Interpretation of the Influence of Substituents on the UV Spectra of Benzofurans

Walter Fabian
Institute of Organic Chemistry, University of Graz

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The electronic excitation energies of twelve isomeric methoxy- and nitrobenzofurans were calculated by means of PPP and CNDO/S-CI method. Based on the results of a configuration analysis a simple molecules-in-molecule-type model is proposed which in a semiquantitative manner completely accounts for the characteristic dependence of the UV spectra of these compounds on the position of the substituent.

Introduction

Nitro as well as methoxy derivatives of benzofuran have attracted considerable interest due to their pharmacological properties, especially their cytostatic or radioprotective action as well as their antimicrobial activity [1–7]. In addition the high fluorescence quantum yields of phenylsubstituted benzofurans have led to their use as analytical reagents [8]. Despite this importance relatively little is known about the electronic structure of substituted benzofurans. So far theoretical work was mainly restricted to benzofuran itself, especially to a comparison of its electronic states with the isoelectronic counterparts indole and indenide anion [9–12]. To the best of our knowledge no systematic theoretical study concerning the effect of substitution upon the electronic structure of this important class of compounds has been published. Experimentally, it has been found that simple substituted benzofurans show a marked dependence of the first electronic absorption band on the position as well as the nature of the substituent (see Table 1) [13]. In continuation of our previous work on the electron spectroscopic properties of heterocyclic compounds [14] we present here an analysis and interpretation of the above mentioned characteristic variation of the longest wavelength absorption band of substituted benzofurans with position and nature of the substituent. For this purpose we have chosen the six isomeric methoxy- and nitrobenzofurans as models for donor and acceptor substituted derivatives.

Calculation Procedure

Excitation energies as well as oscillator strengths were calculated by means of the semiempirical Pariser-Parr-Pople (PPP) [15, 16] as well as the CNDO/S-CI method [17]. The results of the PPP calculations were subjected to the configuration analysis of Baba et al. [18]. Finally, the results obtained by this method are used to develop a simple model based on the molecules-in-molecule approach [19] to describe at least semiquantitatively the effect of position and nature of the substituent on the absorption properties.

Results and Discussion

Table 1 lists the calculated (PPP and CNDO/S-CI) as well as the experimental [13] excitation energies and oscillator strengths of the compounds investigated in this paper. As can be seen from the data presented there the calculated values agree quite satisfactorily with the experimental ones. Especially the marked dependence of the transition energy on the position of the substituent is nearly perfectly reproduced by both semiempirical methods. Only in the case of 3-methoxy- and 7-nitrobenzofuran the PPP method predicts a somewhat too low transition energy. The most striking feature of these data is the fact that within the series of the isomeric methoxy derivatives substitution in position 5 leads to absorption at the longest wavelength whereas in the case of nitro substitution this same isomer is characterized by absorption at the shortest wavelength. The theoretical results are in complete agree-

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Reprint requests to Doz. Dr. Walter Fabian, Institute of Organic Chemistry, University of Graz, Heinrichstr. 28, A-8010 Graz, Austria.

