

Analysis of long-range NMR spin–spin coupling in polyenes and the π -mechanism

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The *J*-OC-PSP (decomposition of *J* into Orbital Contributions using Orbital Currents and Partial Spin Polarization) method is applied to analyze NMR spin–spin coupling constants in polyenes, which were calculated using coupled perturbed density functional theory in connection with the B3LYP hybrid functional and a [7s,6p,2d/4s,2p] basis set. The analysis revealed that the π -mechanism for Fermi contact (FC) spin coupling is based on passive π -orbital contributions. The π -orbitals transfer spin information between σ orbitals (*spin-transport mechanism*) or increase the spin information of a σ orbital by an *echo effect*. The calculated FC(π) values are rather constant for small polyenes ranging between 3.5–5.5 Hz for a double bond. They decay more slowly with the distance between perturbing and responding nucleus than the σ contributions to the FC term. The sign of the passive FC(π) contribution can be assessed from a Dirac vector model. The limits for long-range coupling in a polyene were determined and their practical implications discussed.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is one of the most important tools when determining the structure and conformation of molecules.^{1–8} Most important are the indirect spin–spin coupling constants (SSCCs) since they depend sensitively on geometric features such as bond lengths⁹ and dihedral angles,¹⁰ which is extensively used in the conformational analysis of biomolecules.¹ Clearly, any relationship between NMR SSCCs and geometric parameters has its origin in the dependence of the spin–spin coupling mechanism on the electronic structure of the molecule. The SSCC functions as a sensitive antenna, which probes the electron density close to the nuclei, in the valence regions as well as in the bond regions. It detects charge contraction in the vicinity of electronegative atoms, the larger polarizability of electron-rich atoms, orbital currents caused by multiple bonds, through-bond interactions connecting remote atoms as well as through-space interactions between atoms separated by a long bond chain but being close to each other in space. Although the spin–spin coupling mechanism between two coupling nuclei, A and B, is observed as a whole in experiment, it is useful to partition it according to Ramsey¹¹ into four separate mechanisms. Suppose that the magnetic moment of nucleus B (perturbing nucleus) distorts the zeroth-order electron density around B, this distortion can be transferred to the responding nucleus A in the following ways:

(1) The Fermi contact (FC) mechanism results from the internal magnetic field of nucleus B (which has a finite size). The electron density on the contact surface of nucleus B is spin polarized and this spin polarization travels like a wave through the electron system and interacts at the contact surface of nucleus A with the magnetic moment of A. Only orbitals that have a finite density at the contact surface, *i.e.* orbitals with s-character, can contribute to the FC coupling mechanism in an active way. However, this does not exclude that the spin polarization of the s-density is transferred *via* exchange interactions to orbitals without any s-character and that these orbitals contribute to the FC coupling mechanism in a passive way.

(2) The spin dipole (SD) mechanism is connected to the external magnetic dipole field of nucleus B, which causes spin polarization of the surrounding density. The spin-dipole mechanism is carried preferentially by p-orbitals for first- and second row molecules. This is a result of the form of the quadrupole potential at the responding nucleus bearing in mind that the components of the nuclear dipole fields have the same form as the potential of a suitably chosen quadrupole (d-orbital shape).¹⁸ Hence, the responding nucleus can detect only the spin polarization transferred by orbitals with p-character. Excitations supporting the SD mechanism involve p-orbitals of the same magnetic quantum number (denoted by $p_x \rightarrow p_x^*$).

(3) The spin orbit (SO) mechanisms are associated with orbital currents (equivalent to electron currents) generated by the magnetic moment of nucleus B; the electron currents are accompanied by a magnetic field, which is experienced by nucleus A. The diamagnetic SO (DSO) mechanism is carried by circular currents corresponding to a Larmor precession for each electron, which depend on the form of the orbital and the associated orbital density in the molecular ground state. All orbitals can contribute to the DSO spin–spin coupling mechanism.

(4) The paramagnetic SO (PSO) spin–spin coupling mechanism is carried by orbital currents that result from electron excitations into low-lying excited states where p-orbitals with different magnetic quantum number must be involved (*e.g.* $p_x \rightarrow p_y^*$).

