DETERMINATION BY POLARIZED NEUTRON DIFFRACTION OF THE SPIN DENSITY DISTRIBUTION IN A NON-CENTROSYMMETRICAL CRYSTAL OF DPPH:C₆H₆

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Résumé. - La densité de spin du radical libre DPPH (diphénylepicrylhydrazyle) a été étudiée dans la forme cristallisée DPPH:C₆H₆, avec les moments paramagnétiques orientés, à basse température, par un champ magnétique extérieur. Comme la structure cristalline est non centrosymétrique, il n'est pas possible d'obtenir directement les facteurs de structure magnétiques à partir des rapports de "flipping" mesurés par diffraction de neutrons polarisés. Pour cette raison, la densité de spin a été représentée par un développement multipolaire sur chaque atome. Les paramètres de ce développement sont déterminés directement par une comparaison avec les rapports de "flipping" mesurés.

La plus grande partie de la densité de spin est partagée entre les deux atomes d'azote du groupe hydrazyl (N_α et N_β). La partie restante est délocalisée sur les 2 cycles phenyl et sur le cycle picryl. Ces résultats sont comparés aux mesures de résonance magnétique.

Abstract. - The spin density of the free radical DPPH (diphenylpicrylhydrazyl) has been studied in the crystallized form DPPH C₆H₆ with the paramagnetic moments orientated, at low temperature, by an external magnetic field. As the crystal structure is not centro-symmetrical, it is not possible to obtain directly the magnetic structure factors from the experimental flipping ratios measured by polarized neutron diffraction. For this reason we have represented the spin density by a multipole expansion on the different atoms, and determined directly the parameters of this expansion by comparing with the observed flipping ratios.

A large amount of the spin density is shared between the 2 nitrogen atoms (N_α and N_β) of the hydrazyl group. The remaining part is delocalized on the 2 phenyl and the picryl rings. These results are compared to magnetic resonance data.

1. Introduction. - The stable aromatic free radical α,α-diphenyl β-picryl hydrazyl (DPPH) was among the first paramagnetic species investigated by electron spin resonance (ESR) [1], and its remarkable chemical stability and narrowness of its resonance line have made it a widespread standard for measuring unpaired spin concentrations and effective gyromagnetic ratios [2]. DPPH crystallizes in several different forms, with [3a] or without [3b] the inclusion of solvent molecules. Complete X-ray determination of the crystal structure at room temperature was first performed on the best grown crystal form, the DPPH : C₆H₆ complex [4], and later extended to acetone-containing DPPH crystals [5], revealing in both cases a rather twisted conformation (Fig. 1, table II).

Fig. 1 - Overall view of DPPH structure as deduced from neutron diffraction data at 10K (paragraph 3)

The DPPH molecule is one of the most widely investigated molecules using magnetic resonance techniques [6]. ESR measurements on dilute solutions have mainly yielded the hyperfine couplings of the central nitrogen atoms in a large variety of physical conditions. Both the contact and dipolar parts of these couplings have been shown to depend significantly on the solvent composition, rigidity and structure, and the spin densities to be almost as large on the nitrogen linked to the two phenyls as on the nitrogen linked to the picryl [7]. Nuclear magnetic resonance (NMR) of concentrated samples has essentially provided the magnitudes and signs of the hyperfine couplings of the ring protons [8] and of the picryl nitrogens [9], revealing an extensive spin delocalization and polarization on the whole molecule. Contact hyperfine couplings have been determined most accurately by electron-electron double resonance (ELDOR) for the hydrazyl nitrogens [10] and by electron-nuclear double resonance (ENDOR) for the ring protons [11]. The hydrazyl nitrogens appear to share about 70 % of the total spin density, the remaining part being delocalized on the 2 phenyl and the picryl rings, with alternating positive and negative signs on the ring carbons, in agreement with quantum mechanical calculations [12].

One remarkable feature of the magnetic resonance results for the hydrazyl nitrogens is that their hyperfine coupling tensors appear consistently quasiallial and nearly parallel [7], whereas, in the few cases where the exact molecular geometry has been determined from X-ray diffraction data [4,5], the corresponding trigonal planes are at an angle close to 30°.

