Tetrahedron Vol. 35, pp. 1019 to 1025. Pergamon Press 1979. Printed in Great Britain

APPLICATION OF THE ADDITIVE INCREMENTS METHOD TO THE CALCULATION OF CHEMICAL SHIFT OF OLEFINIC PROTONS IN AROMATIC OLEFINES

ADDITIVE INCREMENTS FOR *PARA* AND *META* SUBSTITUENTS IN THE AROMATIC RING

MARIAN MIKOŁAJCZYK,* SŁAWOMIR GRZEJSZCZAK and ANDRZEJ ZATORSKI
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 Łódź, Boczna 5, Poland

(*Received in UK 18 September 1978*)

Abstract—Additive increments for *para* and *meta* substituents in the aromatic ring were calculated on the basis of 332 examples of chemical shifts and were correlated with Hammett's constants. Examples of calculation of chemical shifts of olefinic protons in substituted aromatic olefines by means of the increments are given.

The method for calculating chemical shifts of protons at the double bond by means of additive increments[1-4] is often very useful in the determination of the configuration around the double bond and in the assignment of resonance signals to the corresponding protons. The additive increments method is based on the independence and additivity of the shielding effects of substituents at the double bond. According to this method the chemical shift of an olefinic proton is given by eqn (1)

$$\delta_{ppm} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans} \qquad (1)$$

where 5.25 is the chemical shift of ethylene and Z_{gem}, Z_{cis} and Z_{trans} are additive increments of substituents R in the corresponding positions with respect to the proton. Until the present time the additive increments have been calculated for 44 functional groups,[2,5] i.e. for the majority of substituents usually encountered at the double bond. In the case of 36 functional groups the increments have been calculated by the least squares method on the basis of 4298 chemical shifts and in the case of the remaining 8 groups on the basis of simple additivity.

The parent compound method proposed by Tobey[4] is a variant of the additive increments method, in which the additive increments of the substituent are calculated on the basis of chemical shifts of compounds having the structure related as closely as possible to that of the examined compound. This method makes it possible to use additive increments also in the cases where steric or electronic interactions between the substituents interfere with the simple additivity.

Among olefinic compounds the compounds containing aromatic substituents at the double bond are of particular importance. In this case the situation is complicated by the fact that substituents can be present also in the aromatic ring, which has a profound effect on the chemical shifts of olefinic protons. Pascual[1] gave in his first work only one increment for all the aromatic substituents:

$$Z_{gem} = 1.35, \quad Z_{cis} = 0.37, \quad Z_{trans} = -0.10.$$

For comparison, according to Tobey[4] a phenyl group which is not sterically crowded shows the following increments:

$$Z_{gem} = 1.43, \quad Z_{cis} = 0.39, \quad Z_{trans} = -0.06.$$

In their next publication Pascual *et al.*[2] introduced subgroups of aromatic substituents in order to make the method more exact and to extend its applicability.

Substituent	Z_{gem}	Z_{cis}	Z_{trans}
Aromatic	1.38	0.36	−0.07
Aromatic crowded	1.60	—	−0.05
Aromatic *ortho*-substituted	1.65	0.19	0.09

However, we have found that when a substituent (particularly a substituent exerting a strong electronic effect) is present in the aromatic ring, the differences between the observed and the calculated chemical shifts of olefinic protons are considerable. This is not surprising, since the aromatic system is very sensitive to the effect of substituents. The effect of a substituent on the chemical shift of *meta* and *para* protons in substituted benzene is usually by one order of magnitude stronger than that on γ and δ protons in aliphatic compounds.[6] Several linear relationships between chemical shifts of olefinic protons and σ Hammett's constants of substituents in the aromatic ring have been proposed.[7]

We have found that (within the accuracy limits of the additive increments method) substituents in the aromatic ring in the *meta* or *para* positions exert a constant additive effect on the chemical shifts of the corresponding protons at the double bond and that this effect is independent of other substituents. This can be expressed in the form of eqn (2) which gives chemical shift (δ) of the olefinic proton in an aromatic olefine containing

substituent S in the aromatic ring:

$$\delta_{ppm} = \delta_0 + \Delta S_i^j \quad (2)$$

where δ_0 is the chemical shift of the olefinic proton in the unsubstituted compound; ΔS_i^j is the increment due to substituent S in the aromatic ring; *i* is the *gem*, *cis* or *trans* position of the substituted aromatic ring with respect to the olefinic proton; *j* is the *para* or *meta* position of the substituent in the aromatic ring.

