# Secondary steric effects in $S_NAr$ of thiophenes: a coordinate kinetic, thermodynamic, UV–VIS, crystallographic and *ab initio* study

PERKIN 2

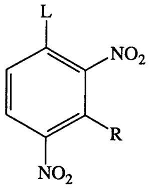
**Giovanni Consiglio,[a] Vincenzo Frenna,[b] Angelo Mugnoli,[c] Renato Noto,[b] Marcella Pani[c] and Domenico Spinelli[a]**

[a] *Dipartimento di Chimica Organica 'A. Mangini', Via S. Donato 15, Bologna, I-40127, Italy*
[b] *Dipartimento di Chimica Organica 'E. Paternò', Via Archirafi 20, Palermo, I-90123, Italy*
[c] *Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, Genova, I-16146, Italy*

**The reactivity of some dinitro-benzene and -thiophene derivatives with piperidine and sodium benzenethiolate has been examined giving evidence that benzenes show large and thiophenes show small kinetic secondary steric effects, respectively. The acid dissociation reaction and the UV–VIS spectra of some nitrothiophenamines have also been studied. The crystal structure and the absolute conformation of 2-iodo-3,5-dinitrothiophene and of 2-iodo-4-methyl-3,5-dinitrothiophene have been determined. For different conformations of the analogous chlorodinitro derivatives in the thiophene and benzene series, *ab initio* energy calculations have been performed. The results collected show that steric strain among adjacent groups affects the benzene and thiophene compounds and the kinetic, thermodynamic and spectroscopic properties of the molecules examined differently. Differences in geometry of the two aromatic rings and then in rotation of nitro groups with respect to the rings themselves as well as differences along reaction coordinates (essentially depending on hybridation changes) are used to explain the above data.**

Activated aromatic nucleophilic substitution in halogenobenzenes can be subject to secondary steric effects.[1] In fact a strong decrease of reactivity is observed when the activating group (electron-withdrawing groups such as $NO_2$, CN, COR, *etc.* in the *ortho* and/or *para* position with respect to the halogen) cannot exert its total potential electronic effect because of steric effects.

On comparing the piperidinodechlorination rates in ethanol of 2,4-dinitrochlorobenzene **1** and of 3-chloro-2,6-dinitrotoluene **2** ($k_H/k_{Me}$ *ca.* 800 at 30 °C), Capon and Chapman[1b] showed a classical example of the secondary steric effect. This is related to the torsion and/or to the out-of-plane bending of the nitro groups determined by the intramolecular hindrance of the methyl group inserted between the two nitro groups.

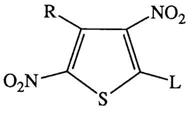


**1,2,7,8**

**1**: L = Cl; R = H **2**: L = Cl; R = Me
**7**: L = $SO_2Ph$; R = H **8**: L = $SO_2Ph$; R = Me

We have recently determined the crystal structure of **2**[2] (that of **1** was already known)[3] and the results obtained have confirmed the importance of the steric inhibition of resonance in connection with the observation of secondary steric effects in $S_NAr$ reactions.

On the other hand some of us have pointed out that in $S_NAr$ reactions of thiophene derivatives secondary steric effects are not important.[4] In fact 2-halogeno-3,5-dinitrothiophenes **3** and 2-halogeno-4-methyl-3,5-dinitrothiophenes **4** show similar reactivities with piperidine ($k_H/k_{Me}$ *ca.* 2 at 20 °C).[4a,c] This behaviour has been blamed on the peculiar geometry of five-membered ring derivatives,[4a] which strongly lowers the steric interactions between the substituents of the thiophene ring.

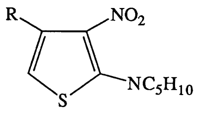


**3–6**

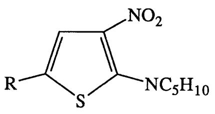
**3**: L = Cl (**a**), Br (**b**), I (**c**); R = H
**4**: L = Cl (**a**), Br (**b**), I (**c**); R = Me
**5**: L = $SO_2Ph$; R = H
**6**: L = $SO_2Ph$; R = Me

In order to confirm this view about the poor weight of secondary steric effects in $S_NAr$ reactions of thiophene derivatives and to correlate molecular geometry with reactivity we have carried out a crystal structure analysis of 2-iodo-4-methyl-3,5-dinitrothiophene **4c** (which should show the highest steric interactions among compounds **4** on account of the size of iodine) and of 2-iodo-3,5-dinitrothiophene **3c**.

To extend the comparison between the behaviour of five- and six-membered ring derivatives we have also collected the following data: (*a*) further kinetic data in methanol on $S_NAr$ with different nucleophiles (piperidine and sodium benzenethiolate) of some thiophene (**3a** and **4a**, **5** and **6**) and benzene (**1** and **2**, **7** and **8**) derivatives; (*b*) $pK_{BH^+}$ measurements of some thiopheneamines to provide evidence for the effect of the alkyl group present at C(4) on the through-conjugation between the amino group at C(2) and the nitro groups at C(3) and/or at C(5); (*c*) *ab initio* calculations of compounds **2, 4a** with the aim of leaving out the effect of packing forces on the molecular conformation; (*d*) UV–VIS spectra of some model compounds (nitrosubstituted thiophenamines **9–12**).



