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The role of sulphur 3d orbitals in spin-orbit coupling of thiopurines and thiopyrimidines

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We present a theoretical and experimental investigation of the spin-orbit coupling mechanisms in sulphur-substituted nucleic acid components. If the sulphur 3d orbitals take part in π -electron configuration, new spin-orbit coupling paths appear. We have studied the phosphorescence of sulphur-containing pyrimidines and purines at 77 K and in the range 1.42-4.2 K.

1. INTRODUCTION

Sulphur-substituted purines and pyrimidines are of some importance in biological systems. Thionucleosides are found as minor constituents in transfer ribonucleic acids [1] and in ribosomic ribonucleic acids [2]. Thiopurine derivatives have been shown to have anti-tumour and other inhibitory properties. The optical properties of these compounds have been used successfully [3] for analytical and structural applications. It was therefore of interest to investigate in more detail the electronic structure and spectra of these molecules. In previous papers [4-6] absorption and luminescence spectra of thiopurines and pyrimidines were presented. The replacement of an oxygen by a sulphur atom in caffeine was shown to induce a red shift of the absorption, a quenching of the fluorescence and a drastic shortening of the phosphorescence lifetime. Polarization studies showed that the phosphorescence of 6-thioxanthine, 2,6-dithiopurine and 2-thiouracil is mainly polarized in the molecular plane, in contrast with the case of the parent oxy-compounds where it is mainly out-of-plane polarized. These experimental results showed that the spin-orbit coupling (S.O.C.) mechanisms were different in oxygen and sulphur derivatives. We suggested [4-7] that the sulphur 3d orbitals could take part in the π -electron system. In this paper we present a detailed theoretical investigation of this conjecture along with a study of the phosphorescence of sulphur derivatives in the liquid helium temperature range. We conclude that the sulphur 3d orbitals indeed provide an efficient S.O.C. path for the deactivation of the triplet state in these compounds.

2. Experimental

6-Thiopurine was purchased from Cyclo Chemical Co. or from Schwarz Bioresearch Co., and was used as received. 6-Thiocaffeine was prepared by the reaction of phosphorus pentasulphide on caffeine in pyridine [8]. 2,6-Dithiocaffeine was obtained by reacting caffeine with P_2S_5 in kerosene at 220°C to 250°C, following a method described by Khalestskii and Estman [9]. Unreacted caffeine was removed by chromatography on silica. The products were crystallized from chloroform. A similar synthesis, starting from 1,3-dimethyluracil, yielded 1,3-dimethyl 6-thiouracil. All samples were made from ethanolether (1 v/1 v) solutions. Concentrations were kept close to $2.5 \times 10^{-4} \text{ M}$, which corresponds to an optical density of one for the thickness of our samples Absorption spectra were recorded on a Cary 14 spectrophotometer, $(2 \text{ mm})^{+}$. equipped with a cryostat which could be used in the range 70 K-300 K. Luminescence and polarization studies were performed with an automatic spectrophotometer built in this laboratory. Excitation spectra were automatically corrected for changes in exciting light intensity by means of a quantum counter [7, 10]. Emission spectra were corrected by means of a calibration This curve was derived from a comparison of the experimental spectra curve. of quinine sulphate, naphthalene and anthracene with published spectra at room The polarization ratio p was obtained from the following temperature [11]. relation [12]:

$$p = \frac{I_{\rm vv} - I_{\rm vh}(I_{\rm hv}/I_{\rm hh})}{I_{\rm vv} + I_{\rm vh}(I_{\rm hv}/I_{\rm hh})}.$$
(1)

The I's are signal intensities, the first (second) subscript denotes the polarization direction of the exciting (analysing) beam. Our apparatus automatically measures the four intensities and computes p for a given wavelength. A detailed description will appear elsewhere.

