Substitution Effects on Electronic Structure of Thiophene

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The He(I) photoelectron (PE) spectra of the following methoxy (-MeO) and nitro (-NO₂) thiophenes: 2-MeO, 3-MeO, 2,5-di-MeO, 2-NO₂, 3-NO₂, 2,4-di-NO₂ and 2,5-di-NO₂ have been recorded and their electronic structure is discussed in terms of inductive and mesomeric effects of substituent on the electronic energy levels of thiophene.

Introduction

Thiophene, a heterocycle with remarkable benzenoid ("aromatic") character has intrigued both experimentalists and theoreticians for a long time. Many exciting and surprising facts have resulted from these investigations. Last years molecular photoelectron (PE) spectroscopy [1–7] and most recently Penning ionization electron spectroscopy [8] (PIES) played a dominant role in the conclusive assignment of the valence electronic structure of this molecule and also helped greatly in developing sophisticated methods for quantum chemical calculations of such medium-sized molecules [9]. Thus, there is a general agreement that the electronic structure of thiophene may be considered as confirmed. In view of our interest in the electronic structure, chemical behavior and structure activity relationship of thiophenes [7, 10–12] we have investigated the effects of mono- and di-, methoxy-, and -nitro substitution on thiophene. These substituents were chosen as typical representatives of electron donating and electron withdrawing groups whose mode of action has been elucidated repeatedly in benzene ring substitution and quantified in terms of the well known Hammett relationship. To date only few papers have reported on the effect of substituents (methyl and halogen) in thiophene [11, 13–16].

Experimental

Compounds

3-Nitrothiophene was supplied by K & K Laboratories, Inc. 2-Methoxythiophene [17], 3-methoxythiophene [18], 2-nitrothiophene [19], 2,4-nitrothiophene [20] and 2,5-dinitrothiophene [20] were synthesized by described procedures.

2,5-Dimethoxythiophene was prepared by a modification of a procedure published earlier [21]. Dry copper (II) oxide (9.7 g) and 2,5-dibromothiophene (18.5 g) were added into a methanol solution of sodium methoxide prepared from 19.4 g of sodium and 150 ml of absolute methanol. After four days of stirring under reflux, the mixture was cooled, filtered, poured in water and extracted with ether. The combined ether solutions were dried, and solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel; petrolether 30–50 °C) and distilled to yield 0.6 g of product, b.p. 96–98 °C (25 Torr); ¹H NMR (CDCl₃): 5.88 (s, thienylic, 2H), 3.80 (s, OMe, 6H).

All compounds were recrystallized or redistilled *in vacuo* prior to spectroscopic measurement, and purity checked by the ¹H NMR spectra.

Spectra

The He(I) photoelectron spectra were recorded on a Vacuum Generators UVG 3 spectrometer [22] with a resolution of approx. 35 meV FWHM and at 100 °C of the inlet system. The energy scale was calibrated by admission of small quantities of iodomethane and/or xenon to the sample flow during the measurement. The quoted ionization energies are accurate within 0.05 eV.

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Results and Discussion

The low resolution He(I) PE spectra of 2,5-dinitrothiophene, 3-nitrothiophene, 2-nitrothiophene, 2,5-dimethoxythiophene, 3-methoxythiophene and 2-methoxythiophene (top to bottom) are shown in Fig. 1, the numbers on top of the observed band systems corresponding to ionization energies, E_i /eV.

The outer valence structure of thiophene is $1a_2$ (π_3), $2b_1$ (π_2), $6a_1$ (n_s), $1b_1$ (π_1), $4b_2$ (σ), $5a_1$ (σ), and $3b_2$ (σ), corresponding to observed ionization energies of 8.85, 9.45, 12.0, 12.46, 13.11, 13.8, and 14.23 eV, respectively [7]. Compared to thiophene

itself, the PE spectra of methoxythiophenes are shifted to lower ionization energies, and those of nitrothiophenes to higher ionization energies as a result of the substituent effects on the n_s and three ring orbitals. The correlation diagram for these molecules is shown in Fig. 2. Throughout the ensuing discussion, the symbols π_3 , π_2 , π_1 and n_s denote the ring orbitals, while symbols like π_{NO_2} , n_0^+ *etc.* denote the substituent orbitals. Although these orbitals do retain some of their “ring” or “substituent” character, such a classification is, strictly speaking, not possible due to the fact that, in an imagined process of as-

Fig. 1. He(I) spectra of methoxy and nitro substituted thiophenes.

sembling a molecule from a ring and a substituent part, all of the ring and substituent orbitals of the correct symmetry will interact and, consequently, mix with one another. Nevertheless, keeping the distinction between “ring” and “substituent” orbitals is useful and adequate for the purpose of generalizing and classifying the substituent effects.

The introduction of a single methoxy group exhibits a rather dramatic effect on the ring orbitals. Although the average shift of the highest four thiophene orbitals is 0.25 eV for 3-methoxythiophene and 0.35 eV for 2-methoxythiophene, the distribution of these shifts among the four orbitals is quite uneven. The most marked effect is exerted by the highest (π_3) orbital which is destabilized from its thiophene position by nearly 0.5 eV in 3-methoxy and approximately 0.7 eV in 2-methoxythiophene. The second highest orbital (π_2) is shifted by 0.25 eV toward lower E_i in both 3- and 2-methoxythiophene, the net effect being an increase of the gap between π_3 and π_2 from the original 0.6 eV in thiophene to approximately 0.8 eV and to a little over 1 eV in 3- and 2-methoxythiophene, respectively. The behavior of the n_s orbital parallels that of the π_2 orbital, *i.e.* it is shifted toward lower E_i by approximately 0.2 eV in both 3- and 2-methoxythiophene. This keeps the energy gap between π_2 and n_s at an almost constant value of approximately 2.6 eV, the main difference from thiophene being the fact that the additional π_0 orbital (the oxygen lone pair orbital roughly perpendicular to, and conjugated with the ring) arises in this region. The corresponding ionizations are, in fact, found at 11.30 eV and 11.19 eV in 3- and 2-methoxythiophene, respectively.