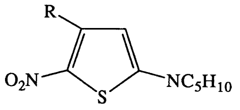
**9**



**10**

**a** : R = H

**b** : R = Me

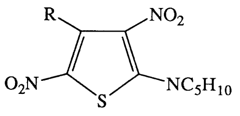


**11**

**a**: R = H  **d**: R = Pr$^i$

**b**: R = Me  **e**: R = Bu$^t$

**c**: R = Et



**12**

**a**: R = H  **b**: R = Me  **c**: R = Pr$^i$

## Results and discussion

### Kinetic data

The influence of the nature of the leaving group and of the steric interactions in the reaction area on the kinetic secondary steric effects in thiophene derivatives has been widely studied.[4c–d] Moreover the effect of the size of the alkyl group inserted at C(4) between the two activating nitro groups has also been investigated.[4e]

All results pointed to the following: (*i*) by comparing the reactivity of 2-halogeno-3,5-dinitrothiophenes **3** and 2-halogeno-4-methyl-3,5-dinitrothiophenes **4** with piperidine and other amines $k_H/k_{Me}$ ratios ranging from 1.1 to 1.9 have been measured;[4c] (*ii*) by comparing the reactivity of 3,5-dinitro-2-phenylsulfonylthiophene **5** and of 3,5-dinitro-4-methyl-2-phenylsulfonylthiophene **6** with piperidine and other amines $k_H/k_{Me}$ ratios of 5.6–16 have been measured, which shows in this case the occurrence of small but significant kinetic secondary steric effects;[4c] (*iii*) $k_H/k_{Me}$ ratios measured in the reactions with various nucleophiles (some amines, sodium methoxide and benzenethiolate) with both bromine and phenylsulfonyl as leaving groups are practically independent of the nature of the atom (or group) linked at C(5) (hydrogen, bromine or nitro group), and this shows that the steric interactions are restricted to those between the leaving group at C(2) (bromine or phenylsulfonyl), the nitro group at C(3) and the methyl group at C(4) and that the substituent at C(5) does not affect steric interactions by an enhanced buttressing effect;[4c] (*iv*) the insertion at C(4) between the two activating nitro groups of a bulky alkyl group (*e.g.* the Pr$^i$ group) causes an enhancement of the kinetic secondary steric effects: in fact with some amines $k_H/k_{Pr^i}$ ratios increase to *ca.* 7 and to 60–110 when the leaving groups are bromine or phenylsulfonyl, respectively.[4e] However, these reactivity ratios are much lower than those expected for six-membered ring derivatives, indicating that in thiophenes the strain between the four adjacent substituents is markedly lower than in benzenes and is presumably at least in part relieved on going from substrates to $S_NAr$ transition states.[4e]

To confirm this point we have measured (see data in Table 1) the reactivities in methanol of benzene derivatives **1**, **2**, **7** and **8** with piperidine and sodium benzenethiolate and of thiophene derivatives **3a**, **4a**, **5** and **6** with sodium benzenethiolate, so extending the study of dinitrothiophenes to an anionic nucleophile.

2,4-Dinitrochlorobenzene **1** and 3-chloro-2,6-dinitrotoluene **2** give with piperidine and with sodium benzenethiolate in methanol comparable results concerning the occurrence of kinetic secondary steric effects: in fact in both instances high $k_H/k_{Me}$ ratios have been measured (850 and 1500 at 20 °C, respectively), confirming the results obtained by Capon and Chapman on the reactivity with piperidine in ethanol ($k_H/k_{Me}$ 960 at 20 °C).[1b]

An interesting confirmation of our previous findings concerning the leaving group effect on the kinetic secondary steric effect[4c] has been obtained by comparing the reactivity of 2,4-dinitrophenyl phenyl sulfone **7** and of 3-methyl-2,4-dinitrophenyl phenyl sulfone **8** with piperidine in methanol: in fact the $k_H/k_{Me}$ ratio obtained is significantly larger (12 800 *versus* 850 at 20 °C) than that observed with chlorine as leaving group, so duplicating the situation observed in thiophene compounds [compare previous points (*i*) and (*ii*)]. In contrast the same comparison with the nucleophile sodium benzenethiolate furnishes similar values of the $k_H/k_{Me}$ ratios (930 *versus* 1500 at 20 °C) probably because now the early nature of the transition states of the two reactions studied makes the change of leaving group (from chlorine to phenylsulfonyl) unable to affect the reactivity.

Moreover the kinetic data obtained by measuring the reactivities in benzenethiolate substitution reactions of thiophene derivatives **3a** and **4a**, **5** and **6** in methanol have confirmed the absence of kinetic secondary steric effects in $S_NAr$ of thiophenes: in fact $k_H/k_{Me}$ 3.8 and 5.1 at 20 °C have been obtained, respectively, *i.e.* values similar to those measured in piperidino substitution of the same thiophene compounds.[4c]

### p$K_{BH^+}$ and UV–VIS data

The p$K_{BH^+}$ values measured for some 3-nitro-2-piperidyl-4-R- or -5-R-thiophenes (**9**, **10**: R = H, Me), 5-nitro-2-piperidyl-4-R-thiophenes (**11**: R = H, Me, Et, Pr$^i$, Bu$^t$) and 3,5-dinitro-2-piperidyl-4-R-thiophenes (**12**: R = H, Me, Pr$^i$) have been collected in Table 2. The obtained p$K_{BH^+}$ values were calculated by the modified Hammett method[5a] (Hammett acidity functions method: HAFM, *i.e.* using $H_0'''$ as acidity function for tertiary aromatic amines) and by the Marziano–Cox–Yates method[5b] (excess acidity method: EAM). The data obtained by the two methods are nearly coincident.

The presence of an alkyl group causes in each case, as expected on the basis of its electronic effects,[6] a decrease in the acidity of the protonated amines to an extent which depends essentially on the relative position of nitro and alkyl groups, and ranges from 0.4 to 6.6 units in p$K_{BH^+}$ values. Apparently, this is in contrast with the observation that the electronic effects of alkyl groups are very similar to each other. Indeed, the variations observed in p$K_{BH^+}$ values indicate either a very large sensitivity of the dissociation reaction to the electronic effect (*e.g.* considering the series of 5-nitro-2-piperidyl-4-R-thiophenes **11**, where R varies from hydrogen, to methyl, ethyl, isopropyl and *tert*-butyl, this implies that the Hammett type relationship would require a susceptibility constant greater than 10)† or the occurrence of effects different from the expected electronic ones (*e.g.* steric, solvation or polarization-type effects).

