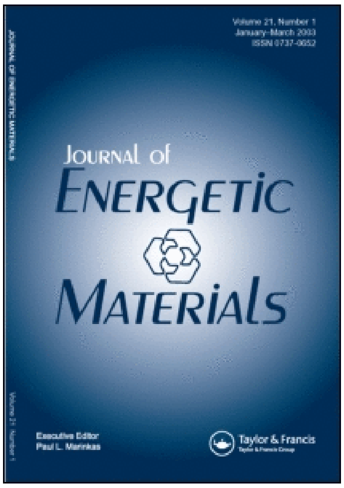

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Method of calculation of the heats of formation of new energetic compounds (containing NO_2 and/or NF_2 groups) by a benson's like additive scheme

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METHOD OF CALCULATION OF THE HEATS OF FORMATION OF NEW ENERGETIC COMPOUNDS (CONTAINING NO_2 AND/OR NF_2 GROUPS) BY A BENSON'S LIKE ADDITIVE SCHEME

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ABSTRACT

In the present work, the origin of the energy content of some energetic molecules, the heats of formation of which have been previously determined, is analyzed in terms of stabilization energy (SE). This concept is shown to be very fruitful for describing the interactions between substituents and it is found that: (i) the global SE decomposes into local (one center) and non-local (polycenter) contributions and (ii) both contributions are reasonably transferable.

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These observations allow us to use a Benson's like additive scheme for estimating the gaseous heats of formation of new energetic molecules containing NO_2 and/or NF2 groups, some examples of which are reported.

INTRODUCTION

In the research field of new solid energetic compounds, there has been a considerable interest for years in the synthesis of cyclic and polycyclic nitro- and nitramine molecules[1]. Before undertaking such a difficult and generally expensive synthesis, it is highly desirable as far as possible to predict its basic properties, in particular its energy content measured by the heat of formation in the condensed state $\Delta H^\circ_f(c)$, which is the difference between the heat of formation in the gaseous state ΔH°_f and the heat of sublimation. This last quantity can be estimated in an approximate way, by the use of chemical engineering methods[2], so the main difficulty is to evaluate ΔH°_f. To carry out easily such a calculation, one has at disposal energy increment methods, the best known being Benson's one[3, 4]. In fact, for nitro-compounds, the results are not always satisfactory because of strong interactions between NO_2 groups.

This is the reason why we reconsidered the problem in a preceding paper[5] and determined by quantum chemistry calculations the heats of formation in the gaseous state of nitro-, nitramine and/or fluoramine molecules (these last ones are also energetic) containing up to 12 heavy atoms (i.e. other than H atoms).

The purpose of the present work is to use these results for calculating Benson's like enthalpy increments in the first step and to evaluate the heats of formation of new energetic compounds having a number of heavy atoms far greater than the reference molecules' one in the second step. To meet this goal, we first analyze the energy content origin of nitro-, nitramine and/or fluoramine molecules using the stabilization energy (SE) concept and we show SE can be decomposed into a local (monocenter) and a non-local (polycenter) term in the description of the interactions between the main substituents (NO_2, NF_2...) in the molecules. We find both terms are transferable to other molecules, which allows us to calculate new Benson's like energy increments and to use them in the estimation of the heats of formation of large-sized new energetic molecules.

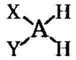
ENERGY CONTENT ANALYSIS

A) Heat of Atomization and Stabilization Energy

As already shown in other works[6], the concept of stabilized energy is quite useful to understand the origin of the molecular energy content. Even if this concept has received different definitions, we adopt the type of formulation introduced by Cox and Pilcher without splitting stabilization and destabilization contributions[7]. Then, for a compound in the gaseous state, the molar heat of atomization ΔHa can be written as the sum of two terms :

$$\Delta Ha = \sum_{AB} N_{AB} E(A - B) + SE \qquad (1)$$

where E(A - B) are standard bond energy terms derived from the heat of atomization of reference compounds, N_{AB} the number of A - B bonds in the chemical species under consideration and SE the stabilization energy of the compound. In relation (1), where the E(A - B) values depend on the nature of A and B, the multiplicity of the A - B bond and the nature of the connected atoms with A and B, SE appears therefore as a non-linearity in the bond energy model. For bonds between hydrogen and heavy atoms, a distinction is made for primary (p), secondary (s) and tertiary (t) surrounding of the non-hydrogen atoms and corrections are applied to the A-H bond energy depending on the nature of the A-connected atoms. For example:

in the molecule 

$XYAH_2$, $E(A^{XY} - H)s = E(A - H)s + \Delta(A^{X}\text{-}H)s + \Delta(A^{Y} - H)s \quad (2)$

where the susperscripts X and Y recall the nature of the surrounding atoms. With these notations, some standard bond energies and Δ corrections are reported in table 1.

Finally the heat of atomization is related to the heat of formation of the chemical species by:

$$\Delta Ha = \sum \Delta H^{\circ}_{f}(\text{atom}) - \Delta H^{\circ}_{f}(\text{chem. species}) \qquad (3)$$

where $\Sigma\Delta H^{\circ}_{f}$(atom) is the sum of the heats of formation for the gaseous atoms of the chemical species in their ground state at 298.15 K.

To sum up, the knowledge of the E(A - B) and SE (table 1) allows the calculation of the ΔHa value which, reported into equation (3), gives ΔH°_{f}(chem. species). The main difficulty is therefore to evaluate the SE term.