For the temperature range 1.4-4.2 K, the sample was contained in a quartz tube which was dipped into a liquid helium bath. Temperatures below the boiling point were obtained by pumping on the bath and were determined from They are accurate to within measurements of the helium vapour pressure. To record phosphorescence decays, the exciting light was cut off ± 0.01 K. with a rotating sector which also triggered the sweep of a digital averager. This apparatus (RE 10 unit, custom modified by the maker REE) uses either a The latter proved useful when several linear or a pseudo-logarithmic sweep. Moreover, a variable delay $(10^{-6} \text{ to } 1 \text{ s})$ decay times were present in the sample. could be introduced before the start of a sweep. About 16 decays were accumulated for each sample and temperature; the contents of the memory were then printed and plotted on semi-log paper. Quantum yields were determined by comparison with benzophenone ($\phi_p = 0.8$) and 9,10-diphenylanthracene ($\phi_F =$ 1.0). If τ_{pn} is the natural lifetime, the radiative lifetime τ_{pr} was computed from the relation $\tau_{pr} = \tau_{pn} \cdot \phi_{isc} / \phi_p$, where ϕ_{isc} is the intersystem crossing yield. For 6-thiopurine, we have shown previously [6] that $\phi_{isc} = 1$. In other cases, $\phi_{\rm isc}$ is unknown. We therefore give the limiting values of τ_{pr} , computed, assuming either $\phi_{isc} = 1$ or $\phi_{isc} = \phi_p$.

3. Absorption and emission properties at 77 K

The formulae of the four sulphur derivatives studied in the present work are collected in figure 1. Among these, 6-thiopurine can be found under several tautomeric forms. We compared its spectra with those of 6-methylthiopurine and could thus ascertain that 6-thiopurine is, in our case, in the thione form.



Figure 1. Formulae of 6-thiopurine (6 TP), 6-thiocaffeine (6 TC), 2,6-dithiocaffeine (2,6 TC) and 1,3-dimethyl-6-thiouracil (6 TU).

Bergmann *et al.* [13] have obtained absorption spectra of 6-thiopurine and of several methyl derivatives : their results confirm our assignment. Absorption and emission spectra were presented in previous papers [4-6]. For 1,3-dimethyl 6-thiouracil similar spectra are obtained (figure 2). Relevant results are collected in tables 1 and 2. We mention orbital assignments for the first two singletsinglet bands, on the assumption that these molecules are planar and remain so in their singlet excited states. The choice between $n\pi$ and $\pi\pi$ was made on the basis of the oscillator strength. Two values are given for each phosphorescence



Figure 2. Absorption (left) and phosphorescence (right) spectra of 1,3-dimethyl-6-thiouracil at 77 K in a glass of ethanol-ether (1 v/1 v). Broken line: polarization spectra of phosphorescence upon exciting the 0-0 band of absorption (353 nm.)

polarization ratio: p_1 and p_2 correspond to excitation into S_1 and S_2 respectively. From the value of p_i (i=1, 2) we derive the angle θ_i between the absorption (\mathbf{M}_i) and phosphorescence (\mathbf{M}_n) transition moments, through the formula [14]

$$p_i = \frac{3\cos^2\theta_i - 1}{\cos^2\theta_i + 3}.$$
(2)

If the angle between \mathbf{M}_1 and \mathbf{M}_2 were known, the direction of \mathbf{M}_p could be determined. Since this is not the case, we have computed the range of allowed orientations for \mathbf{M}_p when the angle $(\mathbf{M}_1, \mathbf{M}_2)$ is varied between 0 and 90°. Our results are shown in table 2, in the following form. The length of \mathbf{M}_p was assumed to be unity, the components of \mathbf{M}_p in the molecular plane (M_p^{\parallel}) and perpendicular to this plane (M_p^{\perp}) were computed. Limiting values of M_p^{\parallel} and M_p^{\perp} are given for each compound. The in-plane component of \mathbf{M}_p is seen to be rather large.

