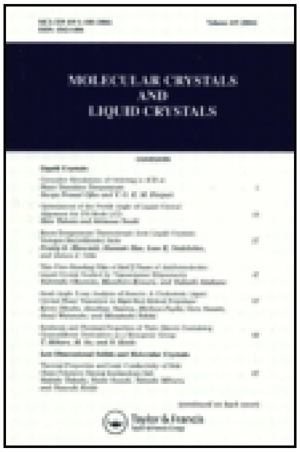

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Exchange Interactions in Nitroxide Biradicals

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EXCHANGE INTERACTIONS IN NITROXIDE BIRADICALS

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Abstract It has been shown by experimental and theoretical studies that exchange interactions in non planar π systems are strongly dependent on the geometrical parameters characterizing the non planarity.

A study of the exchange interaction in isolated nitroxide biradicals is presented for non planar paraphenylene bis nitroxide **3** [1,4-di-*t*-butyl-2,5-bis(*t*-butylaminoxyl) benzene (*anti*)], non planar metaphenylene bis nitroxides **7** and planar metaphenylene bis nitroxide **9**.

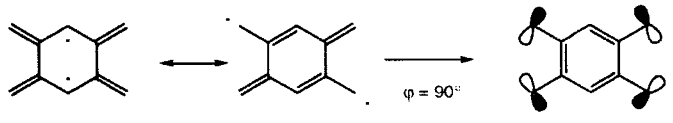
Determination of positive or weak negative exchange interactions in isolated molecules in dilute solution is difficult and can be inaccurate. **3** is a ground state singlet $2J/k = -35K$. Metaphenylene bis nitroxide **7g** [1-*t*-butyl,3,5-bis(*t*-butylaminoxyl) benzene] and **9** [1,2,9-tetrahydro 2,2,4,4,6,6,8,8-octamethyl-4H,6H-benzo[1,2d; 4,5d']bis(1,3 oxazine)-1,9 dioxyl] are probably ground state singlets, the triplet-singlet separation being smaller than 10K, contrary to theoretical predictions. X-Ray structure of **7a A** [1,3,5-trimethyl-2,6-bis(*t*-butyl aminoxyl)benzene (*syn*)], **7g** and **9** are reported. In pure crystalline solid, however, these three biradicals have a susceptibility characteristic of triplet radical-pairs in weak antiferromagnetic interaction with their neighbours.

The problems (including the transferability of the exchange interaction) raised by these apparently contradictory results are discussed.

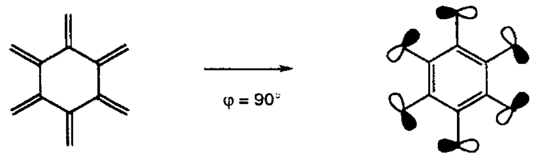
Although it is generally accepted (1) that metaphenylene is a ferromagnetic coupling unit, it has been reported that some non planar metaphenylene bisnitroxides are ground-state singlets (2). Conformational effects on the singlet-triplet energy difference ($E_S - E_T = 2J$) (twice the exchange interaction J) in metaphenylene biradicals have been rationalized by molecular orbital calculations (3) : this splitting decreases from positive values in planar biradicals ($\varphi_1 = \varphi_2 = 0$) to negative values for perpendicular *syn* or *anti* conformations ($\varphi_1 = \pm\varphi_2 = 90°$). ($\varphi_i$ are the torsion angle between the π orbitals of the aromatic ring and of the radical centre *i*).

Similar effects have been found in simpler systems such as ethylene, in para phenylene biradicals or in more complex systems like **A** or **B**, where a 90° torsion would change the π system of the radical centres into a σ system.

A



B



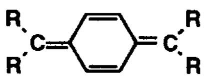
In this article, we would like discuss some examples of such effects and to point out some discrepancies between theory and experiment in metaphenylene bisnitroxides and ask some questions on their possible origin.

1) Twisted ethylene :

The simplest conformation effect on the singlet-triplet energy gap in an isolated molecule, may be found in non planar ethylene : assuming rigid CH_2 groups, Mulliken (4) suggested on the basis of Hund's rule that perpendicular ethylene ($\varphi = 90°$) has a triplet ground-state. Further experiments and calculations (5) showed that in fact the negative singlet-triplet gap increases from $2J/k = -32700K$ (experimental) to ca $-1000K$ (calculated) as φ changes from zero to 90° but never becomes positive. (For experimental work on related biradicals see (6)).

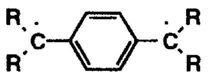
2) Paraphenylene derivatives :

Conformational effects have also been discussed (7) (1b) in paraphenylene derivatives, such as **1** where the aromatic ring is expected to change from a quinonoid structure **1a** to a benzenoid structure **1b** as the molecule changes from a planar ($\varphi_1 = \varphi_2 = 0$) to a bis-perpendicular conformation ($\varphi_1 = \varphi_2 = 90°$), while the singlet-triplet gap increases from large negative to smaller negative or positive values.



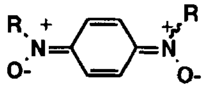
φ = 0

1a

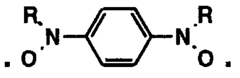


φ = 90°

1b

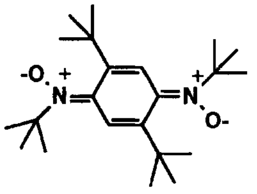


2a

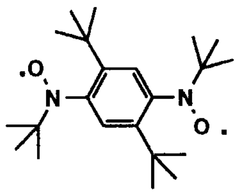


2b

Bisnitrone **2a**, a quinonoid molecule is diamagnetic (as shown for **2a**, R = C_6H_5 (8)). Although to our knowledge the energy of its first triplet state as not been reported, the singlet-triplet gap may be estimated as $0 << -2J / k \leq 42450K$. This last value is the one reported for the benzene molecule (9), but $-2J / k$ may be smaller because of a positive contribution from a bisnitroxide structure **2b** : in C_6H_6 the triplet state has one π-bond less than the ground state molecule ; similarly, **1a** has four π-bonds while **1b** has only three, while there are four π-bonds in **2a** as well in **2b** because each nitroxide group has a $\frac{1}{2}\pi$-bond.