In order to evaluate the electronic effects exerted by a methyl group, free from steric, solvation and/or polarization-type effects, we have compared the p$K_{BH^+}$ of 3-nitro-2-piperidylthiophene **10a** and of 5-methyl-3-nitro-2-piperidylthiophene **10b**: the introduction of the methyl group causes a decrease of only 0.4 p$K_{BH^+}$ units. The decrease in acidity is

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† This is not consistent with the literature data (*e.g.* for the p$K_{BH^+}$ of a series of 5-substituted 3-nitro-2-piperidylthiophenes a $\rho^-$ value of around 4 has been calculated).[5c]

**Table 1** Rate constants and activation parameters for the reactions of compounds **1**–**8** with nucleophiles in methanol

| Substrate | Nucleophile[a] | $k$/l mol$^{-1}$s$^{-1\,b}$ (at various temperatures) | | | $\Delta H^{\ddagger c}$/kJ mol$^{-1}$ | $-\Delta S^{\ddagger d}$/JK$^{-1}$ mol$^{-1}$ | $k_H/k_{Me}$ (at 20 °C) |
|---|---|---|---|---|---|---|---|
| **1** | PIP | $2.01 \times 10^{-3}$ (0.9)[e] | $4.19 \times 10^{-3}$ (10.08) | $8.44 \times 10^{-3}$ (20.05) | 43.4 | 129 | 850 |
| **2** | PIP | $9.94 \times 10^{-6}$ (20.05) | $2.58 \times 10^{-5}$ (30.07) | $6.59 \times 10^{-5}$ (40.10) | 69.4 | 103 | |
| **3a**[f] | PIP | 0.866 (0.03) | 1.88 (9.99) | 3.74 (20.03) | 46.0 | 76 | 1.9 |
| **4a**[f] | PIP | 0.494 (0.02) | 1.05 (10.00) | 1.93 (20.00) | 42.7 | 93 | |
| **5**[f] | PIP | 2.43 (0.02) | 4.14 (10.02) | 6.80 (20.03) | 31.8 | 118 | 7.7 |
| **6**[f] | PIP | 0.257 (0.02) | 0.485 (10.00) | 0.878 (20.03) | 38.9 | 115 | |
| **7** | PIP | $1.36 \times 10^{-3}$ (0.01)[g] | $2.96 \times 10^{-3}$ (9.94) | $6.46 \times 10^{-3}$ (20.01)[h] | 49.4 | 118 | 12 800 |
| **8** | PIP | $5.70 \times 10^{-7}$ (21.70) | $1.14 \times 10^{-6}$ (29.99) | $2.38 \times 10^{-6}$ (39.95) | 57.3 | 169 | |
| **1** | NaBT | 3.51 (0.03) | 7.31 (9.95) | 15.8 (19.89)[i] | 47.7 | 59 | 1500 |
| **2** | NaBT | $10.0 \times 10^{-2}$ (19.88) | $2.32 \times 10^{-2}$ (29.99) | $5.65 \times 10^{-2}$ (39.95) | 61.5 | 72 | |
| **3a**[h] | NaBT | | 34 200 (20) | | | | 3.8 |
| **4a** | NaBT | | 9000 (20) | | | | |
| **5** | NaBT | | 1 640 000 (20)[j] | | | | 5.1 |
| **6** | NaBT | | 320 000 (20) | | | | |
| **7**[h] | NaBT | | 2400 (20) | | | | 930 |
| **8** | NaBT | 0.573 (−0.02) | 1.22 (9.93) | 2.57 (19.95) | 61.5 | 74 | |

[a] PIP = piperidine; NaBT = sodium benzenethiolate. [b] The rate constants are accurate to within ±3%. [c] At 20 °C; the maximum error is 2.1 kJ mol$^{-1}$. [d] At 20 °C; the maximum error is 7 JK$^{-1}$ mol$^{-1}$. [e] This datum compares well with a previous kinetic result (at 0 °C, $k$ $1.95 \times 10^{-3}$) of J. F. Bunnett, E. W. Garbisch, Jr. and K. M. Pruitt, *J. Am. Chem. Soc.*, 1957, **79**, 385. [f] Data from ref. 4*c*. [g] This datum compares well with a previous kinetic result (at 0 °C, $k$ $1.43 \times 10^{-3}$) of AA. of note *e*. [h] Datum from ref. 10. [i] This datum compares well with a previous kinetic result (at 20 °C, $k$ 14.4) of AA. of note *e*. [j] A value of 770.000 was previously reported[10] for kinetic experiments carried out with benzenethiol solutions in the presence of an excess of sodium methoxide. The observed difference in $k$ values is due to the fact that operating with an excess of methoxide ion some, probably reversible, interaction occurs that affects absorbance and then the $k$ value measured. Now the reaction substitution has been carried out with benzenethiolate solutions in the presence of an excess of benzenethiol thus eliminating every secondary reaction.

