Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information to: Theoretical analysis of the solvent effects on the magnetic exchange coupling in bis-nitroxides

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1 Structures

The following coordinates are given in Å.

2IN-W0

C	0.079268	0.036911	0.083138
C	0.015650	-0.073673	1.443613
C	2.140799	-0.053382	1.025111
N	1.435095	0.052982	-0.219448
H	-0.657761	0.105748	-0.699934
H	-0.869075	-0.118685	2.063209
C	3.566952	-0.075183	1.179630
C	4.500079	-0.002004	0.198299
O	1.946809	0.144367	-1.378797
N	1.279972	-0.129119	2.014531
C	8.120635	-0.011647	0.022753
C	7.876943	-0.116125	1.366186
H	9.016428	0.029748	-0.574329
H	8.603044	-0.183993	2.164380
N	6.518148	-0.129925	1.647482
C	5.904890	-0.034221	0.491758
N	6.866425	0.043194	-0.566379
O	6.593898	0.142790	-1.802893
H	3.886761	-0.161178	2.214060
H	4.224778	0.084786	-0.845483

2IN-W1a

C	-0.044955	0.001282	-0.054271
C	-0.122090	0.005572	1.308697
C	2.010174	-0.009680	0.911171
N	1.315176	-0.007759	-0.344291
H	-0.773348	0.002306	-0.848506
H	-1.011687	0.012384	1.922717
C	3.436145	-0.016021	1.087385
C	4.363388	0.002751	0.094641
O	1.832048	-0.014125	-1.504822
N	1.138106	-0.000660	1.893155
C	7.969998	0.003934	-0.237900
C	7.799427	0.015483	1.119813
H	8.833668	-0.001866	-0.881575
H	8.564850	0.020820	1.882889
N	6.457565	0.019292	1.467886
C	5.775747	0.006353	0.341429
N	6.688000	-0.000834	-0.762834
O	6.354588	-0.009270	-1.987827
H	3.741744	-0.042673	2.134066
H	4.073250	0.015065	-0.948931
O	4.996376	-0.066896	3.992887
H	5.625773	-0.066358	3.245667
H	4.890945	0.868816	4.206099

2IN-W1b

C	-0.074614	-0.152465	-0.065872
C	-0.111015	-0.158846	1.300683
C	2.002300	-0.048774	0.840628
N	1.272389	-0.082721	-0.395377
H	-0.825989	-0.188512	-0.837375
H	-0.982700	-0.205503	1.938588
C	3.428896	0.024165	0.967507
C	4.341464	0.073540	-0.035045
O	1.759954	-0.054097	-1.568421
N	1.161640	-0.094803	1.849944
C	7.952927	0.261113	-0.292975
C	7.740683	0.246348	1.059089
H	8.849830	0.308560	-0.886862
H	8.494020	0.282183	1.832516
N	6.389214	0.175814	1.373732
C	5.750442	0.145356	0.228142
N	6.687172	0.196489	-0.854451
O	6.382445	0.183158	-2.088291
H	3.769432	0.039124	1.998740
H	4.044477	0.060740	-1.076534
O	10.996334	0.423591	0.300142
H	11.624957	-0.303700	0.387613
H	11.540088	1.219471	0.353783

2IN-W1c

C	-0.047460	0.115155	-0.185706
C	-0.045304	-0.138281	1.156798
C	2.057878	-0.012560	0.652027
N	1.291283	0.209924	-0.542827
H	-0.821880	0.251647	-0.922442
H	-0.898600	-0.277599	1.805633
C	3.490728	-0.011336	0.738831
C	4.366485	-0.031822	-0.296692
O	1.740500	0.508112	-1.692784
N	1.245763	-0.208432	1.664407
C	7.978138	0.050119	-0.647114
C	7.795591	0.004463	0.710369
H	8.845998	0.089614	-1.284192
H	8.557676	-0.006039	1.477245
N	6.452246	-0.032146	1.052071
C	5.784454	-0.016207	-0.076088
N	6.702349	0.039057	-1.182430
O	6.392260	0.098734	-2.414016
H	3.864648	-0.012806	1.758582
H	4.031905	-0.108252	-1.323484
O	3.750087	-0.970488	-3.464081
H	3.101189	-0.256551	-3.416994
H	4.606097	-0.521804	-3.404672