3a



3b

We have prepared (10a) a related compound **3** in the hope that steric hindrance inducing a torsion of the nitrone groups in **3a** would stabilize the bisnitroxide structure **3b** and reduce the triplet singlet gap. This is indeed the case. In the isolated molecule, $2J / k = -35K$ (measured by esr in ethanol solution) : the molecule is not a triplet ground-state but the triplet is stabilized relative to the planar molecule. (In pure crystal, SQUID measurements yield for an isolated-pair model $2J / k = -159K$, quite different from the value found for the isolated molecule in solution). In the crystal at room temperature (10b) (Figure 1), the planar benzene ring is not quinonoid but has equal C-C bonds ; the (aromatic C)-N bonds (1.442 Å) are in the range of (sp^2 C)-N single bonds and much longer than (sp^2 C)=N double bonds (11). Calculations (12) on **2b**, (R = H) with the experimental geometry (*anti*) adapted for H substituents give $2J / k = -600K$ while for the *syn* compound with similar torsion angles, the calculated value is -723 K). (Similar examples of relative stabilization of the triplet state by torsion in non disjoint p-phenylene biradicals have been recently reported (13)).

Other ground-state singlet p-phenylene biradicals of (at least partially) disjoint type are known (14).

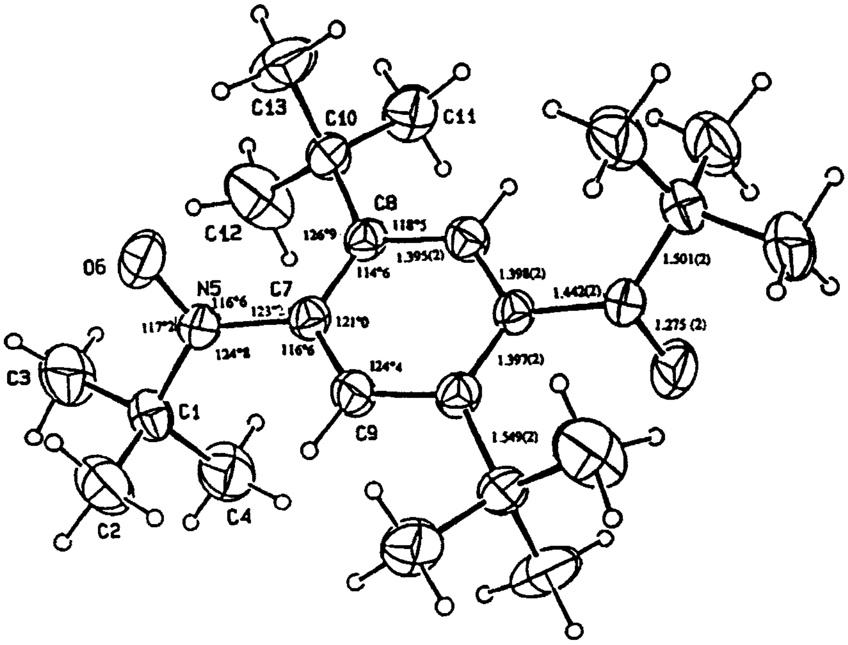
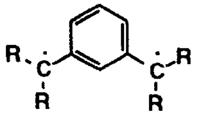


FIGURE 1 : X-Ray structure of biradical **3** (ref. 10b)

Metaphenylene derivatives :

Experimentally, bismethylene-metaphenylene **4a** has been found to be a ground state triplet (15). However, to our knowledge, no experimental quantitative determination of the singlet-triplet gap has been published (16).



4

a R = H

b R = ϕ

The theory of this non-kekuléan molecule was first studied by H.C. Longuet-Higgins (17) and calculations on its planar conformation (18) (3b) ($\varphi_1 = \varphi_2 = 0$) confirmed his proposal. The calculated values ($2J/k = 3370K$ (18a); 1380 K, 5410 K (3b); 5700 K (18b)) may be compared to the the highest value for a molecular ground state triplet found in O_2 where $2J/k = 11312K$ (19).

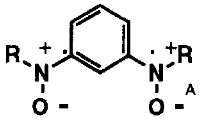
Torsion of the CH_2 groups changes the singlet-triplet gap : for the perpendicular ($\varphi_1 = \varphi_2 = 90°$) conformation, the calculated values are : $2J/k = -130K$ and - 50 (3b) or 0 (18b).

Some non planar metaxylylene biradicals have been studied experimentally : in *syn* and *anti* perchloro derivatives of **4b** (20a), with $\varphi_1 \approx \pm\varphi_2 \approx 50°$ (21), it was found that either $2|J|/k < 4K$ or $2J/k > 300K$ in solution and that in the solid state $2J/k > 300K$. These values may be compared to those estimated in **4a** assuming on symmetry grounds a variation $2J/k = A + B\cos^2\varphi$ for symmetrical metaphenylene derivatives **4** : with $\varphi_1 = \varphi_2 = \varphi$ the calculated results (3b) for $\varphi = 0$ and $\varphi = 90°$ give (A,B) = (- 131, 1514) or (-91, 5503) (in K) so that in **4a** for $\varphi = \pm 50°$, $2J/k = 500$ or 2180 K.

Other derivatives of **4b** (20b-f) (some of which presumably with $\varphi \approx 90°$ (20e) or $\varphi = 0°$ (20f)) are known, but the temperature dependence of the esr spectra in dilute solution was not quantitatively studied or was not conclusive, the solid state results (20d, e, f) being interpreted as originating from ground-state triplet molecules.

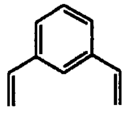
Methaphenylene bisnitroxides :

Although when written as **5a** metaphenylene bisnitroxides may seem nitrogen atoms



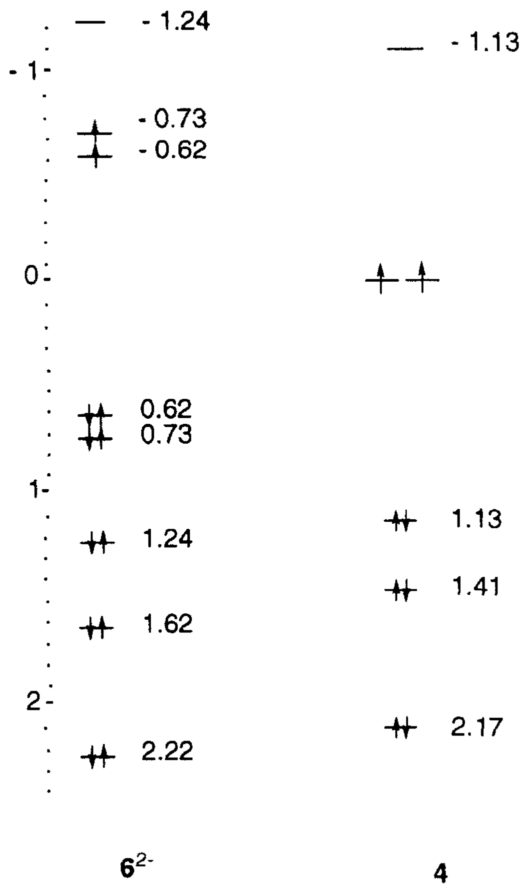
5a

5b



6

analogs of **4**, they may also be considered as analogs of the dianion of a bisvinylidenephenylene molecule **6** (22).