Let us now analyze the heats of atomization of energetic compounds, listed in table 2, we theoretically determined in a previous work[5].

B) <u>One-center Substitution Effect on Stabilization Energy</u>

First of all, compounds of molecular formula $CH_{4-n}X_n$ where X stands for substituents NH_2, NO_2, NF_2, OH or F, are considered. When ΔHa is plotted against n for each substituent (figure 1), a linear relationship is obtained in a first approximation.

TABLE 1
Standard bond Energies.

Bonds		E_b(kcal mol^{-1})	Δ(kcal mol^{-1})	
CC	E(C-C)	85.05		
	$E(C-H)_p$	98.25		
	$E(C-H)_s$	97.50		
	$E(C-H)_t$	96.78		
CN	E(C-N)	76.61		
	$E(N-H)_2$	91.31		
	$E(N-H)_1$	90.29		
	$E(C^N-H)_p$	96.75	$\Delta(C^N-H)_p$	-1.50
	$E(C^N-H)_s$	96.27	$\Delta(C^N-H)_s$	-1.23
	$E(C^N-H)_t$	95.87	$\Delta(C^N-H)_t$	-0.91
NN	E(N-N)	47.88		
	$E(N-NO_2)$	266.95	$\Delta(N-NO_2)$	8.26
CO	E(C-O)	91.33		
	E(O-H)	108.12		
	$E(C^O-H)_p$	95.86	$\Delta(C^O-H)_p$	-2.39
	$E(C^O-H)_s$	95.49	$\Delta(C^O-H)_s$	-2.01
	$E(C^O-H)_t$	95.35	$\Delta(C^O-H)_t$	-1.43
NO	E(N-O)	47.12		
	$E(NO_2)$	210.81		
	$E(C^{NO2}-H)_p$	97.07	$\Delta(C^{NO2}-H)_p$	-1.18
	$E(C^{NO2}-H)_s$	95.79	$\Delta(C^{NO2}-H)_s$	-1.71
	$E(C^{NO2}-H)_t$	95.71	$\Delta(C^{NO2}-H)_t$	-1.07
CF	E(C-F)	109.50		
	$E(C^F-H)_p$	97.79	$\Delta(C^F-H)_p$	-0.46
	$E(C^F-H)_s$	97.26	$\Delta(C^F-H)_s$	-0.24
	$E(C^F-H)_t$	96.56	$\Delta(C^F-H)_t$	-0.22
NF	E(N-F)	66.48		
	$E(C^{NF2}-H)_p$	96.39	$\Delta(C^{NF2}-H)_p$	-1.86
	$E(C^{NF2}-H)_s$	95.69	$\Delta(C^{NF2}-H)_s$	-1.81
	$E(C^{NF2}-H)_t$	95.02	$\Delta(C^{NF2}-H)_t$	-1.76

TABLE 2

Heat of Formation, Heats of Atomization and Stabilization Energies for Materials here considered (values in kcal.mol^{-1}).

Compounds	ΔH_f(298.15K)	ΔH_a(298.15K)	SE	Determination	References
NO_2CH_3	-19.30	578.62	-0.01	Exp.	12
NO_2CH_2F	-59.63	585.71	-2.31	Th.	6
NO_2CHF_2	-111.82	604.66	2.97	Th.	6
$NO_2CH_2CH_3$	-24.38	858.80	0.00	Exp.	13
$NO_2CH(CH_3)_2$	-33.21	1142.73	0.00	Exp.	13
$NO_2C(CH_3)_3$	-42.20	1426.82	0.00	Exp.	15
$NO_2CH_2NH_2$	-17.28	741.70	5.93	Th.	6
$NO_2CH_2NF_2$	-17.06	675.00	-11.11	Th.	6
NO_2CH_2OH	-53.50	672.38	-2.05	Th.	6
NO_2CHFCH_3	-68.98	870.16	-2.05	Th.	5
NO_2CHFOH	-109.31	694.95	4.52	Th.	5
$NO_2CF_2CH_3$	-118.35	886.29	0.07	Th.	5
$NO_2CF_2CH_2OH$	-154.13	981.63	-0.27	Th.	5
NO_2CF_2OH	-153.75	706.15	0.28	Th.	5
$NO_2CH_2CH_2NO_2$	-22.90	1037.34	-5.71	Exp.	8
$NO_2CH_2CH_2NF_2$	-25.30	958.34	-8.77	Th.	5
$NO_2CH_2CH_2CH_2NO_2$	-31.60	1321.14	-1.96	Exp.	8
$(NO_2)_2CH_2$	-14.20	753.54	-9.46	Exp.	12
$(NO_2)_2CHCH_3$	-24.10	1038.54	-10.74	Exp.	8
$(NO_2)_2C(CH_3)_2$	-27.00	1316.54	-17.90	Exp.	8
$(NO_2)_2C(CH_3)NF_2$	-19.85	1132.91	-31.30	Th.	5
$(NO_2)_2CHF$	-56.10	762.20	-16.56	Exp.	9
$(NO_2)_2CFCH_3$	-66.48	1047.68	-16.46	Th.	5
$(NO_2)_2CFCH_2OH$	-101.50	1142.26	-17.56	Exp.	11
$(NO_2)_2CFOH$	-114.57	880.23	-3.56	Th.	5
$(NO_2)_2CFOCH_3$	-107.28	1148.04	-6.54	Th.	5
$(NO_2)_2C(NH_2)_2$	-26.60	1096.14	2.81	Th.	5
$(NO_2)_2CHCH_2NO_2$	-14.40	1208.86	-21.25	Th.	5
$(NO_2)_3CH$	-0.20	919.56	-36.27	Exp.	12
$(NO_2)_3CCH_3$	-12.40	1206.86	-35.20	Exp.	8
$(NO_2)_3CCH_2NH_2$	-6.99	1366.55	-32.53	Th.	5
$(NO_2)_3CCH_2OH$	-41.13	1295.15	-42.59	Th.	5
$(NO_2)_4C$	18.50	1080.88	-68.80	Exp.	12
NF_2CH_3	-20.81	498.73	-0.01	Th.	6
$NF_2CH_2CH_3$	-27.73	780.75	0.00	Th.	6
NF_2CH_2F	-63.28	507.96	-3.17	Th.	6
NF_2CHF_2	-116.12	527.56	3.72	Th.	6
$NF_2CH_2CH_2NF_2$	-29.08	880.72	-8.55	Th.	5
$(NF2)2CH_2$	-20.96	597.50	-11.72	Th.	6
$(NF_2)_2CHCH_3$	-29.70	881.34	-10.86	Estimated	Relation on Fig. 3
$(NF_2)_2CHF$	-66.63	609.93	-13.45	Th.	5
$(NF_2)_2CF_2$	-109.04	619.10	-19.04	Th.	5
$(NF_2)_2CHOH$	-59.44	695.54	-16.58	Th.	5
$(NF_2)_2C(CH_3)_2$	-41.00	1167.74	-11.01	Th.	5
$(NF_2)_2CHCH_2NHNO_2$	-7.52	1204.28	-13.00	Th.	5
$(NF_2)_2CHCH2NF_2$	-20.74	971.00	-30.26	Th.	5
$(NF_2)_2C(CH_3)NO_2$	-25.06	1056.72	-29.94	Th.	5
$(NF_2)_3CH$	-11.12	686.28	-36.48	Th.	5
$(NF_2)_3CCH_3$	-24.11	974.37	-34.14	Th.	5
$(NF_2)3COH$	-49.93	784.65	-43.51	Th.	5
$(NF_2)_3COCH_3$	-44.90	1054.72	-44.23	Th.	5
$(NF_2)_4C$	0.50	773.28	-65.00	Exp.	16

