

# Electronic States of Naphthazarin and Related Compounds. UV–VIS Linear Dichroism Spectroscopy and Quantum Chemical Model Calculations†

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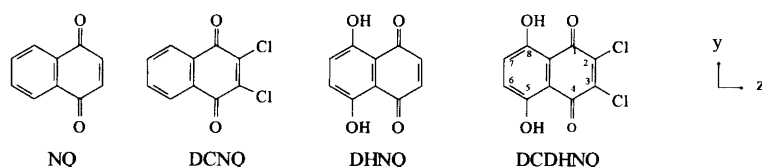
Andersen, K. B., 1999. Electronic States of Naphthazarin and Related Compounds. UV–VIS Linear Dichroism Spectroscopy and Quantum Chemical Model Calculations. – Acta Chem. Scand. 53: 222–229. © Acta Chemica Scandinavica 1999.

The four 1,4-naphthoquinones, 1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin) and 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone have been investigated by UV–VIS linear dichroism spectroscopy in uniaxially stretched polyethylene sheets. Experimental results are compared with theoretical predictions using the ZINDO/S and LCOAO quantum chemical models. Excellent agreement with observed data is obtained. The observed shift of bands due to chlorine substitution is also satisfactorily described using a new set of chlorine parameters in the ZINDO/S model. Analyses of the substituent effects are used in the assignment of transitions for naphthoquinone and naphthazarin for which conclusive LD results are missing. The combined results lead to a determination of transition moment directions for the lowest (observed) electronic transitions.

The spectral and structural features of naphthoquinones have earlier been the subject of several experimental and theoretical investigations.<sup>1–14</sup> The great interest in these compounds is due to their many biological and medical applications. In particular, naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) has attracted interest because some substituted naphthazarins have been found to be cytotoxic and potent inhibitors of different types of tumour.<sup>15–23</sup> 1,4-Naphthoquinone is found as a chromophore in naturally occurring compounds such as the K vitamins and 2,3-dichloronaphthoquinone is a potent organic fungicide.<sup>24–27</sup> This group of compounds also contains many dyes or dye-intermediates.<sup>28</sup> Naphthazarin has been investigated frequently in an attempt to elucidate the structure and symmetry of this

compound. The molecular structure of the compound can, owing to the two intramolecular H-bonds, be formulated in several ways.<sup>10,29</sup>

In this paper we report the results of an investigation of the electronic transitions of four related compounds: 1,4-naphthoquinone (NQ), 2,3-dichloro-1,4-naphthoquinone (Dichlone, DCNQ), 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin, DHNQ) and 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (DCDHNQ), the latter two having bifold intramolecular H-bonding. These compounds were investigated by UV–VIS linear dichroism spectroscopy using stretched polyethylene as an anisotropic solvent and by quantum chemical calculations. Special interest is devoted to substituent effects and intramolecular H-bonding.



Scheme 1.

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## Experimental

Samples of 1,4-naphthoquinone, 96% [77498-75-4], 2,3-dichloro-1,4-naphthoquinone, 98% [117-80-6], 5,8-dihydroxy-1,4-naphthoquinone, 95% [475-38-7] and 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone, 95% [14918-69-5] were obtained from commercial sources (Aldrich). DHNQ was purified by column chromatography (silica gel 60 H) using dichloromethane as the eluent (LAB-SCAN, HPLC Grade) yielding red needles. DCDHNQ was purified by vacuum sublimation. NQ and DCNQ were used without further purification.

**Spectroscopic data.** The purity of the compounds was checked by comparison of their UV-VIS absorption spectra with literature data<sup>1,9,30</sup> and/or by <sup>1</sup>H NMR spectroscopy [250 MHz, CDCl<sub>3</sub>, TMS (1%) Merck UVASOL]:

DCNQ:  $\delta$  7.79–7.83 (m, 2 H), 8.18–8.22 (m, 2 H).  
 DHNQ:  $\delta$  7.14 (s, 4 H), 12.34 (s, 2 H). DCDHNQ:  $\delta$  7.33 (s, 2 H), 12.34 (s, 2 H).

The UV-VIS absorption spectra were recorded at room temperature with a Shimadzu Model MPS-2000 spectrophotometer connected to a personal computer. A rotatable Glan prism was used as a polariser in the sample and in the reference beam. The LD spectra were measured for samples in stretched low-density polyethylene (PE) sheets. The PE used was a 100  $\mu$ m thick material (HinumPlast, Denmark).

To remove additives and ensure purity the PE sheets were washed in chloroform (Merck UVASOL) before use. Samples of the four different compounds were prepared by placing a PE film in a concentrated chloroform solution for a few hours. The film was then stretched uniaxially 400%. In the LD investigation two experiments were performed, with the light polarised parallel or perpendicular to the uniaxial stretching direction of the sheet. Sample and reference spectra were recorded independently using identical procedures. Light polarised parallel to the stretching direction of the sheet resulted in the  $E_U$  spectrum and light polarised perpendicular to the stretching direction resulted in the  $E_V$  spectrum. In all cases the beam was perpendicular to the surface of the sheet. Subtraction of the reference spectra was performed manually. All spectra were recorded with a constant slit width of 1 nm and as an average of four scans. The resulting LD spectra are shown in Figs. 1, 2, 4 and 5. Liquid solution spectra were recorded for samples in cyclohexane (Merck UVASOL) with a slit width of 1 nm (the spectra are not shown).

