Experimental and Theoretical Spin Densities in Two Alkyl Nitroxides*

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The spin density in the two alkyl nitroxide compounds 4-oxo- and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (tempone and tempol) has been determined by polarised-neutron diffraction and compared to theoretical predictions obtained in both the Unrestricted Hartree-Fock and the Local Spin Density approaches.

Key words: Nitroxide free radicals; Polarised-neutron diffraction; Spin density; Unrestricted Hartree-Fock calculations; Local-spin-density calculations.

Spin density determination by means of polarised-neutron experiments has been shown to be a critical test for theoretical ab-initio calculations [1].

We have determined the spin densities in two alkyl nitroxides, derivatives of 2,2,6,6-tetramethyl piperidine: tempone (4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, CAS registry no. 2896-70-0) and tempol (4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy, CAS registry no. 2226-96-2) [2]. These two radicals contain six-membered rings, and the unpaired electron arises from an $N{-}O^{\cdot}$ group and occupies an antibonding π-orbital. The two molecules look very similar (Fig. 1) and differ mainly by their chemical function (ketone for tempone and alcohol for tempol). Both compounds crystallise in an acentric space group. In the first compound the molecules are isolated, whereas in the second one the hydrogen of the alcohol function induces hydrogen bonds between the H of the alcohol group and the O of the nitroxide group of the next molecule. As a result, tempone exhibits Curie behaviour and shows antiferromagnetic interactions between neighbouring molecules [3], whereas the magnetic susceptibility of tempol reaches a maximum at $T = 5$ K.

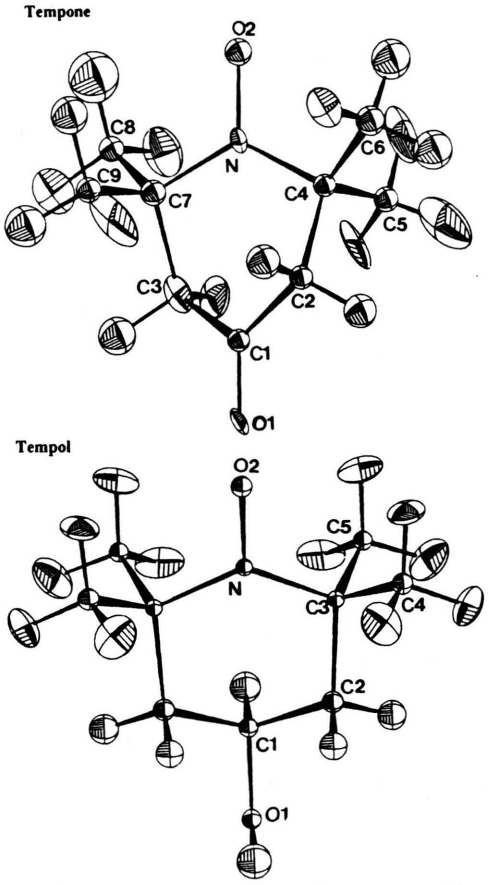

Fig. 1. View of the two molecules tempone (a) and tempol (b).

