Crystal Structure and Reactivity of 2-Chloro-3,5-dinitrothiophene and of 2-Phenylsulphonyl-3,5-dinitrothiophene with Nucleophiles

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The geometry obtained by a crystal structure determination of the title compounds, as compared with that of the analogous benzene derivatives, along with results of *ab initio* calculations, is used to interpret the different S_NAr reactivities in some thiophene and benzene compounds. The smaller rotation of the nitro groups with respect to the aromatic rings observed in thiophene derivatives should be considered a relevant factor in the higher reactivity in the thiophene series.

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Introduction.

Halonitrothiophenes [1] react with nucleophiles in S_NAr reactions through the attachment-detachment mechanism [2-4] faster than halonitrobenzenes [5] containing the same number of activating nitro groups. *E.g.*, 2-chloro-3,5-dinitrothiophene reacts with piperidine in methanol at 273 K [6] and with $^{36}Cl^-$ in sulpholane (tetrahydrothiophene 1,1-dioxide) at 298 K [7] faster than 2,4-dinitrochlorobenzene [3,8] by a factor of 446 and 1.4×10^5, respectively.

A similar behaviour has been generally observed in S_NAr reactions of various thiophene derivatives, containing different leaving (halogens, phenylsulphonyl, alkoxy, aryloxy, *etc.*) and activating (electron-withdrawing) groups, with various neutral and anionic nucleophiles (see the data reported in Table I). A high reactivity in S_NAr reactions has been observed with aromatic five-membered ring derivatives containing one heteroatom of either the V (nitrogen [9]) or the VI (oxygen [10], sulphur [1] or selenium [11]) group.

Table I

Ratios between the Kinetic Constants for the Nucleophilic Substitutions in Some Thiophene (k_T) and Benzene (k_B) Derivatives

Substrate L =	1-L-Ar or 2-L-Het Ar [a] or Het [b]	Nucleophile [c]	Solvent [d]	Temperature °C	Kinetic Constant (ℓ mol^{-1} s^{-1})	Rate Ratio (k_T/k_B)	Reference
Cℓ	DNT	PIP	MeOH	0	0.870	446	[18f]
Cℓ	DNB	PIP	MeOH	0	1.95×10^{-3}		[3]
Br	DNT	PIP	MeOH	0	0.478	243	[18e]
Br	DNB	PIP	MeOH	0	1.97×10^{-3}		[3]
I	DNT	PIP	MeOH	0	4.16×10^{-2}	92	[18f]
I	DNB	PIP	MeOH	0	4.51×10^{-4}		[3]
SO_2Ph	DNT	PIP	MeOH	0	2.43	1,700	[18f]
SO_2Ph	DNB	PIP	MeOH	0	1.43×10^{-3}		[3]
SO_2Ph	DNT	PIP	MeOH	20	6.80	1,050	[e]
SO_2Ph	DNB	PIP	MeOH	20	6.46×10^{-3}		[e]
$OC_6H_4NO_2$-*p*	DNT	PIP	MeOH	0	4.71	3,510	[18f]
$OC_6H_4NO_2$-*p*	DNB	PIP	MeOH	0	1.34×10^{-3}		[3]
Cℓ	*o*-MNT	PIP	MeOH	80	1.57×10^{-2}	1,090	[18f]
Cℓ	*o*-MNB	PIP	MeOH	80	1.44×10^{-5}		[f]
Cℓ	*p*-MNT	PIP	EtOH	90	9.85×10^{-3}	912	[1]

Table I (continued)

