The Molecular Structure of Allenes and Ketenes. Part 16.[1] Phenyl Carbon Chemical Shifts of γ-Substituted Phenylallenes as a Probe for the Transmissions of Substituent Effects across the Allenic System

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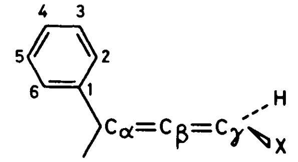
^{13}C Chemical shifts of γ-substituted phenylallenes PhHC=C=CHX have been measured. In order to investigate how substituent effects are transmitted across the allenic system emphasis is on the ^{13}C chemical shifts of the phenyl site. Analysis of the data using the dual substituent parameter approach reveals that inductive effects (polarizations) originating from the substituents' dipole moments are predominant. For the phenyl *ipso*-atom, however, delocalization effects are non-negligible. In order to account for the observations several types of ' hyperconjugative interactions ' are discussed. Semiempirical CNDO/S molecular orbital calculations are used to inquire further into the electron density distributions of phenylallenes and into the modes of the transmissions of substituent effects across the allenic system. Electron density distributions of phenylallenes turn out to be significantly affected through hyperconjugation.

Previous investigations [2] of electronic structures of allenes and bonding situations involving cumulated double bonds have concentrated mainly on energetical aspects [orbital/ionization energies measured by photoelectron (p.e.) spectroscopy [3] or excited state energies from u.v. absorption or c.d. spectroscopy].[1,3-5]

This contribution seeks to extend the knowledge of the ways in which different subunits of substituted allenes interact. The emphasis is on substituent effects on electron density distributions. For this purpose the ^{13}C chemical shifts of the phenyl sites in γ-substituted phenylallenes (1)—(9) have been examined. This means that the experimental method of choice is an indirect one referring to the modes of transmitting substituent effects across the allenic ($>$C=C=C$<$) system.

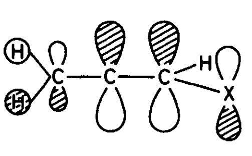


(1) X = H
(2) X = C_6H_5
(3) X = CH_3
(4) X = CH_3O
(5) X = Cl
(6) X = Br
(7) X = I
(8) X = CO_2H
(9) X = CN

In general, in a series of related molecules ^{13}C chemical shifts reflect changes of a variety of factors (for instance, electron densities, bond orders, excitation energies).[6] For the particular type of molecules under consideration with the distant sites Ph and X, however, all the conditions [6] seem to be met which should allow employment (at least qualitatively) of the phenyl carbon chemical shifts as a monitor of mainly charge density fluctuations.

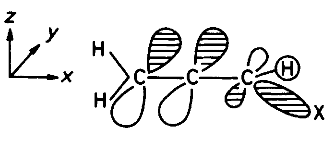
In order to support and complement the findings on electron densities from n.m.r. spectroscopy semiempirical quantum-chemical CNDO/S calculations [for (1)—(5), (8), (9)] have been performed. So far, the common approach to deal with molecular properties of allenes has been based upon perfect reductionism, properties of an allene $R^1R^2C{=}C{=}CR^3R^4$ being related to those of the two isolated constituent ethylenic subunits $R^1R^2C{=}CH_2$ and $H_2C{=}CR^3R^4$. Analytical descriptions of allenic orbitals usually refer to ' two perpendicular, isolated π systems ' which, in the above sense, are identified as the π orbitals of the corresponding ethylenic subunits (for more details *cf.* refs. 2, 3*b*, and *d*). Recently, however, objections against this approach and the model of allenes dissecting the molecules into two ethylenes have been raised.[2-4]

π(a'') orbital



(A)

π̄(a') orbital



(B)

To assist in the understanding of the molecular properties of allenes RHC=C=CH_2 or $R^1R^2C{=}C{=}CH_2$, respectively, with a methylene group the significance of ' hyperconjugation ' of the two-centre CC π orbital with the CH_2 group orbital of corresponding symmetry [symbolized in (A)] has been recognized for more than 20 years.[5] In these molecules (of symmetry C_s or C_{2v}) one has perfect π—σ separability,[2,5] *i.e.* all the orbitals are either antisymmetric (a'', π) or symmetric (a', $\sigma = \bar{\pi}$) with respect to mirror reflection in the molecular plane (xy). Here, π electron delocalization across the whole allenic skeleton *via* π-type interactions between the ligand X π orbitals and the π CH_2-group orbital is possible.

On the other hand, symmetry criteria allow overlap-dependent electronic interactions between the perpendicular $\bar{\pi}$ (σ) CC group orbitals and appropriate σ orbitals of the

Table 1. Carbon chemical shifts of phenylallenes PhHC=C=CHX (in $CDCl_3$) [a]

	Compound								
$\delta_{C\text{-}k}$	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
C-*i*	133.68	133.56	135.18	133.20	131.92	131.54	131.43	130.63	131.56
C-*o*	126.60	127.00	126.73	127.25	127.72	127.78	127.61	127.64	127.66
C-*m*	128.55	128.76	128.55	128.70	128.62	128.64	128.70	128.94	128.87
C-*p*	126.60	127.37	126.73	127.97	128.47	128.45	128.10	128.36	128.87
$\Sigma\delta_{C\text{-}k}$ [b]	770.58	772.45	772.47	773.07	773.07	772.83	772.15	772.15	773.49
C-α	93.98	98.49	94.17	109.00	103.60	102.45	98.26	99.04	99.75
C-β	209.59	207.86	206.21	194.69	203.32	202.77	205.43	216.29	217.56
C-γ	78.83	98.49	89.49	126.08	91.14	74.67	38.56	91.44	71.08
C-X			14.04	55.80				171.18	128.20

[a] In p.p.m. relative to Me_4Si. [b] $\Sigma\delta_{C\text{-}k} = \Delta$.