TABLE 2, continued.

Compounds	ΔH_f(298.15K)	ΔH_a(298.15K)	SE	Determination	References
CH_3NHCH_3	-4.43	823.93	-0.08	Th.	13
CH_3NFCH_3	-13.94	800.20	0.00	Th.	17
NO_2NH_2	-0.77	450.09	0.52	Th.	6
NO_2NHCH_3	-0.99	725.41	1.31	Th.	5
NO_2NFCH3	0.14	691.04	-9.25	Th.	5
$NO_2N(CH_3)_2$	-1.15	1000.67	0.00	Exp.	14
$(NO_2NH)_2CH_2$	22.81	1046.73	-11.05	Th.	5
$(NO_2NHCH_2)_2$	11.84	1332.80	-5.03	Th.	19
$(NO_2)_2NH$	15.80	613.54	-10.65	Th.	5
$(NO_2)_2NCH_3$	12.79	891.65	-9.11	Th.	10
NH_2CH_3	-5.50	549.90	0.42	Exp.	13
$NH_2CH_2CH_3$	-11.35	830.85	-0.72	Exp.	13
NH_2CH_2OH	-49.78	653.74	6.54	Th..	6
$NH_2CH_2CH_2NH_2$	-4.20	988.80	0.21	Exp.	14
$(NH_2)_2CH_2$	-2.19	711.69	3.15	Th..	6
$(NH_2)_3CH$	-2.31	876.91	5.17	Th.	6
$(NH_2)_4C$	-10.21	1049.91	12.99	Th.	6
$OHCH_3$	-48.07	486.93	-0.10	Exp.	13
$OHCH(CH_3)_2$	-65.12	1054.18	-0.22	Exp.	13
$OHCH_2CH_3$	-56.24	770.20	-0.03	Exp.	13
$HOCH_2CH_2OH$	-92.64	866.16	0.25	Exp.	14
$(OH)_2CH_2$	-93.50	591.92	6.06	Exp.	6
$(OH)_2CHF$	-151.59	616.77	14.67	Th.	17
$(OH)_3CH$	-144.37	702.35	11.51	Th.	6
$(OH)_3CF$	-207.31	732.05	24.20	Th.	17
$(OH)_4C$	-98.64	816.18	18.38	Th.	6
CH_3OCH_3	-43.99	757.95	0.13	Exp.	13
CH_3F	-56.80	402.86	0.00	Estimated	6
CH_2F_2	-108.13	420.95	7.91	Exp.	13
CHF_3	-166.30	445.88	21.26	Exp.	13
CF_4	-223.30	469.64	31.64	Exp.	13
FCH_2CH_2F	-103.88	691.80	-1.29	Th.	18
CH_4	-17.89	397.19	0.00	Exp.	13
CH_3CH_3	-20.24	674.64	0.09	Exp.	13
$(CH_3)_2CH_2$	-24.83	954.33	-0.27	Exp.	13
$(CH_3)_3CH$	-31.58	1236.18	0.83	Exp.	13

In fact, this only corresponds to a crude description, the "fine structure" of this relation being hidden by large variations in the heats of atomization. Refining the analysis, ΔHa is expanded in powers of n:

$$\Delta Ha(CH_{4-n}X_n) = a + bn + cn^2 + dn^3 + en^4 \qquad (4)$$

The quadratic, cubic and quartic terms describe the interaction between atom groups. So another way to write ΔHa is:

$$\Delta Ha(CH_{4-n} - X_n) = \sum_{i=o}^{n} C_n^i I_i \qquad (5)$$

where I_0 is the independent term, I_1 the linear term and I_i ($i \geq 2$) the interaction term between i groups. These two expressions are equivalent as the I_i can be expressed in terms of a, b, c, d, e ($I_0 = a$, $I_1 = b + c + d + e$, $I_2 = 2c + 6d + 14e$, $I_3 = 6d + 36e$, $I_4 = 24e$) but in the latter, the physical meaning is more familiar.

