

## Comparisons of Circular Dichroism in Liquid Solution and in the Crystal State with Reference to Conformations of 3,3'-Bithienyls

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The electronic structures as well as the nuclear arrangements in bithienyls have been the subject of recent studies by several workers, in the gas, liquid, and solid states.<sup>1-7</sup> However, in contrast to the corresponding biaryls,<sup>8-10</sup> which have a higher *quasi*-symmetry, no complete theory has been developed for the origin of the optical activity of the resolvable 3,3'-bithienyls. Consequently, the use of circular dichroism (CD) has been in general restricted to decisions between the two possible absolute configurations, on an empirical basis.<sup>7</sup> A correlation of the CD with a more precise structural assignment requires either a bridged compound<sup>11,12</sup> in which the conformation can be estimated from molecular models, or an independent structure determination.

In this paper we wish to report that the CD spectrum of 4,4'-dibromo-2,2'-dicarbomethoxy-3,3'-bithienyl (I) and that of 2,2'-dibromo-4,4'-dicarbomethoxy-3,3'-bithienyl (II), as obtained by the randomised crystal powder technique<sup>13</sup> on crystal fractions previously used in an X-ray structure determination,<sup>4</sup> closely resemble the corresponding solution CD spectra (Figs. 1-2).

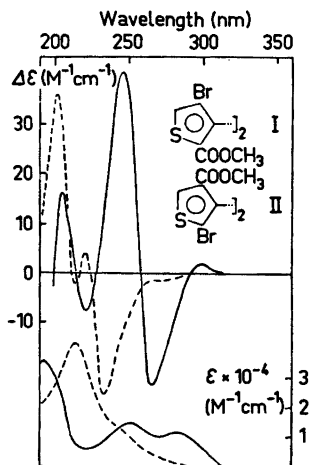


Fig. 1. Liquid solution (acetonitrile) CD and UV spectra of *R*(+)-I — and *R*(-)-II - - -.

Acta Chem. Scand. B 28 (1974) No. 6

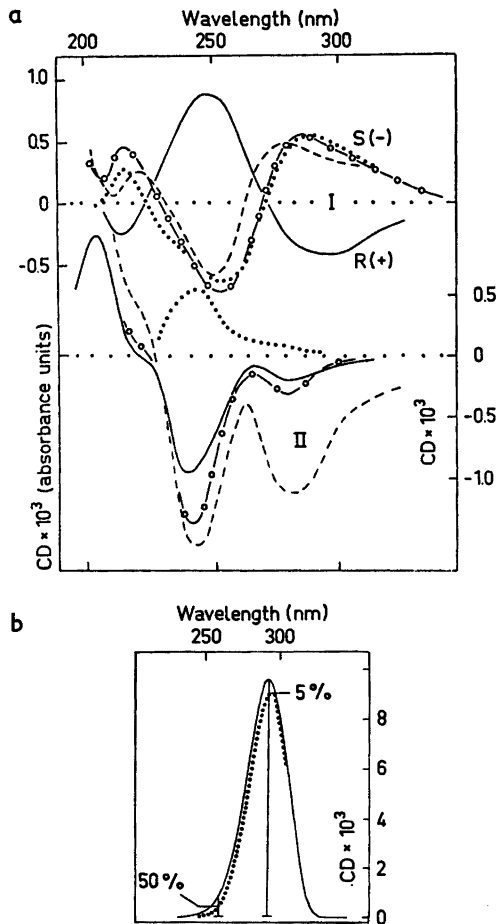
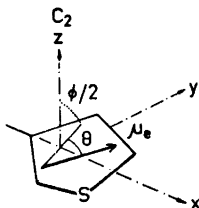


