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Thermally-induced paramagnetism of spiropyrane iodides†

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Thermally stimulated paramagnetism has been found in the iodides of organic spiropyrane molecules, namely 1-isopropyl-3,3,5′,6′-tetramethylspiro(indolino-2,2′-[2*H*]pyrano[3,2-*b*]-pyridinium) (***Sp***) and spiro(1,3,3,7′-tetramethyl-indolino-2,3′-3*H*-pyrano[3,2-*f*]quinolinium) (***Sp2***). The activation energy of their triplet states was determined from the temperature dependence of their magnetic moments: 0.023 and 0.032 eV, respectively. It was found that the magnetic moment, μ_{eff}, increases under UV light (250–400 nm) due to the formation of high-spin ($S = 3$) states of the molecules.

1. Introduction

Great efforts are being made at present in the design of organic and organometallic photomagnetic compounds.[1–3] Example "building blocks" for such bifunctional compounds are photochromic spiropyrane molecules whose structure changes under light.[4–8] Organometallic materials based on spiropyrane cations have been developed, in which their coercive force and residual magnetization change under light.[4] There are two sublattices in such materials, one of which is formed by photochromic molecules and the other involves transition metal ions. Only one mechanism of the photomagnetic effect *a priori* predicts spiropyrane opening and changes in the distances between metal ion spins. It has been shown[9] that the photomagnetic effect in $Sp_3Cr(C_2O_4)_3$ cannot be interpreted by this phenomenon alone. Of essential importance is the paramagnetism of the initial spiropyrane molecules. Detailed information on the physical properties of the light controlled element, namely the spiropyrane cation, is needed to interpret the observed effects, develop photomagnetic materials and improve their parameters (magnetic ordering temperature, the value of the photomagnetic effect, *etc.*).

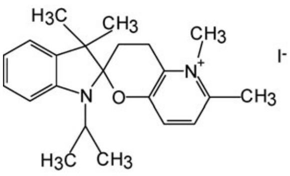
Prior to our experiments, spiropyrane molecules were considered to be diamagnetic. Efforts to find paramagnetism in spiropyranes were undertaken in the liquid phase, and were unsuccessful. Nevertheless, the data were published, which showed that spiropyrane molecules can exhibit paramagnetic properties in the solid state. For example, it was reported[10,11] that ESR spectra were measured for neutral spiropyrane molecules. Moreover, thermochromism is known for spiropyrane molecules[12,13] that is realized through low-lying excited triplet states.[14,15] The observed phenomenon is also proved by quantum chemical calculations.[16] Therefore, one might expect spiropyrane molecules to show high temperature paramagnetism in the solid state and become diamagnetic at low temperatures. Since the physical and chemical properties of molecules are dependent of their charge state, we chose ionic salts of spiropyrane molecules. It is necessary to understand the contribution of spiropyrane ions to the magnetic properties of transition metal compounds.[9] Spiropyrane iodides ***Sp***$^+$***I***$^-$ and ***Sp2***$^+$***I***$^-$ are used as components in the synthesis of photomagnetic compounds with transition metals.

This work aims to establish the nature of the paramagnetic states of spiropyrane ions ***Sp***$^+$ and ***Sp2***$^+$, and the mechanism of the photomagnetic effect in spiropyrane iodides.

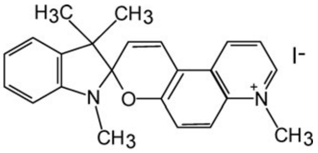
2. Experimental

1-Isopropyl-3,3,5′,3′-tetramethylspiro(indolino-2,2′-[2*H*]pyrano-[3,2-*b*]pyridinium) iodide (***SpI***) was obtained according to published methods.[4,17]

Spiro(1,3,3,7′-tetramethylindolino-2,3′-3*H*-pyrano[3,2-*f*]-quinolinium) iodide (***Sp2I***) was prepared as follows. A mixture of spiro(1,3,3-trimethylindolino-2,3′-3*H*-pyrano[3,2-*f*]quinoline) (0.328 g, 1 mmol) and MeI (0.213 g, ~0.09 ml, 1.5 mmol) in absolute acetone (15 ml) was refluxed for 3 h and left for 2 d. The precipitated solid was filtered off and washed with absolute acetone.[18] M.p. >250 °C (acetone); yield 80%.