So numerical values of I_i (in kcal.mol^{-1}) obtained for compounds of interest are reported in table 3:

TABLE 3
Additive Terms in the Decomposition of ΔHa ($CH_{4-n}X_n$)

X→	NH_2	NO_2	NF_2	OH	F
I_0	397.190	397.190	397.190	397.190	397.190
I_1	152.710	181.430	101.540	89.740	5.670
I_2	9.080	-6.510	-2.770	15.521	12.421
I_3	-5.649	-2.389	-7.220	-9.808	-5.578
I_4	10.001	6.590	15.430	7.771	-2.429

In every case, the obtained values prove the existence of large interactions between groups (in the range -10.5, +15 kcal.mol^{-1}). If the additive scheme cannot be considered as an accurate model in itself, this model nevertheless enables to separate, in ΔHa, contributions due to the substituents themselves from those arising from the interactions between the substituents.

Let us now analyze the origin of such a curvature in the relation ΔHa(n) rewriting it in a third form where the explicit expression for the bond energy increments are taken into account, the calculation being done by substitution of the hydrogen atoms in the methane molecule for groups of interest (NO_2, ...):

$$\begin{aligned}\Delta Ha(CH_{4\text{-}n}X_n) = \; & 4(E(C\text{-}H) + n\{E(C\text{-}X) + E(X) - E(C\text{-}H)\} \\ & + (4 - n)\{E(C\text{-}X)_{p,s,t} - E(C - H)\} + n(4 - n)\Delta(C^x - H)_{p,s,t} \\ & + SE(n)\end{aligned} \tag{6}$$

or, in an abbreviated way:

$$\Delta Ha(CH_{4\text{-}n}X_n) = A + B + C$$

Term A is evidently quite linear with n but the other two are not,

Term B expresses the change in C-H type (p, s or t) in C surrounding,

Term C, the stabilization energy, is in most cases numerically the highest.

So it can be concluded that in the curvature of ΔHa(n), SE plays the essential part. Moreover, as SE is close to zero for monosubstituted compounds (see figure 2 where SE(n) is plotted against n) it can be said that SE gives the measure of interactions between two or more substituents.

In figure 2, it can also be observed that the nitro- and difluoramino- compounds have similar and large destabilization effects (large negative values of SE); accumulation of such groups leads to lower the heats of atomization and to improve the energetics of these molecules. On the other hand, the three remaining groups (NH_2, OH and F) exhibit stabilization energies, sometimes small but always positive. In general, from an energetic point of view, similarities between NF_2 and NO_2 can be seen on a large scale (see table 2 and figure 3).

So the relation between SE(NF_2) and SE(NO_2) may be useful for a qualitative estimate of the heats of atomization of unknown species. Figure 3 suggests that SE for difluoramino- compounds (and consequently for ΔHa) can be nicely evaluated as long as stabilization energies for corresponding nitro- derivatives are available.

C) Non-local Contribution to the Stabilization Energy

Let us now consider the long-range interaction of X groups through the carbon chain. Table 4 contains SE values for compounds of general formula $X(CH_2)_mX$ (m = 1, to 3).

TABLE 4
Long-range Interactions along the Carbon chain in Terms of Stabilization Energy (kcal.mol^{-1})

X →	NH_2	NO_2	NF_2	OH	F
XCH_2X	3.15	-9.46	-11.72	6.06	7.91
XCH_2CH_2X	0.21	-5.71	- 8.55	0.25	-1.29
$XCH_2CH_2CH_2X$		-1.96			

It can be observed that SE goes down rapidly when the carbon chain length increases. For NH_2, OH and F, only two CH_2 are needed between the substituents to cancel the interaction, but substituents such as NO_2 or NF_2 request at least three CH_2 groups. The stabilization energy of $NO_2CH_2CH_2NF_2$ (-8.77 kcal.mol^{-1}) exhibits a similar long-range interaction. From table 1, small stabilization energies can also be calculated for compounds such as NO_2CH_2F, NO_2CH_2OH, NF_2CH_2F,...

The non-local and the local terms equally play an important role in the global SE. So, if we assume for the local gem di-NO_2 or gem di-NF2 contributions to the stabilization energy a value close to -11 kcal.mol^{-1} (value got from $(NO_2)_2CHCH_3$) and if alpha di-NO_2 and alpha di-NF_2 non-local contributions are respectively chosen as -5 and -8 kcal.mol^{-1} (values got from $NO_2CH_2CH_2NO_2$ and $NF_2CH_2CH_2NF_2$ respectively), the following stabilization energies are calculated:

$$SE[(NO_2)_2CHCH_2NO_2] \approx -11 + 2(-5) = -21 \text{ kcal.mol}^{-1}$$
$$SE[(NF_2)_2CHCH_2NF_2] \approx -11 + 2(-8) = -27 \text{ kcal.mol}^{-1} \quad (7)$$

Those values are qualitatively close to the exact values reported in table 1 (namely -21.25 and -30.26 kcal.mol^{-1}). This suggests that stabilization energies can really be split into local (centered on one atom) and non-local (long-range interaction) contributions. Such an idea is used to build a Benson's like incremental thermochemical model as explained in the next paragraph.