Substrate L =	1-L-Ar or 2-L-Het Ar [a] or Het [b]	Nucleophile [c]	Solvent [d]	Temperature °C	Kinetic Constant (ℓ mol^{-1} s^{-1})	Rate Ratio (k_T/k_B)	Reference
Cℓ	*p*-MNB	PIP	EtOH	90	1.08×10^{-5}		[5]
Br	*p*-MNT	PIP	EtOH	90	4.49×10^{-3}	323	[1]
Br	*p*-MNB	PIP	EtOH	90	1.39×10^{-5}		[5]
I	*p*-MNT	PIP	EtOH	90	1.51×10^{-2}	3,780	[1]
I	*p*-MNB	PIP	EtOH	90	4.0×10^{-6}		[5]
Cℓ	DNT	NaBT	MeOH	20	34,200	2,380	[e]
Cℓ	DNB	NaBT	MeOH	20	14.4		[g]
Br	DNT	NaBT	MeOH	20	32,200	1,400	[e]
Br	DNB	NaBT	MeOH	20	23.0		[g]
I	DNT	NaBT	MeOH	20	9,360	463	[e]
I	DNB	NaBT	MeOH	20	20.2		[g]
SO_2Ph	DNT	NaBT	MeOH	20	770,000	321	[e]
SO_2Ph	DNB	NaBT	MeOH	20	2,400		[e]
$OC_6H_4NO_2$-*p*	DNT	NaBT	MeOH	20	55,000	7,910	[e]
OC_6H_4-NO_2-*p*	DNB	NaBT	MeOH	20	7.08		[g]
Cℓ	*p*-MNT	NaBT	MeOH	25	0.193	9,190	[15]
Cℓ	*p*-MNB	NaBT	MeOH	25	2.1×10^{-5}		[h]
Br	*p*-MNT	NaBT	MeOH	25	0.211	4,140	[15]
Br	*p*-MNB	NaBT	MeOH	25	5.1×10^{-5}		[h]
I	*p*-MNT	NaBT	MeOH	25	0.134	2,130	[15]
I	*p*-MNB	NaBT	MeOH	25	6.3×10^{-5}		[h]
Cℓ	*o*-MNT	NaBT	MeOH	35	0.289	12,000	[i]
Cℓ	*o*-MNB	NaBT	MeOH	35	2.41×10^{-5}		[f]
Cℓ	DNT	Cℓ	SO_2	25	8.33×10^{-2}	142,000	[7]
Cℓ	DNB	Cℓ	SO_2	25	5.85×10^{-7}		[8]
Cℓ	DNT	Cℓ	SO_2	40	0.332	107,000	[7]
Cℓ	DNB	Cℓ	SO_2	40	3.10×10^{-6}		[8]
Cℓ	DNT	Cℓ	SO_2	55	1.17	83,600	[7]
Cℓ	DNB	Cℓ	SO_2	55	1.40×10^{-5}		[8]
Cℓ	*o*-MNT	Cℓ	SO_2	25	1.21×10^{-9}	2,040	[7]
Cℓ	*o*-MNB	Cℓ	SO_2	25	5.92×10^{-13}		[8]
Cℓ	*o*-MNT	Cℓ	SO_2	140	1.19×10^{-3}	992	[7]
Cℓ	*o*-MNB	Cℓ	SO_2	140	1.20×10^{-6}		[8]
Cℓ	*p*-MNT	Cℓ	SO_2	25	1.96×10^{-8}	515	[ℓ]
Cℓ	*p*-MNB	Cℓ	SO_2	25	3.77×10^{-11}		[8]
Cℓ	DNT	Cℓ	Me_2CO	−1	6.6×10^{-2}	45,500	[7]
Cℓ	DNB	Cℓ	Me_2CO	−1	1.45×10^{-6}		[8]

[a] DNB = 2,4-dinitrophenyl; *o*-MNB = 2-nitrophenyl; *p*-MNB = 4-nitrophenyl. [b] DNT = 3,5-dinitrothienyl; *o*-MNT = 3-nitrothienyl; *p*-MNT = 5-nitrothienyl. [c] PIP = piperidine; NaBT = sodium benzenethiolate; Cℓ = ^{36}Cℓ. [d] MeOH = methanol; EtOH = ethanol; SO_2 = sulpholane; Me_2CO = acetone. [e] This work. [f] A. Porto, L. Altieri, A. J. Castro and J. A Brieux, *J. Chem. Soc. (B)*, 963 (1966). [g] J. F. Bunnett and W. D. Merritt, Jr., *J. Am. Chem. Soc.*, **79**, 5967 (1957). [h] G. Bartoli and P. E. Todesco, *Acc. Chem. Res.*, **10**, 125 (1977) and references therein. [i] G. Guanti, C. Dell'Erba and P. Macera, *J. Heterocyclic Chem.*, **8**, 537 (1971). [ℓ] P. H. Gore, D. Spinelli and G. Consiglio, unpublished results.

