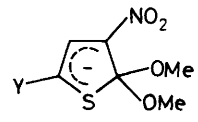
A ^{13}C N.M.R. Study of 5-Cyano-, 5-Methoxycarbonyl-, 5-Carbamoyl-, and 5-Acetyl-3-nitro-2-X-thiophenes: Substituent Effects and their Relation to the Charge Distribution in Corresponding 2,2-Dimethoxy Meisenheimer Adducts

Carlo Dell'Erba,* Fernando Sancassan,* and Marino Novi
Instituto di Chimica Organica, CNR Centro di Studio sui Diariloidi e loro Applicazioni, Corso Europa 26, 16132 Genova, Italy
Domenico Spinelli, Giovanni Consiglio, Caterina Arnone, and Fiammetta Ferroni
Dipartimento di Chimica Organica, Via S. Donato 15, 40127 Bologna, Italy

A ^{13}C n.m.r. study in $(CD_3)_2SO$ has been carried out on 5-cyano- (**5**), 5-methoxycarbonyl- (**6**), 5-carbamoyl- (**7**), and 5-acetyl-3-nitro-2-X-thiophenes (**8**) in order to investigate the 2-X-substituent effect on the C(α) chemical shifts of the different 5-probes. The results obtained show that, unlike the case of the acetyl group, the α-carbon chemical shifts of the cyano, methoxycarbonyl, and carbamoyl groups are not appreciably affected by through-conjugation with the 2-X-substituents, π-polarization being the more important outcome of the substituent effect on the probe group. The analysis of both the C(5) and C(α) chemical-shift variations in the series (**5**)–(**8**), by means of a gradual modification of the electron-releasing power of the substituents, reveals a trend which has been interpreted as a useful indicator of the electronic effects in play on the distribution of the π-electron densities in the corresponding Meisenheimer adducts (**1**)–(**4**).

In a previous ^{13}C n.m.r. study[1] we reported that the formation of Meisenheimer adducts (**1**)–(**4**) from the corresponding 2-methoxy-3-nitro-5-Y-thiophenes in $(CD_3)_2SO$ is accompanied by significant shielding of the α-carbon of the Y group when Y = COMe, but by a deshielding of the same carbon when Y = CN, CO_2Me, or $CONH_2$. A similar dichotomy has previously been observed,[2] but not interpreted, in the formation of Meisenheimer adducts from 2,6-dinitro-4-Y-anisoles when Y = COPh or CN. To explain our results we have advanced the hypothesis that, unlike the acetyl group, the CN, CO_2Me, and $CONH_2$ functions stabilize the corresponding adducts not so much by charge-transfer from the ring, but mainly by stabilizing a larger π-electron density at C(5) through an enhancement of their internal polarization, as depicted in Figure 1 for Y = CN. In other words, Meisenheimer adducts (**1**)–(**3**) could be substantially regarded as dipole-stabilized carbanions.†



(**1**) Y = CN
(**2**) Y = CO_2Me
(**3**) Y = $CONH_2$
(**4**) Y = COMe

The hypothesis of a lower contribution of resonance structures involving conjugation of some Y functions with the ring in stabilizing the corresponding adducts has recently received support from our ^{13}C n.m.r. study[4] on *p*-substituted benzonitriles and methyl benzoates and on their 2,6-dimethyl derivatives. The results obtained showed that the α-carbons of the cyano and methoxycarbonyl groups are not appreciably affected by through-conjugation with *p*-substituents, π-polarization being the more important outcome of the substituent resonance effect on the probe group. Successive work carried out on benzamides led to analogous conclusions.[5]

In the present paper we report on a ^{13}C n.m.r. study carried out on thiophene derivatives (**5**)–(**8**) in $(CD_3)_2SO$ to investigate the substituent effect on the C(α) chemical shifts of the Y probes The main purpose was to test whether, on going through appropriate series of thiophene derivatives, the trends of C(α) chemical shifts were consistent with the data obtained[1] for the corresponding Meisenheimer adducts (**1**)–(**4**).

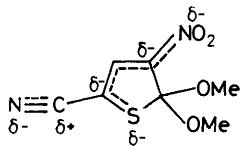
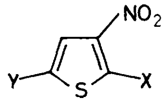


Figure 1. Possible charge distribution in Meisenheimer adduct (**1**).