## Calculations

The electronic transitions of the four compounds were calculated by using the ZINDO/S<sup>31</sup> and LCOAO (linear combination of orthogonalised atomic orbitals)<sup>32,33</sup> semi-empirical all-valence electrons models. The ZINDO/S model is included in the HyperChem<sup>34</sup> software package. The overlap weighting factors in the ZINDO/S procedure

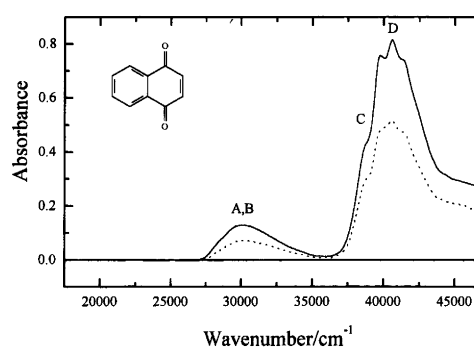


Fig. 1. Baseline-corrected LD spectra of 1,4-naphthoquinone (NQ) aligned in stretched polyethylene. The full curve  $E_U(\nu)$  and broken curve  $E_V(\nu)$  are measured with polarised light parallel (U) and perpendicular (V) to the stretching direction.

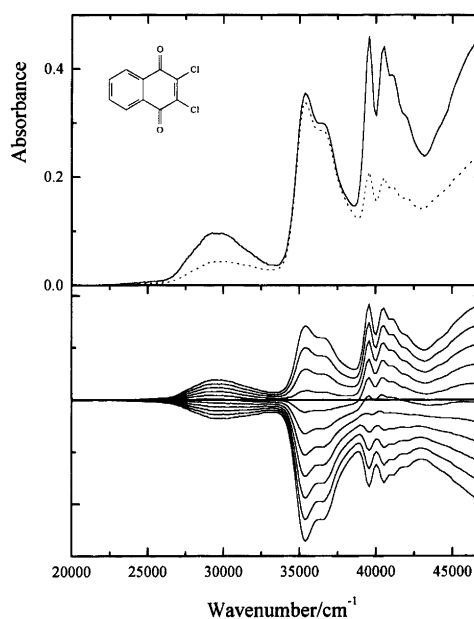


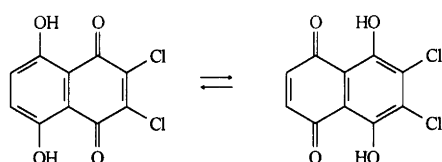
Fig. 2. Top: baseline-corrected LD spectra of 2,3-dichloro-1,4-naphthoquinone (DCNQ) aligned in stretched polyethylene. The full curve  $E_U(\nu)$  and broken curve  $E_V(\nu)$  are measured with polarised light parallel (U) and perpendicular (V) to the stretching direction. Bottom: family of reduced absorbance curves  $r_K(\nu) = (1-K)E_U(\nu) - 2KE_V(\nu)$  with  $K$  ranging from 0 to 1 in steps of 0.1.

were taken as 1.267 and 0.585 for  $\sigma$ - and  $\pi$ -type overlaps, respectively, and the configuration interaction (CI) procedure included configurations derived from the promotion of an electron from the eight highest occupied MOs to the eight lowest unoccupied ones. In the LCOAO calculations only  $\pi$ - $\pi^*$  configurations were included, considering promotion from the six highest  $\pi$  MOs to the six lowest  $\pi^*$  MOs. In ZINDO/S chlorine is not parametrised and the parameters were taken as follows:  $\xi = 2.03333$ ,  $I_s = 26.85$  eV,  $I_p = 13.86$  eV,  $\beta = -19.00$  eV,  $F_0 = 10.8662$  eV,  $F_2 = 6.44670$  eV,  $G_1 = 8.80224$  eV.<sup>34</sup> Some of the parameters were selected by tentative extrapolation procedures. This set of parameters seems to work well for the two chlorine substituted naphthoqui-

nones but has not been tested on a wider range of compounds.

The theoretically predicted transitions are very sensitive to the input geometry, especially for the two compounds with intramolecular H-bonds (DHNQ and DCDHNQ). For these compounds the geometry has been computed with three different procedures, PM3,<sup>35</sup> PM3-FF<sup>36,37</sup> and ZINDO/1.<sup>38,39</sup> PM3 predicts 'weak', PM3-FF predicts 'strong' while ZINDO/1 predicts 'very strong', nearly symmetrical, H-bonds (Table 1). The PM3-FF method is designed to predict stronger and therefore more symmetrical H-bonds than PM3. It consists of the standard PM3 method with the addition of a force field associated with each pair of O and H atoms engaged in H-bonding.<sup>36</sup> For the two compounds without hydroxy groups, NQ and DCNQ, the PM3-geometry is in best agreement with the crystal structures.<sup>40,41</sup>

DCDHNQ exists in an equilibrium between two tautomeric species, 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone and 6,7-dichloro-5,8-dihydroxy-1,4-naphthoquinone.



