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POLYENYL-SUBSTITUTED FURANS AND THIOPHENES. A STUDY OF THE ELECTRONIC SPECTRA[1]—II[2a]

J. W. van Reijendam[2b] and M. J. Janssen

Department of Organic Chemistry, The University, Bloemsingel 10, Groningen, The Netherlands

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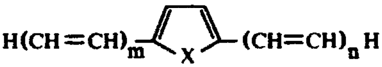
Abstract—LCI-SCF-MO calculations on furans and thiophenes which bear ethylene, butadiene or hexatriene groups at the 2 position or at the 2 and 5 positions have been performed. The excitation energies calculated are almost independent of the presence or the nature of the heteroatom and thus reflect the experimental results of the previous paper.[2a] Orbital diagrams show that a fundamental difference is expected between compounds where heterocyclic 5-membered rings are conjugated with a π electron system and compounds where these rings are part of a larger condensed ring system.

INTRODUCTION

In part I,[2a] the synthesis of the title compounds (**1a**–**f** and **2a**–**f**) and some qualitative aspects of their electronic spectra were described. In this paper we report the results of a theoretical treatment.



1; X = O
2; X = S

a; m = 0, n = 1 **d**; m = n = 1
b; m = 0, n = 2 **e**; m = n = 2
c; m = 0, n = 3 **f**; m = n = 3

*Calculations**

The spectra of the title compounds were calculated by the PPP method,[3] that is, b interaction between a limited number of singly excited configurations built from self consistent MO's, using the approximations introduced by Pople[4] and Pariser an Parr.[5]

Apart from the many applications to hydrocarbons,[3] this method has been applie recently by Zahradník and coworkers to a large number of sulfur-containing molecule with good results.[6] For furans, the applications have until now been restricted t furan itself.[7]

The values of the integrals in this paper were taken from the work of Zahradník,[6,] and are given in Table 1. For sulfur the *p*-orbital model was used.

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[*] The calculations were performed on a Telefunken TR-4 computer of the Computing Center of th University, Groningen, and, in part, by the facilities of the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences, Prague. One of the authors (Van Reijendam) gratefully acknowledges a sta of two months in this Institute, on invitation of the Czechoslovak Academy of Sciences.

TABLE 1. VALUES OF INTEGRALS (eV)

Atom	α_x	γ_{xx}	β
C	11·22	10·53	$\beta_{CC} = \beta_0 = -2{\cdot}318$
O	32·9	22·9	$\beta_{CO} = 0{\cdot}8\,\beta_0$
S	20·0	10·84	$\beta_{CS} = 0{\cdot}7\,\beta_0$

The two-electron repulsion integrals were calculated with the approximation of Mataga and Nishimoto.[9] The molecular geometry was taken to be equal to that of furan[10] and thiophene[11] for the ring part, whereas the side chains were assumed to be in a completely trans configuration and transoid conformation, with bond angles of 120° and bond lengths as in butadiene[12] (1·48 Å for single bonds, 1·34 Å for double bonds). The relative orientation of the 2,3-bond of the ring and the first double bond of the side chain was also taken transoid.

