B3LYP/6-31G(d,p) level. The B3LYP/6-31G(d,p) optimized geometries were used for the NICS calculations.

Geometry optimizations of the molecules were performed by the above-mentioned methods without any geometrical restriction. For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

Results and Discussion

Energetics

The total energies (zero point energy corrected) of the molecules under present consideration with different correlation functions and basis sets are given in Tables 1–4. According to the results of the calculations with all the correlation functions, the lowest energies are obtained by 6-311G(d,p) basis set. When the total energies of all the molecules are considered, 2-nitropyridine (1), 2,6-dinitropyridine (7), 3,4,5-trinitropyridine (13), and 2,3,4,5-tetranitropyridine (16) have been found to be the most stable ones among the mono-, di-, tri-, and tetra-nitropyridine derivatives, respectively. The most stable isomer of each of the series showed that when the nitro groups are close to the heteroatom of the main skeleton (except for the tri-nitro derivatives), the stability of that isomer increases. This is quite reasonable because the electrons located on the electronegative pyridine nitrogen atom can be pulled away into the ring by the attachment of very strong electron-withdrawing

Table 1
The zero-point energy corrected total electronic energies of the nitropyridine derivatives, calculated with B3LYP correlation function with different basis sets (energies are in hartrees)

	B3LYP			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	−452.689532	−452.709845	−452.80113	−452.717338
2	−452.689602	−452.709798	−452.800617	−452.717122
3	−452.688901	−452.70916	−452.800036	−452.716564
4	−657.047314	−657.075353	—	−657.144494
5	−657.174446	−657.203641	−657.342775	−657.223184
6	−657.174836	−657.204063	−657.343051	−657.218521
7	−657.174686	—	−657.341403	−657.223462
8	−657.14516	−657.173299	−657.312698	−657.19437
9	−657.174884	−657.203899	−657.342522	−657.223279
10	−861.580508	−861.616593	−861.806221	−861.652558
11	−861.626906	−861.663862	−861.851957	−861.697594
12	−861.626781	−861.66409	−861.852224	−861.697568
13	−861.655015	−861.692949	−861.880401	−861.725182
14	−861.57952	−861.615112	−861.804144	−861.651299
15	−861.626347	−861.663222	−861.851214	−861.697103
16	−1066.099564	−1066.147338	−1066.382092	−1066.190398
17	−1066.058708	−1066.1035	−1066.341774	−1066.152564
18	−1066.078437	−1066.123341	−1066.360738	−1066.170578
19	−1270.226295	−1270.274305	−1270.546198	−1270.329301

nitro groups. The nitro groups increase the electron density as well as the aromatic character of the main pyridine skeleton that was partially lost by the insertion of one nitrogen atom into a benzene ring, to construct pyridine from benzene theoretically.

NICS

Aromaticity continues to be an actively investigated area of chemistry. The simplest criterion for aromatic compounds is

Table 2

The zero-point energy corrected total electronic energies of the nitropyridine derivatives, calculated with B3P86 correlation function with different basis sets (energies are in hartrees)

	B3P86			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	−453.831438	−453.847361	−453.937954	−453.862569
2	−453.831348	−453.847152	−453.937346	−453.891451
3	−453.830634	−453.846507	−453.936743	−453.890744
4	−658.576338	−658.597268	−658.731951	−658.671927
5	−658.705314	−658.728616	−658.86677	−658.757868
6	−658.705745	−658.729056	−658.804212	−658.758251
7	−658.704685	−658.729219	−658.86753	−658.758376
8	−658.671074	−658.698375	−658.836685	−658.728869
9	−658.705578	−658.728698	−658.868533	−658.757819
10	−863.499713	−863.528902	−863.721224	−863.621552
11	−863.546587	−863.576413	−863.7631	−863.5759
12	−863.546653	−863.546653	−863.763524	−863.621712
13	−863.574994	−863.605566	−863.800016	−863.649475
14	−863.498918	−863.527659	−863.714993	−863.574835
15	−863.546143	−863.575942	−863.762502	−863.62115
16	−1068.408277	−1068.447361	−1068.680777	−1068.504338
17	−1068.366954	−1068.403462	−1068.639588	−1068.465355
18	−1068.387043	−1068.423651	−1068.659034	−1068.484801
19	−1272.91901	−1272.958433	−1273.227441	−1273.026394

that they possess cyclic conjugated π-systems containing the proper number of π-electrons (i.e., the Hückel rule). Though this criterion is robust enough to predict the aromaticity of a host of neutral and charged ring systems, it is not always a clear indicator of aromaticity for more complex systems (as in our case).

Aromaticity is expressed by a combination of properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural, and magnetic criteria [22–27].

Table 3
The zero-point energy corrected total electronic energies of the nitropyridine derivatives, calculated with B3PW81 correlation function with different basis sets (energies are in hartrees)

	B3PW81			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	−452.516185	−452.53241	−452.621037	−452.546942
2	—	−452.532059	−452.620289	−452.546411
3	−452.51526	−452.53145	—	−452.545836
4	−656.912428	−656.937264	−657.072302	−656.964245
5	−656.924728	−656.948509	−657.084042	−656.976443
6	−656.925126	−656.948905	−657.084405	−656.976798
7	−656.925282	−656.949229	−657.084914	−656.977077
8	−656.8949	−656.91785	−657.053552	−656.947048
9	−656.924827	−656.948433	−657.083611	−656.976236
10	−861.306026	−861.338123	−861.520528	−861.378995
11	−861.317853	−861.350028	−861.532151	−861.390926
12	−861.317236	—	−861.532027	−861.39046
13	−861.329266	−861.360504	−861.543463	—
14	−861.252321	−861.281643	−861.465709	−861.402415
15	−861.314994	−861.346942	−861.52933	−861.387976
16	−1065.697384	−1065.737299	−1065.966667	−1065.791732
17	−1065.707991	−1065.74746	−1065.97739	−1065.802579
18	−1065.707389	−1065.747957	−1065.977127	−1065.802326
19	−1270.086847	−1270.134829	—	−1270.202933

In 1996, Schleyer et al. introduced a simple and efficient probe for aromaticity: nucleus-independent chemical shift (NICS) [28], which is the computed value of the negative magnetic shielding at some selected point in space, generally at a ring or cage center. Negative NICS values denote aromaticity (−11.5 for benzene, −11.4 for naphthalene), positive NICS values denote anti-aromaticity (28.8 for cyclobutadiene), and small NICS values indicate non-aromaticity (−2.1 for cyclohexane, −1.1 for adamantane). NICS may be a useful indicator of

Table 4
The zero-point energy corrected total electronic energies of the nitropyridine derivatives, calculated with BH and HLYP correlation function with different basis sets (energies are in hartrees)

	BH and HLYP			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	−452.41912	−452.435923	−452.524552	−452.4493
2	−452.4197	−452.436412	−452.524562	−452.4495
3	−452.418499	−452.43527	−452.523507	−452.448455
4	−656.777152	−656.802181	−656.937656	−656.82857
5	−656.790278	−656.814338	−656.95036	−656.841853
6	−656.790993	−656.815064	−656.951046	−656.84252
7	−656.790379	−656.814632	−656.950808	−656.842063
8	−656.758741	−656.782138	−656.91832	−656.810767
9	−656.79174	−656.81566	−656.951208	−656.842873
10	−861.131131	−861.163061	−861.346486	−861.204209
11	−861.144701	−861.176914	−861.359904	−861.217824
12	−861.143204	−861.17549	−861.358905	−861.216564
13	−861.156297	−861.187625	−861.371525	−861.229801
14	−861.074822	−861.104552	−861.289541	−861.149775
15	−861.141221	−861.172941	−861.356453	−861.214442
16	−1065.482782	−1065.52222	−1065.753055	−1065.577593
17	−1065.493661	−1065.532784	−1065.764208	−1065.588892
18	−1065.493139	−1065.533491	−1065.764042	−1065.588449
19	−1269.83074	−1269.878052	−1270.15661	−1269.947728

aromaticity that usually correlates well with the other energetic, structural, and magnetic criteria for aromaticity [29–32]. Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of individual rings of polycyclic systems.