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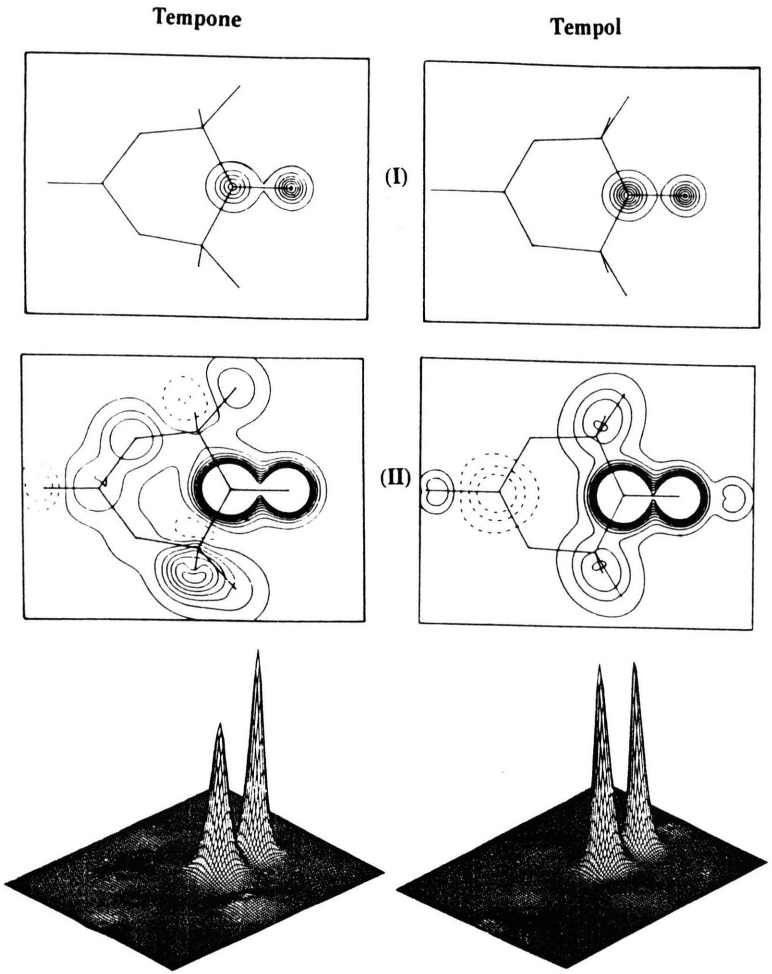

Fig. 2. Spin density projections along the π-direction for tempone and tempol. All plots are normalised to a total magnetisation of 1 μ_B per molecule. High-level plots (I): $100 \pm n \cdot 200$ mμ_B/Å. Low-level plots (II): $5 \pm n \cdot 10$ mμ_B/Å.

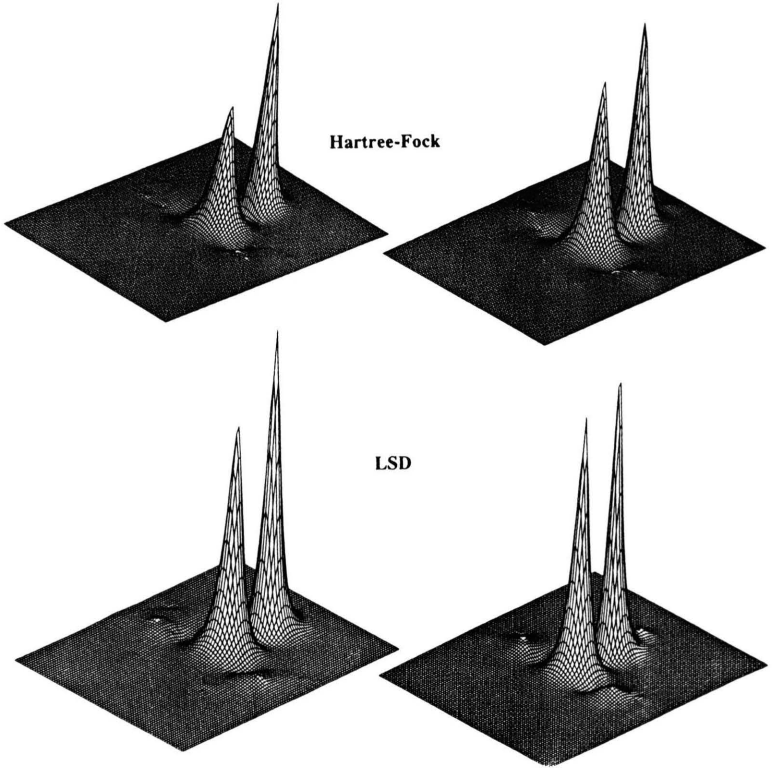

Fig. 3. Theoretical spin density projections along the π-direction for tempone and tempol. All plots are normalised to a total magnetisation of 1 μ_B per molecule.

Table 1. Experimental conditions of the polarised-neutron experiments.

	Tempone	Tempol
Spectrometer	D3 (ILL)	D3 (ILL)/5C1 (Saclay)
Temperature	2 K	4.2 K
Applied field *B*	4.6 T	4.6 T/4.2 T
No. of observations	219	262

Table 2. Refined spin populations (magnetic moments in multiples of μ_B) from polarised-neutron data.