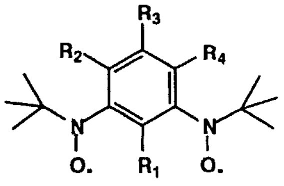
Scheme 1

Scheme 1 gives a comparison of the Hückel levels for **4** and **6** : simple Hund's rule arguments favor a ground state singlet for planar $(\mathbf{6})^{2-}$ without excluding the possibility of a ground state triplet because if the weak splitting (0.11β) between the two lowest antibonding levels.

Calculations (3b) for *syn* and *anti* **5** (R = H) found in fact a positive splitting for $\varphi = 0$, $2J/k = 110K$ decreasing to $0 \leq -2J/k \leq 20K$ for $50 \leq \varphi \leq 130°$ $(\varphi = \varphi_1 = \pm\varphi_2)$, another calculation (13) for $\varphi = 0$ giving $2J/k = 400K$. For dihydroxy derivative **7h** (2b) at $\varphi = 0$, $2J/k = 90K$. These positive values are much smaller than those calculated for planar **4a**.

Ground-state singlet :

Five metaphenylene bis nitroxides **7 a A**, **7a B** (2a), **7b** (2b), **7c** (23) and **7d** (24) with



7

a $R_1 = R_2 = R_4 = Me$ $R_3 = H$ (A : *syn*, B : *anti*)
b $R_1 = R_3 = H$ $R_2 = R_4 = OMe$
c $R_1 = R_2 = OMe$ $R_3 = Br$
d $R_2 = R_4 = Me$ $R_1 = R_3 = H$
e $R_1 = R_2 = R_3 = R_4 = H$
f $R_1 = R_2 = R_4 = H$ $R_3 = Br$
g $R_1 = R_2 = R_4 = H$ $R_3 = tBu$
h $R_1 = R_3 = H$ $R_2 = R_4 = OH$

singlet ground state are known (Table 1). Crystal structure have been resolved for **7a A** (25) and **7b** (27) only : $\varphi_1 = 89°$, $\varphi_2 = 83°$ and $\varphi_1 = 65°$, $\varphi_2 = 75°$ have been found for *syn* **7a** (crystalline **A** of ref. 2a) (figure 2) (25) and **7b** (2b) respectively.

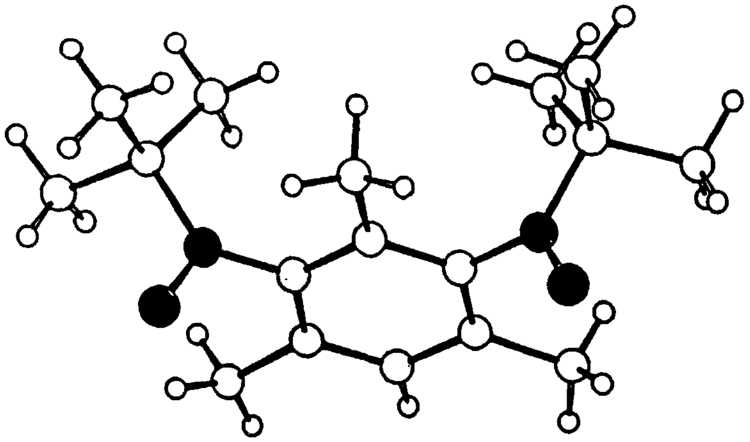


FIGURE 2 : X-Ray structure of biradical **7a A** (*syn*) (ref. 25)

In solution, the conformations of these biradicals may differ from the one found in the crystal (the variation of the dipolar interaction with temperature found (2a) in *syn* **7a A** and *anti* **7a B** shows that even in these highly hindered molecules conformational mobility may exist).

In the average, the molecule may be symmetrical and the torsion angle φ $(= \varphi_1 = \pm\varphi_2)$ in solution is probably not very different from the average of the solid-state values $\frac{|\varphi_1| + |\varphi_2|}{2} = 86°$ for **7a A**. Using the calculated $2J(\varphi)$ (3b), an order of magnitude of

TABLE 1 : Comparison of the singlet-triplet splitting ($2J/k$) found in solution and in pure solid. Data obtained by esr (a) or magnetic susceptibility (b). *Solution results* : (c) singlet-triplet splitting in kelvin obtained by fitting results to a Bleaney-Bowers formula (ref. 27). *Solid state results* : (d) Curie law (ref. 28) C in emu Kmole^{-1}. (e) Curie-Weiss formula (ref. 28) C as in (d), θ in kelvin. (f) Bleaney-Bowers ($\theta = 0$) or modified Bleaney-Bowers formula (ref. 54) : $\chi_{\mathrm{para}} = Ng^2\mu_B^2 / \left\{k(T-\theta')\left[3+\exp(-2J'/kT)\right]\right\}$; $[-]$:θ' was not reported. (g) ref. 2a. (h) ref. 10a. (i) ref. 32. (j) ref. 2b. (k) ref. 23. (l) ref. 24. (m) ref. 26a. (n) ref. 26b. (p) ref. 29. (q) ref. 22 c.

	$2J/k$ K (c)	C (d)	C[θ] (e)	$2J'/k[\theta']$ (f)
7a A	- 63 (ethanol) (a) (g)			- 76 [0] (a) (b) - 64 [0] (b) (j)
7a B	- 50 (ethanol) (a) (g)			- 54 [0] (a) (h)
7b	- 7 (polycarbonate) (b) (j)			- 73.8 [0](b) (j)
7c				- 450 [0] (b) (k)
7d				- 80 [−] (b) (l)
7e	+ 6000 (ethanol) (a) (m) $2J/k > 300$K (a) (j) $2\|J\|k < 5$ (b) (ethanol)		0.90 [−19] (b) (n) 0.98 [−7.8] (b) (p)	
7f	(a) (j) $2J/k > 300$K (a) (j) $2\|J\|k < 5$ (b) (ethanol)			
7g	- 12 (ethanol) (a) (c) - 1.3 (polycarbonate) (b) (c)	0.94(b) c)	0.96 [−5] (b) (c)	+ 840 [−] (b) (q) + 730 [−5] (b) (i)
9	- 12 ethanol (a) (c) - 1.1 polycarbonate (b) (c)	0.8 (b) (c)	0.87 [−0.38] (b) (c)	+ 100 [−7.5] (b) (c)

$2J/k$ for the isolated molecules **2a** may be obtained for these symmetrical conformations : $-10K$ for **7a A** and $-15K$ for **7a B**. These may be compared to the experimental values ($-66K$ and $-81K$). It was calculated that for $\varphi = 70°$, $2J/k = 0\,K$ in the dihydroxyderivative **7h**, a model of **7b**. This value is close to $-7K$ found in solution, but an order of magnitude smaller than $-74K$ found in the pure solid (2b).

