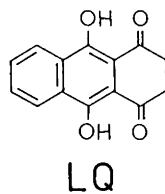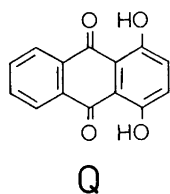*Short Communication*

Ultraviolet–Visible Linear Dichroism of Leucoquinizarin Aligned in Stretched Polyethylene

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Quinizarin (1,4-dihydroxy-9,10-anthraquinone, **Q**) is of particular interest as a model chromophore for the anthracycline antitumor drugs.[1–3] In a recent optical investigation,[2] the binding geometry of anthracycline–DNA intercalation was thus studied by specific reference to previously published linear dichroism (LD) data for **Q**.[4] However, it has subsequently been suggested that *in vivo*, the active form of the drug may be a reduced form with a model chromophore corresponding to leucoquinizarin (2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione, **LQ**).[3]

It is therefore of importance to establish precise LD reference data for **LQ**. In this communication, we report the results of a UV–VIS–LD spectroscopic investigation of **LQ** aligned in stretched polyethylene (PE).

Experimental

A sample of **LQ** was obtained from Aldrich; the purity of the compound was checked by ^{1}H and ^{13}C NMR spectroscopy.[5] The UV–VIS LD spectra were measured at room temperature in uniaxially stretched (400 %) low-density PE on a Shimadzu Model MPS-2000 spectrophotometer equipped with a rotatable Glan prism polarizer in the sample beam as previously described.[4,6] An attempt to obtain the corresponding IR LD spectra failed, apparently because of poor solubility of the compound in PE.

LQ was introduced into the polymer from solutions in

chloroform (Merck, spectral quality). However, under the experimental conditions, **LQ** was slowly oxidized to **Q**, leading to the presence of trace amounts of **Q** in the PE samples. The characteristic visible absorption band of **Q**[4] thus appeared around 20000 cm^{-1} in the observed LD spectra, partly overlapping the onset of the **LQ** absorption close to 23000 cm^{-1}. Contributions from **Q** to the observed LD spectra were removed by the subtraction of appropriately scaled[7] LD absorption curves, obtained independently for pure **Q** under identical experimental conditions.[4]

Results and discussion

The observed LD absorption curves $E_U(\tilde{v})$ and $E_V(\tilde{v})$ for **LQ** aligned in stretched PE are shown in Fig. 1. The curves indicate the two linearly independent spectra obtained with the electric vector of the polarized sample beam parallel (U) and perpendicular (V) to the uniaxial stretching direction of the polymer. The directional properties that can be obtained from the LD spectra are the orientation factors K_i for the observed transitions i,[8,9] [eqn. (1)].

$$K_i = \langle \cos^2(M_i, U) \rangle. \tag{1}$$

The K_i values express the averages over all solute molecules of $\cos^2(M_i, U)$, where (M_i, U) is the angle between the transition dipole moment of transition i and the uniaxial stretching direction of the sample. Provided a spectral feature (a peak or a shoulder) associated with transition i can be recognized in $E_U(\tilde{v})$ and $E_V(\tilde{v})$, it is possible to determine K_i, even in the case of overlap with absorption due to other, differently polarized transitions, by using the 'stepwise reduction' procedure.[8,9] In the present application, we form linear combinations [6,10]

$$r_K(\tilde{v}) = (1 - K) E_U(\tilde{v}) - 2K E_V(\tilde{v}) \tag{2}$$

[eqn. (2)] by systematic variation of K between 0 and 1, as shown in Fig. 2. $r_K(\tilde{v})$ is a reduced absorption curve in

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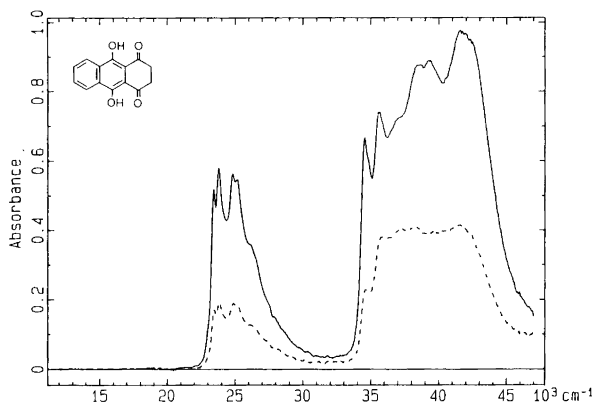* To whom correspondence should be adressed.

