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### **Molecular Physics**



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# Evaluation of nuclear quadrupole interactions as a source of magnetic anisotropy in the radical pair model of the avian magnetic compass

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*Running title:* 

Radical pair avian magnetic compass

### Abstract

One of the principal proposed biophysical mechanisms put forward to explain the avian magnetic compass sense centres around magnetically sensitive chemistry. Based a large number of *in vitro* studies of the effects of applied magnetic fields on the yields and rates of chemical reactions, it has been suggested that the anisotropic magnetic interactions in spin-correlated radical pairs could be the source of the directional information that allows migratory birds to use the Earth's magnetic field as a navigational aid. Here we employ numerical quantum mechanical simulations to explore the possibility that the hitherto neglected nuclear quadrupole interaction may provide directional information in a radical pair magnetoreceptor. It is concluded that although nuclear quadrupole interactions could fulfil this function, they are unlikely to influence significantly the reaction yield anisotropy in the flavin-tryptophan radical pair that has been proposed as the *in vivo* magnetoreceptor.

### Keywords:

Cryptochrome; Electron transfer; Flavoprotein; Magnetic field effect; Magnetoreception; Photoreceptor.

### 1. Introduction

Although it has been known for forty years that migratory birds can detect the direction of the geomagnetic field, the biophysical mechanism responsible for this magnetic compass is still poorly understood [1-4]. One of the most promising proposed mechanisms is based on specialised light-dependent chemical reactions whose product yields are magnetically sensitive [5-8]. The idea is that photoinduced radical pair reactions take place in an ordered array of photoreceptor molecules in the eye, and that their anisotropic response to the Earth's magnetic field enables the bird to orient itself during migration.

Almost all previous discussions of anisotropic radical pair magnetic field effects in the context of magnetoreception [5,9-11], including Schulten's original proposal [6], have assumed that the electron-nuclear hyperfine interaction (HFI) is the source of the magnetic anisotropy needed to extract directional information from the geomagnetic field. Two other possibilities are the electron Zeeman interaction with the external field and the magnetic dipole-dipole interaction of the two unpaired electrons, one in each radical. The anisotropy of the former is almost certainly too small to be important for the weak fields involved in magnetoreception. The latter can be much larger, depending on the separation of the radicals, but has the general effect of suppressing rather than promoting sensitivity to applied magnetic fields [12]. The only other plausible source of anisotropy in organic radicals, the nuclear quadrupole interaction (NQI), seems to have been ignored in previous treatments of radical pair magnetic field effects, whether in the context of magnetoreception or not. This is obviously legitimate for radicals devoid of quadrupolar nuclei (those with spin quantum number  $I \ge 1$ , e.g. <sup>14</sup>N). It is also acceptable for molecules tumbling rapidly in solution, where the NQI is usually averaged to zero, but is questionable for the immobilised radicals that are essential for a directional magnetic response, and in particular for biologically relevant free radicals that often contain one or more <sup>14</sup>N atoms.

At first sight, it might seem that the NQI, being a purely nuclear spin interaction, could not affect the electronic spin state of a radical pair or therefore the reaction

product yields. However, if the nucleus also has a hyperfine interaction, the NQI can exert an indirect influence on the electron spin evolution analogous to the electron spin echo envelope modulations (ESEEM) observed for radicals containing quadrupolar nuclei [13]. There are thus good reasons to expect that the NQI should modify the response of a radical pair to an external magnetic field.

Here, we report the use of computer simulations to investigate whether nuclear quadrupole interactions could be a source of suitable directional information in a radical pair compass magnetoreceptor and in particular whether <sup>14</sup>N NQIs are likely to play an important role in the flavin-tryptophan radical pairs that are currently favoured as the magnetically sensitive species [5,11,14].