On the other hand, the higher reactivity of five-membered rings, compared to benzene derivatives, has also been observed in S_EAr reactions [12].

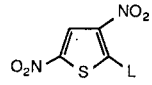
The parallel behaviour shown in both S_NAr and S_EAr reactions by five-membered ring derivatives points out two factors affecting the energy content of the transition states of both reactions: i) The five-membered ring compounds considered (pyrrole, furan, thiophene and selenophene) are characterized by a lower resonance stabilization energy than benzene derivatives [12c,13]; this implies a lower loss of stabilization energy, with respect to benzene, on going from starting compounds to transition states [14]. Thus, the iso-π-electronic cogeners 2-bromo-5-nitrothiophene [15], -selenophene [11] and -furan [10] react at 293 K with piperidine in benzene and with sodium benzenethiolate in methanol, giving the reactivity ratios 1:8.5:300 and 1:4:12, respectively: indeed, the reactivity increases as the resonance stabilization energy decreases. ii) Generally, in both S_EAr and S_NAr reactions the rate-determining step is the formation of the σ-complex: during this step a reorganization of the ring skeleton occurs and the carbon atom of the reaction centre gradually assumes a sp^3 hybridization. In five-membered ring derivatives the internal bond angles along the ring carbon atoms are about 111-112° (figures similar to those of sp^3 hybridized carbon atoms) and this causes a lower contribution, with respect to benzene, to the energy necessary for the reorganization of the ring skeleton in the formation of the reaction intermediate [16].

Among the other factors which determine the reactivity pattern, a lower F-strain to the approach of the nucleophile to the reaction centre of five-membered rings, compared to benzene, certainly plays a role [17].

Moreover, an examination of the molecular models together with kinetic studies concerning the steric effects in S_NAr reactions of thiophene derivatives [18] has allowed us to infer that in nitro-substituted five-membered ring derivatives the nitro group(s) is (are) nearer to coplanarity with the aromatic ring than in nitrosubstituted benzene compounds [19]. This is a critical factor in determining the activation of S_NAr reactions, *e.g.*, in thiophene derivatives, because the nitro group(s) is (are) more efficient than in benzene compounds in exerting the activating electronic effects.

In crystals of 2,4-dinitrohalobenzenes, *e.g.*, 2,4-dinitrochlorobenzene (**1**) [20], both the *ortho*- and *para*-nitro groups are markedly rotated with respect to the plane of the benzene ring (see later). However, the molecular models show that in five-membered ring compounds the distances between two adjacent substituents are larger than in benzene compounds [18d]; this reduces the interactions between the halogen and the nitro group or between the nitro group and the hydrogen which prevent, in benzene derivatives, the coplanarity of the nitro group(s) with the ring.

In order to clarify this point we have determined the crystal structure of 2-chloro- (**2**) and 2-phenylsulphonyl-3,5-dinitrothiophene (**3**) by X-ray diffraction. The phenylsulphonyl group in **3** has already attracted our attention as a leaving group in S_NAr reactions because of its peculiar behaviour in connection with steric effects [18a,b,f,g,i] and catalysis [21].



2, L = Cl

3, L = SO_2Ph

We have also collected some more kinetic data with the aim to make a wider comparison between analogous thiophene and benzene derivatives. Moreover, to leave out the effects of packing forces on the molecular conformation, we have compared the energies obtained for different geometries of 2-chloro-3,5-dinitrothiophene by *ab initio* calculations.

