^{13}C-NMR SPECTRA OF MONOSUBSTITUTED
AND SYMMETRICALLY 1,2-DISUBSTITUTED ETHENES

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^{13}C-NMR data on olefinic carbons in monosubstituted and symmetrically 1,2-disubstituted ethenes were compiled and linear correlations among the chemical shifts in these compounds were found. The chemical shifts or differential shieldings in 1,2-disubstituted ethenes can be estimated according to these correlations from the shifts in the corresponding monosubstituted ethenes. Deviations from the regression lines are indicative of steric crowding or of substituents with multiple bonds. Steric crowding is thought to be responsible for the paramagnetic shift of the olefinic carbons in *cis*-2,2,5,5-tetramethyl-3-hexene. It is inferred from the correlations that the same factors which control the shielding in monosubstituted ethenes control also the shielding in the disubstituted ethenes. The carbon chemical shifts in substituted ethenes are also found to correlate linearly with the shifts of substituent-bearing carbons in substituted benzenes and with the Q parameter of the substituent. It is concluded that a full account of these chemical shift must consider both energy and charge distribution terms.

Chemical shifts of olefinic carbons have been of steady concern since the early days of ^{13}C-NMR spectroscopy[1,2]. As a result several trends in these shifts have been empirically established (*e.g.* additivity rules for calculation of the shifts in alkenes[3,4] and unsaturated acids[5,6], correlations with charge densities[7] and shifts in benzene derivatives[7,8], linear correlation between the shifts of β and γ carbons in allyl compounds[9], and others[10,11]) but, with an exception of recent work on fluoroethylenes[12,13], theoretical understanding of these shifts and trends is in a rather chaotic state. This is most apparent in the case of differential shielding in *cis* and *trans* isomers of symmetrical 1,2-disubstituted ethenes.

The analytically important[6,10,11,14−16] differential shielding, $\overline{\Delta}$, is defined as the difference between the chemical shifts of the corresponding nuclei in *cis* (or *Z*), δ (*cis*), and in *trans* (or *E*), (*trans*), geometric isomers, *i.e.* $\overline{\Delta} = \delta \ (cis) - \delta \ (trans)$. Depending upon the substituent the experimental values of $\overline{\Delta}$ vary between −8 to +17 p.p.m. — in alkenes they are close to −1·1 p.p.m. (ref.[4]). Since a chemical shift difference of this magnitude cannot be interpreted in terms of long-range effects of magnetic anisotropy (as proton differential shieldings are[17]) other explanations have been sought.

Based on their measurements of four isomeric pairs of XCH=CHX type (X = Cl, Br, I, $COOC_2H_5$) Savitsky and Namikawa[18] suggested that the steric inhibition of resonance in the *cis* isomers leads to higher shielding in the case of mesomerically electron-releasing substituents (X = Cl, Br, I) and to lower shielding in the case of mesomerically electron-withdrawing substituent (X = $COOC_2H_5$) relatively to the shielding in the corresponding *trans* isomers. Although this argument was consistent with the signs of observed differential shieldings it was incompatible

with the values and the trend in the halogen series and so additional factors had to be taken into account (enhanced magnetic anisotropy of C—X bond due to its double bond character and a competition of steric and mesomeric effects)[18]. Later, however, the study of unsymmetrical 1,2-disubstituted ethenes, XCH=CRY (R = H, CH_3 or C_2H_5), led to the results that required essentially opposite interpretation, *i.e.* exaggeration rather than inhibition of resonance in the *cis* isomer[19]. It was therefore assumed[19] that repulsive forces between *cis* substituents bring about greater polarity and lower bond order in the central C=C bond and greater bond order in the C—X bond. The attempt[20] to interpret along this line the differential shielding in the series of XCH=CHX compounds, in which the symmetry of the molecules is not compatible with the charge polarization in the C=C bond, failed probably because the theory has assumed constant average electronic excitation energy[20], ΔE_{av}, and did not considered *d* orbitals[20]. Actually, it was variation in the former factor that was suggested already in 1967 by Lippmaa and co-workers[21] as a probable explanation of the differential shieldings in isomeric octenes[21] and in unsaturated acids some years later[6].

Such an explanation cannot satisfy the chemist since it does not specify which structural factors or effects contribute to the variation in ΔE_{av}. It only replaces the uninterpreted variation in the chemical shifts by an uninterpreted variation in an ill-defined quantity of average excitation energy.

After reviewing the literature it became clear that the previous studies suffered from the following inadequacies: *1*) series of studied compounds were too limited, *2*) some of the compounds had composite substituent groups with multiple bonds (*e.g.* X = CN, COOR) and therefore the corresponding data (being affected by conformational and conjugational effects) were rather special than typical for this type of compounds, *3*) the explanation of the differential shielding was sought only in special effects present in *cis* isomers without paying attention to the factors determining the shifts in *trans* isomer and especially in monosubstituted ethenes and at their time, *4*) very little was known about energy levels in ethene derivatives.

