The Whiffen effect of symmetry-enhanced and symmetry-forbidden hyperconjugation in spin-paired molecules

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In the EPR spectroscopy of organic radicals, the Whiffen effect describes the way in which the hyperconjugative β-proton coupling of an H–C σ-bond in a cyclic radical can be enhanced or forbidden according to the symmetry of the π-orbital with which it hyperconjugates. This principle of the symmetry-control of hyperconjugation has been largely ignored in the context of spin-paired molecules. It is examined here as it applies to H–C and M–C (M = metal) hyperconjugation in spin-paired carbocations and neutral molecules, where the effect shows up principally in relative isomer stabilities, in bond lengths and angles, and in one-bond NMR coupling constants.

Systems in which the effect has important consequences include the Wheland intermediates of electrophilic aromatic substitution, the loose complexes formed between metal cations and arenes, and η^1-cyclopentadienylmetal compounds.

Introduction

The proton hyperfine coupling in the EPR spectrum of an organic radical provides a measure of the interaction of the spin of the unpaired electron with the protons in the locality of the electron, and the coupling constant to Hβ gives a quantitative measure of H–C hyperconjugation. The magnitudes of the coupling constants can be predicted according to well-established rules, but when the spectrum of the cyclohexadienyl radical was first recorded, the hyperconjugative β-coupling was found to be double the expected value.[1,2] This enhancement (or cancellation) of the β-coupling is commonly called the Whiffen effect after D.H. Whiffen who, in 1963, provided the interpretation: in a cyclic π-conjugated radical, hyperconjugation can be enhanced or forbidden depending on the symmetry of the SOMO.[3]

This phenomenon is well recognised in free radical chemistry, but it has been largely ignored in the context of spin-paired molecules where it should be equally relevant. The purpose of this article is to survey the consequences of the phenomenon of symmetry-control of hyperconjugation in spin-paired systems, and to draw attention to the circumstances where it can be important.

In the following sections, relevant aspects of H–C and M–C (M = metal) hyperconjugation in radicals and spin-paired molecules are briefly reviewed. The Whiffen effect in EPR spectroscopy is outlined, then examples are presented from the literature for the operation of the effect, and for its consequences, in spin-paired systems.

Carbon–hydrogen and carbon–metal hyperconjugation

Hyperconjugation in an alkyl radical can be described by the valence bond representation **1**. It involves interaction of the σ H–C bond with the singly occupied 2p orbital (**2**), and is the major factor which gives rise to hyperfine coupling by
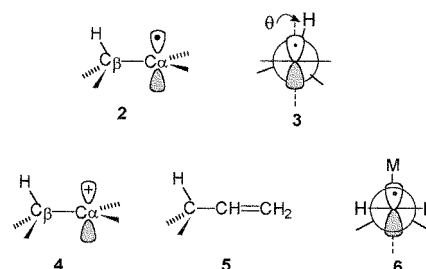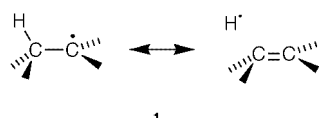
β-protons in the EPR spectra. This β-coupling is described by the Heller–McConnell equation [eqn. (1)].[4,5]

$$a_{H\beta} = \rho_{C\alpha}(A + B\cos^2\theta) = c_\alpha^2(A + B\cos^2\theta) \qquad (1)$$

The term $\rho_{C\alpha}$ represents the unpaired π-electron spin density at Cα, which is equal to the square of the linear combination of atomic orbitals (LCAO) coefficient c_α, and θ is the dihedral angle between the axis of the singly occupied 2p orbital and the C_β–H bond (**3**). The term A is small (*ca.* 1 G) and is often neglected, and relates to transmission of the spin through the intervening bonds, and B, the dominant term (*ca.* 60 G in a neutral radical), arises from hyperconjugation.

Similar H–C hyperconjugation occurs, and more strongly, in alkyl cations (**4**), but it is usually accepted to be negligible where the p orbital is part of an uncharged olefinic π-system as in propene (**5**).[6]

Hyperconjugation by a metal–carbon bond, M–C (M = *e.g.* R₃Si, R₃Ge, R₃Sn, R₃Pb, RHg) is more effective than by H–C.[7–10] In radicals it imparts a special stability to the β-metalloalkyl radicals and gives rise to a barrier to rotation about the C_α–C_β bond (**6**).[11] It is a lot more effective in stabilising β-metalloalkyl cations,[12–14] and hyperconjugative interaction in the eclipsed form of the β-silylethyl cation is calculated to confer a stabilisation of *ca.* 121 kJ mol⁻¹.[13,15,16] This substantial stability which hyperconjugation confers on cationic intermediates makes it important in the use of vinyl-, allyl- and aryl-metallic compounds, particularly silanes[17–20] and stannanes,[21] in organic synthesis, and under favourable circumstances hyperconjugative activation by an Sn–C bond can accelerate a reaction by a factor of >10¹⁴.[15,22] Symmetry-control of hyperconjugation therefore can be an important

factor in determining structure, molecular physical properties and reactivity in organic cations, radicals and radical ions, and in organometallic compounds.

