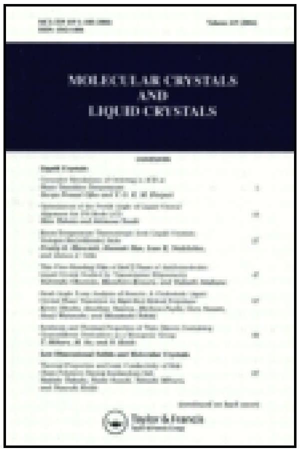

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Magnetic Properties of Iminonitroxide and Nitronylnitroxide Based Diradicals

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MAGNETIC PROPERTIES OF IMINONITROXIDE AND NITRONYLNITROXIDE BASED DIRADICALS

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Abstract The properties of a series of stable diradicals based either on iminonitroxide (IN) or nitronylnitroxide (NN) are described. Both radical fragments are coupled by various phenylene and phenylethynylene (triple bond) bridges. They are characterized by EPR studies both in solution and in glassy state. Magnetic coupling is evidenced at a very large distance between both radical fragments (up to 36 Å). The intramolecular coupling is found to be antiferromagnetic in all cases and in particular for meta- or ortho- substituted phenylene. Semiempirical calculations using configuration interaction show that the linkers with triple bonds induce a stronger conjugated character than the corresponding ones involving a double bond, in agreement with the experimental optical spectra, and that the relevant geometrical parameters are the twist angles; the corresponding barriers of rotation are then evaluated. Calculations show that, for some values of the twist angle, an antiferromagnetic state may be stabilized.

INTRODUCTION

The existence of intramolecular long range spin exchange has been reported previously in iminonitroxide diradicals; a magnetic coupling in a diradical in which the distance between both radicals is as large as 21 Å has been shown by EPR.[1] The peculiarity of the diradicals, we are interested in, is that both fragments are linked with triple bonds. Even if the alternation of triple bonds with single bonds is known to be less conjugated than double-single bonds, such a linker has been shown to be efficient for nonlinear optics.[2] The purpose of this study is then: i) to extend spatially the molecular coupling as far as possible; ii) to obtain informations about the relative contributions of various coupling mechanisms; iii) to determine the nature of the coupling (ferro- or antiferromagnetic) as a function of the topology of the molecules and/or their geometry (twist angles in particular); iv) to establish the role of the triple bonds (i.e. *sp* vs sp^2 hybridization) in the extension of the magnetic coupling. We present here results obtained mainly by EPR on a series of