We have therefore attempted to compile more data than it was previously possible and tried to determine whether the factors that are usually thought as responsible for the shifts in monosubstituted ethenes also control the differential shielding.

Data Compilation

For the sake of consistency in compiling the data for Table I and II preference was given to the source which gave more data to be included even if some other source gave more precise individual pieces of data. For this reason we have retained in Table I the values given by Savitsky and Nami-kawa[18] for dichloroethenes despite that Miyajima and Takahashi[25] published a reverse assignment for these two compounds. If this reverse assignment is correct, then the points for chlorine derivatives fall somewhat off the correlation lines discussed further, but the deviations do not invalidate the following discussion. On the other hand, other data that were published for tert--butyl derivatives[37] would bring the corresponding points on the correlation lines and eliminate the deviations noticed here but these data were shown convincingly to be in error[27].

The data shown in Table I were obtained using different techniques with different precisison, they were all converted into δ scale using the factors indicated. It seems reasonable to expect that the values of differential shieldings ($\overline{\Delta}$) and internal shifts (Δ) are less affected by all the involved errors and are therefore more suitable for the comparisons. When two values were found an average value was used in the correlations (X = CH_3 and C_2H_5).

There are many more data available for mono- and disubstituted ethenes. The limiting factor for the size of Table I was the availability of the data for both isomers of 1,2-disubstituted ethene.

Included are also data on monosubstituted ethenes for which the value of the Q parameter was available.

TABLE I

^{13}C-NMR Chemical Shifts of Olefinic Carbons^a

No^c	Substituent X^d	X—C$_\alpha$H = C$_\beta$H$_2$			X—HC = CH—X			Q^b
		$\delta(\alpha)$	$\delta(\beta)$	Δ^e	$\delta(cis)^f$	$\delta(trans)^f$	$\overline{\Delta}^g$	
1	H	122·8^h	122·8^h	0·00	122·8^h	122·8^h	0·00	2·28^i
2	F	152·1^j	92·0^j	59·24	140·3^j	148·6^j	−8·30	1·04^i
3	Cl	126·1^k	117·2^k	8·9	121·3^l	119·4^l	1·9^m	2·55^i
4	Br	114·3^k	122·4^k	− 8·1	116·4^l	109·4^l	·7·0	3·16^i
5	I	85·4^n	130·5^n	−45·1	96·5^{l,o}	79·4^{l,o}	17·0	3·98^i
6	CN	108·2^k	138·0^k	−29·8	120·8°	120·2°	0·6	3·43^p
7	CH$_3$	136·2^q	115·9^q	20·3	123·3°	124·5°	−1·20	1·77^p
					124·22^r	125·42^r		
8	C$_2$H$_5$	140·7^q	113·3^q	27·4	131·02^r	131·18^r	−0·16	—
		140·2^s	113·5^s	26·7				
9	t-C$_4$H$_9$	149·7^s	109·8^s	39·9	139·35^t	135·78^t	3·57	2·50^p
10	n-C$_3$H$_7$	138·5^u	114·4^u	24·1	130·06^r	130·64^r	−0·58	—
11	n-C$_4$H$_9$	138·7^u	114·4^u	24·3	130·18^r	130·77^r	−0·59	—
12	COOCH$_3$	129·0^k	130·2^k	− 1·2	128·7°	132·4°	−3·7	—
13	COOC$_2$H$_5$	129·7^k	130·1^k	− 0·4	130·5°	134·1°	−3·8^v	—
14	COCH$_3$	137·7^k	129·5^k	8·2				5·20^{p,x}
15	CHO	138·6^k	137·6^k	1·0				4·90^{p,x}
16	NO$_2$	145·6^k	122·4^k	23·2				6·33; 4·00^{p,y}
17	OCH$_3$	153·8^k	84·6^k	69·2				0·54^p