SpI



Sp2I

X-Ray structural investigations were carried out on single crystals of light-pink or brown color, respectively, of arbitrary shape (size: 0.1 × 0.25 × 0.1 at 200 K (***SpI***, Fig. 1) and 0.2 × 0.2 × 0.2 mm at 293 K (***Sp2I***, Fig. 2)) on a KUMA Diffraction KM4 diffractometer (λ Mo-K$_\alpha$ = 0.71073 Å, $\omega/2\theta$-scanning). Structures were solved by the direct method. The positions and temperature parameters of the non-hydrogen atoms were refined in an anisotropic approximation by the full matrix least-squares method. The positions of the hydrogen atoms emerged from difference syntheses and were subsequently

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† CCDC reference numbers 290280 and 721088. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b822567b

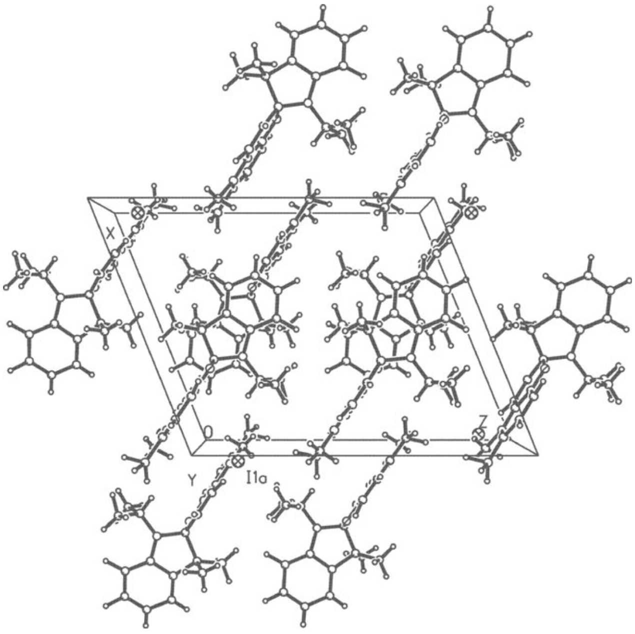

Fig. 1 Projection of the crystal structure of ***SpI*** on the X0Z plane.

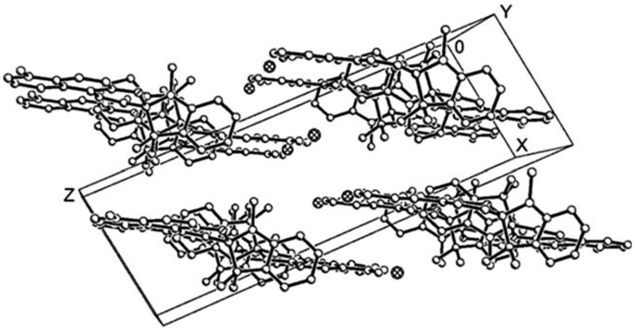

Fig. 2 Projection of the crystal structure of ***Sp2I*** on the X0Z plane. Hydrogen atoms are omitted for clarity.

refined with superpositions according to the riding model, allowing for the randomization of the hydrogen atoms at the C(12′) methyl atom in two positions, located equivalently relative to the plane of the ring. The crystallographic data and main parameters of the refinements are given in Table 1.†