### 2. Methods

Spin-correlated radical pairs have the potential to be magnetically sensitive because their reactivity is subject to the requirement to conserve spin angular momentum. The singlet (S) and triplet (T) states of the radical pair therefore generally have distinct reaction pathways whose relative yields are determined by the coherent quantum mechanical interconversion of the S and T states that results from a variety of weak (<<  $k_BT$ ) magnetic interactions [15-17]. The influence of an applied magnetic field on a radical pair reaction may be determined by calculating the fraction of pairs that recombine from the S state (the 'singlet yield') as described previously [10,18]:

$$\Phi_{\rm S}(\theta,\phi) = \frac{1}{M} \sum_{n=1}^{4M} \sum_{m=1}^{4M} \frac{k^2}{k^2 + (\omega_n - \omega_m)^2} \left| \left\langle n \right| \hat{P}^{\rm S} \left| m \right\rangle \right|^2 \tag{1}$$

The S and T states were assumed, for simplicity, to recombine at equal rates (first order rate constant k), and M is the total number of nuclear spin configurations.  $|n\rangle$  and  $|m\rangle$  are eigenstates, and  $\omega_n$ ,  $\omega_m$  eigenvalues (expressed as angular frequencies), of the spin Hamiltonian  $\hat{H}$ , all of which depend on the direction of the external magnetic field ( $\theta$ ,  $\phi$ ) with respect to the molecular frame.  $\hat{P}^{s}$  is the singlet projection

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operator. The radical pair was considered to be formed instantaneously in a pure S state and its lifetime (=  $k^{-1}$ ) was 1 µs in all calculations presented here.

The anisotropy of the singlet yield, defined as [10]

$$\Gamma = \frac{\max_{\theta,\phi}[\Phi_{\rm S}] - \min_{\theta,\phi}[\Phi_{\rm S}]}{\max_{\theta,\phi}[\Phi_{\rm S}]} \times 100\%, \qquad (2)$$

was obtained by computing  $\Phi_{\rm S}(\theta, \phi)$  for several thousand combinations of the polar angles  $\theta$  and  $\phi$ . The spherically averaged singlet yield was calculated using a trapezium rule approximation to the integral

$$\langle \Phi_{\rm s} \rangle = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \Phi_{\rm s}(\theta, \phi) \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\phi$$
 (3)

 $\hat{H}$  is the sum of three terms representing the electron Zeeman, electron-nuclear hyperfine and nuclear quadrupole interactions respectively (all expressed here as angular frequencies)

$$\hat{H}_{Z}(\theta,\phi) = \gamma_{e} B_{0} \sum_{i=1}^{2} \left[ \hat{S}_{x}^{(i)} \sin \theta \cos \phi + \hat{S}_{y}^{(i)} \sin \theta \sin \phi + \hat{S}_{z}^{(i)} \cos \theta \right]$$
(4)

$$\hat{H}_{\rm HF} = \sum_{i=1}^{2} \sum_{j=1}^{N} \left[ a^{(i,j)} \hat{\mathbf{S}}^{(i)} \cdot \hat{\mathbf{I}}^{(j)} + \hat{\mathbf{S}}^{(i)} \cdot \mathbf{T}^{(i,j)} \cdot \hat{\mathbf{I}}^{(j)} \right]$$
(5)

$$\hat{H}_{NQ} = \sum_{j=1}^{N} \hat{\mathbf{I}}^{(j)} \cdot \mathbf{Q}^{(j)} \cdot \hat{\mathbf{I}}^{(j)}$$
(6)

where  $\hat{\mathbf{S}}^{(i)}$  (i = 1, 2) and  $\hat{\mathbf{I}}^{(j)}$  (j = 1, ..., N) are, respectively, the electron and nuclear spin angular momentum operators, and  $B_0$  is the strength of the external magnetic field  $(B_0 = 50 \ \mu\text{T}$  in all calculations). The quantities  $a^{(i,j)}$  and  $\mathbf{T}^{(i,j)}$  are respectively the isotropic hyperfine coupling constant and the anisotropic HFI tensor for nucleus *j* in radical *i*. The hyperfine axiality  $\alpha^{(i,j)}$  and rhombicity  $\beta^{(i,j)}$  are defined in terms of  $T_{pp}^{(i,j)}$ , the principal values of  $\mathbf{T}^{(i,j)}$ , as [19]

$$\alpha^{(i,j)} = -\frac{2T_{zz}^{(i,j)} - T_{xx}^{(i,j)} - T_{yy}^{(i,j)}}{6a^{(i,j)}}; \qquad \beta^{(i,j)} = \frac{T_{xx}^{(i,j)} - T_{yy}^{(i,j)}}{T_{zz}^{(i,j)}}$$
(7)