Results and Discussion.

Kinetic Data.

Literature data allow us to make a comparison between the reactivities with nucleophiles of structurally similar thiophene and benzene derivatives. The most significant kinetic results concerning some mono and dinitro derivatives of thiophene and of benzene containing the halogen(s), the phenylsulphonyl and the aryloxy groups as the leaving groups, have been assembled in Table I. The measured reactivity ratios range between 10^2 and 10^5 depending on the leaving group, the nucleophile, the solvent, and the reaction temperature.

To make possible the comparison within a large range of reactivities we have collected additional kinetic data which are also reported in Table I.

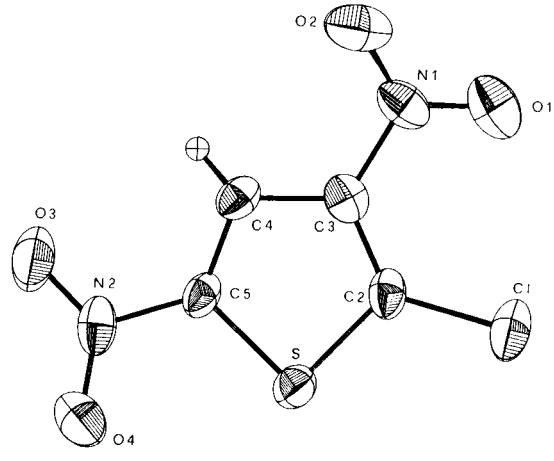


Figure 1. The molecule of compound **2** with the atom-numbering scheme and thermal ellipsoids at the 40% probability level. The H atom is represented as a sphere of arbitrary size.

Crystal Structures and *ab initio* Calculations.

Final atomic coordinates of the heavier atoms (with their estimated standard deviations) for compounds **2** and **3** are listed in Tables II and III; bond lengths and bond angles are reported in Tables IV and V for **2** and **3**, respectively. The numbering of atoms is shown in Figures 1 and 2, which have been drawn using the ORTEP program [22]. Hydrogen atoms have been named according to the numbering of the bonded carbon atoms.

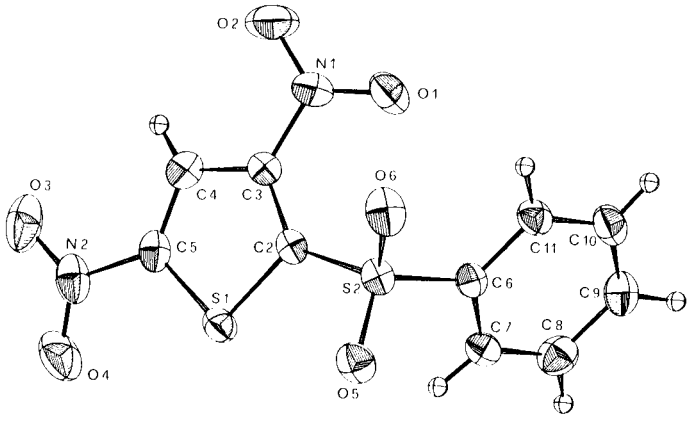


Figure 2. The molecule of compound **3** with the atom-numbering scheme and thermal ellipsoids at the 40% probability level. The H atoms are represented as spheres of arbitrary size.

Table II

Atom Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U eq
S	634(3)	2500(0)	3623(2)	49(1)
C(2)	516(11)	4668(13)	2460(8)	46(2)
C(3)	2113(11)	4640(12)	1769(7)	44(2)
C(4)	3445(9)	2828(14)	2136(7)	43(2)
C(5)	2821(9)	1572(15)	3151(7)	42(2)
Cℓ	−1452(4)	6455(5)	2310(2)	66(1)
N(1)	2428(12)	6199(13)	690(7)	55(2)
N(2)	3785(10)	−394(12)	3805(8)	54(2)
O(1)	1533(14)	7968(14)	633(9)	80(3)
O(2)	3541(14)	5659(16)	−103(9)	85(3)
O(3)	5300(12)	−1029(16)	3415(8)	79(3)
O(4)	2957(12)	−1301(13)	4701(9)	75(3)