Table I shows some sets of values obtained for the hyperfine couplings of DPPH under various conditions. The first column summarizes the most accurate values measured for the contact couplings using appropriate techniques. The second column recalls the values measured in dilute glassy samples by ESR [7b] and in pure crystalline powders by NMR [8a]. The third column provides the corresponding values for DPPH : C₆H₆ in dilute [7a,c] or pure [8c] crystals. The signs and assignments are confirmed by the theoretical results given in the fourth column ; here, we have used the UHF spin populations ρ^π calculated for an extended structure [12b] together with the semi-empirical relations :

$$a_H = Q_{CH} \rho_C^\pi \quad a_N = Q_{NN} \rho_N^\pi \quad (1)$$

with the spin polarization constants :

$$Q_{CH} = -23 \text{ G [13a]}, \quad Q_{N\alpha} = 36 \text{ G and } Q_{N\beta} = 25 \text{ G [12b]}, Q_{NO_2} = 48 \text{ G [13b]}$$

As has been shown for nitroxide free radicals [14], the direct determination of the spin density distribution by neutron diffraction techniques can reveal new and important results, complementary to those obtained with magnetic resonance techniques. Contrary to nitroxide radicals, where the spin density is concentrated on the N-O group, DPPH offers a case of large delocalization, which makes it a stimulating challenge for neutron diffraction. Unfortunately, all the crystal forms of DPPH are non-centrosymmetrical and this has prevented any study with polarized neutrons to be done so far.

Recently a new technique for data reduction has been proposed [15], which makes use of a multipolar expansion for the spin density. This method makes it possible to study non-centrosymmetrical crystals by polarized neutron diffraction. We have undertaken such an experiment on a DPPH single crystal, the results of which are reported in this paper.

In the following Section we show how multipolar expansions make it possible to measure spin densities in non-centrosymmetrical crystals. Section 3 describes the determination of the crystal structure of the DPPH:C₆H₆ complex using unpolarized neutron diffraction. In Section 4 we describe the polarized neutron experiments and the derivation of spin density maps. In the last Section we discuss the results of neutron diffraction in relation to those of magnetic resonance.

	Liquid (I)	Glass or powder (II)	DPPH:C ₆ H ₆ crystal (III)	Calculations (IV) [12b,13a]	
Hydrazyl nitrogens	[10] 7.93 9.74	[7b] 7.6 (b=5.9) 9.9 (b=7.8)	[7a,c] 6.3 (b=6.3) 13.0 (b=7.3)	[12b] +8.11 +9.24	N _α N _β
Phenyl protons	[11] 2.01 (x2) 1.90 (x4) 0.68 (x2) 0.75 (x2)	[8a] -2.2 (x4) -1.3 (x2) +0.6 (x4)	[8c] -2.6 (x3) -1.5 (x3) +0.6 (x2) +1.1 (x2)	[13a] -1.89 (x2) -1.79 (x2) -1.64 (x2) +0.86 (x2) +0.91 (x2)	H ortho outer H ortho inner H para H meta inner H meta outer
Picryl protons	1.02 (x1) 1.12 (x1)	+1.4 (x2)	+1.6 (x2)	+0.87 (x2)	H meta
Picryl nitrogens	[9] -0.39 (x1) -0.48 (x2)			[13b] -0.24 (x3)	N

Table I : Contact hyperfine coupling a (in Gauss) of the nitrogen and hydrogen nuclei in DPPH (the numbers of nuclei are given in parenthesis).

I - ELDOR [10] and ENDOR [11] do not provide the coupling signs whereas NMR [9] does.
 II, III - For N_{α,β} one obtains also the dipolar coupling b (in Gauss) by ESR [7a,b] and for the H's, the intermediate value of the anisotropic tensor by NMR [8a,c].
 The measured values for the hyperfine couplings of the hydrazyl nitrogens range from $a=6.3$, $b=5.0$ to $a=8.7$, $b=7.0$ for N_α and $a=9.4$, $b=5.0$ to $a=13.0$, $b=8.0$ for N_β [6].
 IV - UHF calculation for planar DPPH.