The principal values of the quadrupole coupling tensors are related to the components of the electric field gradient  $(\partial^2 V^{(j)} / \partial p^2)$  by

$$Q_{pp}^{(j)} = \frac{eQ}{2I(2I-1)\hbar} \left(\frac{\partial^2 V^{(j)}}{\partial p^2}\right); \quad p = x, y, z$$
(8)

where Q is the nuclear quadrupole moment (2.044 × 10<sup>-30</sup> m<sup>2</sup> for <sup>14</sup>N [20]) and *I* is the nuclear spin quantum number (I = 1 for <sup>14</sup>N). The components of the nitrogen quadrupole tensors (in millitesla) were obtained from the electric field gradients (in atomic units) using the conversion:  $Q_{pp}^{(j)} = 0.08575 (\partial^2 V^{(j)} / \partial p^2)$ . By convention, the nuclear quadrupolar coupling constant  $\chi^{(j)}$  (= 2 $Q_{zz}^{(j)}$ ) and the asymmetry  $\eta^{(j)}$  are defined as

$$\chi^{(j)} = \frac{eQ}{h} \left( \frac{\partial^2 V^{(j)}}{\partial z^2} \right)$$
(9)

$$\eta^{(j)} = \frac{Q_{xx}^{(j)} - Q_{yy}^{(j)}}{Q_{zz}^{(j)}}$$
(10)

Density functional theory methods were used to determine the interaction tensors for the neutral and cationic tryptophan radicals,  $TrpH^{\bullet+}$  and  $Trp^{\bullet}$ , and the anionic and neutral flavin adenine dinucleotide radicals,  $FAD^{\bullet-}$  and  $FADH^{\bullet}$ . The quadrupolar and hyperfine tensors were calculated *in vacuo* at the GGA/PBE/TZ2P and GIAO UB3LYP/EPR-III levels of theory, using Gaussian 03 [21] and ADF 2006.01 respectively. For the flavin radicals, the sidechain at N10, which carries no significant spin density beyond the first carbon atom, was replaced by methyl (for FAD<sup> $\bullet-$ </sup>) or an ethyl (for FADH<sup> $\bullet$ </sup>) (see Figure 1). In the following, the superscripts *i* and *j* are omitted when it is not necessary to distinguish between the two electron spins or amongst the *N* nuclear spins.

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### 3. Results

The only candidate currently under discussion as a putative chemical magnetoreceptor is cryptochrome, a flavoprotein thought to play host to a photoinduced radical pair comprising the semi-reduced form of the FAD cofactor and a semi-oxidised tryptophan residue, Trp [5,11]. Since the protonation states of these radicals are not clear, we consider both neutral and anionic flavin radicals (FADH<sup>•</sup> and FAD<sup>•-</sup>) and the neutral and cationic Trp radicals (Trp<sup>•</sup> and TrpH<sup>•+</sup>). The sites of (de)protonation are N5 in FADH<sup>•</sup> and N1 in TrpH<sup>•+</sup> (Figure 1).

Table 1 gives the calculated <sup>14</sup>N hyperfine interactions for N1 in TrpH<sup>•+</sup> and Trp<sup>•</sup> and for N5 and N10 in FAD<sup>•-</sup> and FADH<sup>•</sup>. Four features are apparent: (i) all three nitrogens have significant isotropic and anisotropic HFIs irrespective of the protonation state of the radical; (ii) the HFI tensors are all close to axial ( $|\beta| < 0.03$ ); (iii) the axiality,  $\alpha$ , is close to -1; (iv) the *z*-axis of the hyperfine interaction is approximately parallel to the ring normal ( $\zeta_{HF} \approx 0$ ). Graphical representations of the nitrogen HFI tensors are given in the Supplementary Information.

