INTERACTIONS IN ACETYLENES

AN NMR APPROACH

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Abstract—Proton magnetic resonance data and ^{13}C chemical shifts of numerous acetylenes are presented and analyzed. For 1-alkynylphosphines and -phosphinoxides also ^{31}P shifts are given.

It is concluded, that electronic charge shift *from* triple bond to substituent occurs in phenylethyne, ethylthioethyne, triethynylphosphine, triethynylphosphinoxide and ethynyltriethylgermanium. In 1-alkynyl ethers and amines a charge shift *to* the triple bond is present.

A relatively high shielding of C, F, and P, attached to the triple bond, is observed. This effect is ascribed to a reinforcement of diamagnetic anisotropy caused by π-overlap between triple bond and substituent. To explain this reinforcement the hypothesis of coupling of ring currents is introduced.

INTRODUCTION

THIS paper presents a critical evaluation of previously published[1] and recently acquired NMR data on acetylenes. The purpose was to obtain insight into the charge changes that occur in the triple bond on substitution. Measurements were performed on hydrogen, carbon and phosphorus atoms.

RESULTS

Proton chemical shifts of a variety of monosubstituted acetylenes, HC≡C—X, and of their saturated counterparts, CH₃CH₂—X, are collected in Table 1. Coupling constants are listed in Table 2. Measurements of ^{13}C and of ^{31}P resonances are given in Tables 3 and 4, respectively.

DISCUSSION

Acetylenic proton chemical shift

The different effects on proton chemical shifts will be estimated quantitatively.

Electric field effects. The electric field effects were calculated for monosubstituted acetylenes, in which a carbon atom is attached to the triple bond, using the equation given by Schweitzer *et al.*[5] The results are collected in Table 5.

Comparison with the experimental chemical shift values, using propyne as reference, shows that the electric field effect does not exceed a fraction of 35% of the measured chemical shift difference. In all cases a deshielding effect was calculated, because the positive end of the dipole moment vector is nearest to the acetylenic proton.

Diamagnetic anisotropy effects from ring currents in substituents at the triple bond. These anisotropy effects on the acetylenic proton can be estimated with the equation

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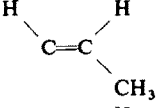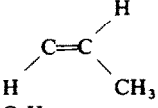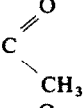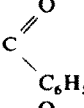TABLE 1. EXPERIMENTAL PROTON CHEMICAL SHIFTS
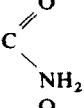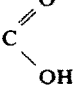
Acetylenic compounds of type HC≡C—X			Ethyl derivatives of type CH₃—CH₂—X		
Atom of X. linked to C≡C	X	δ(HC≡C—X). ppm	$\delta(\alpha CH_2)$. ppm	$\delta(\beta CH_3)$. ppm	$\Delta\delta = \delta(\alpha CH_2) - \delta(\beta CH_3)$. ppm
—	H	1·80[a]	0·86[b]	0·86[b]	0
C sp³	CH₃	1·76	1·45[b]	0·91[b]	0·54
	C₂H₅	1·76	1·23[b]	0·90[b]	0·33
	C₃H₇	1·79	1·26[b]	0·89[b]	0·37
	n-C₄H₉	1·73	1·27[b]	0·90[b]	0·37
	CH₂CH₂OH	1·92	1·38[c]	1·00[c]	0·38
	CH₂OH	2·33	1·57[b]	0·92[b]	0·65
	CH₂I	2·19	1·88	1·04	0·84
	CH₂Br	2·33	1·90	1·04	0·86
	CH₂Cl	2·40	1·83	1·04	0·79
	CH₂CN	2·15	1·71	1·11	0·60
	CH₂OCH₃	2·28	1·54[b]	0·92[b]	0·62
	CH(C₆H₅)(OH)	2·46			
	C(CH₃)₃	1·87	−1·20[c]	−0·85[c]	0·35
	C(C₆H₅)₃	2·54			
	cyclo-C₆H₁₁	1·88			
	CF₃	2·80	2·15[d]	1·27[d]	0·88
C sp²	CH=CH₂	2·92	2·00	1·00	1·00
	H, H / C=C \ CH₃	2·95	2·00[c]	0·95[c]	1·05
	H / C=C \ / \ H CH₃	2·60	1·95[c]	0·95[c]	1·00
	C₆H₅	2·93	2·63	1·21	1·42
	pNO₂—C₆H₅	3·21			
	pNH₂—C₆H₅	2·71			
	2.4.6-trimethylphenyl	3·27			
	O ‖ C \ CH₃	3·50	2·47[e]	1·05[e]	1·42
	O ‖ C \ C₆H₅	3·33	2·92[f]	1·18[f]	1·74
	O ‖ C \ NH₂	2·90	2·23[e]	1·13[e]	1·10
	O ‖ C \ OH	3·02[h]	2·36[f]	1·16[f]	1·20