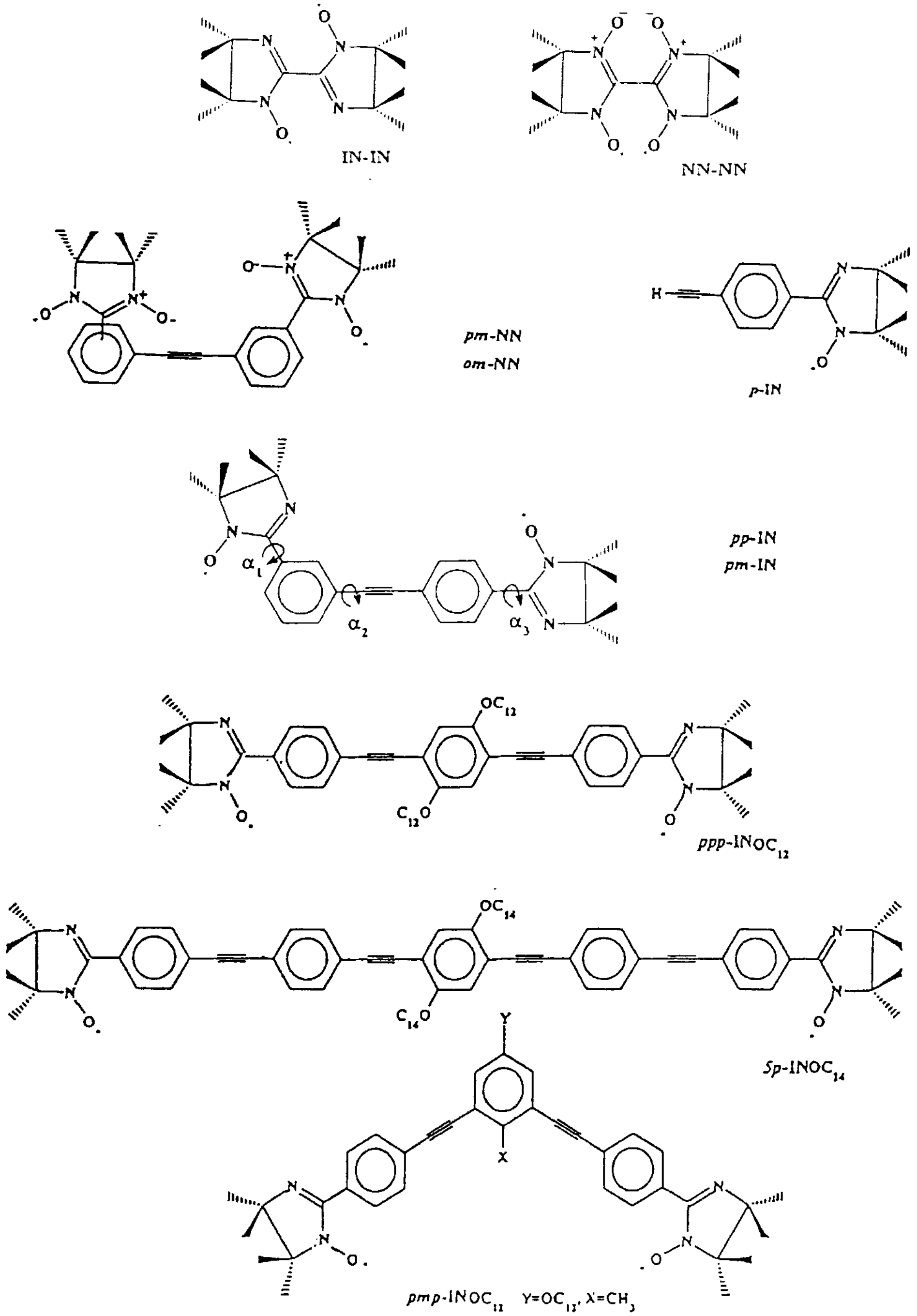


FIGURE 1 Different iminonitroxide and nitronylnitroxide derivatives discussed in this work.

original molecules; they are compared with some model molecules reported in the literature and the discussion is based on electronic structure calculations carried out with semi-empirical methods.

Diradicals are defined as systems having two odd electrons in degenerate or nearly degenerate molecular orbitals.[3,4,5] This degeneracy of the localized odd orbitals may be either accidental or related to some symmetry element and may be obtained for two chemically equivalent radical fragments coupled with a "linker". For alternated hydrocarbons it is possible to predict the multiplicity of the ground state using a simple topological rule based on Hückel or Valence Bond theory.[6,7]. According to this rule, phenylene substituted with radicals in meta position should be in the triplet state; this is generally the case. In order to explain the antiferromagnetic coupling observed in some cases the role of σ orbitals has been invoked.[8]

In this study we are concerned with iminonitroxide or nitronylnitroxide rings which are chemically stable. In both cases most of the spin density is concentrated on these rings and is located on the ON groups in a π^* orbital. In nitronylnitroxide derivatives (NN) both NO groups carry equal spin density. Both nitrogen are inequivalent in iminonitroxide ones (IN). In diradicals both radicals interact and the signature of this interaction is obtained from EPR on isolated molecules in solution.