Fig. 2. a. CD spectra (selected from some 50 representative of cases of varying confidence: Above: *R*(+) I — (3.0 × 10<sup>-3</sup> %, KCl), *S*(-) I ··· (2.0 × 10<sup>-3</sup> %, KCl), - O - (1.5 × 10<sup>-3</sup> %, KCl), - - - (0.5 × 10<sup>-3</sup> %, KCl). Below: *R*(-) II - - - (3.7 × 10<sup>-3</sup> %, KBr), - O - (0.7 × 10<sup>-3</sup> %, KBr), — (0.5 × 10<sup>-3</sup> %, KCl), *S*(+) ··· (0.3 × 10<sup>-3</sup> %, KBr). b. Depolarisation test: A camphersulphonic acid/PVA standard<sup>17</sup> following the specimen in the light path ··· only standard —. The decrease (50 % at 260 nm) is a measure of the percentage of the light intensity which is not acting as in a circularly polarized mode.

Before we may have confidence in an ordinary "pressed KBr disc" CD spectrum, it is necessary to minimize the influence of two principal errors, *viz.* the optical artifacts due to anisotropic CD or refraction (birefringence) of the crystallites, and those due to a stress birefringence induced by pressing the disc. The

first error is minimized by the randomisation procedure, while the second is detected by measuring the depolarisation.<sup>13</sup> An additional effect seems to be the scattering due to different refractive indices in substance and matrix. Preliminary experiments indicate that more reliable results are obtained by extrapolation to a zero substance concentration (*cf.* Fig. 2). On this basis Fig. 2 yields the following CD features for the *R*-configurations of I and II, in absorbance units (wavelengths, nm, in parentheses): I: -0.2 (225), +0.6 (250), -0.5 (275); II: +0.7 (200), ±? (230), -0.9 (240), -0.3 (275).



By analogy with, *e.g.*, biphenyls, a tentative conclusion which may be drawn from the great similarity between these features and the spectra in Fig. 1a, is that on the average the same structures of I as well as of II exist in both the solution and the crystal, *viz.* *cisoid* conformations with a dihedral angle  $\phi = 75 - 90^\circ$  in I and  $60 - 70^\circ$  in II.<sup>4</sup>

This conclusion is correct as long as any of the CD bands considered is due to a transition polarised at an angle  $\theta$  (in the present notation) fairly close to zero, and if the CD is governed by a dipole-dipole coupling<sup>14</sup> ("exciton") mechanism. Such an origin of the CD may be of predominant importance considering the high oscillator strengths of the transitions involved and the probably small electronic exchange between the thiophene nuclei.

The dipole coupling between the two equivalent transition moments  $\mu_{e1}$ ,  $\mu_{e2}$ , directed as denoted above, gives rise to two components A and B (point group  $C_2$ ) with rotational strengths given by eqn. (1) and at relative energies determined by (2).<sup>15</sup> It is thus obvious that CD bands due to transitions with  $|\theta| > 35.3^\circ$  will not depend in sign or energy on a conformational change ( $0 < \phi < 180^\circ$ ). However, it is most improbable that this is the trivial explanation for the

$$R_A = -R_B = \frac{\pi\nu}{2c} r_{12} \mu_e^2 \cos^2 \theta \sin \phi \quad (1)$$

$$\nu_A - \nu_B = \frac{2\mu_e^2}{hcr_{12}^3} (1 - 2 \cos^2 \theta \cos^2 (\phi/2) - 3 \sin^2 \theta) \quad (2)$$

similarities between Fig. 1 and Fig. 2. Firstly, there is evidence for an intensive low-energy transition with  $\alpha = +30^\circ$ ,<sup>15</sup> implying a "con-

formational" CD sign change due to eqn. (2) when  $\phi$  exceeds  $131.8^\circ$ . Secondly, with a low  $\nu_A - \nu_B$  the A and B components mutually cancel to a great extent, leading to an apparent CD spectrum whose features are very sensitive to changes in *R*, and consequently also to conformational changes.

Experimental details are to be described elsewhere.<sup>13,16</sup> KBr was found more suitable than KCl giving birefringence free discs with high transmission down to 230 nm. Close to 200 nm KCl was superior to KBr with respect to transparency. Discs with depolarisations (defined in Fig. 2) exceeding 5% were discarded.

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