Magnetic moments M for powder-like samples ***SpI*** and ***Sp2I*** were measured at $B = 0.1$ T ($T = 2$–300 K) and at $T = 2$–3 K ($B = 0$–5 T) using a MPMS 5XL (Quantum Design) SQUID magnetometer. All experimental values were corrected for the diamagnetic contribution of the sample holder. The experimental values of the magnetic moment at each point in the temperature dependence experiments, M(T), were recalculated to an effective magnetic moment, μ_{eff}, using the following formula: $\mu_{\text{eff}} = (8MT/\nu\text{B})^{\frac{1}{2}}\mu_{\text{B}}$ where μ_{B} is the Bohr magneton, T is temperature and ν is the number of moles; the M/νB ratio characterizes the molar static magnetic susceptibility.

To determine the type of paramagnetic particles, we used a Bruker EMX ESR spectrometer operating at X band (~9.4 GHz) and 100 KHz modulation frequencies, and equipped with a rectangular resonator of H_{102} type. ESR spectra were measured as the dependence of the first derivative of the microwave absorption, $\delta I/\delta H$, for irradiated and non-irradiated powder-like samples of ***SpI*** and ***Sp2I*** at $T = 300$ K.

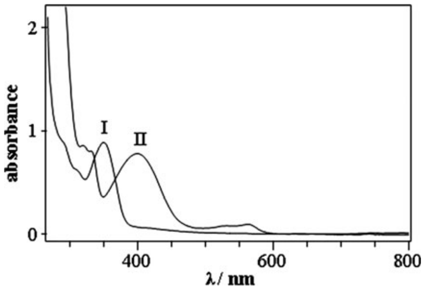

Fig. 3 Absorption spectra of non-irradiated (I) ***SpI*** in ethanol (6.7×10^{-5} mol L^{-1}) and (II) ***Sp2I*** in ethanol (5.2×10^{-5} mol L^{-1}).

The samples were irradiated by an Hg lamp using a filter transmitting light at $\lambda = 250$–450 nm. The light intensity was mainly in the wavelength range corresponding to the absorption of samples ***SpI*** and ***Sp2I*** (Fig. 3). The samples were irradiated for 2 h at room temperature. Samples of ***SpI*** and ***Sp2I*** were stirred upon irradiation to provide light access to all of the powder microcrystals. A water filter was used to exclude sample heating and avoid effects in the IR range.

3. Results

The results of the X-ray structural investigations of ***SpI*** and ***Sp2I*** have been published (CCDC 290280, 721088 correspondingly).†[17,18] The temperature dependence of the magnetic moment was determined for samples of ***SpI*** and ***Sp2I***. The effective magnetic moment, μ_{eff}, of non-irradiated ***SpI*** is equal to 0.002 μ_{B} at $T = 2$ K (Fig. 4a). The temperature increase results in a monotonic growth of μ_{eff} to 0.73 μ_{B} at $T = 300$ K. The effective magnetic moment of irradiated ***Sp2I*** at $T = 2$ K is 0.08 μ_{B} and increases with the temperature increase up to 1.1 μ_{B} at $T = 300$ K. The effective magnetic moment, μ_{eff}, of non-irradiated ***Sp2I*** is equal to 0.25 μ_{B} at $T = 2$ K and monotonically increases with the temperature increase up to 2.11 μ_{B} at $T = 300$ K (Fig. 4b). The effective magnetic moment, μ_{eff}, of irradiated ***Sp2I*** grows from 0.27 μ_{B} to 2.18 μ_{B} with increasing temperature from 2 to 300 K (Fig. 4b).

To determine the spins of particles mainly contributing to the magnetic properties at low temperatures, we measured the dependence of the molar magnetic moment, M, for ***SpI*** and ***Sp2I*** on the external magnetic field, B, before and after irradiation. The dependence M(B) for ***SpI*** (Fig. 5a) was measured prior to irradiation at $T = 2$ K and approximated by the Brillouin function, which describes the properties of paramagnetic particles. The dependence M(B) was measured for ***Sp2I*** before and after irradiation, and approximated using the Brillouin function. An increase in magnetic moment, M, was observed in irradiated ***Sp2I*** (Fig. 5b).