EPR STUDY

Molecules discussed in this work are presented in figure 1.[9] The sign and the strength of the intramolecular spin exchange coupling J , have been estimated from the temperature dependence ($4K - 300K$) of the integrated X-band EPR absorption signal of the molecules in solution. In order to insure that the molecules are isolated in solution, thus avoiding the molecular aggregates, we prepared degassed solutions of c.a. $10^{-3} mole.l^{-1}$ diradicals in 1:1 p-xylene/CH_2Cl_2. The EPR signal usually consists of a single line spreading over a few gauss with a distorted shape. In

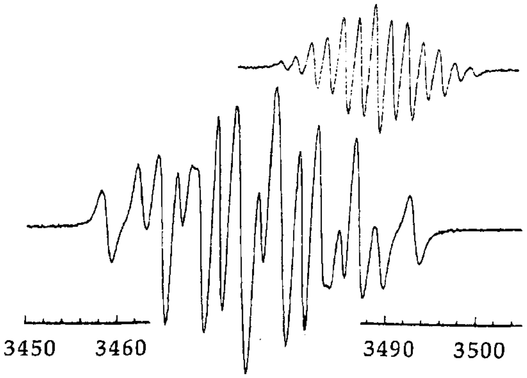


FIGURE 2 EPR spectrum of 5p-INOC$_{14}$ in solution in 1:1 p-xylene/CH_2Cl_2 mixing revealing the intermediate exchange coupling limit; inset: characteristic spectrum obtained in the strong exchange limit of iminonitroxide derivatives (13 lines). Magnetic fields are expressed in gauss.

TABLE 1 Experimental triplet-singlet splitting in imnonitroxide diradicals. Left side: linear oligomers; right side: broken chain oligomers (see figure 1 for the molecular structures).

Molecule	J/kB [K]	Molecule	J/kB [K]
IN-IN	-279	pmpIN-H	-6.56
2pIN	?	pmpIN-OCH$_3$	-2.55
3pIN-OC$_{12}$	-3.13	pmpIN-NO$_2$	-1.36
5pIN-OC$_{14}$	-0.002		

* ref. 14

most cases the EPR susceptibility is Curie-Weiss like. Therefore, the singlet-triplet splitting is always smaller than the measurement temperature range.

We failed to report on the temperature dependence of the EPR susceptibility of the pp-IN molecule. Different trials were unsuccessful, since they revealed the growing of a very broad line below the diradical signal as the temperature decreases. Such a feature has been attributed to residual metal catalyst from the chemical synthesis. As already reported for the 3p-IN and the pmp-IN compounds,[10] the EPR signal at room temperature of the synthesized diradicals is typical of radical spins in the limit of strong exchange coupling (see inset in figure 2). Within this limit, a nitronylnitroxide is expected to exhibit 9 lines for two equivalent sets of two equivalent ^{14}N nuclei, whereas 13 lines do occur for the iminonitroxide derivatives with two inequivalent sets of two equivalent ^{14}N nuclei. However, the behavior of the 5p-IN molecule is quite different (figure 2). The EPR spectrum clearly consists of more than the expected 13 lines. The observation of these extra lines may reveal the intermediate exchange limit achieved in this diradical.[11-14] Following this analysis, $|J|$ may be estimated from the splitting of the outer extra lines assigned to S resonance. It yields $|J| \approx 2mK$. The 5p-IN diradicals is the limit of the measurable exchange coupling; the distance between radical centers is 36 Å. The sign of this coupling could not be determined and has been assumed to correspond to an AF coupling according to the above mentioned topological rule.

Following the same rule, pmp-IN derivative should show a ferromagnetic coupling which is not found experimentally. A substitution with an electron acceptor or donor group induces a small decrease of the coupling constant. For diradicals with a linker having one triple bond (pm-IN), the EPR spectra are in agreement with the strong exchange limit but the temperature variation of the susceptibility does not allow to determine the coupling constant, which is less than 1 K (i.e. $10^{-4}eV$). All the results are collected in table 1.

Underlying all our studies is the question how the exchange coupling does occur: through bond or through space? The through space interaction can hardly be invoked for the series of the linear chain derivatives in which the inter radical distance