TABLE 1—*continued*

Acetylenic compounds of type HC≡C—X			Ethyl derivatives of type CH₃—CH₂—X		
Atom of X. linked to C≡C	X	δ(HC≡C—X). ppm	$\delta(\alpha CH_2)$. ppm	$\delta(\beta CH_3)$. ppm	$\Delta\delta = \delta(\alpha CH_2) - \delta(\beta CH_3)$. ppm
	C (=O, OC₂H₅)	2·75[h]	2·28[f]	1·12[f]	1·16
C sp	C≡CCH₂CH₃	1·78	1·90[g]	0·96[g]	0·94
	CN	2·48[h]	2·35[f]	1·31[f]	1·04
Si	Si(CH₃)₃	2·19	0·50[b]	0·92[b]	−0·42
	Si(C₆H₅)₃	2·32			
	Si(C₆H₅)₂C≡CH	2·52[i]			
Ge	Ge(nC₄H₉)₃	2·09	−0·60	−0·90	0·30
	Ge(C₆H₅)₃	2·51			
Sn	Sn(C₂H₅)₃	2·07	−0·80	−1·20	0·40
	Sn(C₆H₅)₃	2·32[j]	1·40	1·40	0·0
Pb	Pb(C₆H₅)₃	2·16	0·80	1·15	−0·35
N	N(C₂H₅)₂	2·15	2·42[b]	0·95[b]	1·47
	N(CH₃)(C₆H₅)	2·75[j]	3·38[e]	1·13[e]	2·25
	N(C₆H₅)₂	2·71[j]			
P	P(C₂H₅)₂	2·70	1·20[i]	0·96[i]	0·24
	P(tC₄H₉)₂	2·65			
	P(sC₄H₉)₂	2·62			
	P(C₆H₅)₂	3·07[k]	1·98	1·04	0·94
	P(C≡CH)₂	3·0			
	P(O)(C₂H₅)₂	3·18	1·65[l]	1·10[l]	0·55
	P(O)(tC₄H₉)₂	3·08			
	P(O)(nC₄H₉)₂	2·97			
	P(O)(C₆H₅)₂	3·33[k]			
	P(O)(C≡CH)₂	3·50			
As	As(C₆H₅)₂	2·82[j]	1·50[m]	1·15[m]	0·35
	As(C≡CH)₂	2·65			
O	OC₂H₅	1·33	3·38	1·15	2·23
	OCH=CH₂	1·89	3·68	1·19	2·49
	OC₆H₅	1·92[j]	3·98[f]	1·38[f]	2·60
S	SC₂H₅	2·64	2·49	1·24	1·25
	SCH=CH₂	3·11	2·72	1·30	1·42
	SC₆H₅	3·13[j]	3·00	1·35	1·65
	SO₂C₄H₉	3·80	2·86[n]	1·36[n]	1·50
Se	SeC₂H₅	2·70			
F	F	1·57[p]	4·35[b]	1·27[b]	3·08

[a] H. Dreeskamp. E. Sackmann and G. Stegmeier. *Ber. Bunsenges. Phys. Chem.* **67**. 860 (1963)

[b] H. Suhr. *Anwendungen der kernmagnetischen Resonanz in der organischen Chemie.* Springer. Berlin (1965)

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[d] D. D. Elleman. *J. Mol. Spectros.* **7**. 307 (1961)

[e] Varian NMR Spectra Catalog (1962)

[f] L. M. Jackman and S. Sternhell. *Appl. of NMR in Org. Chem.* Pergamon Press. Oxford (1969)

[g] W. Zeil and H. Heel. *Ber. Bunsenges. Phys. Chem.* **64**. 962 (1960)

[h] A. A. Petrov. N. V. Elsakov and V. B. Lebedev. *Opt. Spektrosk.* **16**. 1013 (1964)

[i] S. M. Fedin. *Dokl. Akad. Nauk, S.S.R.* **175**. 879 (1967)

[j] M. P. Simonnin. *Bull. Soc. Chim. France* 1774 (1966)

[k] M. P. Simonnin. C. Charrier. W. Chodkiewicz and P. Cadiot. *C.R. Acad. Sci.* **258**. 1537 (1964)

[l] J. B. Hendrickson. M. L. Maddox. J. J. Sims and H. D. Kaesz. *Tetrahedron* **20**. 449 (1964)

[m] Values of As(C_2H_5)$_3$; A. G. Massey. E. W. Randall. D. Shaw. *Spectrochim. Acta* **20**. 379 (1964)

[n] F. Taddei. P. Biscarini and C. Zauli. *Bull. Sci. Fac. Chim. Ind. Bologna* **21**, 169 (1963)

[p] W. J. Middleton and W. H. Sharkey. *J. Amer. Chem. Soc.* **81**. 803 (1959)

TABLE 2. PROTON COUPLING CONSTANTS IN MONOSUBSTITUTED ACETYLENES, $HC^2{\equiv}C^2{-}X$

Atom of X. linked to $C{\equiv}C$	X	$J(^1H{-}^{13}C^1)$. Hz	$J(^1H{-}^{13}C^2)$. Hz
—	H	249[a]	
C sp^3	CH$_3$	248	
	CH$_2$Cl	252	50
	CH$_2$Br	252	50
	CH$_2$OCH$_3$	253	49
	C(CH$_3$)$_2$OH	253[b]	
	CH$_2$CN	251	
C sp^2	C$_6$H$_5$	251	50
C sp	C≡CH	259[b]	
	C≡C—tC$_4$H$_9$	257	52
Si	Si(CH$_3$)$_3$	236[c]	42[c]
	Si(C$_6$H$_5$)$_3$	239[c]	42·5[c]
Ge	Ge(C$_2$H$_5$)$_3$	236[c]	42[c]
Sn	Sn(C$_6$H$_5$)$_3$	238[c]	41[c]
N	N(C$_6$H$_5$)CH$_3$	258[c]	52·5[c]
	N(C$_6$H$_5$)$_2$	259[c]	55·5[c]
P	P(nC$_3$H$_7$)$_2$	244	45
	P(iC$_4$H$_9$)$_2$	246	
	P(sC$_4$H$_9$)$_2$	246	46
	P(C$_6$H$_5$)$_2$	247[c]	45·8[c]
	P(sC$_4$H$_9$) (C≡CH)	243	45
	P(C≡CH)$_2$	250	48
	P(O) (tC$_4$H$_9$)$_2$	252	49
	P(O) (tC$_4$H$_9$) (C≡CH)	250	
	P(S) (iC$_3$H$_7$)$_2$	250	46
O	OC$_2$H$_5$	263	
	OC$_6$H$_5$	269[c]	61[c]
S	SC$_2$H$_5$	253	
	SC$_6$H$_5$	256[c]	51·6[c]
	SO$_2$(nC$_4$H$_9$)	266	

