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Ground and excited state dipole moments of pyranthione and xanthione by the electro-optic method

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Electric field-induced changes in the absorption spectrum (electrochromism) have been used to obtain the ground (S_0) and second excited (S_2) state dipole moments of two sulphur-containing heteroaromatics, pyranthione and xanthione, which have C_{2v} symmetry. The magnitude of the change in the dipole moment ($\Delta\mu = |\mu(S_2) - \mu(S_0)|$) was found to be nearly 2 D for both compounds, which is consistent with results reported previously based on microscopic solvent shifts. The transition dipole moment for the S_0 - S_2 transition is parallel to the direction of the ground state dipole moment (μ_g), i.e. along the C_2 axis which contains the C=S bond. For comparison the ground state dipole moments of both compounds have also been calculated using the AM1 method with full geometry optimization.

1. Introduction

Aromatic thioketones, such as pyranthione (PT) and xanthione (XT) (fig. 1), have unusual excited state properties, which are distinctly different from their ketone analogues [1,2]. For example, thioketones exhibit relatively large quantum yields of fluorescence from the $S_2(\pi, \pi^*)$ state and intense phosphorescence from T_1 in fluid, deoxygenated solution at room temperature. Consequently, thioketones are particularly useful model compounds for carrying out detailed multi-state, photophysical and photochemical studies.

The lowest excited singlet states of the aromatic thioketones and the aromatic ketones are both of $^1(n, \pi^*)$ (1A_2 in C_{2v} local symmetry) character, whereas the second excited singlet states are $^1(\pi, \pi^*)$ (1A_1). However CNDO/2-CI MO calculations by Huber and co-workers [3], indicate that there is apparently a striking difference between the

ketones and thioketones in the nature of their S_2 - S_0 transitions. These calculations suggest that the S_2 - S_0 transition is localized mainly in the rings in the ketones, whereas in thioketones this transition appears to have considerable charge transfer character involving a displacement of electron density from the thiocarbonyl sulphur atom to the adjacent carbon atom and carbon atoms in the rings. If this prediction is true one would expect a decrease in the electric dipole moment of the thioketone upon excitation to its S_2 state, similar to an $n \rightarrow \pi^*$ transition. Even though recent results based on the analysis of both macroscopic [4] and microscopic [5] solvent shifts support this prediction, the actual magnitude of the change in the dipole moment has not yet been experimentally measured.

Electro-optic techniques are the excellent ways of obtaining excited state dipole moments and transition moment directions of dipolar molecules [6,7]. This electro-optic method has been employed here to gain more insight into the excited state properties of the aromatic thioketones. These data are of importance in interpreting the photophysical properties of thiones, a subject which is under active investigation in this laboratory.

For dipolar molecules in solution the electronic absorption intensity can be perturbed by subjecting

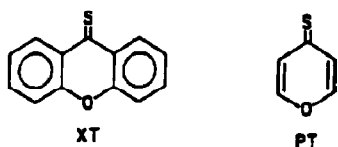


Fig. 1. Thione structures, XT, xanthione; PT, pyranthione.

the solution to a strong external electric field. Two factors are mainly responsible for the electric field-induced perturbations; (i) the production of an anisotropic molecular distribution and (ii) a change in the electronic transition energy if the ground state electric dipole moment, μ_g , is different from the excited state dipole moment, μ_e . The theoretical expression relating the change in the extinction coefficient, $\Delta\epsilon$, to the frequency, ν , of the incident light, the internal field strength, F_{int} , and the angle χ , between the direction of the applied field and the plane of polarization of the incident light, according to Liptay [6], is

$$\Delta\epsilon = F_{int}^2 \epsilon \left(A_\chi + \frac{B_\chi}{15h} \frac{1}{\epsilon/\nu} \frac{d}{d\nu} (\epsilon/\nu) + \frac{C_\chi}{30h^2} \frac{1}{\epsilon/\nu} \frac{d^2}{d\nu^2} (\epsilon/\nu) \right), \quad (1)$$

where A_χ , B_χ and C_χ are related to the dipole moment parameters of the molecule by the following expressions:

$$A_\chi = \frac{1}{30} (3 \cos^2 \chi - 1) \beta^2 [3(\hat{m} \cdot \mu_g)^2 - \mu_g^2] + 3\beta(\alpha_{gm} - \bar{\alpha}_g), \quad (2)$$

$$B_\chi = 5\beta(\mu_g \cdot \Delta\mu) + \frac{15}{2} \Delta\bar{\alpha} + (3 \cos^2 \chi - 1) \beta [3(\hat{m} \cdot \mu_g)(\hat{m} \cdot \Delta\mu) - (\mu_g \cdot \Delta\mu)] + \frac{3}{2} (\Delta\alpha_m - \Delta\bar{\alpha}), \quad (3)$$

$$C_\chi = 5\Delta\mu^2 + (3 \cos^2 \chi - 1) [3(\hat{m} \cdot \Delta\mu)^2 - \Delta\mu^2]. \quad (4)$$