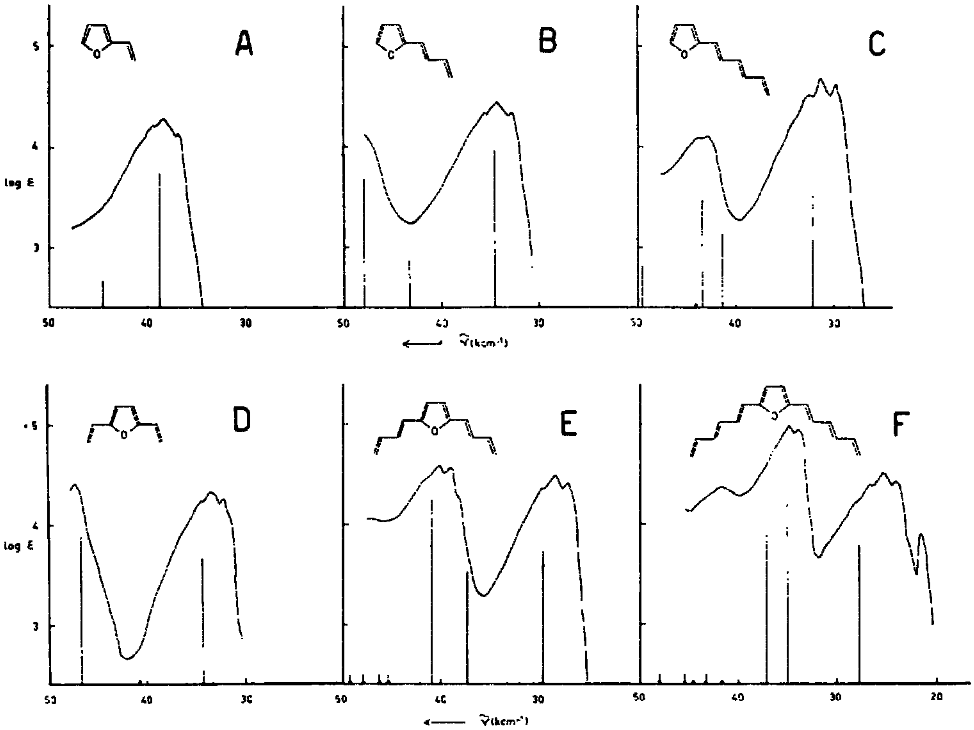


FIG. 1 Experimental and calculated spectral data for polyenyl-substituted furans (1a–f). The calculated transitions are represented by vertical lines. The height of the lines corresponds to the calculated intensity, for which the relation[6] $\log \varepsilon = 4 + \log f$ was used (ε = molar extinction coefficient, f = calculated oscillator strength). Transitions with $\log f < -1{\cdot}6$ are indicated by arrows.

For 1f the zero point of the ordinate is not fixed, as the concentration of the soln was unknown.

The peculiar low-frequency maximum at 21·5 kcm^{-1} decreases in intensity when the soln is allowed to stand for some time; see footnote j to Table 3 of Part I of this series.

The alteration between single and double bonds in the molecules was taken into account by adjusting the value of β_{CC} to the bond length. This was done by means of a relation which has formerly been used in connection with calculations on linear polyenes:[8, 13]

$$\beta_{CC} = \beta_0 \exp(2{\cdot}597 - 1{\cdot}862\, r)$$

where β_0 is the "standard" value of β_{CC} (Table 1) and r is the bond length (in Å).

In the configuration interaction part of the calculations 16 mono-excited configurations were considered, namely those obtained by excitation of an electron from one of the four highest occupied MO's to one of the four lowest vacant MO's.

Results

The results of the calculations are given in graphical form in Figs 1 and 2, together with the experimental spectra and require little comment.

The position of the long wavelength maximum is calculated correctly for the lower members of both series. For the disubstituted furan compounds (**1d–f**) the calculated frequencies are too high by 1–3 kcm^{-1}.

The calculated second transition follows the first one at a closer distance in the thiophene series than in the furan series. It is seen that in 2-vinyl-thiophene (**2a**) and