^{a} Chemical shifts in δ scale (*i.e.* p.p.m. relative to Si(CH$_3$)$_4$, paramagnetic shifts positive). ^{b} The Q parameter, 10^{-21} Js^{-1}. ^{c} The number by which the substituent is identified in the graphs. ^{d} The structure of the substituent. ^{e} The internal shift $\Delta = \delta(\alpha) - \delta(\beta)$. ^{f} The label refers to the isomer. ^{g} The differential shielding $\overline{\Delta} = \delta(cis) - \delta(trans)$. ^{h} Value from ref.[10]. ^{i} Value from ref.[22]. ^{j} Original data[12] converted using $\delta(CH_4) = -1\cdot8$ (ref.[23]). ^{k} Original data[7] converted using $\delta(CS_2) = 193\cdot7$ (ref.[24]). ^{l} Original data[18] converted using $\delta(C_6H_6) = 128\cdot7$ (ref.[24]). ^{m} Value of $-1\cdot8$ follows from data of ref.[25]. ^{n} Original data[8] converted using $\delta(C_6H_6) = 128\cdot7$ (ref.[24]). ^{o} Original data[20] converted using $\delta(CS_2) = 193\cdot7$ (ref.[24]). ^{p} Value from ref.[26]. ^{q} Original data[19] converted using $\delta(CS_2) = 193\cdot7$ (ref.[24]). ^{r} Value from ref.[15]. ^{s} Original data[9] converted using $\delta(C_6H_6) = 128\cdot7$. ^{t} Value from ref.[27]. ^{u} Original data[2] converted using $\delta(CS_2) = 193\cdot7$ (ref.[24]). ^{v} Value given in the source[20], but the chemical shifts given there yield $\overline{\Delta} = -3\cdot6$. ^{x} Reasonably a different Q value would be required as Q (2) for this substituent. ^{y} The two values are Q (1) and Q (2) values[26].

TABLE II
One-Bond ^{13}C—^{1}H Coupling Constants of Olefinic Carbons[a]

No	Substituent X	X—C_αH = C_βHa			X—HC = CH—X	
		$J(C_\alpha—H_{gem})$	$J(C_\beta—H_{trans})^b$	$J(C_\beta—H_{cis})^b$	$J(cis)^c$	$J(trans)^c$
1	H[d]	156·4	156·4	156·4	156·4	156·4
2	F	200·2[e]	162·2[e]	159·2[c]	—	—
3	Cl	194·9[e]	160·9[e]	162·6[e]	198·5[f]	199·1[f]
4	Br	196·6[e]	160·3[e]	163·6[e]	200[g]	204[g]
5	I	190·9[e]	159·2[c]	164·1[e]	187·9[h]	194·2[h]
6	CN	176·7[i]	165·4[i]	163·2[i]	—	—
7	CH_3	—	—	—	153·4[j]	148·7[j]
9	$t-C_4H_9$	150·1[k]	—	—	150·4[j]	149·4[j]
12	$COOCH_3$	168[l]	—	—	—	—
13	$COOC_2H_5$	—	—	—	167·6[m]	168·6[m]

[a] All values in Hz. [b] Positions are labeled relative to the substituent. [c] Index denotes the isomer. [d] Values from ref.[28]. [e] Value from ref.[29]. [f] Value from ref.[30]. [g] Value from ref.[31]. [h] Value from ref.[32]. [i] Value from ref.[33]. [j] Value from ref.[34]. [k] Value from ref.[35]. [l] Value from ref.[7]. [m] Value from ref.[36].

RESULTS

The compiled literature data on monosubstituted and 1,2-disubstituted ethenes are listed in Tables I – II. In treating these data we have started with the following working hypothesis: *1*) the factors that are the cause of the shifts of the α and β carbons and of their difference (the internal shift, Δ) in vinylic compounds should also operate in 1,2-disubstituted ethenes (probably to a different extent in *cis* and *trans* isomers). *2*) The same factors are dominant in disubstituted ethenes except in the cases of extremely bulky substituents (tert-butyl derivatives) or those with multiple bonds (nitriles or carbonyl derivatives).

If this hypothesis is true then one should observe some relationship between the carbon shifts in disubstituted and monosubstituted ethenes. Since the values of differential shielding, $\bar{\Delta}$, between *cis* and *trans* isomers and the values of internal shift, Δ, in vinylic compounds are less affected by all the errors involved we tested these two quantities first. It is apparent from Fig. 1 that a simple linear correlation exists between these quantities if the data for the substituents mentioned in the second hypothesis are excluded from consideration. (Some statistical characteristics of this and of other correlations to be discussed latter are given in Table III. In this case the correlation is significant even at 99% confidence level.) In addition to proving our hypothesis, this correlation has an important analytical application — it allowes us to esti-

mate the differential shielding (or at least its sign) from the internal shift in the corres-
ponding vinyl derivative and *vice versa*. According to this correlation the substituents
which cause the extreme values of internal shift also cause extreme differential