[a] G. S. Reddy and J. H. Goldstein. *J. Chem. Phys.* **39**. 3509 (1963)

[b] J. W. Emsley. J. Feeney and L. H. Sutcliffe. *High Resolution NMR*. Pergamon Press. Oxford (1966)

[c] M. P. Simonnin. *Bull. Soc. Chim. France* 1774 (1966)

of McConnell.[6] which involves the dipole approximation. This is a fairly good approximation here. for the distance between the acetylenic proton and the aniso-tropy centre, X, in HC≡C—X, is large (4 Å) compared with the dimensions of the

TABLE 3. CARBON-13 CHEMICAL SHIFTS IN PPM UPFIELD FROM CS_2
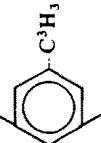
Compounds	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$\delta(C^4)$	$\delta(C^5)$	$\delta(C^6)$	$\delta(C^1)+\delta(C^2)$	$\delta(C^1)-\delta(C^2)$
H—C^1≡C^2—C_4H_9	128·0	111·0					239·0	+17·0
H—C^1≡C^2—S—CH_2—CH_3	112·6	121·4					234·0	−8·8
H·C_1≡C^2—O·C^3H_2—C^4H_3	170·8	104·6	121·6	184·2			275·4	+66·2
H—C^1≡C^2—Ge(nC_4H_9)$_3$	101·3	108·0					209·3	−6·7
H—C^1≡C^2—Pt(SC_4H_9)$_2$	101·3	110·8					212·1	−9·5
H—C^1≡C^2—P(O)(C^3H_2—C^4H_3)$_2$	100·6	113·0	168·6	186·6			213·6	−12·4
(H—C^1≡C^2)$_3$P	96	118					214	−22
(CH_3—C^1≡C^2)$_2$P(O)	92	117					209	−25
H C^1≡C^2—C_6H_5	115·7	109·4					225·1	+6·3
H—C^1≡C^2—⟨aryl⟩—C^3H_3 (C^3H_3 substituents)	110·4	113·6	176·6				224·0	−3·2
C^3H_3, C^4H_2—C^1≡C^2—C^4H_2—C^3H_3	112·0	112·0	183·3	185·1			224·0	0
C^3H_3—C^4H_2—C^1≡C^2—S—C^3H_3	101·3	126·7	184·8	185·2	179·7		228·0	−25·4
C^3H_3—C^4H_2—C^1≡C^2—O—C^5H_2 C^6H_3	158·0	105·9	182·5	186·9	121·7	183·7	263·9	+52·1
C^3H_3—C^1≡C^2—O·C^4H_3	166·0	105·6	198·4	131·6			271·6	+60·4

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TABLE 4. Phosphorus-31 chemical shifts in ppm upfield from H_3PO_4

Compounds	$\delta(^{31}P)$
$(iC_3H_7)_2P-C\equiv C-CH_3$	$+13\cdot2$
$(iC_3H_7)_2P-C\equiv C-nC_4H_9$	$+13\cdot9$
$(nC_4H_9)_2P-C\equiv C-C_2H_5$	$+50\cdot6$
$(nC_4H_9)_2P-C\equiv C-C_6H_5$	$+49\cdot8$
$(iC_4H_9)_2P-C\equiv C-H$	$+56$
$sC_4H_9-P(C\equiv C-H)_2$	$+53$
$(C_6H_5)_2P-C\equiv C-H$	$+33\cdot3$
$(C_6H_5)_2P-C\equiv C-CH_3$	$+34\cdot3$
$P(C\equiv C-H)_3$	$+91$
$P(C\equiv C-CH_3)_3$	$+87$
$tC_4H_9-P(O)(C\equiv CH)_2$	$-6\cdot5$
$(tC_4H_9)_2P(O)-C\equiv C-H$	$-48\cdot2$
$iC_3H_7-P(O)(C\equiv C-H)_2$	$-0\cdot7$
$(cycloC_6H_{11})_2P(O)-C\equiv C-H$	-36
$cycloC_6H_{11}-P(O)(C\equiv C-H)_2$	$+3$
$(sC_4H_9)_2P(O)-C\equiv C-H$	$-36\cdot4$
$(nC_4H_9)_2P(O)-C\equiv C-H$	$-23\cdot7$
$(C_2H_5)_2P(O)-C\equiv C-H$	$-29\cdot4$
$(nC_4H_9)_2P(O)-C\equiv C-CH_3$	$-21\cdot2$
$P(O)(C\equiv C-H)_3$	$+56$
$(tC_4H_9)_3P(O)$	$+41$
$(iC_3H_7)_2P(S)-C\equiv C-H$	-53
$(tC_4H_9)_2P(S)-C\equiv C-H$	-67
$(tC_4H_9)_2P-C\equiv C-P(tC_4H_9)_2$	$-14\cdot5$
$(C_6H_5)_2P(O)-C\equiv C-P(O)(C_6H_5)_2$	$-9\cdot25$
$(nC_3H_7)_2P(O)-C\equiv C-P(O)(nC_3H_7)_2$	-28