2IN-W1d

C	-0.004905	0.045932	-0.034877
C	-0.037231	-0.058680	1.326507
C	2.078655	-0.023983	0.859623
N	1.344642	0.070810	-0.368268
H	-0.759522	0.105203	-0.801875
H	-0.906818	-0.107565	1.966756
C	3.508107	-0.034535	0.982143
C	4.417396	0.039374	-0.022339
O	1.828451	0.161797	-1.539558
N	1.241072	-0.100855	1.868607
C	8.034882	0.055096	-0.296592
C	7.821858	-0.044892	1.055515
H	8.903950	0.098325	-0.937075
H	8.569845	-0.104271	1.833938
N	6.471263	-0.066037	1.375715
C	5.827197	0.018442	0.237736
N	6.767179	0.097197	-0.847100
O	6.446631	0.189159	-2.077382
H	3.852681	-0.112056	2.009205
H	4.114412	0.116393	-1.059086
O	9.162473	0.316301	-3.202651
H	9.279801	1.243345	-3.445267
H	8.198803	0.215485	-3.128504

2IN-W2a

N	0.010125	0.037493	0.023989
C	-0.002988	0.030908	1.409397
C	1.315514	-0.017309	1.775142
N	2.162180	-0.041424	0.674320
C	1.384612	-0.008712	-0.382197
C	1.727339	-0.013624	-1.775552
C	3.017366	-0.056722	-2.193640
C	3.495379	-0.066637	-3.545758
N	2.675641	-0.032010	-4.724963
C	3.534849	-0.056646	-5.814717
C	4.791622	-0.103352	-5.280756
N	4.762594	-0.109329	-3.891562
O	1.405617	0.012503	-4.764291
O	-0.986228	0.076505	-0.764318
O	-0.740597	0.040661	4.441820
H	3.172590	-0.039251	-6.828547
H	5.723629	-0.133394	-5.825639
H	-0.914174	0.059870	1.982276
H	1.705787	-0.036226	2.782424
H	3.813992	-0.088372	-1.455910
H	0.902781	0.018865	-2.476956
H	-0.997692	0.811507	4.962761
H	-1.052820	-0.713143	4.957550
O	5.065950	-0.131787	-8.537142
H	5.314225	0.602104	-9.112809
H	5.246585	-0.921289	-9.062189

2IN-W2b

C	0.524880	0.226441	-0.916810
C	0.197259	-0.150078	0.356943
C	2.361668	-0.111812	0.384373
N	1.911850	0.261170	-0.930569
H	-0.021114	0.476739	-1.816936
H	-0.792640	-0.290228	0.768138
C	3.728162	-0.206868	0.807717
C	4.838284	0.030786	0.065123
O	2.655325	0.565791	-1.919709
N	1.322401	-0.355886	1.147043
C	8.420991	-0.054760	0.607441
C	7.916218	-0.419189	1.826921
H	9.417000	0.078353	0.218987
H	8.469550	-0.667941	2.721835
N	6.528621	-0.447187	1.826775
C	6.156444	-0.102990	0.616670
N	7.308302	0.155575	-0.193475
O	7.286389	0.509184	-1.413167
H	3.836417	-0.505996	1.846226
H	4.776434	0.330802	-0.973479
O	0.463355	1.027998	-3.916317
H	1.351089	1.011898	-3.526669
H	0.436455	0.242468	-4.491233
O	0.274280	-0.674364	-6.188811
H	0.503429	0.166895	-6.607288
H	-0.682674	-0.741668	-6.307607