In these equations μ_g and α_g are the ground state dipole moment and polarizability, $\Delta\mu$ and $\Delta\alpha$ are the change in the dipole moment and polarizability upon electronic excitation, \hat{m} is a unit vector in the direction of the transition moment, α_{gm} is the component of the polarizability along the transition moment, $\Delta\alpha_m$ is the change in the polarizability along the transition moment, and $\beta = (kT)^{-1}$, where k is the Boltzmann constant and T is the temperature.

2. Methods and materials

Detailed descriptions of the electric field apparatus and the data analysis methods can be found elsewhere [7,8]. The value of the effective external field,

F_{ext} , is 3.768×10^4 V/cm for both compounds studied here. The externally applied field was converted to an internal field by using the spherical cavity approximation [9]. The absorption spectrum in the absence of the field was measured and its first and second derivative terms as a function of wavelength were computed numerically. For each molecule the spectra with electric field applied were then collected at three different values of χ and for each of several wavelengths within the S_2 - S_0 absorption band. The values of A_χ , B_χ and C_χ were then obtained by making a least-squares fit of the observed $\Delta\epsilon$ spectrum to a sum of the absorption spectrum and its first and second derivatives (see eq. (1)). The contribution from the second derivative term to the electric field signal was found to be very small, as observed for several other polar molecules [10-12]. This term was therefore neglected in the regression analysis. Finally, the molecular parameters were calculated from the slopes and intercepts of least squares plots of A_χ , B_χ versus $(3 \cos^2 \chi - 1)$ (see eqs. (2) and (3)).

Xanthione (XT) and pyranthione (PT) were synthesized and purified by previously reported methods [13]. Carbon tetrachloride solvent (BDH Omnisolve) was used as received. The solution was continuously circulated by a micro-pump from a reservoir to avoid significant photochemical decomposition.

3. Results and discussion

The electric field spectra of PT and XT in the S_2 - S_0 region at $\chi = 0^\circ$, 25° and 50° are shown in figs. 2 and 3, respectively. The discrete points are the values of $\Delta\epsilon$ obtained from the electric field measurements and the solid lines are obtained from the multiple linear regression fit of the experimental points to eq. (1). The excellent fit between the experimental data points and the theoretical curve indicates that the experimental results are adequately described by eq. (1).

Assuming that the polarizability terms are sufficiently small, the dipole moment terms can be obtained directly from eqs. (2)-(4). However, the data obtained in this way should be treated with caution since the magnitudes of α for the sulphur-containing heteroaromatics are expected to be significant. No

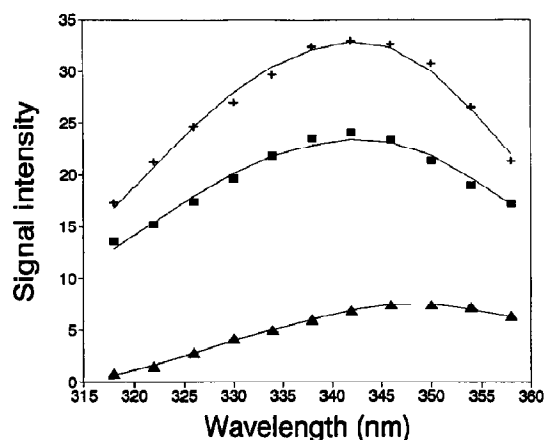


Fig. 2. Electric field spectra of XT in carbon tetrachloride at $\chi=0^\circ$ (+); 25° (■); and 50° (▲) and $T=298$ K.

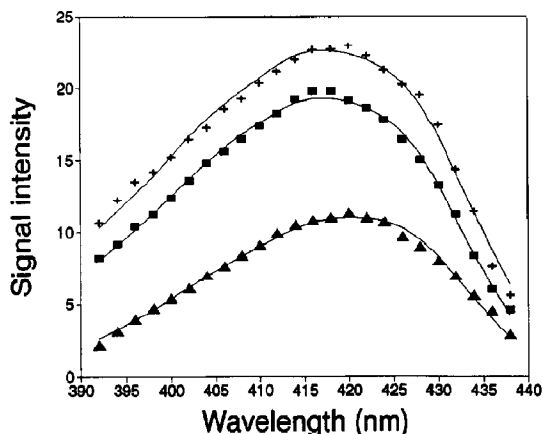


Fig. 3. Electric field spectra of PT in carbon tetrachloride at $\chi=0^\circ$ (+); 25° (■); and 50° (▲) and $T=298$ K.