	$\frac{{\nu_{00}}^1}{{ m cm}^{-1}}$	nature	$\frac{{\nu_{00}}^2}{\mathrm{cm}^{-1}}$	nature	$\frac{\nu_{00}^{P}}{\mathrm{cm}^{-1}}$	$\Delta E_{\mathrm{ST}}/\mathrm{cm}^{-1}$ $^{1}\pi\pi^{*}-\mathrm{T})$	$\Delta E_{ m ST}/ m cm^{-1}$ $^{1}n\pi^{*}- m T)$
6-thiopurine	28 550	$\pi\pi^*$	44 050†	$\pi\pi^*$	21 980	6570	
6-thiocaffeine	23 260	$n\pi^*$	28 400	$\pi\pi^*$	20 790	7620	2470
2,6-dithio- caffeine	22 470	$n\pi^*$	27 750	$\pi\pi^*$	20 260	7490	2210
1,3-dimethyl- 6-thiouracil	28 330	$l \rightarrow a_{\pi}$ or $\pi \pi^*$	39 200‡	$l \rightarrow a_{\pi}$ or $\pi \pi^*$	20 830	7500	

Table 1. Absorption and phosphorescence 0-0 bands of sulphur-containing purines and pyrimidines derivatives. † The second absorption band of 6-thiocaffeine is detected as a shoulder. ‡ Energy of the maximum of absorption.

	Φ_p	$\frac{\tau_{pn}}{ms}$	$\frac{\tau_{pr}}{ms}$	Þ 1	Þ2	M_p^\perp	M_p
6-thiopurine	0.25 ± 0.02	13.5	54	-0.21	-0.10	00.88	1-0.48
6-thiocaffeine	0.43 ± 0.05	24	24–56	+0.12	+0.10	0-0.73	1-0.67
2,6-dithiocaffeine	0.65 ± 0.05	13.5	13.5-21	-0.05	+0.11	0-0.73	1-0.53
1,3-dimethyl- 6-thiouracil	$0{\cdot}30\pm0{\cdot}05$	3	3–10	+0.35		0-0-48	1-0.88

Table 2. Luminescence characteristics of sulphur-containing purine and pyrimidine derivatives in a glass of ethanol-ether at 77 K. τ_{pn} is the natural phosphorescence lifetime. The radiative lifetime τ_{pr} is computed from the relation: $\tau_{pr} = \tau_{pn} \cdot \phi_{\rm isc}/\phi_p$ (see text). p_1 and p_2 are polarization ratios of the 0-0 band of phosphorescence upon excitation into the first or second absorption band respectively. Under the headings M_{\perp} and M_{\parallel} , we give the computed limiting values of the outof-plane and in-plane components of \mathbf{M}_p , the phosphorescence transition moment.

Spin-orbit coupling

The data of tables 1 and 2 show that sulphur-substituted purines and pyrimidines have a high quantum yield and short radiative lifetime for phosphorescence. This efficient S.O.C. could be due to an enhancement of mechanisms already present in the parent (oxy) compound [5, 15] by the heavy atom effect. However, the two series of compounds differ by the polarization of phosphorescence, the sulphur derivatives showing a distinct in-plane polarization. This is a hint that different S.O.C. mechanisms are operative in thiopyrimidines and thiopurines.

4. PHOSPHORESCENCE AT LIQUID HELIUM TEMPERATURE

Spin-lattice relaxation between the triplet sublevels is strongly temperature dependent. At 77 K it is fast enough to maintain Boltzmann equilibrium among the sublevels. Since the zero-field splittings are small compared to kT, the populations of the sublevels are almost equal, and the lowest triplet manifold appears as a single level in optical experiments. At 4 K or lower, spin-lattice relaxation is slow, the sublevels are isolated from each other. It is then, in principle, possible to determine population and depopulation rates for each sublevel [16]. When three decay rates τ_1 , τ_2 , τ_3 are observed, they must fulfil the condition

$$1/\tau_1 + 1/\tau_2 + 1/\tau_3 = 3/\tau_{77}.$$
(3)



Figure 3. Decay of phosphorescence of 6-thiocaffeine observed at 481 nm in a mixture of ethanol-ether (1 v/1 v) at 1.52 K. Right: decay observed 200 ms after the cutoff of the excitation beam $(\bigcirc \bigcirc \bigcirc \bigcirc$). Left: decay observed immediately after the cut-off of the excitation beam $(\bigcirc \bigcirc \bigcirc \bigcirc$). The fast decay (+ + +) is computed by subtraction of the long decay (see text). The excitation beam is cut in 15 ms.

The definite space \otimes spin symmetry of a given sublevel should then allow one to unravel the relevant S.O.C. mechanisms. Our attempts in this direction are described in this section.