TABLE III
Parameters of Linear Correlations $Y = A + B . X$

X^a	Y^a	A^b	B^c	r^d	N^e	Omitted^f	Fig.^{g}
Δ	$\overline{\Delta}$	4·6	− 0·23	0·960	9	6, 9, 12, 13	1
$\delta(\alpha)$	$\delta(cis)$	50·3	0·58	0·949	13	—	3
$\delta(\alpha)$	$\delta(trans)$	21·3	0·81	0·911	13	—	4
$\delta(\beta)$	$\delta(cis)$	396·5	− 2·34	0·972	5	g	—
		234·2	− 0·98	0·897	5	h	—
$\delta(cis)$	$\delta(trans)$	− 58·0	1·45	0·979	13	—	6
$\delta(cis)$	$\delta(C_X)$	− 11·4	1·01	0·986	9	—	7
Q	$\delta(\alpha)$	168·9	− 18·79	0·975	8	9, 14, 15, 16	8
Q	$\delta(\beta)$	85·4	12·16	0·911	10	14, 16	8
Q	$\delta(cis)$	152·6	− 13·14	0·959	6	6, 9	9
Q	$\delta(trans)$	169·9	− 21·32	0·971	6	6, 9	9
Q	Δ	89·3	− 32·45	0·934	9	14, 15, 16	—
Q	$\overline{\Delta}$	− 17·3	8·18	0·982	7	6	—

^{a} Type of NMR variable. ^{b} Intercept of the least-squares line. ^{c} Slope of the least-squares line.
^{d} Correlation coefficient. ^{e} Number of data points induced. ^{f} Numbers of substituents that were
not included into the least-squares fit though the appropriate data were available in Table I
and II. ^{g} Figure on which the dependence is depicted. ^{g} All but alkyls. ^{h} All but halogens and
hydrogen.

FIG. 1

Correlation of the Differential Shielding, $\overline{\Delta}$,
with the Internal Shift, Δ

The errors are smaller than indicated
by the size of the points. The solid line is
a least-squares fit of full circles, open circles
not included. For the parameters of the fit
see Table III.
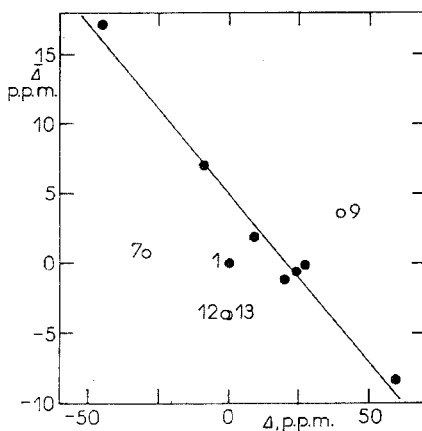
shielding. Approximately, the substituents which cause positive internal shift cause a negative differential shielding and *vice versa*. It should be noted that the deviations from the regression line are in the oposite directions for the substituents the first atom of which is multiple bonded and for bulky substituents without multiple bonds.

Assumptions analogous to our hypothesis are being implicitly made in direct additivity rules for chemical shift that are frequently used in ^{13}C-NMR spectroscopy. Direct additivity was successfully applied also to olefins[3,4] and their derivatives[5,6]. Though in the simple case of 1,2-disubstituted ethanes direct additivity cannot reflect the geometrical isomerism, it can be used in assigning carbon resonances in un-symmetrically substituted ethenes[19]. In the scale used here, the direct additivity means that the chemical shift $\delta(XHC{=}CHX)$ in a 1,2-disubstituted ethene can be expressed as

$$\delta(XHC{=}CHX) = Z(\alpha) + Z(\beta) + \delta(H_2C{=}CH_2) ,$$

where $Z(\alpha)$ and $Z(\beta)$ are the shielding contributions of the substituent X to the shield-ing of α and β carbons, resp. They are evaluated as the shifts of these carbons in vinyl derivatives relatively to the chemical shift of ethene, $\delta(H_2C{=}CH_2)$.

Yonemoto[9] has shown that the olefinic carbon chemical shifts (and hence the shielding contributions) are linearly correlated in allyl compounds in which the substi-tuent X is separated from the vinylic system by one carbon atom. As is apparent from Fig. 2 correlation of such a type is very poor for vinyl compounds though some points are clustered along the Yonemoto's regression line. In general, the two con-tributions $Z(\alpha)$ and $Z(\beta)$ are not linearly correlated in vinyl compounds. With the exception of fluoro compounds the shifts calculated according to this additivity rule fall within a few p.p.m. from the shift of one or the other isomer (Table IV) with no
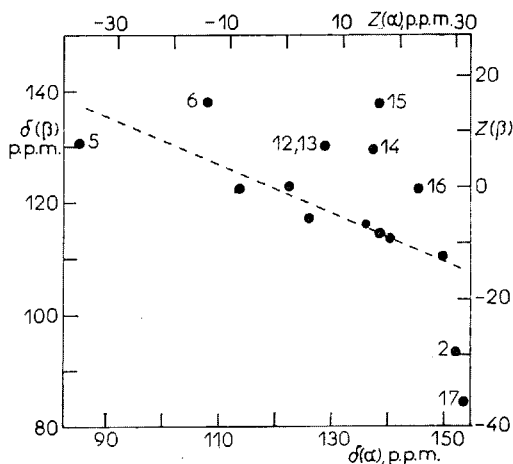