Bond distances and bond angles in the thiophene rings and in the nitro groups are normal; the geometry of the phenylsulphonyl group in **3** is in good agreement with that reported for other thiophene phenylsulphones, *e.g.*, for 5-benzsulphonyl-4-bromo-2-sulphamylthiophene and for 5-(2,5-dichloro)benzsulphonyl-2-sulphamylthiophene [23]. However, in **3** the C(2)-S(2) bond length (1.785 Å) and the distance of S(2) from the thiophene plane (0.26 Å) are appreciably larger than the corresponding distances determined for the two above quoted compounds (1.752 Å, 0.094 Å; and 1.749 Å, 0.065 Å). These results can be explained as due to an internal strain present in **3**, as discussed below.

Table III

Atom Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$) for **3**

	x	y	z	U eq
C(2)	1277(1)	1450(2)	−272(2)	32(1)
C(3)	1831(1)	2064(2)	−23(3)	35(1)
C(4)	2319(1)	1582(2)	806(3)	42(1)
C(5)	2103(1)	609(2)	1171(3)	40(1)
C(6)	14(1)	2459(2)	−692(2)	34(1)
C(7)	−390(1)	2076(2)	349(3)	39(1)
C(8)	−872(2)	2721(3)	897(3)	52(1)
C(9)	−957(2)	3752(3)	407(3)	53(1)
C(10)	−557(2)	4128(2)	−647(3)	48(1)
C(11)	−66(2)	3488(2)	−1200(3)	42(1)
N(1)	1926(1)	3132(2)	−555(3)	46(1)
N(2)	2472(2)	−153(2)	2004(3)	56(1)
O(1)	1438(1)	3633(2)	−922(3)	65(1)
O(2)	2501(2)	3466(2)	−608(3)	84(1)
O(3)	3049(1)	73(3)	2291(3)	76(1)
O(4)	2172(2)	−962(2)	2340(3)	76(1)
O(5)	302(1)	543(2)	−1468(2)	49(1)
O(6)	859(1)	2042(2)	−2662(2)	54(1)
S(1)	1335(0)	250(1)	539(1)	41(0)
S(2)	596(0)	1590(1)	−1443(1)	36(0)

The S(2)-O(5), S(2)-O(6) bond distances are in good agreement with the value of 1.43 Å predicted by Bent [24], and with the values found in other phenylsulphones. The S(2)-C(6) bond distance and the C(7)-C(6)-C(11) bond angle are in excellent agreement with values obtained by Domenicano, Vaciago, and Coulson [25] for benzene derivatives bearing an SO_2 substituent, *i.e.*, 1.7534(14) Å and 121.19(14)°.

In both compounds **2** and **3** the thiophene ring is almost planar; deviations of plane-defining atoms from the least-squares planes and the dihedral angles between least-squares planes are summarized in Table VI. The rotation angle, τ [26] of the 5-nitro group with respect to the thiophene plane is rather small in both compounds. This seems to be a common feature in crystal structures of 4-unsubstituted-5-nitrothiophenes, as in 4-(5-nitro-2-thienyl)-but-3-en-2-one (τ = 6.5°) [27] and in 5,5'-dinitro-2,2'-bithienyl (τ = 3.3°) [28].

Table IV

Bond Lengths (Å) and Bond Angles (°) for **2**

S-C(2)	1.71(1)	C(3)-N(1)	1.44(1)
C(2)-C(3)	1.37(1)	C(5)-N(2)	1.43(1)
C(3)-C(4)	1.41(1)	N(1)-O(1)	1.23(1)
C(4)-C(5)	1.36(1)	N(1)-O(2)	1.21(1)
C(5)-S	1.71(1)	N(2)-O(3)	1.21(1)
C(2)-Cl	1.68(1)	N(2)-O(4)	1.24(1)

E.s.d.'s range between 0.007 and 0.012 Å (average 0.010 Å).