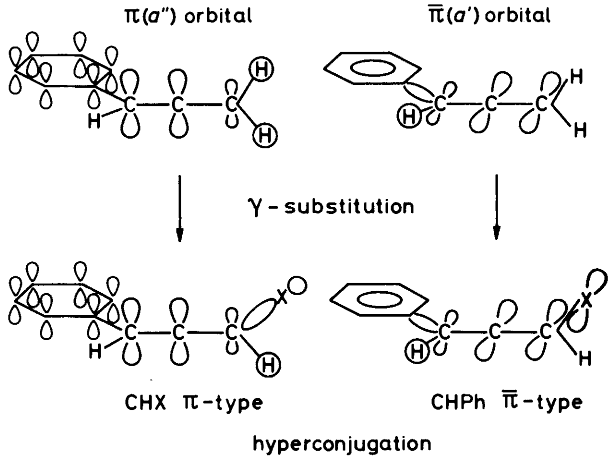


Figure 1. Types of 'hyperconjugative' interactions between the Ph and X sites in γ-substituted phenylallenes PhHC=C=CHX

remaining part of the molecule, *i.e.* there may arise 'π̄-type hyperconjugations' as visualized in (B). This particular interaction may also generate electron delocalization across the allenic system. The significance of π̄-type hyperconjugation for the electronic structure of allenes naturally depends upon the nature of the substituent X. π̄-Type hyperconjugation involving the terminal allenic atom and the neighbouring vinylic atom has been revealed recently by p.e. spectroscopy of vinylallene (X = $HC{=}CH_2$).[3c] A similar through-bond interaction between the allenic π̄ orbital and the carboxy *n* orbital has also been observed for methoxycarbonylallene (X = CO_2CH_3).[3b] Hence, one may suppose that such an interaction involving the *ipso*-atom of the aromatic ring may also play a role for phenylallenes.

Accordingly, this investigation of the transmissions of substituent effects across the allenic system examines how the ideal (π-type) CH_2 hyperconjugation in phenylallene (1) is affected through substitution. This means that we are concerned with the role of CHX π-type hyperconjugations in allenes (Figure 1). These particular conjugative interactions are similar to those discussed for benzyl derivatives $PhCH_2X$ with a *gauche*-arrangement of the groups X.[7] Furthermore, we discuss whether CHPh π̄-type hyperconjugation (Figure 1) is relevant for the transmissions of substituent effects in allenes.

From a general point of view this paper represents a contribution to the study of non-planar unsaturated 'π-systems' where characteristic interactions are intermediate between pure π and pure σ, which became an important field of chemical and spectroscopic research.[8]

Experimental and Computations

Carbon-13 resonances for (1), (3), and (8) are reported in ref. 8 and those of (2) are in ref. 9. In both these studies the shifts are reported to be accurate to within ±0.1 p.p.m. For the present investigation more accurate data are necessary. Furthermore, in order to obtain a consistent set of experimental data the carbon shifts of the above compounds have been remeasured.

All the compounds were obtained according to the procedures outlined in refs. 10 [(1), (3), (4), (8)], 11 [(2)], and 12 [(5)—(7)]; compound (9) was synthesized in the manner described in ref. 12 using CuCN. N.m.r. spectra were recorded on Bruker HX-90 and Bruker WP-200 spectrometers with 8K data points, spectral width 5 000 Hz, pulse delay 3 s, acquisition time 0.82 s, and number of transients 500. Measurements from both instruments agreed to within ±0.04 p.p.m.

In the case of liquid compounds the samples were prepared usually at a concentration of *ca.* 3% v/v in $CDCl_3$ containing *ca.* 5% tetramethylsilane as internal standard. For solid compounds [(2) and (8)] concentrations of *ca.* 0.2M were used.

The assignment of the aromatic carbon atoms was as follows. The *ipso*-atom (C-*i*) is readily identified by its low intensity. In the case of the cyano-compound (9), however, there remains a certain ambiguity concerning the assignments of the C-*i* and the CN atoms.

The assignment of the *meta*-carbons could be established *via* intensity considerations and their positions near to those of styrene $PhHC{=}CH_2$, whose ^{13}C chemical shifts have been remeasured to be comparable with those of phenylallene (1). The *para*-carbon atoms were identified *via* intensity considerations since they are only about one-half the area of the *ortho*- and *meta*-atoms.

Quantum-chemical CNDO/S calculations were done as described in refs. 2 and 3*a* and *b*. CNDO/S electron densities for (1) and (3) are also given in ref. 3*a*. CNDO/S electron densities for the allenic carbon and hydrogen atoms of (1)—(5), (8), and (9) are already summarized in ref. 2.

Results and Discussion

(1) ^{13}C *N.m.r. Spectroscopy.*—The ^{13}C chemical shifts of the allenes (1)—(9) are given in Table 1. Substituent effects on the chemical shifts of the allenic carbon atoms have been treated in detail for monosubstituted compounds.[2] In the phenyl-

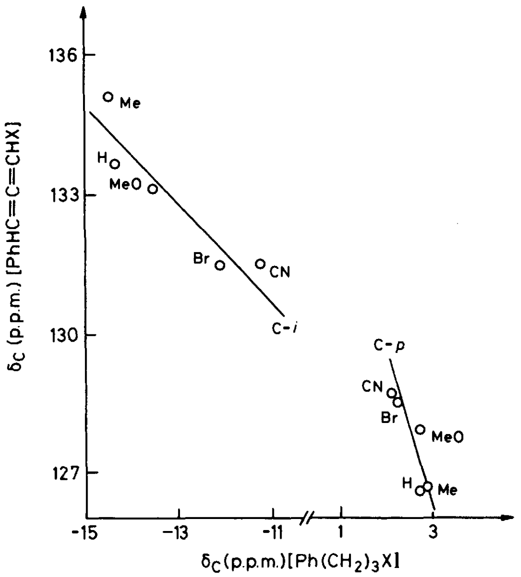


Figure 2. Correlations between ^{13}C chemical shifts of aromatic carbon atoms in correspondingly substituted γ-phenylallenes and 3-phenylpropanes

allenes these substituent effects are similar and, therefore, will not be discussed explicitly in this paper.

The proton decoupled ^{13}C n.m.r. spectra of all the phenylallenes (1)—(9) exhibit four resonances for the aromatic carbon atoms which are attributed to the *ipso* (1), *ortho* (2,6), *meta* (3,5), and *para* (4) carbon atoms, *i.e.* the inequivalent *ortho*- and *meta*-carbon atoms are not distinguished by ^{13}C n.m.r. spectroscopy.

