A Linear Dichroism Study of the 1,4-Naphthoquinone Chromophore

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The visible-u.v. absorption and linear dichroism spectra of 1,4-naphthoquinone and of several substituted naphthoquinones have been recorded using a nematic liquid crystal as an orientating matrix. The spectra can be satisfactorily interpreted assuming that four transitions are present in the region down to 240 nm. The effect of substituents on the four bands is discussed.

The 1,4-naphthoquinone chromophore is present in several natural compounds including interesting derivatives such as K vitamins and ansacycline antibiotics. Although several studies on the electronic absorption spectrum of this chromophore have appeared,[1-8] a detailed study of the polarisation of the transitions of 1,4-naphthoquinone and substituted naphthoquinones in the region between 240 and 550 nm is still lacking. Such a study could be generally useful as many interesting derivatives bear several substituents and show considerable variations in both the $\lambda_{max.}$ value and intensities of all transitions connected with the substitution pattern.

Precise knowledge of the polarisation of the transitions is particularly interesting in connection with the study of the c.d. of ansacycline antibiotics.[9,10]

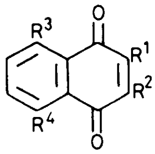
Singh *et al.*[1] carried out a detailed study on the isotropic absorption of 1,4-naphthoquinone and several substituted derivatives. From considerations on the substituents' effect on both $\lambda_{max.}$ and intensities of the observed bands, they concluded that four transitions are present down to 240 nm in addition to the weak $n \longrightarrow \pi^*$ transition (in the region between 400 and 500 nm). The transitions are classified as 'quinonoid' and 'benzenoid' and in unsubstituted naphthoquinone the absorption at *ca.* 330 nm is due to the overlapping of one quinonoid (weak) and one benzenoid (medium) transition. The shoulder at *ca.* 257 nm is associated with a strong quinonoid transition and the maximum at *ca.* 250 nm with a strong benzenoid one.

Electron-releasing substituents in positions 2 and 3 shift both quinonoid transitions to the red while similar substitution of the benzene ring shifts the benzenoid transitions in the same direction. Other work based on MO computations,[2-5] m.c.d. spectroscopy,[6] phosphorescence polarisation,[7] and considerations based on Platt's theory[8] substantially confirmed the assignments of Singh *et al.*[1] However, experimental data reported for unsubstituted 1,4-naphthoquinone in refs. 6 and 7 allowed only the relative polarisation of the four transitions to be deduced.

Recently, Hatano and his co-workers[11] reported the polarized absorption of unsubstituted 1,4-naphthoquinone in stretched polyethylene film. The long-wavelength broad absorption was found to be composed of two transitions, one at lower energy, polarized along the two-fold symmetry axis (A_1; long axis), and one, at slightly higher energy, polarized perpendicularly (B_2; short axis). In the region around 250 nm, the shoulder at *ca.* 256 nm is short axis, while the band at *ca.* 250 nm is long-axis polarized.

These findings are in agreement with the assignments of quinonoid and benzenoid transitions of Singh *et al.*;[1] however, an unequivocal assignment of the bands of substituted derivatives, which, in several cases undergo dramatic changes with respect to the parent 1,4-naphthoquinone, is still necessary.

In the present investigation the polarized spectra were recorded with a modified dichrograph which affords a signal directly related to the differential absorption of plane-polarized light [$E_{\parallel}(\lambda) - E_{\perp}(\lambda)$, l.d.] by a modulation technique with very high sensitivity.[12,13a] Alignment of the molecules under investigation was obtained by using a liquid crystal as orientating matrix; the liquid crystal solvent (nematic phase ZLI 1167) does not contain aromatic rings and is transparent down to 200 nm.



