DUAL SUBSTITUENT PARAMETER TREATMENT OF ^{13}C SUBSTITUENT CHEMICAL SHIFTS IN
5-SUBSTITUTED 2-THENYLIDENEMALONONITRILES AND MOLECULAR ORBITAL THEORETICAL
ANALYSIS AT THE CNDO/2 LEVEL

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Abstract- DSP treatment of ^{13}C SCS among the members of the title compound indicated the
dominance of the resonance effect at Cβ and the presence of both localized and extended
polarization in the side chain. MO calculations at the CNDO/2 level corroborated the
observed SCS trends.

The importance attributed to thiophene among the heteroaromatics subjected to Hammett type corre-
lation[1] is largely due to its similarity with benzene and numerous were studies comparing the
transmission of substituent effects in the two molecules[2]. Besides reactivity studies, correlation
of spectral data[1-4] involving single and dual substituent parameter[3,4] (SSP and DSP) treatment as
well as multivariate statistics[5] e.g. principal component analysis, are reported in the literature
although some of the data sets are too small. Meta or para substituted styrenes with or without
substituents in the α- or β-positions in the side-chain, have frequently been investigated, parti-
cularly by those interested in the correlation of n.m.r. data with substituent parameters[6]. Easy
accessibility, well-defined geometry and easily interpretable spectra account for the popularity
enjoyed by this class of compounds. Our choice fell on the series (1) and (2) while looking for a
suitable model in the thiophene series. Apart from their relatively easy accessibility (although
more difficult compared to the corresponding benzene analogues) and simple spectra, they provide
an opportunity to compare the transmissivity of the substituent induced electronic effects in thio-
phene and benzene with side-chains which enter into conjugation with the aromatic rings, since an
abundance of data on the benzene analogues of (1) and (2) is currently available[6].

(1) X= CN (2) X=CONH₂

(3)

(4)

(5)
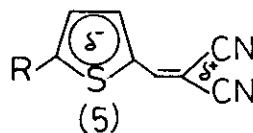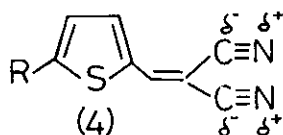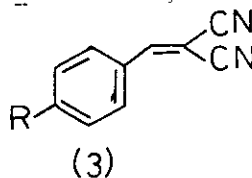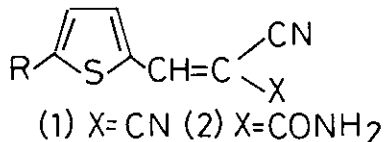
RESULTS AND DISCUSSION

Unlike the earlier study, we correlated the SCS instead of chemical shifts as such and confined ourselves to the DSP treatment whose superiority over the SSP treatment is now irrefutably establi- shed[7]. Nor does the principal component analysis appear to accrue any additional information in this type of system[8]. Suitability of the DSP treatment for thiophene derivatives has been favoura- bly commented upon[1]. As polar substituent parameters we have used Reynold's σ_F values[9] representing a pure field effect while, as resonance parameters, σ_Ro values of Reynolds[9] and σ_R+ values of both Taft[6] and Charton[10] were used. The data set consisting of only those substituents which have well established values of these parameters, included most of the substituents recommended for a "mini- mal basis set"[6] and contained donor, acceptor and neutral substituents.

The SCS are given in Table 1. Assignments were made using broad band, off resonance and gated coupled spectra. The SCS of the three carbon atoms in the side-chain Cβ, CN$_Z$ and CN$_E$ show strictly analogous behaviour with the same carbon atoms in the corresponding benzene series[11] (3) according to the equation :

$$\underline{S} \text{ (thiophene)} = a \ \underline{S} \text{ (benzene)} + b$$

The result of the correlation are given in Table 2, indicating a greater transmissivity in the thiophene series apparent from the values of a. The results of the DSP analysis are summarized in Table 3. SCS Cα and C-2, show no correlation although SCS C-1 in (3), could be correlated[11] against (σ_F + σ_Ro). For the other three carbon atoms in the side-chain only the use of σ_R+ as resonance parameter led to meaningful correlations, the quality of fit being almost indentical for the two σ_R+ scales. The dominance of the mesomeric effect at the β-position, which is approximately twice that of the polar effect is clear from the magnitude of the ρ_R value. From the sign of the ρ value the "reverse" substituent effect at the two nitrile carbons is evident as well as the direct pola- risation of the nitrile Π-electrons as the dominant field effects exerted by the substituents R (4). It is difficult to pronounce about the polarization of the C_α-C_β double bond in the absence of a reliable correlation of SCS C_α but the ρ_F at C_β is large enough to indicate a significant contribution from the extended polarization of the type (5).

The molecular electronic structure of six members of (1) were investigated by M.O. calculations at the CNDO/2 level for a better understanding of the SCS trends. The scope of the present investiga- tion is larger compared to our earlier study[3] through examination of a greater number of substitu- ents and by making the geometrical parameters more reliable by using the data available from a X-ray crystallographic study[12] of (1, R=H). The results summarized in Table 4 indicate :

(i) C_α and C_β are respectively rich in σ or Π-electrons.