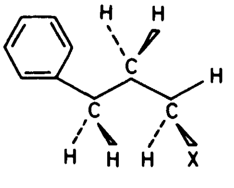
Furthermore, in Table 1 the sum Δ of the ^{13}C chemical shifts of all the six phenyl carbon atoms is given. Δ may be viewed as a rough measure of the electron density transfer between the phenyl ring and the γ-ligand X. As in the symmetrical 1,3-diphenylallene (2) no gain or loss of electron density may occur, the Δ value for (2) represents a reference point and, for instance, Δ values greater than $\Delta(2) = 772.45$ p.p.m. (Table 1) would indicate electron density loss of the aromatic ring.

From the Δ values in Table 1 one may infer that there is some charge transfer between phenyl and the group X. In rationalizing the substituent effects in (1)—(9) electron delocalization across the allenic system therefore should be taken into account.

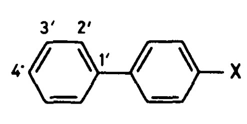
The phenyl carbon positions whose ^{13}C resonances are mostly affected by the substituents X are the *ipso*- and *para*-positions ($\delta_{C\text{-}i}$, $\delta_{C\text{-}p}$). The total variation of the ^{13}C chemical shifts amounts to 4.55 (C-*i*) and 2.27 p.p.m. (C-*p*), respectively. On the other hand, the total variation of the *ortho*-carbon resonances is only 1.20 p.p.m. As usually observed for substituted phenyl compounds the shifts of the *meta*-atoms vary only little ($\delta_{C\text{-}m}$ 128.75 ± 0.20 p.p.m.).

The ^{13}C chemical shifts of the aromatic nuclei of (1)—(9) represent substituent effects where the sites are separated by four to seven bonds. The substituent effects observed for phenylallenes are qualitatively similar to those of 3-phenylpropanes (10)[13a] which is seen from the correlations between the *ipso*- and *para*-carbon shifts in both types of molecules (Figure 2). In the phenylallenes the absolute magnitudes of the observed shift variations are greater than in the 3-phenylpropanes.

Molecules (10) are saturated analogues of the phenylallenes



(10)



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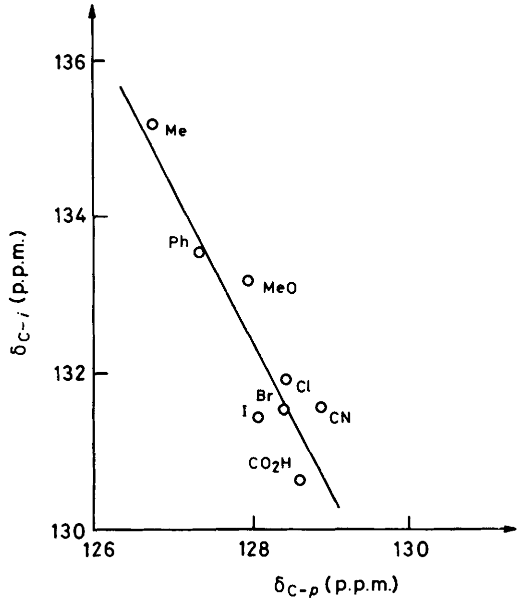


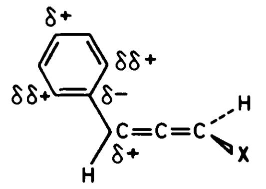
Figure 3. Correlation of the *ipso*- and *para*-phenyl carbon chemical shifts of γ-substituted phenylallenes PhHC=C=CHX

with the same numbers of intervening bonds between the Ph and X sites. The distances between the aromatic carbon atoms and the X site in (10), however, are smaller than those in the phenylallenes by 15—20%. In (10) resonance effects should not contribute to the observed substituent effects. On the other hand, the substituent effects on the aromatic carbon atoms in (1)—(9) are also more pronounced than those of C-1' in 4-substituted biphenyls (11)[14] where resonance effects are operative. [In (11) C-1' exhibits by far the largest shift variations of the remote phenyl carbon atoms.]

Except for X = Me in the γ-substituted phenylallenes the *ipso*-atoms show highfield ^{13}C shifts relative to that of (1). For the *para*-carbon atoms a reverse substituent effect is observed [downfield shifts relative to that of (1)]. The ^{13}C chemical shifts of both these atoms exhibit a crude linear correlation (1) (linear correlation coefficient *r* 0.8875) (Figure 3) if one disregards phenylallene (1). Owing to perfect CH$_2$ hyperconjugation compound (1), however, has an exceptional position in the series of phenylallenes (see below).

$$\delta_{C\text{-}i} = 377.66 - 1.92\,\delta_{C\text{-}p} \qquad (1)$$

The observation that, for instance, the strong π-donor MeO and the strong π-acceptor CN, groups which both withdraw electron density inductively, influence the ^{13}C chemical shifts in the same direction suggests that it is largely the inductive character (the polarity) of the group X which determines the chemical shifts of the phenyl carbon atoms. This is further supported considering the data for the methyl compound (3). Here, the direction of the substituent-induced shifts is



(C)

reversed. This is expected if the shifts are mainly influenced by the group moments as the sign of the methyl group moment is reversed relative to those of the other groups X.

In terms of electron density redistributions in the phenyl ring the substituent effects on the ^{13}C resonances, except X = Me, indicate withdrawal of electron density from the *para*- and *ortho*-positions with the flow of electron density essentially to the *ipso*-atom. On the other hand, inductively withdrawing groups seem to induce a positive charge at the α-carbon of the allene moiety, whereas a positive or a negative charge is built at the β-carbon depending upon whether X is a π-acceptor or π-donor, respectively. The electron density redistribution associated with an inductively withdrawing group is depicted in (C).