In recent work, we have formulated and implemented the theory for calculating SSCCs in the framework of DFT,¹² using SSCCs as conformational descriptors,^{13–15} and analyzing the mechanism of NMR spin–spin coupling in terms of orbital contributions, spin density distributions, electron excitations, orbital (electron) currents, and intramolecular magnetic fields.^{16–24} The quantum chemical basis for this analysis is summarized in the *J*-OC-PSP (= *J*-OC-OC-PSP: decomposition of *J* into Orbital Contributions using Orbital Currents and Partial Spin Polarization) method. This method makes it possible to analyze the four spin–spin coupling transmission mechanisms associated with the four Ramsey terms of the

indirect SSCC in terms of orbital contributions, spin density distributions, orbital currents, and energy densities. *J*-OC-PSP distinguishes between active and passive orbital contributions,¹⁹ which is important for the FC coupling mechanism. For the purpose of demonstrating this point, we will investigate in this work the role of the π -orbitals for long-range coupling in polyenes.

Since the π -orbitals of a polyene possess a zero amplitude at the contact surface of the carbon and hydrogen nuclei (equivalent to a zero π -density), they cannot play any active role for the FC spin coupling mechanism. Nevertheless, one knows that long-range spin-spin coupling leading to sizable values of SSCCs 4J or 5J in conjugated hydrocarbons is dominated by a π -mechanism.^{4,5,25-31} The π -density can be spin-polarized by the s -density and then the NMR spin-spin coupling mechanism is transferred *via* the π -electrons to the σ spin density at the responding nucleus.^{4,5,25-31} This passive contribution of the π -electrons proves to be very effective according to measured SSCCs for long-range coupling in polyenes.

Clearly the π -electrons participate in the FC coupling mechanism in a passive rather than active way, *i.e.* they are not directly affected by the internal magnetic field of the perturbing nucleus. This passive contribution has been shown to be always present in any π -system where differing statements about the magnitude of the π -mechanism have been made.^{4,5,25-31} There is of course also a passive σ -contribution, which transmits spin polarization through one or more intermediate bonds not involving the coupling nuclei. It is known that this σ -mechanism for long-range coupling requires a zigzag arrangement of the bonds along the coupling path, which guarantees that the back lobes of the bond orbitals overlap through-space thus passing spin information along the bond path.^{4,26} Also, it is known that the σ -mechanism is not as effective as the π -mechanism.

In this work, we will focus on the π -mechanism, quantitatively determine the magnitude of the passive FC(π) contribution of the total FC term, and describe the π -mechanism in detail. In this connection we will investigate the following problems and questions:

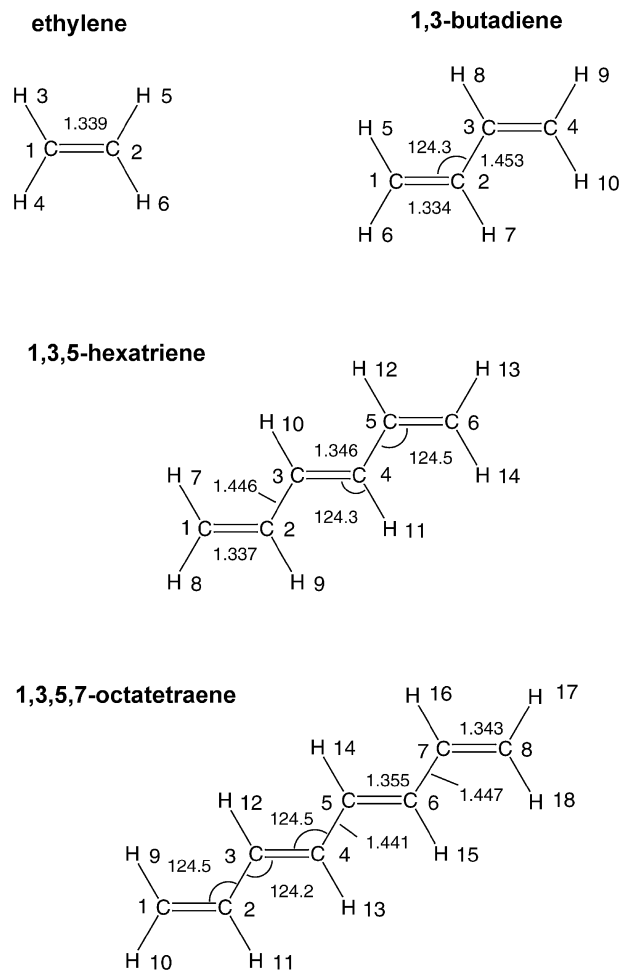
(1) How can the π -orbitals contribute to the FC coupling mechanism, how can the contribution of the π orbitals to the FC coupling mechanism be quantified, and how can it be visualized?

