Journal of Organometallic Chemistry, 291 (1985) 335–340
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

^{13}C NMR STUDY OF POLARIZATIONS AND POLARIZATION RANGES OF VINYLENE GROUPS IN SEVEN SERIES OF RELATED COMPOUNDS

AGNES G. NAGY

Department of Chemistry, Central Research Institute for Physics, 1121 Budapest (Hungary)

(Received February 26th, 1985)

Summary

Polarizations, polarization ranges and ratios of polarization ranges for vinylene groups in seven series, namely chalcone derivatives, ferrocene analogues of chalcone, stilbene derivatives, ferrocene analogues of stilbene, and styrene derivatives, were studied. The polarization ranges spanning the intervals between ^{13}C NMR chemical shifts of the derivatives substituted by p-NO_2 and p-NMe_2 groups are compared in these related compounds. The influence of the side-chain groups in the vinylene moiety and of the sign of the polarization on the substituent-effect are discussed.

Introduction

A number of compounds containing a vinylene group were recently studied by the ^{13}C NMR technique [1–5]. In these compounds, namely chalcone derivatives, ferrocene analogues of chalcone, stilbene derivatives, ferrocene analogues of stilbene and styrene derivatives, the effect of the substituents has been studied (Fig. 1). Much information was collected and this gives a good opportunity to study and compare the polarization of the vinylene groups and the polarization ranges of the carbon atoms in the vinylene groups as well as the factors influencing these properties.

Discussion

Chemical shift values, listed in refs. 1–5, of substituted derivatives of the seven related series are used to study the properties of the vinylene groups. We plotted the δ values of the carbon atoms, C_α * and C_β, in the vinylene groups of these substituted compounds against the Hammett constants of the substituents [6]. The chemical shift values and the Hammett constants are found to correlate well. The $\delta(\sigma)$ line equations for C_α and C_β atoms are calculated and listed in Table 1 together

* In these series the carbon atom of the vinylene group which is near to the X substituents is marked by α (see Fig. 1).

0022-328X/85/$03.30

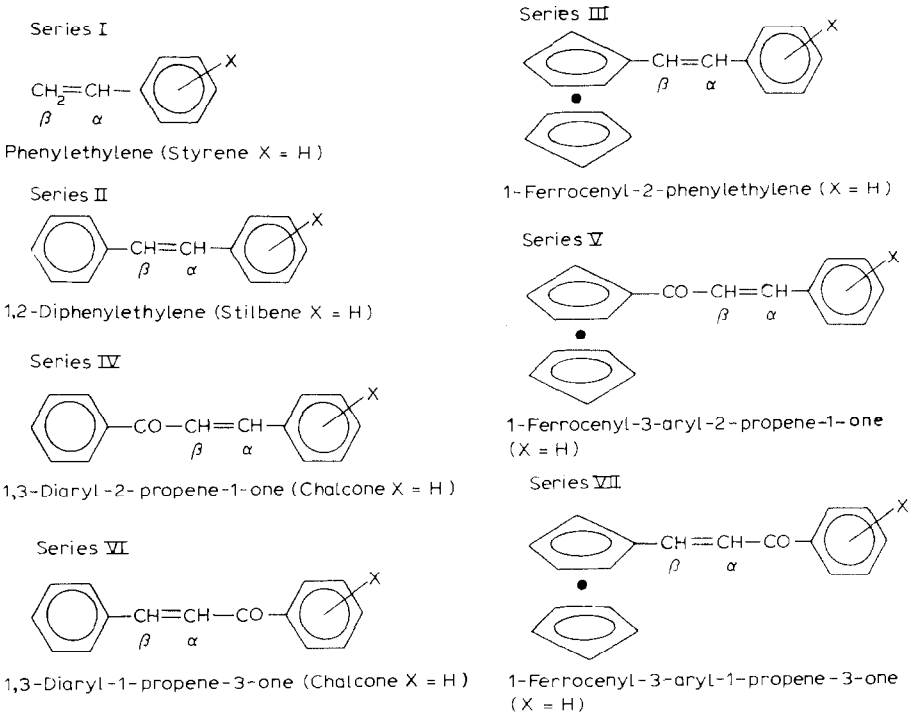


Fig. 1. Schematic representations of chalcone derivatives, ferrocene analogues of chalcone, stilbene derivatives, ferrocene analogues of stilbane and styrene derivatives.