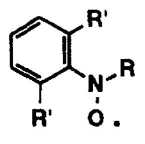
Ground-state triplets :

7e was the first metaphenylene bisnitroxide reported to have a triplet ground-state with "an approximate value" of the singlet-triplet splitting $2J = 12\text{kcal/mole}$ (26a). The experimental evidence came from an esr study of the intensity (I_2) of the $|\Delta m| = 2$ transition in a temperature range not reported but probably between 300 to 77 K according to the experimental set-up. The numerical data were not reported but a Bleaney-Bowers (27) fit for $2J = 12\text{kcal/mole}$ means that in fact, it was found that I_2T was constant in this temperature range. There were thus two possible interpretations : $2|J|/k < 77K$ or $2J/k > 300K$ and the authors choosed the second without discussing the first one. A proof of the presence of a ground-state triplet in the solid was obtained by a temperature study of the magnetic susceptibility of a crystalline sample between 60 and 300 K with a magnetic torsion balance (26b) : a Curie-Weiss (28) plot of the results gave a Curie constant $C = 0.90 \pm 0.04/\text{emuKmole}^{-1}$ slightly lower that the theoretical value for a pure triplet (C = 1) and $\theta = -19 \pm 2K$. This was attributed to a strongly coupled intramolecular triplet ($2J/k > 300K$) in weak antiferromagnetic interaction with its neighbours. These results were confirmed (29) on a sample reported to be of higher purity.

This proof of the triplet multiplicity of the ground state of the isolated molecule relies on some hypothesis : 1) The ferromagnetic interaction observed in the crystal is the intramolecular one. 2) The intramolecular exchange interaction is the same in a dilute solution and concentrated phases. 3) The conformations of the molecule (specially the torsion angle φ_1 and φ_2) in solution and in the crystal do not differ much.

We shall discuss later the two first hypothesis. About the third one, there was no possibility to obtain an X-Ray structure because the crystal decomposes (26a). (In an X-Ray study on a related trisphenylnitroxide triradical, a torsion angle $\varphi = 37.5°$ was found (22c)).

Two different frozen-solution spectra were observed in toluene and in ethanol solution : the dipolar interactions clearly show the presence of a single conformation $2|D| = 262G$ in toluene and of two conformations with $2|D| = 262$ and $366G$ in ethanol. The two conformations were not determined but the presence of large torsions were suggested. On the basis of Mc Lachlan calculations, possible values $\varphi_1 = \pm\varphi_2 = 46°$ were estimated. If we ignore the problem of two conformations, we may obtain an average conformation in solution from other esr data, the nitrogen (a_N) and proton (a_H) hyperfine splittings (hfs)


8

a R = R' = H
b R = Me R' = H
c R = Et R' = H
d R = isoPr R' = H
e R = tBu R' = H
f R = tBu R' = Me

reported for a series **8** of phenyl nitroxides (table 2).

TABLE 2 : Estimation of an average torsion angle $\tilde{\varphi}$ between the nitroxide and phenyl π orbitals from the nitrogen a_N and aromatic (ortho (o), meta (m) or para (p)) proton a_H hyperfine splitting (in gauss) in a series of phenylnitroxides **8**.
(a) assumed (b) calculated (c) assumed : (83° and 85° was found in **2a** (ref. 25).

	$\tilde{\varphi}$	a_N	$a_{H_{o,p}}$	$a_{H,m}$
8a	0° (a)	9.9	3.1	1.0
8b		11.0	2.9	1.0
8c		11.1	2.9	1.0
8d		11.1	2.8	0.9
8e	$40° < \tilde{\varphi} < 63°$(b)	13.3	1.8	0.9
8f	90° (c)	14.2	not detected	

Assuming a $\cos^2\varphi$ variation, $a_X = A_X + B_X \cos^2 \tilde{\varphi}_X$ ($X = N$ or $H_{o,p}$, $\cos^2\tilde{\varphi} = <\cos^2\varphi>$, the average being taken on the internal motions of the molecule) with $\tilde{\varphi} = 0$ for the parent compound **8a** and $\tilde{\varphi} = 90°$ for **8f** (as in **7aA** (25) (i.e. neglecting internal motions), the nitrogen hfs and the aromatic proton hfs (with $0 < a_H < 1G$ for **8f**) yield $\tilde{\varphi}_N = 63°$ and $40° < \tilde{\varphi}_H < 52°$ respectively, suggesting a rather broad estimate, $40° < \tilde{\varphi} \leq 63°$, slightly higher than 37.5° (22c). For these angles, the theoretical estimates (3b) are $2J/k \approx +50K$, much smaller than the values of deduced from the solid state results (2b).

Since the temperature dependence of the esr $|\Delta m| = 2$ line was studied between 77 and 300 K only (26a), we have investigated this variation at lower temperature. Figure 3 shows the esr spectrum of **7e** in a toluene/dimethyl formamide mixture at 160 and 3.6 K.

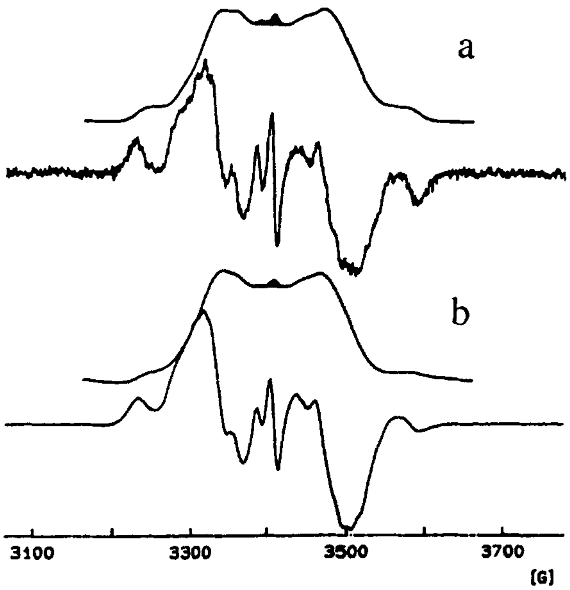


FIGURE 3 : X-Band esr spectrum of biradical **7e** in M/100 toluene/dimethylformanide solution at 160 K (a) and 3.6 K (b). (monoradical signal in black).