(2) How important is the π -mechanism in polyenes? Previous semiempirical investigations²⁸⁻³¹ suggest that a significant portion of the FC part of $^1J(C,C)$ in unsaturated hydrocarbons (up to 20% or 15 Hz) is related to contributions from the π electrons. To what extent can these findings be confirmed by DFT calculations with an extended basis set?

(3) How does the FC(π) term decay with increasing distance between the two coupling nuclei? Is it possible to establish simple rules for the sign and magnitude of the FC(π) term based on the length and topology of the bond chain between the coupling nuclei?

(4) The double bonds in polyenes are separated by formal CC single bonds. Does the π -electron coupling mechanism bridge these formal single bonds (π -delocalization) or does it branch to transmit spin polarization partly *via* the delocalized π -orbitals and partly *via* the σ -bond orbital of the formal CC single bond? More generally, if there is more than one orbital path for the coupling mechanism, which of them is dominating? Are the path contributions to FC(π) additive or is there just one dominating π orbital mechanism?

(5) What are the practical implications of understanding long-range FC coupling? Can one, *e.g.*, use the calculated FC(π) values as a measure for the degree of π delocalization in a conjugated system? At what length of the coupling path is FC(π) identical to $^nJ(AB)$? Can one predict the value n , for which long-range SSCCs are no longer (still) measurable? Is the measurement of long-range coupling of any relevance for structure determination?



Scheme 1

(6) What orbitals are most strongly affected by the spin polarization of the π -orbital? Are these just the σ -orbitals at the responding nucleus or also its core orbitals? Is the spin polarization interaction localized to certain regions in the molecule (just the atomic or also the bond regions)? Does one have a feedback in spin polarization in form of a σ - π - σ interaction involving the same σ -orbital (echo effect)?

These and other questions will be investigated in this work. For this purpose, we will briefly review in Section 2 some essentials of the *J*-OC-PSP analysis method. In section 3, we will discuss the importance of the π -mechanism for long-range SSCCs and analyze in this connection the SSCCs of ethylene, *trans*-1,3-butadiene, *trans-trans*-1,3,5-hexatriene, and *trans-trans-trans*-1,3,5,7-octatetraene (Scheme 1). Finally, we will investigate whether passive σ -electrons can play a similar role for either FC, PSO or SD term as passive π -electrons do for the FC term.

2. Theory of the spin-spin coupling mechanism

The *J*-OC-PSP method used in this work is tightly connected with the CP-DFT approach for calculating NMR SSCCs.¹² Since *J*-OC-PSP is described in detail elsewhere,^{16,19} we report here just some of its essentials. *J*-OC-PSP can be carried out with any type of orbital, however it is advantageous to use localized molecular orbitals (LMOs) rather than canonical MOs as was shown in previous work.¹⁶⁻²⁴ It should be noted that this choice is relevant for the occupied MOs only. The unoccupied orbitals are used only as a basis to expand the deformations of the occupied orbitals, and can be used either in canonical or localized form without an impact on the results. In the current work, we will use canonical unoccupied MOs.

