
THEORETICAL INVESTIGATION OF A POSSIBLE NEW CLASS OF STABLE AMINYL RADICALS

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

We show in this paper that nitrogen-centred radicals carrying two electron-donor substituents constitute a possible new class of stable aminyl radicals. An interpretation of this original result is given by using a general definition of the thermodynamic stabilization energy.

In a previous paper¹, we have shown that nitrogen-centred radicals carrying two electron-donor substituents ($\cdot\text{N}(\text{OH})_2$ and $\cdot\text{N}(\text{NH}_2)_2$, for example) constitute a possible new class of stable aminyl radicals. Moreover, these species should be easily obtained from their parent molecule by hydrogen abstraction reactions. In order to confirm these results, we consider, in this work, the series of (more realistic) compounds shown in Fig. 1. It concerns four yet unknown heterocyclic free radicals, the parent molecules and the corresponding dimers. We shall use here the same theoretical approach to the effects of substituents on the structure, stability and reactivity of nitrogen-centred radicals as that described in literature¹.

RESULTS*Total Energies and Optimized Geometries*

All the radicals ($\text{c}\cdot\text{NXY}$) considered in this work and the corresponding positive ions (c^+NXY) and parent molecules (cNHXY) have been studied at the *ab initio* 4-31G UHF and RHF levels, respectively, with full geometry optimization, using the GAUSSIAN-82 series of programs². The dimers of the radicals [$(\text{cNXY})_2$] have also been studied by the same procedure but only the parameters outside of the cycles were optimized, the remaining ones being taken identical to those of the corresponding parent molecules. The total energies obtained in this way are collected in Table I.

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Some typical structural parameters of the aminyl radicals and related species are listed in Table II. It is seen that, in the open shell systems, the distances between the radical center and the neighbouring heteroatoms are significantly shorter than in the parent molecules. This result is consistent with a three-electron bond character for the corresponding NO and NN bonds. This shortening is still generally much larger in the positive ions.

Thermochemical Properties

Unknown heats of formation can be obtained by using the procedure of Pople et al., based on the concept of isodesmic reaction³. By definition, in this type of process,