(I) $R^1 = R^2 = R^3 = R^4 = H$
(II) $R^1 = R^2 = Me,\ R^3 = R^4 = H$
(III) $R^1 = R^2 = Cl,\ R^3 = R^4 = H$
(IV) $R^1 = R^2 = OMe, R^3 = R^4 = H$
(V) $R^1 = R^2 = H,\ R^3 = R^4 = OH$
(VI) $R^1 = Me,\ R^2 = CH_2CH{=}CMe(CH_2CH_2CH_2CHMe)_3Me,$
$R^3 = R^4 = H$
(VII) $R^1 = Me,\ R^2 = R^3 = R^4 = H$
(VIII) $R^1 = R^2 = R^3 = H,\ R^4 = OH$

If the symmetry of the molecules under investigation is at least C_{2v} [as for derivatives (I)—(V)], the possible directions of the three perpendicular transition moments lie along the $u = x,y,z$ molecular axes which define the orientation of the whole molecule with respect to the optical axis of the sample (Z) through the Saupe order parameter[12] S_{uu}.[14] For bands having no mixed polarisation the 'degree of dichroism' is given by equation (1). Positive dichroism therefore indicates transitions

$$\frac{E_{\parallel}(\lambda) - E_{\perp}(\lambda)}{E_{\parallel}(\lambda) + E_{\perp}(\lambda)} = \frac{3\,S_{uu}}{2 + S_{uu}} \qquad (1)$$

polarized along the optical axis direction; negative dichroism is instead associated with polarisation perpendicular to it.

Symmetric Derivatives.—1,4-*Naphthoquinone* (I). The l.d. spectrum of this derivative is reported in Figure 1. One observes in particular a positive l.d. band at *ca.* 335 nm in correspondence with an absorption maximum. This band shows at the higher energy edge a negative l.d. component which becomes more evidenct after the reduction procedure (see Experimental section).

A negative l.d. band is observed at *ca.* 260 nm to correspond with the shoulder in the absorption, followed by a strong positive l.d. 1,4-Naphthoquinone can be considered as a 'rod-like' molecule and should be orientated with the C_2 axis parallel to the nematic director;[13] therefore the positive l.d. corresponds to transitions polarized along the two-fold

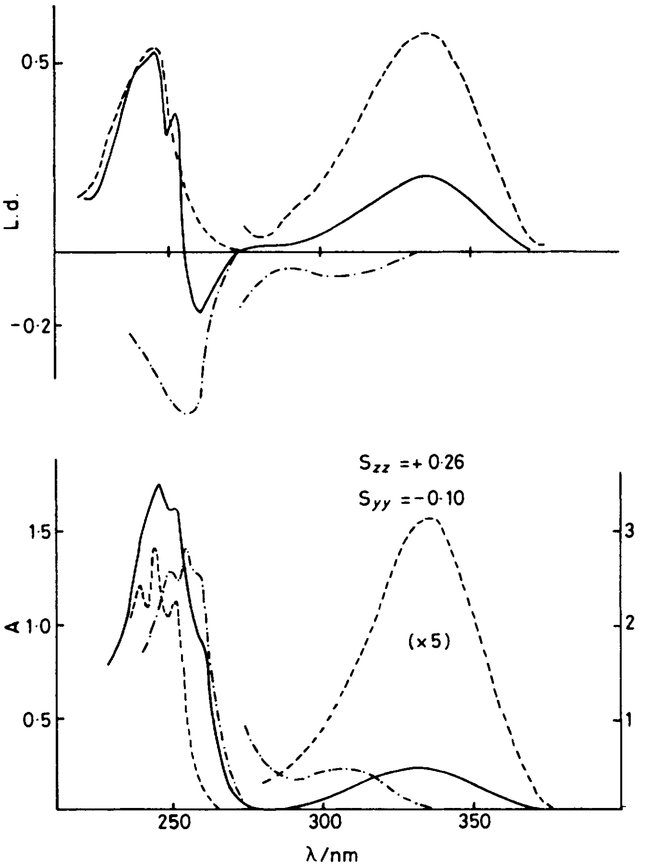


Figure 1. Upper. The l.d. spectrum of (I) (———) in the orientated liquid crystalline matrix and the reduced spectrum, in arbitrary units, showing negative (– · – · –) and positive (– – – – – –) contributions to the l.d. derived from transitions polarized along the short and long axes respectively. Lower. The average absorption spectrum (———, left-hand scale) in the orientated liquid crystalline matrix and the absorption components (right-hand scale) polarized along the short (A_y, – · – · –) and long (A_z, – – – – – –) molecular axes

symmetry axis, the negative l.d. to transitions polarized perpendicular to it. The former polarisation corresponds to benzenoid, the latter to quinonoid $\pi \longrightarrow \pi^*$ transitions (if a polarisation perpendicular to the molecular plane is not considered), in agreement with that reported in ref. 11 and with previous assignments.[1-8]