Fig. 1. LD absorption curves for LQ aligned in stretched polyethylene. The figure shows $E_U(\tilde{v})$ (———) and $E_V(\tilde{v})$ (— — — —) obtained with the electric vector of the polarized light parallel and perpendicular, respectively, to the stretching direction of the sample.

the sense that contributions from transitions with an orientation factor equal to K cancel. Hence, a spectral feature due to transition i simply disappears from $r_K(\tilde{v})$ for $K = K_i$.[6,10] By visual inspection of the curves in Fig. 2, K_i values close to 0.61 can be determined for the peaks observed at 23 350, 23 650, 24 650, 25 350, 34 500, 36 650, and 42 000 cm^{-1}. Unfortunately, it does not seem possible to obtain K_i values for differently polarized transitions from the present LD curves.

The presence of molecular symmetry elements greatly simplifies the analysis of the LD data. Because of the puckering of the $-CH_2-CH_2-$ moiety, the molecular symmetry of LQ is probably not higher than C_2, but it seems reasonable to assume that the conjugated chromophore is effectively planar with local C_{2v} symmetry. In this case, allowed transitions must be polarized along the three mutually orthogonal symmetry axes s of the chromophore, $s = x, y, z$, and the K_i values should adopt only three different values, corresponding to the orientation factors for the three molecular axes: $K_s = \langle \cos^2(s, U) \rangle$; $s = x, y, z$. These K_s values may deviate
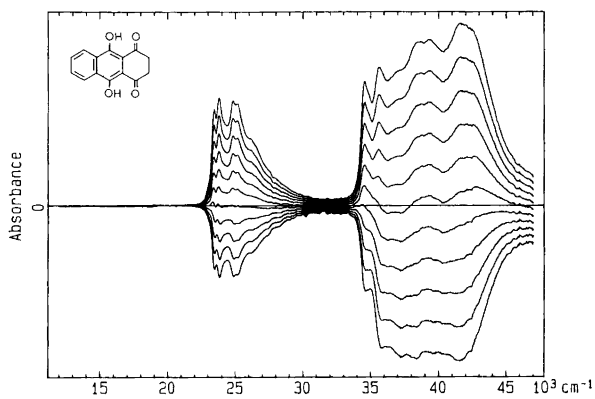

Fig. 2. Reduced absorption curves $r_K(\tilde{v}) = (1 - K) E_U(\tilde{v}) - 2K E_V(\tilde{v})$ with K ranging from 0 to 1 in steps of 0.1 (see the text).

slightly from the corresponding principal values of the orientation tensor K,[9] but as long as the optical tensor of the chromophore can be considered to be diagonal in the coordinate system $s = x, y, z$, this does not affect the validity of the ensuing analysis in terms of partial absorbance curves (see below).[9] The sum of the three K_s values must be equal to unity, $K_x + K_y + K_z = 1$, and labeling of the axes is, by convention, chosen such that $K_x \leqslant K_y \leqslant K_z$. The alignment of a compound in stretched PE generally reflects its molecular shape;[8,9] hence, for LQ, z is the 'long' in-plane axis, y the 'short' in-plane axis, and x the out-of-plane axis (Fig. 3).