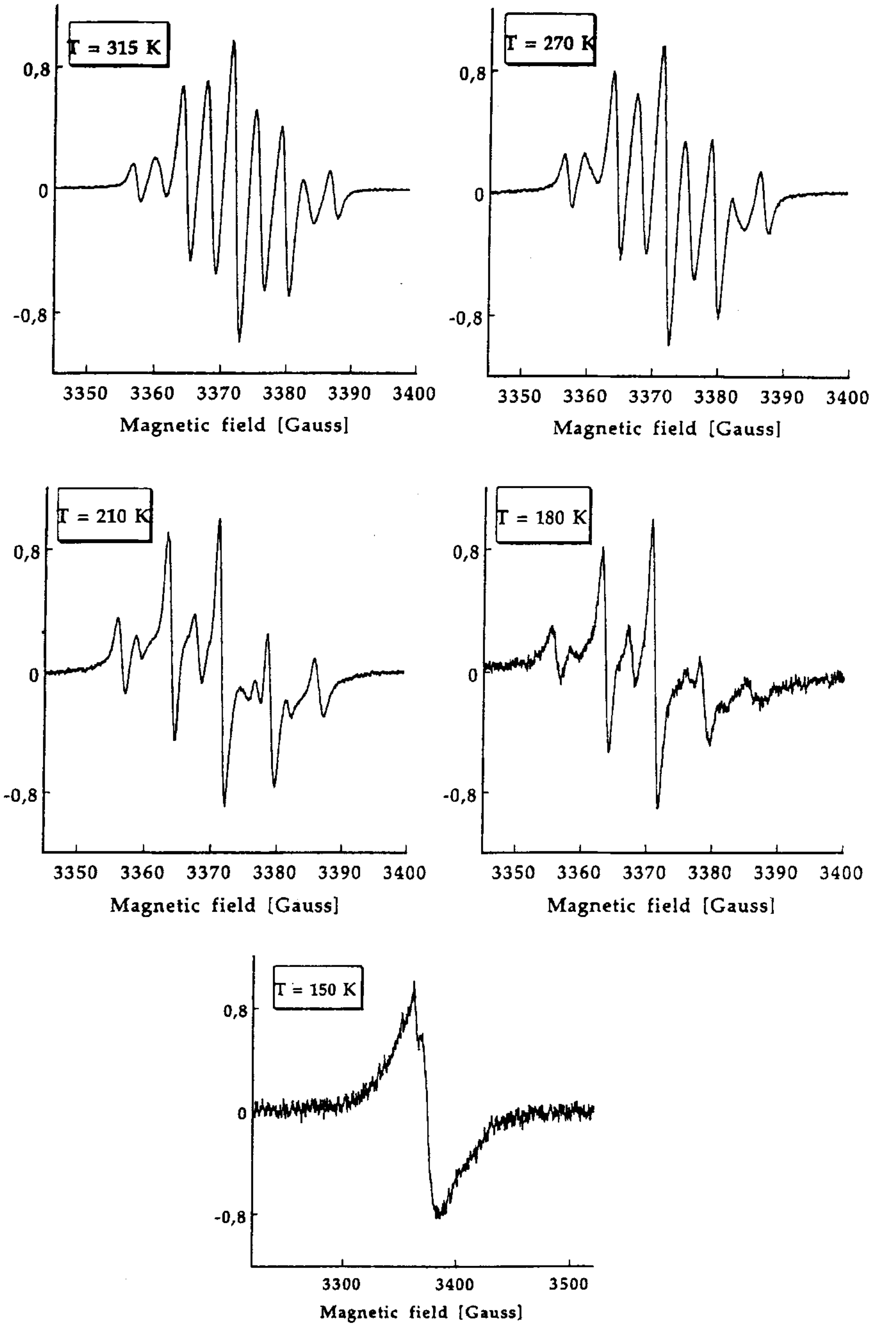


FIGURE 3 Evolution with temperature of the EPR spectra of om-IN in solution in 1:1 p-xylene/CH_2Cl_2 mixing (See text).

is larger than 9Å. However, it may be of utmost importance in the broken chain compounds (such as pmp-IN derivatives). An unambiguous answer concerning the importance of both contributions is brought about upon recording the EPR spectra of different derivatives as a function of temperature (figure 3). Due to steric hindrance, the radical spins within the om-NN derivative may obviously interact through space and/or through bond. The through space exchange coupling must be strongly temperature dependent in the solution, since the inter radical distance is not fixed depending upon molecular motion. The apparent spin decoupling within the diradical om-NN is well observed as the temperature is lowered. It is worth noting that the shape of the EPR spectra remains unchanged in the case of the pmp-IN derivatives as the temperature is lowered in the course of similar studies. Therefore, any variation of the spin-spin distance due to the molecular motion does not modify significantly the exchange interaction in these compounds. The route for the exchange interaction is mainly through bond rather than through space.