DETERMINATION OF NEW BENSON'S LIKE INCREMENTS

The heat of atomization of a gaseous compound can be split into a sum of groups. According to Benson's idea, these groups include at least one atomic center and its next neighbors characterizing the surrounding. So it can be written:

$$\Delta Ha = \sum_g E_g + SE_{nl} \quad (8)$$

where E_g is a g group increment and SE_{nl} the non-local contribution to stabilization energy of the compound. In its turn E_g can be decomposed into group increments ΣE_b and local contributions to stabilization energy SE_g :

$$E_g = \sum_{b \in g} E_b + SE_g \quad (9)$$

so that relations (1), (8) and (9) imply:

$$SE = \sum_g SE_g + SE_{nl} \quad (10)$$

In small compounds, both SE_g and SE_{nl} are vanishing and the group energy can be defined from the standard bond energies listed in table 1. Then using the conventional Benson's notation, one can write, to build table 5:

$[C-(C)(H)_3] = 1/2\ E(C\text{-}C) + 3\ E(C\text{-}H)_p$

$[C-(C)_2(H)_3] = E(C\text{-}C) + 2\ E(C\text{-}H)_s$

$[C-(N)(H)_3] = 1/2\ E(C\text{-}N) + 3\ E(C^N\text{-}H)_p$

. . . .

For larger compounds with general polysubstitution, the local stabilization energies are no longer vanishing but the non-local contributions remain negligible. So new group increments can be calculated to build table 6 starting from ΔHa for a new compound and previously determined increments taken out of table 5.

For example:

$[C-(N)_2(H)_2] = E(C-N) + 2\ E(C-H)_s + 2\ \Delta(C^N-H)_s + SE([C-(N)_2(H)_2]$

where the term $(SE[C-(N)_2(H)_2]$)is such that:

$\Delta Ha(NH_2CH_2NH_2) = [C-(N)_2(H)_2] + 2[N-(C)(H)_2]$.

Let us now consider compounds where alpha- or beta-substitutions exist, specially molecules containing NO_2 or/and NF_2 groups. As these groups show non negligible long-range interactions, it is necessary to introduce additional non-local stabilization term SE_{nl}. The numerical importance and nature of SE_{nl} for some compounds is reported in table 7 where the heats of formation have been estimated using Benson's like increments (tables 5 and 6). Comparison with exact values of ΔH_f, liste in table 2, gives SE_{nl} values.

We are now in a position to predict the heats of formation of a few energetic compounds still actually beyond the scope of theoretical capabilities. To obtain table 8, we used table 7 (interactions) and tables 5 and 6 (Benson's like increments). So far as possible, for each $\Delta H°_f$ calculated, the experimental value in the gaseous state (or in the

TABLE 5

Some Benson's like Increments (Based on Values from Table 1) for Compounds in which SE_g and SE_{nl} are vanishing. $E_g(f)$ are Group Increments in Terms of Heats of Formation, $E_g(a)$ are the Corresponding Values in Terms of Heats of Atomization; Values are in kcal.mol^{-1}.

Group	$E_g(f)$	$E_g(a)$
[C-(C)(H)$_3$]	-10.075	337.275
[C-(C)$_2$(H)$_2$]	-4.950	280.050
[C-(C)$_3$(H)]	-1.355	224.355
[C-(N)(H)$_3$]	-1.355	328.555
[C-(N)(C)(H)$_2$]	1.730	273.370
[C-(N^{NO_2})(H)$_3$]	-2.315	329.515
[C-(N^{NO_2})(C)(H)$_2$]	2.690	272.410
[C-(N^{NO_2})(C)$_2$(H)]	3.935	219.065
[C-(N^{NO2})(C)$_3$]	5.020	165.880
[C-(N^{NF_2})(H)$_3$]	-0.275	327.475
[C-(N^{NF_2})(C)(H)$_2$]	2.892	272.208
[C-(O)(H)$_3$]	-6.045	333.245
[C-(O)(C)(H)$_2$]	-4.070	279.170
[C-(O)(C)$_2$(H)]	-3.065	226.065
[N-(C)(H)$_2$]	-3.725	220.925
[N-(F)$_2$(C)]	-20.545	171.265
[N-(N^{NO_2})(H)$_2$]	10.122	207.078
[NO$_2$-(C)]	-16.995	249.115
[NO$_2$-(N)]	-10.89	243.01
[O-(C)(H)]	-42.125	153.785
[O-(C)$_2$]	-31.770	91.330

TABLE 6

Some Benson's like Increments for Compounds in which only SE_{nl} are vanishing. $E_g(f)$ are Group Increments in Terms of Heats of Formation, $E_g(a)$ are the Corresponding Values in Terms of Heats of Atomization; Values are in kcal.mol^{-1}.