The effect of carbon–metal σ–π* hyperconjugation can be detected even in neutral spin-paired molecules such as allyl- or cyclopentadienyl-metal compounds, where there is a better match between the energies of the σ and π orbitals than in the hydrocarbon systems. For example, allylstannanes are most stable in the conformation where the M–C bond eclipses the π-orbital (7), and this hyperconjugation is reflected in the photoelectron spectra.[23]
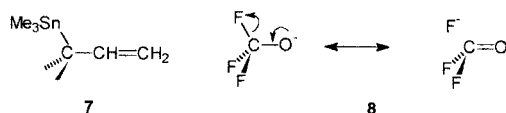
The phenomenon of negative hyperconjugation is also recognised, in which a vacant σ* orbital interacts with an occupied π orbital; a simple example is provided by the trifluoromethoxy anion 8.[24,25]

### The Whiffen effect in the EPR spectra of radicals

The Whiffen effect in the EPR spectra of radicals or radical ions relates to the situation (9) where the C–H bond is flanked by p-orbitals which form the ends of a singly-occupied π-MO.
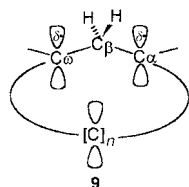
Whiffen showed that the hyperfine coupling is now described by the modified Heller–McConnell equation [eqn. (2)].[3]

$$a_{H\beta} = (c_\alpha + c_\omega)^2 (A + B \cos^2 \theta) \qquad (2)$$

If c_α and c_ω have the same sign and magnitude, as they have in the cyclohexadienyl radical 10, the spin density term when the
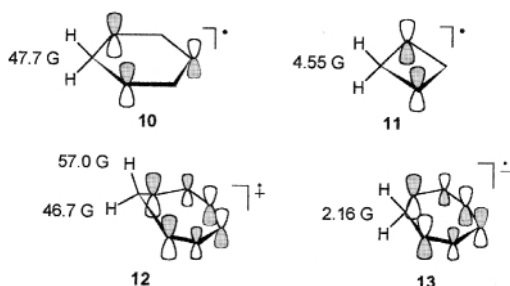
two act in concert ($c_\alpha^2 + c_\omega^2 + 2c_\alpha c_\omega$) is twice what it would be if they acted independently ($c_\alpha^2 + c_\omega^2$), and the hyperfine coupling is double what would otherwise be expected. If c_α and c_ω have opposite sign and magnitude, as in the cyclobutadienyl radical 11, the spin density term is zero, and the hyperfine coupling is negligible. Thus the observed values of $a_{H\beta}$ in 10 and 11 are 47.7 G [2] and 4.45 G [26] respectively, compared with predicted values, using the simple Heller–McConnell equation and ignoring the Whiffen effect, of *ca.* 28 G and *ca.* 42 G respectively. Similarly, in the cycloheptatrienyl radical cation 12, in which the SOMO is the symmetric MO ψ_3 (and the methylene protons are non-equivalent because the molecule is non-planar), $a_{H\beta}$ has the values of 46.7 and 57.0 G,[27] whereas in the corresponding radical anion 13, where the SOMO is the antisymmetric MO ψ_4, $a_{H\beta}$ is 2.16 G.[28] It is possible that orbital overlap between C(1) and C(6) may give 12 some degree of homoaromatic character,

but this will not change the symmetry of the SOMO, and the argument in favour of symmetry-enhanced hyperconjugation still holds. In 12, the positive charge has the effect of increasing the value of *B* in eqn. (2).

If a CH group is bonded to three carbon atoms, Cα, Cμ and Cω which form part of a π-SOMO, the spin density term c_α^2 in eqn. (1) is replaced by $(c_\alpha + c_\mu + c_\omega)^2$ with the appropriate signs for the coefficients. An important example of such a system is the radical HC$_{60}$·, shown in part in 14, which is obtained by
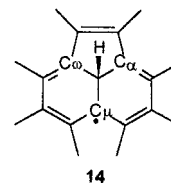

adding a hydrogen atom to C$_{60}$, when about two thirds of the unpaired electron spin is located on the Cα, Cμ and Cω atoms; $a(H)$ is 33.07 G, the value of θ for all three p atomic orbitals is zero, and c_α, c_μ and c_ω all have the same sign, but interpretation in terms of the Whiffen effect is complicated by the curvature of the surface of the π-system which reduces the orbital overlap.[29]

Many further examples of the operation of the Whiffen effects are to be found in the EPR spectra of radicals and radical ions.[30] These are the effects which we will refer to as symmetry-enhanced (*e.g.* 10 and 12) and symmetry-forbidden (*e.g.* 11 and 13) hyperconjugation. If c_α and c_ω have opposite signs but different magnitudes, the hyperconjugation will be symmetry-reduced but not forbidden.

Symmetry-control of hyperconjugation in spin-paired neutral molecules and ions

Spin-paired cyclic neutral molecules and ions should be subject to symmetry-control of hyperconjugation in the same way as radicals, but in the literature we can find only a few papers in which it has been explicity recognised that hyperconjugation is zero when a CH group lies in the nodal plane of an MO (*e.g.* refs. 31–34), and none that hyperconjugation can be symmetry enhanced. The effect should be stronger when M–C rather than H–C bonds are involved, it should increase down the series Si < Ge < Sn < Pb, Hg, and it should be stronger in cations than in neutral molecules.