The ESR spectra of ***SpI*** (Fig. 6a) and ***Sp2I*** (Fig. 6b) before and after irradiation at room temperature show a single Gaussian line. The position of the line in the ESR spectrum of ***SpI*** corresponds to $g = 2.23$ with a half-width $\Delta H_{\frac{1}{2}} =$ 49 mT. The position of the line in the ESR spectrum of ***Sp2I*** corresponds to $g = 2.35$ with a half-width $\Delta H_{\frac{1}{2}} = 120$ mT.

Table 1 Crystallographic data and main parameters of the refinements

Parameters	***SpI***	***Sp2I***
Empirical formula	$C_{22}H_{27}N_2OI$	$C_{23}H_{23}N_2OI$
M_w	462.36	470.33
Temperature/K	200	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	12.862(3)	7.925(1)
b/Å	11.025(2)	11.338(2)
c/Å	16.019(3)	23.147(5)
α (°)	90.00	90.00
β (°)	112.00(3)	98.14(3)
γ (°)	90.00	90.00
V/Å^3	2106.1(7)	2058.9(7)
Z	4	4
ρ_{calc}/g cm^{-3}	1.458	1.517
μ/mm^{-1}	1.5	1.570
Scanning region	1.71–26.04	1.78–25.05
Number reflections measured	4146	3659
Number reflections with intensities $I > 2\sigma(I)$	2025	2021
R_1	0.0749	0.0458
R_w	0.2166	0.1204
GOOF	1.015	0.978

No changes in g-factor value, amplitude or linewidth were found for ***SpI*** and ***Sp2I*** irradiated with UV light.

4. Discussion

A detailed discussion of the crystal structures can be found in refs. 17 and 18.† Non-interacting paramagnetic particles whose concentration is temperature-independent should follow Curie's law. In this case, the magnetic moment, M, is inversely proportional to temperature, corresponding to the temperature-independent effective magnetic moment μ_{eff}. It can be seen from Fig. 4 that the effective magnetic moment, μ_{eff}, increases with temperature, *i.e.* ***SpI*** and ***Sp2I*** do not follow Curie's law. The μ_{eff}(T) dependencies cannot be interpreted by an exchange interaction, since the expected Curie temperature for ***SpI*** and ***Sp2I*** is several Kelvin. Therefore, the μ_{eff}(T) dependencies should be interpreted by considering intramolecular processes. Spiropyrane molecules are characterized by a singlet ground state with $S = 0$ and molecules that are diamagnetic in the ground state. Nevertheless, spiropyrane molecules show low-lying triplet ($S = 1$) excited states. Such triplet states with $S = 1$ can be populated to provide paramagnetic properties under thermal fluctuations. The temperature increase is accompanied by a growing number of triplet molecules and an increasing magnetic moment, μ_{eff}, which we observed in the experiments. At low temperatures, the number of excited molecules is negligibly small and spiropyrane molecules are diamagnetic *in toto*.

The temperature dependence of the magnetic susceptibility, χ(T), for molecules with triplet excited states is usually described by the following equation:[19]

$$\chi(\mathrm{T}) = \frac{2\mu_B^2 g^2 N_A}{\mathrm{k}T}\exp\left(-\frac{E^{\mathrm{T}}}{\mathrm{k}T}\right) + \frac{c}{T} \qquad (1)$$

where μ_B is the Bohr magneton, g is the g-factor, k is the Boltzmann constant, T is the temperature and E^{T} is the energy of the triplet state. The second sum in eqn (1) corresponds to a contribution of the paramagnetic additive, which satisfies Curie's law. Therefore, μ_{eff}(T) can be written as follows:

$$\mu_{\text{eff}}(\mathrm{T}) = 4\sqrt{\frac{\mu_B^2 g^2 N_A}{\mathrm{k}}\exp\left(-\frac{E^{\mathrm{T}}}{\mathrm{k}T}\right) + c} \qquad (2)$$