FIG. 2
Plot of $\delta(\beta)$ *versus* $\delta(\alpha)$
     Only data of Table I are included though other data are available. The dashed line is Yonemoto's regression line for allyl com-pounds.

apparent regularity. According to the additivity rule, which assumes constant shielding contributions, one should not expect good correlation between the experimental shifts in *cis* or *trans* isomers of 1,2-disubstituted ethenes on one side and one of the contribution $Z(\alpha)$ or $Z(\beta)$ on the other, especially as the two contributions are of comparable magnitude and their values are not correlated. Inspection of Figs 3 and 4 and Table III reveals, however, significant linear correlations between $Z(\alpha)$ (or $\delta(\alpha)$) and both $\delta(cis)$ and $\delta(trans)$. In both cases all data points can be included, points corresponding to composite substituents with multiple bonds deviate all in the same direction (which is opposite to the direction of tert-butyl derivative deviation on Fig. 4). No such simple relationship was found for $\delta(\beta)$, only $\delta(trans)$ shows a non-linear correlation with $\delta(\beta)$ (Fig. 5) according to which shielding in the *trans* isomer increases as the shielding of $C(\beta)$ in the corresponding vinyl compound decreases.

Good linear correlations of Figs 3 and 4 support our hypothesis that the shieldings in the two types of compounds are governed by the same factors. Any further rationalization of these correlations and absence of such for $C(\beta)$ shielding encouters with a difficulty. The correlations seem to indicate a dominating influence of the α substituent on the shielding in 1,2-disubstituted ethenes but the shielding contributions to α and β carbons are of similar magnitude and it has been shown[19] that the additive rule holds well for 1,2-disubstituted ethenes. Comparison with one-bond

TABLE IV

[13]C Shielding Contributions $Z(\alpha)$ and $Z(\beta)$ of Substituents in Vinylic Compounds and Calculated Shifts in 1,2-Disubstituted Ethanes[a]

Substituent	$Z(\alpha)^{b}$	$Z(\beta)^{b}$	$\delta(XHC:CHX)^{c}$
F	29·3	− 29·9	122·2
Cl	3·3	− 5·6	120·5
Br	− 8·5	− 0·4	113·9
I	−37·4	7·7	93·1
CN	−14·6	15·2	123·4
CH_3	13·4	− 6·9	129·3
C_2H_5	17·7	− 9·4	131·1
$t\text{-}C_4H_9$	26·9	−13·0	136·7
$n\text{-}C_3H_7$	15·7	− 8·4	130·1
$n\text{-}C_4H_9$	15·9	−8·4	130·3
$COOCH_3$	6·2	7·4	136·4
$COOC_2H_5$	6·9	7·3	137·0

[a] All values are in p.p.m. [b] Values calculated from the shifts in vinyl derivatives, positive value indicates deshielding relative to ethene. [c] The values calculated according to Eq. $\delta(XHC:CHX) = Z(\alpha) + Z(\beta) + \delta(H_2C:CH_2)$.

coupling constants ^{13}C—^{1}H (Table II) which have in 1,2-disubstituted ethenes values similar to those of α carbon couplings in vinyl compounds might be misleading. The coupling constants are affected by a substitution on a β carbon much less than by a substituent on the α carbon[38].

Correlations on Figs 3 and 4 suggest that there might be a linear correlation between $\delta(cis)$ and $\delta(trans)$. Indeed, Fig. 6 shows how well all the 13 pertinent data points fit the regression line, in most cases the deviation is considerably smaller than the differential shielding. The only appreciable deviation is seen in the case of $X =$ = tert-butyl. This correlation, which might be also analytically usefull, has no direct relation to our hypothesis but it brings out another point. Linear dependence on Fig. 6 means that the two shifts $(\delta(trans)$ and $\delta(cis))$ are controlled by a common factor and if there are any special interactions present in the *cis* compounds then their effect upon the shielding is either negligible or proportional to the factor controlling the shift in the *trans* compounds. This statement is true both for the compounds in which steric inhibition (or exaggeration) of resonance are assumed and for compounds in which interactions of non-bonding electrons are possible. Only in the compound in which a sterical crowding without the mentioned electronic effects is recognized[27] a sizable deviation is observed. According to the chemical shift $\delta(trans)$ the shift in *cis*-2,2,5,5-tetramethyl-3-hexene should be $\delta(cis) = 133$, while the observed chemical shift is by 6 p.p.m. more paramagnetic. We suggest that this paramagnetic shift (or at least some part of it) is due to the sterical crowding in the
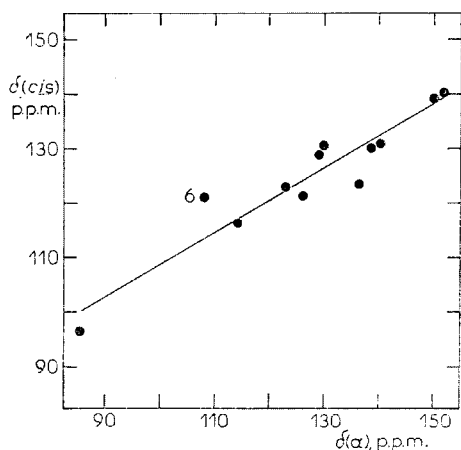