Hyperconjugation has the effect of changing bond orders (*e.g.* 15a and b), and this shows up particularly in measurements
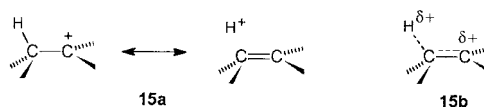
of bond lengths and angles, ^1J NMR coupling constants, NMR chemical shifts, and vibrational frequencies. These criteria however are not as quantitative as that of EPR spectroscopy, and it is often difficult to decide what value of a particular property corresponds to normal hyperconjugation, and what to symmetry-enhanced or symmetry-forbidden hyperconjugation.

A second difficulty is that the effect of symmetry-control is to be sought in cyclic systems, which may be subject to ring strain or homoaromaticity which can itself have an important effect on these properties. The most convincing demonstration of the effect might be found in the comparison between members of a family of closely related compounds, similar to 10 and 11, or 12 and 13 above, in which the interacting vacant π-orbital is symmetric or antisymmetric, respectively.

An important model is provided by Lambert and Singer's investigation of the NMR $^1J(M–C)$ and $^1J(C–C)$ values of a series of benzylmetallic compounds (16) in a search for

Me₃M ... CH₂—⟨benzene ring⟩—X ⟷ Me₃M⁺ ... CH₂=⟨ring⟩=—X

M = C, Si, Ge, Sn   X = NO₂, CN, H, Me, OMe

16
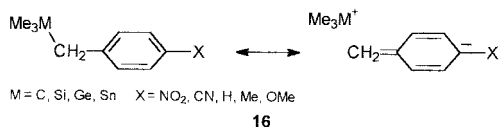
evidence of hyperconjugation in neutral organometallic compounds.[35]

They found that the value of ^1J(M–C) did correlate inversely with the ability of X to stabilise a negative charge (*e.g.* M = ^{119}Sn, X = OMe, 294 Hz; X = CN, 239 Hz), but the values of ^1J(H₂C–C) did not show the expected reverse effect.[36,37]

A second important model has been provided by Kelly,[38,39] who has used an interesting approach to the analysis of hyperconjugation in carbocations, H–C–C⁺, in which the NMR ^1J(H–C) coupling constant is broken down into two terms [eqn. (3)] similar to those in the Heller–McConnell equation [eqn. (1)].

$$\Delta^1 J = A - B \cos^2 \theta \qquad (3)$$

$\Delta^1 J$ Is the difference in ^1J(H–C) values between the carbocation H–C–C⁺ and the corresponding ketone, H–C–C=O; ketones were chosen as the standard because the geometry about the carbonyl carbon atom is similar to that about the carbocation centre. A Is the increment arising from the inductive effect on the H–C bond of the unit positive charge, B is the decrement due to weakening of the H–C bond by hyperconjugation, and θ, as in the Heller–McConnell equation, is the dihedral angle between the H–C σ-bond and the axis of the 2p orbital.

Within a limited number of corresponding cations and ketones, the values of A and B were found to be 22.5 Hz and 33.1 Hz respectively. This approach is particularly promising as it aims to provide, through ^1J(H–C) values, a quantitative measure of hyperconjugation similar to that which is available through EPR coupling constants, a(Hβ). One difficulty is that, in contrast to eqn. (1), the term A in eqn. (3) cannot be neglected, and the effects of the A and B terms may be difficult to distinguish.

## Organometallic neutral compounds

Electrically neutral allyltin and allylmercury compounds show evidence of hyperconjugation, and suitable cyclic compounds would be expected to show symmetry-enhanced or symmetry-forbidden hyperconjugation. In particular, the many η¹-cyclopentadienylmetal compounds which are known,[40] which have a symmetrical LUMO (**17**), should show symmetry-enhanced hyperconjugation.

17   **18**   **19**
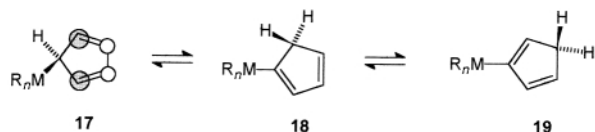
Cyclopentadienyl derivatives of the Group 14 metals are usually prepared as the 5-isomers **17**. The rapid metallotropic shift is degenerate, but the slower shift of hydrogen is non-degenerate, and gives in equilibrium the 1- and 2-isomers **18** and **19**. For example, when RₙM = Me₃Si, the ratio of **17**, **18** and **19** in the gas phase, at 63.2 °C, is 17.38 : 2.85 : 1.00.[41]

However, the metal–alkyl bonds are weaker than the metal–vinyl bonds (*e.g.* Me₃Sn–Me 297, Me₃Sn–Et 279, Me₃Sn–Prⁱ 261, Me₃Sn–CHCH₂ 327 kJ mol⁻¹): why then should the metal prefer the 5-position? The metal–carbon bonds are long and steric hindrance should not be important, and the principal factor which stabilises the structure **17** is probably symmetry-enhanced hyperconjugation.