Approximation of the μ_{eff}(T) dependencies by eqn (2) showed a noticeable discrepancy between the experimental values of μ_{eff} and the calculated ones. One can assume that the discrepancy is mainly because of the wide distribution of energies of the triplet state for different spiropyrane molecules, *i.e.* there is a statistical distribution of E^{T} in molecules in non-homogeneous solid phases. If this distribution is considered to be typically Gaussian in eqn (1), then dependence χ(T) can be written as follows:[19]

$$\chi(\mathrm{T}) = \frac{2\mu_B^2 g^2 N_A}{\mathrm{k}T}\left(\pi^2\frac{E^{\mathrm{T}}}{\mathrm{k}T}\right)^{1/4}\exp\left[-2\left(\frac{E^{\mathrm{T}}}{\mathrm{k}T}\right)^{1/2}\right] + \frac{c}{T} \qquad (3)$$

Correspondingly, dependence μ_{eff}(T) can be written as:

$$\mu_{\text{eff}}(\mathrm{T}) = \frac{4\mu_B g}{T^{1/8}}\sqrt{\left(\frac{\pi^2 E^{\mathrm{T}}}{\mathrm{k}^{5/4}}\right)^{1/4} N_A}\exp\left(-\sqrt{\frac{E^{\mathrm{T}}}{\mathrm{k}T}}\right) + c \qquad (4)$$

The energy of the triplet state, E^{T}, was determined from an approximation of μ_{eff}(T) for ***SpI*** (Fig. 4a) and ***Sp2I*** (Fig. 4b) by eqn (4). The energy of the triplet state was found to be 0.023 eV for ***SpI***, 0.032 eV for ***Sp2I***, respectively. The E^{T} values are in good agreement by way of their order of magnitude with those reported by other authors for the magnetism of similar cyclic molecules. For example, the activation energy of the triplet states of bis-hydrazine is 0.018 eV.[20] Thus, the origin of the observed magnetic phenomena is the thermal populating of triplet states of the spiropyran molecules. The temperature dependencies of the effective magnetic moment, μ_{eff}(T), are described satisfactorily in terms of the thermally stimulated triplet paramagnetism of organic molecules.

It can be derived from eqn (4) and from the calculated E^{T} values that μ_{eff} should decrease to a value lower than 0.01 μ_B