In the present case, NICS values of the various nitropyridine derivatives have been calculated by the application of density functional theory using the standard 6-31G(d,p) basis set (Table 5). All the molecules have been found to be aromatic. Due the electronegativity of the pyridine nitrogen, the ring does not have homogeneous electron distribution, in contrast to benzene, and thus possesses relatively poor aromaticity. The aromaticity of pyridine itself is expected to be improved by the substitution of nitro groups because insertion of a nitro group into the system will pull the electrons located on the nitrogen

Table 5
NICS(0) values (ppm) of the pyridine and nitropyridine systems

	B3LYP/6-31G(d,p)
Pyridine	−8.08
1	−9.45
2	−9.22
3	−9.51
4	−10.54
5	−10.81
6	−10.12
7	−10.78
8	−10.44
9	−9.84
10	12.61
11	−12.00
12	−12.46
13	−11.91
14	−11.99
15	−11.87
16	−12.79
17	−13.47
18	−13.61
19	−13.08

atom of the pyridine ring and let these electrons delocalize over the ring better (even much better in symmetrically nitro substituted pyridines), which will lead to an improved aromaticity. Therefore, the greater the number of nitro groups properly oriented in the pyridine system, the more aromatic the structure will be. As can be seen in Table 5, the NICS values of the systems increase (absolutely) as the number of nitro groups in the structures increases.

Heats of Formation

Thermochemical and molecular properties are critical parameters in many aspects of gas kinetics, and the accuracy to which these parameters are determined can greatly affect the determination of a variety of parameters including rate coefficients, rates of heat release, and branching ratios, all of which are critical in the accurate simulation of reactive gas-phase systems.

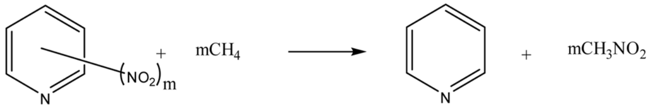
HOF of a molecule has significant practical application to explore reactivity and equilibrium of a chemical reaction. It is important to find the heats of formation of various compounds correctly. For the aromatic nitro compounds, although some of their heats of formation can be found experimentally, certain nitro compounds are very difficult to synthesize and some are highly unstable. Hence, it would be useful to develop a reliable theoretical means to calculate the heats of formation of these energetic materials.

HOF values have been calculated by ab initio methods for many years, especially for some high-level theories, such as G2, G3, QCISD (T), CCSD (T), and MP4SDTQ approaches [33–39]. However, these approaches require long computation times and can only be used for small to medium-size molecules. DFT has emerged as a reliable theoretical method to calculate geometries of molecules. Hence, it has been used to evaluate the heats of formation of interested molecules [40–44] and the results indicate that DFT is a reliable method. Rice et al. [42] reported methods to predict gas-phase heats of formation of energetic materials using quantum mechanical calculations.

Among these methods, predictions for gas-phase heats of formation are based on Hess's law [45], combined with quantum mechanical and experimental information. The application of the Hess's law requires building a chemical reaction scheme. The isodesmic reaction, in which numbers of electron pairs and chemical bond types are conserved in the reaction, allows canceling of errors inherent in the approximate treatment of electron correlation in the solutions to quantum mechanic equations. Hence, various reports of the heats of formation of the molecules have been given by various isodesmic reaction schemes [37–51]. Ventura et al. [52] and Ventura and Kieninger [53] pointed out that DFT methods using modest basis sets and isodesmic reactions can produce very accurate thermochemical information, in many cases superior to results from G2 and even CCSD (T).

Chen et al. [54] investigated the HOF values of various aromatic nitro compounds and they found that the results were quite close to the experimental data. In the present study, the complete series of nitropyridine derivatives was selected to calculate the heats of formation through the selected isodesmic reaction, using various DFT methods and basis sets. Because these kinds of calculations are reliable, as pointed out before, the heats of formation of compounds whose heats of formation cannot be determined by experimental techniques can be obtained theoretically.

As indicated by Foresman and Frisch [55], different isodesmic reactions would predict different values of HOF for the same molecule. Therefore, it is necessary to properly select the isodesmic reaction of the studied molecule. Because isodesmic reactions require as many experimental data as possible in order to be applied conveniently, we have chosen the isodesmic reaction shown in Scheme 1 because of its convenience to get the required HOF data for pyridines. We could find the experimental HOF values for pyridine, methane, and nitromethane in the literature. Additionally, in an isodesmic reaction, the bonding in both sides of the reaction must be as similar as possible. Therefore, after a detailed survey of various possible isodesmic reactions, the following isodesmic reaction (Scheme 1) has been



Scheme 1. Isodesmic reaction considered presently.

selected in order to calculate the HOF values of nitropyridine systems (1–19) presently considered.

The general bond separation reaction of the systems under consideration is presented in Scheme 1 and the calculated energies of all species are listed in Tables 1–4. The energy difference between the products and reactants shown in Scheme 1 has been calculated as the heat of reaction (ΔH_{rxn}). From the calculated ΔH_{rxn} and experimental heats of formation at 298 K of methane, pyridine, and nitromethane, heats of formation (ΔH_f) values of all the molecules (1–19) can be calculated and the results of various DFT methods are listed in Tables 6–9. It is well known that DFT methods underestimate the energies by 1–3 kcal/mol only [56]. Because they are all difficult to synthesize, the experimental gas-phase enthalpies of formation values of the present systems are not available in the literature. Thus, no comparison with the experimental values has been done.

The HOF values obtained by different DFT methods and basis sets are mostly close to each other. However, for some molecules there are differences in the heats of formation between the applied methods (see Figs. 2–5 for the variation of HOF data with the applied DFT method). Each method has its own approximation scheme. Therefore, the deviation of the HOF data from one to another is not surprising.