Table 2 summarizes the results of NQI calculations for the same four radicals (see also the Supplementary Information). Four general points are evident: (i) the quadrupole coupling constants ( $\chi^{(j)} = 2Q_{zz}^{(j)}$ ) are smaller than the corresponding HFIs; (ii) the NQIs are approximately axial ( $|\eta| < 0.2$ , except for Trp<sup>•</sup> N1, for which  $\eta = 0.31$ ); (iii) the axis of the NQI interaction is approximately perpendicular to the plane of the ring ( $\zeta_{NQ} \approx 90^\circ$ ) if the nitrogen has a directly bonded substituent (N1 in TrpH<sup>•+</sup>, N5 in FADH<sup>•</sup>, and N10 in both FADH<sup>•</sup> and FAD<sup>•-</sup>); (iv) the axis of the NQI interaction is approximately in the plane of the ring ( $\zeta_{NQ} \approx 0^\circ$ ) if the ring nitrogen has no directly bonded substituent (N1 in Trp<sup>•</sup> and N5 in FAD<sup>•-</sup>). Scant experimental data exist with which to compare these figures. Investigating flavin radicals in flavoproteins, both Martinez *et al.* [22] and Hung *et al.* [23] report  $\chi \approx 3$  MHz for either N1 or N3, and the former estimate  $\chi \approx 5$  MHz for N10. These compare reasonably well with our values of 3.9 MHz for N10 (Table 2), and 3.4 MHz for both N1 and N3, in both FAD<sup>•–</sup> and FADH<sup>•</sup> (Supplementary Information). Martinez *et al.* [22] also find  $\eta = 0.5$  for either N1 or N3; our calculations give  $\eta = 0.72$  and 0.61 for N1 in FAD<sup>•–</sup> and FADH<sup>•</sup> respectively and 0.08 and 0.05 for N3, suggesting, perhaps, that  $\eta = 0.5$  should be assigned to N1 rather than N3.

Before presenting simulations of the reaction yields, we derive some straightforward results directly from Equations (4)-(6) and the form of the singlet projection operator,

$$\hat{P}^{\mathrm{S}} = \frac{1}{4} - \hat{\mathbf{S}}^{(1)} \cdot \hat{\mathbf{S}}^{(2)} \tag{11}$$

It can easily be shown that  $\hat{H}_{NQ}$  commutes with  $\hat{H}_{Z}$  and  $\hat{P}^{S}$  but not, in general, with either part of  $\hat{H}_{HF}$ . As a consequence, a NQI can modify the S  $\leftrightarrow$  T interconversion of the radical pair even though  $\hat{H}_{NQ}$  does not include an electron spin operator provided the quadrupolar nucleus has a hyperfine coupling to one of the electron spins. It is therefore acceptable to ignore the NQIs of N1 and N3 in the FAD radicals and the amide nitrogen in the Trp radicals, as all three have small HFIs ( $|a^{(i,j)}|$  and  $|A_{pp}^{(i,j)}| < 0.1 \text{ mT}$ ).

A special case arises when the HFI and NQI tensors are both axial ( $\beta = \eta = 0$ ), with collinear axes, and  $\alpha = -1$ . Under these conditions,

$$\hat{H}_{\rm HF} = 3a\hat{S}_z^{(1)}\hat{I}_z$$
 and  $\hat{H}_{\rm NQ} = \frac{1}{2}Q_{zz}[3\hat{I}_z^2 - \hat{I}^2]$  (12)

with the consequence that the commutator  $[\hat{H}_{NQ}, \hat{H}_{HF}]$  vanishes and the singlet yield becomes independent of  $\hat{H}_{NQ}$ .

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In the light of this last conclusion and the data in Tables 1 and 2, we consider the effect of a NQI on the anisotropic singlet yield of a radical pair containing one I = 1 nuclear spin. Figure 2 shows how the reaction yield anisotropy  $\Gamma$  varies with the axiality of the HFI for three values of  $\chi$  and three relative orientations of the axial NQI and HFI tensors. Two important features may be discerned: (i) when  $\alpha = -1$ , the NQI has no effect at all when the HFI and NQI axes are parallel (as predicted above), only a small effect when they are perpendicular, and a large effect when they are at 45° to one another; (ii) Except for the 45° case,  $\Gamma$  does not change much in the range  $-1.25 < \alpha < -0.75$ , especially when a NQI is present, and in particular when the HFI and NQI axes are collinear.

The conditions for  $\Gamma$  to depend weakly on the strength of the NQI ( $\alpha \approx -1$ ,  $\beta \approx 0$ ,  $\eta \approx 0$ , and  $\Delta \zeta \equiv \left| \zeta_{NQ} - \zeta_{HF} \right| \approx 0$  or 90°) are satisfied rather well by the FAD and Trp radicals (Tables 1 and 2). Given that, in addition, the NQIs in the FAD and Trp radicals are weaker than the corresponding HFIs, it seems reasonable to anticipate that NQIs may make a minimal contribution to the anisotropic magnetic response of a cryptochrome-derived radical pair.