If K_y and K_z can be determined, partial absorbance curves corresponding to absorbance $A_y(\tilde{v})$ due to y-polarized transitions and $A_z(\tilde{v})$ due to z-polarized transitions can be produced[8,9] [eqn. (3), (4)]. In these expressions, it has

$$A_y(\tilde{v}) = (K_y - K_z)^{-1} r_{K_z}(\tilde{v}),\qquad(3)$$

$$A_z(\tilde{v}) = (K_z - K_y)^{-1} r_{K_y}(\tilde{v}).\qquad(4)$$

been assumed that all significant intensity in the near-UV and VIS regions is of $\pi-\pi^*$ type and thus is polarized along y or z in the plane of the chromophore. Out-of-plane (x) polarized intensity, for example associated with $n-\pi^*$ transitions of the keto groups in LQ, is expected to be negligibly weak;[4] if present, it will result in positive contributions to $A_y(\tilde{v})$ and negative contributions to $A_z(\tilde{v})$.[4,6]

However, only one K value (0.61) can be determined from the present LD curves for LQ. Since $K_x + K_y + K_z = 1$ and $K_x \leqslant K_y \leqslant K_z$, this must correspond to K_z. We thus have $K_z = 0.61$, a value that is essentially identical with that observed for Q, $K_z = 0.60$.[4,11] In order to estimate K_y for LQ, we notice that the experimental value for Q is $K_y = 0.30$.[4,11] In view of the non-planarity of LQ,

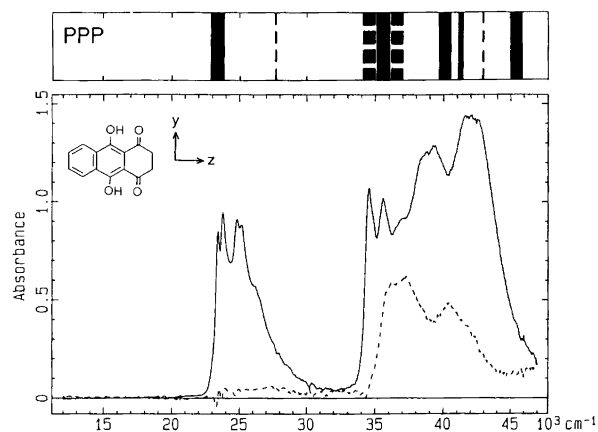*Fig. 3.* (a) Graphical representation of $S_n \leftarrow S_0$ transitions in LQ calculated by the PPP method.[12,13] Full and broken bars indicate z- and y-polarized transitions, and the thickness of the bars corresponds to different values of oscillator strengths f ($f < 0.05$, $0.05 < f < 0.3$, $0.3 < f$). (b) Partial absorbance curves $A_z(\tilde{v})$ (———) and $A_y(\tilde{v})$ (— — — —) indicating z- and y-polarized absorption (see the text).

we expect that its K_y is somewhat smaller, corresponding to a slightly more rod-like orientation distribution.[8,9] We shall adopt the value $K_y = 0.27$ for LQ. The partial absorbance curves $A_y(\tilde{v})$ and $A_z(\tilde{v})$ produced with $(K_y, K_z) = (0.27, 0.61)$ are shown in Fig. 3; the results are insignificantly affected by variation of K_y between, say, 0.25 and 0.30.

The partial absorbance curves in Fig. 3 clearly indicate that the long-wave absorption band ($\tilde{v}_{max} = 23650$ cm^{-1}, $\varepsilon_{max} \simeq 15000$) is almost purely z-polarized, whereas the 34000–45000 cm^{-1} region is characterized by several overlapping, differently polarized contributions. All y-polarized features of the LQ chromophore in the near-UV and VIS are completely overlapped by stronger z-polarized absorption.

The general structure of the spectrum is consistent with the results of a standard PPP π-electron calculation, [12,13] as indicated in Fig. 3(a) where the calculated transitions are illustrated graphically. According to the PPP results, the z-polarized long-wave band of LQ can be assigned to the HOMO–LUMO transition of the π-system, with partial hydroxy–carbonyl charge-transfer character.

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13. PPP parameters for LQ (16 π-centers): $I_C = 11.42$, $I_{OH} = 32.9$, $I_{=O} = 13.6$, $A_C = 0.58$, $A_{OH} = 10.0$, $A_{=O} = 2.3$, $\beta_{X-Y} = -2.312$ eV, $R_{X-Y} = 1.4$ Å, $\theta_{X-Y-Z} = 120°$; 16 singly excited configurations in the CI treatment.