S-C(2)-C(3)	111.7(6)	C(3)-N(1)-O(1)	117.7(7)
C(2)-C(3)-C(4)	113.9(6)	C(3)-N(1)-O(2)	117.5(8)
C(3)-C(4)-C(5)	109.8(6)	O(1)-N(1)-O(2)	124.8(9)
C(4)-C(5)-S	114.2(6)	C(4)-C(5)-N(2)	126.5(6)
C(5)-S-C(2)	90.4(4)	S-C(5)-N(2)	119.3(5)
S-C(2)-Cl	118.4(4)	C(5)-N(2)-O(3)	117.4(7)
C(3)-C(2)-Cl	129.9(6)	C(5)-N(2)-O(4)	116.3(7)
C(2)-C(3)-N(1)	125.6(7)	O(3)-N(2)-O(4)	126.4(8)
C(4)-C(3)-N(1)	120.4(6)		

Average e.s.d. 0.65°.

Table V

Bond Lengths (Å) and Bond Angles (°) for **3**

S(1)-C(2)	1.706(3)	S(2)-O(5)	1.437(3)
C(2)-C(3)	1.366(3)	S(2)-O(6)	1.424(2)
C(3)-C(4)	1.403(4)	C(3)-N(1)	1.450(4)
C(4)-C(5)	1.342(4)	C(5)-N(2)	1.456(4)
C(5)-S(1)	1.709(2)	N(1)-O(1)	1.210(3)
C(2)-S(2)	1.785(2)	N(1)-O(2)	1.219(4)
S(2)-C(6)	1.752(2)	N(2)-O(3)	1.215(4)
		N(2)-O(4)	1.221(4)

Average e.s.d. 0.004 Å

S(1)-C(2)-C(3)	111.1(2)	C(3)-N(1)-O(2)	117.0(2)
C(2)-C(3)-C(4)	114.7(2)	O(1)-N(1)-O(2)	124.2(3)
C(3)-C(4)-C(5)	109.0(2)	C(4)-C(5)-N(2)	125.8(2)
C(4)-C(5)-S(1)	115.4(2)	S(1)-C(5)-N(2)	118.8(2)
C(5)-S(1)-C(2)	89.9(1)	C(5)-N(2)-O(3)	117.0(3)
S(1)-C(2)-S(2)	116.0(1)	C(5)-N(2)-O(4)	116.8(3)
C(3)-C(2)-S(2)	132.2(2)	O(3)-N(2)-O(4)	126.3(4)
C(2)-C(3)-N(1)	124.1(2)	C(2)-S(2)-C(6)	107.0(1)
C(4)-C(3)-N(1)	121.1(2)	O(5)-S(2)-O(6)	119.9(1)
C(3)-N(1)-O(1)	118.8(2)	C(7)-C(6)-C(11)	121.3(2)

Average e.s.d. 0.2°.

Intermolecular distances are in the normal range, with the exception of a slightly short contact in **2** between Cl and O(3) in $x-1, y+1, z$ (3.02 Å). In the same compound some internal strain due to an 1...5 intramolecular contact [O(1)...Cl, 2.95 Å] is relieved by a broadening of the C(3)-C(2)-Cl bond angle (129.9°) in addition to the rotation of the 3-nitro group (τ = 17.5°). In **3** a rather short O(1)...S(2) intramolecular distance (3.10 Å) is found; in this case the strain is relieved, in addition to the rotation of the 3-nitro group (τ = 21.0°), by an increase of the C(2)-S(2) bond length (1.785 Å), by a deformation of the C(3)-C(2)-S(2) bond angle (132.2°), and by a N(1)-C(3)-C(2)-S(2) torsion angle of 11.5°, which puts the S(2) atom 0.26 Å out from the thiophene least-squares plane, on the opposite side with respect to the O(1) atom.