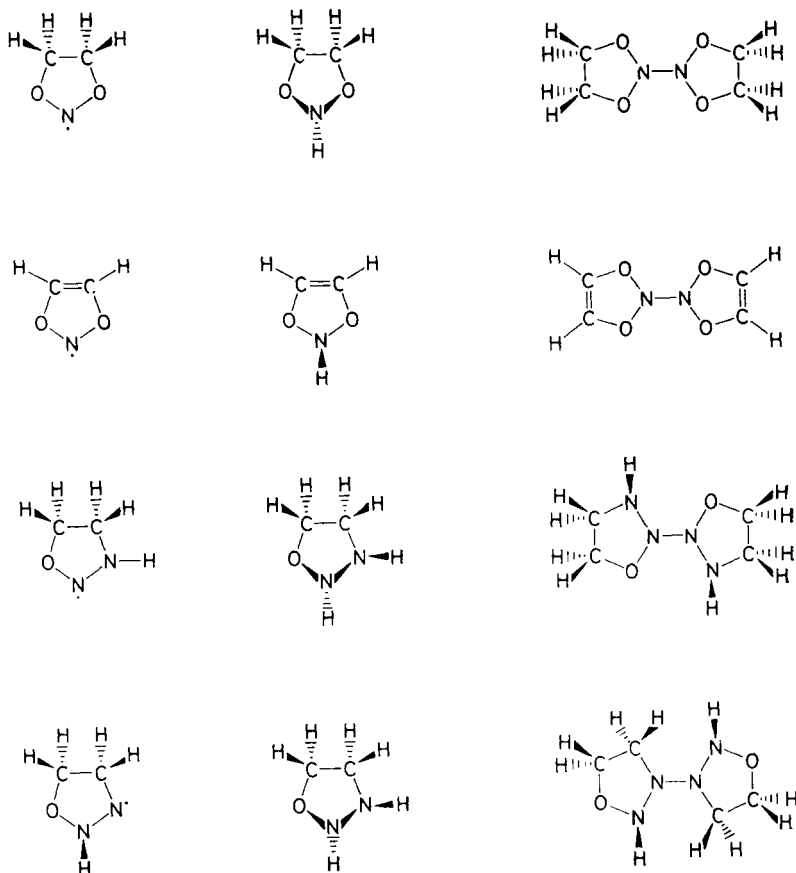


FIG. 1

Cyclic aminyls, parent molecules and corresponding dimers

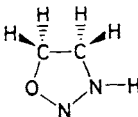
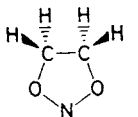
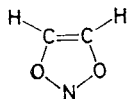
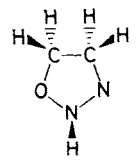
all the bonds are conserved in number and nature, which leads to approximate cancellations of correlation errors and also of zero point energy and thermal corrections. Thus, the energy change theoretically obtained at the SCF level is approximately equal to the experimental heat of reaction at 298.15 K.

$$\Delta E(\text{SCF}) \simeq \Delta H_0^\circ(298.15) = \sum_i k_i N_i [\Delta H_f^\circ(298.15)] \quad (1)$$

So, one can use a semiempirical procedure for estimating unknown heats of formation. It simply consists in introducing experimental heats of formation of reference compounds in the above equation as explicitly described elsewhere⁴.

The total energies and the heats of formation of the reference compounds involved in the isodesmic processes are given in Table III. The chosen isodesmic reactions, the corresponding thermal effects and the deduced semiempirical heats of formation are collected in Table IV, for all the species considered in this work.

TABLE I
Total energies (a.u.)* of the chosen aminyls and related species (4-31G)

Radical skeleton	c [•] NXY	c ⁺ NXY	cNHXY	(cNXY) ₂
	-261.89091	-261.63975	-262.47010	-523.74585
	-281.67198	-281.35800	-282.25267	-563.30448
	-280.47867	-280.15544	-281.05337	-560.92107
	-261.87543	-261.62281	-262.47010	-523.74380

* 1 a.u. = 2 625.5 kJ mol⁻¹.

These results allow us to calculate the stabilization energies E_s° of the chosen aminyls and related compounds by using the definition recently proposed by one of us⁵, namely:

$$E_s^\circ = \Delta H_a^\circ - \sum N_{AB} E_{AB}, \quad (2)$$

where ΔH_a° is the heat of atomization of the species under consideration and E_{AB} represents a standard bond energy term.

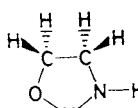
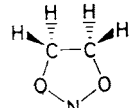
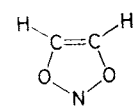
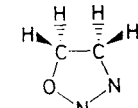
In the case of neutral species, molecules or radicals, ΔH_a° is classically written as:

$$\Delta H_a^\circ = \Delta H_f^\circ(\text{atoms}) - \Delta H_f^\circ(\text{neutral species}). \quad (3)$$

For the positive ions of the aminyl radicals, we shall use the relation⁵:

$$\Delta H_a^\circ(c^+NXY) = \Delta H_a^\circ(c^*NXY) - I(c^*NXY) + I(N), \quad (4)$$

TABLE II
Typical bond lengths (Å)* in the chosen aminyls and related species

Radical skeleton	Bond	c*NXY	c ⁺ NXY	cNHXY	(cNXY) ₂
	NN	1.38	1.24	1.42	(1.42)
	NO	1.41	1.30	1.48	(1.48)
	NN inter	—	—	—	1.41
	NO	1.40	1.26	1.45	(1.45)
	NN inter	—	—	—	1.43
	NO	1.41	1.28	1.46	(1.46)
	CO	1.40	1.39	1.41	(1.41)
	CC	1.31	1.33	1.31	(1.31)
	NN inter	—	—	—	1.47
	NN	1.37	1.20	1.42	(1.42)
	NO	1.46	1.38	1.48	(1.48)
	NN inter	—	—	—	1.41

* 1 Å = 0.1 nm.

where $I(\dot{c}'NXY)$ and $I(N)$ represent the ionization potentials of the considered aminyl radical and the nitrogen atom, respectively.

Using the data of Table IV and the bond energy terms given elsewhere¹, one obtains the results collected in Table V. It is seen that the aminyls where the radical center is carrying two electron-donor substituents have a relatively large thermodynamic stabilization energy, in accordance with previous results concerning their open chain analogues¹. However they are considerably less stabilized than the latter; moreover their parent molecules are much destabilized. This is at least partly due to the ring strain of the five membered heterocycles. One will also notice that the destabilization of the dimers is generally larger than twice that of the corresponding parent molecules.