with the correlation coefficients of the $\delta(\sigma)$ lines. The theoretical * chemical shift values of the C_α and C_β atoms (δ_{th}) for two compounds substituted by p-NO_2 and p-NMe_2 groups in each series are also calculated utilizing the equations mentioned

TABLE 1

EQUATIONS OF $\delta(\sigma)$ LINES AND CORRELATION COEFFICIENTS IN SERIES I–VII

Series	Equation of C_α [a] (ppm)	Correlation coefficient for (n) points	Equation of C_β (ppm)	Correlation coefficient for (n) points
I	$\delta = -1.00\sigma + 136.17$	0.84 (13)	$\delta = 5.64\sigma + 113.05$	0.99 (14)
II	$\delta = -1.39\sigma + 127.95$	0.89 (15)	$\delta = 5.45\sigma + 128.56$	0.99 (14)
III	$\delta = -2.34\sigma + 125.29$	0.96 (11)	$\delta = 7.36\sigma + 126.55$	0.99 (12)
IV	$\delta = -2.70\sigma + 143.87$	0.94 (14)	$\delta = 5.24\sigma + 121.33$	0.99 (14)
V	$\delta = -2.57\sigma + 140.08$	0.93 (13)	$\delta = 5.08\sigma + 122.41$	0.99 (13)
VI	$\delta = -1.02\sigma + 121.62$	0.91 (12)	$\delta = 2.87\sigma + 144.59$	0.99 (13)
VII	$\delta = -1.63\sigma + 118.98$	0.90 (13)	$\delta = 3.63\sigma + 146.64$	0.99 (13)

[a] The equations were calculated by the least squares method.

* The calculation of these theoretical δ values is necessary because the δ values of the derivatives substituted by p-NMe_2 or p-NO_2 are not available for the measured δ sets of some series, refs. 1 and 2.

TABLE 2

^{13}C NMR DATA OF VINYLENE GROUPS IN THE SEVEN SERIES (δ (ppm))

Series	Chemical shift $\delta_{th}(C_\alpha)$		*PR* $\Delta\delta(C_\alpha)$	Chemical shift $\delta_{th}(C_\beta)$		*PR* $\Delta\delta(C_\beta)$	*PR* Ratio	Polarization (*P*)			Chemical shift (δ_{th}) X = H		Ref.
								X = *p*-NMe_2	X = *p*-NO_2	X = H	C_α	C_β	
Phenylethylene (styrene)	*p*-NMe_2	137.00	1.61	*p*-NMe_2	108.37	9.07	5.63	28.63	17.95	23.76	136.17	113.05	5
(I)	*p*-NO_2	135.39		*p*-NO_2	117.44								
1,2-Diphenylethylene (stilbene)	*p*-NMe_2	129.11	2.24	*p*-NMe_2	124.04	8.76	3.91	5.07	5.93	0.61	127.95	128.56	3
(II)	*p*-NO_2	126.87		*p*-NO_2	132.80								
1-Ferrocenyl-2-phenylethylene	*p*-NMe_2	127.23	3.76	*p*-NMe_2	120.44	11.83	3.15	6.79	8.80	−0.83	125.29	126.55	4
(III)	*p*-NO_2	123.47		*p*-NO_2	132.27								
1,3-Diaryl-2-propene-1-one (chalcone)	*p*-NMe_2	146.11	4.34	*p*-NMe_2	116.98	8.43	1.94	29.13	16.36	22.57	143.87	121.33	1
(IV)	*p*-NO_2	141.77		*p*-NO_2	125.41								
1-Ferrocenyl-3-aryl-2-propene-1-one	*p*-NMe_2	142.21	4.13	*p*-NMe_2	118.19	8.17	1.98	24.02	11.72	17.9	140.08	122.41	2
(V)	*p*-NO_2	138.08		*p*-NO_2	126.36								
1,3-Diaryl-1-propene-3-one (chalcone)	*p*-NMe_2	122.47	1.65	*p*-NMe_2	142.11	4.61	2.79	19.64	25.90	−22.57	121.62	144.49	1
(VI)	*p*-NO_2	120.82		*p*-NO_2	146.72								
1-Ferrocenyl-3-aryl-1-propene-3-one	*p*-NMe_2	120.33	2.62	*p*-NMe_2	143.63	5.83	2.23	23.30	31.75	−27.08	118.98	146.64	2
(VII)	*p*-NO_2	117.71		*p*-NO_2	149.46								