data are yet available concerning the change in the polarizability upon electronic excitation in these molecules. Since both PT and XT are of C_{2v} symmetry, the transition dipole moment vector must be either parallel or perpendicular to the principal symmetry axis of the molecule (C_2) which is colinear with the dipole moment vector. The positive slopes obtained in the plots of A_χ versus $(3 \cos^2 \chi - 1)$ (see eq. (2)) indicate that μ_g and \bar{m} are parallel. This observation confirms the fact that the S_0 - S_2 transitions in PT and XT are polarized along the C_2 axis of the molecule, i.e. parallel to the C=S bond. This observation agrees with the theoretical predictions of Huber et al. [3] as well as with the results of ex-

perimental studies of the polarization of the optical transition in XT [3]. The values of $\Delta\mu \cdot \mu_g$ obtained independently from the slope and intercept using eq. (3) are nearly the same for both PT and XT, revealing that within experimental error $\Delta\mu$ is parallel both to μ_g and to the transition moment.

The value of μ_g obtained for XT (2.9 D) is much smaller than the experimental value obtained previously by a dielectric method (5.4 D) [14]. However, the present value is similar in magnitude to that of xanthone (3.0 D) (the ketone analogue of XT) obtained by Liptay [6] from an electro-optic measurement. We suspect that there may be an error in the value of μ_g reported earlier for XT for the following reasons. (i) The ground state dipole moments of PT and XT should be similar because the pyranthione ring is mainly responsible for the separation of charge. In fact, μ_g of XT is expected to be slightly smaller than that of PT, since additional aromatic rings generally tend to lower μ_g due to increased charge delocalization [7]. The ground state dipole moment of PT has been determined accurately by gas-phase second-order Stark effect measurements and has a value of 3.95 D [15]. Thus the existing value of 5.4 D for XT appears to be too large, whereas 2.9 D obtained here is more reasonable^{#1}. (ii) AM1 molecular orbital calculations with full ground state geometry optimization reproduce the μ_g of PT accurately, and predict the μ_g of PT (4.1 D) to be larger than that of XT (2.6 D), as observed in the present experiment (see table 1). (iii) For xan-

^{#1} Although no correction has been made for the effect of dipole reaction field or for the contribution of molecular polarizability to the electric field signals in the calculation of the dipole moment parameters, such corrections are not expected to change the results reported here significantly.

Table 1
Ground and excited state dipole moments of XT and PT^{a)}

	μ_g	$\Delta\mu \cdot \mu_g$	$\Delta\mu$	$\mu_c(S_2)$
XT	2.9 ± 0.3 2.6 ^{b)}	5.5 ± 0.2	1.9 ± 0.2	1.0 ± 0.5
PT	3.3 ± 0.3 4.1 ^{b)} , 3.9 ^{c)}	6.1 ± 0.2	1.8 ± 0.2	1.5 ± 0.5

^{a)} Dipole moments are in D.

^{b)} Obtained using AM1 method.

^{c)} Ref. [13].

thone, the ketone analogue of xanthione, Liptay [6] obtained $\mu_g = 3.0$ D which is similar in magnitude to our value of μ_g in XT. The experimental dipole moments of PT (3.95 D) [15] and its ketone counterpart (3.79 D) [15] are also similar so that the present results and those of Liptay et al. and the calculated results for μ_g are all apparently self-consistent.

The change in the dipole moment $\Delta\mu$ upon electronic excitation to the S_2^1 , (π , π^*), state is moderate (nearly 2 D) and similar in magnitude for both PT and XT. The quantity $\Delta\mu \cdot \mu_g$ is positive for both molecules indicating that $\Delta\mu$ and μ_g are parallel to each other. However, these results are not conclusive with respect to the magnitude of μ_e , i.e. whether μ_e is smaller or larger than μ_g . This is unlike the situation in azulene where $\Delta\mu \cdot \mu_g$ is negative confirming that the dipole moment reverses direction upon excitation to the S_2 state and that the absolute magnitude of μ_e is smaller than μ_g [16]. Other experimental evidence such as calculation of the microscopic solvent shifts induced by van der Waals complexation of rare gases with XT [5] and macroscopic solvent shift measurements [4] indicate clearly that the dipole moment of XT in its S_2 electronic state must be smaller than in the ground state. Based on these observations we conclude that the dipole moments of XT and PT decrease by nearly 2 D upon excitation to their S_2 states. The smaller μ_e values are mainly caused by charge transfer from the sulphur atom to the ring carbon atoms in accord with the CNDO/2-CI calculations. Unlike azulene, the respective directions of μ_e and μ_g remain the same in XT and PT, although $\mu_e < \mu_g$.

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