It was found that the values of increments ΔS_i^j of substituents are perfectly linear functions of Hammett's σ constants of substituents S. Using 332 examples of chemical shifts of protons in olefinic compounds containing phenyl substituents we have derived eqns (3)–(8) expressing ΔS_i^j as functions of the σ value.[8] The standard deviation of the chemical shift has been found to be 0.03 ppm.

$$\Delta S^p_{gem} = 0.162\ \sigma_p - 0.005 \quad (3)$$

$$\Delta S^p_{cis} = 0.252\ \sigma_p - 0.022 \quad (4)$$

$$\Delta S^p_{trans} = 0.321\ \sigma_p - 0.010 \quad (5)$$

$$\Delta S^m_{gem} = 0.119\ \sigma_m - 0.032 \quad (6)$$

$$\Delta S^m_{cis} = 0.239\ \sigma_m - 0.027 \quad (7)$$

$$\Delta S^m_{trans} = 0.291\ \sigma_m - 0.027 \quad (8)$$

Table 1 shows the values of ΔS_i^j calculated by means of the above equations for substituents in the aromatic ring, which were taken into account in the derivation of eqns (3)–(8). The increments of other substituents can be calculated by means of eqns (3)–(8) and the corresponding Hammett's σ constants.

The values of the increments shown in Table 1 indicate that only substituents exerting strong electron accepting or electron donating effects, e.g. NMe_2, CN, NO_2, etc. have a significant influence on the olefinic proton shift. It should be observed that the strongest vinyl proton shielding effect have substituents in the aromatic ring in position *trans* with respect to the proton. The effect of substituents in position *cis* is slightly smaller and that of substituents in position *gem* is considerably smaller. The effect of a substituent in position *para* in the aromatic ring is stronger than the effect of the same substituent in position *meta*. On the basis of many examples we have found that deviations from the calculated values ΔS_i^j are most frequently observed in the case of substituents Cl, Br and CN in the aromatic ring in the *gem* position with respect to the olefinic proton.

Utilising the determined additive increments of shielding ΔS_i^j of substituents in the aromatic ring we can express the equation determining the chemical shift of the olefinic proton in an unsaturated compound containing substituent S in the aromatic ring in the form of eqn (9).

$$\delta_{ppm} = 5.25 + \Sigma_i Z_i + \Sigma \Delta S_i^j. \quad (9)$$

Examples of calculations of chemical shifts of vinyl protons by means of eqn (9) are given in Table 2. Examples 1–14 illustrate the possibilities of assigning signals in the ABC and AB systems to the corresponding protons in substituted aromatic olefines, whereas examples 15–17 illustrate the assignment of configuration around the double bond on the basis of vinyl proton chemical shift. It is of interest that the additivity rule is also valid in the case when both aromatic rings contain a substituent (examples 9–12).

The increments of substituents in the aromatic ring ΔS_i^j determined by us can be used also in the case when the additive increments method fails but the chemical shift of the olefinic proton in the unsubstituted compound is known. In this case the procedure is based on the parent compound principle. In a series of analogous compounds it gives a better agreement between the calculated and the observed values of chemical shifts.

Examples of calculations of chemical shifts of vinyl protons by means of eqn (2) are shown in Table 3. The vinyl proton in compound 18 shows the difference between the calculated and the observed values of chemical shift equal to 0.26 ppm, but the application of the procedure discussed above makes it possible to calculate with good accuracy the chemical shifts of vinyl protons in the substituted analogues 19–21. Similarly in the case of 1,1-diphenylethylene (22) the difference between the observed and the calculated values of the chemical shift is 0.15 ppm, which makes it impossible to carry out the calculations for substituted derivatives. The parent compound method can be used for calculating with good accuracy the chemical shifts in examples 21–25 and for assigning the resonance signals in the AB system to the corresponding protons in examples 26 and 27.