2IN-W2c

C	0.120580	-0.070325	0.086718
C	0.177888	0.009757	1.448759
C	2.259259	-0.059349	0.850073
N	1.443216	-0.109856	-0.332778
H	-0.702942	-0.091138	-0.606978
H	-0.658131	0.059726	2.130706
C	3.693789	-0.083064	0.879613
C	4.524641	-0.370633	-0.153831
O	1.849497	-0.117627	-1.536991
N	1.489746	0.023543	1.910299
C	8.113927	-0.478140	-0.662917
C	7.995249	-0.203527	0.675514
H	8.951368	-0.612059	-1.327206
H	8.793613	-0.059243	1.390384
N	6.670772	-0.120642	1.073423
C	5.949884	-0.346070	0.000764
N	6.815148	-0.574807	-1.126719
O	6.446268	-0.791218	-2.324395
H	4.111942	0.143329	1.856219
H	4.144027	-0.672396	-1.120663
O	3.747260	-2.011737	-3.016912
H	3.101469	-1.293646	-3.040325
H	4.604783	-1.565497	-3.072378
O	-2.960768	-0.095663	0.353408
H	-3.617295	0.602132	0.236039
H	-3.473225	-0.913477	0.335343

2IN-W2d

C	-0.041553	-0.011854	-0.076483
C	-0.036980	0.074831	1.285822
C	2.068262	0.027689	0.764675
N	1.298108	-0.035983	-0.446995
H	-0.816615	-0.044924	-0.824498
H	-0.888016	0.117734	1.950803
C	3.502813	0.017122	0.852092
C	4.350950	-0.299549	-0.162088
O	1.741974	-0.034258	-1.637039
N	1.256483	0.106934	1.792759
C	7.928058	-0.485596	-0.717662
C	7.847452	-0.112070	0.598264
H	8.748031	-0.681444	-1.388140
H	8.662699	0.071272	1.283912
N	6.533855	0.019976	1.013988
C	5.776175	-0.274818	-0.021965
N	6.618517	-0.595699	-1.143393
O	6.222279	-0.895125	-2.313393
H	3.882477	0.267962	1.843517
H	3.977332	-0.636580	-1.120582
O	3.514386	-2.164716	-2.852145
H	2.906016	-1.437856	-3.038076
H	4.393020	-1.775122	-2.968094
O	5.259901	0.754498	3.538938
H	5.221896	1.716683	3.468975
H	5.832503	0.489226	2.793623

2IN-W2e

C	3.814949	-0.026284	-0.468911
C	3.987642	-1.250571	0.109215
C	1.837811	-1.060349	-0.073319
N	2.442662	0.122102	-0.612655
H	4.486958	0.747524	-0.801200
H	4.916710	-1.730505	0.382345
C	0.428209	-1.314560	0.008016
C	-0.550004	-0.390977	-0.162140
O	1.853310	1.093900	-1.176091
N	2.771092	-1.884484	0.338096
C	-4.161017	-0.251086	-0.048729
C	-3.894361	-1.581337	0.174804
H	-5.067988	0.326351	-0.115732
H	-4.610884	-2.374004	0.341328
N	-2.537448	-1.849436	0.170447
C	-1.940071	-0.702074	-0.051208
N	-2.925880	0.342048	-0.196098
O	-2.685310	1.571623	-0.423726
H	0.173351	-2.337570	0.268009
H	-0.299336	0.639802	-0.357621
O	-0.132543	3.092337	0.061326
H	0.420634	2.851591	-0.694958
H	-0.997752	2.693088	-0.128495
O	1.425515	1.487916	1.819636
H	1.027702	1.438891	2.696582
H	0.870901	2.130433	1.335697

2IN-W2f

C	0.040761	-0.000142	-0.062334
C	0.021000	-0.034612	1.310371
C	2.129889	-0.016335	0.846093
N	1.382068	0.011472	-0.390639
H	-0.739741	0.012957	-0.821332
H	-0.850444	-0.055097	1.949981
C	3.557144	-0.014549	0.962494
C	4.468352	0.013160	-0.043038
O	1.897669	0.038874	-1.557961
N	1.295712	-0.043391	1.857698
C	8.083793	0.026399	-0.306335
C	7.874993	-0.002057	1.045595
H	8.963535	0.041271	-0.928123
H	8.620216	-0.016409	1.828607
N	6.522132	-0.011676	1.360658
C	5.879859	0.010700	0.217158
N	6.813468	0.034957	-0.866190
O	6.511027	0.058396	-2.099704
H	3.902274	-0.039127	1.992116
H	4.168965	0.038508	-1.083186
O	0.197348	0.069399	-3.880907
H	0.816518	0.110951	-3.127573
H	0.383474	-0.779135	-4.302109
O	-2.111023	0.029073	-2.360781
H	-2.482032	0.916406	-2.442708
H	-1.387239	0.013680	-3.024639