GEOMETRICAL CONSIDERATIONS

Single crystals allowing a crystallographic study have been obtained only for two systems namely the monoradical p-IN substituted in para position with $-C \equiv CH$ group and the biradical ppp-INOC$_{12}$. As already observed for similar systems, the atoms ONCN are already planar and the heterocycle is slightly distorded. In the diradical the central fragment is planar. The angle between the heterocycle and the adjacent phenyl is 24° for the monoradical (a common value) and 6° for ppp-INOC$_{12}$ (an unusually small value). This angle is very important for the stabilization of the magnetic states; we will focus on this parameter in the following.

At this stage of the discussion, the following questions arise: What is the particularity of the systems? Is it possible to predict the strength of the coupling? Is the ground state singlet or triplet? What is the role of the molecular geometry? And which are the relevant parameters?

We shall try to answer some of these questions keeping in mind that only a few data on the molecular geometries are available, that large molecules are involved in the spatial extension of the intramolecular coupling, and that only C, N, O, H atoms are concerned.

COMPUTATIONAL METHODOLOGY

We undertaken the determination of the electronic structure of the whole family of diradicals described above by means of semiempirical calculations. Let us emphasize from the outset that our aim at the present stage, is to find out the relevant parameters and the general trends, if any, concerning the intramolecular magnetic coupling between the radical fragments of the diradicals. The relevant parameters may either of geometrical nature, such as the twist angles between the different rings, the conjugated character of the triple bonds, the **planarity** of the heterocycles, ... or of topological nature, such as the branching of cycles at ortho, meta and para positions. Moreover the substitution and the chemical nature of the radical (IN vs NN) may play a role. Unfortunately, in view of the size of the diradicals we are interested in, we cannot use ab initio methods reasonably adapted to the study of magnetic coupling. [8,15] We have therefore used a semiempirical methods based on the NDDO approximation. [16–18] In this paper, we focus mainly on IN-IN and pm-IN diradicals and we report results obtained within the AM1 parametrization; [19,16,20] a detailed discussion about the other diradicals will be published elsewhere. In order to investigate the behavior of the singlet-triplet splitting as a function of the twist angles, the most reasonable methodology appears to be the optimization of the lowest singlet or triplet state for a series of fixed values of the twist angles; this implies to optimize the geometry including some configuration interaction (CI) in order to take account of the correlation which is crucial in such systems.[21,15,22] Within the NDDO approximation, CI enables to study the non dynamic correlation [23] i.e. configurational mixing (for a excellent discussion see ref. 24). However this turns out to become rapidly very difficult to carry out for two different reasons: i) to our knowledge there is no definite and clear criteria which enables to select the most important configurations to be retained in the CI; ii) the numerical computation becomes very heavy, if not untractable, when the number of configurations becomes large. For instance, in the case of pm-IN, a minimum number of six or seven molecular orbitals (CI=6,7 in figure 5b), depending upon the value of the twist angles, has to be retained in the calculation; otherwise the singlet and triplet states remain completely or nearly degenerate. Let us first discuss the ground state optimization. Full optimization[25,26] of the ground state with CI=2 to CI=7 yields geometries which differ only by the values of the α_2 twist angle (see figure 1 for a definition): α_2 decreases when the size of the CI increases. and becomes close to the experimental value when known in solid state. Moreover, we also optimized the ground state geometry within the UHF scheme, once for $N_\alpha - N_\beta = 0$ and once for $N_\alpha - N_\beta = 2$, where N_α, N_β are the number of occupied α and β orbitals respectively. The most stable ground state we obtained satisfy for all diradicals the well known topological rules[7] and show, for NN derivatives, the highest spatial symmetry. For a fixed twist angle, CI and UHF optimized geometries are very similar. We have therefore explored the potential energy surface within the UHF scheme. We have thus identified several minima corresponding to the conformations which differ with respect to the orientation of the NO groups; we have determined the path relating the different conformations and the transition states[27] which occur for 90° for α_1 and α_3.

