

¹³C-NMR AND CNDO/2 CALCULATIONS OF COMPOUNDS CONTAINING
SP-HYBRIDISED CARBON. ACETYLENES AND CUMULENES.

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(Received in UK 27 February 1973; accepted for publication 8 March 1973)

The extremely low field shift (about 200 ppm relative to internal TMS^{1,2,3}) of the central sp hybridised carbon in allenes, prompted us to a study of compounds with more extended cumulated double bond systems in order to find out whether or not this resonance position is unique for sp hybridised carbon in such a carbon chain.

Table 1 summarises the ¹³C-NMR data for the compounds

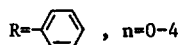
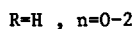
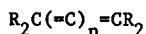


Figure 1 shows the alternation in the chemical shifts of corresponding carbon atoms, in the functional system $C(=C)_n=C$, with n.

An upfield shift of the C_α carbon, when we go to the next higher homologue, is always accompanied by a downfield shift of the C_β carbon and an upfield shift of the C_γ carbon (if present), and vice versa. As a consequence the internal shift $\delta C_\beta - \delta C_\alpha$ is much larger for the cumulenes with n odd than for those with n even.

A close correlation is observed between the mentioned variations of δC_α , δC_β and δC_γ and the total charge densities, calculated by the CNDO/2 method, on the corresponding atoms of the unsubstituted systems with n=0-5 (table 1, fig. 2). For all calculations known geometries were used, except for the cumulenes with $n \geq 3$ for which bond lengths and bond angles were estimated from the data for the cumulenes with $n \leq 2$. However, within the limits of the CNDO/2 approximations, the results are not critically dependent of those geometries. The calculated charges on C_β in allene and pentatetraene are the same, but the measured shifts in the corresponding tetraphenyl derivatives, for which no CNDO/2 calculations could be performed because of computer limitations, are not. However, this may be explained by the fact that in the case of the allene four phenyl groups occupy similar positions with respect to the one C_β atom, whereas in the pentatetraene a C_β atom has two phenyl groups in a β and two phenyl groups in a δ position. In the tetraphenylsubstituted cumulenes, the shifts of the C_α atoms are paralleled by the shifts of the corresponding C_1 and C_2 carbons of the phenyl groups, whereas the meta and para carbons, C_3 and C_4 , remain more or less at the same position (fig. 3). This indicates that, at least in

Table 1. ^{13}C chemical shifts^{a,b} and charge densities^c for the systems $\text{R}_2\text{C}(\text{=C})=\text{CR}_2$ and $\text{R}-(\text{C}\equiv\text{C})_n-\text{R}$

Compound	Functional system ^d			Phenylgroup ^{e,f}				Calculated charge densities in 10^{-3} e.u.
	δC_α	δC_β	δC_γ	δC_1	δC_2	δC_3	δC_4	
$\text{Ph}_2\text{C}=\text{CPh}_2$	141.01 (123.13)			143.72	131.31	127.62	126.39	$\alpha:-28$
$\text{Ph}_2\text{C}=\text{C}=\text{CPh}_2$	112.53 (73.57)	208.26 (212.47)		136.28	128.38	128.52	127.33	$\alpha:-101$ $\beta:+67$
$\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{CPh}_2$	122.74 (118.00)	152.03 (171.10)		138.81	129.46	128.42	127.94	$\alpha:-48$ $\beta:-1$
$\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2$	117.77	181.61	119.25	136.22	129.15	128.53	128.21	$\alpha:-95$ $\beta:+67$ $\gamma:-85$
$\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2$	124.71	149.42	127.33	137.96	129.16	128.35	128.35	$\alpha:-65$ $\beta:+19$ $\gamma:-13$
$\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CH}_2$								$\alpha:-93$ $\beta:+58$ $\gamma:-71$ $\delta:+66$
$\text{PhC}\equiv\text{CPh}$ ^g	89.69 (73.16)			123.52	131.67	128.54	128.43	$\alpha:-64$
$\text{PhC}\equiv\text{C}=\text{C}\equiv\text{CPh}$ ^h	81.50 (66.30)	74.37 (67.52)		121.88	132.35	128.42	129.10	$\alpha:-83$ $\beta:+14$