TABLE 5. Electric field effect, δ_E, on acetylenic proton in $HC\equiv C-X$ by X

X	group moment μ_X, D	δ_E ppm	$\delta(HC\equiv)_{exp}$ of $HC\equiv CX$ ref. to $\delta(HC\equiv)$ of propyne, ppm
CH_3	0·30	0·01	0
CH_2Cl	2·0 $(\mu C-Cl)$	0·08	0·64
CH_2CN	4·0 $(\mu C-CN)$	0·14	0·39
CF_3	2·35	0·16	1·04

TABLE 6. Hybridisation effect on $\delta(HC\equiv)$ in $HC\equiv C-X$

X	$J(^{13}C-^1H)$ Hz	$J(^{13}C-^1H)$, compared with propyne. Hz	corresp. $\delta(HC\equiv)$. ppm	exp. $\delta(HC\equiv)$. ppm
CH_3	248	0	0	0
CH_2Cl	252	4	0·20	0·64
CH_2Br	252	4	0·20	0·57
CH_2OCH_3	253	5	0·25	0·74

substituted magnetic dipole (0·5 Å). For most substituents, anisotropy values. Δ_{χ}, necessary for the application of McConnell's equation are not known. Only in the case of acetylene there is an estimate of $5 \cdot 10^{-29}$ cm³ for Δ_{χ}.[7,8] For the acetylenic proton in butadiyne an anisotropy contribution to higher shielding compared with propyne, of 0·25 ppm was calculated. As the anisotropy contribution of a triple bond will be large compared with other groups considered here, CH_3, CH_2CN, CH_2OCH_3 and CF_3,[9] this contribution may be neglected.

Hybridisation effects. Changes of the hybridisation of the acetylenic carbon atom attached to the proton can be estimated from changes in the $^{13}C—^1H$ coupling constant. From investigations of Reddy and Goldstein[10] an increase of 1% in s character of the acetylenic carbon orbital, participating in the $\equiv C—H$ bond, gives an increase in proton shift of 0·2–0·3 ppm. Furthermore, an increase of 1% in s character corresponds to an increase in $J(^{13}C—^1H)$ of 5 Hz, assuming a difference of 25% s character between CH_4 and $HC\equiv CH$, which have $J(^{13}C—^1H)$ of 125 Hz and 250 Hz, respectively. For this reason an increase of 1 Hz in the coupling constant means an increase of 0·04–0·05 ppm in proton shift.

Comparison of the data in the last two columns of Table VI shows that changes in the hybridisation of the acetylenic carbon atom, reflected in the coupling constant, constitute sometimes a considerable but not preponderant, part of the shift changes.

Inductive effects. In a previous paper[1] the internal chemical shift as defined by Dailey and Shoolery[11] for compounds $CH_3CH_2—X$

$$\Delta\delta = \delta(CH_2) - \delta(CH_3)$$

was used as a measure of the electronegativity of the substituent X. As was shown by Spiesecke[12] this is allowed only if the first atom of group X is a first row element. For other elements diamagnetic anisotropy contributions cannot, *a priori*, be neglected. For the latter elements $\Delta\delta$ values will be corrected to eliminate anisotropy
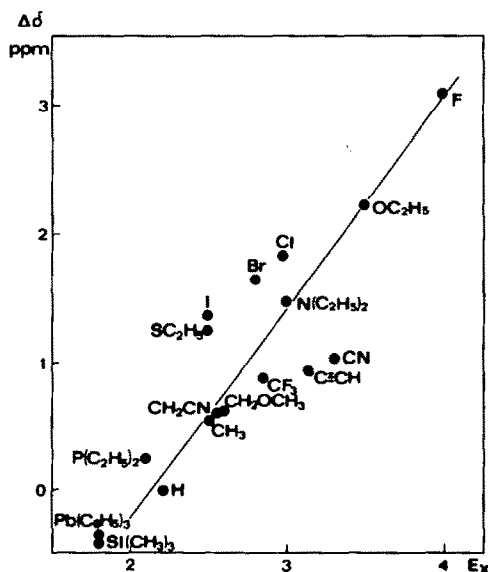

FIG 1. Experimental internal chemical shifts versus Pauling electronegativity of X, E_X.

contributions. To this end $\Delta\delta$ values are plotted *versus* Pauling electronegativity of group X (Fig 1). The straight line indicates linear behaviour for the saturated substituents X=H, CH_3, $N(C_2H_5)_2$, OC_2H_5 and F of which the first atom is a first row element. The corresponding equation is

$$\Delta\delta_X = 1.64\,E_x - 3.48 \qquad\qquad 1$$

The correlation coefficient amounts to 99.9%.