Group	$E_g(f)$	$E_g(a)$	SE(g)	Reference compound
$[C-(N)_2(H)_2]$	5.263	269.837	3.147	$NH_2CH_2NH_2$
$[C-(O)_2(H)_2]$	-9.250	284.350	6.060	$CH_2(OH)_2$
$[C-(O)(N)(H)_2]$	-3.929	279.029	6.539	NH_2CH_2OH
$[C-(N^{NO_2})_2(C)(H)]$	19.965	203.035	-10.740	$CH_3CH(NO_2)_2$
$[C-(N^{NO_2})(F)(C)(H)]$	-41.905	283.765	-2.055	$CHFNO_2CH_3$
$[C-(N^{NO_2})(F)(O)(H)]$	-50.190	292.050	4.520	NO_2CHFOH
$[C-(N^{NO_2})(F)_2(C)]$	-91.279	299.899	0.069	$NO_2CF_2CH_3$
$[C-(N^{NO_2})(F)_2(O)]$	-94.634	303.254	0.280	NO_2CF2OH
$[C-(N^{NO_2})_2(C)(F)]$	-22.419	212.179	-16.456	$(NO_2)_2CFCH_3$
$[C-(N^{NO_2})_2(C)_2]$	27.140	143.760	-17.900	$(CH_3)_2C(NO_2)_2$
$[C-(N^{NO_2})_2(N)_2]$	14.870	156.030	2.810	$(NO_2)_2C(NH_2)_2$
$[C-(N^{NO_2})_2(NF_2)(C)]$	44.780	126.120	-31.300	$(NO_2)_2C(CH_3)NF_2$
$[C-(N^{NO_2})_2(O)(F)]$	-38.458	228.218	-3.557	$(NO_2)_2CFOH$
$[C-(N^{NO_2})_2(F)(H)]$	-22.110	263.970	-16.560	$(NO_2)_2CHF$
$[C-(N^{NO_2})_3(H)]$	50.785	172.215	-36.270	$CH(NO_2)_3$
$[C-(N^{NO_2})_3(C)]$	48.660	122.240	-35.200	$CH_3C(NO_2)_3$
$[C-(N^{NF_2})_2(F)(H)]$	-25.540	267.400	-11.750	$(NF_2)_2CHF$
$[C-(N^{NF_2})_2(F)_2]$	-67.950	276.570	-19.040	$(NF_2)_2CF_2$
$[C-(N^{NF_2})_2(O)(H)]$	23.775	199.225	-14.880	$(NF_2)_2CHOH$
$[C-(N^{NF_2})_2(C)(H)]$	21.465	201.535	-10.860	$CH_3CH(NF_2)_2$
$[C-(N^{NF_2})_2(C)_2]$	20.250	150.650	-11.010	$(CH_3)_2C(NF_2)_2$
$[C-(N^{NF_2})3(H)]$	50.514	172.486	-36.479	$CH(NF_2)_3$
$[C-(N^{NF_2})_2(N^{NO2})(C)]$	43.110	127.790	-29.940	$(NF_2)_2C(CH_3)NO_2$
$[C-(N^{NF_2})_3(C)]$	47.600	123.300	-34.140	$CH_3C(NF_2)_3$
$[C-(N^{NF_2})_3(O)]$	53.834	117.066	-43.514	$(NF_2)_3COH$
$[N-(C)_2(H)]$	-1.720	166.820	-0.080	$(CH_3)_2NH$
$[N-(N^{NO_2})(C)(H)]$	11.257	153.843	1.308	CH_3NHNO_2
$[N-(N^{NO_2})_2(H)]$	37.584	127.516	-10.650	$NH(NO_2)_2$
$[N-(N^{NO_2})_2(C)]$	35.925	77.075	-9.110	$N(CH_3)(NO_2)_2$
$[N-(F)(C)_2]$	-11.226	143.086	-0.004	CH_3NFCH_3
$[N-(N^{NO_2})(F)(C)]$	12.382	119.478	-9.247	NO_2NFCH_3
$[N-(N^{NO_2})(C)_2]$	12.450	100.550	0.000	$(CH_3)_2NNO_2$
$[C-(O)_2(F)(H)]$	-67.342	309.202	14.672	$CHF(OH)_2$
$[C-(O)_3(H)]$	-17.990	240.990	11.505	$CH(OH)_3$
$[C-(O)_3(F)]$	-80.936	270.696	24.201	$CF(OH)_3$
$[C-(O)_4]$	-30.140	201.040	18.380	$C(OH)_4$
$[C-(N)_3(H)]$	8.863	214.137	5.172	$(NH_2)_3CH$
$[C-(N)_4]$	4.687	166.213	12.993	$(NH_2)_4C$

TABLE 7

Long-range Corrections to the Benson's like Increments due to the Non-vanishing SE_{nl}; Values are in kcal.mol-1.