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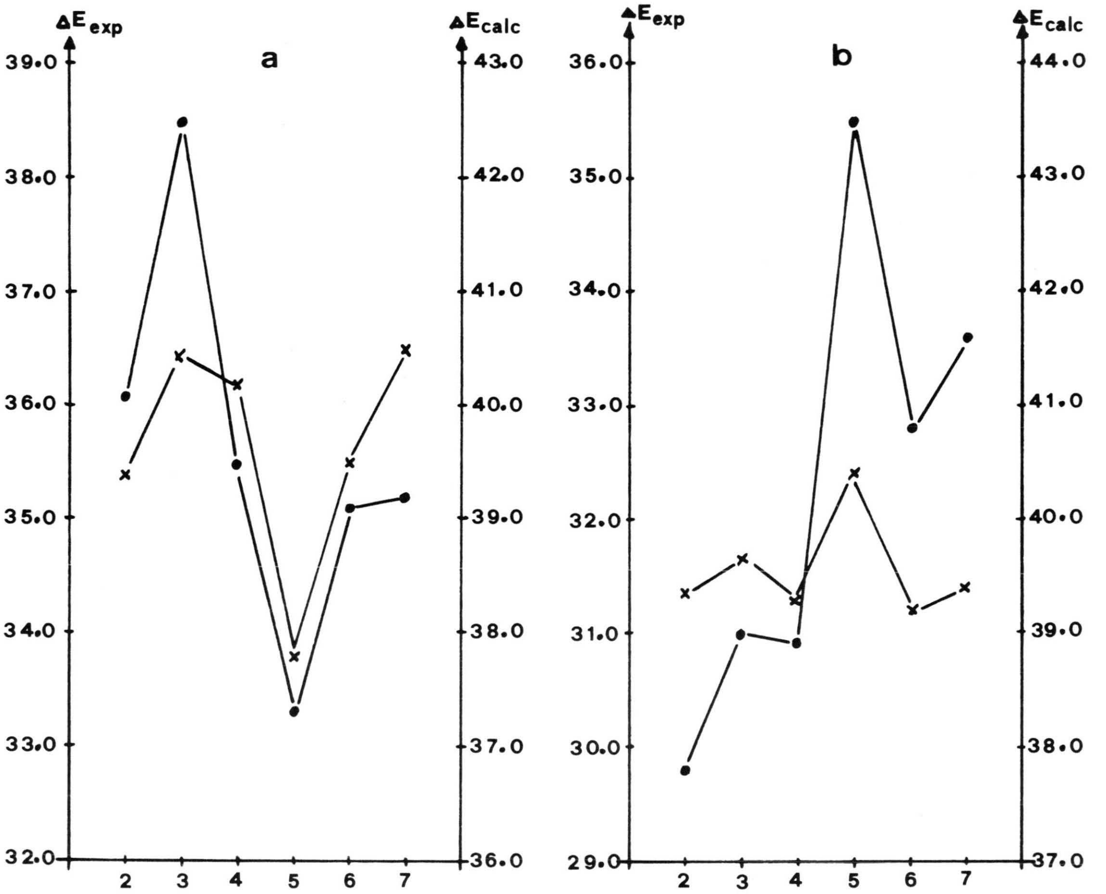

Fig. 1. Experimental (●, left scale) and calculated (×, right scale) by the model (see text) variation of the first excitation energy with the position of the methoxy (Fig. 1 a) and nitro group (Fig. 1 b), respectively.

Table 1. Experimental and calculated $\pi\pi^*$-transition energies of substituted benzofurans (in $10^3\,\text{cm}^{-1}$).

Substituent	$\tilde{\nu}_{\text{exp}}$	$\log \varepsilon$	$\tilde{\nu}_{\text{calc}}$ (f)	
			PPP	CNDO/S
2-MeO (**1**)	36.1	3.20	36.2 (0.14)	32.8 (0.12)
3-MeO (**2**)	38.5	3.80	35.9 (0.22)	33.0 (0.09)
4-MeO (**3**)	35.5	3.35	35.8 (0.15)	32.8 (0.10)
5-MeO (**4**)	33.3	3.51	34.9 (0.09)	32.7 (0.04)
6-MeO (**5**)	35.1	3.68	35.7 (0.10)	32.8 (0.11)
7-MeO (**6**)	35.2	3.14	36.0 (0.05)	32.8 (0.07)
2-NO_2 (**7**)	29.8	3.92	30.8 (0.41)	31.8 (0.30)
3-NO_2 (**8**)	31.0	4.25	33.3 (0.18)	33.4 (0.08)
4-NO_2 (**9**)	30.9	3.97	31.8 (0.27)	31.4 (0.18)
5-NO_2 (**10**)[a]	35.5	3.83	36.0 (0.04)	33.3 (0.01)
6-NO_2 (**11**)	32.8	4.03	33.1 (0.22)	32.0 (0.15)
7-NO_2 (**12**)	33.6	3.87	31.6 (0.24)	32.6 (0.12)

[a] For this compound both PPP and CNDO/S-CI predict a transition of very low intensity ($f < 0.01$) at longer wavelength (PPP: 33.7; CNDO/S: 32.9).

ment with this remarkable effect of the nature of the substituent. From the results of the configuration analysis presented in Table 2 immediately some qualitative conclusions can be drawn. First of all, the ground state of all compounds can almost completely be described by the no bond (NB) configuration with a small admixture of charge transfer (CT) configurations. Within the series of methoxybenzofurans the S_1 state is represented by a mixture of the first and second locally excited (LE) states of the benzofuran parent chromophore and varying amounts of CT configurations. Since, in contrast to the other isomers **1** and **3–6,** in 3-methoxybenzofuran **2** the first excited state is mainly composed of the second locally excited state (see Table 2) one may expect absorption at considerably shorter wavelength as compared to the other isomers. On the other hand, 5-methoxybenzofuran **4** shows the

Table 2. Results of the configuration analysis (in %, NB: no bond, LE: locally excited, CT: charge transfer).