2,3-*Dimethyl*-1,4-*naphthoquinone* (II). The absorption spectrum of (II) shows a new structured band at *ca.* 270 nm, while the rest of the spectrum is practically identical to that of (I). The l.d. of this new band is negative like that corresponding to the shoulder observed in derivative (I), showing that methyl substitution in positions 2 and 3 shifts to the red the quinonoid transition which thus becomes better defined. In the low-energy region the negative component corresponding to the other quinonoid transition is no longer evident in the l.d. spectrum: this is in agreement with the red shift discussed above which displaces the low-energy quinonoid transition towards the higher intensity benzenoid which now completely masks the former absorption.

2,3-*Dichloro*-1,4-*naphthoquinone* (III). The situation is very similar to that of the dimethyl derivative (II).

2,3-*Dimethoxy*-1,4-*naphthoquinone* (IV). Relative to derivative (I) the absorption spectrum shows a band at *ca.* 275 nm, similar to that observed for derivatives (II) and (III) and a weak broad absorption at *ca.* 400 nm. The l.d. of the band at 275 nm is

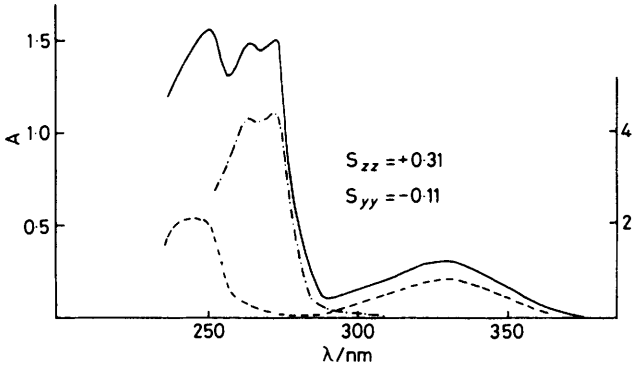


Figure 2. The average absorption spectrum of (II) (———, left-hand scale) in the orientated liquid crystalline matrix and the absorption components (right-hand scale) polarized along the short (A_y, – · – · – · –)- and long (A_z, – – – – – – – –) molecular axes

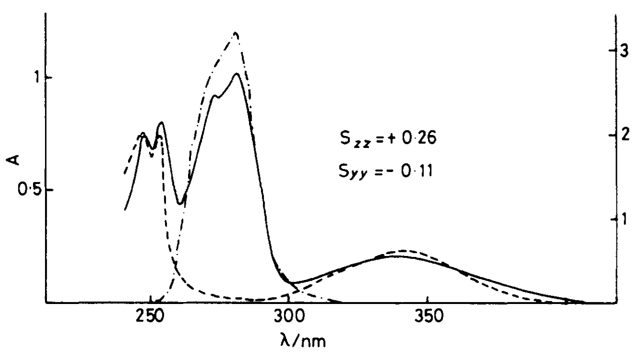


Figure 3. The average absorption spectrum of (III). Details as in Figure 2

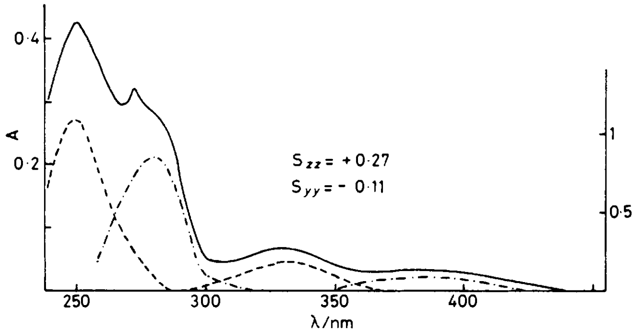


Figure 4. The average absorption spectrum of (IV). Details as in Figure 2

again negative and so is that of the low-energy band. This shows that crossing has occurred between the low-energy quinonoid and benzenoid transitions, the former being now unequivocally defined.