Tempone		Tempol	
N	0.402(18)	0.092(2)	N
O2	0.355(17)	0.060(2)	O2
C1	0.036(20)	−0.009(3)	C1
C2	0.012(17)	0.001(2)	C2
C3	0.051(25)		
C4	−0.056(20)	0.003(2)	C3
C7	0.027(23)		
C5	0.123(21)	0.007(2)	C4
C9	−0.036(18)		
C6	0.025(17)	0.001(2)	C5
C8	0.033(14)		
O1	−0.015(12)	0.004(2)	O1
		−0.002(2)	H1

Table 3. Experimental and theoretical integrated spin populations in the $\mathrm{N{-}O^{\cdot}}$ group in multiples of μ_B, normalised to 1 μ_B per molecule.

		Tempone	Tempol
UHF	N	0.452	0.533
	O	0.583	0.487
LSD	N	0.456	0.475
	O	0.475	0.409
Exper.	N	0.411	0.544
	O	0.370	0.354

Polarised-neutron diffraction measurements have been performed on single crystals of the compounds, with a magnetic field applied to the samples in order to induce a long-range order of the spin density, and at low temperature in order to make the magnetic signal as large as possible. The experimental conditions are summarised in Table 1. Since the two compounds crystallise in acentric space groups, direct determination of the magnetic structure factors is not possible from the measurements. We have used a model that consists in refining the unpaired-electron populations and magnetic moments from the flipping ratios [4]. The results are summarised in Table 2, and Fig. 2 represents spin-density projections, derived from the refined parameters, along the π-direction.

In the two compounds, the spin density is localised mainly on the $\mathrm{N{-}O^{\cdot}}$ groups, in $2\,p_z$ orbitals centred on the oxygen and nitrogen atoms. However, the two molecules differ in two points; firstly, the spin delocalisation of the rings is larger for tempone, and secondly, the spin partitioning of the spin density inside the $\mathrm{N{-}O^{\cdot}}$ groups is drastically modified from one compound to the other. While in tempone, where the molecules are isolated, we observe a nearly equal partitioning between N and O (53% on N/47% on O), the spin density is shifted from O to N in tempol, owing to the hydrogen bond, to reach an unbalanced distribution (61% on N/39% on O).

We have compared the experimental densities to theoretical predictions obtained within both the Unrestricted Hartree-Fock (UHF, [5]) and the Local Spin Density (LSD, [6]) frameworks. The basis sets for these calculations have been taken from Gillon et al. [7] (UHF) and from Delley et al. [8] (LSD), respectively. Figure 3 contains theoretical spin density projections in the same plane as for the experimental results. The integrated and renormalised spin populations are collected in Table 3. Both methods are in good agreement with the experiment in localising the major part of the spin density on the $\mathrm{N{-}O^{\cdot}}$ groups. They also reproduce the spin transfer from O to N when passing from tempone to tempol. In either case, UHF overestimates the rôle of the oxygen atom, while LSD remains closer to the experiment.

In conclusion, it appears that in alkyl nitroxides the spin density is equally spread on the oxygen and the nitrogen atom of nitroxide groups when there are no interactions between neighbouring molecules. When an interaction, such as a hydrogen bond, occurs, it results in a spin transfer from O to N. The Local-Spin-Density-theory approach is closer to the experimental results than is the Hartree-Fock one.

[1] B. Gillon and J. Schweizer, in: J. Maruani (ed.), Molecules in Physics, Chemistry and Biology, 3 (1989) 111, Kluwer Academic Publishers.

[2] D. Bordeaux, J. X. Boucherle, B. Delley, B. Gillon, E. Ressouche, and J. Schweizer, in: D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio (eds), Magnetic Molecular Materials, Serie E, Vol. **198,** Kluwer Academic Publ., Dordrecht 1991, pp. 371–384.

[3] Y. S. Karimov, Zh. Eksp. Teor. Fiz., Pis. Red. **8,** 239 (1968).

[4] E. Ressouche, Thesis, Univ. Grenoble 1991.

[5] M. R. Peterson and R. A. Poirier, program MONSTERGAUSS (University of Toronto).

[6] B. Delley, J. Chem. Phys. **92,** 508 (1990).

[7] B. Gillon, P. Becker, and Y. Ellinger, Mol. Phys. **48,** 763 (1981).

[8] B. Delley, P. Becker, and B. Gillon, J. Chem. Phys. **80,** 4286 (1984).