The phosphorescence decay times were monitored between 4.2 and 1.46 K. In each case the largest decay time was seen to reach a plateau at the lower end of the temperature range. We take this as evidence that isolation of the sublevels then obtains, at least approximately.

4.1. 6-Thiocaffeine

The phosphorescence decay of 6-thiocaffeine is exponential at 77 K ($\tau_{77} = 24 \text{ ms}$) and at 4.2 K ($\tau_{4.2} = 38 \text{ ms}$). At lower temperatures it is a sum of two exponentials. Figure 3 shows how the data were handled. Two decay curves were recorded, using light from the 0-0 transition: one recording started immediately after the excitation, the other after a delay of 200 ms. This delayed recording yielded a single lifetime (52 ms). It was then assumed that the latter part of the undelayed recording was exponential with this same lifetime. By subtraction we then determined that the earlier part of the decay was exponential with lifetime 18 ms. Extrapolating back to time zero, we find the relative intensities of the fast and slow components to be 0.39 and 0.61. A similar procedure was followed in all other cases. Using relation (3), we find



Figure 4. Decay of phosphorescence of 2,6-dithiocaffeine observed at 489 nm in a mixture of ethanol-ether (1 v/1 v) at 1.46 K $(\bigcirc \bigcirc \bigcirc)$. The fast decay (+ + +) is obtained by subtraction of the slow component (24 ms) from the observed decay $(\bigcirc \bigcirc \bigcirc)$. The excitation beam is cut in 15 ms.

for the third lifetime $\tau_3 = 20$ ms. This value is so close to 18 ms that the two exponentials cannot be separated. Identical results (except for small changes in the relative weights) are found when the decay is monitored at different wavelengths.

4.2. 2,6-Dithiocaffeine

The phosphorescence decay is here exponential, at 77 K ($\tau_{77} = 14.5$ ms) and at 4.2 K ($\tau_{4.2} = 17.5$ ms). At 1.46 K (figure 4), it appears as a sum of two exponentials: $\tau_1 = 24$ ms and $\tau_2 = 12$ ms, with normalized intensities at time zero 0.73 and 0.27 respectively. The third lifetime is computed as $\tau_3 = 12 \pm$ 2 ms, again indistinguishable from τ_2 . These results are independent of emission wavelength.



Figure 5. Decay of phosphorescence of 1,3-dimethyl-6-thiouracil in a mixture of ethanolether (1 v/1 v) at 1.46 K, recorded at 480 nm, 8 ms and 24 ms after the cut-off of the excitation beam. The fast component ($\bigcirc \bigcirc \bigcirc$) is obtained as the difference between the slow decay and the total decay ($\triangle \triangle \triangle$).

4.3. 1,3-Dimethyl-6-thiouracil

The decay is exponential at 77 K ($\tau_{77} = 2.7$ ms) and at 4.2 K ($\tau_{4.2} = 3.3$ ms). When the temperature is lowered to 1.46 K, the decay curve appears to be made up of three exponentials characterized by lifetimes of 12.7, 4.2 and 1.4 ms and by initial intensities of 0.6, 0.11 and 0.27 respectively (figures 5, 6). The three rates sum to 1104 s⁻¹, close to $3/\tau_{77} = 1110$ s⁻¹. Recording the decay of other vibronic components produced similar lifetimes and slightly different initial intensities.



Figure 6. Decay of phosphorescence of 1,3-dimethyl-6-thiouracil in a mixture of ethanolether (1 v/1 v) at 1.46 K, recorded at 480 nm immediately after the cut-off of the excitation beam (+ + +). The curve (□□) is obtained by subtraction of long decay (12.7 ms) from the total decay (+ + +). The decay corresponding to the short lifetime (4.2 ms) is drawn by comparison with figure 5. The difference between the two previous curves (□□) and (---) gives a third decay (○○○) The excitation beam is cut in 1 ms.