(**5**) Y = CN **a**; X = NMe_2 **e**; X = SMe
(**6**) Y = CO_2Me **b**; X = NC_5H_{10} **f**; X = I
(**7**) Y = $CONH_2$ **c**; X = OMe **g**; X = Br
(**8**) Y = COMe **d**; X = H **h**; X = SO_2Me

Results and Discussion

In Table 1 are reported the ^{13}C chemical shift values of the probe α-carbons [$\delta_{C(\alpha)}$] for compounds (**5**)–(**8**) and the relevant values for Meisenheimer adducts (**1**)–(**4**). Examination of the data obtained reveals that the substituent effect on $\delta_{C(\alpha)}$ is small, variations being in the range 1.4–2.1 ppm. Such variations are significantly smaller than those previously observed for the C(α) of the corresponding probe groups in *p*-substituted benzene derivatives: the less marked substituent effect in compounds (**5**)–(**8**) could be rationalized by the presence of the strongly interacting nitro group in position 3.

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† For the importance of charge–dipole interactions in stabilizing carbanions see, *e.g.*, ref. 3.

Table 1. Chemical shifts (δ) of the α-carbon of the Y groups in Meisenheimer adducts[a] (**1**)–(**4**) and in 3-nitro-2-X-5-Y-thiophenes (**5**)–(**8**) [0.3 mol dm^{-3} in $(CD_3)_2SO$].

X	Y = CN	Y = CO_2Me	Y = $CONH_2$	Y = COMe
	(**1**)	(**2**)	(**3**)	(**4**)
	117.94	163.46	164.96	188.26
	(**5**)	(**6**)	(**7**)	(**8**)
NMe_2	113.84	161.06	162.19	189.63
NC_5H_{10}	113.69	160.96	162.06	189.69
OMe[a]	113.19	160.65	161.63	190.26
H	112.77	160.49	161.32	190.81
SMe	112.62	160.07	161.12	189.75
I	112.39	159.86	160.73	189.87
Br	112.22	159.78	160.64	190.07
SO_2Me	111.70	159.61	160.65	190.56

[a] Data from ref. 1.

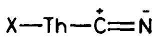
Table 2. Chemical shifts (δ) of the C(5) in Meisenheimer adducts[a] (**1**)–(**4**) and in 3-nitro-2-X-5-Y-thiophenes (**5**)–(**8**) [0.3 mol dm^{-3} in $(CD_3)_2SO$].

X	Y = CN	Y = CO_2Me	Y = $CONH_2$	Y = COMe
	(**1**)	(**2**)	(**3**)	(**4**)
	79.62	104.93	113.37	116.67
	(**5**)	(**6**)	(**7**)	(**8**)
NMe_2	89.40	112.23	120.46	123.56
NC_5H_{10}	91.03	113.79	122.20	124.76
OMe[a]	91.88	114.24	122.28	125.58
H	110.69	133.92	141.50	144.34
SMe	104.15	127.09	135.17	137.94
I	115.23	137.50	145.08	147.78
Br	109.76	132.08	139.92	142.64
SO_2Me	113.63	135.86	142.29	144.46

[a] Data from ref. 1.

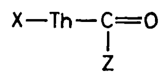
$\mathrm{X{-}Th{-}C{\equiv}N}$

(**9**)



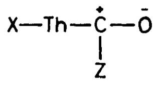
$\mathrm{X{-}Th{-}\overset{+}{C}{=}\overset{-}{N}}$

(**10**)



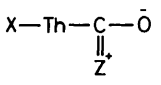
$\mathrm{X{-}Th{-}\underset{\underset{\displaystyle Z}{|}}{C}{=}O}$

(**11**)



$\mathrm{X{-}Th{-}\underset{\underset{\displaystyle Z}{|}}{\overset{+}{C}}{-}\overset{-}{O}}$

(**12**)



$\mathrm{X{-}Th{-}\underset{\underset{\displaystyle \overset{+}{Z}}{\|}}{C}{-}\overset{-}{O}}$

(**13**)