On the other hand, we wanted to compare the HOF data obtained from the isodesmic reaction in Scheme 1 with direct calculation of the HOF using the atomization scheme. The heats of formation of pyridine and 2-nitropyridine (**1**) have been calculated by the application of the G3MP2 method and the atomization scheme. The calculated value of ΔH_f for pyridine is 138.5 kJ/mol, approaching the experimental value of

Table 6
The calculated heat of formation values of the nitropyridine derivatives based on the isodesmic reaction in Scheme 1, with B3LYP functional and different basis sets (energies are in kJ/mol)

	B3LYP			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	118.8	129.0	125.2	123.5
2	118.6	129.1	126.5	124.1
3	120.4	130.8	128.1	125.5
4	447.4	472.0	—	328.4
5	113.6	135.2	126.9	121.8
6	112.6	134.1	126.2	134.1
7	112.9	—	130.5	121.1
8	190.5	214.8	205.9	197.5
9	112.4	134.5	127.6	121.6
10	315.4	353.6	334.0	320.9
11	193.6	229.5	213.9	202.7
12	193.9	228.9	213.2	202.8
13	119.8	153.1	139.2	130.3
14	318.0	357.5	339.4	324.3
15	195.1	231.2	215.8	204.0
16	220.6	262.7	245.8	235.3
17	327.9	377.8	351.7	334.6
18	276.1	325.8	301.9	287.3
19	1155.8	1232.0	1238.8	1197.0

140 kJ/mol [18] (there is only a 1.07% error for ΔH_f of pyridine). Therefore, the reliability of the G3MP2 method has been confirmed. Thereafter, ΔH_f for 2-nitropyridine has been calculated (by the atomization scheme with the G3MP2 method) and found to be 128.8 kJ/mol, which is very close to our value (129.0 kJ/mol) obtained by the B3LYP/6-31++G(d,p) method. Therefore, the B3LYP/6-31++G(d,p) method can be regarded as the best among all the methods applied in this

Table 7
The calculated heat of formation values of the nitropyridine derivatives based on the isodesmic reaction in Scheme 1, with B3P86 functional and different basis sets (energies are in kJ/mol)

	B3P86			
	6-31G(d,p)	6-31++G(d,p)	6311G(d,p)	cc-pvdz
1	117.4	125.9	124.2	122.0
2	117.6	126.5	125.8	46.2
3	119.5	128.2	127.4	48.0
4	450.0	474.1	479.5	345.3
5	111.4	129.3	125.5	119.7
6	110.2	128.1	289.8	118.6
7	113.0	127.7	123.6	118.3
8	201.3	208.7	204.5	195.8
9	110.7	129.1	120.9	119.8
10	314.0	345.3	322.2	200.3
11	191.0	220.5	212.2	320.2
12	190.8	298.6	211.1	199.9
13	116.4	144.0	115.3	127.0
14	316.1	348.5	338.5	323.0
15	192.1	221.7	213.8	201.4
16	217.0	251.0	242.8	230.9
17	325.5	366.2	351.0	333.2
18	272.7	313.2	299.9	282.1
19	1164.4	1226.3	1247.6	1208.5

study for the determination of the HOF values of nitro derivatives of pyridine.

Predicted Densities and Detonation of the Nitropyridine Derivatives

Density (ρ), detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the performances

Table 8

The calculated heat of formation values of the nitropyridine derivatives based on the isodesmic reaction in Scheme 1, with B3PW91 functional and different basis sets (energies are in kJ/mol)

	B3PW91			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	118.6	127.1	125.2	123.0
2		128.1	127.1	124.4
3	121.0	129.7	140.1	125.9
4	146.0	161.3	158.4	153.9
5	113.8	131.8	127.6	121.9
6	112.7	130.7	126.7	121.0
7	112.3	129.9	125.3	120.2
8	192.1	212.3	207.7	199.1
9	113.5	132.0	128.7	122.4
10	180.5	205.9	199.7	191.5
11	149.4	174.7	169.2	160.2
12	151.1		169.5	161.4
13	119.5	147.2	139.5	
14	321.5	354.2	343.6	130.0
15	156.9	182.8	176.6	167.9
16	220.8	255.0	246.4	234.4
17	193.0	228.3	218.3	205.9
18	194.5	227.0	218.9	206.6
19	266.1	308.4		281.3

of explosion of energetic materials and can be predicted by the empirical Kamlet-Jacobs equations [57] as follows:

$$\mathrm{D} = 1.01(\mathrm{N\ M}^{1/2}\ \mathrm{Q}^{1/2})^{1/2}(1 + 130\rho) \tag{1}$$

$$\mathrm{P} = 1.558\rho^2\mathrm{N\ M}^{1/2}\ \mathrm{Q}^{1/2} \tag{2}$$

Table 9
The calculated heat of formation values of the nitropyridine derivatives based on the isodesmic reaction in Scheme 1, with BHandHLYP functional and different basis sets (energies are in kJ/mol)

	BHandHLYP			
	6-31G(d,p)	6-31++G(d,p)	6-311G(d,p)	cc-pvdz
1	123.0	273.2	129.6	124.6
2	121.5	131.4	129.5	124.1
3	124.6	134.4	132.3	126.8
4	158.0	175.3	170.6	160.9
5	123.5	143.4	137.2	126.1
6	121.7	141.5	135.4	124.3
7	123.3	142.7	136.1	125.5
8	206.3	228.0	221.4	207.7
9	119.7	140.0	135.0	123.4
10	203.6	232.1	222.9	206.8
11	168.0	195.7	187.6	171.0
12	171.9	199.5	190.3	174.3
13	137.6	167.6	157.1	139.6
14	351.5	385.7	372.4	349.7
15	177.1	206.1	196.7	179.9
16	255.4	293.3	281.1	258.5
17	226.8	265.6	251.8	228.8
18	228.2	263.8	252.2	230.0
19	316.8	363.3	347.2	318.8

where D is detonation velocity in km/s, P is detonation pressure in GPa, ρ is density of a compound in g/cm^3, N is moles of gaseous detonation products per gram of explosive (in mol/g), M is average molecular weight of gaseous products (in g/mol), and Q is chemical energy of detonation in kJ/g. Here, the parameters N, M, and Q have been calculated according to the chemical composition of each explosive [58,59] as listed in Table 10. On the other hand, the density of each molecule

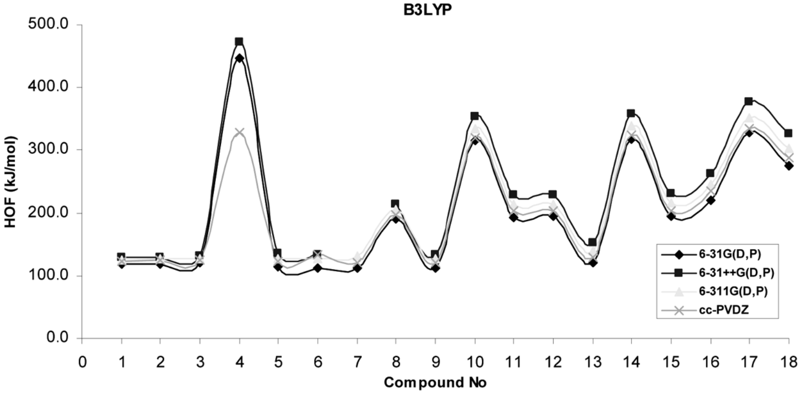


Figure 2. The variation of HOF data with the applied basis set (B3LYP).

has been predicted from the molecular volume, and the molecular volume of each molecule has been obtained from the statistical average of 100 single-point calculations for each optimized structures. The molar volume has been defined as inside a contour of 0.001 electrons/Bohr^3 density that was evaluated using a Monte Carlo integration implemented in the Gaussian 03 package. This method was successfully tested on various CHNO molecules and accurately predicts the explosive properties