In order to inquire into the relative importance of polarity and delocalization (charge transfer) effects the ^{13}C chemical shift data of the *ipso*-, *ortho*-, *para*-, and β-carbon atoms were analysed in terms of the dual substituent parameter (d.s.p.) equations (2).[15-17] Owing to the unfavourable ratio of the overall shift variation (±0.20 p.p.m.) and the experimental error of the measurements (±0.05 p.p.m.) a corresponding correlation analysis has not been performed for the *meta*-carbon shifts. The ^{13}C chemical shifts of the allenic α-carbon atoms could not be analysed in terms of equation (2). Seven substituents (Ph, Me, MeO, Cl, I, CO_2H, CN) were selected as the basis set for the d.s.p. analyses. Parameter values from ref. 2 were employed. The hydrogen atom as a substituent is omitted because in the allenes a hydrogen ligand generates the particular CH_2 arrangement which induces CH_2 hyperconjugation. Hence, hydrogen in that special bonding situation acts as a substituent to which a (hitherto unknown) non-zero resonance substituent constant could be attributed [*i.e.* $\sigma_R(H^\pi) \neq 0$ for π-type hyperconjugation and otherwise $\sigma_R(H) = 0$]. Consequently, as one cannot use the parent hydrocarbon (1) as a reference point for the substituent effects the particular form (2) of the regression equation with an intercept term $\delta^\circ_{C\text{-}k}$ has been used.

$$\delta_{C\text{-}k} = \delta^\circ_{C\text{-}k} + \rho_I\sigma_I + \rho_R\sigma_R \qquad (2)$$

At this time an inherent problem in d.s.p. analyses of molecular properties of allenes is that there are not enough data available to determine a ' best ' set of substituent constants (σ_I, σ_R) for groups with conformational flexibility, such as MeO or CO_2H.[2] Therefore, in correlation analyses it is difficult to decide whether deviations of data points for such groups from otherwise near perfect straight lines indicate the neglect of an important factor, the erroneous assumption that a particular factor is significant, or simply an unfavourable selection of numerical values of the input data (*i.e.* the substituent constants).

Furthermore, in the weak protic solvent $CDCl_3$ complications may arise through hydrogen bond interactions between certain groups and the solvent. Such interactions (possibly also accompanied by conformational effects) may lead to non-negligible solvent dependences of σ_I for particular groups, such as MeO, CO_2H, and CN.[7e,16c,d] For these reasons d.s.p. analyses of ^{13}C chemical shifts of phenylallenes with a fit parameter f (*cf.* Table 2) < 0.1 are regarded as good and ones with f < 0.2 as fair.[17b] Correlations were done for each of the four resonance scales (σ_R^-, σ_R°, σ_R^{BA}, σ_R^+).[16] For each atom the σ_R^- series of substituent constants has turned out to yield the highest correlation coefficients and lowest standard deviations (best fits).

Table 2. Fit parameters of d.s.p. equations (2) for phenyl and allenic carbon chemical shifts of γ-substituted phenylallenes

Carbon atom	$\delta^\circ_{C\text{-}k}$	ρ_I	ρ_R [a]	λ [b]	f [c]
C-*p*	127.01	+3.32	+0.22	+0.07	0.19
C-*o*	126.86	+1.74	+0.06	+0.04	0.18
C-*i*	134.17	−5.80	−1.46	+0.25	0.18
C-β	207.67	+1.27	+26.56	+20.99	0.05

[a] In all cases correlations refer to the σ_R^- series of substituent constants. [b] $\lambda \equiv \rho_R/\rho_I$. [c] The fit parameter $f \equiv$ s.d./r.m.s. where s.d. is the standard deviation of the fit and r.m.s. the root mean square of the data.

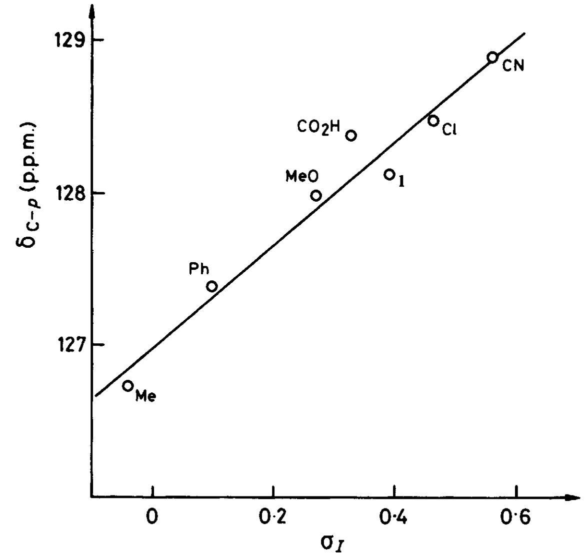
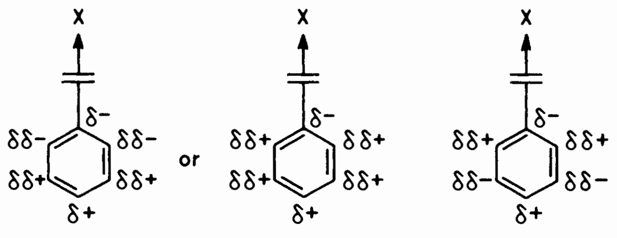


Figure 4. Correlation of the *para*-carbon chemical shifts of γ-substituted phenylallenes and the polar substituent constants

The results of the d.s.p. analyses for the allenic and the aromatic carbon atoms are summarized in Table 2. The quality of the correlations is good for the allenic central atom (C-β) and fair for the phenyl carbon atoms.

For all correlations the intercept term $\delta^\circ_{C\text{-}k}$ is close to the experimental chemical shift of (2), *i.e.* (2) represents an adequate reference point for the discussion of substituent effects as may be anticipated from its symmetrical structure. The allenic central atom is almost entirely affected by resonance substituent effects. For the phenyl carbon atoms it is seen that the *ipso*-atom (C-*i*) contains a small, but distinct resonance contribution. It is, however, influenced to a large extent inductively. The *ortho*- and *para*-carbon chemical shifts are also mainly inductively affected. But in these cases resonance interactions are negligible. If, in particular, $\delta_{C\text{-}p}$ is plotted *versus* only the polar substituent constant σ_I a good linear correlation (3) (*r* 0.9781) is obtained (Figure 4). This means that for the *para*-carbon resonances one substituent

$$\delta_{C\text{-}p} = 126.98 + 3.40\,\sigma_I \qquad (3)$$



(D) (E) (F)

I_{π}^{F} -effect I_{π}^{O} -effect

constant suffices to account for the observed effects and in the corresponding d.s.p. equation for $\delta_{C\text{-}p}$ (Table 2) the inclusion of the second substituent constant ($\sigma_R{}^-$) probably only spreads the deviations for CO_2H and I over all other substituents.