Some monoradical signal (in black) is apparent in the central part of the spectrum. The intensity of absorption I_{mono} of the mono biradical could in principle be used as an internal reference to determine the ground state multiplicity of the biradical : since it follows the Curie law ($I_{mono}T$ =Constant), the ratio I_{bi} / I_{mono} is thus proportional to $I_{bi}T$ (I_{bi} refers to the biradical esr absorption). For instance in **7a** (**A** and **B**) the published esr spectra (2a) show that $(I_{bi} / I_{mono})_{100K} > (I_{bi} / I_{mono})_{10K}$ in accord with the quantitative determination a ground-state singlet.

In the case of **7e**, precise integration was not attempted because saturation occurred at low temperature, but qualitatively $(I_{bi} / I_{mono})_{160K} = (I_{bi} / I_{mono})_{3.6K}$: the isolated biradical follows (at least approximatively) Curie law, either as two degenerate doublets ($2|J| / k < 3.6K$) or as a triplet ($2J / k > 160K$, or even $2J / k > 300K$ if the previous results (26a) are taken into account).

More quantative results should be obtained from the intensity I_2 of the $|\Delta m| = 2$ esr line. However, as shown in figure 4, the I_2T / I_{ref} plot versus temperature T (I_{ref} is the signal of a reference sample) is not conclusive within experimental errors : I_2T / I_{ref} is constant, thus confirming the previous results (2a). (Best fit to a Bleaney-Bowers formula give $2J/k = -1K$).

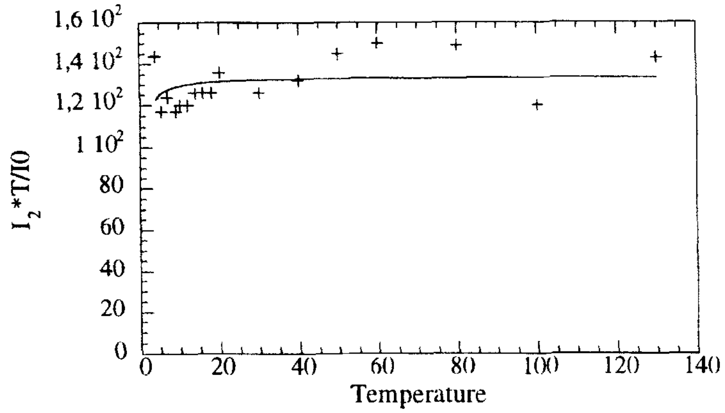


FIGURE 4 : Variation of I_2T / I_0 versus temperature T for a M/50 solution of biradical **7e** in ethanol (I_2 intensity of the $\Delta_m = 2$ esr transition, I_0 reference sample).

Similar results (32) were obtained with another metaphenylenebisnitroxide **7f**, (Table 1). The crystals of **7e** and of **7f** are unstable. Biradical **7g** has been prepared (22c) (33) because the *t*butyl group is expected to prevent the bimolecular decomposition so that stable crystals could be obtained. It was reported (22c) that in the pure solid $2J / k = 840K$. Recently, we have been able to obtain small single crystals suitable for an X-Ray determination. The structure resolution (34) is complicated by some disorder ; preliminary results (R = 0.067) are shown in figure 5. The conformation of the molecule is not symmetrical, $\varphi_1 = 39.35 \pm 1.4°$ and $\varphi_2 = 6.84 \pm 1.5°$ (the incertainties originate from a slight non-planarity of the phenyl ring). The first value is in agreement with other X-Ray data (22c) and of the order of magnitude estimated from an interpretation of the esr data of phenylnitroxides. The smaller value φ_2 is quite unexpected. However, NO groups are strongly polar $[\mu_{NO} = 2.3D\,(35)]$ and the presence of this conformer may be due to intermolecular interactions in the crystal. (An other possibility relating $\varphi = 0$ to the conformer with $2|D| = 280G$ and $\varphi \approx 50°$ to $2|D| = 380G$ is discussed later).

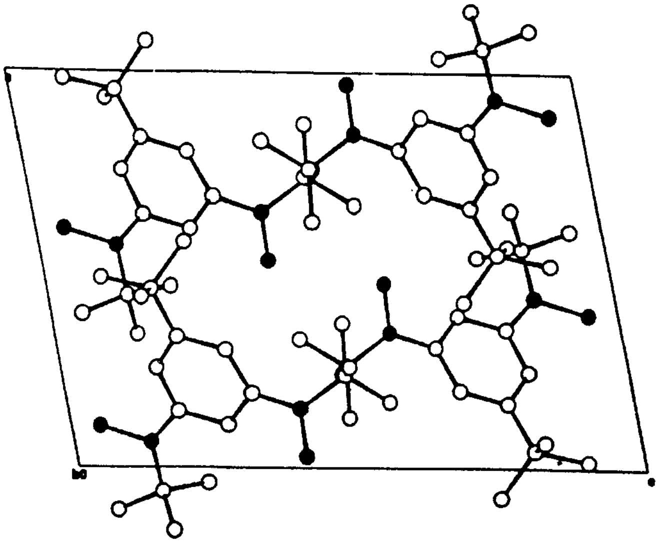


FIGURE 5 : X-Ray structure of biradical **7g** (ref. 34)

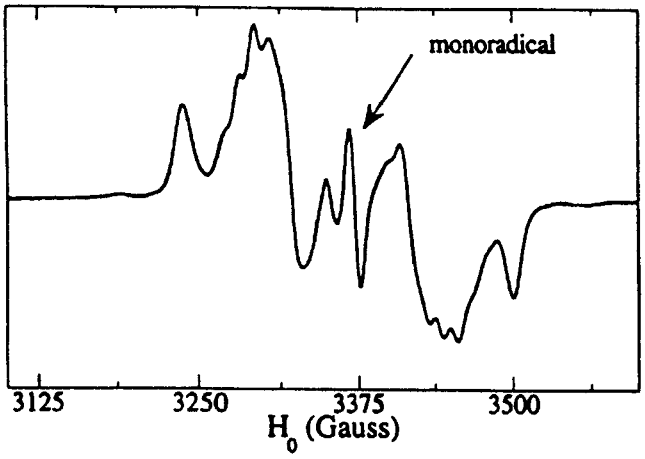


FIGURE 6 : X-Band esr spectrum of biradical **7g** in M/200 ethanol solution at 100 K.