The CP-DFT equations in terms of LMOs read¹⁹

$$|\psi_k^{X,(B)}\rangle = \sum_a \frac{\langle \psi_a^{(0)} | F^{X,(B)} | \psi_k^{(0)} \rangle - \sum_{l,l \neq k} F_{kl}^{(0)} \langle \psi_a^{(0)} | \psi_l^{(B)} \rangle}{F_{kk}^{(0)} - \varepsilon_a} |\psi_a^{(0)}\rangle, \quad (1)$$

where the $\psi_k^{(0)}$, $\psi_a^{(0)}$ and $\psi_k^{X,(B)}$ denote zeroth-order occupied, zeroth-order virtual, and first order occupied orbitals, respectively, whereas ε_a is the energy of the canonical unoccupied orbital a . The superscripts will be used analogously for the components of the operator F . The latter result for a perturbation X ($X = \text{PSO, FC, SD}$) caused by the magnetic moment of nucleus B (we will omit the index X in the following). The operator $F^{(B)}$ comprises (see eqn. (2)) the Ramsey perturbation $h^{(B)}$ and a contribution $\tilde{F}^{(B)}$ that accounts for the feedback of the first-order orbitals to the Kohn–Sham operator. According to eqn. (3), operator $\tilde{F}^{(B)}$ can be decomposed into orbital contributions $\tilde{F}_l^{(B)}$, which are defined in eqn. (4):

$$F^{(B)} = h^{(B)} + \tilde{F}^{(B)}, \quad (2)$$

$$\tilde{F}^{(B)} = \sum_l \tilde{F}_l^{(B)}, \quad (3)$$

$$\tilde{F}_l^{(B)} = \int d^3r \frac{\delta F}{\delta \psi_l^{(0)}} \psi_l^{(B)}(\mathbf{r}). \quad (4)$$

Multiplying eqn. (1) from the left by $\langle \Psi_a^{(0)} |$ and using the notations $C_{ak}^{(B)} = \langle \Psi_a^{(0)} | \Psi_k^{(B)} \rangle$ and $\langle \Psi_p^{(0)} | \hat{O} | \Psi_q^{(0)} \rangle = O_{pq}$ (matrix element of operator \hat{O}), the decomposition of $\tilde{F}^{(B)}$ leads to eqn. (5):

$$C_{ak}^{(B)} = \frac{1}{F_{kk}^{(0)} - \varepsilon_a} \left[h_{ak}^{(B)} + (\tilde{F}_k^{(B)})_{ak} + \sum_{l,l \neq k} \left((\tilde{F}_l^{(B)})_{ak} - F_{kl}^{(0)} C_{al}^{(B)} \right) \right], \quad (5)$$

which is the basic *J-OC-PSP* equation.¹⁹ The reduced SSCC can be expressed in terms of coefficients $C_{ak}^{(B)}$ and the responding potential at nucleus A .

$$K_{AB} = \sum_k \langle \psi_k^{(B)} | h^{(A)} | \psi_k^{(0)} \rangle = \sum_{ak} C_{ak}^{(B)} h_{ak}^{(A)}. \quad (6)$$

Eqn. (6) represents a trivial decomposition of the SSCC and its Ramsey terms into one-orbital contributions, which possesses several disadvantages and will not be used in this work. It is a better approach to consider the structure of $C_{ak}^{(B)}$ in eqn. (5), which is characterized by one- and two-orbital terms where this classification is based on occupied orbitals only. The first two terms on the rhs of eqn. (5) are one-orbital terms, describing (a) the direct impact of the Ramsey perturbation $h^{(B)}$ through $|\psi_k\rangle$ on $h^{(A)}$ and (b) the feedback to this perturbation by *steric self-repulsion* (dynamic correlation plays only a small role for the spin–spin coupling mechanism).¹⁹ The third term in the square bracket of eqn. (5) comprises the two-orbital terms, which describe orbital interactions induced by the Ramsey perturbations. The term containing $\tilde{F}_l^{(B)}$ represents a steric exchange term between orbitals $|\psi_l\rangle$ and $|\psi_k\rangle$. The term containing the non-diagonal elements of $F^{(0)}$ describes a resonance effect reflecting the fact that a local perturbation (as the nuclear spin at the perturbing nucleus) will affect the electron system in the whole molecule rather than just locally around the perturbation. Canonical (delocalized) orbitals can account for this effect directly whereas for localized orbitals the resonance terms are necessary to transport this effect through the electron system of the molecule. The resonance terms vanish for the transfer of spin information between σ and π orbitals for reasons of symmetry.