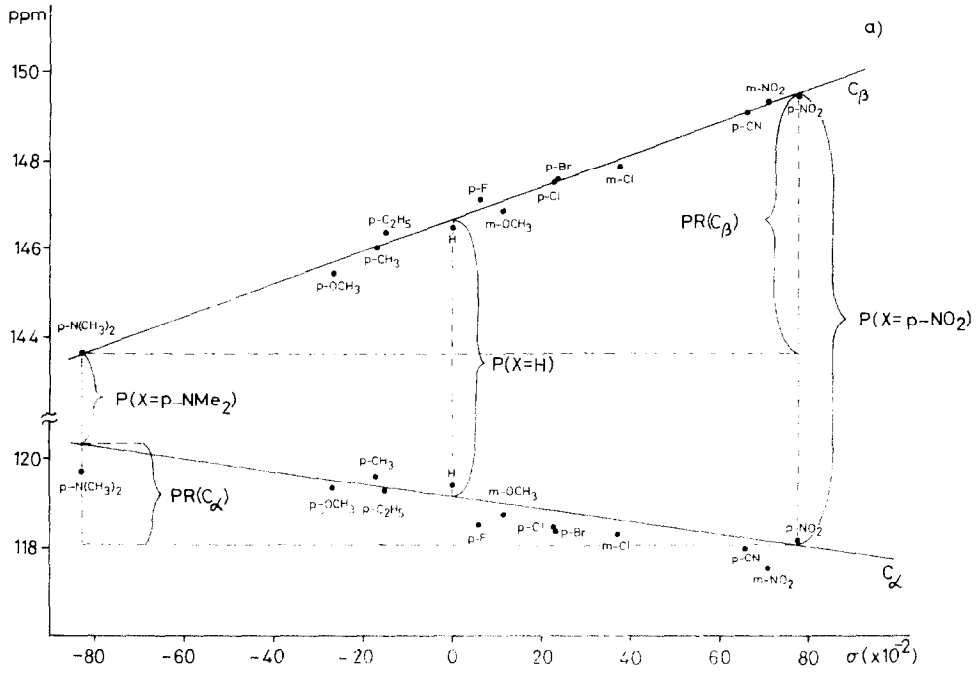


Fig. 2. The $\delta(\sigma)$ lines of C_α and C_β atoms in vinylene groups of Series V (b) and Series VII (a).

above. The intercept values of $\delta(\sigma)$ lines for the C_α and C_β atoms, i.e. the theoretical δ values of the carbon atoms in the vinylene groups of the basic compounds, X = H, are also shown in Table 2. The *p*-NO_2, and the *p*-NMe_2 groups are the strongest electron-withdrawing and electron-donating substituents; their σ values are 0.78 and -0.83 respectively [6]. The polarization values of the vinylene groups given by these theoretical δ_{th} values and the polarization ranges given by the difference between the δ_{th} values of the C_α and C_β atoms are compared in these series. The polarization values of the vinylene groups for the basic compounds and two substituted derivatives (X = *p*-NO_2 and X = *p*-NMe_2) of each series,