This conclusion is supported by simulations of two types of radical pair: (a) model systems of the type  $[X^{\bullet}Z^{\bullet}]$ , in which  $X^{\bullet}$  is one of TrpH<sup>•+</sup>, Trp<sup>•</sup>, FAD<sup>•-</sup> and FADH<sup>•</sup>, and Z<sup>•</sup> is a radical with no magnetic nuclei, and (b) the neutral and ionic species,  $[FADH^{\bullet} Trp^{\bullet}]$  and  $[FAD^{\bullet-} TrpH^{\bullet+}]$ . Values of  $\Gamma$ , computed using the hyperfine and nuclear quadrupole tensors in Tables 1 and 2 and the Supplementary Information, are presented in Table 3 for radical pairs containing N1 in TrpH<sup>•+</sup> and Trp<sup>•</sup> and N5 and N10 in FAD<sup>•-</sup> and FADH<sup>•</sup>. It is plain that the effects of the NQIs are indeed rather small.

Although  $\Gamma$  is a useful measure of the size of the anisotropic magnetic field effect, it gives no information on the dependence of  $\Phi_s$  on the direction of the magnetic field with respect to the molecular frame. Figure 3 shows  $\Phi_s(\theta, \phi) - \langle \Phi_s \rangle$ , the anisotropic part of the singlet yield, for two values of  $\alpha$  for a one-nucleus radical pair. When  $\alpha =$ 

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-1.2, a modest axial NQI has almost no effect on the orientation dependence of the singlet yield whether the NQI axis is parallel or perpendicular to the HFI axis. Moreover, a small NQI rhombicity, comparable to that of N1 in Trp<sup>•</sup> ( $\eta = 0.3$ ), also has little effect. In contrast, the response is much more sensitive to both  $\chi$  and  $\eta$  and the relative orientation of the two interactions when  $\alpha = +1.2$ . These effects are clearly consistent with the changes in  $\Gamma$  shown in Figures 2(a) and (c).

To explore more comprehensively the anisotropic effects of NQIs, we have adopted the Monte-Carlo approach used in a previous study [10]. Values of  $\Gamma$  were calculated for an ensemble of ~10<sup>6</sup> two-nitrogen radical pairs, with and without NQIs, with randomly chosen values of the hyperfine and quadrupolar parameters in the ranges:  $-1 \text{ mT} < a^{(i,j)} < 1 \text{ mT}; -3 < \alpha^{(i,j)} < 3; -1.63 \text{ mT} < \chi^{(j)} < 1.63 \text{ mT}.$  The relative orientations of the two radicals were also selected at random. The other parameters had fixed values:  $B_0 = 50 \mu \text{T}$ ,  $k = 10^6 \text{ s}^{-1}$ ,  $\beta^{(i,j)} = \eta^{(j)} = 0$ ,  $\Delta \zeta^{(i,j)} = 0$  or 90°. The results, in Figure 4, show that the addition of NQIs leads to fairly minor changes in the distribution of  $\Gamma$  values whether the nuclei are in the same radical or in different radicals. In the former case, the NQI produces a small shift of the distribution towards higher values of  $\Gamma$ , as can also be seen from the percentages of radical pairs (quoted in Figure 4) that have  $\Gamma > 10\%$ . As noted previously [10], the reaction yield anisotropy is generally larger when both nuclei are in the same radical (top row of Figure 4). Similar behaviour may be seen in the data summarized in Table 3 (compare rows 1-4 with rows 5 and 6).

### 4. Discussion



The simulations presented above strongly suggest that NQIs are unimportant for the anisotropic magnetic responses of the FAD-Trp radical pairs that have been proposed as the primary magnetoreceptor responsible for the avian compass sense. The outcomes of previous simulations, all of which ignored or neglected NQIs, therefore remain valid. As demonstrated above, this conclusion stems partly from the property of isoalloxazine and indole radicals that the NQI and HFI tensors of each of the ring

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nitrogen atoms are approximately axial, with axes that are either parallel or perpendicular to one another, and partly from the relative weakness of the quadrupolar interactions.