2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone

6,7-dichloro-5,8-dihydroxy-1,4-naphthoquinone

Scheme 2.

According to B3LYP/6-31G\* calculations the 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone structure is predicted to be the more stable by approximately 8 kJ mol<sup>-1</sup> (Jens Spanget-Larsen, personal communication). This is the reason for only considering the most stable 2,3-dichloro structure in the following.

Table 1. Computed and experimental (X-ray) interatomic distances in DCDHNQ (in Å).

	PM3	PM3-FF	ZINDO/1	X-Ray <sup>44</sup>
C1-C8a and C4-C4a	1.475	1.458	1.434	1.453(6), 1.443(6)
C4a-C5 and C8a-C8	1.399	1.398	1.401	1.385(6), 1.385(6)
C1-O1 and C4-O4	1.227	1.241	1.300	1.232(5), 1.247(5)
C5-O5 and C8-O8	1.335	1.338	1.352	1.336(6), 1.350(6)
O5-H and O8-H	0.962	1.097	1.083	0.81(6), 0.83(6)
O5...H and O8...H	1.809	1.489	1.289	1.94(6), 1.86(6)
O1-O8 and O4-O5	2.635	2.484	2.325	2.613(5), 2.617(5)

## UV-VIS linear dichroism (LD) spectroscopy

For each of the four compounds two baseline corrected UV-VIS spectra are recorded corresponding to  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$ .  $E_U(\tilde{\nu})$  is the spectrum recorded with the electric vector of the light polarised along the stretching direction (U) of the PE sample and  $E_V(\tilde{\nu})$  with the light polarised perpendicular to U. The two recorded LD spectra are for a transition  $i$  defined by eqn. (1),

$$E_U(\tilde{\nu}) = A_i(\tilde{\nu}) \langle \cos^2(\mathbf{M}_i, \mathbf{U}) \rangle \quad \text{and} \quad (1)$$

$$E_V(\tilde{\nu}) = A_i(\tilde{\nu}) \langle \cos^2(\mathbf{M}_i, \mathbf{V}) \rangle^{42}$$

where  $A_i(\tilde{\nu})$  is the contribution of the transition to the absorbance of a corresponding sample of molecules, all having their transition moment vectors  $\mathbf{M}_i$  perfectly aligned with the electric vector of the light. The angular brackets indicate averaging over all molecules in the beam of light and  $(\mathbf{M}_i, \mathbf{U})$  is the angle between the transition moment of transition  $i$  and the uniaxial stretching direction of the sample. For uniaxial samples  $\langle \cos^2(\mathbf{M}_i, \mathbf{V}) \rangle$  is equal to  $\frac{1}{2}[1 - \langle \cos^2(\mathbf{M}_i, \mathbf{U}) \rangle]$ <sup>42</sup> and the orientational properties of the transition moment vector  $\mathbf{M}_i$  can be described by one parameter, the orientation factor, defined by  $K_i = \langle \cos^2(\mathbf{M}_i, \mathbf{U}) \rangle$ .  $K_i$  is the experimental information concerning the direction of the transition moment vector compared with the uniaxial stretching direction that is available from an LD experiment. For uniaxial samples the dichroic ratio  $d_i = E_U(\tilde{\nu}_i)/E_V(\tilde{\nu}_i)$  for a non-overlapping transition  $i$  is related to the orientation factor through the equation  $K_i = d_i/(2 + d_i)$ .<sup>42</sup> When the transitions are overlapping, as is frequently observed in UV-VIS spectroscopy, the TEM stepwise reduction procedure can be used to obtain information on the orientation factors.<sup>42</sup> A prerequisite for using the TEM procedure is a recognisable spectral feature in both  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$  associated with transition  $i$ . In the present application, linear combinations  $r_K(\tilde{\nu}) = (1 - K)E_U(\tilde{\nu}) - 2KE_V(\tilde{\nu})$ <sup>43</sup> of the two observed curves are formed by variation of  $K$  between 0 and 1 in steps of 0.1.  $K_i$  is found when the spectral feature due to  $A_i(\tilde{\nu})$  just disappears and  $K = K_i$ .<sup>43</sup>

The presence of molecular symmetry elements greatly facilitates the analysis of the LD-data. Molecules with  $C_{2v}$ ,  $D_2$  or  $D_{2h}$  symmetry ( $C_{2v}$  is expected for the present naphthoquinones) have only optically allowed transitions polarised along the three mutually perpendicular symmetry axes  $x$ ,  $y$  and  $z$ . In this study we expect only to observe orientation factors adopting one of three values corresponding to the three possible transition moment directions,  $K_s = \langle \cos^2(s, \mathbf{U}) \rangle$ ,  $s = x, y, z$ . From their definition it follows that  $\sum K_s = K_x + K_y + K_z = 1$ .

Molecules embedded in stretched PE tend to align according to the molecular shape and, for planar molecules, the 'long' in-plane axis ( $z$ ) tends to align better with the stretching direction than the 'short' in-plane axis ( $y$ ) while the out-of-plane axis ( $x$ ) has the poorest average alignment. It follows that  $K_z \geq K_y \geq K_x$ . Assignment of the observed  $K_i$  to  $K_x$ ,  $K_y$  or  $K_z$  amounts to a determina-

tion of absolute polarisation directions and provides a symmetry assignment of the observed electronic states.