$$P = \delta_{th}(C_\alpha) - \delta_{th}(C_\beta)$$

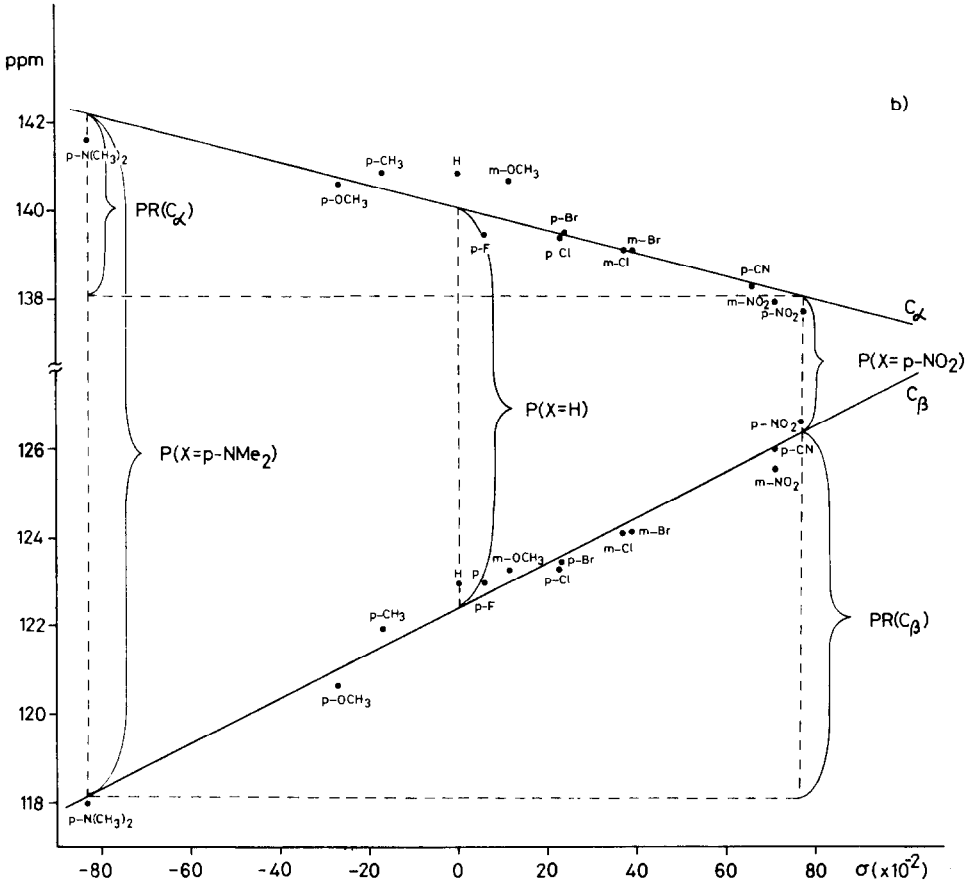
are listed in Table 2. The polarization ranges, *PR*, are given by:

$$PR(C_\alpha) = \delta_{th}[C_\alpha(p\text{-}NMe_2)] - \delta_{th}[C_\alpha(p\text{-}NO_2)] \text{ and}$$

$$PR(C_\beta) = \delta_{th}[C_\beta(p\text{-}NO_2)] - \delta_{th}[C_\beta(p\text{-}NMe_2)],$$

and also the ratios of the polarization ranges $[PR(C_\beta)/PR(C_\alpha)]$ are shown in Table 2.

The polarization ranges of C_α and C_β atoms clearly demonstrate that the effect of the substituents is manifested on the C_β atom of the vinylene group, that is, the polarization range of C_β atom is larger in every case than the polarization range of the C_α atom. It is obvious that the signs of the polarization ranges of the C_α and C_β atoms are opposite. In Figs. 2a and 2b the $\delta(\sigma)$ lines of C_α and C_β atoms in Series V and VII are shown as an example. The polarization values of the vinylene groups for



X = H, *p*-NO_2, *p*-NMe_2 and the polarization ranges of the C_α and C_β atoms are also marked in this Figure.