The cations carrying an NH group on their positive center are better stabilized than the oxygen containing species and their ionization potentials are particularly low. On the other hand, the 6- π electron 5-center cation has an unexpectedly low stabilization energy as compared with the other cations. Although obeying the Hückel $4n + 2$ rule, this compound is clearly non-aromatic. The absence of electronic delocalization is demonstrated by the distribution of the LMO centroid

TABLE III

Total energies (a.u.) and heats of formation (kcal mol^{-1}) of reference compounds

Compounds	$E(4\text{-}31\text{G}/4\text{-}31\text{G})$	$\Delta H_f^\circ(298\text{-}15)$
CH ₄	-40.13977	-17.89 ^a
CH ₃ CH ₃	-79.11593	-20.24 ^a
CH ₃ OH	-114.87152	-48.07 ^a
CH ₃ NH ₂	-95.07166	-5.50 ^a
CH ₂ CH ₂	-77.92216	12.45 ^a
H ₂ O	-75.90864	-57.80 ^a
NH ₃	-56.10669	-10.97 ^b
*NH ₂	-55.47473	45.50 ^b
NH ₂ OH	-130.79188	-9.00 ^c
*NHOH	-130.18798	23.48 ^d
+NHOH	-129.82682	257.48 ^d
NH(OH) ₂	-205.48761	-13.64 ^d
NH ₂ NH ₂	-111.00675	22.80 ^c
*NHNH ₂	-110.40523	54.43 ^d
(HO) ₂ NN(OH) ₂	-409.78459	7.40 ^d

^a Taken from ref.⁶; ^b taken from ref.⁷; ^c taken from ref.⁸; ^d taken from ref.¹.

TABLE IV
Isodesmic reactions and semiempirical heats of formation (kcal mol⁻¹; 298.15 K)

Compound	Isodesmic reaction	ΔE	ΔH_f°
cNH(OCH ₂) ₂	cNH(OCH ₂) ₂ + 2 CH ₄ + NH ₃ + 2 H ₂ O → 2 CH ₃ OH + 2 NH ₂ OH + CH ₃ CH ₃	8.44	19.53
c ⁺ N(OCH ₂) ₂	c ⁺ N(OCH ₂) ₂ + 2 CH ₄ + ⁺ NH ₂ + 2 H ₂ O → 2 CH ₃ OH + 2 ⁺ NHOH + CH ₃ CH ₃	5.39	31.07
c ⁺ N(OCH ₂) ₂	c ⁺ N(OCH ₂) ₂ + ⁺ NHOH → c ⁺ N(OCH ₂) ₂ + ⁺ NHOH	29.60	235.47
[cN(OCH ₂) ₂] ₂	[cN(OCH ₂) ₂] ₂ + 4 CH ₄ + 4 H ₂ O → (HO) ₂ NN(OH) ₂ + 2 CH ₃ CH ₃ + 4 CH ₃ OH	-2.77	80.17
cNH(OCH ₂) ₂	cNH(OCH ₂) ₂ + 2 CH ₄ + 2 H ₂ O → NH(OH) ₂ + CH ₂ CH ₂ + 2 CH ₃ OH	-1.65	55.70
c ⁺ N(OCH ₂) ₂	c ⁺ N(OCH ₂) ₂ + 2 CH ₄ + 2 H ₂ O + ⁺ NH ₂ → 2 CH ₃ OH + CH ₂ CH ₂ + 2 ⁺ NHOH	5.68	63.47
c ⁺ N(OCH ₂) ₂	c ⁺ N(OCH ₂) ₂ + ⁺ NHOH → c ⁺ N(OCH ₂) ₂ + ⁺ NHOH	23.80	273.67
[cN(OCH ₂) ₂] ₂	[cN(OCH ₂) ₂] ₂ + 4 CH ₄ + 4 H ₂ O → (HO) ₂ NN(OH) ₂ + 2 CH ₂ CH ₂ + 4 CH ₃ OH	-0.18	142.96
cNH(OCH ₂)(NHCH ₂)	cNH(OCH ₂)(NHCH ₂) + 2 CH ₄ + 2 NH ₃ + H ₂ O → CH ₃ OH + CH ₃ NH ₂ + NH ₂ OH + NH ₂ NH ₂ + CH ₃ CH ₃	8.73	46.78
c ⁺ N(OCH ₂)(NHCH ₂)	c ⁺ N(OCH ₂)(NHCH ₂) + 2 CH ₄ + NH ₃ + ⁺ NH ₂ + 2 H ₂ O → CH ₃ OH + CH ₃ NH ₂ + ⁺ NHOH + ⁺ NHNH ₂ + CH ₃ CH ₃	5.14	58.01
c ⁺ N(OCH ₂)(NHCH ₂)	c ⁺ N(OCH ₂)(NHCH ₂) + c ⁺ N(OCH ₂) ₂ → c ⁺ N(OCH ₂)(NHCH ₂) + c ⁺ N(OCH ₂) ₂	39.40	228.81
cNH(OCH ₂)(⁺ NCH ₂)	cNH(OCH ₂)(⁺ NCH ₂) + 2 CH ₄ + NH ₃ + ⁺ NH ₂ + 2 H ₂ O → CH ₃ OH + CH ₃ NH ₂ + ⁺ NHOH + ⁺ NHNH ₂ + CH ₃ CH ₃	-4.57	67.72
cNH(OCH ₂)(⁺ NCH ₂)	cNH(OCH ₂)(⁺ NCH ₂) + c ⁺ N(OCH ₂) ₂ → cNH(OCH ₂)(⁺ NCH ₂) + c ⁺ N(OCH ₂) ₂	38.49	239.43
[cN(OCH ₂)(NHCH ₂)] ₂	[cN(OCH ₂)(NHCH ₂)] ₂ + 4 CH ₄ + 6 NH ₃ + 2 H ₂ O → 2 CH ₃ NH ₂ + 2 CH ₃ OH + 3 NH ₂ NH ₂ + 2 CH ₃ CH ₃ + 2 NH ₂ OH	25.17	130.59
[cNH(OCH ₂)(NCH ₂)] ₂	[cNH(OCH ₂)(NCH ₂)] ₂ + 4 CH ₄ + 6 NH ₃ + 2 H ₂ O → 2 CH ₃ NH ₂ + 2 CH ₃ OH + 3 NH ₂ NH ₂ + 2 CH ₃ CH ₃ + 2 NH ₂ OH	23.88	131.88