**Table 2** p$K_{BH^+}$ values of nitropiperidylthiophenes **9–12** in aqueous sulfuric acid

| | HAFM | | EAM | | |
|---|---|---|---|---|---|
| Substrate | $-pK_{BH^+}$ ($\pm s_{pK}$) | $m$($\pm s_m$) | $-pK_{BH^+}$ ($\pm s_{pK}$) | $m^*$($\pm s_m$) | $\varepsilon$ ($\lambda_{max}$/nm)[a] |
| **9a** = **10a**[b] | 1.07 (0.03) | 1.03 (0.02) | 1.06 (0.03) | 1.78 (0.07) | 5 620(398) |
| **9b** | 0.28 (0.03) | 0.98 (0.04) | 0.29 (0.02) | 1.70 (0.04) | 3 700(404) |
| **10b** | 0.65 (0.01) | 1.01 (0.01) | 0.64 (0.01) | 1.72 (0.04) | 6 020 (410) |
| **11a**[b] | 1.92 | 0.81 | 1.87 | 1.20 | 31 600 (448) |
| **11b** | 1.27 (0.03) | 0.78 (0.04) | 1.27 (0.03) | 1.25 (0.02) | 34 900 (440) |
| **11c** | 1.20 (0.03) | 0.73 (0.04) | 1.12 (0.03) | 1.00 (0.03) | 34 700 (438) |
| **11d** | 1.00 (0.08) | 0.90 (0.06) | 1.17 (0.11) | 1.71 (0.18) | 34 700 (444) |
| **11e** | 0.36 (0.01) | 1.08 (0.01) | 0.39 (0.01) | 2.05 (0.01) | 32 900 (450) |
| **12a**[b] | 6.66 | 1.04 | 6.55 | 1.53 | 15 800 (380) |
| **12b** | 2.91 (0.20) | 0.89 (0.05) | 2.86 (0.15) | 1.30 (0.07) | 17 800 (408) |
| **12c** | 1.99 (0.09) | 1.01 (0.04) | 1.87 (0.09) | 1.60 (0.08) | 16 600 (420) |

[a] In methanol. [b] Values from ref. 5*c*.

higher in all other instances: *e.g.* in the series of 5-nitro-2-piperidyl-4-R-thiophenes **11** it is 0.6–1.5 p$K_{BH^+}$ units on going from hydrogen to methyl, ethyl, iso-propyl and *tert*-butyl.

The p$K_{BH^+}$ variations observed in compounds **11** can be interpreted by assuming that alkyl groups cause either a torsion and/or an out-of-plane bending of the nitro group (*i.e.* an electronic secondary steric effect) or a hindrance to the solvation of the nitro group or an electronic effect, whose entity is related to a polarization-type process.‡ In principle all these effects are possible, but taking into account the effects exerted by the same alkyl groups on the piperidinodebromination reactions in methanol of some 2-bromo-5-nitro-4-R-thiophenes **13** one can

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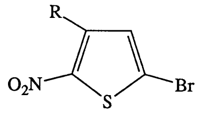
‡ The relevance of solvation effects in acid dissociation equilibria of thiophenes **11** is witnessed by the observed meaningful variations in $m^*$ values.

make a choice among them.[7] In fact, the rates of the nucleophilic substitutions in **13** increase with the size of the alkyl group which behaves as a substituent activating the $\mathrm{S_NAr}$. Thus, the main effect of the alkyl group is not to hinder the coplanarity of the activating nitro group with the thiophene ring, which would cause a strong reduction in the reactivity. Moreover acid dissociation constants of **11a–e** and kinetic rates of piperidinodebromination of **13a–e**[7] give a good linear free energy relationship ($s$ 0.44 ± 0.04, $i$ 0.02 ± 0.03, $n$ 5, $r$ 0.990) showing that the alkyl groups exert similar effects on the dissociation equilibria and on the piperidinodebromination reactions. In a previous paper it has been proposed that the rate acceleration determined by alkyl groups in **13** depends on the hindrance of the orientation of solvent molecules near the nitro group, which 'should act mainly in the initial state rather than in the transition state',[7] or on an electronic effect 'resulting in the stabilization of both positive and negative charge through a polarization-type process',[7] and one can confidently assume that the same effect determines p$K_{\mathrm{BH^+}}$ values variation. According to this interpretation no effect of 4-alkyl groups on the UV–VIS spectra of 5-nitro-2-piperidyl-4-R-thiophenes **11a–e** has been observed (see data in Table 2).

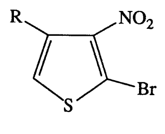


**13**

**a**: R = H **d**: R = Pr$^i$
**b**: R = Me **e**: R = Bu$^t$
**c**: R = Et

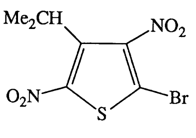
The situation appears different for 3-nitro-2-piperidyl-4-R-thiophenes **9** and 3,5-dinitro-2-piperidyl-4-R-thiophenes **12**. In fact the introduction of the methyl group at C(4) in **9** causes a decrease in p$K_{\mathrm{BH^+}}$ values of 0.8 units, and the insertion at C(4) between the two nitro groups of a methyl or of an isopropyl group causes a decrease of 3.7 and 4.7 units, respectively, in **12**. Note that **12c** shows a p$K_{\mathrm{BH^+}}$ value (−1.99) similar to that of 2-piperidyl-5-nitrothiophene (−1.92).

In principle in **9** and in **12** the introduction of alkyl groups can also affect the coplanarity, the solvation of the nitro group(s) and/or a polarization-type process as in **11**, but both kinetic and spectroscopic data seem to indicate the occurrence of a small secondary steric effect. In fact considering the effect of alkyl groups on the rates of piperidinodebromination in methanol of 2-bromo-3-nitro-4-R-thiophenes (**14**: R = H, Me)[4c] and of 2-bromo-3,5-dinitro-4-*R*-thiophenes (**3b**, **4b**, **15**)[4e] one can observe only a small decrease in the reactivity on introduction of the alkyl groups (in **14**: $k_{\mathrm{H}}/k_{\mathrm{Me}}$ *ca.* 2; in **3b** and **15**: $k_{\mathrm{H}}/k_{\mathrm{Pr^i}}$ *ca.* 7).