The occurrence of one- and two-orbital terms in eqn. (5) suggests a decomposition of the SSCC term into one- and two-

orbital contributions according to

$$K_{AB} = \sum_k K_{AB}^{\text{PSP1}}(k) + \sum_{k \neq l} \sum K_{AB}^{\text{PSP1}}(k \leftrightarrow l). \quad (7)$$

This is the basis of the *J-OC-PSP1* method.^{16,19} The *J-OC-PSP1* contributions can be calculated from a series of SSCC calculations where all except one or two orbitals are set passive, *i.e.* their interaction with the Ramsey perturbation is suppressed:

$$K_{AB}^{\text{PSP1}}(k) = K_{AB}^{\text{pass}}[-k], \quad (8)$$

$$K_{AB}^{\text{PSP1}}(k \leftrightarrow l) = K_{AB}^{\text{pass}}[-(k, l)] - K_{AB}^{\text{pass}}[-k] - K_{AB}^{\text{pass}}[-l], \quad (9)$$

where

$$[-k]$$

and

$$[-(k, l)]$$

indicate that all orbitals except k , or k and l , respectively, are set passive. Steric exchange and resonance interactions lead to a transfer of spin information not only by a pair of orbitals but also along chains (orbital paths) of three and more orbitals involving both active (interacting with perturbing or responding nucleus) and passive orbitals (interacting with other spin-polarized orbitals). *J-OC-PSP1* subsumes such contributions into the one- and two-orbital terms.

An explicit consideration of passive orbital contributions requires a *J-OC-PSP2* analysis.¹⁹ In this approach, one- and two-orbital contributions are redefined and separated from three- and n -orbital contributions. For this purpose, single orbitals, orbital pairs or group of orbitals are frozen (froz) so that they cannot contribute to the spin–spin coupling mechanism in an active or passive way. For example, the *J-OC-PSP2* one-orbital terms are obtained from eqn. (10):

$$K_{AB}^{\text{PSP2}}(k) = K_{AB} - K_{AB}^{\text{froz}}[k]. \quad (10)$$

In a similar way, the two- and three-orbital terms of *J-OC-PSP2* are determined:

$$K_{AB}^{\text{PSP2}}(k \leftrightarrow l) = K_{AB} - K_{AB}^{\text{froz}}[k] - K_{AB}^{\text{froz}}[l] + K_{AB}^{\text{froz}}[k, l], \quad (11)$$

$$\begin{aligned} K_{AB}^{\text{PSP2}}(k \leftrightarrow l \leftrightarrow m) &= K_{AB} - K_{AB}^{\text{froz}}[k] - K_{AB}^{\text{froz}}[l] \\ &\quad - K_{AB}^{\text{froz}}[m] + K_{AB}^{\text{froz}}[k, l] \\ &\quad + K_{AB}^{\text{froz}}[k, m] + K_{AB}^{\text{froz}}[l, m] \\ &\quad - K_{AB}^{\text{froz}}[k, l, m]. \end{aligned} \quad (12)$$

More complicated expressions result for four-orbital and n -orbital interaction terms, which are however of little relevance.

Often it is reasonable to simplify the *J-OC-PSP2* analysis in the way that one considers contributions for a whole group of orbitals alternatively to eqn. (10) or two groups of orbitals alternatively to eqn. (11). This provides *e.g.* the whole contribution of the π -system or of the interaction between the π -system with selected σ -orbitals.

In this work, we will calculate one- and two-orbital (or orbital-group) contributions of the long-range SSCCs (and their Ramsey contributions) in polyenes to obtain the passive π -contributions and the $\pi \leftrightarrow \sigma$ interaction contributions of the FC term, which means that we will apply preferentially *J-OC-PSP2*.