When the orientation factors are found it is possible to express the observed absorption in terms of reduced absorbance spectra  $A_z(\tilde{\nu})$ ,  $A_y(\tilde{\nu})$  and  $A_x(\tilde{\nu})$ .<sup>42</sup> But only when one of the three contributions  $A_x(\tilde{\nu})$ ,  $A_y(\tilde{\nu})$  and  $A_z(\tilde{\nu})$  can be assumed to be negligible can the other two be derived from the observed LD curves  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$ . For planar  $\pi$  systems it can frequently be assumed that all significant spectral intensity in the near-UV and visible regions is of  $\pi$ - $\pi^*$  type and thus is polarised along  $y$  and  $z$  in the molecular plane. In this case,  $A_x(\tilde{\nu})$  can be set equal to zero and we obtain<sup>42</sup>

$$A_z(\tilde{\nu}) = [(1 - K_y)E_U(\tilde{\nu}) - 2K_y E_V(\tilde{\nu})] / (K_z - K_y)$$

$$A_y(\tilde{\nu}) = [(1 - K_z)E_U(\tilde{\nu}) - 2K_z E_V(\tilde{\nu})] / (K_y - K_z)$$

Reduced spectra for DCNQ and DCDHNQ are shown in Figs. 3 and 6.

## Results and discussion

*Naphthoquinones*.<sup>9</sup> The observed baseline corrected UV-VIS LD-spectra  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$  for NQ are shown in Fig. 1. Inspection of the series of reduced curves (not shown) reveals that the orientation factors are almost identical, rendering the construction of partial absorbance spectra  $A_z(\tilde{\nu})$  and  $A_y(\tilde{\nu})$  impossible. Apparently, the molecule aligns like a disc-shaped species

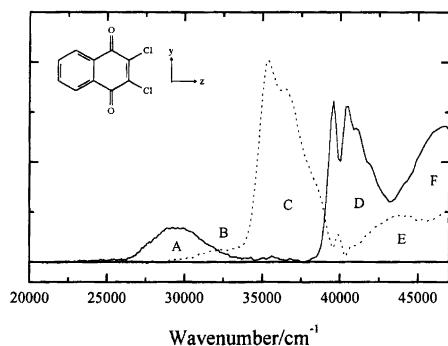


Fig. 3. Reduced absorbance spectra for 2,3-dichloro-1,4-naphthoquinone (DCNQ). The full line is  $A_z(\tilde{\nu})$  and the broken line  $A_y(\tilde{\nu})$  corresponding to  $z$ - and  $y$ -polarised transitions.

Table 2. Observed and calculated  $\pi$ - $\pi^*$  transitions for NQ.<sup>a</sup>

Observed						ZINDO/S <sup>b,c</sup>		LCOAO <sup>b</sup>	
Sym. <sup>d</sup>	Band <sup>e</sup>	$\tilde{\nu}_{\max}$	$A_{\text{iso}}$	$\epsilon_{\max}$	$f$	$\tilde{\nu}$	$f$	$\tilde{\nu}$	$f$
B <sub>2</sub>	A, B	30.1	0.09	3000	0.06	33.0	0.04	33.4	0.04
A <sub>1</sub>	A, B					33.1	0.11	33.0	0.09
B <sub>2</sub>	C	(38.7)	0.35	11 000		42.4	0.65	44.2	0.62
A <sub>1</sub>	D	40.6	0.81	20 500	0.4	42.2	0.26	42.4	0.23
B <sub>2</sub>						48.0	0.04	47.7	0.04

<sup>a</sup> $\tilde{\nu}$ , wavenumber in  $10^3 \text{ cm}^{-1}$ ;  $A_{\text{iso}} = (E_U + 2E_V)/3$ ;  $\epsilon$ , molar absorbance ( $\text{l mol}^{-1} \text{ cm}^{-1}$ );  $f$ , oscillator strength. <sup>b</sup>PM3 geometry. <sup>c</sup>Extremely weak or forbidden  $n$ - $\pi^*$  transitions are predicted at 21 900 and 22 900  $\text{cm}^{-1}$ ; these transitions are not clearly observed in the present spectra. <sup>d</sup>Irreducible representations in the  $C_{2v}$  point group. The  $y$  axis forms a basis for B<sub>2</sub> and the  $z$  axis forms a basis for A<sub>1</sub>. <sup>e</sup>Letters refer to bands in the reduced spectra.

in stretched PE, as would be expected from the molecular shape. This is in contrast with the results of Gotarelli *et al.*<sup>2</sup> who found that NQ behaves like a rod-shaped molecule when oriented in liquid crystals. Fukuda *et al.*<sup>3</sup> have also measured the LD spectra of NQ in stretched PE. The main difference in their results is that they observed some kind of absorption between the two bands which can probably be attributed to insufficient baseline correction.

The calculations were performed with the semiempirical models ZINDO/S and LCOAO using geometrical parameters predicted by PM3 and ZINDO/1. Best agreement is seen between crystal data<sup>40</sup> and PM3-predicted geometry and therefore the latter is used in the calculation of transition energy, intensity and polarisation (Table 2).