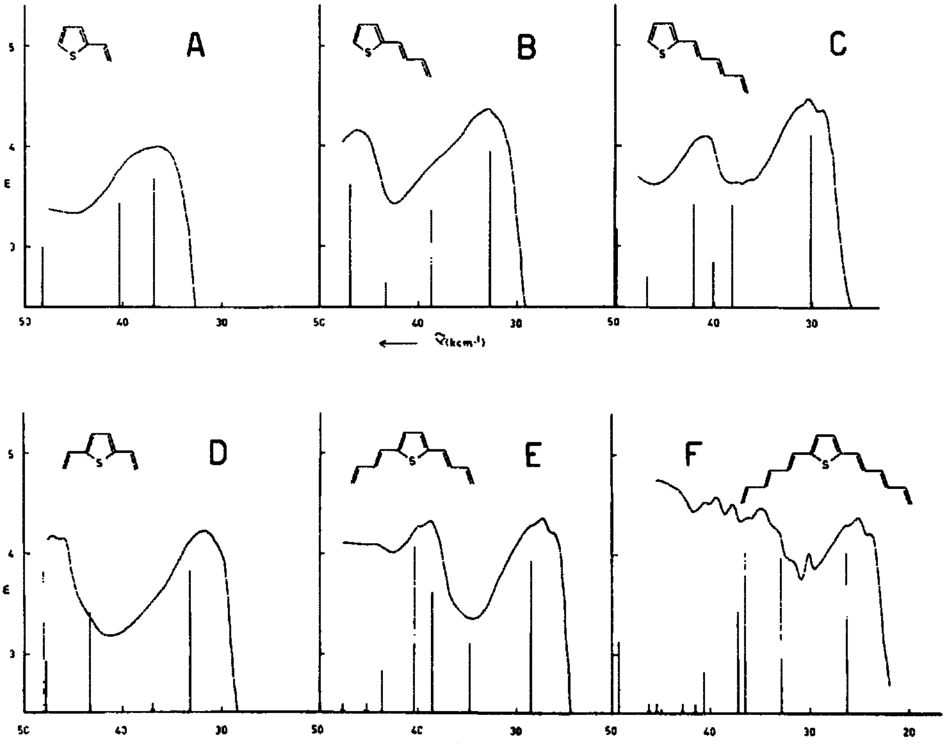


FIG. 2 Experimental and calculated spectral data for polyenyl-substituted thiophenes (**2a–f**). The high-frequency part of the spectrum of **2f** ($\nu > 30$ kcm^{-1}) is uncertain. For this spectrum the zero point of the ordinate is not fixed.

2-(1,3-butadienyl)thiophene (**2b**) the observed long wavelength band in fact consists of two different electronic transitions. Thus the small irregularities, visible on the short wavelength side of this band are nicely accounted for.

In the mono-substituted compounds the second absorption band is always of lower intensity than the first one, whereas in the symmetrical compounds this order is reversed. Also these aspects are correctly reproduced by the calculations.

For all compounds studied, the first transition is a nearly pure N → V_1 transition; the same was found for linear polyenes. For the description of the other transitions configuration interaction is essential.

In Fig. 3 the results of a slightly different parametrization are shown for one representative compound. Raising the value of β_{CO} to β_0 leads to a short-wavelength shift of the first transition and minor shifts in the other transitions. Neglect of the bond alternation has more serious effects. When the same value, β_0, is used for all C—C bonds, the calculated transitions all occur at too low frequencies. These deviations are largest in the compounds with the longest side chains, as might be anticipated.

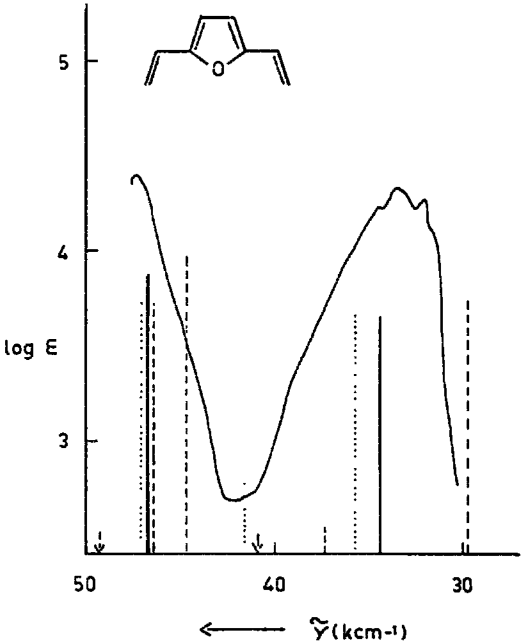


FIG. 3 Experimental spectrum of 2,5-divinylfuran compared with the results of three calculations.

———— Calculation with variable β_{CC} (see text), and $\beta_{CO} = 0{\cdot}8\,\beta_0$.

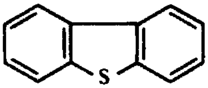
— — – Calculation with $\beta_{CC} = \beta_0$ for all carbon—carbon bonds, and $\beta_{CO} = 0{\cdot}8\,\beta_0$.

………… Calculation with variable β_{CC}, but $\beta_{CO} = \beta_0$.

It can be concluded that also for the compounds under study the PPP method provides a satisfactory interpretation of the spectral characteristics.

The role of the heteroatom

In part I the attention was drawn to the fact that both series of title compounds show their first absorption band at approximately the same wavelengths as the corresponding olefinic substances, i.e., the linear conjugated polyenes in which the same total number of double bonds is present. In contrast, compounds like dibenzothiophene (3) and benzoderivatives thereof, in which the heterocyclic ring is part of a larger condensed aromatic ring system, show a spectrum in which the long wavelength part is strongly dependent on the nature of the heteroatom (O, S, or NH).[14]



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In terms of the LCI-SCF-MO method these facts can be correlated with an important difference between the two groups of compounds.