4.4. 6-Thiopurine

The phosphorescence decays exponentially, with a single lifetime $\tau_{77} = 13.5$ ms in the temperature range 77-4.2 K. At 1.46 K the decay of the 0-0 band is still exponential, with however a lifetime $\tau_1 = 28$ ms (figure 7) and $\tau_1 \neq \tau_{77}/3$. This means that, either isolation of the triplet sublevels is not established, or that the other two levels decay non-radiatively. Here, the phosphorescence spectrum is rather well resolved (figure 8), and more detailed information can be obtained. The same figure also shows a plot of the polarization ratio, for excitation into the 0-0 band of the S_0-S_1 transition. It is a strongly varying function of wavelength. We therefore expect the radiative characteristics of successive vibronic bands to be different. Indeed, when the triplet decay is monitored using a wavelength of 465 nm, it appears as a sum of two exponentials, of lifetimes 28 ms and 12 ms, with relative initial intensities 0.76 and 0.24 respectively (figure 9). This leads us to believe that sublevel isolation indeed obtains for 6-thiopurine at 1.46 K. We compute $\tau_3 = 11$ ms. It is also

interesting to note that the phosphorescence spectrum recorded at 1.6 K is different from that found at 4.2 K. The intensity of non-totally symmetric bands (p>0) decreases compared to that of symmetric components (p<0).

We now turn to a theoretical investigation of the spin-orbit coupling in the above compounds.



Figure 7. Decay of the phosphorescence of 6-thiopurine observed on the 0-0 band (453 nm) in a mixture of ethanol-ether (1 v/1 v) at 1.63 K immediately and 60 ms after the cut-off of the excitation beam. The excitation beam is cut in 3 ms.



Figure 8. Phosphorescence spectrum of 6-thiopurine in ethanol-ether (1 v/1 v) at 1.46 K (-----) and 4.2 K (-----). The broken line gives the polarization ratio p upon excitation in the 0-0 band of $S_0 \rightarrow S_1$ at 77 K.



Figure 9. Decay of the phosphorescence of 6-thiopurine observed at 465 nm (0→600 cm⁻¹ vibronic band) in a mixture of ethanol-ether (1 v/1 v) at 1.63 K (+++) immediately and 60 ms after the cut-off of the excitation beam. The subtraction of the slow component (29 ms) from total decay gives an exponential decay corresponding to a lifetime of 12 ms (○○○○). The excitation beam is cut in 3 ms.

5. Review of spin-orbit coupling mechanisms

Neglecting spin-other orbit coupling, we write the spin-orbit hamiltonian as

$$H_{\rm SO} = \frac{e^2}{2m^2c^2} \sum_{\mu,i} Z_{\mu i} \frac{\mathbf{L}_{\mu i} \cdot \mathbf{S}_i}{r^3_{\mu i}}$$
(4)

where \mathbf{S}_i is the spin angular momentum of electron i, $\mathbf{L}_{\mu i}$ its angular momentum relative to nucleus μ from which it is removed by the distance $r_{\mu i}$. $Z_{\mu i}$ is an effective nuclear charge, for S.O.C. of electron i in the field of nucleus μ . Using $H_{\rm SO}$ as a perturbation of the spinless hamiltonian, we find the well-known first-order approximation to the phosphorescence transition moment :

$$\mathbf{M} = \sum_{i} \frac{\langle {}^{1}\phi_{i} | H_{\rm SO} | {}^{3}\phi_{1} \rangle}{{}^{3}E_{1} - {}^{1}E_{i}} \ \mathbf{M}_{0i} - \sum_{l>1} \frac{\langle {}^{3}\phi_{1} | H_{\rm SO} | {}^{1}\phi_{0} \rangle}{{}^{3}E_{l}} \ \mathbf{M}_{1l} - \frac{\langle {}^{3}\phi_{1} | H_{\rm SO} | {}^{1}\phi_{0} \rangle}{{}^{3}E_{1}} \ \mathbf{M}_{1} + \frac{\langle {}^{1}\phi_{0} | H_{\rm SO} | {}^{3}\phi_{1} \rangle}{{}^{3}E_{1}} \ \mathbf{M}_{0}.$$
(5)

The unperturbed eigenvalues and eigenfunctions have been denoted as ${}^{1}E_{i}$, ${}^{1}\phi_{i}$ or as ${}^{3}E_{l}$, ${}^{3}\phi_{l}$. The M_{0i} are singlet-singlet transition moments, the M_{1l} triplet-triplet transition moments, while M_{0} and M_{1} are the static dipole moments of the ground state and the lowest triplet state.