Th = 2,5-disubstituted thiophene
Z = OMe, NH_2

As regards series (**5**)–(**7**), some significant trends can, however, be observed: (*i*) strong electron-donating X-substituents deshield the C(α) of the Y groups, such effect increasing together with their electron-donating ability; (*ii*) electron-withdrawing X-substituents always cause shielding of C(α). Therefore, if the ^{13}C chemical shift variations mirror the π-electron density changes at the same carbon,[6] the observed substituent effect can be defined as 'reversed'.[6] A deeper analysis of the data shows that, when the $\delta_{C(\alpha)}$ values of compounds (**5**) are plotted *vs.* the Hammett σ_p substituent constants,[7,*] a good straight line is obtained ($r = 0.992$) the negative slope of which (-1.44 ± 0.08) confirms the reversed substituent effect on the same carbons. Analogous linear correlations with negative slopes are also observed for compounds (**6**) (slope $= -1.04 \pm 0.17$, $r = 0.936$) and (**7**) (slopes $= -1.13 \pm 0.20$, $r = 0.931$): the poorer correlation possibly being due to the lower sensitivity of the methoxycarbonyl and carbamoyl probes which results in a smaller range of $\delta_{C(\alpha)}$ variations. The observed linear dependence of $\delta_{C(\alpha)}$ values on the Hammett constants, which are significant anyway in statistical terms for each series examined, confirms that the reversed substituent effect is systematic and therefore electronic in nature. In our opinion, such reversed substituent effect can be appropriately rationalized (as proposed for benzonitriles, methyl benzoates,[4] and benzamides[5]) on the basis of a π-electron polarization of the probe group, the direction and intensity of which is closely dependent upon the nature of the X-substituent; *i.e.* X groups with negative σ_p values induce a π-electron polarization of the probe in such a direction that it causes deshielding of its α-carbon, an opposite effect to that determined for electron-withdrawing substituents.

In connection with the above assumption it is interesting to examine the much more marked substituent effect observed for the $\delta_{C(5)}$ values of compounds (**5**)–(**7**) (Table 2). The data obtained appear to be governed mainly by normal resonance effects of the X-substituents. In fact, even if a more complete treatment of these substituent effects required a dual substituent–parameter analysis,[9] taking account also of polar effects, sufficiently significative linear correlations with positive slopes would be obtained just by plotting the $\delta_{C(5)}$ *vs.* the substituent resonance constants $\sigma_R{}^{BA}$ ($n = 7$, X = NC_5H_{10} being excluded): (**5**): $\delta_{C(5)} = 29.2(\pm 4.4); \sigma_R{}^{BA} = +113.3(\pm 1.8)$; ($r = 0.938$); (**6**): $\delta_{C(5)} = 29.0\ (\pm 4.3)$; $\sigma_R{}^{BA} = +135.8\ (\pm 1.8)$; ($r = 0.940$); (**7**): $\delta_{C(5)} = 27.6\ (\pm 4.5)$; $\sigma_R{}^{BA} = +143.1\ (\pm 1.9)$; ($r = 0.929$).

Therefore the effect of the X-substituents on the π-electron density at C(5) can be considered as being the opposite of that observed for the probe α-carbon.

In terms of resonance contributors [(**9**) and (**10**) for compound (**5**) and (**11**)–(**13**) for compounds (**6**) and (**7**)] the experimental results obtained can be explained in terms of the electron-donating substituents, which increase the π-electron density at C(5), and so enhance the relative weight of structures (**10**) and (**12**) which consistently account for the observed deshielding at the probe α-carbon. Conversely, the observed shielding induced by electron-withdrawing substituents can be rationalized on the grounds that such substituents, by bringing about a decrease in the π-electron density at C(5), make the contribution of structures (**9**), (**11**), and (**13**) relatively more important.

