Furan and Thiophene Analogs of Phenanthrene
A Theoretical Study of the Absorption Spectra of Benzodifurans, Benzodithiophenes and Thiienobenzofurans

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The light-induced cyclisation of cis-stilbene yielding, in presence of an oxidizing agent, phenanthrene has been widely studied and discussed in the last few years. Although the mechanistic aspects of the ring closure are not clear the synthetic potential of this reaction has drawn the attention of organic chemists since its extension to heterocyclic and substituted stilbene analogs. However, excluding those compounds having the heteroatom in β-position to the benzene ring, which from chemical arguments are not expected to be products of such cyclisation three different benzodifurans, three benzdithiophenes and four thiienobenzofurans might be prepared. These are benzodifuran (1), -dithiophene (2), benzodifuran (1,2-b: 3,4-b'), -dithiophene (3) and -dithiophene (4), benzo(1,2-b: 3,4-b')-difuran (5) and -dithiophene (6), thieno(2,3-e)benzofuran, thieno(3,2-e)benzofuran, thieno(3,2-g)benzofuran, benzofuran, benzothiophene and phenanthrene. The calculated π-electron transitions and their oscillator strengths are in good agreement with known absorption spectra. The resemblance of these spectra to the absorption spectra of phenanthrene and phenanthrolines is discussed.

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1 For a detailed review on the photocyclisation of stilbene analogs see: E. V. BLACKBURN and C. J. TIMMONS, Quart. Rev. 23, 482 [1969], and references cited therein.
to be of considerable interest. It was stated that the spectra of 2 and phenanthrene resemble each other in the shape and nature of fine structure, that the spectrum of 7 bears resemblance to that of benzo-
thiophene (12) and that neither phenanthrene, benzo-furan (11), nor 12 serve as models for 3 or 4. These statements have neither theoretical nor deeper experimental foundation except the feeling that the introduction of a heteroatom should not essentially change the spectral behaviour of a π-electron ring system. Thus several factors remain to be explained and we thought it worthwhile to start a theoretical study of these spectra applying the LCAO—MO—SCF —CI method to compounds 1—12. This method is so far one of the best for the calculation and prediction of absorption spectra of π-electron systems. Especially we were interested to which extent the spectra of 1—10 could be related to the spectrum of phenanthrene and the possibility of a fortuitous resemblance to it. For this reason we also calculated the spectrum of phenanthrene.

Calculations

As mentioned before, we applied the LCAO—MO—SCF formalism within the framework of the Pariser—Parr and Pople (PPP) approximation. Several authors have shown that extension of the PPP method to oxygen and especially sulphur heterocycles is rather difficult since lack of data makes the parameter choice in some way arbitrary. However, a number of successful correlations between PPP calculation results and experimental data for oxygen and sulphur heterocycles made the application of this method a standard and reliable tool for the study of molecular properties. At this place we wish to point out the thorough work of Bloor et al. who already calculated compounds 11 and 12 and whose parameters we used, with slight changes, in our calculations (Table I). With this parameter set and evaluating the two-centre Coulomb integrals, γ_{XY}, by the Nishimoto-Mataga approximation we calculated the ground state SCF orbitals of each molecule and then the singlet π-electron energy levels by the standard configuration interaction procedure including all singly excited configurations. The reported oscillator strengths for all transitions were evaluated from

\[ \mathcal{f}_{nm} = 0.0875 (E_m - E_n) |M_{nm}|^2 \]

and the usual method was employed to obtain transition moments.

Results and Discussion

The calculated electronic transitions for the studied molecules are given together with their absorption spectrum (if it was known) in Figs. 1—13. The lengths of the lines representing the calculated spectrum correspond to calculated oscillator strengths. The orientation respective to the orthogonal coordinate system in the calculation is indicated only for phenanthrene in Fig.1 but is the same for all molecules.

Before starting a discussion of the theoretical and experimental results on benzodifurans, benzodithiophenes and thienobenzofurans we shall consider the spectrum of phenanthrene. Using the nomenclature proposed by Platt it consists of following absorption bands (in order of ascending energy): \(1\text{L}_b, 1\text{L}_a, 1\text{B}_b, 1\text{B}_a, 1\text{C}_b, 1\text{C}_a\). The sequence of these bands has been established by theoretical and experimental results since \(1\text{L}_a\) and \(1\text{B}_a\) are polarised in the long axis (x) whereas \(1\text{L}_b\) and \(1\text{B}_b\) are polarised along the short axis (y) of the molecule. In phenanthrene the maxima of the absorption bands are at \(1\text{L}_b: 28960 \text{ cm}^{-1}; 1\text{L}_a: 34200 \text{ cm}^{-1}; 1\text{B}_b: 39830 \text{ cm}^{-1}; 1\text{B}_a: 40970 \text{ cm}^{-1}; 1\text{C}: 45350 \text{ and 47300 cm}^{-1}\). The structured \(1\text{L}_b\) band is of very low intensity (\(\varepsilon < 250\)) and is therefore

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Atom & \(W_{X^+}(\text{eV})\) & \(\gamma_{X^+}(\text{eV})\) & \(\beta_{cX}(\text{eV})\) & \(r_{cX}(\text{Å})^*\) \\
\hline
C & 11.16 & 11.13 & -2.39 & 1.40 \\
O & 33.00 & 21.53 & -1.80 & 1.37 \\
S & 22.20 & 13.05 & -1.50 & 1.74 \\
\hline
\end{tabular}
\caption{Summary of Parameters. The assumption was made that all investigated molecules are planar.}
\end{table}


Fig. 1. Observed (in cyclohexane) and calculated absorption spectrum of phenanthrene. Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. The observed spectrum is given arbitrary.