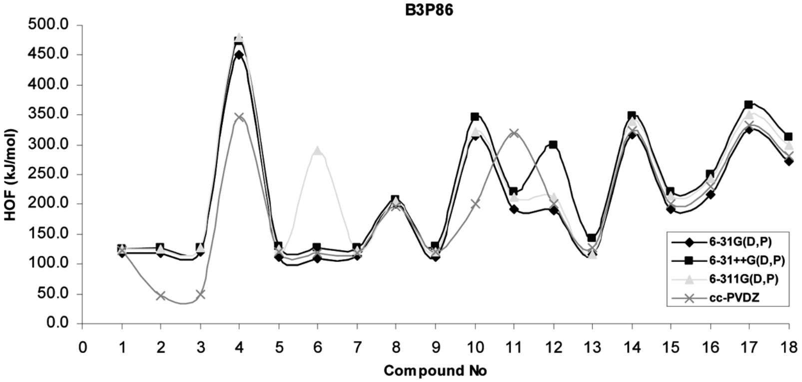


Figure 3. The variation of HOF data with the applied basis set (B3P86).

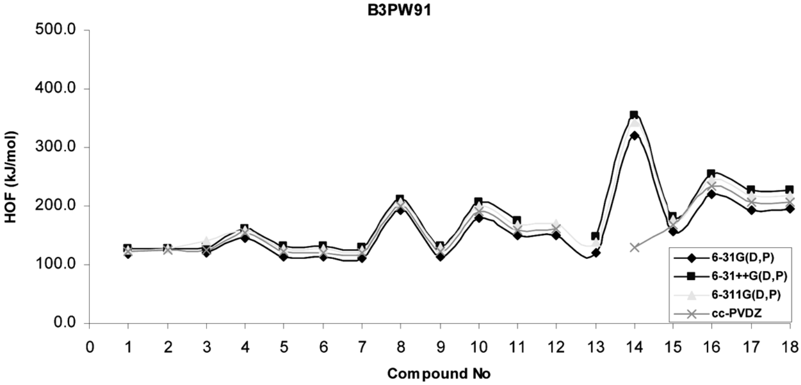


Figure 4. The variation of HOF data with the applied basis set (B3PW91).

[59–64]. We have calculated the densities of two well-known explosives trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) with the method mentioned in the text. The calculated values for TNT and TATB are 1.68 and 1.90 g/cm^3, respectively, whereas the experimental values are 1.64 and 1.88 g/cm^3 for TNT and TATB, respectively. Thus, the method applied here is successful for determination of the densities of compounds within the limits of some small errors.

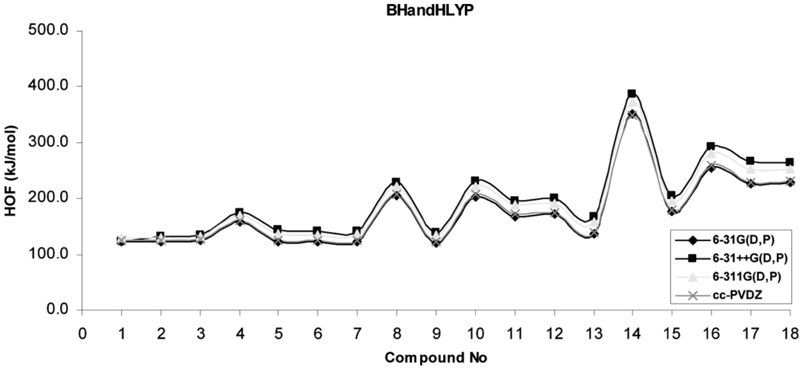


Figure 5. The variation of HOF data with the applied basis set (BHandHLYP).

Table 10
Methods for calculating the N, M, and Q parameters of the $C_aH_bO_cN_d$ explosive[a,b]

	stoichiometric ratio		
paraneters	$c \geq 2a+b/2$	$2a+b/2 > c \geq b/2$	$b/2 > c$
N	$(b+2c+2d)/4MW$	$(b+2c+2d)/4MW$	$(b+d)/2MW$
M	$4MW/(b+2c+2d)$	$(56d+88c-8b)/(b+2c+2d)$	$(2b+28d+32c)/(b+d)$
Q	$(28\ 9b+94.05a+0.239\ \Delta Hf^{\circ})/MW$	$[28\ 9b+94.05(c/2-b/4)+0.239\ \Delta Hf^{\circ}]/MW$	$57.8c+0.239\ \Delta Hf^{\circ})/MW$

[a] $C_aH_bO_cN_d$ denotes the compound composed of the C, H, O, and N elements; a, b, c, and d stand for the number of C, H, O, and N atoms in the compound.

[b] N is moles of gaseous detonation products per gram of explosive (in mol/g); M is the average molecular weight of the gaseous products (in g/mol); Q is the chemical energy of detonation (in kJ/g); MW in the formula is the molecular weight of the title compounds (in g/mol); ΔH^* is the standard heat of formation of the studied compound (in kJ/mol).

In the present study, single-point molecular volume calculations at B3LYP/6-31G(d,p) have been performed based on the B3LYP/6-31G(d,p) geometry optimized structures. Table 11 shows the predicted densities and detonation properties of the nitropyridine derivatives together with the TG index (see Appendix). The PM3 calculated HOF values were also calculated and listed in Table 11. The previously reported studies have proven that the heats of formation calculated by the PM3 method are reliable [65–68]. All these data in Table 11 provide some clue about the explosive character of the molecules derived from pyridine.

It was clear that from monosubstituted to pentasubstituted nitropyridines, density (ρ), velocity of detonation (D), and detonation pressure (P) all increase with the increasing number of the nitro groups. This might show good group additivity on

Table 11
Predicted densities and detonation properties of the nitropyridine derivatives (HOF values are obtained from PM3 calculations, V data are obtained from 100 single-point calculations at the 6-31G(d,p) level)

	HOF (kJ/mol)	Q (kJ/g)	V (cm^3/ mol)	ρ (g/cm^3)	D (km/s)	P (GPa)	TG Index
1	117.25	1,158.24	79.09	1.57	7.17	23.46	2,482
2	103.93	1,132.58	78.25	1.58	7.21	23.32	1,946
3	108.59	1,141.57	78.76	1.57	7.18	23.34	2,398
4	145.82	1,414.87	101.03	1.67	8.87	32.56	11,363
5	113.08	1,368.58	101.96	1.66	8.72	31.87	10,425
6	112.66	1,367.99	103.56	1.63	8.58	31.62	12,544
7	122.59	1,382.02	102.25	1.65	8.71	31.99	10,095
8	160.28	1,435.33	104.77	1.61	8.58	32.20	10,647
9	102.78	1,354.01	101.42	1.67	8.74	31.79	10,708
10	249.99	1,648.01	121.30	1.76	10.16	39.49	31,926
11	163.92	1,551.88	124.71	1.72	9.74	37.79	34,283
12	178.55	1,568.23	121.95	1.75	9.98	38.42	35,437
13	129.24	1,513.15	123.98	1.73	9.73	37.43	31,658
14	241.85	1,638.91	125.01	1.71	9.85	38.79	35,018
15	179.11	1,568.85	124.07	1.72	9.82	38.10	30,539
16	190.48	1,649.08	140.37	1.85	10.91	42.58	81,158
17	293.20	1,743.87	141.58	1.83	10.97	43.60	78,592
18	241.09	1,695.79	143.26	1.81	10.77	42.75	86,254
19	512.22	1,949.58	159.91	1.90	11.93	48.66	170,430

the detonation properties and supports the claim that introducing more nitro substituents into a molecule usually helps to increase its detonation performance. To visualize the power of the compounds presently investigated, the respective values of hexogen (RDX) and octogen (HMX) are considered. For RDX and HMX [69], experimental values of D and P are 8.75 km/s ($\rho = 1.8\,g/cm^3$), 9.11 km/s ($\rho = 1.89\,g/cm^3$), and 34.70 GPa ($\rho = 1.8\,g/cm^3$), 39.00 GPa ($\rho = 1.89\,g/cm^3$), respectively. Furthermore, at the same theoretical level (B3LYP/6-