The same argument can be used to account for the structure of bis(trimethylstannyl)dihydropentalene which is most stable as the isomer **20** in which the LUMO coefficients are as shown,

0·418   H   SnMe₃
0·521   0·521
H   0·418
SnMe₃   **20**
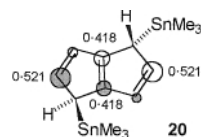
and which should be stabilised by enhanced hyperconjugation. The low value of ^1J(^{119}Sn–C) of 300 Hz, compared with 338 Hz in Me₃Sn–CH₃, is in accord with the hyperconjugative weakening of the Sn–C bond, as is the distortion of the 5-membered rings into an envelope conformation (X-ray diffraction) which favours the σ(Sn–C)–π* interaction.[42]

Ustynyuk's research group have studied the structure and fluxionality of dimetallated cyclopentadienes, C₅H₄(MMe₃)(M′Me₃) (M, M′ = Si, Si; Ge, Ge; Sn, Sn; Si, Sn; Ge, Sn) and C₅H₄(MMe₃)(M′Me₂) (M, M′ = Si, Sb; Sn, Sb), in which the rapid metallotropic shift is non-degenerate. The equilibrium position in all these compounds lies well to the side of the geminal 5,5-isomer; at −30 °C, *e.g.* **21**, M, M′ = Si, 95%, M,

21   **22**   **23**   **24**
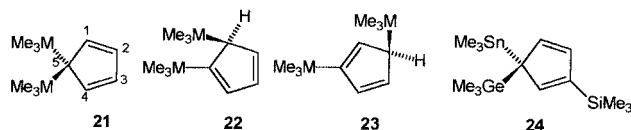
M′ = Ge, "almost completely", M, M′ = Sn, "only detectable isomer".[43] If one R₃M group moved to the 1- or 2-position to give **22** or **23**, the remaining group would be left in the nodal plane, and the (symmetry-enhanced) hyperconjugation would be halved. The situation is analogous to that in homolytic metal-for-metal aromatic substitution (*e.g.* Me₃Si for R₃Si) which similarly involves the geminal *ipso* intermediate for the same reason.[44]

With three different organometallic groups in the ring, they are arranged at equilibrium so that the the two heaviest metals occupy the 5-position (*e.g.* **24**), which maximises the enhanced hyperconjugation.[45]

This suggests a possible criterion for symmetry-control of hyperconjugation in vinylogues of cyclopentadienylmetallic compounds. If the LUMO is symmetric, a metallic substituent should be located preferentially at the methylene position to maximise hyperconjugation, but if the LUMO is antisymmetric the metal should be bonded to sp² carbon because the bond strength then would be greater and hyperconjugation would be symmetry-forbidden.

7-Triphenylstannylcycloheptatriene has an antisymmetric LUMO (**25**), with rapidly (degenerate) fluxional tin and more

25   **26**   **27**
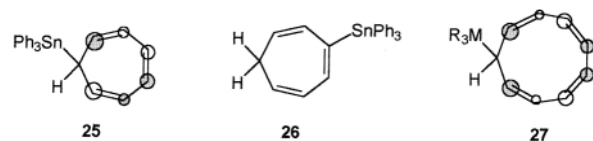
slowly (non-degenerate) fluxional hydrogen. At 160 °C it slowly rearranges to the 3-stannyl isomer **26** (together with Ph₃SnSnPh₃ and C₇H₇C₇H₇ as products of the thermal cleavage of the Sn–C bond).[46] This is consistent with the above criterion; it might be protested that the cycloheptadienyl ring is not planar,[47] but this does not appear to be important in the present context in the case of the cycloheptadiene radical cation **12** and anion **13**.

Cyclononatetraene has a symmetric LUMO (**27**). The trimethylsilyl and trimethylgermyl derivatives are prepared as the 9-metallo isomers **27** (R₃M = Me₃Si or Me₃Ge), but they

Table 1 Structures of η^1-cyclopentadienylmetal compounds[a]

Compound	$r(R_nM–Cp)$/Å	$r(R_3M–Me)$/Å	φ^b (°)	Ref.
$C_5H_5SiH_3$	1.881(10)	1.857(7)	116.5(7)	49
$C_5H_5SiMe_3$	1.897	1.875(2)	118.5	42
$C_5H_5GeH_3$	1.969(5)	1.9453(5)	115.9(7)	52
$C_5H_5SnMe_3$	2.16(1)	2.144(3)	111.6	42
$3\text{-}Ph_3CC_5H_4SiH_3$	1.89(1)	1.857(7)	125.2(7)	53
$3\text{-}Ph_3CC_5H_4SnH_3$	2.194(6)^c	1.875(2)	121.0(4)	53
$C_5H_5PbPh_3$	2.30(2)^d	2.23	114	54
$C_5H_4(SiMe_3)_2$	1.89(1)	1.875(2)	114, 129	42
$C_5H_4(SnMe_3)_2$	2.16(1)	2.144(3)	114, 129	42
	2.18(4)^e	2.144(3)	117.4, 126.9	55

[a] Earlier electron diffraction measurements which were interpreted to show a non-planar cyclopentadienyl ring in CpSiMe$_3$, CpGeMe$_3$ and CpSnMe$_3$, and which have since been reinterpreted,[42] have not been included. [b] Dihedral angle between the M–Cp bond and the plane of the ring. [c] Bond order[65] ca. 0.83. [d] Bond order ca. 0.76. [e] Bond order ca. 0.86.