Since the molecular geometry is not always planar in the phosphorescent triplet state, it is necessary to study S.O.C. mechanisms leading to radiative deactivation of the phosphorescent triplet state in both the planar and non-planar cases.

5.1. Planar molecule in the $3\pi\pi$ phosphorescent state

Here, we consider molecules having a single plane of symmetry. So, the out-of-plane component of the $T_1 \rightarrow S$ transition moment arises from the wellknown mechanisms ${}^{1}n\pi^{*}$, ${}^{1}\pi\sigma^{*}$, ${}^{1}\sigma\pi^{*}\leftrightarrow^{3}\pi\pi^{*}$ and ${}^{3}n\pi^{*}$, ${}^{3}\pi\sigma^{*}$, ${}^{3}\sigma\pi^{*}\leftrightarrow G.S.$ [17]. As in the oxygen analogue, these mechanisms lead to deactivation of the τ_x and τ_y sublevels [15, 25]. The in-plane components will derive from ${}^{1}\pi\pi^*$, ${}^{1}\sigma\sigma^* \leftrightarrow$ ${}^{3}\pi\pi^{*}$ and ${}^{3}\pi\pi^{*}$, ${}^{3}\sigma\sigma^{*}\leftrightarrow G.S.$ S.O.C. paths. Since the very large energy of $\sigma\sigma^{*}$ states appears in the denominator of formula (5), the S.O.C. mechanisms involving these states will be neglected. On the other hand, it is well known that S.O.C. between $\pi\pi^*$ states which are linear combinations of $2p_z$ atomic orbitals is very small [18]. There remains the possibility that incorporation of sulphur 3d orbitals in the $\pi\pi^*$ wavefunction could lead to large S.O.C. matrix elements [4-7, 19]. Indeed, the sulphur atom possesses 3d orbitals whose energy is close to that of the occupied 3d orbitals. Two of these orbitals $(d_{xz} \text{ and } d_{yz})$ could participate in the π -electron system (x and y are in the molecular plane, z is perpendicular to x and y). The component L_z of the angular momentum is able to mix singlet and triplet $\pi\pi^*$ states, since

$$\begin{bmatrix}
 L_z d_{xz} = i\hbar d_{yz}, \\
 L_z d_{yz} = -i\hbar d_{xz}.
 \end{bmatrix}$$
(6)

For example, considering only the one-centre terms we find

$$\langle {}^{1}\pi_{i}\pi_{j}^{*}|H_{\rm SO}|{}^{3}\pi_{i}\pi_{l}^{*}\rangle = i\frac{\zeta 3d}{2}\sum_{s}\left(C_{is}{}^{xz}C_{ls}{}^{yz} - C_{is}{}^{yz}C_{ls}{}^{xz}\right)$$
(7)

for sublevel τ_z and zero otherwise.

$$\zeta_{3d} = \frac{Z_{3d} e^2 \hbar^2}{2m^2 c^2} \langle 3d_u | r^{-3} | 3d_u \rangle \quad \text{with } u = xz \text{ or } yz. \tag{8}$$

If the 3d orbitals are described by Slater orbitals, we compute $\zeta_{3d} = 3.7 \text{ cm}^{-1}$ with $Z_{3d} = 4$. Wadt and Moomow [19] have shown that two-centre one-electron spin-orbit matrix elements could be of the same order of magnitude as the onecentre terms in the case of the L_z component. So, we conclude that the three sublevels of a $\pi\pi^*$ triplet in a planar molecule could be deactivated radiatively to the G.S. if 3d orbitals are conjugated with the π -electron system and that sublevel τ_z could be radiatively deactivated with in-plane polarization.

5.2. Molecule not planar in the phosphorescent triplet state

In this case, we cannot use the separation between σ and π -electron systems. So, each molecular orbital is a combination of p_x , p_y , p_z and 3d orbitals and S.O.C. induces the radiative deactivation to the G.S. of the three triplet sublevels with in-and-out-of-plane polarization.