2. Measurement of spin density distributions in non-centrosymmetrical crystals - Multipolar expansion

The neutron intensity of a Bragg reflection for a magnetic material contains both the nuclear structure factor F_N and the magnetic structure factor F_M . Accurate determinations of magnetic structure factors are usually performed with polarized neutrons and the flipping ratio technique. One measures, for each reflection, the ratio R obtained for two neutron spin states up and down

$$R = \frac{I^+}{I^-} = \frac{|F_N + F_M|^2}{|F_N - F_M|^2} \quad (2)$$

If the nuclear crystal structure of the sample under investigation has been determined, then the nuclear structure factor F_N is known and hence F_M may be deduced from measurement of R .

In the case of centro symmetrical crystals, for which F_N and F_M are real, F_M is obtained by solving equation (2). In the case of non-centrosymmetrical crystals, both F_N and F_M are complex quantities

$$F_N = F_N' + i F_N'' \quad F_M = F_M' + i F_M''$$

and the expression for the flipping ratio becomes :

$$R = \frac{(F_N' + F_M')^2 + (F_N'' + F_M'')^2}{(F_N' - F_M')^2 + (F_N'' - F_M'')^2} \quad (3)$$

The measurements of R alone cannot provide a knowledge of the two unknown quantities F_M' and F_M'' . To overcome this difficulty we propose to apply a model which provides an analytical description of the spin density. We have chosen an expansion of the density around the nuclei at rest. Such a model, first used to represent charge densities, has already proved to be very well adapted in the case of spin densities in centrosymmetric crystals. The expansion consists of a superposition of aspherical atomic densities, each described by a series expansion in real spherical harmonic functions :

$$s(\vec{r}) = \sum_{\text{atoms}} \sum_{\ell=0}^{\infty} R_{\ell}(r) \sum_{m=-\ell}^{\ell} P_{\ell m} Y_{\ell m}(\vec{r}) \quad (4)$$

The $P_{\ell m}$ are population coefficients. The radial functions $R_{\ell}(r)$ are of Slater type :

$$R_{\ell}(r) = \frac{\zeta^{n+3}}{(n+r)!} r^n e^{-\zeta r} \quad (5)$$

The magnetic structure factors corresponding to eqs. (1) become

$$F_M(\vec{H}) = \sum_{\text{atoms}} e^{2\pi i \vec{H} \cdot \vec{r}} \left[\sum_{\ell=0}^{\infty} \phi_{\ell}(H) \sum_{m=-\ell}^{\ell} P_{\ell m} Y_{\ell m}(\hat{H}) \right] e^{-w} \quad (6)$$

$$\text{with } \phi_{\ell}(H) = 4\pi i^{\ell} \int_0^{\infty} R_{\ell}(r) j_{\ell}(2\pi H r) r^2 dr \quad (7)$$

To establish the spin density map, the set of parameters (ζ , $P_{\ell m}$) which characterize the spin density and fit the experimental data must be determined. To do this, given a set of parameters, F_M' and F_M'' , are calculated and a value R_{cal} for the flipping ratio of each measured reflection is obtained from equations (3). By comparing R_{cal} with the measured flipping ratios R_{obs} it is possible to refine the parameters (ζ , $P_{\ell m}$) which best fit the data.

3. The crystal structure of the DPPH:C₆H₆ complex

DPPH is paramagnetic and its magnetic susceptibility follows a Curie law, with a magnetic moment of 1 μ_B per molecule. For the present investigation, one intends to measure the magnetic amplitude F_M ($F_M = F_M' + iF_M''$) scattered by the component of the magnetic moment aligned by an external magnetic field, and compare it with the nuclear amplitude F_N ($F_N = F_N' + iF_N''$) scattered by all the nuclei of the DPPH molecule. The magnetic moment is small compared to the nuclear signal, and only part of it is aligned by the field. To obtain a degree of alignment large enough to make the magnetic signal measurable, it is necessary to perform the neutron diffraction experiment at very low temperature, in order to take advantage of the increase of susceptibility with decreasing temperature.

At very low temperatures, however, the static susceptibility reveals strong deviations from the Curie law, due to antiferromagnetic exchange coupling between adjacent molecules : for pure DPPH crystals a maximum occurs around 10K [17a], whereas for the DPPH-C₆H₆ complex (where the free radicals are kept apart by the benzene molecules) the susceptibility reaches a maximum around 1K [17b] (see Figure 2). This latter form is therefore better suited for a polarized neutron study made at the helium temperature $T = 4.2K$.