undergo intramolecular ring closure to the corresponding 1-metallo-3a,7a-dihydroindenes above −45 °C, before any equilibration by hydrogen shift can be observed. The 9-trimethylstannyl compound (**27** R$_3$M = Me$_3$Sn) undergoes spontaneous metallotropic shift on the NMR time scale at −90 °C, but again ring closure occurs at a higher temperature, and the structure at equilibrium under conditions of sigmatropic shift of hydrogen is not known.[48]

A refinement of this approach therefore would be to investigate the compounds with two metallic substituents in the ring, when the equilibrium concentration of positional isomers would be dependent only on the (non-degenerate) shift of the more mobile organometallic groups, which could be achieved at a temperature below that where thermal decomposition occurs.

The cyclopentadienylmetallic compounds would be expected to show a lengthening of the M–C bond and a decrease in the dihedral angle φ which it forms with the axis of the π-system from the "natural" angle 125.5°, to maximise the σ–π* overlap.

A good example is provided by cyclopentadienylsilane, the structure of which has been determined in the gas phase by electron diffraction.[49]

In cyclopentadiene itself (**28**), hyperconjugation is negligible;
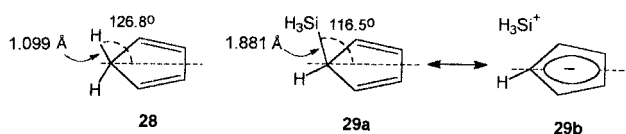
the methylene H–C bonds have a normal length of about 1.1 Å, and a normal ^1J(H–C) value of 125 Hz, and φ is 126.8(3)°.[50] In cyclopentadienylsilane (**29a**), the angle φ is reduced to 116.5(7)°, and the Si–C bond length is increased from 1.857(7) Å in H$_3$Si–Me[51] to 1.881(10) Å.[49] In valence bond terms, the canonical form **29b** makes a substantial contribution to the structure.

Further examples of similar cyclopentadienylmetal structures are given in Table 1. In each case the M–Cp bond is longer than it is in the corresponding M–CH$_3$ compounds, but for most compounds it is not justified to calculate quantitative bond orders because the probable errors which are involved are too large.

Symmetry-enhanced hyperconjugation would be expected to lead to a progressive reduction in bond order and in the dihedral angle φ, in the sequence Si, Ge, Sn, Pb. The data in Table 1 are not inconsistent with this, but the probable errors are too large to allow definite conclusions to be drawn. Similar considerations which can be ascribed to symmetry-enhanced hyperconjugation apply to the structures of CpAlMe$_2$, CpGaMe$_2$, Cp$_3$Ga, Cp$_3$Sb and Cp$_3$Bi, though there are now complications from steric hindrance or from the formation of polymers in the solid state.[40]

To maximise symmetry-enhanced hyperconjugation, the

geminally dimetallated cyclopentadiene molecules **21** would be expected to have structures with local C_{2v} symmetry, long M–C bonds and a large M–C–M angle. In 5,5-bis(trimethylstannyl)-cyclopentadiene (**21**, M = Sn) in both the gas phase and in the crystal, the bond order is indeed low, and the Sn–C–Sn angle is large (Table 1), but the molecule does not have C_{2v} symmetry, and the two angles φ are about 117 and 129°. The reason for this lack of symmetry is not clear. The structure of the corresponding disilyl compound is similar (Table 1).

In solution at room temperature, **21** shows a ^{1}H NMR singlet for the methyl groups, implying that the two angles φ are vibrationally averaged to ca. 122°.[55,56] The coupling constants $^1J(^{119}Sn–^{13}CH_3)$ and $^1J(^{119}Sn–^{13}C1)$ are 347.7 and 193.9 Hz respectively, confirming that the Sn–C1 bond is weakened by (enhanced) hyperconjugation, but direct comparison with the values for the distannadihydropentalene **20** is not possible because of its molecular distortion.

It would be interesting to look for supporting evidence for symmetry-enhanced hyperconjugation in the other compounds in Table 1 in their ^1J(M–C) values (which should be reduced) and ^1J(H–C) values (which should be near normal). Unfortunately, although the ^{13}C NMR spectra of many cyclopentadienylmetal compounds are in the literature, the ^1J values are usually not listed.

^1J Values have however been reported for the stannylcycloheptene, -heptadiene and -heptatriene **30**,[23] **31**[57] and **32**;[57]
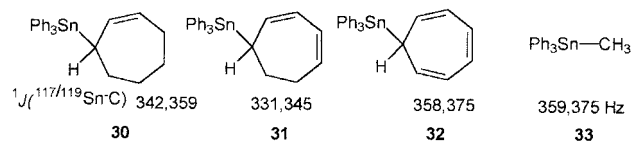
simple hyperconjugation in **30** and **31** should weaken the Sn–C(ring) bond and reduce $^1J(^{117/119}Sn–C)$ below their values in Ph$_3$Sn–Me (**33**),[58] but the LUMO in **32** is antisymmetric, hyperconjugation should be symmetry-forbidden, and the value of ^1J should return to the unperturbed value which it shows in **33**. The observed coupling constants match this prediction, but this has doubtful significance as the triene **32** has a boat-shaped structure with a quasi-axial Ph$_3$Sn group,[47] and the usual inverse correlation between ^1J and the Sn–C bond length breaks down, r(Sn–C) being 2.185(5) Å in **30**, and 2.21 Å in **33**.[47]

