Tetrahedron Letters No. 30, pp 3093 - 3096, 1972. Pergamon Press. Printed in Great Britain.

POLARISED ABSORPTION SPECTRA OF BENZENE, NAPHTALENE AND ANTHRACENE OBTAINED WITH A HIGH SENSITIVE LINEAR DICHROISM TECHNIQUE.

Davidsson, Å. and Nordén, B.

Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden.

(Received in UK 17 March 1972; accepted for publication 22 June 1972)

Linear dichroism effects several hundred times smaller than those obtainable with conventional techniques have been studied by a new method. This has been described in a recent report[1] and is based on an oriented polymer matrix (a stretched polyethylene sheet). The conditions for linear dichroism are <u>optical anisotropy</u> and <u>anisodimensional molecular shape</u>, but as was shown from the metal complexes investigated, detectable effects can be obtained even with small deviations from spherical shape.

In conventional linear dichroism studies, the absorbances $A(\|)$ and $A(\perp)$ are recorded separately; $A(\|)$ is the absorbance when the light vector is oscillating parallel to the direction of orientation (stretch) of the film and $A(\perp)$ is the perpendicular absorbance.[2,3] However, the 90° polariser turning or sample turning in that method introduces considerable errors. In the technique used here, $A(\|) - A(\perp)$, called LD (with sign), is directly measured with a circular dichroism spectrometer supplemented with a quarter wave modulator.[1] LD can take both positive and negative values depending on whether the transition studied is polarised parallel or perpendicular, respectively, to the effective long-axis of the molecule, or for a planar molecule with high symmetry whether it is polarised in the plane or perpendicular to it.[1,2,5]

The benzene molecule is not of negligible thickness, the ratio D/a between the diameter and thickness of a cylinder circumscribing the molecule is only about 2.1. However, this is sufficient to give a detectable orientation, as is shown by the non-zero LD in Fig. 1, for the in-plane polarised $\pi - \pi^*$ transitions (positive LD).

If a band with, e.g. positive LD, is pure, i.e. is not superimposed by bands with opposite signs, the ratio LD/A (A = ordinary absorbance) is directly related to the degree of orientation,[1-5] f ($LD/A = 2(A(\|) - A(\perp))/(A(\|) + A(\perp)) = 2(R_D - 1)/(R_D + 1)$; $R_D = A(\|)/A(\perp)$, e.g., with $\beta = 0$, $LD/A = \frac{6f}{f+8}$, eq. 8 ref. 2).

This is shown by a comparison of LD/A, determined at a fixed orientation of the matrix polymer (R = 3.00),[2,3] with D/a for the bands corresponding to the ^1L_b transition:

	D/a	LD/A
benzene	2.1	0.043
naphthalene	3.6	0.080
anthracene	5.4	0.121

Benzene. The polyethylene begins to absorb at about 220 nm but there is evidence for a strong positive LD band at shorter wavelengths, probably (^1B, $^1E_{1u}$). The small shifts towards lower wavelength of the strong positive LD bands (^1L_b, $^1B_{2u}$) in comparison with the corresponding absorbance bands, may be explained by weak, intermediately positioned negative bands (Cf. absorption spectrum) due to vibronic transitions polarised perpendicular to the molecular plane.[6]

Naphthalene, anthracene. The LD spectra in Fig. 2 and 3 both consist of one strong positive band at short wavelength, and, in principle, two weak bands with positive and negative signs which might be assigned (^1B_b, B_{1u}), (^1L_b, $^1B_{3u}$) and (^1L_a, $^1B_{2u}$), respectively. Contrary to benzene, these molecules have a defined long-axis which is oriented parallel to the stretch-direction of the film. Thus, the negative bands are due to transitions polarised perpendicular to the long-axis but which may still be polarised in the aromatic plane.

Conventional polarised measurements on stretched films[7] have been reported to give short axis-polarisation for the 330 - 380 nm transitions of anthracene, but fluorescence studies on solutions by Zimmermann et al[8] indicate long-axis polarisation for the transitions below 350 nm, agreeing with our result in Fig. 3. Thus, $^1B_{3u}$ is probably split into the positive LD bands at about 330 nm and at 390 nm (in naphthalene at 260 and 310 nm). The negative band at 370 nm (in naphthalene at 290 nm) is $^1B_{2u}$.

