The Lanthanoid-Induced Shifts of Proton NMR Spectra and the Conformations of β-(2-Thienyl)acrylic Esters and Related Compounds

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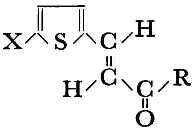
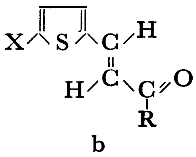
The most predominant conformation of 4-(2-thienyl)-3-butene-2-one and methyl β-(2-thienyl)acrylates were determined by the analysis of their LIS's. The LIS's toward higher fields were observed with some ring protons (H_3's and some of H_4's), and were best interpreted by assuming that about 20% of the shift reagent coordinates on the methoxyl oxygen atom and the rest on the carbonyl oxygen atom.

β-(2-Thienyl)acrylic esters are considered to take a planar conformation in order to minimize pi-electronic energy of the whole conjugated system. However, the rotation about the two $C(sp^2)$–$C(sp^2)$ single bonds (C_β–C_2 and C_α–$C_{carbonyl}$) produces the possibility to exist as the four conformers **1a**—**1b**. As the rotational barriers around these essential single bonds are relatively low,¹⁾ the interconversion among these occurs rapidly, and the ester exists as an equilibrium mixture in which the most stable conformer predominates over the others. Thus, it is of considerable significance to determine which of the four is the most predominant conformer. The stereochemistry of conjugated unsaturated ketones have been discussed by several authors,2,3) and it is concluded that the *s-trans* conformation is, in general, more stable than *s-cis* one from the ultraviolet spectroscopic evidences. However, the conformation around the other essential single bond is less certain. The molecular models and the molecular diagrams2) suggest that the conformer (a or b) in which the C_2–C_3 bond of the thiophene ring is *s-trans* with respect to the ethylenic bond of the enone system is considerably less hindered than the *s-cis* one (c or d), since the H_α–H_3 repulsion operating in the *s-cis* conformer is substituted by much less H_β–H_3 repulsion in the former conformer.



a



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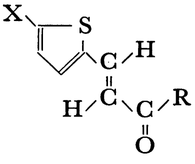

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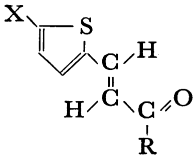

d

Thus, the stereochemistry of some *trans*-β-(2-thienyl)acrylic esters (**1**) and *trans*-4-(2-thienyl)-3-buten-2-one (**2**) has been investigated by measuring the LIS (lanthanoid induced shift) values of their proton NMR spectra.

Experimental

Materials used in this investigation were synthesized according to the methods previously reported,10) or obtained by purification of commercially available materials. Proton NMR spectra were measured in carbon tetrachloride employing a JNM C-60H spectrometer operating at 60 MHz. The concentrations of the solutions were adjusted approximately at 0.3 mol l^{-1} with respect to substrates. Tris(dipivaloylmethanato)europium [$=Eu(dpm)_3$] was used as a shift reagent throughout this investigation, and it was added in small portions to a solution containing an excess of the substrate in order to obtain the $\Delta\delta$ *vs.* [shift reagent]/[substrate] plots.

Results and Discussion

The LIS values and their proportions to the largest were given in Table 1. In order to determine the privileged conformation of *trans*-4-(5-bromo-2-thienyl)-3-buten-2-one, the most probable locations of the Eu(III) ion to reproduce the observed LIS values of 2 were calculated with all of four conformations **2a**—**2d** (where X is Br) by evaluating the agreement factors (R-values) defined by Eq. 1,4) where $(S_{obsd})_i$ and $(S_{calcd})_i$ are the observed and the calculated LIS's of proton i, respectively.

$$R = \left\{\frac{[(S_{obsd})_i - (S_{calcd})_i]^2}{(S_{obsd})_i^2}\right\}^{1/2} \qquad (1)$$

Reasonable results given in Fig. 1 were obtained only when the substrate molecule takes the *s-trans*, *s-trans* conformation (**2a**). As shown in Fig. 1, the location of Eu(III) in the enone–$Eu(dpm)_3$ complex is 2.3 Å apart from the carbonyl oxygen atom and not so far from the C=O axis.

The relative values of the LIS's of the thienylacrylic esters, as a whole, are similar to those of the thienylbutenone (**2**). However, a remarkable differences are observed with the signs of the LIS's of some ring protons (H_3's and some H_4's in Table 1) and with the relative magnitudes of the LIS's of α- and β-protons. The difference is interpreted by assuming that the complexation of $Eu(dpm)_3$ also occurs on the methoxyl oxygen atom to some extent. To estimate roughly the relative abundances of the complexes in which the Eu(III) ions are bonded to the carbonyl and the alkoxyl oxygen atoms, the LIS's of the equimolar mixture of acetone and diethyl ether is measured and, by comparing with the LIS's of each component under the same conditions, the 80% of the shift reagent is shown to coordinate to the carbonyl oxygen atom of acetone.5) Employing the results of the intermolecular competition, the LIS's of the thienylacrylic ester (**1**) were estimated as

Table 1. The LIS's of methyl β-(5-substituted-2-thienyl)-acrylates and related compounds