Table 1. Additive shielding increments for *para* and *meta* substituents in the aromatic ring

Substituent S	ΔS^p_{gem}	ΔS^p_{cis}	ΔS^p_{trans}	ΔS^m_{gem}	ΔS^m_{cis}	ΔS^m_{trans}
NMe_2	-0.14	-0.23	-0.27	-0.06	-0.08	-0.09
NH_2	-0.11	-0.19	-0.22	-0.05	-0.07	-0.07
OH	-0.06	-0.12	-0.13	-0.02	0	0.02
OCH_3	-0.05	-0.09	-0.09	-0.02	0	0.01
CH_3	-0.03	-0.06	-0.06	-0.04	-0.04	-0.05
Br	0.03	0.04	0.06	0.01	0.07	0.09
Cl	0.03	0.04	0.06	0.01	0.06	0.08
COOR	0.07	0.09	0.13	0.01	0.06	0.08
CN	0.10	0.14	0.20	0.04	0.10	0.14
NO_2	0.12	0.17	0.23	0.05	0.14	0.18

Table 2. Assignments of proton resonance position in ABC and AB systems and structural assignments to geometrical isomers in aromatic olefines using shielding increments

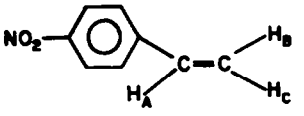
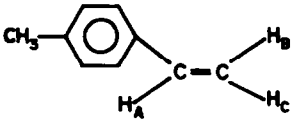
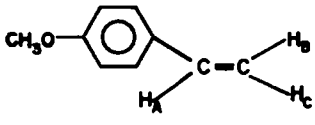
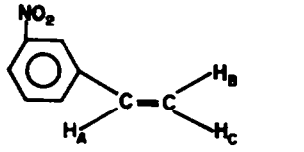
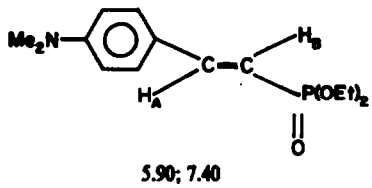
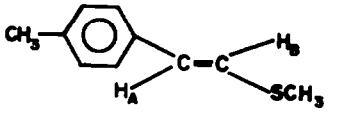
No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
1	9	 5.44; 5.87; 6.27	H_A: 5.25 1.38 (aromatic *gem*) 0.12 (Δ^p_{gem} NO_2) 6.75 (Δ = −0.03) H_B: 5.25 0.36 (aromatic *cis*) 0.17 (Δ^p_{cis} NO_2) 5.78 (Δ = 0.09) H_C: 5.25 −0.07 (aromatic *trans*) 0.23 (Δ^p_{trans} NO_2) 5.41 (Δ = 0.03)
2	9	 5.18; 5.50; 6.66	H_A: 5.25 1.38 (aromatic *gem*) −0.03 (Δ^p_{gem} CH_3) 6.60 (Δ = 0.06) H_B: 5.25 0.36 (aromatic *cis*) −0.06 (Δ^p_{cis} CH_3) 5.55 (Δ = −0.05) H_C: 5.25 −0.07 (aromatic *trans*) −0.06 (Δ^p_{trans} CH_3) 5.12 (Δ = −0.06)
3	9	 5.03; 5.50; 6.55	H_A: 5.25 1.38 (aromatic *gem*) −0.05 (Δ^p_{gem} OCH_3) 6.58 (Δ = −0.03) H_B: 5.25 0.36 (aromatic *cis*) −0.09 (Δ^p_{cis} OCH_3) 5.52 (Δ = −0.02) H_C: 5.25 −0.07 (aromatic *trans*) −0.09 (Δ^p_{trans} OCH_3) 5.09 (Δ = −0.06)
4	9	 5.37; 5.82; 6.69	H_A: 5.25 1.38 (aromatic *gem*) 0.05 (Δ^m_{gem} NO_2) 6.68 (Δ = 0.01) H_B: 5.25 0.36 (aromatic *cis*) 0.14 (Δ^m_{cis} NO_2) 5.75 (Δ = 0.07) H_C: 5.25 −0.07 (aromatic *trans*) 0.18 (Δ^m_{trans} NO_2) 5.36 (Δ = 0.01)
5	10	 5.90; 7.40	H_A: 5.25 1.38 (aromatic *gem*) −0.14 (Δ^p_{gem} NMe_2) 0.88 ($PO(OEt)_2$ *cis*) 7.37 (Δ = 0.03) H_B: 5.25 0.36 (aromatic *cis*) −0.23 (Δ^p_{cis} NMe_2) 0.66 ($PO(Et)_2$ *gem*) 6.04 (Δ = −0.14)
6-E	11	 6.20; 6.62	H_A: 5.25 1.38 (aromatic *gem*) −0.03 (Δ^p_{gem} CH_3) −0.29 (SR *cis*) 6.31 (Δ = −0.11) H_B: 5.25 0.36 (aromatic *cis*) −0.06 (Δ^p_{cis} CH_3) 1.11 (SR *gem*) 6.66 (Δ = −0.04)