Organometallic cations

As carbon–metal hyperconjugation is more effective than carbon–hydrogen hyperconjugation, symmetry-enhanced hyperconjugation would be expected to be more apparent in cyclohexadienylmetal cations, ArHM$^+$, than in the corresponding hydrocarbon cations ArH$_2^+$, the principal interaction involving the M–C rather than the H–C bond. Evidence supporting this

has come from recent attempts to generate free R_3Si^+ and R_3Sn^+ ions.

The structure of the adduct formed between Et_3Si^+ and toluene has been the subject of some controversy,[59–64] but it can more readily be accepted if symmetry-enhanced hyperconjugation is invoked.

The structure (X-ray diffraction) of $[Et_3Si\cdot C_6H_5Me]^+$ is shown in **34a**.[61] The Et_3Si–C bond is stretched and weakened by


34a   **34b**   **35**
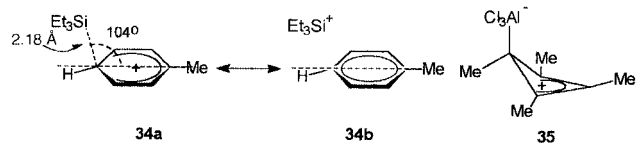
symmetry-enhanced hyperconjugation: it subtends an angle of 104° with the plane of the ring, whereas the natural angle is 125°, to maximise the σ–π* overlap, and the very long bond implies, on Pauling's criterion,[65] a bond order of *ca.* 0.28. The ^{29}Si NMR chemical shift is intermediate between that for Et_3Si–R and that calculated for Et_3Si^+, and the interaction of the cation with the toluene molecule is very weak. In valence bond terms, the canonical form **34b** is the major contributor to the structure, and the R_3Si^+ cations rapidly exchange between arene molecules in solution.

Symmetry-enhanced hyperconjugation with the Sn–C bond should be more effective than with the Si–C bond, and the ^{119}Sn NMR chemical shift of R_3Sn^+ cations in benzene shows "that their 3-coordination is perturbed but not fundamentally altered",[62] and no $[R_3Sn\cdot ArH]^+$ adducts have yet been isolated.

Similar principles apply to the loose complexes formed between arenes and other metal cations (*e.g.* of Hg^{66}).

It is commonly recognised that electrophilic substitution of arylmetallic compounds usually occurs by *ipso* attack because only then can the Wheland intermediate **36** be stabilised by

36
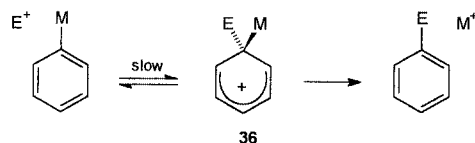
M–C hyperconjugation.[67] This argument carries even more weight when it is appreciated that symmetry-enhanced hyperconjugation, which will be twice as effective, can be involved.

The Wheland-type intermediate formed by addition of an electrophile E^+ to a substrate $(MC=CH)(CH=CH)_{n-1}$, where *n* is even, would have an antisymmetric LUMO. Hyperconjugation with the M–C, H–C or E–C bonds would be symmetry-forbidden (Scheme 1) and the hyperconjugative factor in favour of *ipso* substitution of the metal would be lost. On this basis alone, electrophilic attack on cyclooctatetraenylmetal compounds would be expected to show a smaller *ipso* partial rate factor than phenylmetal compounds do, though of course other factors such as the inductive and dπ–pπ effect of the metal, and the homoaromatic character (see **46**) of the intermediate,[68,69] and its possible transannular reaction have also to be taken into account. The literature does not appear to provide any clear examples of the consequences of this predicted diversion of attack from the *ipso* position.

Dimethylacetylene reacts with aluminium chloride to give the adduct of $AlCl_3$ and tetramethylcyclobutadiene, which has been shown by X-ray crystallography to have the structure **35**.[70] The Al–C bond length is normal at 2.141 Å, which would be consistent with the fact that the propenyl LUMO is antisymmetric and hyperconjugation is symmetry-forbidden, but again the molecule is non-planar, with some homoaromatic character, and the different stereoelectronic effects cannot be separated.
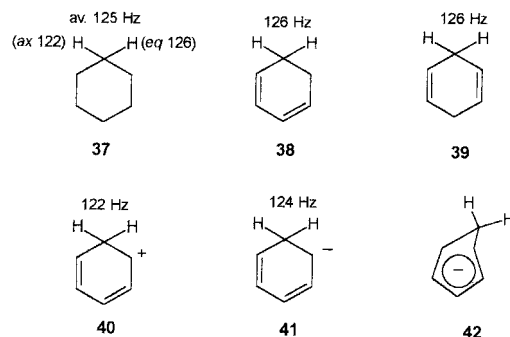
Hydrocarbon cations

Experimental structural evidence for CH hyperconjugation is more difficult to obtain than for CM hyperconjugation: it is limited to cations which may not be easy to prepare and to isolate, and X-ray crystallography is poor at accurately locating the position of the hydrogen atoms. Also the energy of σ–π* interaction is less, and the stretching and bending force constants are larger than for CM bonds, so that the effect on C–H bond lengths and angles is less.