5.3. Strong vibronic coupling

When two triplet states $({}^{3}n\pi^{*}$ and $\pi\pi^{*}$ for example) of a planar molecule are very close, the nuclear interaction could be sufficiently strong to mix these two electronic levels. The study of this case is developed by Hochstrasser and Marzzacco [20]. The wavefunction of the phosphorescent triplet state is written as

$$\psi_{\rm T} = \alpha^3 \pi \pi^* + \beta^3 n \pi^*. \tag{9}$$

Since the vibration which leads to mixing of the ${}^{3}n\pi^{*}$ and ${}^{3}\pi\pi^{*}$ states is outof-plane and antisymmetric, the new geometry which arises after a small deplacement along the normal coordinate is no longer planar. As in § 5.2, the three sublevels of the phosphorescent state could be radiatively deactivated to the G.S. with in-plane and out-of-plane polarization.

6. Discussion

6.1. 6-Thiocaffeine, 2,6-dithiocaffeine

Figure 10 shows the lower part of the energy level diagram for 2,6-dithiocaffeine. Since the ${}^{3}\pi\pi^{*}$ and ${}^{1}n\pi^{*}$ states are separated by 2200 cm⁻¹, the $n\pi^{*}$ singlet-triplet interval has to be smaller than this value. Assuming for this gap a reasonable value of 2000 cm⁻¹ [21], we find that the ${}^{3}n\pi^{*}$ and ${}^{3}\pi\pi^{*}$ must be 200 cm⁻¹ from each other. This small energy difference could lead to strong vibronic mixing between these two states, and to a non-planar distortion of the phosphorescent state. The three triplet sublevels would then be radiatively deactivated towards the vibrationless ground state, in agreement with experimental results. We believe that a similar state of affairs holds for 6-thiocaffeine.



Figure 10. Energy of the first two singlet and triplet states of 2,6-dithiocaffeine.

6.2. 1,3-Dimethyl-6-thiouracil

Saenger and Scheit [22] have shown by X-ray diffraction that 6-thiouridine is not planar in the crystal (the C = S band is out of the molecular plane). We

will assume that the analogous molecule 1,3-dimethyl-6-thiouracil is also not planar in its triplet state. So, using the results of § 5.3, we find that the three sublevels could be deactivated to the 0-0 band of the G.S. with in-plane and out-of-plane polarization in accordance with the experimental results.

6.3. 6-Thiopurine

Since the characteristics of the phosphorescence of 6-thiopurine are independent of polarity of solvents, we have ascribed a pronounced $\pi\pi^*$ character to the triplet state of this compound. On the other hand, the lower excited singlet state is $\pi\pi^*$ in nature and the large gap of energy (6570 cm⁻¹) with the lower triplet state is another good argument for reaching this conclusion. Moreover, the phosphorescence polarization shows a transition moment perpendicular to the molecular plane. These properties, added to the fact that Sletten et al. [23] and Brown [24] have shown that 6-thiopurine is planar in the crystal, suggest that S.O.C. mechanisms are as described in \S 5.1, without an important participation of 3d sulphur orbitals. On the other hand, this mechanism suggests the deactivation of two sublevels to symmetric levels of the G.S. Since this is not experimentally the case, we shall assume that the radiative deactivation of one of these two levels is too small to be observed in our experiments. The third lifetime observed on unsymmetrical vibronic levels of G.S. shows a very efficient spin-orbit vibronic coupling. These characteristics can be described by the well-known mechanisms :

or

${}^{H_{SO}}_{3\pi\pi^* \leftrightarrow^1 n\pi^* \leftrightarrow^{1}\pi\pi^*} {}^{H_{ve}}_{3\pi\pi^* \leftrightarrow^3 n\pi^* \leftrightarrow^{1}\pi\pi^*}.$

7. Conclusion

We have seen that the inclusion of sulphur 3d orbitals in the π -electron system is not needed to explain the large phosphorescent quantum yield of thiopyrimidines and thiopurines. On the other hand, the participation of sulphur 3d orbitals leads to an enhancement of the in-plane component of the phosphorescent transition moment. This mechanism should not be neglected with respect to other paths of radiative deactivation.

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