The above rationalization agrees well with that previously[1] advanced to explain the π-electron distribution in the Meisenheimer adducts (**1**)–(**3**). It is worth noting that in the series of compounds (**5**)–(**7**), as the electron-donating power of the substituent is increased, both the C(5) and the C(α) chemical shift values show a trend, the superior limit of which appears to be that of the corresponding Meisenheimer adduct, where the displacement of a whole negative charge onto the ring brings about a markedly larger shielding of the C(5) with consequent greater deshielding of cyano, methoxycarbonyl, and carbamoyl α-carbons. In this regard, it is relevant that good linear correlations with positive slopes are observed by plotting either $\delta_{C(\alpha)}$ or $\delta_{C(5)}$ of compounds (**2**) and (**6**) [or (**3**) and (**7**)] against the analogous values of the compounds (**1**) and (**5**) [for (**2**) and (**6**) *vs.* (**1**) and (**5**): $\delta_{C(\alpha)}$ (slope 0.63 ± 0.02; $n = 9$; $r = 0.993$); $\delta_{C(5)}$ (slope 0.95 ± 0.02; $n = 9$; $r = 0.998$); for (**3**) and (**7**) *vs.* (**1**) and (**5**): $\delta_{C(\alpha)}$ (slope 0.73 ± 0.03; $n = 9$; $r = 0.993$); $\delta_{C(5)}$ (slope 0.91 ± 0.02; $n = 9$; $r = 0.997$)]. These results indicate that the adducts (**1**)–(**3**), in spite of their anionic character and the different hybridization of C(2), can be formally regarded as thiophene derivatives, like (**5**)–(**7**), in which the 2-position is

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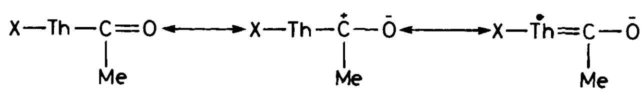
[*] The literature values[7b] for $\sigma_{p\text{-}NC_5H_{10}}$ (-0.12 and -0.57) appear low compared with the corresponding values for NMe_2 (-0.83) and NEt_2 (-0.90) groups.[7b] Therefore this substituent has not been included in the data calculations. We have calculated a σ_p constant of -0.72 ± 0.04 ($n = 4$, $i = 0.01 \pm 0.04$, $r = 0.997$) for the NC_5H_{10} group by using a method equivalent to the extended selectivity treatment.[8]



(14) (15) (16)

occupied by a substituent with an extremely strong $+R$ effect. In fact, the slight influence caused by the change in hybridization at C(2) is not unexpected on the basis of literature data on other cyclic systems.[10]

As far as the substituent effect on the $\delta_{C(\alpha)}$ of compounds (**8**) is concerned, the data collected exhibit, at first glance, a pattern different from that of compounds (**5**)–(**7**): shielding of the acetyl α-carbon is observed whatever the electronic effect of the 2-substituent. As a consequence, no correlation of the data with the Hammett σ_p constants is possible in this case. The substituent effect on $\delta_{C(5)}$ of compounds (**8**), in contrast, proves to be very similar to that observed in the series (**5**)–(**7**): the $\delta_{C(5)}$ values likewise being governed mainly by the normal resonance effects of the 2-substituents [$\delta_{C(5)} = 26.7\ (\pm 4.5);\ \sigma_R^{BA} + 145.6\ (\pm 1.9); n = 7; r = 0.925$]. On the whole, the substituent effects in series (**8**) show tight analogies with those observed in *p*-substituted acetophenones[4,6] and such effects can be consistently rationalized on the grounds of an effective conjugation between the thienyl ring and the acetyl group in compounds (**8**). Thus both electron-withdrawing and electron-donating substituents cause shielding of the probe α-carbon by increasing, respectively, the relative weight of structures (**14**) and (**16**). That makes undetectable the contribution of structure (**15**) which would account for a π-electron polarization effect similar to that observed for the cyano, methoxycarbonyl, and carbamoyl functions.