Nonfirst row elements as well as acetylenic and cyanide substituents and CF_3 do not meet this equation, because of diamagnetic anisotropy contributions. The

TABLE 7. ANISOTROPY CONTRIBUTION IN $\Delta\delta$, A_X, FOR COMPOUNDS CH_3CH_2—X CALCULATED FROM ELECTRONEGATIVITY OF X. E_X

X	E_X	$\Delta\delta_X$ calc. from eq. (1). ppm	$\Delta\delta_{exp.}$, ppm	A_X. ppm
CF_3	2.86^a	1.21	0.88	-0.33
CH_2CN	2.56^a	0.72	0.60	-0.12
CH_2OCH_3	2.60^a	0.78	0.62	-0.16
C_6H_5	2.70^b	0.95	1.42	0.47
$C\equiv CH$	3.15^c	1.69	0.94	-0.75
$C\equiv N$	3.30^c	1.93	1.02	-0.91
SCH_3	2.50^d	0.62	1.25	0.63
$P(CH_2CH_3)_2$	2.10^d	-0.04	0.24	0.28

[a] calculated by the method of Gallais[13]
[b] estimated from values for C sp^3 and C sp
[c] ref. 14
[d] Pauling electronegativities for S and P

difference between $\Delta\delta$, calculated by eq. 1 and the experimental value, or in other words, the deviation from the straight line in Fig 1, A_X, is a measure of the diamagnetic anisotropy contribution. The data are collected in Table 7.

Positive and negative values of A_X indicate deshielding and shielding, respectively, of the αCH_2 protons by the group X in CH_3CH_2—X.

Values of $\Delta\delta$ for nonfirst row elements, corrected for anisotropy contributions, were calculated from eq. 1. In Fig 2 acetylenic hydrogen chemical shifts of compounds $HC\equiv C$—X, $\delta(HC\equiv)$, were plotted *versus* these corrected $\Delta\delta$ values, which are a measure of the electronegativity of substituent X.

An analysis of this figure is made starting from derivatives of propyne. It can safely be assumed, that in these compounds the substituent at the saturated carbon atom neither changes the anisotropy of the triple bond, nor influences the internal chemical shift of the corresponding n-propyl derivatives by substituent anisotropy effects. Thus, in these acetylenes only an inductive effect of the substituent at the triple bond remains. This effect is expressed by the linear equation.

$$\delta(HC\equiv) = 1.20\,\Delta\delta + 1.38 \qquad\qquad 2$$

correlation coefficient 91.8%. The line corresponding to this equation is plotted in Fig 2.

Mesomeric effects. Deviations from this line expressed by eq. 2, can be attributed

to mesomeric effects in a quantitative way. The distance to the line or, equivalently the difference, M_X, between the experimental acetylenic proton shift and the shift calculated from eq. 2, is a measure of the mesomeric effect. In Table 8 values for M_X are collected. The M_X value is positive if the acetylenic proton in $HC\equiv C$—X is more
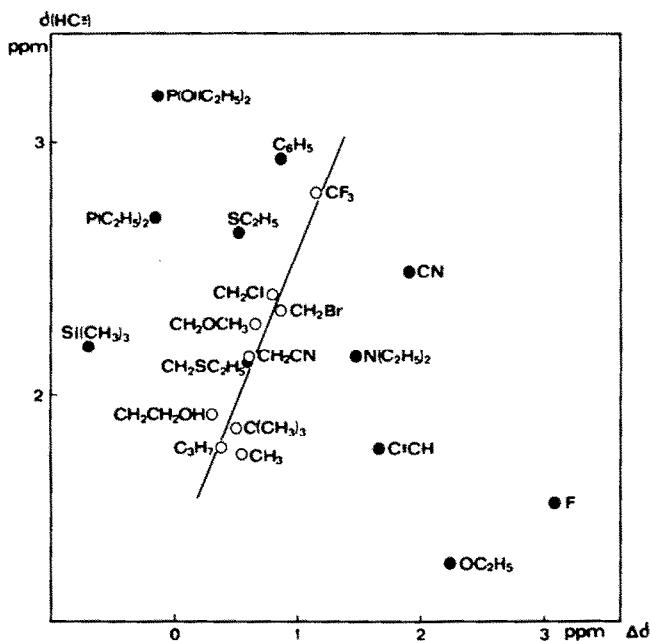

Fig 2. Acetylenic proton chemical shifts of $HC\equiv C$—X versus $\Delta\delta$ values of CH_3CH_2—X. Open circles refer to experimental $\Delta\delta$ values; black circles to $\Delta\delta$ values corrected for anisotropy.

deshielded than can be expected from inductive effects only. A negative M_X value indicates a shielding of the acetylenic proton which is higher than expected from the inductive effect of X. Mesomeric interaction between the π orbitals of the triple bond and of X can influence the chemical shift of the acetylenic proton in several ways:

TABLE 8. CALCULATED MESOMERIC CONTRIBUTIONS FOR COMPOUNDS $HC\equiv C$—X

| X	$\Delta\delta_{corr.}$ ppm	$\delta(HC\equiv)_{calc.}$ from eq. 2, ppm	$\delta(HC\equiv)_{exp.}$ ppm	mesom. contr. M_X, ppm
F	3·08	5·08	1·57	−3·51
OC_2H_5	2·26	4·09	1·33	−2·76
$N(C_2H_5)_2$	1·44	3·11	2·15	−0·96
$C\equiv CH$	1·69	3·41	1·78	−1·63
$C\equiv N$	1·93	3·70	2·48	−1·22
C_2H_5	0·47	1·80	1·76	−0·04
SC_2H_5	0·62	2·12	2·64	+0·52
C_6H_5	0·95	2·52	2·93	+0·41
$Si(CH_3)_3$	−0·53	0·74	2·19	+1·45
$P(C_2H_5)_2$	−0·04	1·33	2·70	+1·37
$P(O)(C_2H_5)_2$	0·00	1·38	3·18	+1·80

i. charge transfer to or from the triple bond will change the charge at C^1, in $HC^1\equiv C^2$—X, and therefore $\delta(HC\equiv)$. Increase of charge at C^1 increases the shielding of the acetylenic proton.