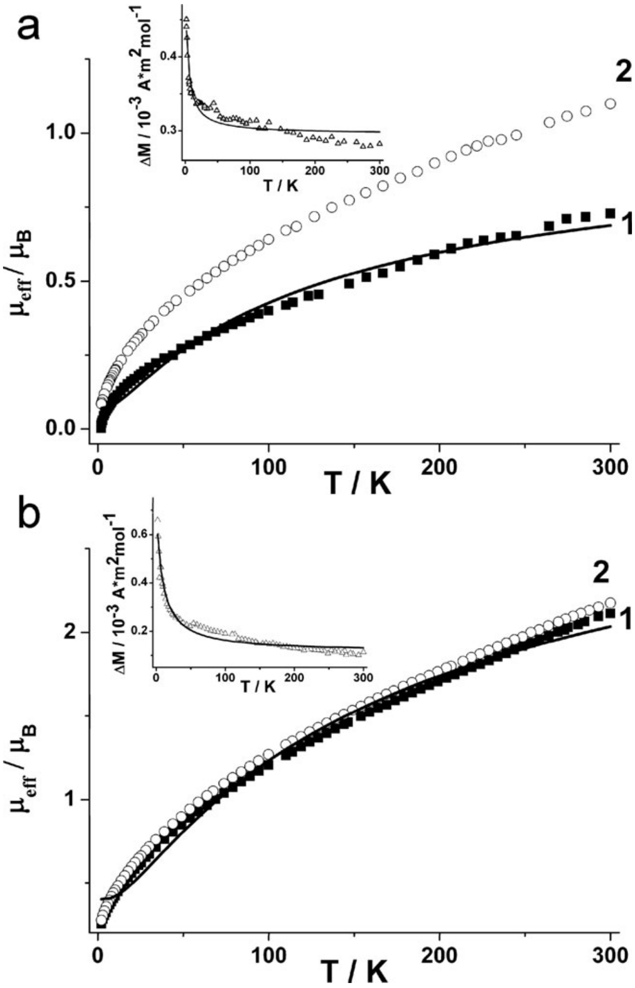

Fig. 4 The temperature dependence of the effective magnetic moment, μ_{eff}, for (a) ***SpI*** and (b) ***Sp2I*** (1) before and (2) after irradiation. Approximations by eqn (4) are shown using solid lines. The insets show the temperature dependence of the increment of the magnetic moment, ΔM, under light irradiation and their approximations by Curie's law.

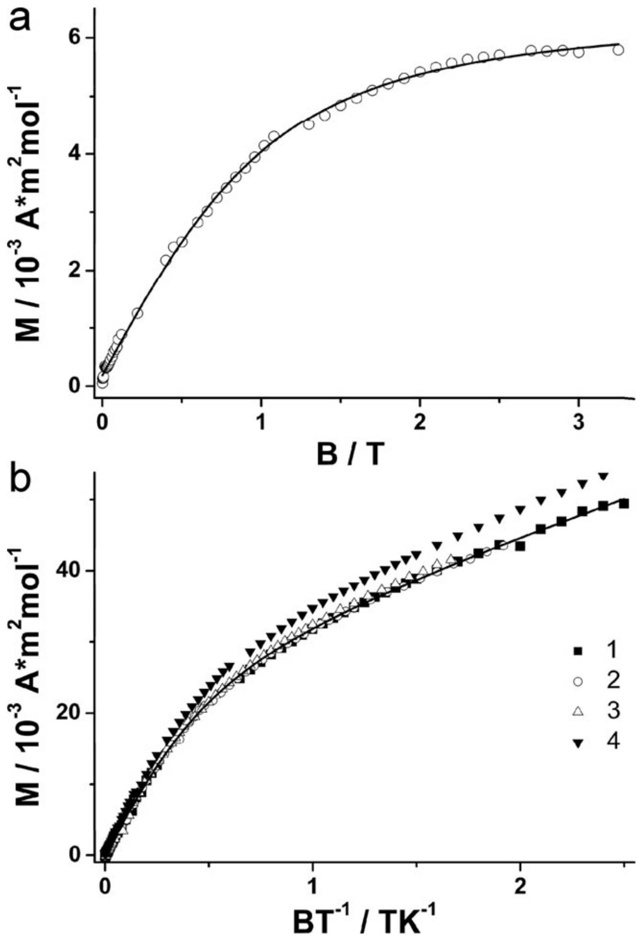

Fig. 5 (a) The dependence of magnetic moment M on magnetic field B for ***SpI*** before irradiation at $T = 2$ K. The approximation by the Brillouin function is shown using a solid line. (b) The dependence of magnetic moment M on B/T for ***Sp2I*** measured before irradiation at $T =$ (1) 2 K, (2) 2.5 K and (3) 3 K, and (4) after irradiation at $T = 2$ K. The approximation by the Brillouin function is shown using a solid line.