As all other forms of DPPH, the DPPH:C₆H₆ complex is non-centrosymmetrical : its space group is Pc with 2 molecules of both DPPH and C₆H₆ in the crystal cell ($Z = 2$). For the spin density determination, the crystal structure, as determined at room temperature by X-rays [4] is not accurate enough. In particular one has to know the location of the hydrogen nuclei and also the exact values of all the thermal para-

Fig. 2 - Magnetic susceptibility χ as a function of the inverse of the temperature $1/T$ for DPPH solvent free and for the DPPH: C_6H_6 complex [17a,b]

meters at the temperature for which the spin density is measured. For this reason, we have first undertaken a low temperature unpolarized neutron crystal study, on a DPPH- C_6H_6 single crystal.

This experiment was performed on the 4 circle diffractometer D15 of the ILL. The temperature, produced by a two stage refrigerator, was 10K. The lattice constants at this temperature are reported in Table II. 1270 independent reflections were collected and corrected for absorption. We have refined the positions and anisotropic thermal parameters of all atoms in the cell. The final weighted agreement factor for all reflections was 3.6 %.

The main features of the crystal structure thus measured are similar to those reported by Williams (Fig. 1, Table II). The main difference between the 2 sets of results is in a systematic contraction of bond lengths at 10K. The deviation from planarity of the environment of N_α is about 3° . The 2 phenyl rings are completely planar, but with different twist angles with respect to the N_α plane.

Lattice constants		Reference [4]	This work
	a	7.764 Å	7.542 Å
	b	10.648 Å	10.416 Å
	c	14.780 Å	14.295 Å
	β	109.05°	108.80°
Structural parameters	$N_\alpha - N_\beta$	1.334 Å	1.318 Å
	$N_\alpha - C_7$	1.422 Å	1.416 Å
	$N_\alpha - C_{13}$	1.419 Å	1.395 Å
	$N_\beta - C_1$	1.370 Å	1.337 Å
	$C_7 N_\alpha N_\beta$	121.8°	121.7°
	$C_{13} N_\alpha N_\beta$	115.1°	116.3°
	$N_\alpha N_\beta C_1$	118.5°	119.2°
	$C_7 N_\alpha N_\beta / N_\alpha N_\beta C_1$	34.4°	33.6°
	$C_{13} N_\alpha N_\beta / N_\alpha N_\beta C_1$	23.2°	22.8°
	phenyl $C_7 / C_7 N_\alpha C_{13}$	54.3°	54.3°
	phenyl $C_{13} / C_7 N_\alpha C_{13}$	15.6°	14.9°
	picryl $N_\alpha N_\beta C_1$	32.9°	33.7°

Table II : Lattice constants, bond lengths, planar angles and dihedral angles defining the structure of DPPH syncrystallized with C_6H_6 as determined by X-rays at room temperature [4] and by neutrons at 10 K.

Finally, as it was reported [4] that a certain amount of benzene may evaporate from the mixed crystals, we have refined the exact stoichiometry of the C_6H_6 molecules, and found exactly 1:1. As our crystals had been stored at $-20^\circ C$, we concluded this was enough to prevent evaporation.

4. Polarized neutron measurements and data treatment

The polarized neutron experiment was performed at a temperature of 4.2K, with an applied magnetic field of 4.65T provided by a cryomagnet on the D3 diffractometer of the ILL Grenoble. The wavelength of the neutron beam was 0.90 Å. The sample was a single crystal of DPPH: C_6H_6 , of dimensions 1x2x6 mm, with the long dimension close to the $\hat{a}$ axis of the cell. The crystal was oriented with this axis vertical, parallel to the magnetic field. The flipping ratios of 425 inequivalent Bragg reflections were measured, lifting when necessary the counter above the horizontal plane to measure in layers other than the zero layer.

The treatment of the flipping ratios was conducted as explained in Section II. The spin density was expanded in atomic multipoles according to relation (4), and the parameters ζ and P_{lm} were refined. Experimental corrections due to imperfect polarization and flipping efficiency, $\lambda/2$ contamination and nuclear polarization of hydrogen atoms were included, modifying slightly relation (3). At the present time no diamagnetic contribution to the magnetization density has been removed. This remains to be done.