FIG. 3

Linear Correlation between $\delta(cis)$ and $\delta(\alpha)$
    The solid line is a least-squares fit with the
parameters given in Table III.
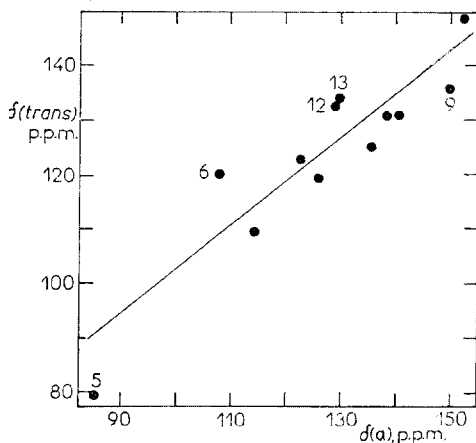
FIG. 4

Linear Correlation between $\delta(trans)$ and $\delta(\alpha)$
    The solid line is a least-squares fit with the
parameters given in Table III.

cis compound. Sterical shifts to lower field have been recently reported for other types of compounds containing tert-butyl groups[15,39-42]. Very often a comparison with one-bond ^{13}C—^1H coupling constants proved fruitful thanks to their relation to hybridization. Perhaps due to very limited data available (Table II) we have been unable to find any definite relationship between the shifts and coupling constants in 1,2-disubstituted ethenes though some similarity is readily apparent.

DISCUSSION

The above results show that there are interesting and analytically useful linear correlations between ^{13}C-NMR chemical shifts in symmetrical 1,2-disubstituted and monosubstituted ethenes. These correlations prove that the shifts in the two types of ethene derivatives are controlled by the same factors and that the observed differential shielding is dominated by these factors except in cases of substituents with multiple bonds and extremely bulky substituents. Deviations from the correlation lines are observed for the two types of anomalous substituents, sometimes the deviations are of opposite signs for the two types (Figs 1, 4) and in other cases only anomalous substituents of one type deviate (Figs 2, 3, 6).
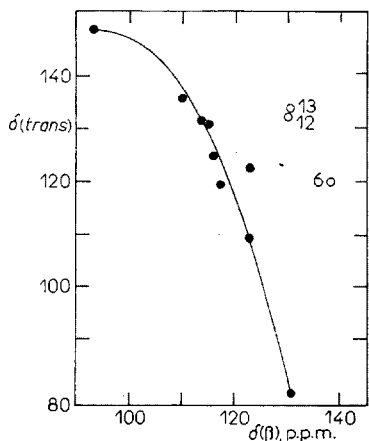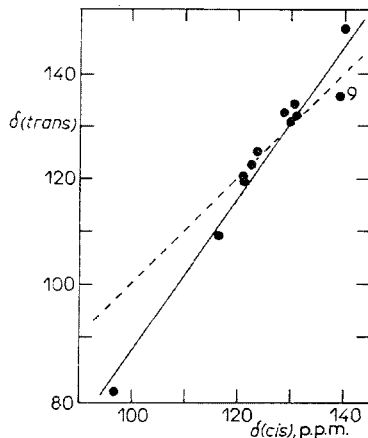

FIG. 5

Plot of $\delta(trans)$ *versus* $\delta(\beta)$

The solid curve is a least-squares fit of the full circles. The curve is given by the equation $\delta(trans) = -352\cdot03 + 10\cdot41\delta(\beta) - 0\cdot5417(\delta(\beta))^2$.


FIG. 6

Linear Correlation between $\delta(trans)$ and $\delta(cis)$

The solid line is a least-squares fit with the parameters given in Table III. The dashed line is $\delta(trans) = \delta(cis)$ line. The deviation from the regression line of the points in the area between the two lines are smaller than their differential shielding.

We shall turn our attention now to assessing which of the factors suggested in literature as the causes of the shifts in olefinic compounds are compatible with the observed correlations.