A further point worth considering is that in this case, as above reported for the series (**5**)–(**7**) and the corresponding Meisenheimer adducts, the assumptions previously made to explain the π-electron distribution in the adduct (**4**) are in line with the trend observed in the series (**8**). The marked shielding at both C(α) and C(5) once again allows us formally to relate the adduct (**4**) to a 5-acetyl-3-nitro-2-X-thiophene with an extremely strong electron-donating 2-X substituent. With regard to electron-donating substituents alone, plots of either $\delta_{C(\alpha)}$ or $\delta_{C(5)}$ values of compounds (**4**), (**8a**–**d**) against the analogous values of compounds (**1**), (**5a**–**d**) give consistantly significant linear relationships [$\delta_{C(\alpha)}$ (slope -0.43 ± 0.07; $n = 5$; $r = 0.948$); $\delta_{C(5)}$ (slope 0.91 ± 0.05; $n = 5$; $r = 0.995$)]. In the case of the $\delta_{C(\alpha)}$ linear correlation, while the negative value of the slope reflects the opposite sensitivity of $\delta_{C(\alpha)}$ of the cyano and of the acetyl groups to the substituent effects, the rather unsatisfactory correlation could be accounted for by the opposing dominant role played by conjugation or by π-electron polarization in the above two systems.

In conclusion, the analysis of $\delta_{C(5)}$ and $\delta_{C(\alpha)}$ variations in the series (**5**)–(**8**), by means of a gradual modification of the electron-releasing power of the substituents, reveals a trend which can be a useful indicator of the electronic effects in play on the distribution of the π-electron densities in the corresponding Meisenheimer adducts. We also feel that, in other aromatic series, to regard formal Meisenheimer adducts as the upper limit of a series of consistent aromatic substrates with substituents of increasing electron-donating power could contribute usefully to the interpretation of the factors operative on the π-electron distribution of the corresponding Meisenheimer adducts.

Experimental

Syntheses.—Pure samples of compounds, (**5a**),[11] (**5b**),[12] (**5d**),[13] (**5f**),[8] (**6a**),[11] (**6b**),[14] (**6d**),[15] (**6f**),[16] (**6g**),[14] (**7a**),[11] (**7b**),[12] (**7f**),[8] (**7g**),[17] (**8a**),[11] (**8b**),[12] (**8d**),[18] (**8f**),[8] and (**8g**)[19] were prepared as reported.

5-*Methylthio*-4-*nitrothiophene*-2-*carbonitrile* (**5e**).—Sodium methanethiolate (0.42 g, 6 mmol) was added to a stirred solution of (**5g**) (0.47 g, 2 mmol) in diethyl ether (20 ml). After the reaction had been stirred for 24 h, the ether was distilled off and the residue was purified by column chromatography on silica gel using toluene as the eluant. The *nitrile* (**5e**) (33% yield) had m.p. 151 °C (from MeOH) (Found: C, 35.8; H, 2.0; N, 14.0. $C_6H_4N_2O_2S_2$ requires C, 36.0; H, 2.0; N, 14.0%).

5-*Bromo*-4-*nitrothiophene*-2-*carbonitrile* (**5g**).*—5-Bromothiophene-2-carbonitrile[12] (1.9 g) was added dropwise to a stirred solution of fuming HNO_3 (17 cm^3) in Ac_2O (34 cm^3), at 20 °C. The mixture was stirred at 25–30 °C for 2 h and then heated at 60 °C on a water bath. After being cooled, the reaction mixture was poured into crushed ice and the white precipitate was filtered off and washed with water. The *nitrile* (**5g**) (65% yield) had m.p. 123 °C (from MeOH) (Found: C, 25.8; H, 0.45; N, 12.0. $C_5HBrN_2O_2S$ requires C, 25.8; H, 0.4; N, 12.0%).

5-*Methylsulphonyl*-4-*nitrothiophene*-2-*carbonitrile* (**5h**).—A solution of (**5e**) (1.8 g, 9 mmol) in acetic acid (7.2 cm^3) was treated with 30% hydrogen peroxide (3.7 cm^3) and refluxed for 3 h. The acetic acid was removed *in vacuo* and the residue was taken up with water, filtered off, and washed with water. The *nitrile* (**5h**), after purification by chromatography on a silica-gel column [eluants: toluene and toluene–ethyl acetate (4:1)], was obtained in 80% yield, m.p. 176 °C (from MeOH–dioxane) (Found: C, 31.1; H, 1.7; N, 12.1. $C_6H_4N_2O_4S_2$ requires C, 31.0; H, 1.7; N, 12.1%).