The evidence for H–C hyperconjugation is therefore more dependent on MO calculations and on NMR ^1J values; information might also come from NMR chemical shifts, but these are usually less easy to interpret than coupling constants.

The cyclohexadienyl cation **40** has been intensively studied because it is the prototype of the Wheland intermediate in aromatic electrophilic substitution. The LUMO in **40** is the same as the SOMO in the radical **10**, and should participate in enhanced hyperconjugation. This raises the question as to what effect symmetry-enhanced hyperconjugation may have on the formation, structure and reactions of these important intermediates.

Many MO calculations have been carried out on **40** over the years at progressively increasing levels of refinement. In 1976 Mulliken estimated the hyperconjugation energy to be about 27 kJ mol^{-1},[33] and, most recently, *ab initio* calculations by Schleyer at the MP2/6-31G* level showed that hyperconjugation between the CH_2 group with the pentadienyl cation moiety reduced the CH bond order to 0.83.[32]

Formulae **37**–**41** show ^1J(H–C) values for a series of cyclohexane derivatives.[32] Cyclohexane (**37**), cyclohexa-1,3-diene

37   **38**   **39**

40   **41**   **42**

(**38**) and cyclohexa-1,4-diene (**39**) all show values of ^1J(H–C) of *ca.* 125 Hz, consonant with the principle that H–C hyperconjugation in neutral spin-paired hydrocarbons is negligible, and they provide a standard value of ^1J for a methylene group in a hydrocarbon, unperturbed by ring strain, charge or hyperconjugation.

For conjugated systems where the charge and LCAO coefficient at Cα are not unity, Kelly's eqn. (3) can be rewritten in the form of eqn. (4), where q_j is the charge, and c_j^2 is the square

$$\Delta^1J = q_j A - c_j^2 B \cos^2 \theta \qquad (4)$$

of the LCAO coefficient of the LUMO at the π centre, which gives a measure of the σ–π* overlap.

Thus for a simple example, the 1,3-dimethylallyl cation, $CH_3CH=CH-CH^+CH_3$, q_j would be 0.5 and c_j would be $\sqrt{0.5}$ at both C(1) and C(3). Unfortunately there are no examples in the literature of this equation being put to the test.

In the LUMO of the constituent pentadienyl cation of **40**, the charges q_1 and q_5 are +0.333, and the coefficients c_1 and c_5 are each +0.577; the ring is flat with the angle C(1)C(6)C(5) 114.5° (MINDO/3)[31] and θ can be taken to be *ca.* 31°.

If the value of c_j^2 is taken to be $c_1^2 + c_5^2$, eqn. (4) gives $\Delta^1J = -1.21$ Hz, whereas if, following Whiffen, c_j^2 is taken to be $(c_1 + c_5)^2$, Δ^1J is predicted to be -16.21 Hz, with ^1J for the

α-methylene groups of cyclohexanone as 129 Hz[36] as the reference standard.

Thus, if symmetry-enhanced hyperconjugation is invoked, the predicted value of ^1J(H–C) in the cyclohexadienyl cation is 113 Hz, rather than 128 Hz for simple hyperconjugation. This is to be compared with the observed value of 122 Hz. At the present stage of its development, this approach does not appear to be useful, but if the values of the constants A and B could be determined more accurately, and eqn. (4) could be shown to hold for cations which are not cyclically conjugated, an approach along these lines might provide a useful quantitative measure of hyperconjugation in H–C bonds. An extension of this method might also be used to measure hyperconjugation by M–C bonds in both cations and neutral molecules.

The cyclohexadienyl anion **41** represents the corresponding Meisenheimer intermediate for nucleophilic aromatic substitution (though in practice the methylene group usually carries two electronegative substituents). Previous interest has focused largely on the possibility that the molecule might have the character of a non-planar homocyclopentadienyl anion **42**, but NMR[32] and *ab initio*[32,71] studies agree that it is planar and not homoaromatic.

The LUMO is now antisymmetric and could not interact with the methylene group, but the HOMO is high in energy and a σ*–π (negative hyperconjugation) interaction could be envisaged. Kelly's approach has not yet been applied to anions or to negative hyperconjugation. Population of σ* should weaken the H–C bond and reduce ^1J(H–C), and the inductive effect of the negative charge should reduce it further. As ^1J(H–C) is normal at 124 Hz, this cannot be an adequate description of the interaction.