The inductive component of substituent effects. Inductive effects are defined as all those which contribute to the σ_I term of a d.s.p. equation through bond or through space. As the σ-inductive effect [13,15] of a substituent X is only important for neighbour and nearest-neighbour carbon atoms [13,15] the inductive effects operating at the phenyl site can only be induced by the action of the group X dipole moments μ(X) through the space of the molecular cavity (π-inductive effects).[13,15] For unsaturated molecules there are two mechanisms which are discussed under the heading of π-inductive effects.[13,15,17] First, a π-system may be polarized by a through-space electrostatic charge density attraction (or repulsion) of a remote (point) charge or dipole ($I_\pi{}^F$-effect, π-polarization). Such a field-induced (geometry-dependent) disturbance would affect all the positions in the π-system, however, to different extents. The polarization is towards the positions nearest to the charge or dipole [as in (D) [13a] or (E) [13b]].

A second mechanism affects all the individual positions to a comparable extent leading to an alternating polarization of the π-system [as represented in (F)]. This effect may be explained in terms of quantum-chemical perturbation theory as a mixing of various orbitals of corresponding symmetry under the disturbing influence of a substituent X ($I_\pi{}^{\circ}$-effect, π-orbital effect).[13,15] The essential difference between the two effects would be represented by the magnitudes of the charge density reorganisations at the *ortho-* and *meta-*positions.

In case of the phenylallenes the polarization diagram (C) and the very small ^{13}C chemical shift variations of the *meta*-atoms do not give conclusive evidence in favour of one of the two π-inductive effects. In order to evaluate the role of the $I_\pi{}^{\circ}$-effect for allenes adequately, however, one must take into account that, owing to a (at least partial) breakdown of the $\pi - \sigma - (\pi, \bar{\pi})$ separability in 1,3-disubstituted allenes,[2,5] for allenes the $I_\pi{}^{\circ}$-effect may represent an effect which is different from that discussed for planar unsaturated π-systems. For these last systems the $I_\pi{}^{\circ}$-effect is generally thought to result from a mixing of occupied and unoccupied orbitals of corresponding symmetries, for instance π,π^* (HOMO − LUMO) mixing.[13,15] As in γ-substituted phenylallenes the occupied (or unoccupied) π and $\bar{\pi}$ orbitals are energetically more close lying than the occupied π and unoccupied π^* (or $\bar{\pi}$ and $\bar{\pi}^*$) orbitals, $\pi,\bar{\pi}$ (and π^*, $\bar{\pi}^*$) orbital mixings are more favourable than π, π^* and $\bar{\pi}, \bar{\pi}^*$ mixings.[5] In this way all the resulting orbitals in PhHC=C=CHX would cover the whole molecular systems (Figure 5) and electron delocalization between the Ph and X sites would be possible, for instance, *via* electron exchange.

Owing to its C_2 rotational symmetry such a $\pi,\bar{\pi}$ mixing is perfect in 1,3-diphenylallene (2),[5] whereas in phenylallene (1) of symmetry C_s there is a strict separation of π and $\bar{\pi}(\sigma)$ orbitals (Figure 1). If in the phenylallenes (3)—(9) $\pi,\bar{\pi}$ mixings were significant, electron delocalization effects should influence the ^{13}C resonances of all the aromatic nuclei to a comparable extent. From the results of the d.s.p. analyses in Table 2 [and equation (3)], however, one can see that this is not the case. One, therefore, may infer that for the ground-state electron density distributions of γ-substituted phenylallenes the $I_\pi{}^{\circ}$-effect can only play a minor role and that the inductive component of the substituent effects on the aromatic ^{13}C chemical shifts is essentially a polarization ($I_\pi{}^F$-effect). This also means that the substituent effects may be discussed to a good approximation separately for the π and $\bar{\pi}$ electronic subsystems of the allenes and that the notion of π-polarization remains meaningful.

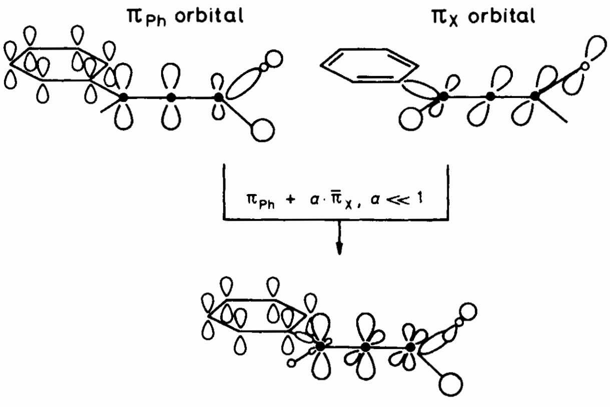


Figure 5. Mixing of π and $\bar{\pi}$ orbital subsystems in γ-substituted phenylallenes PhHC=C=CHX (● = C, ○ = X)

The effect of π-induction on the carbon chemical shifts at the *para*-site is directly seen from the linear correlation (4)

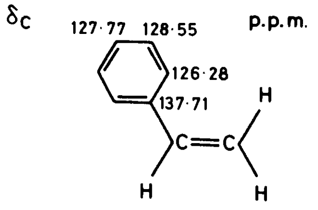
$$\delta_{C\text{-}p} = 127.32 + 0.43\ \mu(X) \qquad (4)$$

(r 0.9193) between the *para*-carbon resonances and the group dipole moments μ(X) (using the basis set of seven substituents and data from ref. 2). Correlation (4) is considerably improved if the acceptors CO_2H and CN, which both have large dipole moments, are omitted [using X = Me, Ph, MeO, Cl, and I one finds $\delta_{C\text{-}p} = 127.13 + 0.74\ \mu(X)$ (r = 0.9843)]. As is found for $\delta_{C\text{-}p}$ electric group dipole moments have also been shown to be the origins of substituent effects in allenes in case of orbital (ionization) energies.[2,3b]

Equation (4) is in line with the D_{2d} model of allenes [2] which, for the particular situation, uses a fixed origin for all the various group dipole moments μ(X) and also fixed orientations for all the μ(X).[2,3b] In the framework of this model the linear electric field (l.e.f.) effect ($\delta_C = A \cdot E_z$) [18] on the carbon atom resonances of γ-substituted phenylallenes can only be determined by the magnitudes of the group dipoles as the variations of the field do not exhibit any angle or distance dependences [$E_z \sim \mu(X)$].