with a temperature reduced to 2 K. However, an order of magnitude higher value of $\mu_{\mathrm{eff}} \sim 0.1\ \mu_B$ is observed in the experiments at $T = 2$ K. Since the contribution of thermally-stimulated triplet paramagnetism in spiropyrane molecules is negligibly small at low temperatures ($T < 10$ K), the discrepancy between the experimental effective magnetic moment, μ_{eff}, and the calculated one is due to the presence of other paramagnetic particles in the samples. To determine the spin of these particles, we approximated the field dependencies, M(B), for ***SpI*** and ***Sp2I*** using the Brillouin function (Fig. 5). It was found that the main contribution to the magnetic moment is made in non-irradiated ***SpI*** at $T = 2$ K by particles with an average spin value of $S = 2.7$ (Fig. 5a). The number of particles determined from the approximation is four orders of magnitude lower than the concentration of spiropyrane molecules calculated from the mass and molar mass of the sample. The spin value was found to be $S = 3$ for the paramagnetic particles from the approximation of the M(H) dependence using the Brillouin function for ***Sp2I*** at $T = 2$ K. The concentration of the particles is 1.5×10^3 lower than that of the ***Sp2I*** molecules. Since the value $S = 3$ is much higher than the spin of triplet states $S = 1$, the M(B) dependencies were additionally measured at 2.5 and 3 K to verify the Brillouin dependence. After this, all of the M(B) dependencies for the non-irradiated and irradiated ***Sp2I*** molecules were built into M(B/T) coordinates (Fig. 5b). The M(B/T) dependencies for the paramagnetic particles were built in such way for the different temperatures that they fitted within the same curve, as described by the Brillouin function. Obviously, the M(B/T) dependencies for the non-irradiated ***Sp2I*** molecules are highly accurate within the same curve (Fig. 5b). It can be derived that neither the concentration nor the spin of the particles are temperature-independent, *i.e.* both of them follow Curie's law and their paramagnetism is not of thermally-stimulated origin. The M(B/T) dependence for irradiated ***Sp2I*** (Fig. 5b, experimental data points set 4) is not within the same curve as those measured before irradiation. An approximation of M(B/T) for ***Sp2I*** allowed us to conclude that the deviation of the field dependence after irradiation from similar dependencies measured before

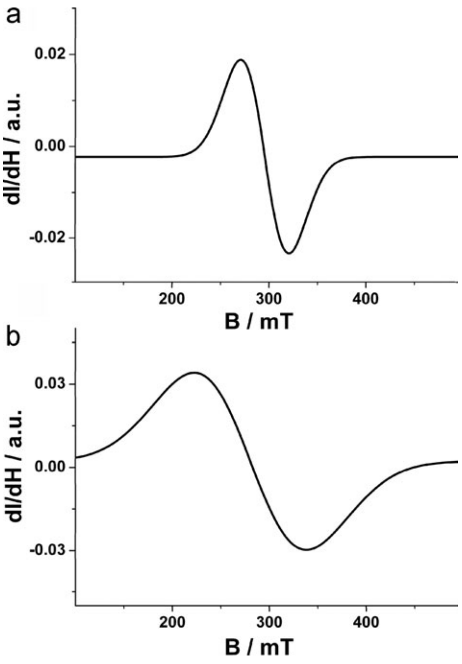

Fig. 6 The ESR spectrum of (a) ***SpI*** and (b) ***Sp2I*** at $T = 300$ K.

irradiation is not due to the changes in spin, but that it instead corresponds to the 15% increase in the number of paramagnetic centers. This implies that the concentration of stable paramagnetic particles with $S = 3$ increases under light irradiation.

The low concentration of high spin ($S = 3$) paramagnetic centers and their increasing number under light irradiation indicates that these centers are radiation defects. If the atoms of impurities that are inevitably present in a compound are such centers, their number would be constant and no increase in their concentration under light irradiation would be observed. Another possible source of paramagnetic centers are spiropyrane molecules with broken intrinsic bonds that bear paired electrons with non-zero spins. The number of broken bonds and unpaired electrons would grow under light irradiation to provide increasing numbers of paramagnetic centers. Similar high-spin organic molecules are well known and widely reported. For example, ref. 21 reports a detailed investigation of trinitrene compounds, formed as a result of photolysis, whose spin is $S = 3$.