5,8-*Dihydroxy*-1,4-*naphthoquinone* (*naphthazarin*) (V). The absorption spectrum shows an intense structured band at *ca.* 500 nm, an inflection at *ca.* 340 nm, and another strong band at *ca.* 270 nm. The l.d. is positive for the low-energy band, a negative contribution is observed at *ca.* 340 nm, while the 270 nm band does not show relevant l.d., thus indicating mixed polarisation. It is worth noticing that, assuming the band at *ca.* 500 nm to be purely long-axis polarized, as for the low-energy benzenoid transitions of the other symmetric derivatives, one

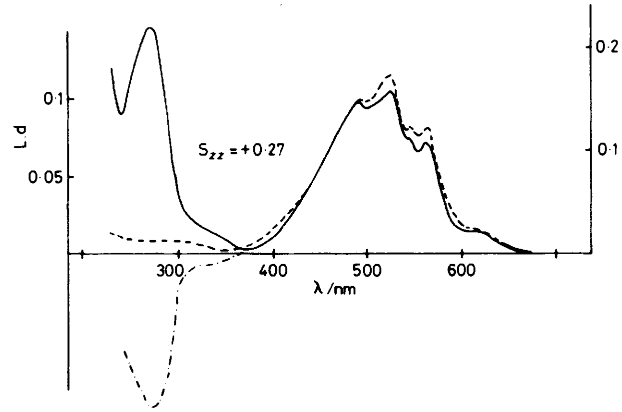


Figure 5. The l.d. (- - - - - - -) and the average absorption (———) of (V). The reduced spectrum (-·-·-·-·-) displays the negative contribution to the l.d. derived from transitions polarized along the short axis. Owing to the strong overlap of the absorption bands and the very weak l.d. signal in the 250—350 nm region, the other reduced spectrum could not be calculated

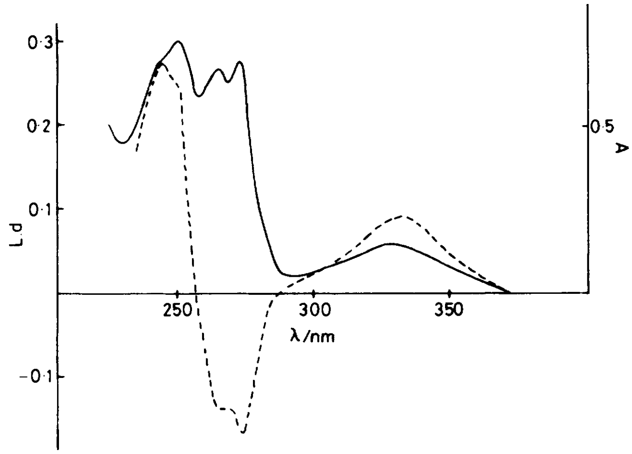


Figure 6. The l.d. spectrum (- - - - - - - -) and the average absorption (———) of (VI) in the orientated liquid crystalline matrix

obtains an order parameter (S_{zz} = 0.27) very similar to those found for the other derivatives.

The structure of naphthazarin is a subject of continuous controversy, some authors being in favour of a 'normal' 1,4-quinone structure[15,16] (C_{2v} symmetry), others 1,5-quinone (C_{2h} symmetry).[17,18] Our data suggest that the transition moment direction of the band at *ca.* 500 nm is along the molecular long-axis which, in the C_{2v} group, is a symmetry axis; this seems to support the C_{2v} symmetry hypothesis. In fact in C_{2h} symmetry the polarisation of the $\pi \longrightarrow \pi^*$ transitions should have components along both long and short axes and the coincidence of the moment with the long axis could be possible, but is not necessary as for C_{2v} symmetry.

Accordingly, the 500 nm band corresponds to the low-energy benzenoid transition shifted to the red by the substituents in the benzene ring. The negative contribution at *ca.* 340 nm is related to the low-energy quinonoid transition which is practically at the same energy as in the unsubstituted derivative (I). The mixed polarisation of the band at *ca.* 270 nm is likely to be related to the almost complete overlap of the high-energy quinonoid and benzenoid transitions as a consequence of the red shift of the latter caused by the substituents in the benzene ring.