In ethanol solution at 100 K, the frozen esr spectra (figure 6) show the presence of two dipolar interactions $2|D| = 261$ and $386G$, evidence of two different conformations, as was found in biradical **7e**. The variation of the intensity I_2 of the $|\Delta m| = 2$ absorption of frozen M/200 ethanol solutions with temperature between 120 and 4 K may be fitted to the Bleaney-Bowers expression with $2J / k = -12K$ (figure 7), while the paramagnetic

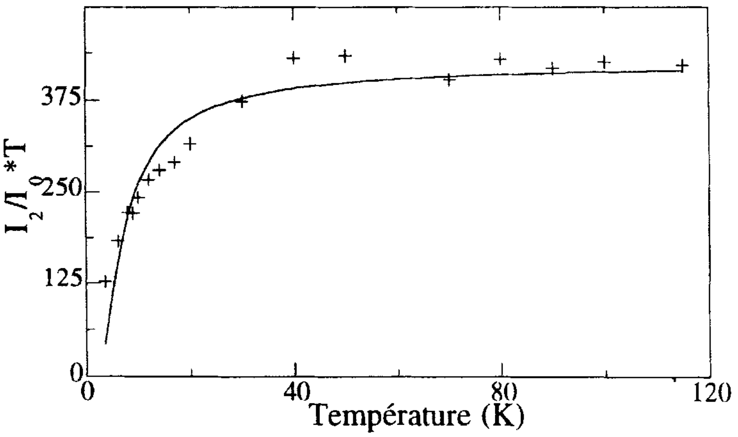


FIGURE 7 : Variation of I_2T / I_0 (arbitrary units) versus temperature for a M/100 solution of biradical **7g** in ethanol (I_2, I_0 as in figure 4).

part of the total static susceptibility $\chi_{dia} + \chi_{para}$ of a M/100 solution in a polycarbonate polymer matrix is smaller at low temperature than the value extrapolated in a χ, 1 / T graph from the high temperature value (figure 8). This small decrease may be due to experimental errors. If taken into account, fit to the Bleaney-Bowers expression gives $2J / k = -1.3K$

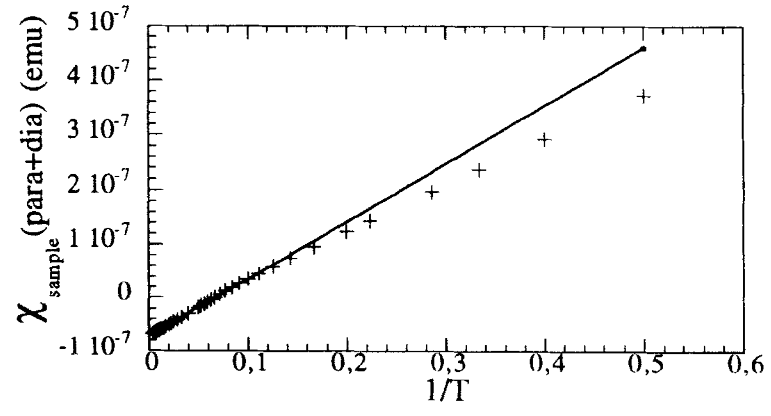


FIGURE 8 : $\chi_{para}T$ (arbitrary units) versus plot of the SQUID results for a M/100 solution of biradical **7g** in a polycarbonate matrix.

corresponding to a ground state singlet. If this small variation is neglected, esr and magnetization results yield $2J / k > 170K$ or $2|J| / k < 25K$.

In pure crystal, the Curie-Weiss plot (figure 9) corresponds to a spin 1 as previously

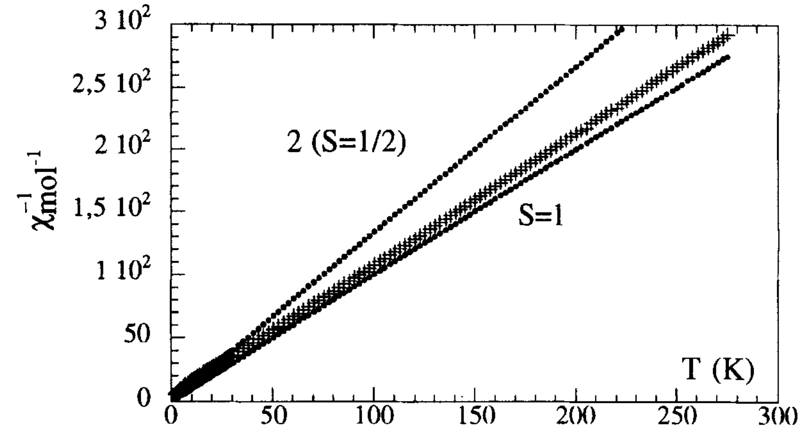
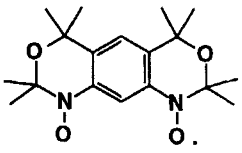


FIGURE 9 : Curie-Weiss plot of the static susceptibility of crystalline sample of biradical **7g**. The dotted lines correspond to an assembly of independent doublets [(S = 1/2) x 2] or of independent triplets (S = 1).

found (22c, 33) in weak antiferromagnetic interaction with its neighbours (C = 0.96 emuKmole^{-1}, $\theta = -5\text{K}$). The solid state results are thus in favour of a ground state triplet. However, this result depends upon the same hypotheses presented before for **7e**. Because the three biradicals **7e, f, g** are conformationally mobile, we have also investigated a biradical **9** expected to be more rigid and planar. It had been prepared more



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than twenty years ago, but at that time, only its esr spectrum was published and discussed (36). An X-Ray structure of its crystals has now been resolved (34). As shown in figure 10, the molecule is nearly planar in the crystal, ($\varphi_1 = \varphi_2 \approx 0$).