The value of the photoinduced magnetic moment, ΔM (see insets in Fig. 4a and b), decreases with increasing temperature and qualitatively follows Curie's law rather than the dependence of triplet paramagnetism. The photoinduced growth of μ_{eff} in ***Sp2I*** is 0.021 μ_B at $T = 2$ K. Since the increase in magnetic moment at low temperatures is due to the appearance of additional high-spin ($S = 3$) "defective" spiropyrane molecules, it is reasonable that the positive ΔM value and the magnetic moment growth under light irradiation at high temperatures are also due to the formation of "defective" spiropyrane molecules with temperature-independent spins. In other words, after UV irradiation, the number of radiation defects that obey Curie's law is increased (Fig. 4b) and the effective magnetic moment, μ_{eff}, also increases at all temperatures. That is to say, the influence of UV irradiation on the magnetic properties is reduced to increasing the number of paramagnetic radiation defects. A similar mechanism is realized in ***SpI***, in which irradiation also provides an increased effective magnetic moment (Fig. 4a).

Thus, the main contribution to the magnetic moment of ***SpI*** and ***Sp2I*** at low temperatures is made by high-spin particles, which are radiation defects. With increasing temperature, the contribution of these particles decreases in accordance with Curie's law and the contribution of triplet paramagnetism increases. Therefore, the main contribution to the magnetic moment at high temperatures is made by thermally-excited spiropyrane molecules.

To prove this assumption we measured room temperature ESR spectra. The g-factor values of the ESR lines (2.23 for ***SpI*** and 2.35 for ***Sp2I***) are larger than $g = 2$, *i.e.* that of a free electron. It was also reported in ref. 10 that an ESR line with a g-factor larger than 2 was observed for spiropyrane molecules. Since the contribution of high-spin ($S = 3$) defects decreases and that of triplet spiropyrane molecules increases with increasing temperature, it is most probable that the ESR lines correspond to spiropyrane molecules. Since spiropyrane molecules ***SpI*** and ***Sp2I*** differ in structure, one might expect differences in their crystal field parameters, and hence different g-factors. Therefore, the different g-factors are indirect evidence that the ESR lines can be ascribed to spiropyrane molecules.

Firstly, attention should be paid to the essential half-width, $\Delta H_{\frac{1}{2}}$, of the ESR lines (49 mT for ***SpI*** and 120 mT for ***Sp2I***) and, secondly, the strongly different $\Delta H_{\frac{1}{2}}$ values for ***SpI*** and ***Sp2I***. Contributions to the ESR linewidth can come from magnetic dipole–dipole interactions between spiropyrane molecules, spin relaxation and the fine structure of the ESR lines. The contribution of dipole–dipole interactions, ΔH_{p}, can be expressed as follows:[22]

$$\Delta H_{\mathrm{p}}{}^2 = 5.1(g\mu_B n)^2 S(S + 1) \qquad (5)$$

where n is the concentration of paramagnetic centers and $S = 1$ (the spin of triplet spiropyrane molecules). The value of dipole broadening, determined from eqn (5), is similar for ***SpI*** and ***Sp2I***, $\Delta H_{\mathrm{p}} = 11$ mT. This value is much lower than the $\Delta H_{\frac{1}{2}}$ values determined experimentally, *i.e.* the observed ESR linewidths cannot be due to dipole–dipole interactions. Therefore, the main contribution to the ESR linewidths is caused by anisotropy of the resonance field of the ESR lines.

5. Conclusion

It was found that a population of excited triplet states in iodide salts of photochromic spiropyrane molecules could be realized, with temperature increases providing the appearance of paramagnetic properties. The energies of the triplet states of the molecules were determined from the temperature dependence of their effective magnetic moment: 0.023 and 0.032 eV, respectively. It was shown that at low temperatures, the main contribution to the magnetic moment is made by high-spin ($S = 3$) paramagnetic particles generated by light irradiation. ESR signals were detected, which were attributed to the spiropyrane cations.

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