From the data of Table 2 and Fig. 2 it can be seen that the polarization ranges of the C_α and C_β atoms depend on (a) the distance between the X substituents and the vinylene group (b) the character of the groups between the X substituents and the vinylene group and (c) the side-chain group of the C_β atom, i.e., the groups which are directly bonded to the C_β atom *.

The importance of the distance between the vinylene group and the substituents, (a) above, is well demonstrated by the polarization ranges of the C_α and C_β atoms in the fifth and the seventh series. They are 4.13 and 2.62, and 8.17 and 5.83 ppm respectively (see Table 2). Because of the carbonyl group between the vinylene, and the phenyl groups, the vinylene group is further from the X substituents in the seventh series than it is in the fifth series. Therefore the potential ranges of C_α and C_β atoms are smaller in the seventh series (see columns 3 and 5 or Table 2). The potential ranges of C_α and C_β atoms in the second and the third series are 2.24 and

* A study of the slight stereo electronic effects in these compounds is in progress [7].

3.76, and 8.76 and 11.83 ppm respectively. The differences between the potential ranges show the different character of the phenyl and the ferrocenyl groups which are the side-chain groups of the C_β atoms in these series. The influence of the side-chain group of the C_β atom depends on the polarization sign in the vinylene group, details to follow.

The polarization of the vinylene groups and the intercept values of the $\delta(C_\alpha, C_\beta)/\sigma$ lines in the basic compounds are also listed in Table 2. It can be seen that the polarizations with a minus sign are increased by the electron-withdrawing substituents. The polarization is marked with a minus sign for those series in which the electron density is shifted to the C_α atom of the vinylene group in the basic compound. The minus polarizations, however, are decreased by the electron-donating substituents. For example, in series VII the polarization of the vinylene is increased to 31.75 ppm by the p-NO_2 substituent and decreased to 23.3 ppm by the p-NMe_2 substituent. In the basic compound of this series the polarization is -27.08 ppm. It follows that the polarization with the positive sign is increased by the electron-donating substituents, while the electron-withdrawing substituents decrease this kind of polarization for the vinylene groups, see the first, fourth and fifth series in Table 2.

It was already mentioned that the influence of the side-chain group of the C_β atom depends on the positive or negative polarization sign in the vinylene group of the basic compound. In the pairs II/III and VI/VII the ferrocenyl moiety, as the side-chain group, increases the polarization ranges of the C_α and C_β atoms related to the phenyl group. The ferrocenyl moiety, however, decreases the polarization ranges in pair IV/V by modifying the effect of the carbonyl on the vinylene group. Details of the interaction between the ferrocenyl and the carbonyl groups is presented in ref. 8.

It can be concluded that the substituent effect on the vinylene group depends significantly on the polarization of the vinylene group in the basic compound, on the sign of the polarization and the side-chain groups of the C_β atom.

Acknowledgements

The author is indebted to Professors S. Toma and J. Márton for valuable discussions and to Miss A. Szuja for her technical assistance.

References

1 E. Solcaniova, S. Toma and S. Gronowitz, Org. Magn. Reson., 8 (1976) 439.
2 A.G. Nagy and S. Toma, J. Organomet. Chem., 266 (1984) 257.
3 D. Cristoforou and D.A.R. Happer, Aust. J. Chem., 36 (1983) 2083.
4 A.G. Nagy and S. Toma, J. Organomet. Chem., 282 (1985) 267.
5 G.K. Hamer, I.R. Peat and W.F. Reynolds, Can. J. Chem., 51 (1973) 897.
6 D.H. McDaniel and H.C. Brown, J. Org. Chem., 23 (1958) 420.
7 A.G. Nagy and J. Márton, KFKI-1985-, in preparation.
8 A.G. Nagy, KFKI-1985-, 23.