ii. charge transfer to or from the triple bond will change the diamagnetic anisotropy contribution of the triple bond. The effect is difficult to estimate, because two effects are counteracting:

(a) an increase in charge on C^1 in $HC^1\equiv C^2$—X will expand the $p\pi$-orbitals and diminish the ring current effect;[15]

(b) the charge increase will reinforce the magnetic field of the ring current by the increase of the rotating charge.

From dipole moment measurements[16] it is known, that in ethoxyethyne a mesomeric effect increases the charge at the triple bond:

$$HC\equiv C\text{—}O\text{—}C_2H_5 \leftrightarrow H\overset{\ominus}{C}=C=\overset{\oplus}{O}\text{—}C_2H_5$$
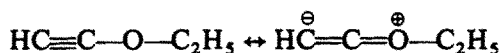
Thus, negative values of M_X (Table 8) correspond with mesomeric electron shifts to the triple bond. The order of the absolute value of M_X for a number of relevant substituents is $F > OR > NR_2 > C\ sp^3$. It is peculiar, that this sequence differs from the order of the absolute value of the Taft substituent constant σ_R which is a measure for mesomeric interaction:[17]

$$NR_2 > OR > F > C\ sp^3$$
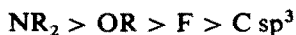
Moreover, there are several arguments against considerable charge transfer from the π orbitals of fluorine to the π orbitals of the triple bond in fluoroethyne:

i. *ab initio* calculations of fluoroethyne[18] do not show charge transfer to the π orbitals of the triple bond, though overlap between fluorine p orbitals and triple bond π orbitals is considerable.

ii. a mesomeric charge transfer, represented by the structure $H\overset{\ominus}{C}=C=\overset{\oplus}{F}$, should involve a shortened C—F bond. Electron diffraction measurements show nearly the same C—F bond lengths for fluoroethyne, 1·34 Å, and fluoroethane, 1·33 Å.[19]

iii. fluorine magnetic resonance shows a high shielding for the fluorine atom attached to the triple bond.[20] This high shielding of the fluorine atom indicates the absence of considerable charge transfer to the triple bond.

Apparently, for fluorine the M_X value is appreciably larger than mesomeric interaction predicts, or in other words, the acetylenic hydrogen resonance signal of $HC\equiv C$—F is at a relatively high shielding position.

This high shielding effect seems to be present, not only for hydrogen and fluorine, but also for other atoms attached to the triple bond (see below). It is ascribed to an extension of the triple bond π orbital system as a result of π orbital overlap between the triple bond and X. Instead of being present at the triple bond only, the system is extended to the atom X as well. Therefore, the ring currents of $C\equiv C$ and X can be considered to be coupled by the π overlap between $C\equiv C$ and X. This coupling will increase the diamagnetic anisotropy effect on the acetylenic proton and carbon atoms as well as on the first atom of group X. For this phenomenon to occur, charge transfer between triple bond and X is not necessary.

This phenomenon also explains the high M_X values of butadiyne and cyano-

ethyne. At least in butadiyne mesomeric charge transfer is not possible and. thus. mesomerism cannot explain the high M_X value. The two molecules are linear and have eight electrons in the π orbitals. Favourable symmetry makes coupling of the triple bond ring currents very likely.

For the acetylenic proton in ethoxyethyne a considerable increase in shielding is found, M_O $-2 \cdot 76$. The presence of considerable charge transfer is concluded from dipole measurements.[16] However. from ^{13}C measurements (see below) it can be concluded that M_O is not entirely the result of this charge transfer.

A similar situation occurs in 1-alkynyl amines.

In phenylethyne and ethylthioethyne the acetylenic proton is deshielded more than could be expected from inductive effects only. A charge transfer from the triple bond to the phenyl ring and the sulfur atom, respectively. is possible. This would indicate electron acceptance by the sulfur atom in the latter compound.

In acetylenes in which the first atom of group X is silicon, phosphorus or phosphorusoxide (P=O). a clear deshielding effect on the acetylenic proton is present. So. charge shift from the triple bond to the hetero atom is probable. These hetero atoms. as well as sulfur, have empty d orbitals the symmetry of which is favourable for accepting electrons from the triple bond. Since d orbitals are contracted by electronegative substituents, charge transfer to phosphorus should be much larger for P=O than for P. Although there is a difference indeed. M_X is $+1 \cdot 80$ ppm and $+1 \cdot 37$ ppm. respectively. it is not striking.