**14**

**a** : R = H **b** : R = Me



**15**

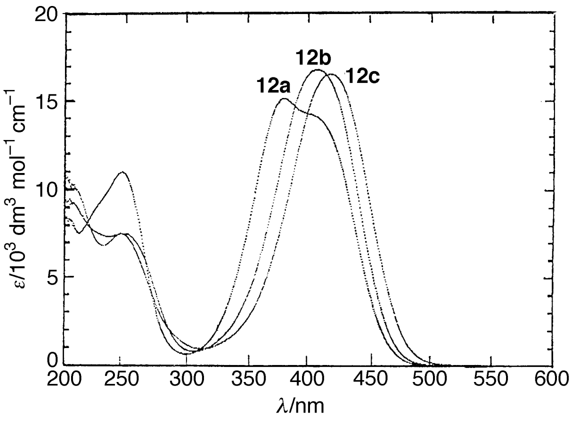


**Fig. 1** UV–VIS spectra of compounds **12a–c** in methanol

The UV–VIS spectra of piperidyl derivatives **9** and **12** agree with this interpretation: in fact the introduction of the methyl group causes in **9** a significant hypochromic effect [$\varepsilon_{9a}$ *ca.* 5600 at $\lambda_{\mathrm{max}}$(398 nm) and $\varepsilon_{9b}$ *ca.* 3700 at $\lambda_{\mathrm{max}}$(404 nm) in methanol]. The spectra of **12** are very interesting: the insertion of alkyl groups causes both a large bathochromic (in methanol $\lambda_{\mathrm{max}}$ shifts from 380 nm in **12a** to 408 and 420 nm, respectively, in **12b** and **12c**) and a hyperchromic (in methanol $\varepsilon_{\mathrm{max}}$ increases from 15 000 in **12a** to 17 800 and 16 600 in **12b** and in **12c**, respectively) effect. These effects can be easily understood by taking into account the spectra in methanol of 3-nitro-2-piperidylthiophene (**10a**) and of 5-nitro-2-piperidylthiophene (**11a**) for which the absorption band can be assigned to $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(3){=}NO_2^-}]$ and to $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(5){=}NO_2^-}]$ electronic transitions, respectively (see Fig. 1). In **12a** the absorption band seems to be affected more by the $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(3){=}NO_2^-}]$ electronic transition than by the $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(5) = NO_2^-}]$ electronic transition, probably because of the through-conjugation which favours electronic interactions between substituents at C(2) and C(3) (hyper-*ortho* effect),[8] as indicated by the wavelength and the molar extinction coefficient observed for the maximum. The insertion of an alkyl group between the two nitro groups as in **12b** and **12c** causes a significant variation in the spectra, which can be easily accounted for by assuming that the alkyl groups hinder the coplanarity of the nitrogroup at C(3): thus making more relevant the electronic transition $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(5){=}NO_2^-}]$ with respect to $[{>}\mathrm{N^+{=}C(2)} \longrightarrow \mathrm{C(3){=}NO_2^-}]$. The proposed torsion and/or out-of-plane bending of the nitro group at C(3) determined by the insertion of an alkyl group between the two nitro groups at C(3) and at C(5) is strongly supported by the comparison of the crystal structures of compounds **3c** and **4c** and by the comparison of '*ab initio*' results for compounds **2** and **4a**.

## Crystal structure analysis of 3c and 4c and *ab initio* calculations for 2 and 4a

To gain further information on the structure of thiophene derivatives and to make a comparison with the previously studied benzene derivatives **1**[3] and **2**[2] we considered it useful to determine the crystal structure of compounds **3c** and **4c**.

An ORTEP view[9] of **3c** and **4c** with the atom numbering scheme is shown in Figs. 2 and 3. Hydrogen atoms have been named according to the numbering of the bonded carbon atom.

Values of bond lengths and bond angles are in the normal range and can be compared with those obtained in previous crystal structure determinations of dinitrothiophene derivatives (*e.g.* 2-chloro-3,5-dinitrothiophene and 3,5-dinitro-2-phenylsulfonylthiophene;[10] 2,5-dimethyl-3,4-dinitrothiophene).[11]

The thiophene ring is planar within experimental errors in both compounds; Table 3 summarizes the deviations from planarity and the dihedral angles between least-squares planes.

**Table 3** Least-squares planes

| | Highest deviation/Å | |
|---|---|---|
| | Compound **3c** | Compound **4c** |
| (A) Thiophene ring | 0.011(7) | 0.006(4) |
| (B) 3-Nitro group | 0.012(7) | 0.002(4) |
| (C) 5-Nitro group | 0.013(7) | 0.003(4) |
| | Dihedral angles (°) | |
| | Compound **3c** | Compound **4c** |
| A–B | 0.8(3) | 44.2(2) |
| A–C | 3.5(3) | 2.0(2) |

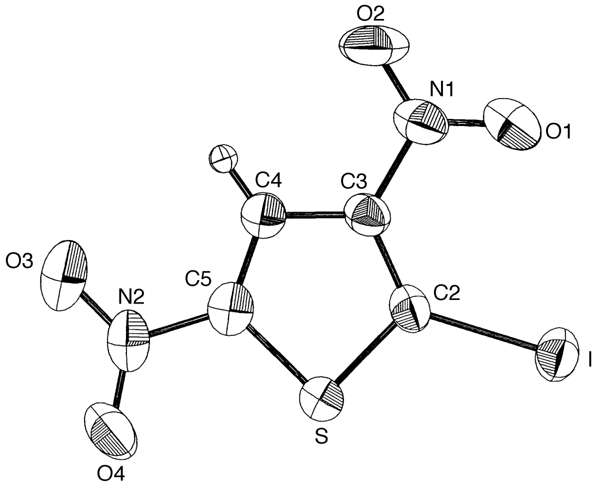


**Fig. 2** ORTEP view of the structure of **3c** in the crystal. Thermal ellipsoids are drawn at the 50% probability level; the hydrogen atom, treated as isotropic, is on an arbitrary scale.