The polyenes investigated in this work are shown in Scheme 1. All SSCC calculations were carried out with the CP-DFT method.¹² For this purpose, the hybrid functional B3LYP^{32–34} and the basis set (11s,7p,2s/6s,2p)/[7s,6p,2d/4s,2p]^{35,36} designed for the calculation of chemical shielding constants was used. Previous experience¹² showed that these basis sets provide reasonable SSCC for alkanes and alkenes even though they are not designed for the calculation of SSCCs. The SSCCs

were calculated at B3LYP/[7s,6p,2d/4s,2p] geometries except for octatetraene for which a B3LYP/6-31G(d,p)³⁷ geometry was used. Bond lengths and bond angles are given in Scheme 1.

The *J*-OC-PSP analysis and the orbital-selected SSCC calculations were carried out for LMOs obtained with a Boys localization³⁸ where however core, σ -, and π -orbitals are separately localized for reasons described elsewhere.¹⁶ All discussions are based on LMOs, which also holds when considering π -orbitals in a conjugated system. Nevertheless, we will make estimates on delocalization effects or excitation energies using what is known for canonical MOs.

For the visualizing of the FC coupling mechanism, we will show diagrams of the FC spin density distribution $\rho^{(B),FC}(\mathbf{r})$ derived recently.¹⁶

$$\rho^{(B),FC}(\mathbf{r}) = 2 \sum_k^{\text{occ}} \psi_k^{(0)}(\mathbf{r}) \psi_k^{(B),FC}(\mathbf{r}). \quad (13)$$

The distribution $\rho^{(B),FC}(\mathbf{r})$ can be split up into orbital contributions. The $\rho^{(B),FC}(\mathbf{r})$ and selected orbital contributions will be represented in form of contour line plots, where the contour levels are given by a geometric progression with the ratio of $100^{1/5}$ between two subsequent contours. All SSCC calculations are performed with the *ab initio* program package COLOGNE 2003.³⁹

3. Results and discussion

In previous work¹⁹ we have shown that all SSCCs of ethylene have a small but significant FC(π) contribution resulting from the passive role of the ethylene π -orbital in the FC coupling mechanism. In Table 1, the calculated FC(π) values are summarized together with the total FC values, the actual SSCCs and the corresponding measured values. The FC(π) values are calculated according to eqn. (10), *i.e.*

$$FC(\pi) = FC - FC^{\text{froz}} [\pi]. \quad (14)$$

The calculated SSCCs of ethylene are in reasonable agreement with the measured ones^{4,5} (see also refs. 28–31).

There is a passive contribution of the π -electrons to the FC term, which, despite the strong variation of the FC term between 0.6 Hz and 153.4 Hz, is in a rather limited range (–2.4 Hz to 4.5 Hz; Table 1). As a result of this, the importance of the π -part of the FC coupling mechanism increases with the length of the coupling path: For one-bond FC(C,H) coupling the π -contribution is just 2% of the total FC term whereas for the three-bond FC terms it is more than 10%.

The involvement of the π -orbitals into FC coupling follows the same mechanism for all SSCCs involving the C=C bond.

Table 1 Passive π contributions to the FC term of the SSCCs of ethylene^a

Coupling nuclei	FC			Total	
	Total	Passive π		CP-DFT	Exp.
		Hz	SI		
C1–C2	79.1	4.5	5.9	72.8	67.6
H3–C1	153.4	2.9	1.0	154.4	156.4
H3–C2	0.6	–2.4	–0.8	–1.2	–2.4
H3–H4	1.9	–1.5	–0.2	2.5	2.5
H3–H5	11.9	1.5	0.2	11.4	11.7
H3–H6	18.5	1.5	0.2	18.4	19.1

^a Experimental values from ref. 30. For nuclei numbering, see Scheme 1. The column labelled “SI” gives reduced SSCCs *K* in SI units of $10^{19} \text{ T}^2 \text{ J}^{-1}$, all other values are *J* values expressed in Hz. CP-DFT/B3LYP/(11s,7p,2d/6s,2p) [7s,6p,2d/4s,2p] calculations. The first nucleus of each pair is the perturbed nucleus.