The computed data using the two models are consistent. The first two transitions predicted by ZINDO/S are  $n$ - $\pi^*$  transitions, one being very weak and polarised out of the molecular plane and the other being symmetry forbidden. No sign of an  $n$ - $\pi^*$  transition in the experimental spectra is observed. These data are not listed in Table 2 since only  $\pi$ - $\pi^*$  transitions are considered.

The observed spectrum of NQ is characterised by a medium intense band (A,B) with a maximum at 30 100  $\text{cm}^{-1}$  followed by a strong, composite band (C, D) around 41 000  $\text{cm}^{-1}$  with considerable fine structure. The 30 100  $\text{cm}^{-1}$  band is easily assigned to the two strongly overlapping transitions predicted at 33 000–33 400 and 33 100–33 000  $\text{cm}^{-1}$ , the first being polarised along  $z$  (A<sub>1</sub>) and the second along  $y$  (B<sub>2</sub>). The composite band with a maximum at 40 600  $\text{cm}^{-1}$  can be assigned to the two strong transitions predicted at 42 200–44 200  $\text{cm}^{-1}$ , one polarised along  $z$  and one along  $y$ . Without additional information assignment of the ordering of the two states is difficult; correlation with the results for DCNQ, however, seems to indicate that the shoulder (C) observed at 38 700  $\text{cm}^{-1}$  in the spectrum of NQ may be assigned to the B<sub>2</sub> state (see below) and the D band to the A<sub>1</sub> state. Previous theoretical studies using the PPP-CI, CNDO/S-CI<sup>14</sup> and CNDO/S<sup>3</sup> semiempirical methods generally give the same picture but the agreement between observed and calculated data is not as good as for the ZINDO/S and LCOAO methods.

Table 3. Observed and calculated  $\pi$ - $\pi^*$  transitions for DCNQ.<sup>a</sup>

Observed							ZINDO/S <sup>b,c</sup>		LCOAO <sup>b</sup>	
Sym. <sup>d</sup>	Band <sup>e</sup>	$\tilde{\nu}_{\max}$	$\epsilon_{\max}$	$f$	$K$	Pol.	$\tilde{\nu}$	$f$	$\tilde{\nu}$	$f$
A <sub>1</sub>	A	29.3	3000	0.1	0.54	<i>z</i>	32.8	0.11	32.9	0.09
B <sub>2</sub>	B	30.0	1500	0.05	0.34	<i>y</i>	31.1	0.001	31.1	0.003
B <sub>2</sub>	C	35.4	19 000	0.3	0.34	<i>y</i>	38.7	0.66	40.3	0.68
A <sub>1</sub>	D	39.6	15 000	0.2	0.54	<i>z</i>	41.9	0.23	42.3	0.25
B <sub>2</sub>	E	43.2	4000	0.1	0.34	<i>y</i>	47.6	0.01	47.5	0.02
A <sub>1</sub>	F	46.8	12 000	$\geq 0.3$	0.54	<i>z</i>	48.8	0.15	50.2	0.37

<sup>a</sup> $\tilde{\nu}$ , wavenumber in  $10^3 \text{ cm}^{-1}$ ;  $f$ , oscillator strength;  $\epsilon$ , molar absorbance ( $\text{l mol}^{-1} \text{ cm}^{-1}$ );  $K$ , orientation factor, defined in the text. Pol, polarisation direction, assignment of the transition moment directions according to the molecular axes defined in Scheme 1. The assignment is based upon  $C_{2v}$  symmetry. <sup>b</sup>PM3 geometry. <sup>c</sup>Two extremely weak or forbidden  $n$ - $\pi^*$  transitions are both predicted at  $22\,500 \text{ cm}^{-1}$ ; these transitions are not clearly observed in the present spectra. <sup>d</sup>Irreducible representations in the  $C_{2v}$  point group. The  $y$  axis forms the basis for  $B_2$  and the  $z$  axis forms the basis for  $A_1$ . <sup>e</sup>Letters refer to bands in the reduced spectra.