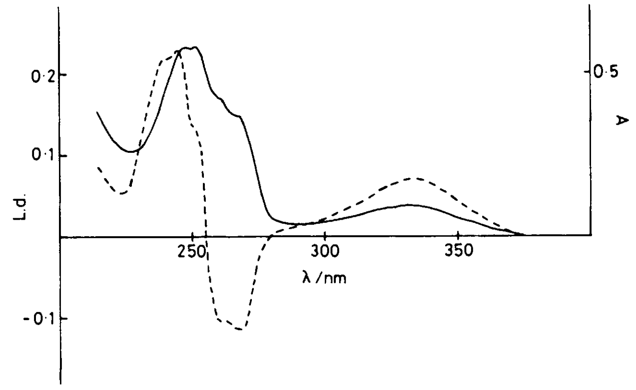


Figure 7. The l.d. spectrum (- - - - - - -) and the average absorption (———) of (VII) in the orientated liquid crystalline matrix

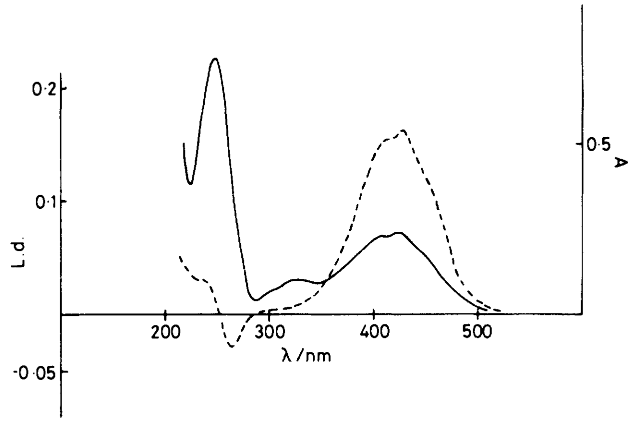


Figure 8. The l.d. spectrum (- - - - - - -) and the average absorption (———) of (VIII) in the orientated liquid crystalline matrix

Derivatives (I)—(V) were all considered to be rod-like molecules and this is confirmed by the similar values of the order parameters reported in Figures 1—5.

Derivatives with Lower Symmetry.—2-*Methyl*-3-*phythyl*-1,4-*naphthoquinone* (*vitamin* K_1) (VI). The absorption and l.d. spectra are reported in Figure 6. Both spectra are very similar to those of the 2,3-dimethyl derivative (II) and analogous considerations on the electronic transitions follow. The effective symmetry of the chromophore and the orientational properties of the molecule are very similar to those of (II).

2-*Methyl*-1,4-*naphthoquinone* (*menadione*) (VII). The spectra reported in Figure 7 are roughly intermediate between those of unsubstituted naphthoquinone (I) and derivative (II). While the benzenoid bands are again similar to those of (I), the higher-energy quinonoid band is at *ca.* 265 nm [*cf.* 267 nm for (II) and 260 nm for (I)] showing a quasi-additive effect of the methyl substitution. The molecule again behaves in a rod-like manner and the rotation of the transition moments caused by the substitution is not appreciable.

5-*Hydroxy*-1,4-*naphthoquinone* (*juglone*) (VIII). The spectra of derivative (VIII) (Figure 8) are again roughly intermediate between those of (I) and (V). The low-energy benzenoid transition is at *ca.* 420 nm [550 nm for (V) and 335 nm for (I)]. The low-energy quinonoid band is at *ca.* 325 nm, again not strongly affected by substitution at the benzene ring. The band at *ca.* 250 nm is this time associated with two dichroic absorptions of opposite polarisation indicating that a single OH substituent is not sufficient to shift the low-wavelength benzenoid transition to the same energy of the quinonoid, as observed in derivative (V).