As the groups showing larger deviations from correlation (4) in the same directions generate the stronger electric fields, one may suppose that the variations of the *para*-carbon chemical shifts should, in general, involve a term of higher order in the electric field, *i.e.* in the group dipole moment. Indeed, taking a term quadratic in the electric field **E** into account (and using the basis set of seven substituents) one obtains a fair correlation (5) (R^2 0.9735).

$$\delta_{C\text{-}p} = 127.16 + 0.84\ \mu(X) - 0.10\ |\mu(X)|^2 \qquad (5)$$



(12)

Generally it is assumed[18] that an electric field **E** exerts essentially a linear effect on the ^{13}C nuclear shielding σ (or chemical shift δ_C, respectively) of unsaturated systems. Our results, however, indicate that a change of σ quadratic in E exists. This would be in agreement with the general theory of the variations of magnetic shieldings with electric fields $[(\sigma)_E = -A\cdot E_z - B\cdot \mathbf{E}^2]$.[19]

The delocalization component of substituent effects. The d.s.p. analyses of the carbon chemical shifts (Table 2) indicate a localization of substituent resonance effects in the allenic moiety. The allenic central atom (C-β) is almost entirely affected by substituent resonance contributions, as has also been observed for the ^{13}C chemical shifts of monosubstituted allenes.[2] The resonance effects on $\delta_{C\text{-}\beta}$ result from the ' normal ' π conjugation of the allenic and the substituent X π group orbitals (which are denoted $\bar{\pi}$ orbitals in the phenylallenes).

For the aromatic carbon atoms only the ^{13}C resonances of the *ipso*-atoms (C-*i*) are affected significantly by delocalization effects. As $\pi,\bar{\pi}$ mixing as an essential mode for electron delocalization and charge transfer has been ruled out, resonance interactions in γ-substituted phenylallenes should involve π-type or $\bar{\pi}$-type hyperconjugations, or both (Figure 1).

If π-type hyperconjugations were relevant, one would expect that the substituent conjugative effect is transmitted to the *ipso*-, *ortho*-, and *para*-carbons to a comparable extent. In particular, in case of π-hyperconjugation C-*p* as the terminal atom of a conjugated system should be influenced markedly by resonance interactions. As the polarization effect decreases with increasing distances between the site X and the particular aromatic carbon atom (which tends to increase $\lambda_{C\text{-}p}$) one would estimate the λ-values for C-*p* and C-*i* to be similar if π-hyperconjugation is operative. Therefore, the data in Table 2 suggest that for the aromatic carbon chemical shifts, except X = H, π-type hyperconjugation can only play a minor role and that the substituent resonance effect observed for the carbon shifts of the *ipso*-atoms results mainly from $\bar{\pi}$-type hyperconjugation.

A further hint that the *ipso*-atom is involved in a special electronic situation in phenylallenes comes from comparisons of the ^{13}C chemical shifts of phenylallene (1) and styrene (12). The similar ^{13}C resonances for the *ortho*-, *meta*-, and *para*-carbon atoms in (1) and (12), but the marked downfield shift of the *ipso*-atom in (12) relative to that in (1) suggests that in (1) the *ipso*-atom gains electron density from the attached group through a special mechanism. According to our analysis this mechanism is essentially $\bar{\pi}$-type hyperconjugation. It must be admitted, however, that in the particular case of phenylallene (1) the CH$_2$ moiety may also exert a π-type hyperconjugative effect on $\delta_{C\text{-}i}$. From the *para*-carbon atom chemical shifts of (1) and (12) one may estimate that CH$_2$ hyperconjugation induces a shift of no more than 1.2 p.p.m., *i.e.* CH$_2$ hyperconjugation can account for only *ca.* 30% of the shift difference observed for C-*i* in (1) and (12).

Table 3. CNDO/S total electron densities of phenylallenes PhHC=C=CHX (in e) [a,b]

	Compound		
$P_{C\text{-}k}$	(1)	(2)	(3)
C-1	3.9703 (+24)	3.9679 (0)	3.9697 (+18)
C-2	4.0267 (−34)	4.0301 (0)	4.0297 (−4)
C-3	4.0125 (−5)	4.0130 (0)	4.0132 (+2)
C-4	4.0237 (−10)	4.0247 (0)	4.0263 (+16)
C-5	4.0121 (−8)	4.0129 (0)	4.0128 (−1)
C-6	4.0276 (−12)	4.0284 (0)	4.0293 (+9)
$\Sigma P_{C\text{-}k}$	24.0729 (−41)	24.0770 (0)	24.0810 (+40)
C-α	4.0565 (−64)	4.0629 (0)	4.0676 (+47)
C-β	3.9358 (−8)	3.9366 (0)	3.9561 (+195)
C-γ	4.1129 (+50)	4.0629 (0)	4.0659 (+30)
$P_{C\text{-}k}$	(4)	(5) [c]	(5a) [d]
C-1	3.9710 (+31)	3.9699 (+20)	3.9538 (−141)
C-2	4.0311 (+10)	4.0255 (−46)	4.0396 (+95)
C-3	4.0140 (+10)	4.0123 (−7)	3.9996 (−134)
C-4	4.0269 (+22)	4.0210 (−37)	4.0334 (+87)
C-5	4.0136 (+7)	4.0125 (−4)	3.9997 (−132)
C-6	4.0290 (+6)	4.0253 (−31)	4.0405 (+121)
$\Sigma_{C\text{-}k}$	24.0856 (+86)	24.0665 (−105)	24.0666 (−104)
C-α	4.0673 (+44)	4.0417 (−212)	4.0533 (−96)
C-β	3.9862 (+496)	3.9344 (−22)	3.9236 (−130)
C-γ	3.9568 (−1 061)	4.0467 (−162)	4.0533 (−96)
$P_{C\text{-}k}$	(8) [e]	(8c) [f]	(9)
C-1	3.9718 (+39)	3.9705 (+26)	3.9720 (+41)
C-2	4.0233 (−74)	4.0208 (−93)	4.0225 (−76)
C-3	4.0108 (−22)	4.0112 (−18)	4.0109 (−21)
C-4	4.0181 (−66)	4.0178 (−69)	4.0174 (−73)
C-5	4.0114 (−15)	4.0119 (−10)	4.0115 (−14)
C-6	4.0230 (−54)	4.0217 (−67)	4.0223 (−61)
$\Sigma P_{C\text{-}k}$	24.0584 (−186)	24.0539 (−231)	24.0566 (−204)
C-α	4.0350 (−279)	4.0261 (−368)	4.0318 (−311)
C-β	3.9118 (−248)	3.9003 (−363)	3.9131 (−235)
C-γ	4.0734 (+105)	4.0786 (+157)	4.0580 (−49)

[a] Values in parentheses give excess charges of the molecule (*j*) relative to (2) $[P_{C\text{-}k}(j) - P_{C\text{-}k}(2)]$ or $[\Sigma P_{C\text{-}k}(j) - \Sigma P_{C\text{-}k}(2)]$ in 10^{-4} e (see Introduction for the numbering of the aromatic carbon atoms). [b] The electron densities of the aromatic hydrogen atoms remain almost constant. [c] Including *d*-atomic orbitals. [d] Without *d*-atomic orbitals. [e] *s-trans* conformation. [f] *s-cis* conformation.