Compounds	ΔH_f(Est.) from $E_0(f)$	ΔH_f(exact) including SE_{nl}	Nature of the long range interaction	SE_{nl}
$NO_2CF_2CH_2OH$	-154.469	-154.13	negligible interaction	0.339
$(NO_2)_2CHCH_2NO_2$	-28.33	-14.40	2-terms alpha-NO_2/NO_2	13.93
$(NO_2)_2CFCH_2OH$	-102.604	-101.50	2-terms alpha-NO_2/OH	1.104
$(NO_2)_2CFOCH_3$	-110.263	-107.28	$\Delta[(NO_2)_2CFOCH_3]$	2.983
$(NO_2)_3CCH_2NH_2$	-4.32	-6.99	3-terms alpha-NO_2/NH_2	-2.67
$(NO_2)_3CCH_2OH$	-48.52	-41.13	3-terms alpha-NO_2/OH	7.39
$NO_2CH_2CH_2NO_2$	-28.61	-22.90	1-term alpha-NO_2/NO_2	5.71
$NO_2CH_2CH_2NF_2$	-31.96	-25.30	1-term alpha-NO_2/NF_2	6.65
$NO_2CH_2CH_2CH_2NO_2$	-33.56	-31.60	1-term beta-NO_2/NO_2	1.96
$(NF_2)_2CHCH_2NHNO_2$	-17.53	-7.52	2-terms alpha-$NF_2/NHNO_2$	10.01
$(NF_2)_2CHCH_2NF_2$	-37.28	-20.74	2-terms alpha-NF_2/NF_2	16.54
$(NF_2)_3COCH_3$	-45.616	-44.90	negligible interaction	0.716
$NF_2CH_2CH_2NF_2$	-35.31	-29.08	1-term alpha-NF_2/NF_2	6.23
$NO_2NHCH_2NHNO_2$	6.00	22.81	1-term gem-$NHNO_2/NHNO_2$	16.82

TABLE 8

Some Predictions of Heats of Formation using both Local and Non-local Stabilization Energies (in kcal.mol^{-1}).

Compounds	Contributions to SE_{nl} (from table VI)	ΔH_f(calc) gas phase	ΔH_f (exp)	State (exp)	Ref. (exp)
$(NO_2CF_2\text{-}CH_2\text{-}O\text{-})_2\text{-}CH_2$	2*0.339	-296.80	-		
$(NO_2CF_2\text{-}CH_2\text{-}O\text{-})_3\text{-}CF$	3*0.339	-512.26	-		
$(CH_3C(NO_2)_2CH_2\text{-})_2\text{-}NH$	unknown	-32.11	-38.24	Gas	21
$(CH_3C(NO_2)_2CH_2\text{-})_2\text{-}N(NO_2)$	unknown	-28.83	-31.7	Gas	21
$(CH_3C(NO_2)_2\text{-}CH_2\text{-}O\text{-})_3\text{-}CF$	unknown	-239.23	-		-
	-				
$((NO_2)_2CF\text{-}CH_2\text{-}O\text{-})_2\text{-}CH_2$	2*1.104	-191.54	-203.1	Liquid	22
			-189.10	Gas (estim. ΔH_v)	
$((NO_2)_2CF\text{-}CH_2OCH_2\text{-})_2\text{-}C(NF_2)_2$	2*1.104	-211.27			
$((NO_2)_2CF\text{-}CH_2\text{-})_2\text{-}NH$	unknown	-111.08	-129.21	Solid	20
			-110.21	Gas (estim. ΔH_v)	
$((NO_2)_2CF\text{-}CH_2\text{-})_2\text{-}NNO_2$	unknown	-107.80	-120.7	Solid	20
$(NO_2)_2CF\text{-}CH_2OCH_2\text{-}N(NO_2)CH_3$	1.104	-94.87	-100	Liquid	24
$((NO_2)_2CF\text{-}CH_2\text{-})_2\text{-}O$	2*1.104	-150.52	-160.3	Liquid	20
			-147.7	Gas (estim. ΔH_v)	2
$((NO_2)_2\text{-}CF\text{-}CH_2\text{-}O\text{-})_3\text{-}CF$	3*1.104	-354.37	-		
$(NO_2)_2CF\text{-}CH_2\text{-}O\text{-}CH_2\text{-}N(NO_2)\text{-}CH_2\text{-}O\text{-}CF(NO_2)_2$	1.104+2.983	-195.089	-		
$((NO_2)_3C\text{-}CH_2\text{-})_2\text{-}NH$	2*-2.670	-8.25	11.3	Gas	21
	if 2*7	11.09	11.3	Gas	21
$((NO_2)_3C\text{-}CH_2\text{-})_2\text{-}N(NO_2)$	2*-2.670	-4.97	21.6	Gas	21
	if 2*7	14.37	21.6	Gas	21
$((NO_2)_3C\text{-}CH_2\text{-}O\text{-})_2\text{-}CH_2$	2*7.39	-70.80	-71.9	Gas	22
$((NO_2)_3C\text{-}CH_2\text{-}O\text{-})_3\text{-}CF$	3*7.39	-173.26	-		
$(C(NO_2)_3\text{-}CH_2\text{-}O\text{-})_3\text{-}CH$	3*7.39	-110.32	-103.5	Gas	22
$(NO_2)_3C\text{-}CH_2\text{-}OH$	7.39	-41.13	-59.7	Liquid	23
$(NO_2)_3CCH_2CH_2CH_2NO_2$	unknown	-26.53	-24.9	Gas	8
$(NO_2)_3C\text{-}CH(CH_3)\text{-}O\text{-}CH_2\text{-}CH_3$	7.39	-53.99	-53.3	Gas	22
$((NO_2)_3C\text{-}CH_2\text{-})_2\text{-}CH\text{-}NO_2$	-	-27.61	-33.7	Liquid	14
$(NO_2)_3C\text{-}CH_2\text{-}CH_2\text{-}C(NF_2)_2CH_3$	-	-43.14	-63.46	Solid	14
$((NO_2)_3C\text{-}CH_2\text{-}N(NO_2)\text{-}CH_2)_2$	unknown	+5.39	-		
$(NO_2)_3C\text{-}CH_2\text{-}O\text{-}C(NF_2)_3$	0.716+7.39	-37.86	-		