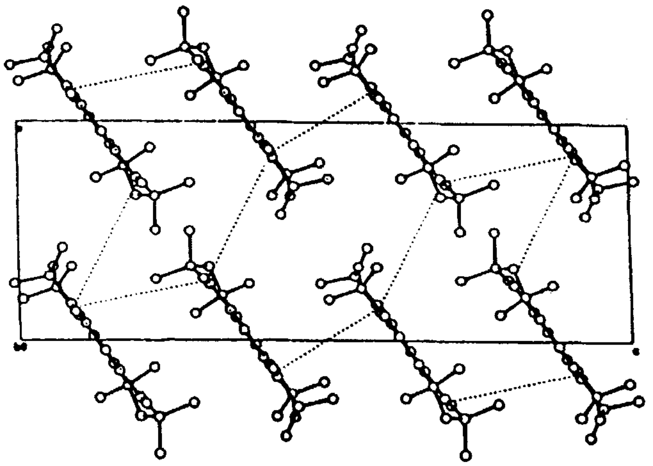


FIGURE 10 : X-Ray structure of biradical **9** (ref. 34)

In frozen solution, the esr spectra show the presence of a single dipolar interaction ($2|D| = 280G$) (36). The corresponding point-dipole value (5.83 Å) of the average distance between the unpaired electrons is larger than expected for the planar conformation where $d_{NN} = 4.79Å \approx d_{OO} = 4.77Å$, $d_{NO} = 4.95Å$ have been found. This had been attributed (36, 37) to non-planar conformations. However although it is reasonable to expect a negative sign for D, this decrease of |D| may be caused by some positive contribution due to a delocalization of the unpaired electrons onto the benzene ring as in photo-excited triplets (38, 39a). Since $2|D| \approx 380G$ was found in biradical **7a** (2a) and **7b** (2b) with large torsion angles and $2|D| \approx 280G$ in planar **9**, this suggests a possibility that the two dipolar interaction observed in **7e**, **7f** and **7g** may correspond to $\varphi \approx 90°$ for the larger one (366 and 386G) and $\varphi \approx 0°$ for the smaller one (262 and 261G).

As before the singlet triplet splitting was studied by two methods : the relative intensity I_2 / I_{ref} of the $|\Delta m| = 2$ transition of a M/50 ethanol is shown in figure 11. Static susceptibility (SQUID) measurements were carried out on a M/100 polycarbonate solution. Figure 12 shows the results.

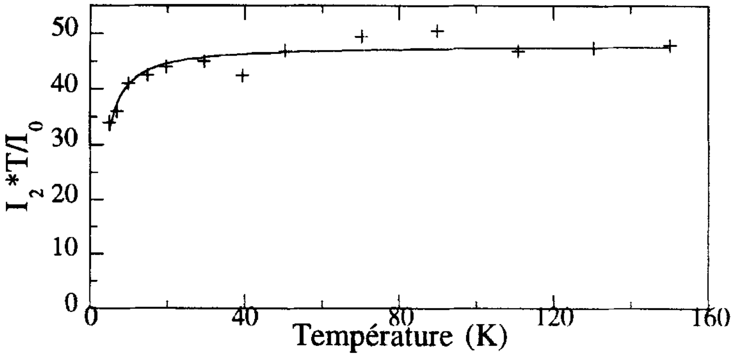


FIGURE 11 : Variation of I_2T / I_0 versus temperature T for a M/50 solution of biradical **9** in ethanol (I_2, I_0 as in figure 4).

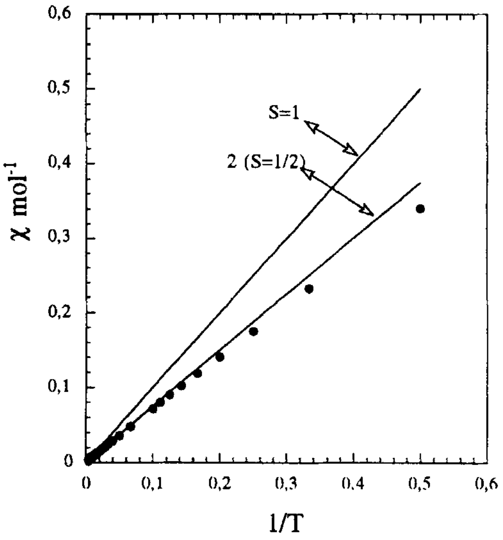


FIGURE 12 : χ_{para} (emu mol^{-1}) versus 1/T plot of the SQUID results for a M/100 solution of biradical **9** in a polycarbonate matrix.

The curvature of χ versus 1/T indicates a singlet ground state, although it may be in the range of the experimental errors. Fit to a Bleaney-Bowers expression gives $2J / k = -5K$ and $-1.1K$ for the esr and SQUID results respectively.

Similar measurements were also made on a crystalline sample (figure 13). Here again, the Curie-Weiss plot ($C = 0.86$ emuKmole^{-1}, $\theta = -0.38$ K) can be interpreted as a spin-one in antiferromagnetic interaction with its neighbours, although the 0.86 value is intermediate between the triplet and the degenerate radical-pair value.

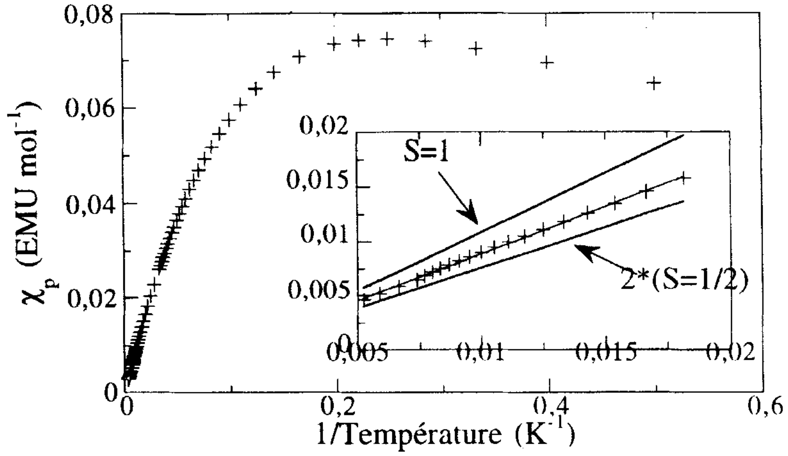


FIGURE 13 : Curie-Weiss plot (χ versus T^{-1})of the static susceptibility of crystalline sample of biradical **9**. Insert : high temperature region.

Discussion

Table 1 summarizes the results obtained for metaphenylene bisnitroxide.

1) Theoretical calculations indicate $2J/k \approx 100$K in the nearly planar case (a) ($0 \leq \varphi \leq 40°$) and $0 \leq -2J/k \leq -20$K in the perpendicular case (b) ($\varphi \approx 90°$).