31G(d,p)), the calculated performance parameters D and P of hexogen (RDX) and Octogen (HMX) were found to be 8.83 km/s, 8.998 km/s and 34.11 GPa, 35.92 GPa, respectively. Comparing these values with tri-nitropyridine compounds, compound **13** has velocity of detonation value of 9.73 km/s and detonation pressure value of 37.43 GPa. All the other tri-nitro derivatives, tetra-nitro and penta-nitro derivatives possess D and P values greater than that of compound **13**. Therefore, one finds them to be more powerful explosives than the well-known explosives HMX and RDX. Furthermore, the relative position of the nitro substituent in the pyridine compounds affects the detonation properties (see Table 11). In particular, di- and tri-nitro-substituted pyridines will be novel potential candidates for HEDMs when they are successfully synthesized.

Correlation with the TG Index

The results of the correlation analysis of the ln(TG) index (see Appendix) with the explosive properties are given in Table 12. The data in the table reveal that the topological (Türker-Gümüş, TG) index can successfully be used for the prediction of the explosive properties of HEDMs, because the correlation coefficient exceeds 0.98 for D and 0.99 for P.

Table 12
The regression equation and the correlation coefficient between the natural logarithm of the TG index and the explosive properties

Property	Regression equation	r^2
Q	$y = 166.96x - 158.21$	0.9540
V	$y = 18.12x - 64.127$	0.9864
ρ	$y = 0.0723x + 0.9921$	0.9178
D	$y = 1.0532x - 1.039$	0.9846
P	$y = 5.6048x - 20.03$	0.9903

Within the set of the equations in Table 12, the lowest correlation is for the density (0.91). In order to figure out the effect of the errors in density calculations by means of TG index on the detonation parameters, we obtained points ultimately off the line from the plot of density versus the ln(TG) index. Then, we calculated new densities including these ± maximum deviations. Thereafter, by means of the Kamlet-Jacobs equations, new ballistic properties were obtained. Then, the percentage errors were found to be at most within the range of ±3.2% for D and ±1.6% for P compared to the calculated D and P values with the Kamlet-Jacobs equations based on quantum chemically calculated ρ values. These values are acceptable if one considers the burden linked to quantum chemical calculation of D and P values by means of the Kamlet-Jacobs equations. However, one can estimate the D and P values directly by using the corresponding equations given in Table 12 and the ln(TG) index. Then there is no need to use the Kamlet-Jacobs equations. One should also keep in mind that the Kamlet-Jacobs equations hold closely only for ideal explosives; for nonideal ones deviations are unavoidable. It is noteworthy that quantum chemically calculated densities bring some errors to results of the Kamlet-Jacobs equations. Rice et al. systematically criticized the method employed to calculate the crystal densities quantum chemically [70]. Their investigation revealed that depending on the type of the structure, errors (root mean square deviations) may vary between 1 and 6.6%. Especially for polynitro compounds, errors are sometimes as high as 4.8% (octanitrocubane), 3.9% (octanitropentane) or as low as 0.1% (heptanitrocubane) [70]. The ballistic properties obtained by means of any calculation method are helpful for design purposes. The real behavior of an explosive is to be determined by field tests.

Conclusion

All possible nitropyridine derivatives have been subjected to theoretical analysis in order to obtain information about their structural and electronic properties. The stabilities of the systems have been investigated by calculating the total electronic energies and NICS values at ring centers. The results of the calculations showed that the closer the nitro group to the heteroatom of the main skeleton, the more stable the system, and attachment of nitro groups stabilizes the parent pyridine structure by increasing the aromaticity of the system. Moreover, the heats of formation of 19 aromatic nitropyridine compounds were calculated by means of selected isodesmic reaction schemes, together with different DFT methods. Generally, the value of HOF for a compound depends on the selected isodesmic reaction and DFT method. However, calculation of the HOF of 2-nitropyridine using the atomization scheme at G3MP2 level showed similar results to that of the B3LYP/6-31++G(d,p) method.

One should note that for an explosive the real interest is the density and other properties in the solid state. However, the present study, in which quantum chemical results are for gas-phase molecules, provides some information about the relative stabilities, enthalpies, and detonation properties of explosives according to one another.

Lastly, a novel topological index has been introduced for modeling the explosive properties of nitropyridines. The calculation of the index is quite simple and not time consuming compared to expensive computational efforts.

References

[1] Bakke, J. M. 2003. Nitropyridines: Synthesis and reactions. *Pure and Applied Chemistry*, 75: 1403–1415.

[2] Friedl, F. 1912. Preparation of nitropyridine. *Chemische Berichte*, 45: 428–430.

[3] Scriven, E. F. V. and G. Jones. 1984. In A. J. Boulton and A. McKillop (eds.), *Comprehensive Heterocyclic Chemistry, Vol. 2*, Oxford: Pergamon.

[4] Bakke, J. M., H. S. H. Gautun, C. Romming, and I. Sletvold. 2001. 5-Nitropyridine-2-sulfonic acid, a new precursor for 2,5-disubstituted pyridines. *ARKIVOC*, 10: 26–34.

[5] Chen, J., G. Ling, and S. Lu. 2003. Synthesis of new unsymmetric N,N′-dipyridylurea derivatives by selenium and selenium

dioxide-catalyzed reductive carbonylation of substituted nitropyridines. *Tetrahedron*, 59: 8251–8256.

[6] Romero, D. L., R. A. Morge, C. Biles, N. Berrios-Pena, P. D. May, J. R. Palmer, P. D. Johnson, H. W. Smith, M. Busso, C.-K. Tan, R. L. Voorman, F. Reusser, I. W. Althaus, K. M. Downey, A. G. So, L. Resnick, W. G. Tarpley, and P. A. Aristoff. 1994. Discovery, synthesis, and bioactivity of bis(heteroaryl)piperazines. 1. A novel class of non-nucleoside HIV-1 reverse transcriptase inhibitors. *Journal of Medicinal Chemistry*, 37: 999–1014.

[7] Millar, R. W., R. P. Claridge, J. P. B. Sandall, and C. Thompson. 2002. Novel synthesis of polynitroaromatic compounds by reversed-dipole ('Umpolong') nitrations. *ARKIVOC*, 19–36.

[8] Youssif, S. 2001. Recent trends in the chemistry of pyridine N-oxide. *ARKIVOC*, 1: 242–268.