DCNQ is elongated compared with NQ and is in this respect more suitable for molecular alignment with the stretched sheet method. The observed LD spectra and a family of reduced curves of DCNQ are shown in Fig. 2. For the ZINDO/S and LCOAO calculations the PM3 geometry is used which is in best agreement with the crystal structure,<sup>41</sup> compared with the ZINDO/1 geometry. The LD spectrum displays three main bands and the start of a fourth one. Substitution with chlorine in the 2- and 3-positions in naphthoquinone does not seem to have any significant effect on the position of the two major bands in the NQ spectra. The main difference is the emergence of a new strong band between these two bands at  $35\,400 \text{ cm}^{-1}$ . This band was also seen in the NQ spectra but only as a shoulder (C) to the strong band due to strong band overlap. Finally a band starts to appear in the high energy part of the spectrum which is not seen in the NQ spectrum. All bands have one of two orientations factors, 0.54 or 0.34, determined by visual inspection of the  $r_x(\tilde{\nu})$  curves (Fig. 2) leading to  $(K_x, K_y, K_z) = (0.12, 0.34, 0.54)$ . This is as expected for a molecule with  $C_{2v}$  symmetry and makes it possible to produce reduced spectra (Fig. 3). These spectra reveal, in addition to the already mentioned bands, a weak transition (B) overlapped by the first band (A) and a transition (E) around  $43\,000 \text{ cm}^{-1}$ . Band A at  $29\,300 \text{ cm}^{-1}$  is clearly  $z$  polarised and is assigned to the medium intense transition predicted at  $32\,800$ – $32\,900 \text{ cm}^{-1}$ . The weak B band, strongly overlapping with A, is assigned to the transition predicted at  $31\,100 \text{ cm}^{-1}$ . Band C is polarised along  $y$  and can easily be assigned to the strong transition predicted at  $38\,700$ – $40\,300 \text{ cm}^{-1}$ . Bands D and F are long-axis polarised and can be assigned to transitions predicted at  $41\,900$ – $42\,300 \text{ cm}^{-1}$  and  $48\,800$ – $50\,200 \text{ cm}^{-1}$ , respectively. The E band is polarised along  $y$  and may tentatively be assigned to the transition calculated at  $47\,500$ – $47\,600 \text{ cm}^{-1}$ . The assignments of observed and calculated transitions for DCNQ are listed in Table 3.

The most remarkably spectral difference on going from NQ to DCNQ is the significant shift, more than

$3000 \text{ cm}^{-1}$ , of the C band. The remaining bands seem to be only slightly red-shifted when chlorine atoms are introduced into the chromophore. The observed substituent effect is well described, both by the LCOAO model and the ZINDO/S model, using a new set of chlorine parameters in the case of ZINDO/S (see the Calculations section). The different effect on the electronic transitions can be explained by consideration of the MOs involved. The MOs involved in transition C are significantly perturbed by the chlorine substitution in DCNQ, thereby explaining the considerable shift of this transition on passing from NQ to DCNQ. Transition D is only slightly changed in the two spectra; this may be explained by the similarity of the MOs involved of NQ and DCNQ.

The experimental results are in agreement with those of Gotarelli *et al.*<sup>2</sup> who found the same transition moment directions for the three main bands A, C and D. However, they did not observe the bands B, E and F. As in the case of NQ they assumed that DCNQ aligns like a rod-shaped molecule. For rod-shaped molecules the average alignment angles of the two short axes  $x$  and  $y$  are equivalent, corresponding to identical orientation factors  $K_x$  and  $K_y$ ; this is in contrast with the orientation factors determined in the present study  $(K_x, K_y) = (0.12, 0.34)$ .

*Naphthazarins.* When hydroxy groups are introduced into the naphthoquinone molecule a whole new chromophore is produced. This can be seen from the emergence of a new visible absorption band around  $20\,000 \text{ cm}^{-1}$  in the spectra of both DHNQ and DCDHNQ. The UV-VIS LD spectra of DHNQ and DCDHNQ are shown in Figs. 4 and 5 and the spectral data in Tables 4 and 5. The appearance of the two spectra is quite similar, not only with respect to the first well resolved band but also the remaining bands, even though substitution with chlorine tends to shift the transition energies to the red.

As pointed out in the Calculations section the computed transitions depend greatly on the input geometry and, for the naphthazarins, it appears crucial that adequate geometrical parameters for the structural elements involved in the H-bonding are used. The trans-

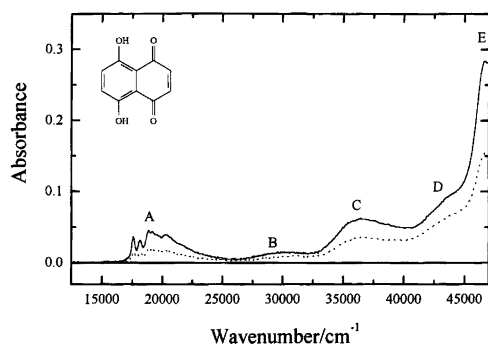


Fig. 4. Baseline-corrected LD spectra of 5,8-dihydroxy-1,4-naphthoquinone (DHNQ) aligned in stretched polyethylene. The full curve  $E_U(\tilde{\nu})$  and broken curve  $E_V(\tilde{\nu})$  are measured with polarised light parallel (U) and perpendicular (V) to the stretching direction.

itions predicted with ZINDO/S as a function of three different input geometries are shown in Fig. 6. It is clear that the low-energy region is particularly affected by the input geometry and that the first predicted band is shifted more than  $4000\text{ cm}^{-1}$  from a geometry with very strong H-bonds (ZINDO/1) to one with weak H-bonds (PM3). Best agreement between observed and predicted transitions is found when a geometry with strong or very strong H-bonds is used (Fig. 6). The sensitivity of the predicted transition energies can be explained by the LUMO (lowest unoccupied molecular orbital) being localised on the carbonyl group and the quinonoid ring and therefore stabilised by strong H-bonding. This is due to the increase in the C=O bond length and increased attraction from the positively charged phenolic hydrogens as the O $\cdots$ H distances decreases. The highest occupied molecular orbital (HOMO) is localised on the phenolic rings and tend to be unaffected or only slightly destabilised by H-bonding. The same phenomenon is seen for anthralin [1,8-dihydroxy-9(10*H*)-anthracenone], a compound with two intramolecular H-bonds to the same carbonyl group.<sup>36</sup>