2) Experimentally, in solution : in the nearly planar case (a), either $2J/k >> 300$K or $2|J|/k < 5$K, a value $2J/k \approx -1$K being possible, but probably beyond the limits of accuracy. In the perpendicular case (b), $2J/k \approx -70$K.

3) Experimentally, the magnetic properties of the pure crystals are in accord with a strongly coupled triplet ($2J/k >> 300$ K) in weak interaction with its neighbours in case (a) and isolated radical pairs with a singlet ground-state in case (b).

The interpretation generally accepted is the following :

For case (a) : the strong positive exchange interaction ($2J/k >> 300$ K) observed in the solid state is the intramolecular one. A Curie law for a spin-one must be chosen as the result of the dilute solution measurements, the other possibility ($2J/k \approx -1$ K) being an experimental artefact. This interpretation is not in accord with the calculations predicting $2J/k \approx 100$ K for this case.

For case (b) : The molecule is a ground state singlet $2J / k \approx -60K$ and behaves as such in the solid state with small negative intermolecular exchange interactions. Calculations predict a smaller value $0 \leq -2J / k \leq 20K$ for this case. There is also a problem with biradical **7b** for which $2J / k = -7K$ in the isolated molecule and $2J / k = -73.8K$ in the solid, the theoretical predictions for a dihydroxy analog (3b) being $-2J / k = 0(\pm 5)K$.

This interpretation rely on an implicit hypothesis, the *transferability* of the intramolecular exchange interaction J (by *definition,* $E_S - E_T = 2J_{Bi}$) :

In an isolated biradical, the isotropic spin "interaction"

$$\mathcal{H}_{\text{spin}} = -2J_{Bi}s(1)s(2)$$

may be used - in esr for instance (39b), (40), (41), (42) - to introduce in an *exact* manner (43) the singlet and triplet levels in a spin hamiltonian $\mathcal{H}_{\text{spin}}$. The situation is even simpler in the Bleaney-Bowers expression for an isolated biradical, where $2J_{Bi}$ is but a symbol for the *exact* energy difference $E_S - E_T$ (see also (44)).

In a crystalline biradical as in any magnetic solid, many model hamiltonians can be used (45) for various types of magnetic phenomena. If for instance, a linear chain model is chosen to reproduce the magnetic properties of a crystal made of biradical molecules k the corresponding Heisenberg hamiltonian $\mathcal{H}$ is

$$\mathcal{H} = -2\sum_{k}\left[J_{\text{intra}}s(2k-1)s(2k) + J_{\text{inter}}s(2k)s(2k+1)\right].$$

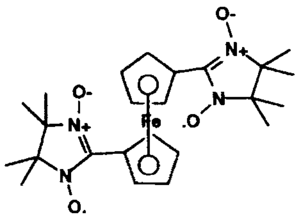
There is transferability if

$$J_{\text{intra}} = J_{Bi}.$$

Is there an evidence of such an equality between an exact value J_{Bi} and a fitting parameter J_{intra} of an approximate (46) hamiltonian ?

Apart from an extreme case where transferability may be verified because interactions between biradicals are comparable to those found in dilute solution, (i.e. $|J_{\text{intra}}| >> |J_{\text{inter}}|$), there may be cases where the magnetic properties of the isolated biradical are strongly perturbed by interactions with its neighbours. (The transformation of an assembly of triplet disulfur S_2 into diamagnetic cyclic S_8 or into a linear polymer can be taken as a very extreme example !).

Experimentally, there have been some reports where $J_{Bi} \approx J_{\text{intra}}$ (2a, 6a, 47) and also where $J_{Bi} \neq J_{\text{intra}}$ (2b, 10a, 48) (Table 3). This raises the question of the transferability of exchange. Similarly, some calculations report a variation of the exchange interaction in n-aggregates of mono radicals as n varies (49, 50).



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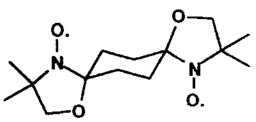

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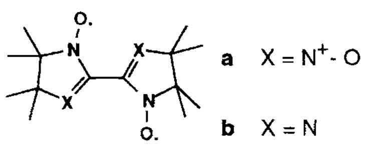

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TABLE 3 : Comparison of the singlet-triplet splitting $2J / k$ (in kelvin) found in solution and in the solid state by fitting to the Bleaney-Bowers expression for various nitroxide biradicals.
(a) ref. 10. (b) ref. 2b. (c) ref. 48. (d) ref. 2a. (e) ref. 32. (f) ref. 47.(g) ref. 6a.

Biradical	(Solution)	Solid state
3a (a)	- 35	- 159
7b (b)	- 7	- 73.8
10 (c)	- 102	- 12
7a A	- 66 (d)	- 64 (e)
7a B	- 81 (d)	- 54 (e)
11 (f)	- 26	- 34
12a (g)	- 422	- 444
12b (g)	- 232	- 277

Some general remarks may also be related to this problem of transferability :

1) When the exchange interactions are calculated in H_2 and equilateral H_3, there is no transferability (51).

2) In the general case of isolated non-symmetrical (of C_1 symmetry or C_s if planar) molecules, made of n monoradicals, the Heisenberg-Dirac spin-hamiltonian $\mathcal{H} = -2\sum_{i<j} J_{ij}s_i s_j$ constructed as in a biradical to reproduce the energy of the $N_E = n! / [(n/2)!]^2 (n \text{ even}) \text{ or } n! / \{[(n+1)/2]!\} (n \text{ odd})$(52) magnetic levels does not exist : it should reproduce the $N_E - 1$ energy splittings with N_J parameters ($N_J = n(n-1)/2$). These two numbers are equal only for $n = 2$. For $n = 3,4$ or 5,

$N_J = N_E + 1$ so that the N_J exchange interaction depend on one arbitrary parameter while for $n \geq 6$, $N_E > N_J$ and there is no possibility to reproduce the $N_E - 1$ energy splittings by the Heisenberg-Dirac spin-hamiltonian (see also 53).

Conclusion :

Going back to metaphenylene bisnitroxides and specially in case (a), it would be important to obtain an accurate determination of the exact value of the singlet-triplet splitting in the isolated molecules (as well as the variation of this splitting with solvation) : comparison of these data with the strong ferromagnetic exchange found in the crystal could solve the transferability problem in these biradicals and settle the discrepancy between calculated and experimental values.

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