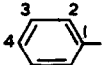

a) δ values in ppm (± 0.05), relative to TMS internal, were measured on a XL 100/15 FT system using ^2H lock, in 1 M solutions in $\text{CCl}_4/\text{CD}_3\text{COCD}_3$ 3:1 b) shifts for the systems with $\text{R}=\text{H}$ are given between parentheses c) calculated by the CNDO/2 method for the systems with $\text{R}=\text{H}$ d) the carbon atoms in the functional system are numbered: $\text{R}_2\text{C}_\alpha=\text{C}_\beta=\text{C}_\gamma=\dots$, $\text{R}-\text{C}_\alpha\equiv\text{C}_\beta-\dots$ e) the carbon atoms in the phenylgroups are numbered:  f) $\delta\text{C}_6\text{H}_6=128.31$ g) $\delta\text{C}_\alpha=89.9$, ref. 5 h) $\delta\text{C}_\alpha=81.7$; $\delta\text{C}_\beta=74.0$, ref. 5

Table 2. ^{13}C chemical shifts^a of substituted butatrienes

R_1	Substituent			δC_α	$\text{R}_1\text{R}_2\text{C}_\alpha=\text{C}_\beta=\text{C}_\gamma=\text{C}_\delta\text{R}_3\text{R}_4$		$\delta\text{C}_{\alpha'}$
	R_2	R_3	R_4		δC_β	$\delta\text{C}_{\beta'}$	
H	H	H	H ^b	118.0	171.1	171.1	118.0
Ph	Ph	Ph	Ph	122.5	152.0	152.0	122.5
CH_3	CH_3	H	OCH_3 ^b	99.4	160.1	137.2	124.5
	H	H	OCH_3 ^b	107.8	158.0	137.8	124.8
CH_3	C_2H_5	H	OCH_3 ^{b,c}	105.8	159.8	139.0	124.4
H	C_2H_5	H	SCH_3 ^{b,c}	105.5	161.5	152.0	102.9
Ph	CH_2OH	SCH_3	SCH_3	113.3	158.3	141.6	120.9
H	H	H	OC_2H_5	76.6	166.5	136.2	128.5
H	H	H	$\text{OC}(\text{CH}_3)_3$	77.4	164.5	138.1	124.1

a) See table 1, note a b) CW measurement c) mean values of the corresponding δ -values of the cis and trans isomers; maximum value of $|\delta_{\text{cis}} - \delta_{\text{trans}}|$ is 0.36 ppm

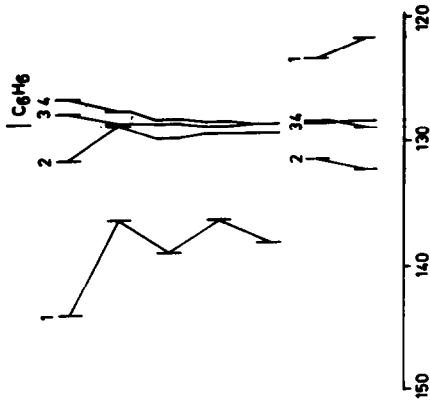
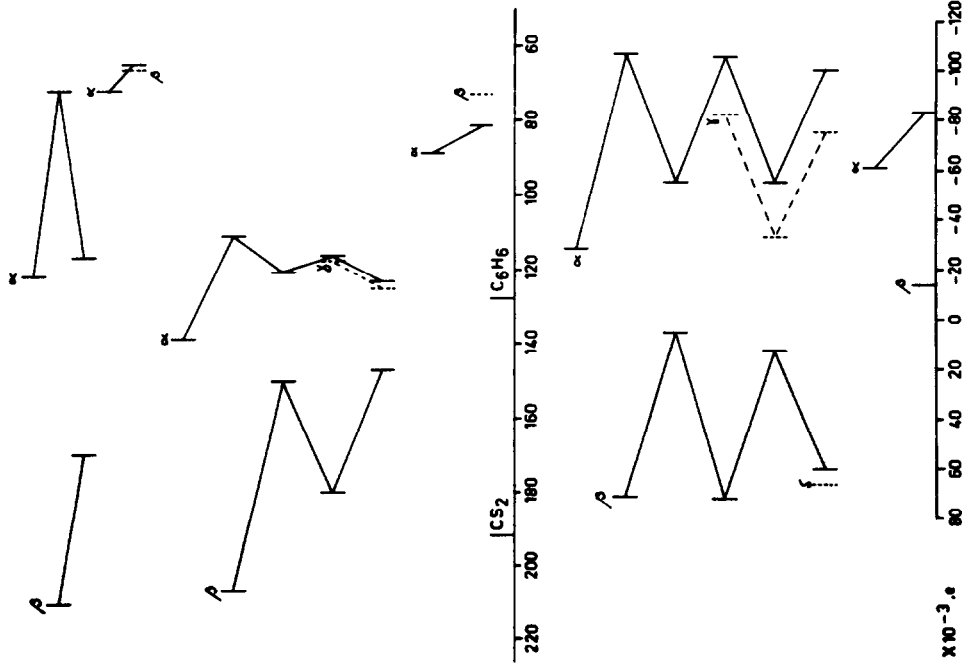