[9] Katritzky, A. R., E. F. V. Scriven, S. Majumder, R. G. Akhmedova, A. V. Vakulenko, N. G. Akhmedov, R. Murugan, and K. A. Abboud. 2005. Preparation of nitropyridines by nitration of pyridines with nitric acid. *Organic and Biomolecular Chemistry*, 3: 538–541.

[10] Chavez, D. E., M. A. Hiskey, and R. D. Gilardi. 2000. 3,3-Azabis(6-amino-1,2,4,5-tetrazine): A novel high-nitrogen energetic materials. 2000. *Angewandte Chemie*, 39: 1971–1973.

[11] Türker, L. and T. Atalar. 2006. Quantum chemical study on 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) and some of its constitutional isomers. *Journal of Hazardous Materials*, 137: 1333–1344.

[12] Johnson, M. A. and T. N. Truong. 1999. Importance of polarization in simulation of condensed phase energetic materials. *Journal of Physical Chemistry B*, 103: 9392–9393.

[13] Zeman, S., W. A. Trcinski, and R. Matyas. 2008. Some properties of explosive mixtures containing peroxides. Part 1. Relative performance and detonation of mixtures with triacetone triperoxide. *Journal of Hazardous Materials*, 154: 192–198.

[14] Türker, L. 2009. Structure-impact sensitivity relation of certain explosive compounds. *Journal of Energetic Materials*, 27: 94–109.

[15] Türker, L., T. Atalar, S. Gümüş, and Y. Çamur. 2009. A DFT study on nitrotriazines. *Journal of Hazardous Materials*, 167: 440–448.

[16] Fried, L. E., M. R. Manaa, P. F. Pagoria, and R. L. Simpson. 2001. Design and synthesis of energetic materials. *Annual Review of Materials Research*, 31: 291–321.

[17] Keshavarz, M. H., Z. Abbas, and S. Arash. 2009. A simple approach for predicting impact sensitivity of polynitroheteroarenes. *Journal of Hazardous Materials*, 166: 1115–1119.

[18] Li, J., Y. Huang, and H. Dong. 2005. A theoretical study of polynitropyridines and their N-oxides. *Journal of Energetic Materials*, 23: 133–149.

[19] Lu, M. and C. Lu. 2000. Synthesis of 2,6-bis(2′,4′,6′-trinitro-3′-aminoanilino)-3,5-dinitropyridine. *Huaxue Shijie*, 41: 135–138.

[20] Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople. 2004. *Gaussian 03, Revision C. 02*, Wallingford, CT: Gaussian, Inc.

[21] Pulay, P., J. F. Hinton, and K. Wolinski. 1993. Mathematical and physical sciences. In J. A. Tossel (ed.), *Nuclear Magnetic Shieldings and Molecular Structure*, NATOASI Series C, Vol. 386, Amsterdam: Kluwer.

[22] Minkin, V. I., M. N. Glukhovtsev, and B. Y. Simkin. 1994. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*. New York: Wiley.

[23] Schleyer, P. R. and H. Jiao. 1996. What is aromaticity? *Pure and Applied Chemistry*, 68: 209–218.

[24] Glukhovtsev, M. N. 1997. Aromaticity today: Energetic and structural criteria. *Journal of Chemical Education*, 74: 132–136.

[25] Krygowski, T. M., M. K. Cyranski, Z. Czarnocki, G. Hafelinger, and A. R. Katritzky. 2000. Aromaticity: A theoretical concept of immense practical importance. *Tetrahedron*, 56: 1783–1796.

[26] Schleyer, P. R. 2001. Introduction: Aromaticity. *Chemistry Reviews*, 101: 1115–1118.

[27] Cyranski, M. K., T. M. Krygowski, A. R. Katritzky, and P. R. Schleyer. 2002. To what extent can aromaticity be defined uniquely? *Journal of Organic Chemistry*, 67: 1333–1338.

[28] Schleyer, P. R., C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. E. Hommes. 1996. Nucleus-independent chemical shifts: A simple and efficient aromaticity probe. *Journal of the American Chemical Society*, 118: 6317–6318.

[29] Jiao, H. and P. R. Schleyer. 1998. Aromaticity of pericyclic reaction transition structures: magnetic evidence. *Journal of Physical Organic Chemistry*, 11: 655–662.

[30] Schleyer, P. R., B. Kiran, D. V. Simion, and T. S. Sorensen. 2000. Does $Cr(CO)_3$ complexation reduce the aromaticity of benzene? *Journal of the American Chemical Society*, 122: 510–513.

[31] Quinonero, D., C. Garau, A. Frontera, P. Ballaster, A. Costa, and P. M. Deya. 2002. Quantification of aromaticity in oxocarbons: The problem of the fictitious ‘‘nonaromatic’’ reference system. *Chemistry – A European Journal*, 8: 433–438.

[32] Patchkovskii, S. and W. Thiel. 2000. Nucleus-independent chemical shifts from semiempirical calculations. *Journal of Molecular Modeling*, 6: 67–75.

[33] Berry, R. J., C. J. Ehlers, D. R. Burgess Jr., M. R. Zachariah, M. R. Nyden, and M. Schwartz. 1998. Halon thermochemistry: Ab initio calculations of the enthalpies of formation of fluoroethanes. *Journal of Molecular Structure (Theochem)*, 422: 89–98.

[34] Francisco, J. S. 1998. The structure and heat of formation of the CH_3OCH_2O radical. *Chemical Physics Letters*, 294: 319–322.

[35] Sudlow, K. P. and A. A. Woolf. 1999. Heats of formation of carbonyl, formyl and trifluoroacetyl fluorides. *Journal of Fluorine Chemistry*, 96: 141–145.

[36] Cheung, T. S., C. K. Law, and W. K. Li. 2001. Gaussian-3 heats of formation for $(CH)_6$ isomers. *Journal of Molecular Structure (Theochem)*, 572: 243–247.

[37] Cheng, M. F., H. O. Ho, C. S. Lam, and W. K. Li. 2002. Heats of formation for the boron hydrides: A Gaussian-3 study. *Chemical Physics Letters*, 356: 109–119.

[38] Cobos, C. J. 2002. Heats of formation for AIH, AlOH, OAlH and OAlOH and their monocations. *Journal of Molecular Structure (Theochem)*, 581: 17–29.

[39] Orlov, Y. D., G. Bouchoux, V. V. Takhistov, and D. A. Ponomarev. 2002. Thermochemistry of organic and hetero-organic species. Part XI. A new estimation scheme of the enthalpies of formation for $RCH_2^{\surd}$ free radicals. *Journal of Molecular Structure (Theochem)*, 608: 109–122.

[40] Jursic, B. S. 1997. The density functional theory evaluation of the heats of formation of some aromatic compounds through the isodesmic approach. *Journal of Molecular Structure (Theochem)*, 417: 99–106.

[41] Ball, D. W. 1997. Density functional calculations on the heats of formation of cyclic hydrocarbons. *Journal of Molecular Structure (Theochem)*, 417: 107–115.

[42] Rice, B. M., S. V. Pai, and J. Hare. 1999. Predicting heats of formation of energetic materials using quantum mechanical calculations. *Combustion and Flame*, 118: 445–458.