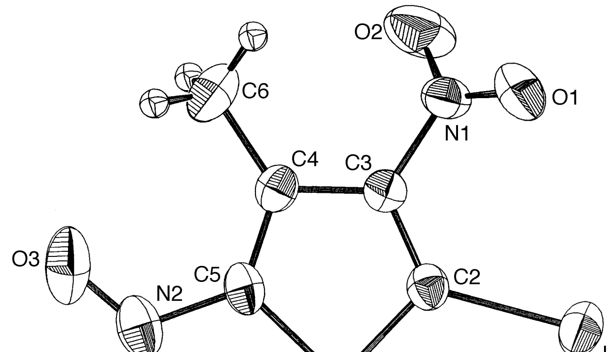


**Fig. 3** ORTEP view of the structure of **4c** in the crystal. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms, treated as isotropic, are on an arbitrary scale.

In both structures one short I···O intermolecular contact has been found, namely: in **3c**, I with O(2) in 2.5 − *x*, 1 − *y*, −0.5 + *z* (3.04 Å); in **4c**, I with O(1) in −0.5 + *x*, 1.5 − *y*, 2 − *z* (3.08 Å). This is however not very unusual and even shorter I···O intermolecular distances can be seen [*e.g.* 2.92 Å in 3-iodo-2-(methylsulfinyl)thiophene].[12] All other non-bonded distances are normal. Atoms I and O(1) are involved even in rather short 1···5 intramolecular contacts (3.143 and 3.243 Å in compound **3c** and **4c**, respectively). In **3c** the strain is relieved by the large I–C(2)–C(3) (132.3°) and C(2)–C(3)–N(1) (124.9°) bond angles; in **4c**, where the corresponding bond angles assume smaller values (129.8° and 121.4°, respectively) the strain is relieved by a rotation of the 3-nitro group, the torsion angle C(2)–C(3)–N(1)–O(1) being −44.7(6)°.

Whereas in both structures the 5-nitro group is substantially coplanar with the thiophene ring, the behaviour of the 3-nitro group is different (see Table 3), as can be foreseen on the basis of steric strain from adjacent substituents; this feature can have influence when considering the $\mathrm{S_NAr}$ reactivity, owing to the fact that the activating effect of the nitro group reaches its maximum in the case of coplanarity with the ring. On the same basis one can predict, in full agreement with experiment, that the reactivity should be even lower for the corresponding halogeno-benzene derivatives, where the higher hindrance between vicinal groups should lead to a larger rotation for the *ortho*-nitro group. This must be true *e.g.* in 2-nitrohalogenobenzenes and, to a larger extent, in 2-nitro-3-halogenotoluenes.

In fact in the crystals of 2,4-dinitrochlorobenzene (alpha form) the 2-nitro group is rotated by *ca.* 40° with respect to the benzene ring[3] and in 3-chloro-2,6-dinitrotoluene the 2-nitro group is rotated by nearly 80°.[2]

These values however could be affected by packing forces in the crystal phase. Indeed, a recent study[13] of crystal structures retrieved from the Cambridge Structural Database[14] has shown that, besides the steric hindrance of adjacent substituents, packing forces can play a noticeable role in modifying the rotation angle of a nitro group bonded to an aromatic six-membered carbon ring. For nitro groups having 0, 1 and 2 adjacent non-H substituents the following ranges of rotation angles have been found: 0–28°; 5–49° for methyl (and methylene), 14–43° for chlorine; and 56–80° for carbon and halogen substituents, respectively. According to De Ridder and Schenk,[13] this behaviour '. . . makes it almost impossible to predict the rotation angle of a nitro group for one or two given adjacent substituents'. In the present case therefore an independent study of the molecular conformation appeared desirable; we deemed it worthwhile to evaluate the change in energy for the isolated molecule of **4c** (or of the corresponding 2-chloro-derivative, **4a**) and for the isolated molecule of 3-chloro-2,6-dinitrotoluene, **2**, when rotating the 3- and the 2-nitro groups, respectively. We adopted the *ab initio* methods using the GAUSSIAN92 program[15] at the HF level and the 6-31G* basis set, with d-type polarization functions on all non-hydrogen atoms. In order to use this basis set we had to consider the chlorine- (**4a**), instead of the iodine-derivative (**4c**). Single point energy calculations were performed for different fixed geometries, each of them corresponding to a different torsion angle of the considered nitro group.

We followed the same protocol previously described.[10] The initial geometry was obtained from the experimental results, with the ring idealized to an exactly planar conformation. The C(2)–I bond distance was substituted, in **4a**, by the corresponding experimental[10] C(2)–C1 value of 1.683 Å. For the 5-nitro group in **4a** the same conformation was assumed as found in **4c**, and for the 6-nitro group in **2** the experimental orientation[2] was adopted; these were held fixed in subsequent calculations. Starting with the 3-nitro group (in **4a**) and the 2-nitro group (in **2**) coplanar to the ring, their torsion angle was decreased until an increase in energy was found. Values of the torsion angles and the resulting differences of energy with respect to the planar conformation are summarized in Table 4.

As a result, the conformation of minimum energy for compound **4a** is fairly similar to that found experimentally for **4c**; the energy differences with respect to the planar molecule lie, however, within 15 kJ mol$^{-1}$, possibly not precluding the nitro group to reach coplanarity with the thiophene ring when the reactants are approaching the transition state.[10] This is in agreement with the large $\mathrm{S_NAr}$ reactivity of **4c** and **4a**. On the other hand for compound **2** the energy well reaches 91 kJ mol$^{-1}$ for a torsion of the 2-nitro group as high as −80° in the minimum energy conformation (again in agreement with the

**Table 4** Energy differences (kJ mol$^{-1}$) with respect to the planar conformation as a function of the nitro group torsion angle

| | Energy difference/kJ mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Torsion angle (°) | −20 | −30 | −40 | −50 | −60 | |
| Compound **4a** | −9.3 | −13.5 | −14.9 | −13.2 | −9.5 | |
| Torsion angle (°) | −20 | −40 | −60 | −70 | −80 | −85 |
| Compound **2** | −33.6 | −73.2 | −89.0 | −90.7 | −90.8 | −90.7 |

experimental result);[2] this barrier to planarity prevents the 2-nitro group from exerting its activating effect, as confirmed from reactivity measurements.