Table 2. (*Contd*)

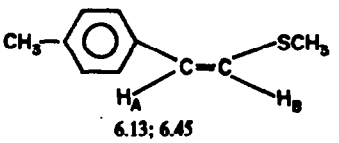
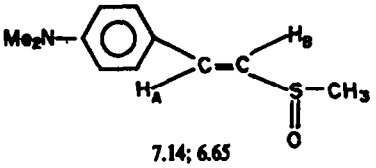
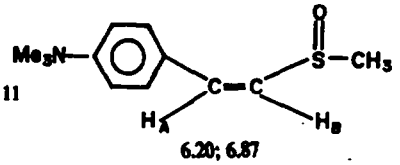
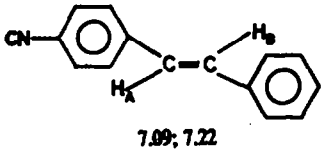
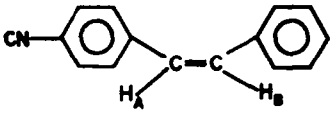
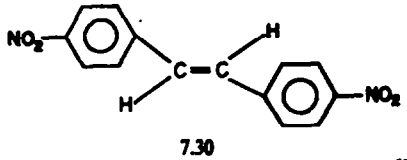
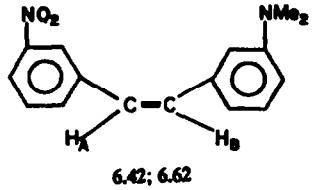
No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
6-Z	11	 6.13; 6.45	H_A: 5.25 1.38 (aromatic *gem*) −0.03 (Δ^p_{gem} CH_3) −0.13 (SR *trans*) 6.47 (Δ = −0.02) H_B: 5.25 −0.07 (aromatic *trans*) −0.06 (Δ^p_{trans} CH_3) 1.11 (SR *gem*) 6.23 (Δ = −0.10)
7-E	11	 7.14; 6.65	H_A: 5.25 1.38 (aromatic *gem*) −0.14 (Δ^p_{gem} NMe_2) 0.67 (RSO *cis*) 7.16 (Δ = −0.02) H_B: 5.25 0.36 (aromatic *cis*) −0.23 (Δ^p_{cis} NMe_2) 1.27 (RSO *gem*) 6.65 (Δ = 0)
7-Z	11	 6.20; 6.87	H_A: 5.25 1.38 (aromatic *gem*) −0.14 (Δ^p_{gem} NMe_2) 0.41 (RSO *trans*) 6.90 (Δ = −0.03) H_B: 5.25 −0.07 (aromatic *trans*) −0.27 (Δ^p_{trans} NMe_2) 1.27 (RSO *gem*) 6.18 (Δ = 0.02)
8-E	12	 7.09; 7.22	H_A: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.10 (Δ^p_{gem} CN) 7.09 (Δ = 0) H_B: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.14 (Δ^p_{cis} CN) 7.13 (Δ = 0.09)
8-Z	13	 6.57; 6.77	H_A: 5.25 1.38 (aromatic *gem*) −0.07 (aromatic *trans*) 0.10 (Δ^p_{gem} CN) 6.66 (Δ = −0.09) H_B: 5.25 1.38 (aromatic *gem*) −0.07 (aromatic *trans*) 0.20 (Δ^p_{trans} CN) 6.76 (Δ = 0.01)
9	12	 7.30	5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.12 (Δ^p_{gem} NO_2) 0.17 (Δ^p_{cis} NO_2) 7.28 (Δ = 0.02)
10	13	 6.42; 6.62	H_A: 5.25 1.38 (aromatic *gem*) −0.07 (aromatic *trans*) 0.05 (Δ^m_{gem} NO_2) −0.09 (Δ^m_{trans} NMe_2) 6.52 (Δ = −0.10) H_B: 5.25 1.38 (aromatic *gem*) −0.07 (aromatic *trans*) −0.06 (Δ^m_{gem} NMe_2) 0.18 (Δ^m_{trans} NO_2) 6.68 (Δ = −0.06)