$\bar{\pi}$-Hyperconjugation in phenylallene (1) would also account for the destabilization of the highest occupied $\bar{\pi}(a')$ orbital of (1) relative to the corresponding orbitals in allene (H$_2$C=C=CH$_2$) or methylallene (MeHC=C=CH$_2$), respectively, as is observed in the p.e. spectrum of (1).[2,3a]

Final support of our analysis comes from the inspections of the LCAO expansions of the CNDO/S MOs of the phenylallenes. They reveal that in phenylallenes $\bar{\pi}$-hyperconjugation as visualized in Figure 1 is indeed operative.

(2) *Electron Densities.*—In order to inquire more quantitatively into the electron redistributions in phenylallenes, semiempirical CNDO/S calculations have been performed for selected compounds. The electron densities thus obtained are comparable to those of common *ab initio* procedures as CNDO/S electron densities correlate with *ab initio* STO-3G gross atomic populations.[2] Owing to the partial breakdown of the $\pi - \sigma$ separabilities in (2)—(9) the discussion will refer only to total electron densities (π electron densities are not strictly defined).

Results of the CNDO/S calculations concerning electron

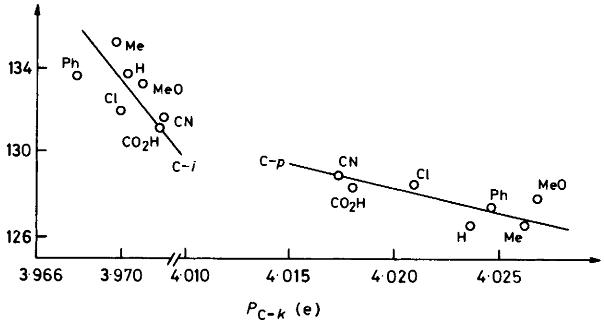


Figure 6. Plots of carbon chemical shifts of aromatic carbon atoms of γ-substituted phenylallenes *versus* their CNDO/S total electron densities

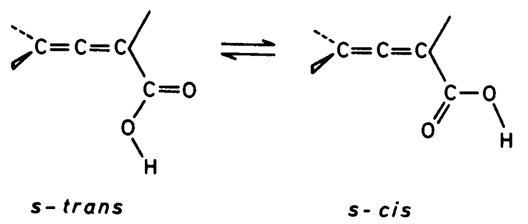


Table 4. Fit parameters of d.s.p. equations (5) for phenyl and allenic CNDO/S total electron densities of γ-substituted phenylallenes

Carbon atom	$P_{C\text{-}k}{}^{\circ}$	ρ_I	ρ_R [a]	λ [b]	f [b]
C-2	4.0288	−0.0102	−0.0104	+1.02	0.10
C-4	4.0244	−0.0115	−0.0117	+1.02	0.10
C-6	4.0280	−0.0094	−0.0080	+0.85	0.06
C-α	4.0617	−0.0526	−0.0392	+0.75	0.09
C-β	3.9382	−0.0353	−0.1067	+3.03	0.13
$\Sigma P_{C\text{-}k}$	24.0756	−0.0308	−0.0365	+1.19	0.08

[a] In all cases correlations refer to the $\sigma_R{}^{\circ}$ series of substituent constants. [b] *Cf.* Table 2.

densities together with the sum $\Sigma P_{C\text{-}k}$ of the electron densities of the phenyl carbon atoms (which represents the charge transfer between the Ph and X sites) are given in Table 3. For the electron densities one observes substituent effects on all the six non-equivalent phenyl carbon atoms, contrary to the ^{13}C chemical shifts. Concerning the phenyl ring by far the largest variations are observed for the charge transfer term $\Sigma P_{C\ k}$ (290×10^{-4} e). Much smaller effects are found for the changes in electron density of the individual phenyl carbon atoms, for C-*p* 95×10^{-4} e, C-*o* 86×10^{-4} e, C-*m* 32×10^{-4} e, and for C-*i* 41×10^{-4} e. Notably, the differences in electron densities of the non-equivalent *ortho*-(2,6) and *meta*-(3,5) atoms may be as large as 21×10^{-4} e [for (4)] and 6×10^{-4} e [for (8), (9)], respectively.

For the allenic carbon atoms far larger electron density changes are found, for C-α $1\,561 \times 10^{-4}$ e, C-β 744×10^{-4} e, and for C-γ 358×10^{-4} e. The allenic central atom (C-β) exhibits a fair chemical shift–electron density correlation (6) (r — 0.9251). From this correlation one may infer that for an

$$\delta_{C\text{-}\beta} = 1314.45 - 280.91\ P_{C\text{-}\beta} \qquad (6)$$

adequate description of the electron density distributions in phenylallenes for second-row atoms *d*-AOs have to be included into the quantum-chemical calculations. If, for instance, chlorine *d*-AOs are neglected, the electron densities of γ-chlorophenylallene (5a) deviate seriously from correlation (6). The necessity to include *d*-AOs for second-row atoms has also been observed for other eigenfunction-related properties of allenes, such as dipole moments.[2,20]

The *para*-carbon electron densities $P_{C\text{-}p}$ seem to be determined to a large extent by charge transfer effects as $P_{C\text{-}p}$ exhibits an excellent correlation (7) (r 0.9968) with the charge transfer term $\Sigma P_{C\text{-}k}$. As, on the other hand, the *para*-carbon chemical shifts $\delta_{C\text{-}p}$ are affected only by π-polarization [equation (3)] there cannot be expected to exist a direct proportionality between chemical shifts $\delta_{C\text{-}p}$ and electron density changes $P_{C\text{-}p}$. Hence, if the *para*-, but also the *ipso*-carbon chemical shifts of the phenylallenes are plotted against the electron densities very crude ^{13}C-resonance–electron density

$$P_{C\text{-}p} = 0.3413\ \Sigma P_{C\text{-}k} - 4.1926 \qquad (7)$$

correlations are observed (Figure 6). This result is contrary to common views that there are close relationships between ^{13}C resonances and charge densities at least for the phenyl *para*-carbon site.[6]