RESULTS

In this discussion we focus on two systems namely IN-IN, for which the $O \ldots O$ distance is short and for which the direct coupling has been invoked, and pm-IN for which both magnetic states are nearly degenerate: singlet-triplet (S-T) or triplet-singlet (T-S) < 1K.

Geometry optimization allows to well reproduce the **planarity** of phenyl groups and the small distortion of the heterocycles, but the atoms ONCN and ONCNO are not strictly planar (deviation of around 15° in all cases). The triple bond is found to be more conjugated than expected; the contiguous single bonds are estimated to be in the range 1.399-1.406Å depending on the system, and the rotation around this linker is not free. When replaced by a double bond this conjugation is decreased:

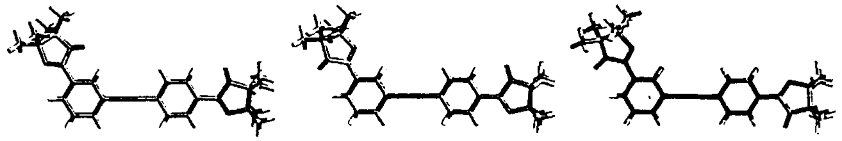
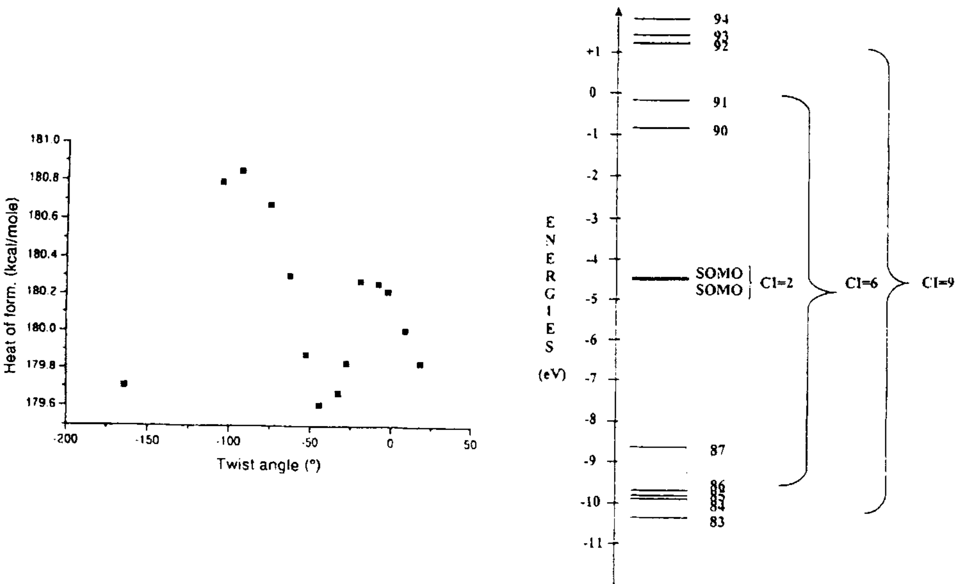


FIGURE 4 Various conformations of pm-IN differing by the orientation of the *NO* groups with their heat of formation obtained in UHF (named from left to right): A (167.32 kcal/mole), B (167.19 kcal/mole) and C (167.15 kcal/mole).



a b

FIGURE 5 a) Barrier of rotation pm-IN for the twist angle α_3 obtained with CI=6 (energies expressed in kcal/mole). b) Molecular orbital energies for pm-IN (conformation C) (energies expressed in eV).

the single bond lengths vary from 1.400Å up to 1.438Å.

In all cases the lowest heat of formation is obtained for geometries corresponding to the spin multiplicity predicted by the topological rule (for example singlet for all the para derivatives and triplet for pm and om derivatives). Moreover related to the low symmetry of most of the molecules there are several stable conformations, especially for IN derivatives such as pm-IN for which the heat of formation of the three calculated conformations are very close (figure 4).