Table 2. (*Contd*)

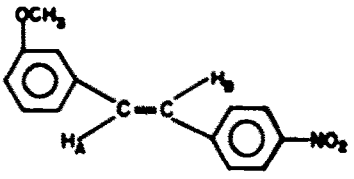
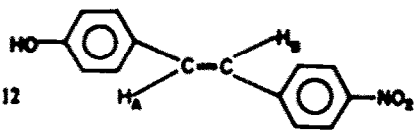
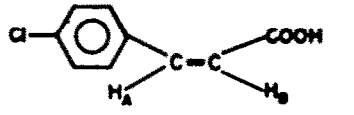
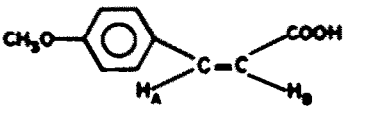
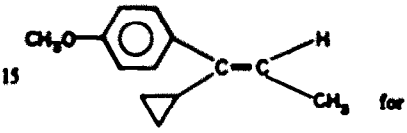
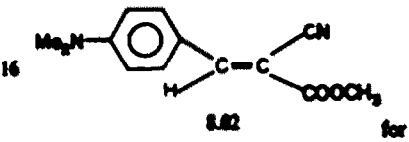
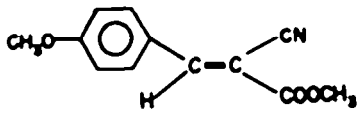
No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
11	12	 7.12; 7.23	H_A: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.17 (A_m' NO_2 *cis*) −0.02 (A_{gem}^p OCH_3) 7.14 (Δ = 0.09) H_B: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.12 (A' NO_2 *gem*) 7.11 (Δ = 0.01)
12	12	 6.97; 7.21	H_A: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.17 (A_m' *cis* NO_2) −0.06 (A_{gem}^p OH) 7.10 (Δ = 0.11) H_B: 5.25 1.38 (aromatic *gem*) 0.36 (aromatic *cis*) 0.12 (A_{gem}^p NO_2) −0.12 (A_{cis}^p OH) 6.99 (Δ = −0.02)
13	14	 6.03; 6.99	H_A: 5.25 1.38 (aromatic *gem*) 0.03 (A_{gem}^p Cl) 0.32 (COOH conjugated *trans*) 6.98 (Δ = 0.01) H_B: 5.25 −0.07 (aromatic *trans*) 0.06 (A_{trans}^p Cl) 0.80 (COOH conjugated *gem*) 6.04 (Δ = −0.01)
14	14	 5.84; 6.87	H_A: 5.25 1.38 (aromatic *gem*) −0.05 (A_{gem}^p OCH_3) 0.32 (COOH conjugated *trans*) 6.90 (Δ = −0.03) H_B: 5.25 −0.07 (aromatic *trans*) −0.09 (A_{trans}^p OCH_3) 0.80 (COOH conjugated *gem*) 5.89 (Δ = −0.05)
15	15	 5.60	for isomer E 5.25 −0.28 (alkyl ring *trans*) 0.45 (alkyl *gem*) 0.36 (aromatic *cis*) −0.09 (A_{cis}^p CH_3O) 5.69 (Δ = −0.09) for isomer Z 5.25 −0.25 (alkyl ring *cis*) 0.45 (alkyl *gem*) −0.07 (aromatic *trans*) −0.09 (A_{trans}^p CH_3O) 5.29 (Δ = 0.31)
16	16	 8.02	for isomer E 5.25 1.38 (aromatic *gem*) −0.14 (A_{gem}^p NMe_2) 0.55 (CN *trans*) 1.01 (COOR conjugated *cis*) 8.05 (Δ = −0.03) for isomer Z 5.25 1.38 (aromatic *gem*) −0.14 (A_{gem}^p NMe_2) 0.75 (CN *trans*) 0.46 (COOR conjugated *cis*) 7.70 (Δ = 0.32)