Although not relevant to flavin-tryptophan radical pairs, it is interesting to consider the reaction yield anisotropy of a radical pair in which the effects of NQIs dominate those of HFIs. One aspect of the radical pair model of magnetoreception about which one can only speculate at the moment is the optimal form of  $\Phi_s(\theta,\phi) - \langle \Phi_s \rangle$ . A reasonable assumption would be that a large and simple orientation-dependence would provide the clearest indication to the bird of the direction of the Earth's field. In mathematical terms, an anisotropic response describable in terms of a small number of low-order spherical harmonics might thus be favoured over a more convoluted pattern. At first sight, these arguably desirable properties might be thought incompatible with most biologically plausible radicals, which are likely to contain many magnetic nuclei with differently oriented hyperfine interactions whose anisotropic effects would tend to cancel one another, resulting in a rather weak and complex orientation-dependence of the product yield. Since most organic radicals contain many fewer quadrupolar nuclei than  $I = \frac{1}{2}$  nuclei (e.g. <sup>1</sup>H), there is the possibility that were the response to the magnetic field to be dominated by NQIs, the resulting anisotropy could be stronger and simpler. Although we have not explored this in great detail, it does indeed seem to be the case if the nuclear quadrupole interactions are larger than the hyperfine interactions.

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### References

- [1] H. Mouritsen and T. Ritz, Curr. Opin. Neurobiol. 15, 406 (2005).
- [2] W. Wiltschko and R. Wiltschko, J. Comp. Physiol. A **191**, 675 (2005).
- [3] R. Wiltschko and W. Wiltschko, Bioessays 28, 157 (2006).
- [4] S. Johnsen and K.J. Lohmann, Phys. Today **61**, 29 (2008).
- [5] T. Ritz, S. Adem, and K. Schulten, Biophys. J. **78**, 707 (2000).
- [6] K. Schulten, C.E. Swenberg, and A. Weller, Z. Phys. Chem. NF 111, 1 (1978).
- K. Schulten and A. Windemuth, *Biophysical Effects of Steady Magnetic Fields*. (Springer, Berlin, 1986), p. 99.
- [8] C.T. Rodgers and P.J. Hore, Proc. Natl. Acad. Sci. USA 106, 353 (2009).
- [9] F. Cintolesi, T. Ritz, C.W.M. Kay, *et al.*, Chem. Phys. **294**, 385 (2003).
- [10] O. Efimova and P.J. Hore, Biophys. J. 94, 1565 (2008).
- [11] I.A. Solov'yov, D.E. Chandler, and K. Schulten, Biophys. J. 92, 2711 (2007).
- [12] A.R. O'Dea, A.F. Curtis, N.J.B. Green, *et al.*, J. Phys. Chem. A **109**, 869 (2005).
- [13] A. Schweiger and G. Jeschke, *Principles of pulse electron paramagnetic resonance* (Oxford University Press, New York, 2001).
- [14] T. Ritz, R. Wiltschko, P.J. Hore, et al., Biophys. J. in press. (2008).
- [15] U.E. Steiner and T. Ulrich, Chem. Rev. **89**, 51 (1989).
- [16] C.R. Timmel and K.B. Henbest, Phil. Trans. Roy. Soc. London, A 362, 2573 (2004).
- [17] B. Brocklehurst, Chem. Soc. Rev. **31**, 301 (2002).
- [18] C.R. Timmel, U. Till, B. Brocklehurst, et al., Mol. Phys. 95, 71 (1998).
- [19] C.R. Timmel, F. Cintolesi, B. Brocklehurst, *et al.*, Chem. Phys. Lett. **334**, 387 (2001).
- [20] P. Pyykkö, Mol. Phys. **106**, 1965 (2008).
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, *et al.*, Gaussian 03. Gaussian, Inc., Wallingford, CT, 2004.
- [22] J.I. Martinez, P.J. Alonso, C. Gomez-Moreno, *et al.*, Biochemistry **36**, 15526 (1997).
- [23] S.C. Hung, C.V. Grant, J.M. Peloquin, *et al.*, J. Biol. Inorg. Chem. 5, 593 (2000).

[24]	C.A. Brautigam, B.S. Smith, Z. Ma, et al., Proc. Natl. Acad. Sci. USA 101,
	12142 (2004).

		<i>a</i> / mT	$T_{xx}$ / mT	$T_{yy}$ / mT	$T_{zz}$ / mT	α	β	$\zeta_{ m HF}/ m deg^{(a)}$
TrpH <sup>•+</sup>	N1	0.322	-0.375	-0.385	0.760	-1.18	0.014	2.1
Trp•	N1	0.371	-0.472	-0.475	0.946	-1.27	0.003	1.0
	N5	0.523	-0.623	-0.610	1.234	-1.18	-0.011	0.0
FAD	N10	0.189	-0.213	-0.203	0.416	-1.10	-0.023	0.0
FADH•	N5	0.431	-0.520	-0.526	1.045	-1.21	0.006	0.0
	N10	0.251	-0.241	-0.255	0.496	-0.99	0.027	2.3

**TABLE 1.** <sup>14</sup>N hyperfine interaction parameters of FAD and tryptophan radicals.

 $^{(a)}\zeta_{\rm HF}$  is the angle between the *z*-axis of the HFI tensor and the normal to the plane of the aromatic part of the radical.