Fig. 2. Calculated absorption spectrum of benzo(1,2-b:3,4-b')-difuran (1). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. Log $\varepsilon$ is given arbitrary.

Fig. 3. Observed (in cyclohexane) and calculated absorption spectrum of benzo(1,2-b:3,4-b') dithiophene (2). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. The observed spectrum is given arbitrary (log $\varepsilon>2.5$).

Fig. 4. Observed (in cyclohexane) and calculated absorption spectrum of benzo(1,2-b:4,3-b') difuran (3). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. The observed spectrum is given arbitrary (log $\varepsilon>2.5$).

Fig. 5. Observed (in cyclohexane) and calculated absorption spectrum of benzo(1,2-b:4,3-b') dithiophene (4). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. The observed spectrum is given arbitrary (log $\varepsilon>2.5$).
Fig. 6 Calculated absorption spectrum of benzo(2,1-b: 3,4-b')-difuran (5). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. Log $\varepsilon$ is given arbitrary.

Fig. 7. Calculated absorption spectrum of benzo(2,1-b: 3,4-b')-dithiophene (6). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. Log $\varepsilon$ is given arbitrary.

Fig. 8. Observed $^3$ (in cyclohexane) and calculated absorption spectrum of thieno (3,2-e) benzofuran (7). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. The observed spectrum is given arbitrary ($\log \varepsilon > 2.5$).

Fig. 9. Calculated absorption spectrum of thieno (2,3-e) benzofuran (8). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. Log $\varepsilon$ is given arbitrary.

Fig. 10. Calculated absorption spectrum of thieno (2,3-e) benzofuran (9). Abscissa: Frequency in cm$^{-1}$. Ordinate: Oscillator strength $f$. Forbidden transitions are indicated by crosses. Log $\varepsilon$ is given arbitrary.
not shown in Fig. 1. The $1^B_a$ and $1^B_b$ bands are close together and are responsible for the most intensive absorption of phenanthrene. The coincidence of these bands is also the reason why phenanthrene exhibits a four—instead in five-band spectrum bellow 50,000 cm$^{-1}$.

In a previous comparative study of phenanthrene and phenanthroline absorption spectra$^{10}$ it was shown that the effect of incorporation of two nitrogens on the phenanthrene spectrum could be described as follows: a) the $1^L_b$ and $1^L_a$ bands practically do not change their position, the intensity of the former being strongly dependent on the position of the heteroatoms and b) the shorter wavelength bands show great differences to those of phenanthrene, the $1^B_b$ and $1^B_a$ as well as the $1^C_b$ and $1^C_a$ bands interchange their position and as a rule the most intensive transition is at a shorter wavelength than in phenanthrene. Here should be mentioned that in the case of phenanthrolines, benzo-difurans and benzodithiophenes this nomenclature and direct comparison holds only for those which belong to the same symmetry group as phenanthrene (C$^{2v}$). In the present case these are compounds 3, 4, 5 and 6. In Table II the position of the calculated lowest transitions (in cm$^{-1}$) of all compounds investigated are quoted together with their oscillator strength, polarisation (the angle respective to the

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Table II. Position, oscillator strength, polarisation and assignment of the calculated lowest electronic transitions of phenanthrene and (1) — (12).

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positive x-axis is given) and proposed assignment in correspondence to that of phenanthrene bands. A comparison of the observed and calculated spectra shows that good agreement can be obtained by the present type of calculation.

The results given in Figs. 1 — 13 and Table II can be summarised as follows:

a) The absorption spectra of benzodifurans, benzodithiophenes and thienobenzofurans appear at shorter wavelength than phenanthrene absorption. Benzodifurans absorb at a higher energy than thienobenzofurans and these at higher energy than benzodithiophenes. This holds with few exceptions.

b) Compounds 3, 4, 5 and 6 of C²ᵥ symmetry have, regarding the order and polarisation of the electronic transitions, essentially also a phenanthrene-type absorption spectrum. Interchange of bands occurs initially at the fourth transition.

c) Compounds 1, 2, 8 and 9 which most deviate from C²ᵥ symmetry are characterized by the very intensive third transition which is polarised nearly in the long axis (x) of the molecules. The similarity of the spectra of 2 and of phenanthrene must only be coincidental.

d) The observed high intensity of the first transition in 7 is also reproduced by the calculation. This band is polarised mainly in the long axis (x) of the molecule as in the case of the first transition in 12 which exhibits a spectrum of similar shape. But in this case too the calculated spectra can hardly support a presumption of a similar nature.

Our results, just as in the previous work on phenanthrolines¹⁰ indicate that the changes occurring in the absorption spectrum of a parent aromatic polycyclic hydrocarbon by the replacement of carbon atoms by heteroatoms in the skeleton depend more on the position of the inserted heteroatoms than on their nature. Similar behaviour was found for the stabilities of condensed five-ring heterocyclic π-electron molecules, where so-called "positional isomers" have the same place in the relative stability scale irrespective the nature of the heteroatoms¹³. Further study of the correlation of molecular properties in positional isomers seems therefore to be of interest.

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