condensed state if the former is missing) has been given for comparison. The results obtained are fairly encouraging specially if we consider that large groups introduced in the empirical procedure can occur up to three times. As it can be seen in table 8, non-local terms corresponding to alpha or beta interactions have been introduced as long as they could have been evaluated from some reference compound (table 7). Some discrepancies between theoretical prediction and experimental data are only found in the two cases containing the sub-structure $(NO_2)_3CH_2N<$; more accurate results seem to be obtained in both cases by using a non-local correction of 7 $kcal.mol^{-1}$ instead of -2.67 as proposed in table 6. This value is more acceptable as it compares with the correction term of the sub-structure $(NO_2)_3CH_2O<$ (7.36 $kcal.mol^{-1}$) and with the value retained by Pepekin (7.10 $kcal.mol^{-1}$). Then a nice correlation between theoretical and experimental values for gas phase appears:

$$\Delta H_f(exp) = 0.382 + 0.985\, \Delta H_f(th)$$

with a correlation coefficient of 1.00.

CONCLUSION

In this work, we have shown that the concept of stabilization energy is of large interest to estimate the heat of formation of energetic molecules. The SE, defined as the deviation between the heat of atomization and the sum of standard bond energies, can be partitioned into local and non-local contributions.

The local SE, also called SE_l measures the interactions between the substituents attached to one center; on the other hand, the non-local contribution to SE (SE_{nl}) measures the long-range interactions of substituents through the main atomic chain. We note that nitro- and difluoramino- substituents show non negligible interactions up to the beta position. The use of SE is fruitful in a Benson's like additive scheme as well as in the more conventional additive standard bond energy model; the predictions of heats of formation are quite accurate compared with known experimental gas phase values. So a quantum chemical approach, as described in a previous paper[5], joined to the present work leads to complementary aspects of the theoretical prediction of energetic properties for molecular compounds specially in the field of energetic materials.

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N.B.: $\Delta H^\circ_f(\text{gas}) = -129.3\text{kcal.mol-1} + \Delta H(\text{sublimation}(\approx 19)) = -110.21\text{kcal.mol}^{-1}$

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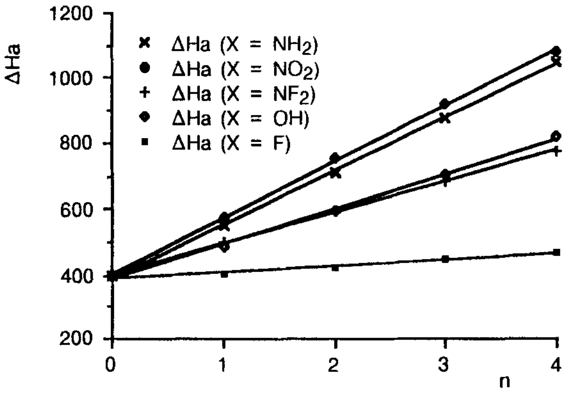

Fig.1. Relation between the heats of atomization (kcal mol^{-1}) and the number of substituents in the series $CH_{4-n}X_n$ where X stands for NH_2, NO_2, NF_2, OH or F.

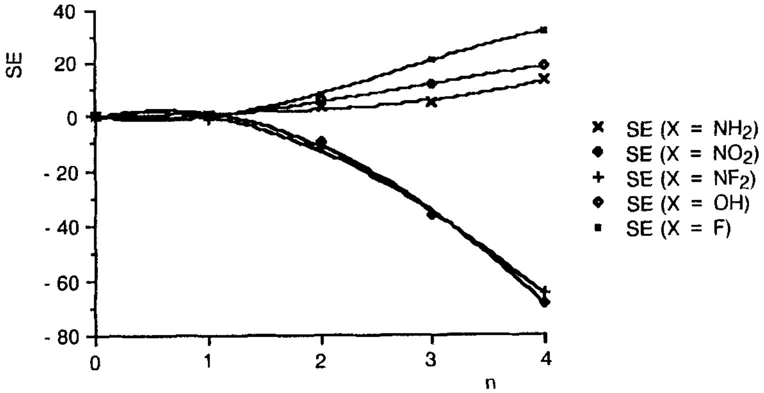

Fig.2. Relation between the stabilization energies (kcal mol^{-1}) and the number of substituents in the series $CH_{4-n}X_n$ where X stands for NH_2, NO_2, NF_2, OH or F.

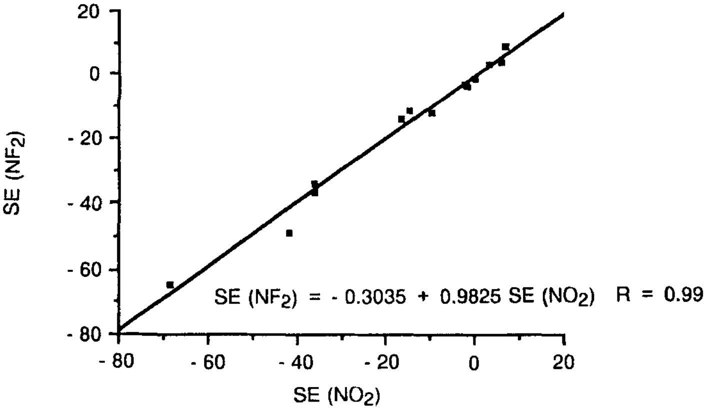

Fig. 3. Relation between the stabilization energies in nitro and di fluoro amino compounds (kcal mol^{-1})