Table VI

Least-squares Planes

	Highest Deviation (Å)	
	Compound **2**	Compound **3**
A) Thiophene ring	0.010(7)	0.005(3)
B) 3-Nitrogroup	0.003(7)	0.002(3)
C) 5-Nitrogroup	0.006(7)	0.002(3)
	Dihedral angles (°)	
	Compound **2**	Compound **3**
A-B	17.5	21.0
A-C	1.0	8.3

Indeed, these points are of interest because the S_NAr reactivity of nitro-activated substrates is affected by the rotation of the nitro group(s); actually the activating effect reaches its maximum for a planar molecule. Therefore, it is worthwhile to compare the different experimental reactivities in the thiophene and in the benzene series with the rotation angles of the nitro group(s). In the benzene series, owing to the high steric hindrance between substituents in adjacent positions, the nitro groups are rotated by a considerable amount [about 40° and 15°, respectively, in 2,4-dinitrochlorobenzene (**1**)] [20]. In the thiophene series, for compounds **2** and **3**, the rotation angle of the nitro group is never larger than 21° (see Table VI); accordingly the ratio between the kinetic constants for the piperidinodechlorination and desulphonylation reactions in methanol at 273 K in the thiophene and in the benzene series has been found to be as high as *ca.* 446 and 1,700 (Table I), respectively.

In **2** and **3** the rotation of the nitro groups and particularly of the 3-nitro group can be explained as due to an internal strain, as discussed before, and possibly to packing forces in the crystal. The first effect in the case of the 3-nitro group should vanish or diminish with the formation of the σ-complex, where the C(2) atom approaches the sp^3 hybridization and the entering and leaving groups are

largely out of the plane of the thiophene ring so that they cannot interact with the 3-nitro group. It is likely that, already in the transition states for the formation of the σ-complexes, the stretching and the bending of the bond between C(2) and the leaving group (chlorine or phenylsulphonyl, in **2** and **3** respectively) are sufficient to allow the 3-nitro group to lie practically in the plane of the thiophene ring. The same effect might not give rise to coplanarity in the formation of transition states of benzene derivatives because of the less favourable geometry, which makes the rotation of the 2-nitro group larger with respect to the benzene ring. The situation should be more favourable in σ-complexes, however. In fact, in going from 2,4,6-trinitrophenetole [29] to the corresponding potassium ethoxide (Meisenheimer) adduct, a decrease of the rotation angle of the *ortho*-nitro groups from 61° and 32° to less than 6° has been observed [30], and it is well known that Meisenheimer adducts are good models for σ-complexes. It appears probable that this trend to coplanarity, which strongly favours the conjugation, is one of the reasons which make these adducts and, in general, the σ-complexes particularly stable.

In order to shut off the effect of packing forces we have investigated the geometry of the 'isolated' molecule of **2** by *ab initio* calculations using the STO-3G basis set [31] for different fixed geometries. To keep computations within bounds, the 3-nitro group only was rotated, with the 5-nitro group always in the thiophene plane.

The initial geometry was constructed by means of the *Z*-matrix procedure starting from the experimental structural results. Atoms of the ring were put in the same plane; nitrogen and oxygen atoms were located at the experimental bond distances and bond angles, with the appropriate torsion angle around the C(3)-N(1) bond for each considered case; the hydrogen atom was located at the experimental bond angles, at a distance of 1.076 Å from the bonded carbon atom. To overcome the instabilities which appeared initially in the SCF procedure, the original program [32] has been modified to implement the level-shifting method [33].

The results can be summarized in terms of energy differences with respect to the planar molecule: for $\tau = 20°$, $\Delta E = +0.13$ kcal/mol; for $\tau = 40°$, $\Delta E = +0.92$ kcal/mole.

For compound **2** the rotation of the 3-nitro group from 0 to 20° is accompanied by a (vanishingly small) energy increase; therefore it is most likely that the experimental rotation found for **2** by X-ray diffraction (and perhaps also that found for **3**) is due mainly to packing forces in the crystal state. On the other hand, for the thiophene derivatives under study in solution, the almost coplanar conformation of the 3-nitro group with respect to the ring would allow the nitro group itself to exert its full power in activating S_NAr reactions, especially in the light of the previous observations on the geometry variations of the nitro group in five-membered ring derivatives on going from the starting material to the transition state.