(ii)   The Π-electron density at C_β responds regularly to a change in the electron demand of R, jus- tifying the large mesomeric contribution in the DSP equation.

(iii) No such change is observed in the σ or Π-electron density at C_α mirroring the failure of correlation of the SCS. One plausible hypothesis is the opposition of substituent effects by secondary polarization caused by the sulphur atom or other localized charges in the ring. The electron density on the sulphur is found to be systematically influenced by the changes in the 5-substituent.

TABLE 1. ^{13}C SCS[a] in 5-Substituted 2-Thenylidenemalononitriles (1).

R	C-2	C-3	C-4	C-5	C-α	C-β	CN$_Z$	CN$_E$
H	135.23	139.99	128.87	138.18	152.96	75.99	113.32	114.11
Me	-1.76	1.51	-0.76	16.03	-0.10	-2.30	0.35	0.31
Cl	-1.13	0.59	0.21	2.40	-0.18	0.58	-0.05	-0.27
Br	1.48	0.02	3.65	-12.91	-0.71	0.63	0.06	-0.19
NO$_2$	3.92	-2.16	0.43	17.70	-0.62	6.41	-0.86	-1.11
OMe	-13.27	8.43	-20.49	39.03	5.41	-7.09	1.03	0.94

[a] Related to the parent compound.

TABLE 2.   Correlation between ^{13}C SCS in Systems (1) and (3)

Carbon	a	b	r[p]	sd[q]	f[m]	n[o]
C$_\beta$	1.46	-0.159	0.998	0.3	0.07	6
CN$_E$	1.24	0.046	0.977	0.1	0.20	6
CN$_Z$	1.28	0.101	0.988	0.1	0.20	6

[p] Correlation co-efficient   [q] Standard Deviation   [m] Tafts' 'f' values   [o] No. of points in the data set.

TABLE 3.   Evaluation of the DSP Model.

Site	Model[a]	ρ_F	ρ_R	c[b]	r[c]	s[d]	sd[e]	f[t]	F[q]	n[m]
C$_\beta$	A	10.56	-7.55	-3.40	0.726	3.90	3.02	1.33	1.68	6
C$_\beta$	B	7.27	13.10	-0.17	0.999	0.22	0.17	0.04	1018.00	6
C$_\beta$	C	7.27	13.10	-0.17	0.999	0.22	0.17	0.04	1018.00	6
CN$_Z$	A	-1.35	1.03	0.53	0.673	0.59	0.46	0.79	1.24	6
CN$_Z$	B	-0.98	-1.29	0.05	0.994	0.09	0.07	0.12	129.00	6
CN$_Z$	C	-0.86	-1.93	0.05	0.996	0.07	0.05	0.09	179.00	6
CN$_E$	A	-1.82	1.23	0.56	0.781	0.56	0.41	0.64	2.35	6
CN$_E$	B	-1.45	-1.29	0.01	0.997	0.07	0.06	0.09	200.00	6
CN$_E$	C	-1.33	-1.93	0.01	0.997	0.06	0.06	0.09	215.00	6

[a] Models A,B and C use σ_Ro (Renyolds)[9], σ_R^+ (Taft)[7] and σ_R^+ (Charton)[10] respectively.   [b] Intercept.
[c] Correlation co-efficient.   [d] Standard error of estimate.   [e] Standard deviation.   [t] Tafts' 'f' value.
[q] F test for variance.   [m] No. of points in the data set.

TABLE 4.   Pi and Total[a] Electron Density in (1) (CNDO/2)

R	C$_\alpha$	C$_\beta$	CN$_E$	CN$_Z$
H	0.6652 (4.2063)	1.3594 (4.1924)	0.9382 (3.8645)	0.9527 (3.8895)
Me	0.6615 (4.2047)	1.3829 (4.2080)	0.9337 (3.8635)	0.9482 (3.8883)
F	0.6679 (4.1991)	1.3677 (4.1998)	0.9380 (3.8641)	0.9525 (3.9089)
Cl	0.6724 (4.2054)	1.3471 (4.1835)	0.9400 (3.8625)	0.9545 (3.8884)
NH$_2$	0.6608 (4.2008)	1.4005 (4.2214)	0.9318 (3.8642)	0.9461 (3.8895)
NO$_2$	0.6824 (4.2070)	1.3258 (4.1706)	0.9452 (3.8648)	0.9598 (3.8917)

[a] Figures within parenthesis indicate total electron density.

EXPERIMENTAL

The physical data of the compounds[13] were reported earlier[3]. The spectra were recorded on a JEOL Fx-100 FT n.m.r. spectrometer operating at 25.05 MHz, with a pulse length of 4μs (33°), a repetition time of 1.2s, a spectral width of 6024Hz and 8K f.i.d. and an average scan of 1500. The central line of DMSO multiplet (39.5 ppm) was used as internal reference.

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