A spectroscopic application of the linear dichroism method has been demonstrated here. The LD spectrum can of course be used in several other ways, e.g. for qualitative chemical analysis, as the spectrum generally has a finer structure than the absorption spectrum. With anthracene, for example, the sensitivity of detection is very high (approx. 10 times that of a sensitive absorption spectrophotometer), i.e. the LD signal can be used also for quantitative analysis.[1]

Experimental: The sample (except for benzene), dissolved in chloroform, was introduced into and oriented in a polyethylene film in the usual way.[3] To prevent the benzene from evaporating, the film was kept in water between quartz wedges. The film was oriented with its direction of stretch 45° from the optical axis of the quarter wave modulator.[1] The linear dichroism from the polymer

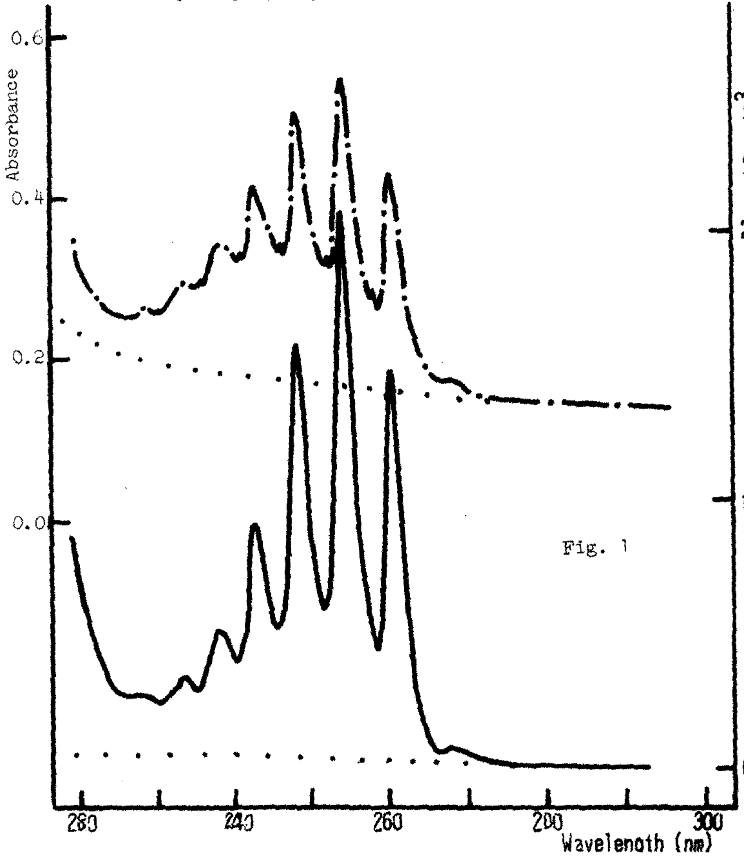


Fig. 1

Benzene in polyethylene (R = 3.00)[3], LD ——, absorbance —— · ——. LD and absorbance of pure polyethylene ·····.