Fig. 1 (upper left) ¹³C chemical shifts in the functional systems $C(=C)_n=C$, $n=0-4$ and $-(C\equiv C)_n$, $n=1,2$

Fig. 2 (lower left) Charge densities (CNDO/2) on the carbon atoms of $H_2C(=C)_n=CH_2$ and $H(C\equiv C)_n$

Fig. 3 (upper right) ¹³C chemical shifts of the phenylgroups of the systems $(Ph)_2C(=C)_n=C(Ph)_2$ and $Ph(C\equiv C)_n$

these compounds, the substituent effects are transmitted mainly by an inductive mechanism. The mesomeric interaction is decreased by the approximately 30-40° rotation of the phenyl groups out of the plane defined by C₁, C_α and C_β.⁴ This steric inhibition of mesomeric interaction is also in accordance with the observation in allenes that the additivity rules for substituent effects break down when two bulky groups (i.e. phenyl groups) are substituted at the same carbon.² In the diphenylsubstituted acetylenes the variation of the shift of the C_α carbons is paralleled too by the variation of the shifts of the C₁ phenyl carbon atoms, reflecting an inductive interaction. However, the shift variation of the C₂ and C₄ carbon atoms of the phenyl groups is opposite to that of carbon C₁, reflecting a mesomeric substituent effect. The large difference in diamagnetic anisotropy of the cumulenenic and acetylenic π systems is mainly responsible for the observed average difference of about 15 ppm between the C₁ phenyl carbons in the tetraphenyl cumulenes and those in the diphenyl acetylenes. This anisotropy difference is of course also largely responsible for, for instance, the shift difference of at least 70 ppm between the C_β in butatriene, tetraphenyl butatriene or tetraphenyl hexapentaene and the C_β in butadiyne or diphenyl butadiyne. The CNDO/2 calculations for the non-substituted butatriene, hexapentaene and butadiyne indicate very similar charges on these C_β atoms. In substituted butatrienes (table 2) there is a reasonable correlation of the C_β resonance position with the C_β resonance position of the corresponding 1- or 1,1-substituted ethylenes. The sensitivity of the C_β resonance position to substitution is, in both systems, almost identical (fig. 4). In allenes the C_β resonance position is about 3 times less sensitive to substitution.² Relative shifts in the butatrienes are easily explained on the basis of mesomeric and inductive substituent effects.

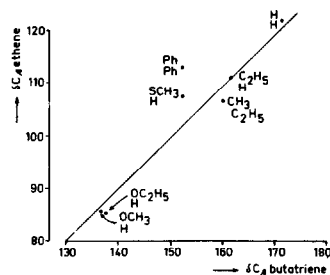


Figure 4. Plot of δC_{β} in substituted butatrienes against δC_{β} in corresponding vinyl compounds.

Acknowledgement. We are indebted to dr. P. Vermeer for his synthesis of tetraphenyl pentatetraene.

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