2 Basis set and integration grid sizes

Electronic density integration. Several integration grids are available in ORCA:
grid0: product grid
grid1: Lebedev 50 (not recommended)
grid2: Lebedev 110 points (default for SCF iterations)
grid3: Lebedev 194 points (more accurate)
grid4: Lebedev 302 points (default for FinalGrid)
grid5: Lebedev 434 points (large)
grid6: Lebedev 590 points (larger)
grid7: Lebedev 770 points (very large)

Table 1: Effect of the grid size on the magnetic coupling constant J (in cm^{-1}) for various implicit solvents.

2IN model	Solvent*	grid1	grid4	grid7
W0	vacuum	-658	-663	-663
	hexane	-706	-710	-710
	acetone	-801	-806	-806
	acetonitrile	-808	-812	-812
	dmso	-810	-814	-814
	water	-812	-817	-817
W1a	vacuum	-685	-687	-687
	hexane	-730	-732	-732
	acetone	-823	-824	-824
	acetonitrile	-829	-830	-831
	dmso	-831	-832	-832
	water	-834	-835	-835
W2a	vacuum	-701	-707	-707
	hexane	-747	-754	-754
	acetone	-835	-841	-841
	acetonitrile	-839	-846	-846
	dmso	-842	-848	-848
	water	-845	-850	-851

*$\varepsilon(hexane) = 2, \varepsilon(acetone) = 20, \varepsilon(acetonitrile) = 37, \varepsilon(dmso) = 47, \varepsilon(water) = 80$.

Enlarging the size of the DFT electronic density integration grid alters very slightly the magnetic exchange value. Using the standard grid4 gives J values in perfect agreement with larger ones.

Basis set. The effect of the basis set size (from double-ζ to triple-ζ including diffuse and polarization functions) on the J solvent shift has been studied.

Table 2: Influence of the basis set size on the magnetic coupling constant J (in cm^{-1}) for various implicit solvents.

2IN model	Solvent*	6-31G	6-31G(d,p)	6-311G(d,p)	6-311G(2d,2p)	6-311+G(2d,2p)
W0	vacuum	-567	-663	-608	-623	-643
	hexane	-614	-710	-656	-672	-708
	acetone	-706	-806	-754	-772	-852
	acetonitrile	-712	-812	-761	-779	-862
	dmso	-714	-814	-763	-780	-866
	water	-717	-817	-766	-784	-870
W1a	vacuum	-589	-687	-629	-645	-660
	hexane	-634	-732	-674	-691	-721
	acetone	-725	-824	-770	-788	-858
	acetonitrile	-731	-830	-777	-795	-868
	dmso	-733	-832	-779	-797	-871
	water	-736	-835	-782	-800	-876
W2a	vacuum	-610	-707	-651	-665	-690
	hexane	-656	-754	-698	-712	-754
	acetone	-742	-841	-788	-803	-886
	acetonitrile	-748	-846	-793	-809	-894
	dmso	-749	-848	-795	-811	-897
	water	-752	-850	-798	-813	-901

*$\varepsilon(hexane) = 2, \varepsilon(acetone) = 20, \varepsilon(acetonitrile) = 37, \varepsilon(dmso) = 47, \varepsilon(water) = 80.$

The J shifts due to the solvent (implicit or explicit) are almost identical whatever the chosen basis set, with the exception of the largest basis set that includes diffuse functions on non-hydrogen atomic centers. Despite the COSMO outlying charge correction, special care must be taken when electrons are free to flow outside the molecular cavity.

3 PBE0 versus B3LYP

The effect of the choice of a DFT functional is checked by comparison of J values obtained with B3LYP and PBE0 functionals. As expected, the absolute values largely depend on the functional. However the solvent contribution is almost independant of the choice of the functional.