In conclusion, our polarisation data on 1,4-naphthoquinone agree with those reported in ref. 11 and confirm previous assignments based on different techniques.[1-8] Polarisation data on substituted derivatives are in excellent agreement with the assignments of Singh *et al.*,[1] based only on absorption spectra. This indicates how good chemical intuition can lead to correct results with the help of simple techniques. Substitution of the benzene ring mainly shifts benzenoid (long-axis polarized) transitions, the low-energy ones being more strongly affected. Substitution at the quinonoid ring mainly shifts quinonoid transitions (short-axis polarized), the low-energy ones to a greater extent. The shifts are roughly proportional to the number of substituents, this result being of interest for the interpretation of the complex c.d. spectra of ansacycline antibiotics.[9,10]

Experimental

The l.d. spectra $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$ and the average absorption spectra $[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2$, where $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are the optical densities of two plane-polarized components parallel and perpendicular to the sample optical axis respectively were recorded with a JASCO J500A spectropolarimeter equipped with a DP500 data processor and with an l.d. attachment.[12,13b]

The absorption spectra were also recorded with a JASCO Uvidec 510 spectrophotometer.

The orientated samples were obtained in the following way. The compounds were dissolved in the nematic phase ZLI 1167 (a mixture of bicyclohexyl derivatives; Merck) and the solutions were inserted in a 10 μm cell, the windows of which were previously coated with polyvinyl alcohol and rubbed with tissue paper in order to give the necessary alignment to the matrix. The thermostatted cell holder was heated to 40 °C as the liquid crystalline solvent is smectic below 32 °C.

The signal recorded by the instrument was converted into linear dichroism by means of the expressions reported in ref. 12. Provided that the symmetry of the chromophore is at least C_{2v} a reduction procedure allows the determination of the order parameter S_{uu} and the absorption components $A_u(\lambda)$, also in the presence of bands with mixed polarisation.

In this case the degree of dichroism is related to the S_{uu} order parameter by equation (2). The reduction procedure consists of

$$\frac{E_{\parallel}(\lambda) - E_{\perp}(\lambda)}{E_{\parallel}(\lambda) + E_{\perp}(\lambda)} = \frac{3\Sigma_u A_u(\lambda)\mathrm{S}_{uu}}{2\Sigma_u A_u(\lambda) + \Sigma_u A_u(\lambda)\mathrm{S}_{uu}} \qquad (2)$$

the computation by means of a trial-and-error method[12,19] of the linear combination (3) in order to get the $d' = d_u'$ value for which the contribution of the *u*-polarized transition to the l.d. spectrum vanishes over all bands. This is to obtain a reduced spectrum, *i.e.* an l.d. spectrum free from mixed polarisation.

$$[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] - d_u'[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2 \qquad (3)$$

From the knowledge of the d_u' value, the S_{uu} order parameter can be obtained by equation (4). Provided that only two polarized components contribute to the l.d. spectrum (in the case of planar molecules without out-of-plane polarisation, as in the naphthoquinone chromophore), the $A_u(\lambda)$ spectra can be computed by means of equation (5).

$$\mathrm{S}_{uu} = 2d_u'/(6 - d_u') \qquad (4)$$

$$A_x(\lambda) = 0$$

$$A_z(\lambda) = \frac{[E_{\parallel}(\lambda) - E_{\perp}(\lambda)](2 + \mathrm{S}_{yy}) - 3\mathrm{S}_{yy}[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]}{2(\mathrm{S}_{zz} - \mathrm{S}_{yy})} \qquad (5)$$

$$A_y(\lambda) = \frac{3\mathrm{S}_{zz}[E_{\parallel}(\lambda) + E_{\perp}(\lambda)] - [E_{\parallel}(\lambda) - E_{\perp}(\lambda)](2 + \mathrm{S}_{zz})}{2(\mathrm{S}_{zz} - \mathrm{S}_{yy})}$$

Compounds (I), (II), (V), (VII), and (VIII) (Fluka) and (VI) (Merck) were used without further purification. Derivative (II) was synthesized as reported in ref. 20 from 2-methyl-1,4-naphthoquinone and lead tetra-acetate, m.p. 119—121 °C (lit.,[20] 120—122 °C). Derivative (IV) was synthesized as reported in ref. 21 from 2,3-dichloro-1,4-naphthoquinone and sodium methoxide, m.p. 114—115 °C lit.,[21] 114—115 °C). Derivatives (II) and (IV) had correct elemental analyses and their n.m.r. spectra were in agreement with the proposed structures.

Acknowledgements

We are grateful to Professor B. Samori for useful discussions. Financial support from the CNR and Ministero PI is gratefully acknowledged.

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Received 4th *November* 1983; *Paper* 3/1963