The perturbing nucleus B (α -spin assumed) spin-polarizes the σ orbitals at this nucleus ($\sigma(\text{CC})$, $\sigma(\text{CH})$, core(1s)) thus leading to a dominance of β -spin (Fermi coupling). Due to an optimization of exchange interactions in the valence sphere of atom B (intraatomic Hund rule), the density in the π -orbital at B preferentially adopts β -spin thus withdrawing β -spin from the valence sphere of atom A. The Pauli pairing principle implies that a dominance of α -spin is generated at A, which causes the σ -orbitals at A also to adopt α -spin preferentially to optimize exchange interactions. Fermi coupling induces β -spin for the nuclear moment and by this a positive π -orbital contribution of 4.5 Hz (corresponding to a reduced SSCC of *K* = 5.9 SI units; “SI units” refer here and in the following to *K* values in units of $10^{19} \text{ J}^{-1} \text{ T}^2$, which are used to show the electronic effect only), *i.e.* by this amount the FC coupling mechanism transmitted through the $\sigma(\text{CC})$ -spin density is increased. Hence, the passive role of the π -orbital corresponds to a spin-transfer effect enhancing the FC term of the SSCC.

The analysis of the FC(π) terms reveals that the spin polarization *via* the π system follows a simple pattern. For example, the total values of the FC terms of ¹*J*(C1H3) (153.4 Hz) and ²*J*(C2C1H3) (0.6 Hz, Table 1) differ by more than a factor of 100. The corresponding FC(π) terms, in contrast, differ by less than 20% in absolute magnitude (2.9 Hz and –2.4 Hz; Table 1) because similar types of passive π -contributions are involved. For the geminal and vicinal H–H coupling constants, this model is even more strongly supported: All three H–H coupling constants are 1.5 Hz in absolute values, with signs following the Dirac vector model. This is even more remarkable keeping in mind that the π contribution in the vicinal H–H coupling follows a different mechanism than that described above for the vicinal H–H couplings (see ref. 19 for a detailed discussion). The exact magnitude of the π -orbital contributions depends on the position of the π -orbital in the coupling path (a π -orbital at both coupling nuclei leads to a larger absolute value than a π -orbital just at one of the coupling nuclei). We will see this more clearly when investigating long-range SSCCs and their FC(π) contributions in polyenes 1,3-butadiene, 1,3,5-hexatriene, and 1,3,5,7-octatetraene.

3.1. The π spin–spin coupling mechanism in *trans*-1,3-butadiene

In Table 2, the 25 SSCCs ^{*n*}*J*(C,C), ^{*n*}*J*(C,H) and ^{*n*}*J*(H,H) of *trans*-1,3-butadiene are listed where CP-DFT/B3LYP/[7s,6p,2d/4s,2p] values for *J* are compared with experimental values.^{4,5} Also given are the FC terms and their passive FC(π) contributions, which are compared with INDO results of Fukui and co-workers.^{30,31} The CP-DFT SSCCs agree better with the measured values than the INDO/SOS2 FC values do.

In Fig. 1, the calculated FC(π) contributions are ordered according to the structural units forming the ^{*n*}*J* coupling path in the polyene (butadiene values are underlined). For the same structural unit and SSCC ^{*n*}*J*, the FC(π) values of butadiene have a slightly increased magnitude compared to the corresponding ethylene value (entry before the underlined butadiene value). The magnitude of the FC(π) contribution decreases by about 1 Hz when the π bond is external rather than directly included into the coupling path. There is also a decrease of FC(π) for increasing *n* in ^{*n*}FC (see section 3.3 for a more detailed discussion).

Fig. 2a and 2b present the total FC and FC(π) spin density distribution, respectively, in the molecular plane of butadiene in form of contour line diagrams. This means that in the case of the FC(π) spin density distribution only the π -impact on the spin polarization of the σ framework (and the core orbitals) can be seen, which of course determines FC(π). The latter changes according to Fig. 2c when only orbital $\pi(\text{C1C2})$ acts in a passive way ($\pi(\text{C3C4})$ is frozen) and according to Fig. 2d when only orbital $\pi(\text{C3C4})$ is passive.