Table 3: Magnetic coupling constant J_{B3LYP} and J_{PBE0} (in cm^{-1}); proportions $\%_{B3LYP}$ and $\%_{PBE0}$ in implicit solvents.

Solvent*	J_{B3LYP}	J_{PBE0}	$\%_{B3LYP}$	$\%_{PBE0}$
Vacuum	-663	-1168	0	0
Hexane	-710	-1236	7	6
Acetone	-806	-1370	21	17
Acetonitrile	-812	-1379	22	18
Dmso	-814	-1382	23	18
Water	-817	-1386	23	19

*$\varepsilon(hexane) = 2, \varepsilon(acetone) = 20, \varepsilon(acetonitrile) = 37, \varepsilon(dmso) = 47, \varepsilon(water) = 80.$

4 Geometry optimizations

The dependence of the J values with the geometry of 2IN in different solvents is analyzed. As expected from a completely conjugated system, 2IN geometry remains almost the same, justifying our choice to keep the gas phase one.

Table 4: Magnetic coupling constant J (in cm^{-1}); overlap S_{ab} between the magnetic orbitals; square of the singly occupied molecular orbital (SOMO) energy splitting in the triplet state (in eV^2) for various implicit solvents with geometry optimizations.

		without optimization			with optimization		
2IN model	Solvent*	J	S_{ab}	$(\varepsilon_1-\varepsilon_2)^2$	J	S_{ab}	$(\varepsilon_1-\varepsilon_2)^2$
W0	vacuum	-663	0.2465	1.2010	-664	0.2469	1.2010
	hexane	-710	0.2589	1.2348	-707	0.2582	1.2263
	acetone	-806	0.2840	1.2971	-805	0.2839	1.2764
	acetonitrile	-812	0.2857	1.3010	-811	0.2857	1.2794
	dmso	-814	0.2862	1.3021	-813	0.2862	1.2807
	water	-817	0.2871	1.3037	-817	0.2870	1.2823
W1a	vacuum	-687	0.2553	1.2371	-690	0.2561	1.2398
	hexane	-732	0.2668	1.2674	-730	0.2663	1.2604
	acetone	-825	0.2905	1.3240	-819	0.2892	1.3055
	acetonitrile	-831	0.2921	1.3276	-825	0.2908	1.3085
	dmso	-833	0.2926	1.3285	-827	0.2914	1.3096
	water	-836	0.2933	1.3301	-830	0.2921	1.3108
W2a	vacuum	-707	0.2579	1.2448	-710	0.2588	1.2467
	hexane	-754	0.2699	1.2726	-752	0.2696	1.2623
	acetone	-841	0.2927	1.3207	-821	0.2914	1.3057
	acetonitrile	-847	0.2941	1.3234	-842	0.2933	1.3064
	dmso	-848	0.2946	1.3243	-838	0.2937	1.3083
	water	-851	0.2952	1.3255	-845	0.2941	1.3075

*$\varepsilon(hexane)=2, \varepsilon(acetone)=20, \varepsilon(acetonitrile)=37, \varepsilon(dmso)=47, \varepsilon(water)=80.$

5 Mulliken spin population analysis

Table 5: Mulliken spin population analysis on water molecules for 2IN-cis-W1 (in |e|)

Atom	W1a	W1b	W1c	W1d
H1	-0.000274	-0.000005	-0.000342	0.000011
O	-0.000143	0.000017	0.003251	-0.000504
H2	0.000016	-0.000004	-0.001676	-0.002601

Table 6: Mulliken spin population analysis on water molecules for 2IN-cis-W1 frozen (in |e|)

Atom	W1a*	W1b*	W1c*	W1d*
H1	-0.000284	-0.000006	-0.000780	0.000003
O	-0.000063	0.000019	0.002015	-0.000431
H2	0.000006	-0.000005	-0.000463	-0.002281

Table 7: Mülliken spin population analysis for W1 (in |e|).