Coupling constants of acetylenic hydrogens

Attempts to correlate $J(^{1}H—^{13}C\equiv)$ with the chemical shift of the proton[21] have not always been successful. because the shift has not been corrected for diamagnetic anisotropy. In the present case a correction can be applied by using $\delta(HC\equiv)$ values calculated from eq. 2. Now. a satisfactory linear relation between J and δ appears:

$$J = 6 \cdot 69 \ \delta(HC\equiv)_{calc} + 235 \text{; correlation coefficient } 97 \cdot 5\%.$$

Carbon-13 chemical shifts

A change in the carbon-13 resonance is mainly determined by a charge change on the carbon atom.[22, 23] Therefore. the sum of the chemical shifts of the two acetylenic carbon atoms. $\delta(C^1) + \delta(C^2)$. for different compounds gives an idea of the charge changes in the triple bond (Table 3). It should be remarked. however. that a relatively small change in this sum. as occurs. for instance. between 1-hexyne and 3-hexyne. of 18 ppm. can be the result of factors other than charge changes. The difference between the shift values. $\delta(C^1)—\delta(C^2)$. is a measure of the polarisation of the charge in the triple bond. The shift values of 1-hexyne are taken as reference. because of the negligible charge transfer from alkyl group to triple bond. Calculations by Newton[24] on propyne support this assumption. According to CNDO calculations by Pople et al..[25] polarisation of the charge in the triple bond is much more important than charge transfer.

Alkyl derivatives. Comparison of $\delta(C^1)—\delta(C^2)$ in 1-hexyne and 3-hexyne as well as in $HC\equiv COC_2H_5$ and $C_2H_5C\equiv COC_2H_5$ and in $HC\equiv CSC_2H_5$ and $C_2H_5C\equiv CSC_2H_5$ shows the polarising effect of an alkyl group on the triple bond to be approximately 16 ppm.

In the disubstituted acetylenes like 3-hexyne. the carbon resonance of the CH_2 group next to the triple bond is shifted by approximately 10 ppm towards higher field compared with propane (176 ppm[12]). This is in agreement with data of Frei and Bernstein,[26] who measured a similar upfield shift for the methyl group in $C_6H_5C{\equiv}CCH_3$. compared to propane.

This relatively high value of the carbon-13 resonance of a carbon atom next to the triple bond. $C{\equiv}C\underline{C}$ relative to $C—C—\underline{C}$. will even be increased if a correction is applied for the difference in electronegativity between carbon sp and carbon sp^3. This correction can be estimated to be 30 ppm. giving an increased chemical shift of the sp^3 carbon atom in $C{\equiv}C—C$ of 40 ppm. Part of this increase will be the result of diamagnetic anisotropy contributions of the triple bond. From McConnell's equation[6] this part is calculated to be 3 ppm. The preponderant part of the shift increase is attributed to the above mentioned coupling of ring currents.

Sulfur derivatives. The ^{13}C chemical shift of the acetylenic carbon atom C^2 in $HC^1{\equiv}C^2SC_2H_5$ is probably not a true measure of its charge because of an anisotropy contribution by the sulfur atom. This contribution can be estimated from a comparison of dimethyl sulfide ($^{13}CH_3$ at 175 ppm) and neopentane ($^{13}CH_3$ at 163 ppm) to be 12 ppm, if electronegativities of sulfur and carbon are the same. If the carbon-13 resonance of C^2 in ethylthioethyne is corrected for this amount. its shielding becomes 109·4 ppm and $\delta(C^1) + \delta(C^2)$ equals 222 ppm, indicating some charge transfer to the sulfur atom. This is in accordance with the acetylenic proton resonances.

Oxygen derivatives. A considerable charge increase is found in the oxygen compounds where $\delta(C^1) + \delta(C^2)$ equals 275 ppm. both for ethoxyethyne and. after correction for the alkyl group. 1-ethoxy-1-butyne. This charge transfer from oxygen to a triple bond increases the shielding of C^1 by 43 ppm with respect to 1-hexyne. With the equation.[22]

$$\Delta\delta(^{13}C) = -160\,\Delta q\pi$$

a charge increase of 0·27 electrons is calculated for this change. This increase of charge is larger than found from dipole measurements on ethoxyethyne. viz. 0·11 electrons.[16] The latter amount corresponds to an increase in shielding of only 17 ppm. The additional shielding of $43 - 17 = 26$ ppm can be attributed to an increase of the diamagnetic anisotropy contribution of the triple bond on C^1.

The low value of C^2 is the result of polarisation by the electronegative oxygen atom. which is even increased by the polar resonance structure $HC^{\ominus}{=}C{=}O^{\oplus}—C_2H_5$. The higher electronegativity of the oxygen atom is also reflected in the deshielding of carbon atom C^3 of ethoxyethyne (121·6 ppm) compared with the methylene carbon atom in diethyl ether[12] (126 ppm).

Phosphorus and germanium derivatives. A diamagnetic contribution of the phosphorus atom to the methyl carbon atoms in trimethylphosphine is negligible. as follows from the fact. that $\delta(^{13}C)$ of CH_3X is linearly correlated[12, 27] with the Pauling electronegativity of X for $X = P(CH_3)_2$. CH_3. $N(CH_3)_2$. OCH_3 and F. From the proton resonances equal deshielding effects were found for phosphines. phosphinoxides and germanium compounds. after correction for inductive effects. This behaviour suggests equal charge transfer from the triple bond. This is confirmed by the carbon resonances. where the sum $\delta(C^1) + \delta(C^2)$. also indicates a charge transfer

of equal magnitude for all these compounds. The small difference in $\delta(C^1) - \delta(C^2)$ between phosphines ($-$ 9·5 ppm) and phosphinoxides ($-$ 13·6 ppm) might indicate approximately equal electronegativity for R_2P and $R_2P(O)$ groups. Obviously. the oxygen atom forms a bond with phosphorus having only little ionic character.