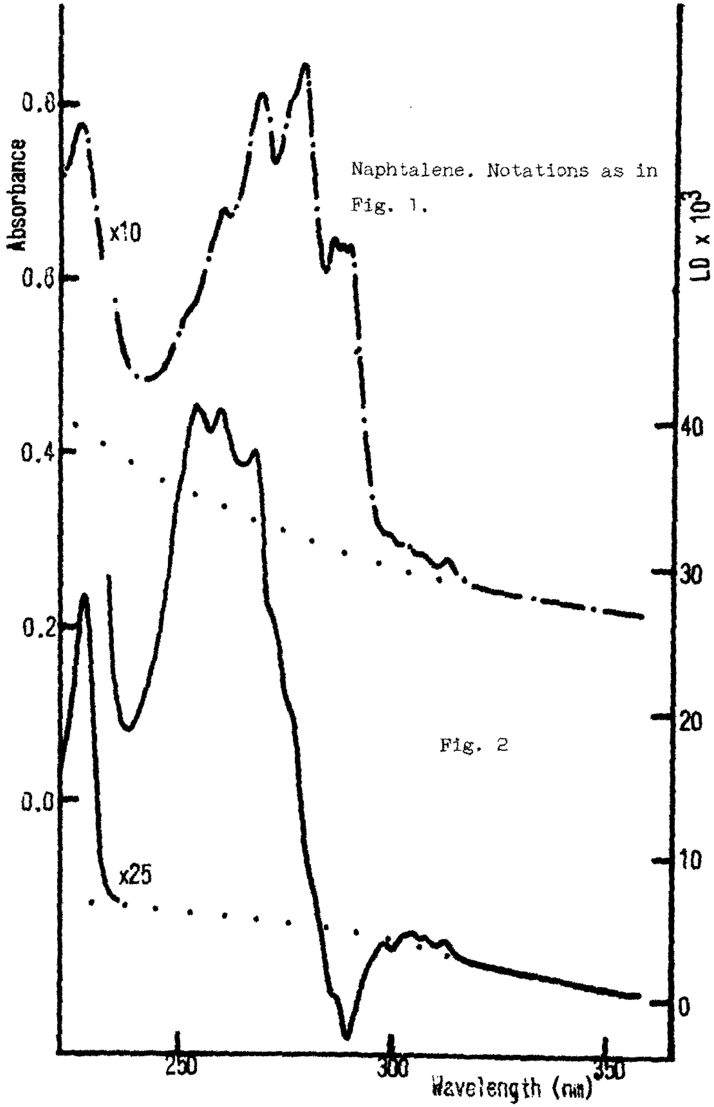
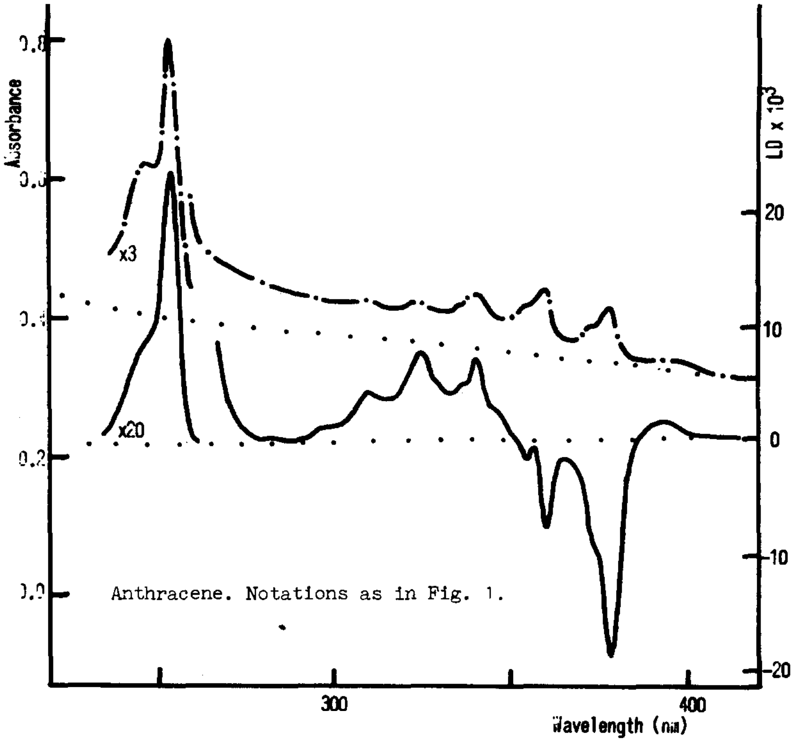


Fig. 2

Naphtalene. Notations as in Fig. 1.



Anthracene. Notations as in Fig. 1.

itself was compensated to approximately zero by inserting a similar film, free of sample, at right angles to the sample-film and after the latter in the light-path.

References:

1. Nordén, B. and Davidsson, Å. Acta Chem. Scand. **26** (1972) 842.
2. Nordén, B. Chemica Scripta **1** (1971) 145.
3. Nordén, B., Håkansson, R. and Sundbom, M. Acta Chem. Scand. **26** (1972) 429.
4. Davidsson, Å. and Nordén, B. Chemica Scripta, to be published.
5. Davidsson, Å., Johansson, L.Y., Larsson, R., Nordén, B., Gouterman, M., Sundbom, M. Acta Chem. Scand. **26** (1972) 840.
6. Sponer, H., Nordheim, G., Sklar, A.L. and Teller, E. J. Chem. Phys. **7** (1939) 207.
7. Eggers, J.H. and Thulstrup, E.W. Lecture presented at the 8th European Congress on Molecular Spectroscopy, Copenhagen August 17, 1965.
8. Zimmermann, H. and Joop, N. Ber. Bunsenges. Physik. Chem. **64** (1960) 1215, 1219.