TABLE V
Some energetic properties of the chosen aminyls and related species (298·15 K)

Compound	$\Delta H_a^{\circ a}$	$E_s^{\circ a}$	I^b
cNH(OCH ₂) ₂	814·89	-19·31	
c ⁺ N(OCH ₂) ₂	751·25	7·34	8·86
c ⁺ N(OCH ₂) ₂	882·14	138·23 ^c	
[cN(OCH ₂) ₂] ₂	1 484·47	-51·23	
cNH(OCH) ₂	674·52	-28·88	
c ⁺ N(OCH) ₂	614·65	1·54	9·12
c ⁺ N(OCH) ₂	739·74	126·63 ^c	
[cN(OCH) ₂] ₂	1 213·28	-60·82	
cNH(OCH ₂)(NHCH ₂)	893·18	-18·91	
c ⁺ N(OCH ₂)(NHCH ₂)	829·85	8·05	7·41
c ⁺ N(OCH ₂)(NHCH ₂)	994·34	172·54 ^c	
[cN(OCH ₂)(NHCH ₂)] ₂	1 645·13	-46·35	
cNH(OCH ₂)(NHCH ₂)	893·18	-18·91	
cNH(OCH ₂)(⁺ NCH ₂)	820·14	-1·66	7·45
cNH(OCH ₂)(⁺ NCH ₂)	983·72	161·92 ^c	
[cNH(OCH ₂)(NCH ₂)]	1 643·84	-47·64	

^a In kcal mol⁻¹; ^b in eV; ^c calculated using Eq. (4) with $I(N) = 14·54$ eV taken from ref.⁹.