The conformation noted C for pm-IN (figure 4) is the most stable one but differences between the heat of formation of the different conformations are less than kT at room temperature. For conformation C the twist angles between successive rings are: $\alpha_1 = -30.1°$, $\alpha_2 = 1.2°$ and $\alpha_3 = -27.7°$.

Barriers of rotation have been calculated for α_1 and α_3 by means of a CI calculation carried out on each UHF optimized geometry. As an example the variation of the heat of formation as a function of α_3 is shown in figure 5. For the energy range corresponding to the room temperature, the twist angle may vary from $-65°$ to $+65°$. The rotation barrier of various systems is nearly of the same order of magnitude; this may explain the large spread over observed for these angles ($+6°$ for ppp-INOC$_{12}$ or $\sim 50°$ for IN-IN or NN-NN). One exception is om-IN for which steric hindrance does not allow a large deviation from the equilibrium geometry ($\alpha_{ortho} = -45°$ and $\alpha_{meta} = -30°$)(figure 6).

Spin densities obtained within INDO approximation for these optimized geometries are quite close for all the systems; for example for pm-IN in conformation A: $\rho_S(O) = 0.641$, $\rho_S(N) = 0.279$, $\rho_S(C) = -0.095$ and $\rho_S(N) = 0.176$ with $< S^2 >= 2.006$ after spin annihilation ($< S^2 >= 2.112$ before spin annihilation). These values reproduce quantitatively the ratio of hyperfine coupling constant observed on both

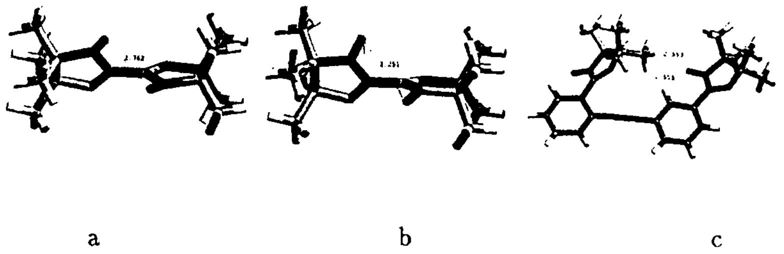


FIGURE 6 Two conformations of IN-IN diradicals differing only by the $O \ldots O$ distances: a) 2.762Å i.e. nearly the Van der Waals distance and b) 3.251Å. Steric hindrance appearing in om-IN: for two H atoms of a methyl group, the distances of $O \ldots H$ (2.56Å) is less than the Van der Waals distance (2.6Å).

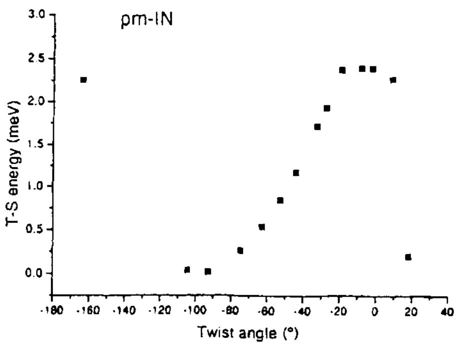


FIGURE 7 Variation of T-S splitting of pm-IN obtained with CI=6.

TABLE 2 T-S splitting (expressed in meV) for a fixed geometry of pm-IN, obtained with CI calculations, as a function of the number of SCF MO energies and the type of excitations (single, double, triple and full within the considered active space) which are taken into account. In the full CI, the number of configurations really used is given in parenthesis.

Number of orbitals (CI)	S + D	S + D + T	Full (Number of configurations)
2			$<10^{-3}$
4			0.747 (36)
5			0.101 (100)
6	0.925 (118)	2.000 (280)	1.776 (400)
7	0.902 (205)	2.054 (637)	1.768 (1225)
8	-0.083 (361)		0.980 (1600)
			0.206 (3360)
10	-0.255 (876)		5.291 (3360)*

* Note that for CI=10, the maximum number of lowest configurations we could use (3360) excluded a series of configurations which are already taken into account with CI=8 CISD. This points out the role of the high energy configurations in the case of pm-IN.