In the following, we present partial results on the spin density, obtained with multipoles limited to $l = 2$. No constraint was imposed to the central nitrogens, but the spin density on the carbon atoms was constrained to their $2p_z$ orbitals, perpendicular to the ring. No spin density was examined on the NO_2 groups. The total number of parameters to be refined was 39. The least square refinement corresponds to $\chi^2 = 2.76$. The spin density map, projected along $\hat{c}$, is represented in Figure 3.

Fig. 3 - Projection of the spin density distribution along the crystallographic axis $\hat{c}$. Adjacent contours are separated by $0.03 \mu_B/\text{\AA}^2$.

5. Discussion

As seen in the map, the largest amount of spin density is located on the two central nitrogen atoms. However, and contrary to the case of nitroxide radicals [14], 30 % of the spin density is delocalized on the two phenyl and the picryl rings.

The spin distribution over the different parts of the molecule is illustrated by the 3 projection maps given in Figure 4. The spin density of the hydrazyl (Fig. 4a) is projected perpendicularly to the plane containing the $N_\alpha-N_\beta$ bond and bisecting the $C_7N_\alpha C_{13}$ angle. It is well separated into two $2p$ -type atomic orbitals and evenly distributed between them. At the present stage of data refinement the axes of the 2 spin distributions appear nearly parallel, whereas the local structure is twisted by over 28° (Figure 1, Table I). This may be linked to the very low value observed by ESR for the angle between the axes of the hyperfine coupling tensors of the two central nitrogens [7]. However, departure of hyperfine couplings from the local structure has been attributed in other systems [18] to dipolar interactions of the considered nucleus with the spin densities surrounding neighbouring nuclei.

Fig. 4 - Projection of the spin density

a) along a direction parallel to the trigonal N_α plane

b) perpendicularly to the phenyl ring (C_{13})

c) perpendicularly to the phenyl ring (C_7)

Adjacent contours are separated by $0.03 \mu_B/\text{\AA}^2$.

Delocalization of the spin density has been observed on the carbon atoms of the three rings of the molecule, in accordance with the magnetic resonance data. The projection maps onto the 2 phenyl planes (Fig. 4b and 4c) show that the spin density on the carbon atoms is alternatively positive and negative, as predicted by theoretical calculations including spin polarization [12b] and in agreement with NMR results [8a,8c]. Table III compares the spin populations of the $2p^\pi$ orbitals for each carbon, as deduced from the hyperfine coupling constants measured on DPPH: C_6H_6 crystals [8c] by the use of McConnell's relation (1), to the monopole populations P_{00} after normalization. All values fit into this scheme and the agreement is quite good. This can be considered as a confirmation of McConnell's constant $Q_{CH} = -23$ G.

Moreover, the inequivalence of the two phenyl rings, already noticed in the NMR of single crystals [8c], is clearly illustrated in Figures 4b and 4c. The spin populations located on the carbon atoms of phenyl ring (C_{13}), which makes a tilt angle of 15° with regard to the N_α trigonal plane, are about twice as large as those relative to phenyl ring (C_7), whose tilt angle is 54° . These delocalized spin populations increase with the overlap between the $2p^\pi(N_\alpha)$ and $2p^\pi(C)$ orbitals [19], that is with $\cos^2\alpha$, where α is the twist angle. Resonance results in DPPH solutions [11], where

no tilt angle can be defined, do not permit to detect an inequivalence between the two phenyl rings.

Table III: Spin populations ρ^π of the $2p^\pi$ orbital of the carbon atoms of DPPH :

I - deduced from the experimental couplings in DPPH-C₆H₆ [8c] by use of the McConnell relation (1)

II - given by the normalized monopole population of each atom in the multipole representation of the spin density

NMR [8c]	(I)	neutrons (this work) (II)		
+0.113	(3)	+0.083 ortho +0.083 para +0.074 ortho	phenyl C ₁₃	
+0.065	(3)	+0.064 ortho +0.049 para +0.020 ortho	phenyl C ₇	
-0.026	(2)	-0.015 meta -0.039 meta	phenyl C ₇	
-0.048	(2)	-0.044 meta -0.049 meta	phenyl C ₁₃	
-0.071	(2)	+0.034 meta -0.005 meta	picryl C ₁	

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