## Conclusion

The results allow the following conclusions to be drawn. In thiophenes[4] the $S_N$Ar reactivity with neutral and anionic reagents is scarcely affected by secondary steric effects at variance with what happens in benzenes.[1] Considering the results of the crystal structure analysis for thiophenes **3c** and **4c** and of the molecular conformation for benzene **2** and thiophene **4a** it appears evident that the differences in the geometry of the two aromatic rings, benzene and thiophene, play a relevant role in the occurrence of kinetic secondary steric effects. In thiophenes the steric strain between the four adjacent substituents is relieved by the rotation of the 3-nitro group (in **4c**: *ca* 45°) and the energy difference with respect to the planar structure is relatively low (in **4a**: *ca.* 15 kJ mol$^{-1}$) and seems to be significantly relieved, as a consequence of the hybridation change at C(2) (from sp$^2$ to sp$^3$), on going from substrates to $S_N$Ar transition states thus determining the absence[4] of kinetic effects or the occurrence[4] of small effects. In contrast, in benzene **2** the same steric strain causes both a larger rotation of the 2-nitro group (*ca.* 80°) and a higher energy difference with respect to the planar structure (*ca.* 91 kJ mol$^{-1}$) which cannot be significantly relieved on going from the substrate to the $S_N$Ar transition state, thus determining the occurrence of a large kinetic secondary steric effect.[1]

Concerning p$K_{BH^+}$ values and UV–VIS data of thiophenes the situation can be different in derivatives containing four adjacent substituents. For example, on going from **12a** to **12b** and **12c** the rotation of the 3-nitro group due to steric strain has a large effect both on the acid dissociation reaction and on the UV–VIS spectra. In fact for the acid dissociation reaction, where no change in hybridation at C(2) occurs, large variations of the relevant p$K_{BH^+}$ are observed because of the insertion between the two nitro groups of a methyl ($\Delta$p$K_{BH^+}$ *ca.* 3.7) or of a bulkier isopropyl group ($\Delta$p$K_{BH^+}$ *ca.* 4.7). The same insertion causes large bathochromic and hyperchromic effects on UV–VIS spectra of compounds **12**.

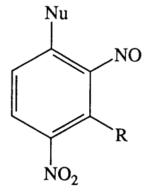
Thus, the kinetic, thermodynamic and UV–VIS data of the thiophene studied can be easily interpreted in the light of crystal structure analysis and *ab initio* calculations and the reasons why an alkyl group adjacent to nitro group(s) can exert a small or a large effect on some chemical and physical properties of thiophenes can be well understood.

## Experimental

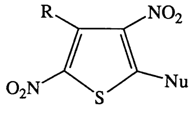
### Materials

Compounds **1**,[1b] **2**,[1b] **3a–c**,[16] **4a**,[17] **4b**,[4a] **4c**,[17] **5**,[16] **6**,[16] **7**,[18] **9a**,[16] **9b**,[4b] **10b**,[7] **11a**,[16] **11b–e**,[7] **12a**,[16] **12b**,[4a] **12c**,[4e] **13a**,[16] **13b–e**,[7] **14a**,[16] **14b**,[4b] **15**,[4e] **16**,[1b] **17**,[1b] **18**,[19] methanol,[20] piperidine[16] and benzenethiol[20] were prepared and/or purified according to the methods reported.

Compound **8** was prepared by refluxing **7** with sodium benzenesulfinate in ethanol for several hours. The precipitate obtained after cooling was filtered off and purified by crystallization from methanol (mp 179–180 °C; exact mass measurement: found 322.0253, $C_{13}H_{10}N_2O_6S$ requires 322.0260). $\delta_H$-$(CD_3)_2SO$ 8.43 [AB-system, 2 H, H(5) and H(6)], 8.02–7.96 [m, 2 H, H(2′) and H(6′)], 7.84–7.79 [m, 1 H, H(4′)], 7.74–7.69 [m, 2 H, H(3′) and H(5′)], 2.31 (s, 3 H, $CH_3$). (*J* in Hz).



**16**: Nu = $NC_5H_{10}$ R = H
**17**: Nu = $NC_5H_{10}$ R = Me
**18**: Nu = SPh R = H
**19**: Nu = SPh R = Me



**20**: Nu = SPh R = H
**21**: Nu = SPh R = Me

Compounds **19–21** were prepared and purified according to the general method reported.[20] Compound **19** was crystallized from methanol, mp 123 °C. UV–VIS spectrum in methanol: log $\varepsilon$ ($\lambda_{max}$) 3.90 (316 nm). Exact mass measurements: found 290.0367, $C_{13}H_{10}N_2O_4S$ requires 290.0361. $\delta_H(CD_3)_2SO$ 8.11 [d, 1 H, H(5), *J* 8.8], 7.70–7.45 [m, 5 H, H(2′)/H(6′)], 7.13 [d, 1 H, H(6), *J* 8.8], 2.42 (s, 3 H, $CH_3$). Compound **20** was crystallized from ethanol–dioxane, mp 158 °C. UV–VIS spectrum in methanol: log $\varepsilon$ ($\lambda_{max}$) 4.22 (360 nm). Exact mass measurements: found 281.9772, $C_{10}H_6N_2O_4S_2$ requires 281.9769. $\delta_H[(CD_3)_2SO]$ 8.56 [s, 1 H, H(4)], 7.85–7.64 [m, 5 H, H(2′)/H(6′)]. Compound **21** was crystallized from methanol–dioxane, mp 185 °C. UV–VIS spectrum in methanol: log $\varepsilon$ ($\lambda_{max}$) 4.16 (362 nm). Exact mass measurements: found 295.9920, $C_{11}H_8N_2O_4S_2$ requires 295.9926. $\delta_H[(CD_3)_2SO]$ 7.86–7.63 [m, 5 H, H(2′)/H(6′)], 2.81 (s, $CH_3$).