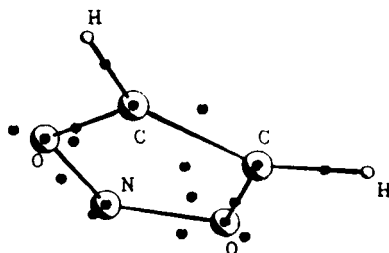
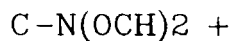
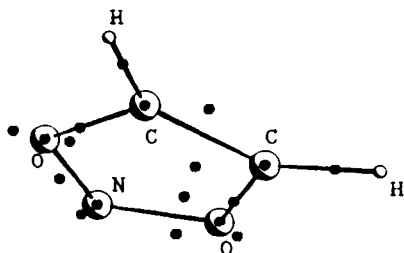
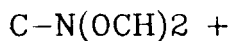
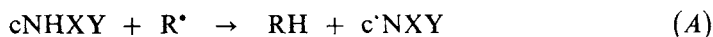


FIG. 2
Electronic structure of the cation c⁺N(OCH)₂ in terms of LMO centroids of charge

of charge shown in Fig. 2. The CC and NO bonds appear to have a localized double bond character which is confirmed by their particularly short length (see Table II).

Thermochemistry and Kinetics of Reactions Involving the Chosen Cyclic Aminyl Radicals

Hydrogen transfer reactions. The hydrogen transfer reactions



are closely related to the breaking of the bonds N-H and R-H involved in these processes. Their heat of reaction actually represents a difference of bond dissociation energies E_{bd}^*

$$\Delta H_0^{\circ} = E_{\text{bd}}(\text{N-H}) - E_{\text{bd}}(\text{R-H}). \quad (5)$$

It is easy to show that $E_{\text{bd}}(\text{N-H})$ can be explicitly written in terms of the stabilization energies of the radical and its parent molecule¹

$$E_{\text{bd}}(\text{N-H}) = \Delta \sum N_{\text{AB}} E_{\text{AB}} + E_s^{\circ}(\text{cNHXY}) - E_s^{\circ}(\text{c}^{\bullet}\text{NXY}). \quad (6)$$

In the case of nitrogen-centred radicals, the term $\Delta \sum N_{\text{AB}} E_{\text{AB}}$ is the standard energy of a given N-H bond. It is strictly constant in the series of cyclic amines considered in this work. Using the data of Table VI, one actually finds the following relation

$$E_{\text{bd}}(\text{N-H}) = 90.29 + E_s^{\circ}(\text{cNHXY}) - E_s^{\circ}(\text{c}^{\bullet}\text{NXY}) \quad r = 1. \quad (7)$$

TABLE VI

Heats of formation and activation energies of hydrogen transfer reactions $\text{cNHXY} + \text{}^{\bullet}\text{CH}_3 \rightarrow \text{c}^{\bullet}\text{NXY} + \text{CH}_4$ (kcal mol⁻¹; 298.15 K)

cNHXY	ΔE_s°	$E_{\text{bd}}(\text{N-H})$	ΔH_0°	E_a
cNH(OCH ₂) ₂	-26.56	63.60	-41.49	1.98
cNH(OCH) ₂	-30.42	59.87	-45.22	1.27
cNH(OCH ₂)(NHCH ₂)	-26.96	63.33	-41.76	1.92
cNHCH ₂ (OCH ₂)(NH)	-17.25	73.04	-32.05	3.74

* All energies are given in kcal mol⁻¹. 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

It is seen that a small $E_{\text{bd}}(\text{N-H})$ may correspond either to a very destabilized amine or to a very stabilized radical but all the intermediate cases can obviously be encountered.

Owing to relations (5) and (6), the thermochemistry of hydrogen transfer reactions can be rationalized in terms of stabilization energies. The following expression can be readily obtained, for any given attacking radical

$$\Delta H_0^\circ = 90.29 + E_s^\circ(\text{cNHXY}) - E_s^\circ(\text{c}^{\bullet}\text{NXY}) - E_{\text{bd}}(\text{R-H}). \quad (8)$$

As shown previously, the activation energies of these processes do obey the next Evans-Polanyi relation¹ (with $\text{R} = \text{CH}_3$)

$$E_a = 9.62 + 0.197 \Delta H_0^\circ \quad (9)$$

which can also be written in terms of stabilization energies

$$E_a = 6.97 + 0.187[E_s^\circ(\text{NHXY}) - E_s^\circ(\text{N}^{\bullet}\text{XY})]. \quad (10)$$

So, we are able to estimate the activation energies of the reactions



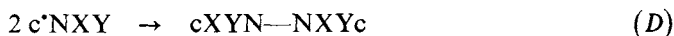
leading to the heterocyclic radicals considered here. The obtained results are listed in Table VI. They show that all these species are easy to prepare by hydrogen transfer reactions using $\text{}^{\bullet}\text{CH}_3$ as attacking radical.