Recently, electric field has been shown to be the source of nonequivalence of ^{13}C chemical shifts of unsaturated acids[43]. The electric field cannot be the source of either internal shift or differential shielding in substituted ethenes in which the functional group is directly attached to the olefinic carbon atom. This can be illustrated best on haloethenes where conformation does not complicate the considerations. The group dipole moments of halogens are all of the same sign and of a very similar magnitude[44] (and with the exception of the C–X bond the corresponding bond lengths do not differ by more than 1% in vinyl halides[38] and still the internal shifts and the differential shieldings of both signs are found amont the haloethenes.

Similarity of spatial relationships in ethenes and benzene derivatives

I   *II*
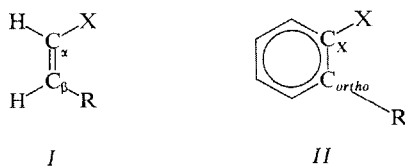
is well recognized and correlations between the corresponding quantities in the two types of compounds have been reported for cases with R = H (*e.g.* carbon shieldings[7,8], electron densities on carbons[7], and proton shieldings[45]). One therefore expects to find a correlation between the carbon chemical shifts if R = X, such linear correlation is shown on Fig. 7 (based on the data of Table I and on compilation of Breitmaier and Voelter[46] supplemented by the data on alkylbenzenes[39]). The fact that the slope of the regression line is close to one should not be taken as indicating "through space" shielding mechanism along the line of thoughts considered in literature[45]. Since the shielding contributions of adjacent substituents are about twice as big as those of β substituents the slope will be close to one independently whether the shielding mechanism is "through space" or "through bonds".

Another consequence of similarity of *I* and *II* is that some NMR parameters in both types of compounds correlate with the Q parameter[22] (^{1}H and ^{19}F chemical shifts of R in *I* and *II* with R = H or F (ref.[22]), C_{ortho} and C_X chemical shifts in *II* with R = H or F (refs[22,26,47])) but no correlation of this type has been reported for the ^{13}C chemical shifts of compounds *I*. It is apparent from Figs 8 and 9 that such correlations hold for the compounds of type *I* both with R = H and with R = X (in addition to the substituents of the two anomalous types, the points for which $Q(1)$ and $Q(2)$ values[26] differ were excluded from the consideration).

The interesting feature of the correlations on Figs 8 and 9 are the slopes of the regression lines. In monosubstituted ethenes (Fig. 8) the slopes of dependences of $\delta(\alpha)$ and $\delta(\beta)$ have similar absolute magnitude, as if they were equally sensitive to the Q parameter, but they are of different signs. The signs agree, however, with the signs reported for analogous dependences of C_X and C_{ortho} carbon shieldings in benzene derivatives[47] *II*. In the two isomers of 1,2-disubstituted ethenes the slopes (Fig. 9) have the same

FIG. 7

Linear Correlation between $\delta(cis)$ of 1,2-Disubstituted Ethene and $\delta(C_X)$ of *ortho* Disubstituted Benzene

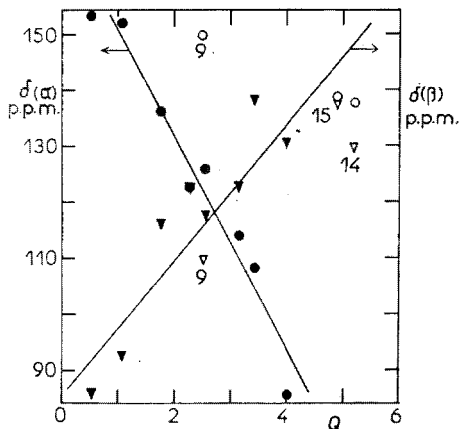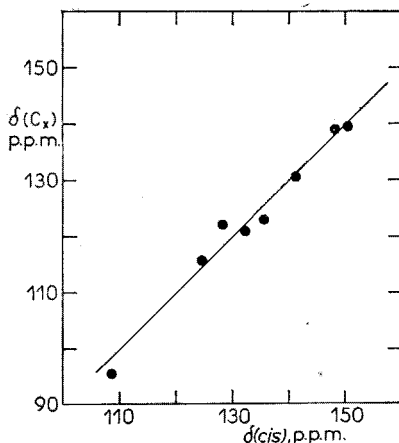The solid line is a least-squares fit with the parameters given in Table III.

