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OPTICALLY ACTIVE AROMATIC CHROMOPHORES. VI (1). THE THIOPHENE AND FURAN CHROMOPHORES.

Lawrence Verbit
Department of Chemistry, State University of New York at Binghamton,
Binghamton, New York, U.S.A.

Emanuel Pfeil and Wolfgang Becker
Institut für Organische Chemie der Universität Marburg, Marburg/Lahn, Germany

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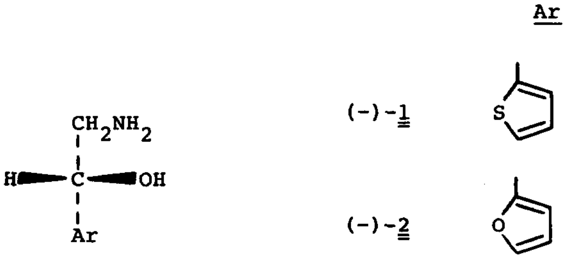
Scant data are available on the ultraviolet spectra of thiophene and furan derivatives and there is lack of agreement on the interpretation of the results which are available (2). The n→π* absorptions are predicted by molecular orbital theory to be relatively strong but, as yet, no such bands have been found. An optical rotatory dispersion (ORD) and circular dichroism (CD) investigation of monosubstituted thiophene and furan compounds was then of interest for two reasons: firstly, Cotton effects in simple open-chain thiophene and furan derivatives have not been reported and, secondly, it might be possible to observe optically active transitions by means of ORD or CD which might be hidden under the broad absorption band in the respective isotropic absorption spectra.

S-(-)-β-(2-Thienyl)ethanolamine, (-)-1, and S-(-)-β-(2-furyl)ethanolamine, (-)-2, were synthesized by the enzyme-catalyzed addition of HCN to the corresponding heterocyclic aldehyde, followed by reduction of the optically



(-)-1

(-)-2

active cyanohydrin with $LiAlH_4$ (3). Final purification of the compounds was best achieved by vacuum sublimation (10^{-2} torr, 35°). In addition to satisfactory elemental analyses, physical data for (-)-**1** and (-)-**2** are given in Table 1.

TABLE 1 Physical Properties of the β-Arylethanolamines (-)-**1** and (-)-**2**

	$[\alpha]_D^{27°}$ (acetonitrile)	m. p.	UV Absorption (acetonitrile)	
			ε_{max}	λ_{max}
(-)-**1**	-36.4°	62.3 - 62.8°	11,600	234
(-)-**2**	-43.3°	83.4 - 84.0°	21,000	217

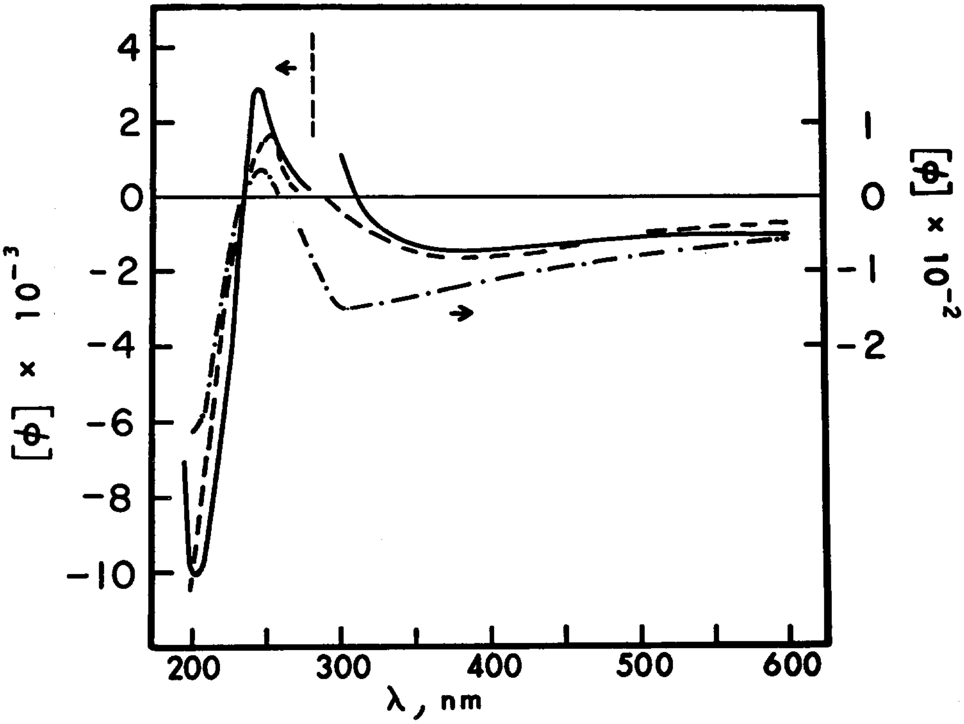


FIG. 1

ORD curves of S-(-)-β-(2-thienyl)ethanolamine, (-)-**1**, in ——— acetonitrile, ----- 2-propanol, and —·—·—·— 0.1 N HCl solution.