TABLE 3 T-S splitting (expressed in meV) for a fixed CI=10 taking account of all single and double excitations in pm-IN for various twist angles (α_3) around the conformation C.

α_3 (°)	-104.5	-92.8	-52.8	-32.7	-27.7
T-S (meV)	-0.02	-0.006	0.49	0.44	0.12
α_3 (°)	-8.3	-2.4	+8.6		
T-S (meV)	-2.11	-0.54	-0.66		

nitrogen by EPR (factor of 2). The small variation of the spin densities from system to system and with the twist angles indicate that they are not a crucial parameter in the intramolecular coupling.

Several geometry optimizations, for a fixed twist angle, of the first excited state have shown that the geometry is very similar to the optimized ground state geometry. We have therefore computed the singlet-triplet splitting by means of CI calculations carried on the optimized geometry of the ground state. For several types of diradicals, the S-T splitting has been studied in this way using small CI active space.[29] In a first step we also computed the S-T splitting using small CI active spaces (up to CI=6 or 7: see figure 5b) for which the degeneracy is lifted. For most of the diradicals we have studied, the triplet state is then the most stable one for all values of the twist angles (figure 7). However it turns out that excitations with much higher energy may play a crucial role: as a typical example the values of the S-T splitting for $\alpha_1 = -35°$ for pm-IN, as a function of the excitations retained in the calculation are shown in table 2. However, to our knowledge, there is no simple criterion which may help to select the most important configurations. For pm-IN we have computed the S-T splitting as a function of α_1 and α_3 retaining all single and double excitations for CI=10. A typical behaviour for the S-T splitting in pm-IN as a function of α_1 is shown in table 3: for some values of twist angles the singlet state may fall below the triplet state and hence a AF state may be stabilized. However at the present stage such a study does not allow to determine unambiguously the S-T splitting.

CONCLUSIONS

This paper is devoted to the properties of some isolated stable diradicals built with two nitroxide radicals linked by phenyl and conjugated triple bonds. Nitroxide radicalar fragments are branched on the neighbouring phenylene either in para position or in meta/ortho position. The exchange coupling between both radicals decreased nearly exponentially with their distance but it is efficient up to 36Å. This coupling is always found to be antiferromagnetic. This is rather surprising for the meta topology for which a ferromagnetic ground state is expected.[8]

The geometry obtained by optimization reproduces very well the characteristics of the systems studied by x-rays in the solid state.[1] The twist angles between the successive rings are the relevant parameters. The barriers of rotation are low (for example 1.4 kcal/mole for pm-IN) and the twist angle obtained in solid state may be in a large range as it is observed experimentally (from 50 to 6°). The lengths of the single bonds contiguous to triple bond show strong conjugated character of this alternant sequence (when compared with double bond); this is verified by the optical absorption shifted towards higher wavelengths.[9]

The calculated spin densities, using the optimized geometries, are in agreement with the hyperfine coupling observed in EPR spectra. They do not strongly depend either on the nature of the linker or on the geometry.

The triplet-singlet splitting has been calculated with semiempirical CI calculations within different active spaces. It is shown that in agreement with reference 8, a change of the sign of the coupling is possible for certain angles but the necessity to take account of configurations with high energy excitations makes a quantitative estimation very questionable.

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25. The UHF calculations have been carried out using the MOPAC version 6 and MOPAC 93 packages.[19,20] The CI calculations have been performed using MOPAC 93 (only revision 2 has been used for CI optimization).

26. SCF convergence criteria which have been chosen are a change in energy between successive iterations less than $10^{-7} kcal.mole^{-1}$ and a change in density matrix elements on two successive iterations less than 10^{-3}. Geometry optimization was stopped when the gradient norm (as defined in 20) was less than 10^{-2} for UHF ground state and transition states calculations. For CI optimization we tried to require the gradient norm less than 10^{-1}; however in several cases it was not possible to reduce the norm below 1.

27. We have checked that the ground states and the transition states are characterized by a Hessian for which all eigenvalues are positive (minima) and for which there is one and only one negative eigenvalue (transition state) respectively.[28]

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