With respect to the transmissions of substituent effects across the allenic system the most important result of the CNDO/S-calculations is the support of the polarization mechanism (through space). Such a mechanism requires that in the phenyl ring, all other effects being equal, through inductive withdrawal of electron density towards the *ipso*-atom the *ortho*-atom C-2 should be more negative than the *ortho*-atom C-6, as C-2 is closer to the substituent's group moment. Except X = H this is observed throughout in the data of Table 3 [disregarding (5a) and (8c)]. For the *meta*-atom electron densities, however, no consistent trend for the substituent effect is observed. The relevance of the polarization mechanism may also be demonstrated by a study of the conformational effect of the carboxy-group in (8). This group may achieve a (locally planar) *s-trans*- (8) or *s-cis*-conformation (8c). In general, the *s-trans*-form (8) is largely preferred[21] and, therefore, comparisons between carbon chemical shifts and electron densities have referred only to this form.

Used as a model for studying the influence of polarization for the electron density distribution in the aromatic ring the conformational effects of the carboxy-group are to be associated with different group dipole moments (μ *ca.* 2.5 D for *s-trans*, μ *ca.* 1.8 D for *s-cis*).[2,20] If polarization (*via* the action of the group moment) makes an essential contribution to the overall substituent effect the *para*- and *meta*-atoms in (8) should be more positive than those in (8c) and the *ipso*- and probably also the *ortho*-atoms should be more negative in (8) than in (8c). This is quantitatively confirmed by the data in Table 3 (except for C-*p* where only small differences between the electron densities are observed).

In order to assess the relative contributions of inductive and charge-transfer effects to the electron density distributions in the phenylallenes, d.s.p. analyses (8) [using data for (2)—(5), (8), (9)] have been performed for the allenic α- and β-atoms as well as the *ortho*- and *para*-phenyl carbon atoms. For the other atoms no statistically significant relationships have been obtained. The results of the d.s.p. analyses are given in Table 4.

$$P_{C\text{-}k} = P_{C\text{-}k}{}^{\circ} + \rho_I\sigma_I + \rho_R\sigma_R \qquad (8)$$

Throughout the $\sigma_R{}^{\circ}$ series of resonance, substituent constants gives the best results.

With the exception of the allenic central atom C-β in all

$H_2C=C=CHCO_2Me$

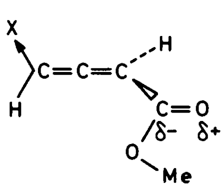
δ_{CO} (13) 165·98 (p.p.m.)

$MeO_2CHC=C=CHCO_2Me$

(14) 163·78

$EtMeC=C=CHCO_2Me$

(15) 167·41



cases the electron densities are affected by polar and resonance effects to a comparable extent. It is noteworthy that also the charge transfer $\Sigma P_{C\text{-}k}$ is influenced comparably by inductive and resonance effects. In monosubstituted benzenes with the ligands directly attached to the aromatic ring the overall charge transfer is dependent almost entirely on $\sigma_R°$.[15a] In ethylenes σ_I contributes 30% to the overall π charge transfer ($\Sigma q_\pi \sim \sigma_R° - 0.32\sigma_I$).[17b]

According to the previous arguments the significant resonance contributions to the electron density redistributions at the *ortho*- and the *para*-positions should come essentially from π-type hyperconjugations. In relation to the d.s.p. results for the carbon chemical shifts the observations with the electron densities suggest the following interpretation. In γ-substituted phenylallenes π-type hyperconjugation affects the electron density distribution of the phenyl ring significantly. This is directly seen from the LCAO expansions of the CNDO/S MOs of the molecules. This means that for eigenfunction-oriented data (electron densities) π-type hyperconjugations play a distinct, non-negligible role. Eigenvalue-oriented data (expectation values of certain operators calculated with the particular eigenfunctions), however, are not necessarily affected in the same way by π-type hyperconjugations. Therefore, depending upon the properties Q_i under investigation, studies of substituent effects in allenes may give widely varying contributions of substituents' inductive and resonance effects, and care is needed if the results are interpreted separately (without discussing relationships between the various properties Q_i) in terms of interactions between sites or in terms of electronic structures of allenes. Qualitative similar problems are encountered, for instance, in the question of the inclusion or neglection of 3*d* AOs of second-row atoms in the discussions or calculations of different molecular properties of allenes, such as dipole moments *versus* orbital energies [2,3b,20] or excitation energies.[1,3b]

Conclusions.—The investigations of ^{13}C-chemical shifts and electron density distributions in γ-substituted phenylallenes have revealed that in allenes the remote molecular unit is significantly influenced by the substituents' group dipole moments, *i.e.* for substituted allenes there is an intrinsic substituent effect operating through space. Through bond substituent effects across the allenic system, which have also been observed, may operate by different types of overlap-dependent interactions separately in either the π or $\bar{\pi}$ orbital subsystems of the molecules (π-type hyperconjugation *versus* $\bar{\pi}$-type hyperconjugation). In phenylallenes both types of hyperconjugations are relevant. Furthermore, in the ground-states of phenylallenes mixing of the π and $\bar{\pi}$ orbitals seems to be small or even negligible. Therefore, this work has demonstrated, at least for the interpretations of spectroscopic properties and electron density distributions, that the widely used model of allenes which decomposes the molecules into two isolated ethylene subunits is not adequate.

Similar effects as in phenylallenes are expected to be found in allenes having other polarizable groups, such as the carboxy- or methoxycarbonyl groups. Indeed, in allenecarboxylic acid esters (13),[22] (14),[9] and (15) [23] inductively electron withdrawing groups make the carboxy-carbon more negative than in the parent compound and, hence, lead to upfield ^{13}C chemical shifts, whereas inductively electron releasing groups make the CO carbon more positive, leading to downfield ^{13}C shifts, as in (15).

Acknowledgements

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