There is good agreement between the theoretically predicted transitions using the two models ZINDO/S and LCOAO, for both DHNQ and DCDHNQ (Tables

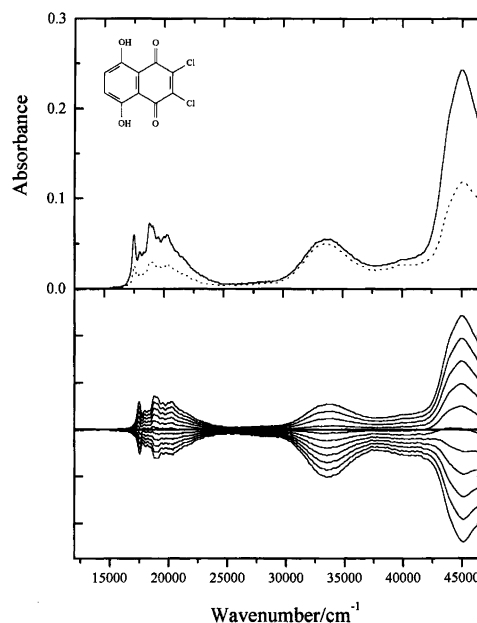


Fig. 5. Top: baseline-corrected LD spectra of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (DCDHNQ) aligned in stretched polyethylene. The full curve  $E_U(\tilde{\nu})$  and broken curve  $E_V(\tilde{\nu})$  are measured with polarised light parallel (U) and perpendicular (V) to the stretching direction. Bottom: family of reduced absorbance curves  $r_K(\tilde{\nu}) = (1-K)E_U(\tilde{\nu}) - 2KE_V(\tilde{\nu})$  with  $K$  ranging from 0 to 1 in steps of 0.1.

4 and 5). The observed spectral similarity between the two naphthazarins can be reproduced by the calculated data.

Inspection of the series of reduced curves for DHNQ (not shown) reveals that all orientation factors are similar, indicating that the molecule aligns like a disc-shaped species in stretched PE. As in the case of NQ, this makes it difficult to construct two reduced spectra and to determine polarisation directions for the transitions. Thus, in the following, we will focus on the chlorine substituted naphthazarin allowing parallels to naphthazarin to be drawn due to the spectral similarity between these two compounds.

All transitions for DCDHNQ have one of two orienta-

Table 4. Observed and calculated  $\pi$ - $\pi^*$  transitions for DHNQ.<sup>a</sup>

Observed						ZINDO/S <sup>b,c</sup>		LCOAO <sup>b</sup>	
Sym. <sup>d</sup>	Band <sup>e</sup>	$\tilde{\nu}_{\max}$	$A_{\text{iso}}$	$\epsilon_{\max}$	$f$	$\tilde{\nu}$	$f$	$\tilde{\nu}$	$f$
A <sub>1</sub>	A	18.9	0.03	4000	0.08	22.6	0.30	20.8	0.30
B <sub>2</sub>	B	31.4	0.01	500	0.01	29.9	0.01	29.2	0.02
A <sub>1</sub>						37.1	0	36.1	0.01
B <sub>2</sub>	C	35.8	0.04	4500	0.1	37.3	0.03	37.3	0.05
B <sub>2</sub>	D	44.2	0.1	8000	0.2	41.1	0.22	42.5	0.26
B <sub>2</sub>						45.4	0.56	48.1	0.30
A <sub>1</sub>	E	46.4	~0.2	15 000	0.2	46.4	0.57	47.9	0.83

<sup>a</sup> $\tilde{\nu}$ , wavenumber in  $10^3\text{ cm}^{-1}$ ;  $A_{\text{iso}} = (E_U + 2E_V)/3$ ;  $\epsilon$ , molar absorbance ( $\text{l mol}^{-1}\text{ cm}^{-1}$ );  $f$ , oscillator strength. <sup>b</sup>PM3-FF geometry. <sup>c</sup>Extremely weak or forbidden  $n$ - $\pi^*$  transitions are predicted at 20 100 and 21 100  $\text{cm}^{-1}$ ; these transitions are not clearly observed in the present spectra. <sup>d</sup>Irreducible representations in the  $C_{2v}$  point group. <sup>e</sup>Letters refer to bands in the reduced spectra.