Table 2. (*Contd*)

No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
17	16		for isomer E 5.25 1.38 (aromatic *gem*) −0.85 (Δ^{p}_{gem} OCH_3) 0.55 (CN *trans*) 1.01 (COOR conjugated *cis*) 7.14 (Δ = 0.02) for isomer Z 5.25 1.38 (aromatic *gem*) −0.85 (Δ^{p}_{gem} OCH_3) 0.75 (CN *cis*) 0.46 (COOR conjugated *trans*) 7.79 (Δ = 0.37)

All chemical shifts are in ppm ex TMS.
A denotes experimental value—calculated value.

Table 3. Calculation of chemical shifts of olefinic protons in aromatic olefines based on the parent compound method

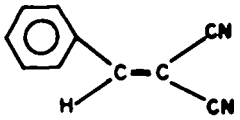
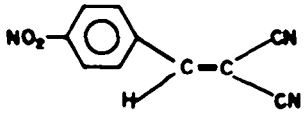
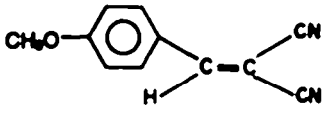
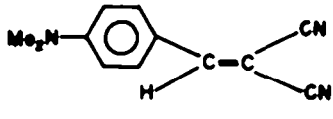
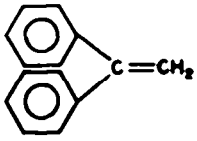
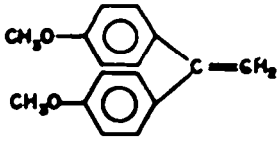
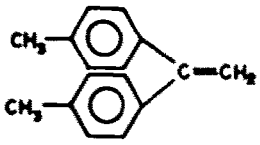
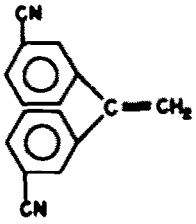
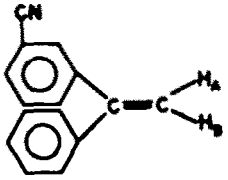
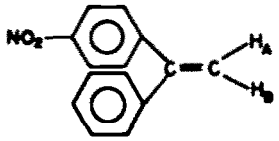
No.	Ref.	Structure and observed chemical shifts	Chemical chemical shifts
18	17	 7.67	5.25 1.38 (aromatic *gem*) 0.75 (CN *cis*) 0.55 (CN *trans*) 7.93 (Δ = −0.26)
19	17	 7.87	7.67 (δ unsubstituted) 0.12 (Δ^{p}_{gem} NO_2) 7.79 (Δ = 0.08)
20	17	 7.64	7.67 (δ unsubstituted) −0.05 (Δ^{p}_{gem} CH_3O) 7.62 (Δ = 0.02)
21	17	 7.42	7.67 (δ unsubstituted) −0.14 (Δ^{p}_{gem} NMe_2) 7.53 (Δ = −0.11)
22	18	 5.39	5.25 0.36 (aromatic *cis*) −0.07 (aromatic *trans*) 5.54 (Δ = −0.15)
	18	 5.19	5.39 (δ unsubstituted) −0.09 (Δ^{o}_{de} OCH_3) −0.09 (Δ^{o}_{gem} OCH_3) 5.21 (Δ = −0.02)