The effect of the addition of a second methoxy group, as in 2,5-dimethoxythiophene, is mostly reflected on the π_3 orbital. This orbital undergoes an additional destabilization of approximately 0.4 eV as compared to 2-methoxythiophene, which brings the total destabilization, as compared to thiophene, to approximately 1 eV (which is, incidentally, almost twice the value of the effect provoked by a single methoxy group in the 2 position). In contrast to this, the π_2 and n_s orbitals stay at roughly the same energies as in the two single substituted methoxythiophenes, which increases the gap between π_3 and π_2 to 1.3 eV while preserving the gap between π_2 and n_s at 2.6 eV. The two π_0 ionizations fill in, of course, some of the region spanned by the latter gap.

Apparently, the most erratic behavior is displayed by the π_1 orbital: a methoxy substitution of thiophene in the 3-position does not alter its position appreciably, while the 2-substitution brings about a destabilization of approximately 0.3 eV. However, the cumulative effect of two methoxy groups in the 2-position (as in 2,5-dimethoxythiophene) results in a destabilization of roughly two third (0.2 eV) of the value of a single substituent.

The introduction of a single nitro group on a thiophene ring exhibits, as expected, an effect opposite in sign to the effect of a methoxy group. However, as we shall see, the underlying logic is not that of a simple reversal of the effects observed for the methoxy group.

In nitrothiophenes, the average shift of approximately 0.8 eV of the four highest thiophene orbitals is distributed much more evenly than in the case of methoxythiophenes. In both 2- and 3-nitrothiophene the position of the ring and substituent π and n orbitals is very much the same. As compared to thiophene, the π_3 orbital is stabilized by 0.9 eV, which is just marginally larger than the amount of destabilization of the remaining ring orbitals, and brings the gap between the two highest orbitals to 0.5 eV. The gap between π_2 and n_s is, however, maintained at the thiophene value. The π_1 orbital is apparently stabilized somewhat less than the remaining ring orbitals, and is very close in energy to the n_s orbital. The energy region between the π_2 and n_s is, as in the case of the methoxythiophenes, partly filled with the substituent orbitals. The nitro group is expected to bring two orbitals in this region: one corresponding to one of the two possible combinations of the two in-plane oxygen lone pairs, n_0 , and the other corresponding to the π -electrons located mainly on the oxygen atoms, π_{NO_2} , and conjugated to the ring π orbitals. The parent orbitals [23] in nitromethane are found at 11.29 and 11.71 eV, respectively, while the other combination of the two in-plane oxygen lone pairs is found at 14.76 eV which is outside the region of interest of this discussion.

The same discussion can be applied to 2,5-dinitrothiophene as it would appear that the electronic structure of this molecule can be rationalized in terms of a second nitro group perturbing 2-nitrothiophene, the main feature being the fact that the effect of the second nitro group upon the ring is somewhat smaller than the effect of the first group. Thus, the ring orbitals experience an additional aver-

Fig. 2. Correlation of vertical ionization energies for π and n orbitals of substituted thiophenes.

Fig. 3. He(I) PE spectra of 2,4-dinitrothiophene and 2,5-dinitrothiophene.

age stabilization of 0.6 eV which is distributed among these orbitals according to the pattern already discussed for a single nitro substitution. This explains a somewhat smaller gap between π_3 and π_2 (0.4 eV) and an unchanged gap between π_2 and n_s . The latter gap is, of course, now filled in by two π_{NO_2} and two n_0^+ band systems.

In conclusion, it is evident that, on the average, the nitro group shows a stronger interaction with the thiophene ring than the methoxy group. The measured inductive shifts are 0.7 eV for the nitro group and -0.3 eV for the methoxy group. Furthermore, it appears that the former is predominantly an inductive substituent, while the latter is predominantly a conjugative substituent, as evidenced by a dramatic splitting of the orbital in methoxythiophenes. Poor conjugation of the ring orbitals with the π_{NO_2} orbital can be rationalized through the fact that π_{NO_2} is localized mainly at the distant oxygen atoms. On the other hand, the inductive effect of the methoxy

group of -0.3 eV can be almost completely attributed to the methyl moiety [24] leaving to the oxygen heteroatom the role of a pure conjugative substituent, whose effect is almost entirely concentrated upon the highest occupied ring orbital.

The effect of the ring heteroatom is negligibly small, as evidenced by the approximate 0.1 eV difference between the energy levels of 2- and 3-substituted thiophenes (with the former being of lower energy). Furthermore, there is obviously no "synergistic" effect, since two substituents exercise, at best, the sum of the single substituent effects (and usually somewhat less than that).

These conclusions allow the prediction that, *e.g.* 2,4-nitrothiophene should exhibit the same PE spectrum as 2,5-nitrothiophene in the low energy region and that is exactly what was found (Fig. 3). Unfortunately, this indicates that UVPE spectroscopy is not the method of the choice for easy distinction of isomers of substituted thiophenes.

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