[43] Vayner, E. and D. W. Ball. 2000. Ab initio and density functional optimized structures, proton affinities, and heats of formation for aziridine, azetidine, pyrrolidine, and piperidine. *Journal of Molecular Structure (Theochem)*, 496: 175–183.

[44] Denis, P. A. and O. N. Ventura. 2001. Density functional investigation of atmospheric sulfur chemistry. II. The heat of formation of the XSO_2 radicals X-H, CH_3. *Chemical Physics Letters*, 344: 221–228.

[45] Atkins, P. W. 1990. *Physical Chemistry*. Oxford: Oxford University Press.

[46] Hehre, W. J., L. Radom, P. V. R. Schleyer, and J. A. Pople. 1986. *Ab Initio Molecular Orbital Theory*. New York: Wiley.

[47] Williams, C. I. and M. A. Whitehead. 1997. Aromatic nitrogen heterocyclic heats of formation: A comparison of semiempirical and ab initio treatments. *Journal of Molecular Structure (Theochem)*, 393: 9–24.

[48] Guthrie, J. P. 2001. Heats of formation from DFT calculations: An examination of several parameterizations. *Journal of Physical Chemistry A*, 105: 9196–9202.

[49] Webber, J. S. and R. Woolley. 1995. Heats of formation for the thienopyridine isomers and their 4-oxygenated derivatives. *Journal of Molecular Structure (Theochem)*, 341: 171–180.

[50] Hammadi, A. El. and M. El. Mouhtadi. 2000. The theoretical determination of heats of formation, proton affinities and gas basicities of N and C-substituted pyrazoles: Analysis of the

substituent effects on the gas-phase basicity. *Journal of Molecular Structure (Theochem)*, 497: 241–266.

[51] Dorofeeva, O. V. and V. S. Yungman. 2002. Enthalpies of formation of biphenyl, 2,2′- and 4,4′-dichlorobiphenyls: Density functional calculations. *Fluid Phase Equilibrium*, 199: 147–151.

[52] Ventura, O. N., M. Kieninger, P. A. Denis, and R. E. Cachau. 2001. Density functional computational thermochemistry: Isomerization of sulfine and its enthalpy of formation. *Journal of Physical Chemistry A*, 105: 9912–9916.

[53] Ventura, O. N. and M. Kieninger. 1995. The FO_2 radical: A new success of density functional theory. *Chemical Physics Letters*, 245: 488–497.

[54] Chen, P. C., Y. C. Chieh, and S. C. Tzeng. 2003. Density functional calculations of the heats of formation for various aromatic nitro compounds. *Journal of Molecular Structure (Theochem)*, 634: 215–224.

[55] Foresman, J. B. and A. Frisch. 1996. *Exploring Chemistry with Electronic Structure Methods*. Pittsburgh, PA: Gaussian, Inc.

[56] Jursic, B. S., J. W. Timberlake, and P. S. Engel. 1996. Computation of bond dissociation energies of substituted methanes with density functional theory. *Tetrahedron Letters*, 37: 6473–6474.

[57] Kamlet, M. J. and S. J. Jacobs. 1968. Chemistry of detonations. I. A simple method for calculating detonation properties of C—H—N—O explosives. *Journal of Chemical Physics*, 48: 23–36.

[58] Zhang, X. H. and Z. H. Yun. 1989. *Explosive Chemistry*. Beijing: National Defense Industry Press.

[59] Qiu, L., H. M. Xiao, X. H. Ju, and X. D. Gong. 2005. Theoretical study of the structures and properties of cyclic nitramines: Tetranitrotetraazadecalin (TNAD) and its isomers. *International Journal of Quantum Chemistry*, 105: 48–56.

[60] Xiao, J. J., J. Zhang, D. Yang, and H. M. Xiao. 2002. DFT comparative studies on the structures and properties of heterocyclic nitramines. *Acta Chimica Sinica*, 60: 2110–2114.

[61] Qiu, L., H. M. Xiao, X. H. Ju, and X. D. Gong. 2005. Structures and properties of hexanitrohexaazatricyclododecane—Molecular design of HEDM. *Chinese Journal of Chemical Physics*, 18: 541–546.

[62] Qiu, L., H. M. Xiao, X. H. Ju, and X. D. Gong. 2005. Theoretical study on the structures and properties of bicyclo-HMX. *Acta Chimica Sinica*, 63: 377–384.

[63] Xu, X. J., H. M. Xiao, X. D. Gong, X. H. Ju, and Z. X. Chen. 2005. Theoretical studies on the vibrational spectra, thermodynamic properties, detonation properties, and pyrolysis mechanisms for polynitroadamantanes. *Journal of Physical Chemistry*, 109: 11268–11274.

[64] Qiu, L., H. Xiao, X. Gong, X. Ju, and W. Zhu. 2006. Theoretical studies on the structures, thermodynamic properties, detonation properties, and pyrolysis mechanisms of spiro nitramines. *Journal of Physical Chemistry A*, 110: 3797–3807.

[65] Williams, C. I. and M. A. Whitehead. 1997. Aromatic nitrogen heterocyclic heats of formation: A comparison of semiempirical and ab initio treatments. *Journal of Molecular Structure (Theochem)*, 393: 9–24.

[66] Xiao, H. M., J. F. Fan, and X. D. Gong. 1997. Theoretical study on pyrolysis and sensitivity of energetic compounds. Part I: Simple model molecules containing NO_2 Group. *Propellants, Explosives, Pyrotechnics*, 22: 360–364.

[67] Ma, X. and H. H. Schobert. 2000. Estimating heats of formation of hydrocarbon radicals by a combination of semiempirical calculation and family correlation with experimental values. *Journal of Physical Chemistry A*, 104: 1064–1074.

[68] Xiao, H. M., J. Fifing, Z. M. Go, and H. S. Dong. 1998. Theoretical study on pyrolysis and sensitivity of energetic compounds: (3) Nitro derivatives of aminobenzenes. *Chemical Physics*, 226: 15–24.

[69] Cooper, P. W. 1996. *Explosive Engineering*. New York: Wiley-VCH.

[70] Rice, B. M., J. J. Hare, and E. F. C. Byrd. 2007. Accurate predictions of crystal densities using quantum mechanical molecular volumes. *Journal of Physical Chemistry A*, 111: 10874–10879.

[71] Türker, L. 1990. An approach to the construction of certain isospectral and subspectral graphs. *Match*, 25: 195–215.

[72] Randic, M. 1975. Characterization of molecular branching. *Journal of the American Chemical Society*, 97: 6609–6615.

[73] Wiener, H. 1947. Correlation of heats of isomerization, and differences in heats of vaporization of isomers, among the paraffin hydrocarbons. *Journal of the American Chemical Society*, 69: 2636–2638.

[74] Wiener, H. 1947. Influence of interatomic forces on paraffin properties. *Journal of Chemical Physics*, 15: 766.

[75] Türker, L. 2003. A novel topological index for coding of alternant systems. *Indian Journal of Chemistry*, 42A: 1295–1297.

[76] Nikolic, S., A. Milicevic, and N. Trinajstic. 2005. Graphical matrices in chemistry. *Croatica Chemica Acta*, 78: 241–250.