Table 3. (*Contd*)

No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
24	18	 5.29	5.39 (δ unsubstituted) −0.06 (Δ^{o}_{calc}, CH_3) −0.06 (Δ^{p}_{calc}, CH_3) 5.27 (Δ = 0.02)
25	18	 5.60	5.39 (unsubstituted) 0.10 (Δ^{o}_{calc}, CN) 0.14 (Δ^{p}_{calc}, CN) 5.63 (Δ = −0.03)
26	18	 5.46; 5.52	H_A: 5.39 (δ unsubstituted) 0.10 (Δ^{o}_{calc}, CN) 5.49 (Δ = −0.03) H_B: 5.39 (δ unsubstituted) 0.14 (Δ^{p}_{calc}, CN) 5.53 (Δ = −0.01)
27	18	 5.54; 5.58	H_A: 5.39 (δ unsubstituted) 0.17 (Δ^{o}_{calc}, NO_2) 5.56 (Δ = −0.02) H_B: 5.39 (δ unsubstituted) 0.23 (Δ^{p}_{calc}, NO_2) 5.62 (Δ = −0.04)

REFERENCES

[1]C. Pascual, J. Meier and W. Simon, *Helv. Chim. Acta* **49**, 164 (1966).
[2]U. E. Matter, C. Pascual, E. Pretsch, A. Proes, W. Simon and S. Sternhell, *Tetrahedron* **25**, 691 (1969).
[3]U. E. Matter, C. Pascual, E. Pretsch, A. Proes, W. Simon and S. Sternhell, *Ibid.* **25**, 2833 (1969).
[4]S. W. Tobey, *J. Org. Chem.* **34**, 128 (1969).
[5]M. Mikołajczyk, S. Grzejszczak and A. Zatorski, *Tetrahedron* **32**, 969 (1976).
[6]J. S. Martin and B. P. Dailey, *J. Chem. Phys.* **39**, 1722 (1963).
[7]M. T. Tribble and J. G. Traynham, *Advances in Linear Free Energy Relationships* (Edited by N. B. Chapman and J. Shorter). Plenum Press, London (1972).
[8]The values of σ were taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).
[9]J. E. Dubois, J. P. Doucet, *J. Chim. Phys.* **64**, 1145 (1967).
[10]M. Mikołajczyk, S. Grzejszczak, W. Midura and A. Zatorski, *Synthesis* 396 (1976).
[11]M. Mikołajczyk, S. Grzejszczak and A. Zatorski, *J. Org. Chem.* **40**, 1979 (1975).
[12]H. Gilsten and M. Salzwedel, *Tetrahedron* **23**, 173 (1967).
[13]H. Gilsten and M. Salzwedel, *Ibid.* **23**, 187 (1967).
[14]T. A. Wittstruck and E. N. Trachtenberg, *J. Am. Chem. Soc.* **84**, 3803 (1967).
[15]A. D. Ketley, A. J. Berlin and L. P. Fisher, *J. Org. Chem.* **31**, 2648 (1966).
[16]T. Hayashi, *Ibid.* **31**, 3253 (1966).
[17]M. A. Weinberger, R. M. Heggie and H. L. Holmes, *Can. J. Chem.* **43**, 2585 (1965).
[18]Y. Tsuno and Y. Yukawa, *Bull. Chem. Soc. Japan* **43**, 1459 (1970).