Namely, in 3 and its three possible mono-benzoderivatives* the highest occupied MO of the ground state is one in which the heteroatom has a very high coefficient (0·6 or more). The energy of this orbital, and the excitation energy of an electron from this orbital, must therefore be strongly dependent on the properties of the heteroatom. Changes in these properties can therefore be expected to have a large influence on the long wavelength part of the spectrum.

The contrary is true for the title compounds 1 and 2. Here the highest occupied MO of the ground state invariably is one in which the heteroatom does hardly participate: its coefficient in this particular MO is zero (in the symmetrical compounds) or 0·1 or less in the other members of the series. This means that in fact this orbital is a polyene orbital, and is very similar in energy and shape to the highest occupied MO of the corresponding polyene. For the lowest unoccupied MO the difference between the title compounds and the appropriate polyenes are larger, but also this orbital has the same form and symmetry characteristics in both groups of compounds.

The effect of these relationships on the long wavelength absorption band is straightforward because for this transition configuration interaction plays hardly any role. Therefore the energy of the first electronic transition can be represented in simplified form† as:

$$\Delta E_i^j = \varepsilon_j - \varepsilon_i - \text{electron repulsion terms} \qquad (1)$$

In this expression ε_j and ε_i are the orbital energies of the lowest unoccupied and highest occupied orbital, respectively, and the electron repulsion terms are determined by the LCAO coefficients of these MO's and the molecular geometry.

In Fig. 4 the quantities occurring in Eq. (1) are given graphically for **1b**, **2b** and the corresponding linear polyene, 1,3,5,7-octatetraene. The energy of the highest occupied MO, ε_i, for each member of 1 and 2 is close to ε_i for the appropriate polyene. The value of ε_j is somewhat lower in the polyene than in the heterocyclic substances, but this is cancelled by a lower value of the electron repulsion terms. The overall result is that the excitation energies are close together for the three compounds.

It is interesting to note that the decrease in the electronic repulsion terms when going from **1b** or **2b** to the linear polyene is largely due to the change from a cisoid structure

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* Calculations by the PPP method of dibenzothiophene and two benzoderivatives have been reported before; see Ref. 6. The calculation of the remaining isomer, 9-thio-3:4-benzofluorene, offers no new important aspects.

† See Ref. 3 for a more rigorous description of the terms used here.

to a transoid. To illustrate this, in Fig. 4 the data are also given for a hypothetical polyene with the same geometry as the carbon atoms in the furan compound **1b**. Compared with the transoid polyene ε_i and ε_j are unchanged, but the repulsion terms are larger, causing a net decrease of the excitation energy of ca. 0·3 eV. These data suggest that, if the title compounds would be compared with the corresponding cyclopentadiene derivatives instead of the linear polyenes, the hydrocarbons would absorb at somewhat longer wavelengths. The differences, resulting from the comparison in Fig. 4, become smaller as the systems compared have a longer polyenic part in common.

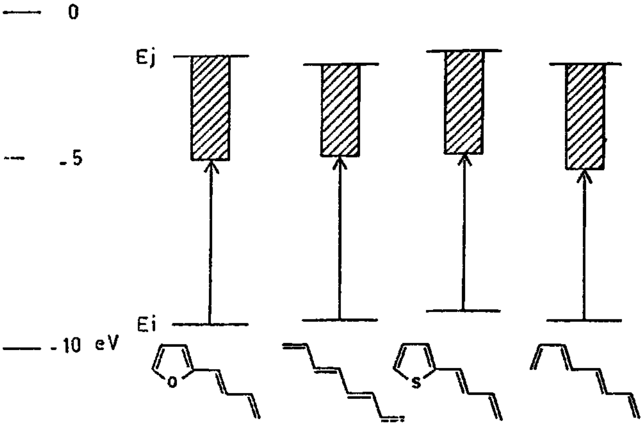

Fig. 4 Orbital energies, electronic repulsion terms and excitation energies for the N → V_1 transition of a set of comparable compounds. The electronic repulsion terms are represented by a shaded area. The resulting excitation energies are given by the length of the arrow.