On the other hand, in the case of the benzene derivatives, true rotation barriers against coplanarity of nitro groups must be expected because of the higher steric hindrance between adjacent substituents in a six-membered ring. As a consequence the favourable geometry of the 3-nitro group in five-membered ring compounds should be one of the factors which make the thiophene derivatives more reactive than the corresponding benzene ones in S_NAr reactions. The observed geometries justify the only small primary or secondary kinetic steric effects measured in the thiophene derivatives [18], at variance with what is observed in the corresponding benzene series [19].

EXPERIMENTAL

Kinetic Measurements.

The kinetic data were obtained spectrophotometrically as previously described [15,34] by measuring the appearance of a piperidyl derivative or of a sulphide.

Crystallographic Measurements.

For crystals of **2** and **3** the X-ray intensities were measured on a CAD4 diffractometer equipped with a graphite monochromator using MoKα radiation. Cell parameters were obtained by the least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.71069 Å.

Crystal Data.

Compound **2**, $C_4H\,C\ell\,N_2O_4S$, fw 208.58. Monoclinic, $a = 6.632(2)$, $b = 6.119(2)$, $c = 9.382(4)$ Å, $\beta = 103.64(2)°$, volume = 370.0 Å^3, space group $P2_1$, Z = 2, Dm = 1.86, Dx = 1.87 g cm^{-3}. Crystal dimensions 0.38 × 0.23 × 0.06 mm, $\mu = 6.9$ cm^{-1}.

Compound **3**, $C_{10}H_6N_2O_6S_2$, fw 314.29. Orthorhombic, $a = 19.887(6)$, $b = 12.535(6)$, $c = 9.816(2)$ Å, volume = 2447.0 Å^3, space group *Pbca*, Z = 8, Dm = 1.71, Dx = 1.71 g cm^{-3}. Crystal dimensions 0.42 × 0.40 × 0.20 mm, $\mu = 4.0$ cm^{-1}.

Data Collection and Processing.

Compound **2**, ω/θ scan mode, scan width 1.05°, scan speed 0.8-5.0 deg min^{-1}; 924 independent reflections measured ($2.5 \leq \theta \leq 27.5°$), 740 with $F \geq 3\,\sigma(F)$, absorption correction [35] (max., min. transmission factors = 0.99, 0.58). Crystal decay *ca.* 10%, corrected during processing.

Compound **3**: $\theta/2\theta$ scan mode, scan width 1.2°, scan speed 1.0-10.0 deg min^{-1}; 3540 independent reflections measured ($3 \leq \theta \leq 30°$), 2132 with $F \geq 3\,\sigma(F)$. Crystal decay *ca.* 11%, corrected during processsing.

Structure Determination and Refinement.

The structures were solved by Patterson synthesis (**2**) and by direct methods [36] (**3**). Refinement was accomplished by full-matrix isotropic, and then anisotropic least-squares [36] on C and heavier atoms. The H atoms (located on difference maps) were not refined, but included in the structure factor calculations with an isotropic temperature factor equal to the U(equivalent) value for the bonded carbon atom. The function minimized was $\Sigma w(\Delta F)^2$, with weights $w = [\sigma^2(F_o) + g\,F_o^2]^{-1}$. In the last cycle (740 observations, 108 parameters for **2**; 2132 observations, 181 parameters for **3**) the greatest shift was less than 0.13 σ, most shifts being less than 0.05 σ. The R factor on observed reflections converged to 0.070 (Rw to 0.064, with g = 0.0249) for **2** and to 0.047 (Rw to 0.053, with g = 0.0047) for **3**.

Tables of anisotropic thermal parameters, hydrogen-atom coordinates, and of the observed and calculated structure factors are available from an author (A.M.) on request.

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