[77] Dankelmann, P., I. Gutman, S. Mukwembi, and H. C. Swart. 2009. The edge-Wiener index of a graph. *Discrete Mathematics*, 309: 3452–3457.

[78] Trinajstic, N. 1992. *Chemical Graph Theory*. Boca Raton, FL: CRC Press.

[79] Barysz, M., G. Jashari, R. S. Lall, V. K. Sarivastava, and N. Trinajstic. 1983. On the distance matrix of molecules containing heteroatoms. In R. B. King (ed.), *Chemical Applications of Topology and Graph Theory*, Amsterdam: Elsevier.

Appendix

A Novel Topological Index for Modeling Properties of Explosion

The TG index (Türker-Gümüş index) is a novel topological index developed by Türker and Gümüş that is constructed on the basis of T(A) graphs [71]. Moreover, the calculation of the topological index makes use of the concepts of both the connectivity (branching), which was introduced by Randic [72], and the path distances, introduced by Wiener [73,74].

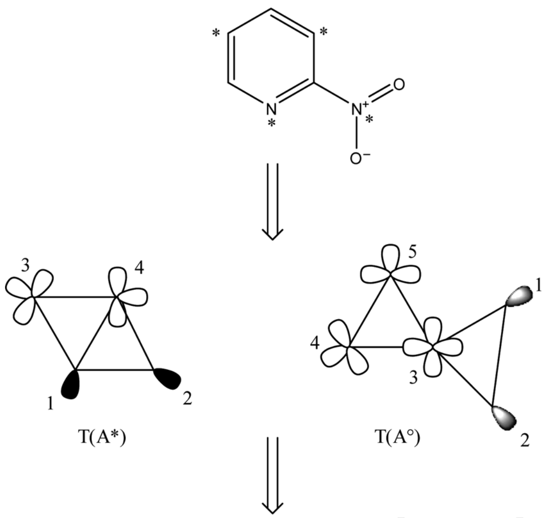
The TG index is defined by the following equation;

$$\mathrm{TG} = \left(\sum_{\mathrm{i}}^{\mathrm{N}}\sum_{\mathrm{j}}^{\mathrm{N}} \mathrm{D}^{*}_{\mathrm{ij}}\right)\left(\sum_{\mathrm{i}}^{\mathrm{M}}\sum_{\mathrm{j}}^{\mathrm{M}} \mathrm{D}^{\mathrm{o}}_{\mathrm{ij}}\right)$$

See below for the meaning of terms.

The calculation of the index is based on a novel type of matrix presently introduced, the distance-degree matrix (D_{ij}). This matrix represents the connectivity in the structure under consideration, so that the distances between the vertices as well as the degrees of the vertices in the parent structure are taken into account.

The calculation of the topological index is presented by an example in Fig. A1. One can calculate the index by following the required steps:



$$\overset{*}{D} = \begin{bmatrix} 0 & n & 3 & 3 \\ n & 0 & 3 & 6 \\ n & 2n & 0 & 3 \\ n & n & 3 & 0 \end{bmatrix} \qquad \overset{o}{D} = \begin{bmatrix} 0 & w & 4 & 6 & 6 \\ w & 0 & 4 & 6 & 6 \\ w & w & 0 & 3 & 3 \\ 2w & 2w & 4 & 0 & 3 \\ 2w & 2w & 4 & 3 & 0 \end{bmatrix}$$

$$\sum_{i}^{N}\sum_{j}^{N} D^{*}_{ij} = 7n+21 \qquad \sum_{i}^{M}\sum_{j}^{M} D^{\circ}_{ij} = 12w+52$$

$$\mathbf{TG} = (7*(13/7)+21) * (12*(14/8)+52) = 2482$$

Figure A1. Illustration of how to calculate the TG index for nitropyridines. (*Note*: the degrees of the vertices for carbon, nitrogen, and oxygen are represented by white, black, and gray self-loops, respectively).

1. Consider a hydrogen-depleted molecular graph.
2. Star the molecule alternatingly (as in the case of alternant hydrocarbons).
3. Obtain T(A*) and T(A$^\circ$) graphs, as shown in Fig. A1 and Türker [71,75] (the number of self-loops is determined by the degree of the corresponding vertex in the original graph).
4. Number the vertices of the newly obtained T(A*) and T(A$^\circ$) graphs.

5. Construct the distance-degree matrix (a newly developed matrix that has not been pronounced in the literature to date) for both $T(A^{*})$ and $T(A^{\circ})$ graphs as follows:

$$D^{*} = \begin{bmatrix} l_{11}d_1 & l_{12}d_2 & l_{13}d_3 & l_{14}d_4 \\ l_{21}d_1 & l_{22}d_2 & l_{23}d_3 & l_{24}d_4 \\ l_{31}d_1 & l_{32}d_2 & l_{33}d_3 & l_{34}d_4 \\ l_{41}d_1 & l_{42}d_2 & l_{43}d_3 & l_{44}d_4 \end{bmatrix}$$

$$D^{o} = \begin{bmatrix} l_{11}d_1 & l_{12}d_2 & l_{13}d_3 & l_{14}d_4 & l_{15}d_5 \\ l_{21}d_1 & l_{22}d_2 & l_{23}d_3 & l_{24}d_4 & l_{25}d_5 \\ l_{31}d_1 & l_{32}d_2 & l_{33}d_3 & l_{34}d_4 & l_{35}d_5 \\ l_{41}d_1 & l_{42}d_2 & l_{43}d_3 & l_{44}d_4 & l_{45}d_5 \\ l_{51}d_1 & l_{52}d_2 & l_{53}d_3 & l_{54}d_4 & l_{55}d_5 \end{bmatrix}$$

   where l_{ij} and d_j represent the shortest distance between the vertices i and j and the degree of the vertex j, respectively. For example, $l_{23}d_3$ is multiplication of the distance between vertices 2 and 3 and the degree of vertex 3. Because the distance between the same atom is zero, all the diagonal elements of the matrix should be zero independent from the degree of that vertex.
6. Sum all the elements of the each matrix to obtain

$$\sum_{i}^{N}\sum_{j}^{N} D^{*}_{ij} \quad \text{and} \quad \sum_{i}^{M}\sum_{j}^{M} D^{o}_{ij}$$

   Summation of half or all of the matrix elements has been frequently pronounced in the literature [73,74,76,77].
7. Use the equation above to calculate the TG index for the compound considered.

Organic compounds containing heteroatoms and/or multiple bonds can be represented as vertex- and edge-weighted molecular graphs [78]. In the case of the TG index, vertex-weighted molecular graphs have been used. A general approach of computing parameters for vertex-weighted graphs was developed by Barysz and coworkers by weighting the contributions of the atoms and bonds with parameters based on the atomic number Z [79]. The application of the atomic number weighting scheme to the TG index includes the calculation of the vertex parameter $Vw(Z)_i$ of the vertex v_i (representing atom i from a molecule). The formula below is used to obtain the parameters for nitrogen and oxygen:

$$Vw(Z)_i = 1 + Z_C/Z_i = 1 + 6/Z_i$$

where Z_i is the atomic number Z of the atom i and $Z_C = 6$ is the atomic number Z of carbon. Therefore, the parameters are 1.857 and 1.750 for nitrogen and oxygen, respectively.