Methyl 5-*Methylthio*-4-*nitrothiophene*-2-*carboxylate* (**6e**).—This was prepared in 85% yield from (**6g**) as for (**5e**). The *ester* (**6e**) had m.p. 119–120 °C (from MeOH–dioxane) (Found: C, 36.15; H, 3.1; N, 6.0. $C_7H_7NO_4S_2$ requires C, 36.0; H, 3.0; N, 6.0%).

Methyl 5-*Methylsulphonyl*-4-*nitrothiophene*-2-*carboxylate* (**6h**).—This was prepared in 70% yield from (**6e**) as for (**5h**). The *ester* (**6h**), purified by chromatography on a silica-gel column (eluant: toluene) had m.p. 134–135 °C (from MeOH) (Found: C, 31.8; H, 2.7; N, 5.3. $C_7H_7NO_6S_2$ requires C, 31.7; H, 2.7; N, 5.3%).

4-*Nitrothiophene*-2-*carboxamide* (**7d**).—Potassium nitrate (1.03 g) was slowly added with stirring to a solution of thiophene-2-carboxamide[20] (1.3 g) in concentrated H_2SO_4 (10 cm^3) at 10 °C. The mixture was stirred at 10 °C for 30 min and then poured onto crushed ice. The precipitate was filtered off, washed with water, and purified by chromatography on a silica-gel column [eluant: benzene–ethyl acetate (1:1)]. The *amide* (**7d**) (74% yield) had m.p. 152–153 °C (from MeOH) (Found: C, 35.0; H, 2.3; N, 16.3. $C_5H_4N_2O_3S$ requires C, 34.9; H, 2.3; N, 16.3%).

5-*Methylthio*-4-*nitrothiophene*-2-*carboxamide* (**7e**).—This was prepared in 90% yield from (**7g**) as for (**5e**). After purification by chromatography on a silica-gel column [eluant: toluene–ethyl acetate (1:1)], the *amide* (**7e**) had m.p. 290–291 °C (from dioxane) (Found: C, 33.1; H, 2.8; N, 12.8. $C_6H_6N_2O_3S_2$ requires C, 33.0; H, 2.8; N, 12.8%).

5-*Methylsulphonyl*-4-*nitrothiophene*-2-*carboxamide* (**7h**).—This was prepared in 70% yield from (**7e**) as for (**5h**). After

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* The preparation of (**5g**) should have been reported in ref. 12 but, owing to some error during press, it was omitted.

purification by chromatography on a silica-gel column [eluant: ethyl acetate–toluene (4:1)], the *amide* (**7h**) had m.p. 256 °C (from dioxane) (Found: C, 28.9; H, 2.45; N, 11.15. $C_6H_6N_2O_5S_2$ requires C, 28.8; H, 2.4; N, 11.2%).

5-*Acetyl*-2-*methylthio*-3-*nitrothiophene* (**8e**).—This was obtained in 75% yield from (**8g**) as for (**5e**). The *ketone* (**8e**) had m.p. 192 °C (from MeOH–dioxane) (Found: C, 38.9; H, 3.3; N, 6.4. $C_7H_7NO_3S_2$ requires C, 38.7; H, 3.25; N, 6.45%).

5-*Acetyl*-2-*methylsulphonyl*-3-*nitrothiophene* (**8h**).—This was prepared in 65% yield from (**8e**) as for (**5e**). The *ketone* (**8h**), purified by chromatography on a silica-gel column [eluants: toluene and then toluene–ethyl acetate (1:1)], had m.p. 163 °C (from MeOH–dioxane) (Found: C, 33.85; H, 2.8; N, 5.65. $C_7H_7NO_5S_2$ requires C, 33.7; H, 2.8; N, 5.6%).

^{13}C *N.M.R. Measurements.*—Samples were prepared in 10 mm sample tubes at a concentration of 0.3 mol dm^{-3} in dry $(CD_3)_2SO$. Spectra were recorded on a Varian FT-80 spectrometer at 20 MHz, 8K data points being collected over a spectral width of 4.5 kHz for acetyl derivatives and 4 kHz for the other compounds, giving a digital resolution of 0.06 and 0.05 ppm, respectively. All chemical shifts were measured relative to $SiMe_4$ in proton–noise decoupling experiments with the temperature controlled at 25 °C. Assignments were assisted by the proton-coupled spectra.

Acknowledgements

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