All new products gave correct analyses (C, H, N, S).

### Kinetic measurements

The kinetics for piperidine- and benzenethiolate-substitution were followed spectrometrically as previously described.[16,20] The concentrations used were $10^{-5}$–$10^{-3}$ M for substrates, 0.2–1 M for piperidine and $10^{-4}$–$10^{-2}$ M for sodium benzenethiolate (in presence of 1–3 times excess of benzenethiol). Excess of benzenethiol had no discernible effect on $S_N$Ar reaction rate.[21] A DU-6 Beckman instrument equipped with a thermostatted cell compartment was used except in the case of benzenethiolate substitution of **3a**, **4a**, **5–7** for which, owing to the high reaction rates, a Durrum D-110 stopped-flow spectrophotometer was used.

### p$K_{BH^+}$ measurements

Acid dissociation constants $K_{BH^+}$ were determined as previously described.[5c] Data treatments (according to HAFM and EAM methods) and corrections were made as previously described.[5c]

### Crystallographic measurements

After taking preliminary Laue photographs, crystals of **3c** and **4c** were mounted on a CAD4 diffractometer; data were collected using graphite-monochromated Mo-K$\alpha$ radiation. Cell parameters were obtained by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.7107$ Å.

### Crystal data

Compound **3c**, $C_4HIN_2O_4S$, $M = 300.03$. Orthorhombic, $a = 6.395(6)$, $b = 10.009(4)$, $c = 12.565(4)$ Å, $V = 804.3$ Å$^3$, space group $P2_12_12_1$, Z = 4, $D_c = 2.478$ g cm$^{-3}$. Crystal dimensions 0.30 × 0.15 × 0.03 mm, $\mu = 42.2$ cm$^{-1}$.

Compound **4c**, $C_5H_3IN_2O_4S$, $M = 314.05$. Orthorhombic, $a = 7.173(2)$, $b = 9.276(3)$, $c = 13.550(6)$ Å, $V = 901.6$ Å$^3$, space group $P2_12_12_1$, $Z = 4$, $D_c = 2.314$ g cm$^{-3}$. Spherical crystal, diameter 0.25 mm, $\mu = 37.7$ cm$^{-1}$.

### Data collection and processing

Compound **3c**, $\omega/2\theta$ scan mode, scan width 1.5°, scan speed 0.7–6.7° min$^{-1}$; 1090 independent reflections measured ($3.0 \leqslant \theta \leqslant 27.5°$), absorption correction[22] (max., min. transmission factors = 0.98, 0.52).

Compound **4c**, $\omega/\theta$ scan mode, scan width 1.2°, scan speed 0.9–20.0° min$^{-1}$; 1209 independent reflections measured ($2.5 \leqslant \theta \leqslant 27.5°$), spherical absorption correction (max., min. transmission factors = 0.51, 0.50).

During the data collection the centring of three reflections was repeated periodically for both structures, to test the crystal orientation, and one reflection was monitored every 60 min to check the crystal stability; no crystal decay was observed.

### Structure determination and refinement

Both structures were solved by the Patterson method. The refinement was accomplished on $F^2$ data by means of isotropic, and then anisotropic full-matrix least-squares process with the program SHELXL 93.[23] For compound **3c** the atom H(4) was located in the calculated position at a distance of 0.93 Å from C(4), and allowed to ride on the bonded carbon atom. For compound **4c** the methyl hydrogen atoms were located by means of a circular difference synthesis calculated for the methyl group at a fixed C−H distance (0.96 Å) and a fixed C−C−H angle (109.47°); both the rotation angle and a common $U$(H) thermal factor were refined.

For both structures the refinement converged well, with a final maximum shift-to-esd ratio of 0.001. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, with $a,b = 0.054$, 0.00 and 0.033, 0.14 for **3c** and **4c**, respectively, with $P = (F_o^2 + 2F_c^2)/3$, and $\sigma(F_o^2)$ from the counting statistics. For compound **4c**, an extinction parameter[23] was refined to a final value of $X = 0.027(1)$. Final reliability factors were $R1 = 0.0297$ on 910 $F_o > 4\sigma(F_o)$, $wR2 = 0.0806$ on all 1090 $F_o^2$ data (110 parameters) for **3c**, and $R1 = 0.0201$ on 1036 $F_o > 4\sigma(F_o)$, $wR2 = 0.0559$ on all 1209 $F_o^2$ data (121 parameters) for **4c**. The values of the goodness of fit were 1.041 and 1.065 for the two structures. The final difference Fourier map showed some residual peaks near to the position of the iodine atom, the two highest values being 1.15 and 0.78 e Å$^{-3}$ for **3c**, and 0.54 and 0.38 e Å$^{-3}$ for **4c**. The Flack parameter[24] was 0.00(5) and −0.09(3) for **3c** and **4c**, respectively. Thus the absolute structure and, in the present cases, the absolute conformation[25] have been established for both compounds.

The scattering factors were taken from SHELXL 93. All geometry calculations were performed with the program PARST 93.[26] Ranges of esds on bond lengths and bond angles are 0.007–0.011 and 0.4–0.8 for **3c**, and 0.004–0.007 Å and 0.2–0.5° for **4c**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/38. Tables of anisotropic thermal parameters and of the observed and calculated structure factors are available from an author (A.M.) on request.

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