The ORD curves for (-)-1 and (-)-2 in acetonitrile, 2-propanol, and 0.1 N HCl solution are given in Figures 1 and 2. Due to the lower sensitivity of our instrument (4) in the CD mode, only part of the Cotton effects could be measured. However, the CD results confirmed that the observed bands were positive. In acetonitrile solution it was possible to carry out measurements to below 200-nm and to observe completely a positive Cotton effect for both (-)-1 and (-)-2. For the thiophene compound the Cotton effect occurs in the 235-nm region while for the furan derivative it is centered near 220-nm. The negative ORD curves in the near ultraviolet and visible regions indicate the presence of

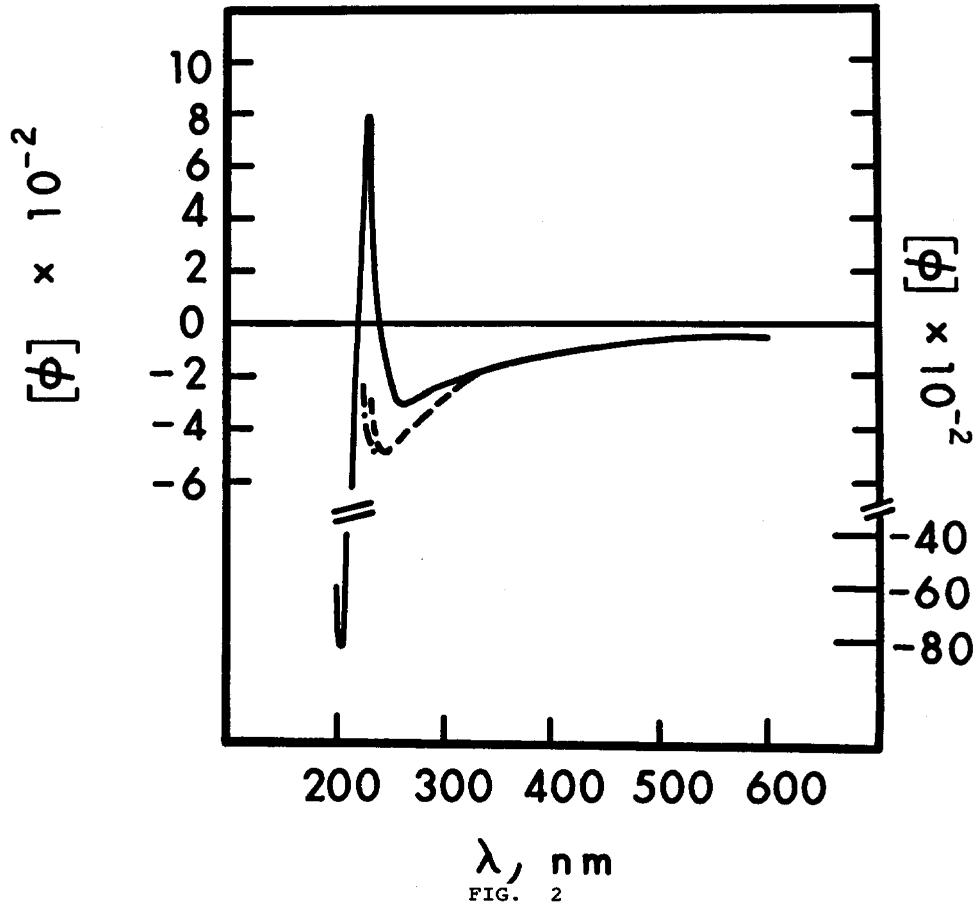


FIG. 2

ORD curves of S-(-)-β-(2-furyl)ethanolamine, (-)-2, in ——— acetonitrile, ----- 2-propanol, and —·—·—·— 0.1 N HCl solution.

strong negative Cotton effects in the presently inaccessible region below *ca.* 190-nm. No other optically active transitions were found and, although spectral solvent shifts were observed, the data, obtained in regions of high absorptivities and relatively low rotational values, do not permit unequivocal assignment of the transitions at this time.

The similar shape of the ORD curves for both compounds in 0.1 N HCl solution in which the amino function is essentially completely protonated, compared to that in acetonitrile solution, indicates that the non-bonding electrons of the amino group do not contribute significantly to the observed Cotton effects.

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(4) A JASCO Spectropolarimeter with CD Recorder operating under the conditions described in L. Verbit, *J. Am. Chem. Soc.*, **89**, 167 (1967) was used.