Nitrogen-nitrogen bond breaking and forming. We consider here the two reverse reactions:

— the nitrogen-nitrogen bond homolyses (dissociations)



— the dimerization reactions (recombinations).



The following relations are readily obtained

$$\Delta H_0^\circ(\text{dissociation}) = -\Delta H_0^\circ(\text{recombination}) = E_{\text{bd}}(\text{N-N}) \quad (11)$$

$$E_{\text{bd}}(\text{N-N}) = E(\text{N-N}) + E_s^\circ(\text{dimer}) - 2E_s^\circ(\text{radical}), \quad (12)$$

where $E_{bd}(N-N)$ is the so-called nitrogen-nitrogen bond dissociation energy and $E(N-N)$, the standard N-N bond energy term ($47.88 \text{ kcal mol}^{-1}$). This equation rationalizes the thermochemistry of homolysis and recombination in terms of stabilization energies. The results obtained for the species considered in this work are collected in Table VII. Due to the large destabilization of the dimers, the N-N bond homolyses are either exothermic or slightly endothermic processes which automatically leads to an activation barrier on the corresponding reaction path.

As a matter of fact, we have shown previously^{4,10} that a relation does exist between the thermodynamic stabilization of nitrogen-centred radicals and the kinetics of their recombination reaction. The next equations have actually been obtained

$$(E_a)_r = 21.526 - 1.466E_{bd}(N-N) \quad (13)$$

and

$$(E_a)_r = -48.666 + 1.466[2E_s^{\circ}(*NXY) - E_s^{\circ}(\text{dimer})]. \quad (14)$$

TABLE VII

Thermodynamic and kinetic parameters of the homolysis and recombination processes involving aminyl radicals (kcal mol^{-1} ; 298.15 K)

c^*NXY	$E_{bd}(N-N)$	$(E_a)_r$	Character
$c^*N(OCH_2)_2$	-18.03	large	stable
$c^*N(OCH)_2$	-16.02	large	stable
$c^*N(OCH_2)(NHCH_2)$	-14.57	large	stable
$cNH(OCH_2)(*NCH_2)$	3.56	16.3	stable

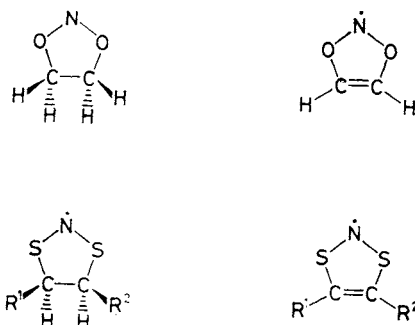


FIG. 3
Known thioanalogues of the presumed stable aminyls

Thus, the recombination reaction of an aminyl radical will have a positive activation energy if $E_{bd}(N-N)$ is less than 15 kcal mol^{-1} or, in other words, if the dimer is relatively much less stabilized (or much more destabilized) than the radical itself, namely

$$2E_s^{\circ}(\cdot NXY) - E_s^{\circ}(\text{dimer}) > 33 \text{ kcal mol}^{-1}. \quad (15)$$

Relation (13) allows us to estimate the activation energy of the recombination reaction of any aminyl radical corresponding to an $E_{bd}(N-N)$ value between 0 and 15 kcal mol^{-1} . In this way, we can also anticipate the character of the species under consideration. As shown in Table VII, all the radicals studied in this work are very likely stable species, essentially because of the large destabilization of their dimer.

It is interesting to notice that the thioanalogues of two radicals of the series considered in this work have been discovered and studied rather recently¹¹. They are represented in Fig. 3. According to the authors of this discovery, the two classes of radicals are persistent and the unsaturated ones can be prepared as pure liquids which have been shown to have a very low enthalpy of dimerization of $-2.4 \text{ kcal per mole}$. These experimental results strongly support the theoretical ones described in this work.

CONCLUSIONS

This work allowed us to confirm a result previously obtained, namely the nitrogen-centred radicals carrying two electron-donor substituents are very likely persistent or stable because the corresponding dimers are relatively much less stabilized than the radicals themselves. Furthermore, the latter are generally easy to generate from the parent molecules by hydrogen exchange reactions.

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