FIG. 8

Linear Correlations of $\delta(\alpha)$ (●) and $\delta(\beta)$ (▼) in Monosubstituted Ethenes with the Q Parameter

The solid lines are least-squares fits of the corresponding full points, for the parameters of the fit see Table III.
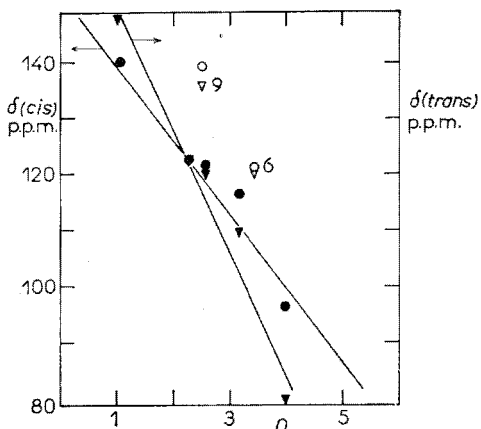

FIG. 9

Linear Correlations of $\delta(cis)$ (●) and $\delta(trans)$ (▼) in 1,2-Disubstituted Ethenes with the Q Parameter

The solid lines are least-squares fits of the corresponding full points, for the parameters of the fit see Table III.

sign as the slope of $\delta(\alpha)$ dependence on Fig. 8. As the dependence of the *trans* isomer is steeper and that of the *cis* isomers is less steeper than that of $\delta(\alpha)$ one can conclude that the β substituent acts in the same direction as the α substituent in the former and in the opposite direction in the latter case. This behaviour seems to support the mentioned idea of dominating influence of the α substituent. As a consequence of good correlations on Figs 8 and 9 similarly good correlations with the Q parameter hold for both internal shift and differential shielding (Table III).

According to the original definition[22] the Q parameter of a substituent X is defined as $Q = P/Ir^3$, where P and r are the polarizability and the length, resp., of the C–X bond and I is the first ionization potential of X. Relationships between the shifts and the Q parameter was rationalized as follows[22]. The paramagnetic term in Ramsey's equation is inversely proportional to an average excitation energy ΔE_{av}. Since ΔE_{av} is not known, one has to use the first ionization potential of the substituent. The quantity P/r^3 is then a factor which corrects for the use of I. With such a rationalization our findings suport the suggestion of Lippmaa and coworkers[21] that ΔE_{av} is the controlling factor in differential shieldings, but the ionization potential is a well defined quantity. We have, however, collected available UV and PE spectral data[48–59] and found no simple relationship between either ionization potentials or transition energies on one side and carbon chemical shifts or coupling constants in substituted ethenes on the other side (though there is apparently a relationship between *I. P.* of the substituent X and *I. P.* of monosubstituted ethenes).

On the basis of correlations of carbon chemical shifts with calculated charges Miyajima and coworkers[7] concluded that the α carbon shieldings depend on the σ electron density which is dominated by inductive effect of the adjacent substituent and that the shielding of β carbon is related to π electron density. In the correlations the points corresponding to halogen and nitril substituted ethenes fell off the line which was attributed[7] to the fact that d-electrons were not considered in the calculations of electron densities. Since at present charge distributions calculated for *cis-trans* pairs of 1,2-disubstituted ethenes with inclusion of d-electrons are not available it is not possible to check whether the charges are the controlling factors or not. But as so many carbon chemical shifts have been found linearly related to the charges[60] it would certainly be worth trying to calculate the charge distribution and try to correlate the charges with the discussed chemical shifts.

The above considerations have shown that both energy and charge distribution have to be taken into account if a full explanation of the chemical shifts in substituted ethenes is attempted. Recent *ab initio* calculations of Ditchfield and Ellis[12] have been very successful in calculating the carbon chemical shifts in mono- and difluoroethenes. It is apparently only a question of time when such calculations could be performed on molecules considered here and when contributions of various factors (diamagnetic, interatomic, multiple-bond *etc.*[61]) could be precisely evaluated.

CONCLUSION

Linear correlations have been found among carbon chemical shifts in mono- and 1,2-disubstituted ethenes and between these and the Q parameter. In analytical applications, chemical shifts can be estimated from these correlations. Deviations from the regression lines may serve as indicating either bulk substituents or those with multiple bonds (in conjugation with the olefinic bond). It has been shown that the chemical shifts in symmetrical 1,2-disubstituted ethenes are controlled by the same factors as the shifts in monosubstituted ethenes and that a full account of these shifts must include both energy and charge distribution terms.

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Translated by the author.

Notes added in proof: 1) The very recent data on methoxy-substituted ethenes (Herberhold M., Wiedersatz G. O., Kreiter C. G.: Naturforsch. *31*b, 35 (1976)) fit the correlations described here, but in some instances the deviations are similar to those of tert-butyl derivatives. *2*) Using data of ref.[7] for styrene the chemical shift of $\delta = 130.9$ is calculated for *cis*-stilbene on the basis of the correlation on Fig. 3. This value is in agreement with the reported value $\delta = 130.8$ (Brown D. A., Fitzpatrick N. J., King I. J., Mathews N. J.: J. Organometal. Chem. *104*, C-9 (1976)).