**TABLE 2.** <sup>14</sup>N nuclear quadrupole interaction parameters of FAD and tryptophan radicals.

		$Q_{xx}$ / mT	$Q_{yy}$ / mT	$Q_{zz}$ / mT	η	$\zeta_{\rm NQ}/{\rm deg}^{(\rm a)}$
TrpH <sup>•+</sup>	N1	0.016	0.020	-0.036	0.100	2.9
Trp•	N1	0.028	0.054	-0.082	0.310	89.9
EAD*-	N5	0.031	0.041	-0.072	0.135	90.0
TAD	N10	0.032	0.041	-0.072	0.121	0.0
FADH•	N5	0.022	0.031	-0.053	0.186	0.0
	N10	0.031	0.038	-0.069	0.095	3.4

<sup>(a)</sup> $\zeta_{NQ}$  is the angle between the *z*-axis of the NQI tensor and the normal to the plane of the aromatic part of the radical.



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	$\Gamma(\chi=0) / \%^{(a)}$	Γ/%
[ Trp• Z• ]	24.0	24.1
[TrpH <sup>•+</sup> Z <sup>•</sup> ]	24.4	24.5
[FADH• Z•]	33.5	34.4
[FAD•- Z•]	38.1	37.7
[FADH• Trp•] <sup>(b)</sup>	17.1	20.1
[FAD <sup>•–</sup> TrpH <sup>•+</sup> ] <sup>(t</sup>	<sup>o)</sup> 19.1	19.3

Singlet yield anisotropies for FAD/tryptophan radical pairs. TABLE 3.

<sup>(a)</sup> $\Gamma(\chi = 0)$  is the value of  $\Gamma$  when the strength of all quadrupolar interactions are set to zero.

<sup>(b)</sup>The relative orientations of the two radicals were as for the FAD cofactor and Trp-324 in the photolyase homology domain of cryptochrome-1 from Arabidopsis thaliana [24].



### **Figure Captions**

**FIGURE 1.** Structures of the neutral Trp<sup>•</sup> (tryptophan, left) and FADH<sup>•</sup> (right) radicals showing the numbering schemes for the ring nitrogen atoms.

**FIGURE 2**. The anisotropy of the singlet recombination yield  $\Gamma$  for a radical pair containing a spin-1 nucleus as a function of the axiality of the hyperfine interaction,  $\alpha$ . Both hyperfine and quadrupole tensors are axial ( $\beta = \eta = 0$ ) with their axes (a) parallel, (b) at 45°, and (c) perpendicular to one another. The values of the nuclear quadrupole coupling constants are as indicated. Other parameter values: a = 1 mT,  $B_0 = 50 \text{ }\mu\text{T}$ ,  $k = 10^6 \text{ s}^{-1}$ . The 'spikes' (e.g. at  $\alpha \approx 0$  and  $\alpha \approx 2$  when  $\chi = 0$ ) arise from avoided crossings of the electron-nuclear energy levels [19].

**FIGURE 3.** Anisotropic parts of the singlet yield,  $\Phi_s^{aniso} = \Phi_s - \langle \Phi_s \rangle$ , for a radical pair containing a spin-1 quadrupolar nucleus. These representations were constructed by plotting a point, for each direction of the applied magnetic field, at a distance from the origin proportional to the absolute value of  $\Phi_s^{aniso}$ . The surface colour is a spectrum in which the maximum (i.e. most positive)  $\Phi_s^{aniso}$  is white and the minimum (i.e. most negative)  $\Phi_s^{aniso}$  is red. Parameter values: a = 0.5 mT,  $\beta = 0$ ,  $B_0 = 50 \text{ }\mu\text{T}$ ,  $k = 10^6 \text{ s}^{-1}$ . Other parameter values are as indicated.