It has been suggested that the π HOMO interacts to nearly equal extents with the σ and σ* H–C orbitals; if the methylene groups carried electronegative substituents, the σ*–π interaction would increase in importance, and both these interactions should lead to symmetry-enhanced hyperconjugation.[71]

The cyclobutadienyl cation (**43**) and the cyclooctatrienyl
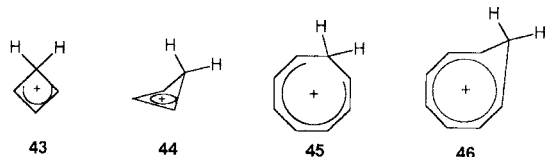
cation (**45**) both have antisymmetrical LUMOs. Hyperconjugation by σ–π* interaction should be symmetry-forbidden, and an increase in ^1J(H–C) would be expected as a result of the effect of the positive charge. Such an attempt to obtain evidence of the symmetry-control of hyperconjugation is frustrated by the fact that both molecules have non-planar homoaromatic structures (**44** and **46**) in which the values of ^1J(H–C) are substantially enhanced by steric strain.[32]

Photoexcited states

In a cyclic alkene $(H/M)_2C(CH=CH)_n$, if n is even, the HOMO is antisymmetric and the LUMO is symmetric; if n is odd, the HOMO is symmetric and the LUMO is antisymmetric. In either case, in the excited state, when one electron is promoted from the HOMO to the LUMO, one of the two SOMOs has the appropriate symmetry to interact by enhanced hyperconjugation with a σ HC or MC bond.

This is illustrated in Scheme 1 for the cyclobutadienyl cation. The HOMO ψ_1 is symmetric but is doubly occupied, and the LUMO ψ_2, though vacant, is antisymmetric. Hyperconjugation with the methylene group is therefore forbidden. Photoexcitation promotes an electron from ψ_1 to ψ_2, and the singly occupied symmetric orbital can now enter into enhanced hyperconjugation.
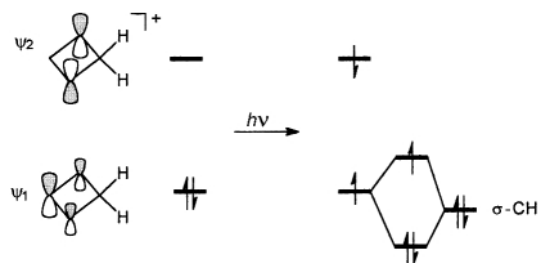
Scheme 1 Enhanced hyperconjugation in the photoexcited cyclobutenyl cation.

It is interesting to speculate what effect this symmetry-controlled hyperconjugation may have on the physical and chemical properties of the singlet or triplet excited states. The cyclopentadienes again provide an example. The alkylated cyclopentadienes show a photosensitivity which is unique among hydrocarbons in that, upon irradiation with light of wavelenth > 300 nm, they dissociate into the cyclopentadienyl radical and a hydrogen atom, *e.g.* $Me_5C_5H \rightarrow Me_5C_5{}^\bullet + H^\bullet$.[72] The HOMO, ψ_2, of cyclopentadiene in the ground state (Scheme 2) is antisymmetric, and although the LUMO ψ_3 is
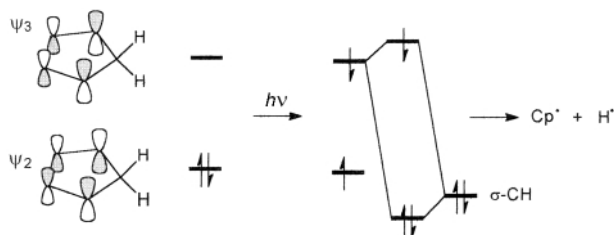
Scheme 2 Photodissociation of a cyclopentadiene.

symmetric and vacant, the hyperconjugative interaction with the methylene group is negligible (**28**) as befits a neutral spin-paired hydrocarbon. Photoexcitation however places an unpaired electron in ψ_3, and symmetry-enhanced hyperconjugation would now be expected to be significant, as it is in a hydrocarbon radical. This enhanced hyperconjugative interaction may be an important factor in differentiating the photochemical properties of the cyclopentadienes from those of the other unsaturated hydrocarbons.

Conclusion

Methods for the quantitative measurement of hyperconjugation, and hence of its symmetry-control, are as yet rudimentary, but the effects of symmetry-enhanced and symmetry-forbidden hyperconjugation are apparent in systems where it would be expected to be important, particularly in the Wheland intermediates which are involved in electrophilic aromatic substitution, in the looser complexes formed between metal cations and arenes, and in η¹-cyclopentadienylmetal compounds.

Recognition of the effect should enable the picture to be rapidly refined. The extension of Kelly's equation to cover charges and LCAO coefficients other than unity needs to be verified. One-bond metal–carbon coupling constants need to be recorded, and Kelly's approach extended to linking ^1J(M–C) values to the LCAO coefficients of the termini of the π-system in neutral organometallic compounds. Organotin and organomercury compounds would be particularly appropriate as the compounds are readily accessible, and the values of ^1J(^{119}Sn–^{13}C) and of ^1J(^{199}Hg–^{13}C) are large and are easily measured, and the polarity term A in eqn. (4) should be small. This should make it possible to establish a quantitative measurement of symmetry-controlled hyperconjugation. The system would also clearly benefit from a focussed study by *ab initio*, semiempirical, or density functional theory calculations.

Longer-range (homohyperconjugative) effects of metals (*e.g.* the "γ-effect" of tin[73]) are also recognised. These should be subject to symmetry-control in the same way as are the β-effects, though the steric demands of the interaction might restrict its operation. Theoretical calculations should again help to identify those systems which would merit investigation.

Acknowledgements

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