Compound	Configuration analysis	Compound	Configuration analysis
1 S_0	$89.1\,NB + 5.3\,CT_1$	**7** S_0	$92.1\,NB$
S_1	$68.7\,LE_1 + 23.0\,LE_2 + 4.8\,CT_1$	S_1	$16.1\,LE_2 + 64.5\,CT_1$
2 S_0	$90.4\,NB + 5.9\,CT_3$	**8** S_0	$92.4\,NB$
S_1	$13.3\,LE_1 + 68.4\,LE_2 + 11.5\,CT_1$	S_1	$6.2\,LE_2 + 71.6\,CT_1$
3 S_0	$88.0\,NB + 6.5\,CT_1$	**9** S_0	$93.2\,NB$
S_1	$68.0\,LE_1 + 19.7\,LE_2 + 5.2\,CT_1$	S_1	$30.0\,LE_2 + 58.0\,CT_1$
4 S_0	$89.2\,NB + 7.3\,CT_2$	**10** S_0	$93.5\,NB$
S_1	$83.0\,LE_1 + 11.9\,CT_1$	S_1	$14.1\,LE_1 + 39.0\,LE_2 + 36.6\,CT_2$
5 S_0	$88.7\,NB + 4.5\,CT_1$	**11** S_0	$93.6\,NB$
S_1	$81.2\,LE_1 + 6.9\,LE_2 + 5.4\,CT_1$	S_1	$14.6\,LE_1 + 26.5\,LE_2 + 49.3\,CT_1$
6 S_0	$89.4\,NB + 5.3\,CT_1$	**12** S_0	$92.4\,NB$
S_1	$85.0\,LE_1 + 3.8\,LE_2 + 5.2\,CT_2$	S_1	$21.2\,LE_2 + 64.1\,CT_1$

largest contribution of the CT configuration thus indicating most effective energy lowering of the first locally excited state, i.e. absorption at the longest wavelength within the series of isomeric methoxybenzofurans. Both conclusions are clearly in agreement with the experimental findings (Table 1). Within the series of nitrobenzofurans much larger contributions of CT configurations are found. This is in complete agreement with the generally longer wavelength absorption of these derivatives as compared to the methoxy analogues. The smallest CT contribution is found for the 5-nitro derivative **10.** In addition, in this case the second, i.e. higher energy, CT configuration is involved. Much less energy lowering of the locally excited state, therefore, will occur, and in striking contrast to 5-methoxybenzofuran **4** this isomer will absorb at considerable shorter wavelength than the other nitrosubstituted isomers (Table 1).

To put these conclusions on an at least semiquantitative footing a simple model is proposed: according to the results of the configuration analysis (Table 2) the ground state of all compounds investigated in this paper is described by a linear combination of the NB and the appropriate CT configuration. Similarly, for the first excited state a linear combination of locally excited states and CT configurations is used, i.e.

$$\Psi(S_0) = c_{00}\,\Phi(NB) + c_{i0}\,\Phi(CT_i)\,,$$
$$\Psi(S_1) = c_{11}\,\Phi(LE_1) + c_{21}\,\Phi(LE_2) + c_{i1}\,\Phi(CT_i)\,.$$

The various matrix elements between the configurations involved in this ansatz were calculated according to [20]. Of course, one cannot expect from such a very limited configuration interaction treatment reliable numerical results. Instead, it is our intention to keep the model as simple as possible while retaining the essential features to unravel the main factors responsible for the influence of the substituents on the excitation energies. The results obtained by this simple model are displayed in Figure 1. As can be seen from Fig. 1 the experimentally observed variation of the energy of the first electronic absorption band with the position of substituents is quite satisfactorily reproduced by the simple model described above. Taking into account additional configurations in the CI treatment thus merely will result in an improvement of the numerical data while the main trend can already be described properly on the basis of this model. In conclusion one, therefore, may safely assume that the main factors governing the distinctly different absorption properties of the isomeric methoxy- and nitrobenzofurans can be completely analyzed and interpreted with the aid of this simple model.

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