**FIGURE 4.** Histograms of the singlet yield anisotropy  $\Gamma$  for an ensemble of ~10<sup>6</sup> radical pairs containing two nitrogen atoms. The two nuclear spins are either in the same radical (top row) or one in each radical (bottom row). The NQI is zero in the left-most column (a, e); in the remaining panels, the NQI and HFI axes are either parallel for both radicals (b, f); parallel for one radical and perpendicular for the other (c, g); or perpendicular for both (d, h). The figure in the top right corner of each panel is the percentage of radical pairs for which  $\Gamma > 10\%$ . In each histogram, the number of  $\Gamma$  bins was equal to the square root of the number of radical pairs in the ensemble.

# Evaluation of nuclear quadrupole interactions as a source of magnetic anisotropy in the radical pair model of the avian magnetic compass

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# SUPPLEMENTARY INFORMATION

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### **Molecular Physics**

	Supplementary Table 1.	<sup>14</sup> N hyperfine tensors of FAD and tryptophan radicals.
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		<i>a</i> / mT	$T_{pp}$ / mT	E	igenvectors	
			-0.375	0.9173	-0.3466	-0.1963
TrpH <sup>•+</sup>	N1	0.322	-0.385	0.3221	0.9353	-0.1463
			0.760	0.2343	0.0710	0.9696
			-0.472	0.9559	-0.0502	-0.2895
Trp•	N1	0.371	-0.475	0.0326	0.9973	-0.0654
			0.946	0.2920	0.0531	0.9549
			-0.623	0.9518	-0.3068	0.0000
FAD•⁻ –	N5	0.523	-0.610	0.3068	0.9518	0.0000
			1.234	0.0000	0.0000	1.0000
			-0.213	0.6845	0.7291	0.0000
	N10	0.189	-0.203	0.7291	-0.6845	0.0000
			0.416	0.0000	0.0000	1.0000
FADH <sup>•</sup> -			-0.520	0.7911	0.6094	-0.0525
	N5	0.431	-0.526	-0.6117	0.7879	-0.0713
			1.045	-0.0021	0.0885	0.9961
			-0.241	-0.2756	0.9534	-0.1225
	N10	0.251	-0.255	0.9613	0.2732	-0.0364
			0.496	0.0012	0.1278	0.9918



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**Supplementary Table 2.** <sup>14</sup>N nuclear quadrupole tensors of FAD and tryptophan radicals.

		$Q_{pp}$ / mT	E	Eigenvectors	
		0.016	0.081	-0.856	-0.511
TrpH <sup>•+</sup>	N1	0.020	0.970	-0.050	0.238
		-0.036	0.229	0.515	-0.826
		0.028	-0.747	0.662	0.064
Trp•	N1	0.054	-0.141	-0.253	0.957
		-0.082	0.650	0.706	0.282
		0.031	-0.507	0.000	0.862
	N5	0.041	0.000	1.000	0.000
FAD•-		-0.072	0.862	0.000	0.507
FAD -		0.032	0.000	0.869	-0.495
	N10	0.041	1.000	0.000	0.000
		-0.072	0.000	0.495	0.869
		0.022	0.083	-0.968	-0.238
FADH' _	N5	0.031	0.997	0.080	0.023
		-0.053	-0.004	-0.239	0.971
		0.031	0.149	-0.910	0.387
	N10	0.038	0.989	0.136	-0.061
		-0.069	0.003	0.392	0.920

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### **Molecular Physics**

**Supplementary Table 3.** Additional <sup>14</sup>N nuclear quadrupole interaction parameters of FAD radicals.

		$\eta$	$Q_{pp}$ / mT	Ei	genvectors	
			0.008	0.000	0.000	1.000
	N1	0.724	0.050	0.555	0.832	0.000
FAD•-			-0.058	0.832	-0.555	0.000
TAD			0.028	0.997	0.073	0.000
	N3	0.082	0.033	-0.073	0.997	0.000
			-0.061	0.000	0.000	1.000
			0.012	-0.032	0.083	0.996
FADH• -	N1	0.613	0.050	0.999	-0.017	0.033
			-0.062	-0.019	-0.996	0.083
			0.028	0.911	-0.409	0.054
	N3	0.050	0.031	-0.413	-0.908	0.077
			-0.060	-0.017	0.093	0.996



**Supplementary Figure 1.** Representations of the HFI and NQI tensors of nitrogen nuclei in FAD (N5 and N10) and tryptophan (N1) radicals. See Fig. 1 for the atom numbering scheme. These ellipsoid plots were generated as described in Kuprov *et al. J. Amer. Chem. Soc.*, **129** (2007) 9004-9013.



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