Table 5. Observed and calculated  $\pi$ - $\pi^*$  transitions for DCDHNQ.<sup>a</sup>

Observed							ZINDO/S <sup>b,c</sup>		LCOAO <sup>b</sup>	
Sym. <sup>d</sup>	Band <sup>e</sup>	$\tilde{\nu}_{\max}$	$\epsilon_{\max}$	$f$	$K$	Pol.	$\tilde{\nu}$	$f$	$\tilde{\nu}$	$f$
A <sub>1</sub>	A	18.8	9000	0.1	0.54	z	22.3	0.31	20.9	0.31
B <sub>2</sub>	B	27.8	1000	0.03	0.35	y	28.3	0.001	27.5	0.001
B <sub>2</sub>						y	36.5	0.03		
A <sub>1</sub>						z	36.8	0.001	36.2	0.01
B <sub>2</sub>	C	38.5	11 000	0.2	0.35	y	37.9	0.42	36.9	0.003
B <sub>2</sub>	D	40.5	6500	0.2	0.35	y	44.4	0.40	38.7	0.5
A <sub>1</sub>	E	44.9	26 000	$\geq 0.4$	0.54	z	45.3	0.56	46.9	0.86
B <sub>2</sub>	F				0.35	y	47.7	0.25	47.2	0.24

<sup>a</sup> $\tilde{\nu}$ , wavenumber in  $10^3 \text{ cm}^{-1}$ ;  $\epsilon$ , molar absorbance ( $\text{l mol}^{-1} \text{ cm}^{-1}$ );  $f$ , oscillator strength;  $K$ , orientation factor, defined in the text. Pol, polarisation direction, assignment of the transition moment directions according to the molecular axes defined in Scheme 1. The assignment is under the assumption of  $C_{2v}$  symmetry. <sup>b</sup>PM3-FF geometry. <sup>c</sup>Extremely weak or forbidden  $n$ - $\pi^*$  transitions are predicted at 20 700 and 21 300  $\text{cm}^{-1}$ ; these transitions are not clearly observed in the present spectra. <sup>d</sup>Irreducible representations in the  $C_{2v}$  point group. The  $y$  axis forms the basis for  $B_2$  and the  $z$  axis forms the basis for  $A_1$ . <sup>e</sup>Letters refer to bands in the reduced spectra.

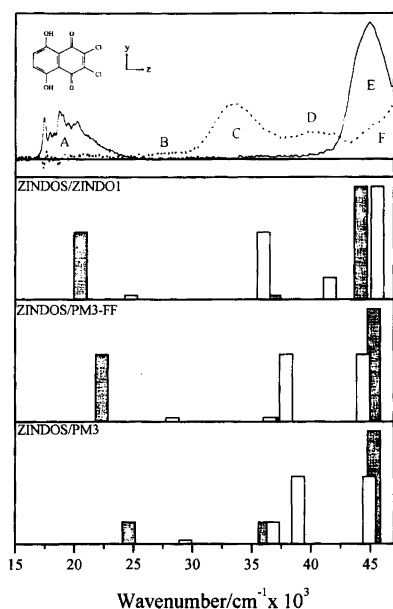


Fig. 6. Upper panel: reduced absorbance spectra for 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (DCDHNQ). The full line is  $A_z(\tilde{\nu})$  and the broken line  $A_y(\tilde{\nu})$  corresponding to  $z$ - and  $y$ -polarised transitions. Lower panels: electronic transitions in 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (DCDHNQ) computed with ZINDO/S for three different input geometries: ZINDO/1 (top), PM3-FF (middle) and PM3 (bottom) corresponding to very strong, strong and weak H-bonding. Shaded bars indicate  $z$ -polarised transitions and the white bars  $y$ -polarised transitions; the length of the bars indicates computed oscillator strength:  $f \leq 0.05$ ,  $0.05 < f < 0.30$ ,  $0.30 < f < 0.50$ , and  $0.50 \leq f$ .

tion factors, 0.54 or 0.34, determined by visual inspection of the  $r_K(\tilde{\nu})$  curves (Fig. 5, lower part). This is consistent with a 'longer' molecular geometry as compared with DHNQ. It is possible to produce two reduced spectra  $A_z$  and  $A_y$  using the above-mentioned orientation factors (Fig. 6 upper panel). The first fine-structured band (A) in the spectra is clearly polarised along  $z$  and this band is therefore assigned to the medium intense  $A_1$  transition

predicted at 20 900–22 300  $\text{cm}^{-1}$ . The second band (B) is weak, but clearly polarised perpendicular to the first band and can be assigned to the  $B_2$  transition calculated at 27 500–28 300  $\text{cm}^{-1}$ . Bands C and D are also  $y$ -polarised and are easily assigned to the  $B_2$  transitions computed at 36 900–37 900 and 38 700–44 400  $\text{cm}^{-1}$ , respectively. Band E is intense and polarised along the  $z$  axis; it may overlap with another band but, since it appears in the less reliable part of the spectra, caution must be exercised. Band E can probably be assigned to the strong  $A_1$  transition calculated at 45 300–46 900  $\text{cm}^{-1}$  while band F, due to the  $B_2$  state, is predicted at 47 200–47 700  $\text{cm}^{-1}$ . The assignment is visualised in Fig. 6 where the reduced spectra for DCDHNQ are compared with the transitions predicted by the ZINDO/S model as a function of three different input geometries.

Assignment of the observed to the predicted transitions for DHNQ was carried out by analogy with the described assignments for DCDHNQ and the transition moment directions are assumed to be the same for the two compounds. Gotarelli *et al.*<sup>2</sup> have also investigated DHNQ by LD spectroscopy using liquid crystals as the solvent and have arrived at the same conclusions for the first two bands but concluded that the third band, corresponding to band C, is of mixed polarisation. This contrasts with our findings and may be caused by the presence of an impurity appearing in the low energy part of their spectrum.

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