	W1a		W1b		W1c		W1d	
Atom	Vacuum	Water	Vacuum	Water	Vacuum	Water	Vacuum	Water
O	0.5275	0.4931	0.5467	0.5270	0.5432	0.5261	0.5577	0.5379
N1	0.1731	0.1843	0.1862	0.1980	0.1945	0.2029	0.1862	0.1982
C	0.1471	0.1621	0.0859	0.0907	0.0756	0.0836	0.0680	0.0741
C	-0.1982	-0.2088	0.0387	0.0483	0.0650	0.0679	0.0692	0.0757
C	0.1808	0.1974	0.0427	0.0399	0.0234	0.0250	0.0169	0.0168
C	-0.1668	-0.1794	0.0906	0.1039	0.1069	0.1168	0.1137	0.1251
N2	-0.1504	-0.1663	0.1740	0.1889	0.1914	0.2002	0.1988	0.2036
O	-0.5243	-0.4872	0.5597	0.5304	0.5283	0.5067	0.5141	0.4945

Table 8: Mülliken spin population analysis for W2 (in |e|).

	W2a		W2b		W2c		W2d		W2e		W2f
Atom	Vacuum	Water	Vacuum	Water	Vacuum	Water	Vacuum	Water	Vacuum	Water	Vacuum
O	0.5522	0.5263	0.5218	0.5047	0.5397	0.5261	0.5489	0.5316	0.5359	0.5220	0.4801
N1	0.1760	0.1893	0.2092	0.2136	0.1986	0.2029	0.1967	0.2043	0.2059	0.2105	0.2209
C	0.0982	0.1081	0.0857	0.0968	0.0702	0.0836	0.0565	0.0700	0.0598	0.0728	0.1128
C	0.0339	0.0355	0.0414	0.0432	0.0739	0.0679	0.0983	0.0924	0.1023	0.0985	0.0182
C	0.0472	0.0528	0.0426	0.0478	0.0161	0.0250	0.0012	0.0072	-0.0035	0.0024	0.0736
C	0.0813	0.0884	0.0927	0.1004	0.1136	0.1168	0.1276	0.1330	0.1304	0.1375	0.0781
N2	0.1888	0.1993	0.1729	0.1876	0.1912	0.2002	0.1822	0.1925	0.1969	0.2013	0.1743
O	0.5459	0.5263	0.5598	0.5344	0.5210	0.5067	0.5173	0.4990	0.4918	0.4795	0.5659

Table 9: Mulliken population analysis for 2IN-W0 system ; proportions %.

atoms	vacuum	cosmo*	%
0C	-0.091537	-0.096695	6
1C	0.196222	0.201226	2
2C	0.078970	0.086579	10
3N	0.185286	0.198009	7
6C	0.046851	0.052721	12
7C	0.033402	0.034985	5
8O	0.553630	0.530887	-4
9N	0.049223	0.050507	2
10C	-0.094432	-0.10404	10
11C	0.197670	0.208135	5
14N	0.036597	0.032751	-10
15C	0.096033	0.106561	11
16N	0.171742	0.187785	9
17O	0.560355	0.530701	-5

*$\varepsilon(water) = 80.$

6 Molcas input for computing exchange integrals over molecular orbitals or magnetic orbitals

Note that the correctness of the magnetic orbitals has been checked by visual inspection (using the Grid_it utility).

```
 &Gateway
Coord = W0.xyz
Basis = 6-31G**
Group = nosym

&Seward

&Scf
charge = 0
uhf
zspin = 2
ksdft = b3lyp

> LINK bisnitro.UnaOrb INPORB

&Grid_it
ASCII
Select = 1:1-50
Name = Natural

&Motra
LumOrb
Frozen = 48
Deleted = 190
Print = 10

&Localisation
NOrbitals = 2
NFrozen = 48

> LINK bisnitro.LocOrb INPORB

&Grid_it
ASCII
Select = 1:1-50
Name = Local

&Motra
LumOrb
Frozen = 48
Deleted = 190
Print = 10
```

By default, the Motra module cannot handle UhfOrb files. In order to compute the exchange integral between the two SOMOs, we copy their coefficients from the UhfOrb file to a fake UnaOrb file that can be read by Motra.