Compounds		(O)CH$_3$	H$_\alpha$	H$_\beta$	H$_3$	H$_4$	5-CH$_3$
BrC$_4$H$_3$SCH=CHCOCH$_3$	S_i[a)]	15.48	13.50	12.70	1.48	0.90	
	$S_i/(S_i)_{max}$	1.00	0.87	0.82	0.096	0.058	
BrC$_4$H$_3$SCH=CHCOOCH$_3$	S_i	15.44	12.26	13.72	−1.04	−0.16	
	$S_i/(S_i)_{max}$	1.00	0.79	0.89	−0.067	−0.010	
ClC$_4$H$_3$SCH=CHCOOCH$_3$	S_i	15.50	12.25	13.30	−1.05	−0.14	
	$S_i/(S_i)_{max}$	1.00	0.79	0.86	−0.068	−0.009	
CH$_3$C$_4$H$_3$SCH=CHCOOCH$_3$	S_i	15.59	12.47	13.72	−0.76	0.00	0.42
	$S_i/(S_i)_{max}$	1.00	0.80	0.88	−0.046	0.00	0.027
BrC$_4$H$_3$SCH=CMeCOOCH$_3$	S_i	13.84	(8.90)	12.52	−0.26	0.24	
	$S_i/(S_i)_{max}$	1.00	(0.64)	0.90	−0.019	0.017	
BrC$_4$H$_3$OCH=CHCOOCH$_3$	S_i	15.04	13.06	13.48	−0.82	0.13	
	$S_i/(S_i)_{max}$	1.00	0.87	0.89	−0.054	0.009	
C$_6$H$_5$CH=CHCOOCH$_3$	S_i	15.62	12.18	13.63	0.78	0.14	
	$S_i/(S_i)_{max}$	1.00	0.78	0.87	0.05	0.01	
Estimated value[b)] for XC$_4$H$_3$SCH=CHCOOCH$_3$	$S_i/(S_i)_{max}$	1.00	0.71	0.79	−0.03	0.03	

a) S_i refers to the LIS value of proton i, which is defined as $S_i = \Delta\delta/([\mathrm{Eu(dpm)_3}]/[\mathrm{Substrate}])$.
b) See text.

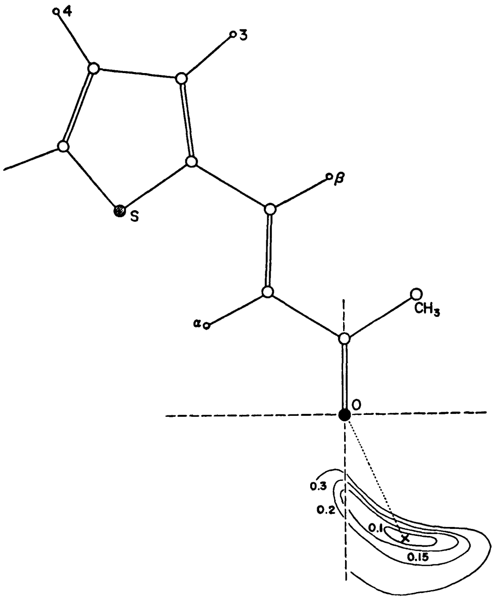

Fig. 1. The most probable position of the Eu(III) ion (x) determined by evaluating the R-values from Eq. 1 for 4-(2-thienyl)-3-buten-2-one.
(The figures show the R-values.)

the weighted sums of the contribution of the Eu(III) ions in two sites calculated by the McConnell Robertson equation,[6)] $\Delta\delta = K(1-3\cos^2\theta)r^{-3}$, by assuming (i) that the shift reagent coordinates to the carbonyl and the methoxyl oxygen atoms of the ester in the ratio of 4: 1, (ii) that the Eu(III) ion is located on the extension of the C=O bond or on the bisector of the C–O–C angle of the methoxyl group, and (iii) that the Eu–O distance is 2.5 Å for the carbonyl oxygen and 3.0 Å for the methoxyl oxygen of the ester group. A conformation in which the two alkyl groups are antiperiplanar, termed "*trans*", is demonstrated to be the most favorable conformation of the carboxylic ester,[7)] and the same conformation is also assumed in the calculation. As the location of the second Eu(III) ion coordinating on the methoxyl oxygen atoms is too close (about 1.9 Å) to realize, its location is modified to be on a line 19° out side from the bisector line and 3.0 Å distant from the oxygen atom (so as to keep the nearest Eu···H distance farther than 2.5 Å). This modification gives a reasonable set of the calculated LIS's of **1** showns together with the observed values, in Table 1. The position of the methoxyl protons are chosen to be the center of gravity of its three protons. In spite of this oversimplification and uncertainty of the position of the methyl group, the agreement between the relative values of the observed and the calculated LIS's are good, and the LIS's of the thienylacrylic esters can be explained by taking into accounts the participation of the alkoxyl oxygen atom in the formation of the shift reagent–substrate complex. The β-(5-bromo-2-furyl)-acrylic esters behave quite similarly with their thia-analogs towards the shift-reagent, and, in consequence with the previous reports,[8,9)] the intra-ring oxygen atom does not participate in the complex formation with the shift-reagent. The LIS's of cinnamic esters are also similar and the participation of the alkoxyl-oxygen atom might be quite general in esters.

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