Polarisation is much more pronounced in triethynylphosphine ($-$ 24 ppm). probably caused by the high electronegativity of the acetylenic group, which is transmitted through the phosphorus atom.

Phosphorus-31 chemical shifts

Phosphorus chemical shifts were measured in order to obtain some quantitative results on the overlap between π orbitals of the triple bond and d orbitals of phosphorus. From proton and carbon-13 measurements it was concluded that an equal charge shift was present in phosphines and phosphinoxides.

Using equations given by Letcher and Van Wazer[28] it is possible to separate inductive and overlap effects in the phosphorus chemical shift.

Phosphines. In phosphines of type PZ_3 the quantity ζ_p in the equation for the phosphorus chemical shift:[28]

$$\delta_{exp} = 11828 - 7719 \, \zeta_p - 417n_\pi$$

is calculated from the electronegativity values of phosphorus and the substituent. Z. and from the bond angle Z—P—Z. In triethynylphosphine the bond angle is 100°.[29] The electronegativity of phosphorus is 2·10.[30] By means of the value 3·15 for the electronegativity of the acetylenic group[14] the calculated shift becomes $-$ 57 ppm. if π bonding is absent. compared with an experimental shift of 91 ppm. If the discrepancy between the two values were the result of π bonding, from the equation above. the amount of π bonding would be $n_\pi - 0.35$ electrons. This negative value is unrealistic. Apparently. the high experimental chemical shift is the result of another effect. Here again. an atom attached to a triple bond shows a relatively high chemical shift. This high shift can be explained qualitatively by the coupling of ring currents.

If there were no π bonding between phosphorus and the triple bond. the difference between calculated and experimental shift of $57 + 91 = 148$ ppm would have its origin in this coupling of ring currents. If π bonding plays a part. the value of 148 ppm will be only a lower limit of this contribution of coupling of ring currents.

Phosphinoxides. In phosphinoxides the shielding of phosphorus increases with increasing electronegativity of the substituent when the substituent electronegativity is higher than the value for phosphorus.[28] For the calculation of ζ_p only the electronegativities of the substituents are needed. because the bond angles are assumed to be tetrahedral in these tetracoordinated molecules. In the equation[31]

$$\delta_{exp} = 11828 - 7940 \, \zeta_p - 149n_\pi$$

n_π equals the total number of electrons occupying the d orbitals of the phosphorus atom. This equation shows. that π bonding to phosphorus gives a negative contribution to the shielding.

A chemical shift for triethynylphosphinoxide of 136 ppm was calculated, using an electronegativity value for the triple bond of 3·15 and for oxygen 3·50, and for the bond angle the value of 109°. This shift is 80 ppm higher than the experimental value of 56 ppm. This latter value can be obtained from the equation of Letcher if either

the unreasonably small electronegativity value of the sp carbon of 2·65 is assumed, or the amount of π bonding of 0·54 electrons per phosphorus atom is present. Part of this π bonding will belong to the P—O bond. If this part is assumed to be equal to the π bonding in trimethylphosphinoxide. it will be 0·35 electrons per phosphorus atom.[28] In triethynylphosphinoxide the remaining part of $0·54 - 0·35 = 0·19$ electrons is due to $\equiv$C—P π interaction. However. the chemical shift of triethynyl-phosphinoxide might have increased by the coupling of the ring currents of triple bond and phosphorus atom. If this is the case, substraction of this contribution lowers the experimental value which is equivalent to a higher amount of π bonding. The value of 0·54 electrons in the π orbitals at phosphorus is, therefore, only the lower limit.

EXPERIMENTAL

Most compounds have been prepared in this laboratory by coworkers of Professor Arens.[2] The phosphorus compounds were prepared by W. Hagens[3] and the germanium compounds by E. J. Bulten according to methods described.[4]

NMR spectra were obtained on a Varian A-60. Shifts were measured in CCl_4 extrapolated to infinite dilution. and are given in ppm from TMS. Coupling constants. expressed in Hz. between acetylenic carbons and hydrogen were measured on a Varian HA-100.

Natural abundance ^{13}C resonances were obtained in neat compounds at a frequency of 15·1 MHz on a Perkin–Elmer R-10 equipped with a time averaging computer. Samples of $HC\equiv CP(O)$ $(C_2H_5)_2$ and $(CH_3C\equiv C)_3PO$ were remeasured on a Varian XL-100 spectrometer at 25·1 MHz. employing proton noise decoupling. Benzene as internal reference. but chemical shifts are expressed in ppm upfield from CS_2. the latter compound being the usual reference δ (referred to CS_2) $= \delta$ (referred to C_6H_6) + 65·5 ppm.

In monosubstituted acetylene. $HC^1\equiv C^2- X$. the assignment of the ^{13}C signal of carbon atoms 1 and 2. was apparent from the differences in the coupling constants $J^1(^{13}C^1$—H) and $J^2(^{13}C^2$—H) having values of approximately 250 Hz and 50 Hz. respectively. In the disubstituted acetylenes the carbon-13 resonances of the triple bonded carbon atoms were assigned by comparison with the values obtained for the mono-substituted compounds.

^{31}P resonances were measured on a Perkin–Elmer R-10 and JEOL JNM-4H-100 machines. operating at 24·28 and 40·48 MHz. respectively. Shifts are expressed in ppm upfield from phosphoric acid as external reference.

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