The findings stated above can be used for predictions concerning other properties than the electronic spectra. For properties dependent on the energy of the highest occupied MO (ionization potentials, polarographic oxidation potentials, charge-transfer spectra) a great similarity should exist between polyenyl-substituted furans and thiophenes on the one hand and linear polyenes on the other hand. For properties connected with the lowest unoccupied MO (electron affinities, polarographic reduction potentials) this similarity will be somewhat less outspoken, but it improves as the systems compared have a larger common polyenic part.

The different importance of the heteroatom in the highest occupied MO of the title compounds **1** and **2** on one hand, and substances like **3** on the other hand, can be clarified by means of Hückel MO correlation diagrams.[15]

Transitions were assumed to involve the following steps:

$$\begin{tikzcd}
\text{Stage A: parent carbon skeleton} + \text{isolated } 2\,p_z \text{ orbital} \arrow[d, "\text{bond formation}"] \\
\text{Stage B: cyclopentadiene anion derivative} \arrow[d, "\text{heteroatom parameters}"] \\
\text{Stage C: thiophene derivative}
\end{tikzcd}$$

The three stages were calculated separately. For sulfur the usual HMO parameters[16] ($\alpha_S = \alpha + \beta$, $\beta_{CS} = 0{\cdot}7\,\beta$) were used. The correlations between the orbitals were possible either by use of their symmetry, or by calculating the slope of the lines by first order perturbation theory.[15]

The two groups of compounds show a very systematic behavior, which is illustrated in Fig. 5 for one representative of both.

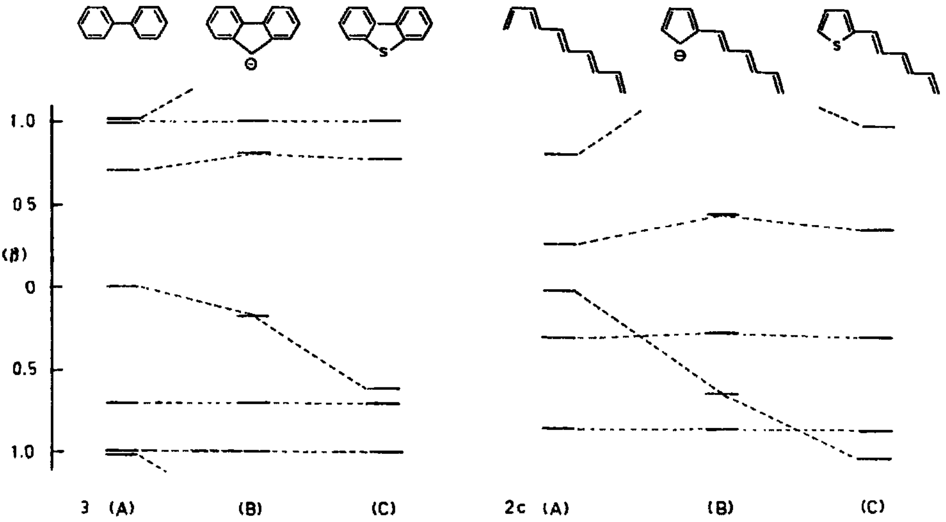

FIG. 5 HMO correlation diagram for the formation of a thiophene ring. Only the orbitals with $|\varepsilon| < 1\beta$ are shown.

The relative position of the orbitals in stage B is determined by two effects. First, the highest occupied MO of the parent system, which carries over practically unchanged from stage A to stage B, is much higher in the polyene system than in the biaryl. This is a well-known property of HMO levels for these types of systems.[15] Second, the orbital which can be correlated with the initially isolated orbital is much lower in **2c** (B) than in **3** (B).

This seems to be a general property for these types of systems. Probably this reflects that in the biaryls the energy situation is already so favorable, that not much is to be gained by the formation of an extra ring, whereas the reverse is true when starting from a polyene.

The adjustment of the parameters for the inserted atom to heteroatom level in the transition from stage B to stage C has about the same effects in both systems. The rudimentary heteroatom orbital goes down $0{\cdot}3$–$0{\cdot}4\,\beta$, because of the increased electronegativity of the atom. For **3** the question which level becomes the highest occupied MO is largely determined by the parameters employed, that is, by the properties of the heteroatom. Consequently the long wavelength part of the spectrum will be influenced strongly, as indeed found. For **2c** the highest occupied MO is largely uninfluenced by the new parameter; here the changes occur only in the lower lying MO's.

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