Table 2 The extent of the π contribution to the transmission of the SSCCs *via* the FC term in 1,3-butadiene^a

Nuclei	# Bonds	INDO			CP-DFT			J	Exp. <i>J</i>
		FC	FC (π)		FC	FC (π)			
	Hz		SI			Hz	SI		
C–C									
1-2	1	78.9	16.3	21.4	80.0	4.9	6.5	74.3	68.6
2-3	1	71.0	7.9	10.4	56.6	3.5	4.6	55.1	53.7
1-3	2	-14.1	-8.2	-10.8	1.0	-2.4	-3.2	-0.4	<1
1-4	3	12.4	8.9	11.7	7.5	1.9	2.5	11.3	9.1
H–C									
5-1	1	163.4	5.6	1.9	152.1	3.3	1.1	153.2	154.9
6-1	1	149.2	5.4	1.8	156.6	3.4	1.1	157.7	159.2
7-2	1	155.2	4.3	1.4	148.8	2.8	0.9	149.8	152.7
5-2	2	-10.6	-4.8	-1.6	-0.1	-2.7	-0.9	-1.9	
6-2	2	-9.8	-4.6	-1.5	1.5	-2.8	-0.9	-0.2	
7-1	2	-10.8	-4.8	-1.6	2.5	-2.3	-0.8	0.8	
8-2	2	-4.0	-2.0	-0.7	5.4	-1.1	-0.4	4.8	4.1
5-3	3	7.7	2.5	0.8	9.2	1.6	0.5	9.1	
6-3	3	14.6	2.5	0.8	13.4	1.7	0.6	13.3	
8-1	3	5.6	2.0	0.7	5.3	0.7	0.2	4.9	
5-4	4	-3.0	-2.7	-0.9	-1.3	-1.2	-0.4	-1.1	-1.2
6-4	4	-1.9	-2.8	-0.9	-0.3	-1.3	-0.4	-0.1	0
H–H									
5-6	2	4.9	-1.6	-0.1	1.2	-1.8	-0.1	1.8	1.7
5-7	3	25.7	1.4	0.1	16.5	1.4	0.1	16.4	17.1
6-7	3	9.2	1.4	0.1	10.4	1.4	0.1	10.1	10.2
7-8	3	17.7	0.5	0.0	10.6	0.3	0.0 ₂	10.4	10.4
5-8	4	-1.5	-0.6	-0.0 ₄	-0.8	-0.5	-0.0 ₄	-0.8	-0.8
6-8	4	-1.3	-0.6	-0.0 ₄	-0.8	-0.5	-0.0 ₄	-0.8	-0.9
5-9	5	1.0	0.8	0.1	0.8	0.9	0.1	0.7	0.6
6-9	5	2.4	0.8	0.1	1.3	1.0	0.1	1.5	1.3
5-10	5	0.9	0.8	0.1	0.8	0.9	0.1	1.0	0.7

^a For nuclei numbering see Scheme 1. Columns labelled "SI" contain reduced SSCCs *K* in SI units of $10^{19} \text{ T}^2 \text{ J}^{-1}$, all other values are *J* values in Hz. SSCCs were calculated using CP-B3LYP with the (11s,7p,2d/6s,2p) [7s,6p,2d/4s,2p] basis. Experimental values from Ref. 36.

The total FC spin density (Fig. 2a) clearly indicates that the perturbing nucleus is H5, which is surrounded by β spin density (dashed contour lines). The signs of the spin polarization at the other nuclei follow the Dirac vector model whereas the amplitudes of the spin polarization decrease with increasing distance from H5 (the contour levels are chosen in geometric progression). The FC(π) part (Fig. 2b) of the FC spin density resembles the latter in the way that the signature of the spin polarization around the nuclei is the same as in Fig. 2a. The regular alternation of negative and positive FC spin densities is in line with the signs of the calculated FC(π) values and the Dirac vector model. Contrary to the total FC spin density (Fig. 2a), the amplitudes of the FC(π) spin polarization decay only slowly with increasing distance from H5. There is no indication in Fig. 2b that the perturbation is at H5; the corresponding contour plot for the perturbation at H6 (not shown) reveals hardly any difference to Fig. 2b within the graphical resolution. Fig. 2b reflects the fact that the response of the π orbitals to magnetic perturbations is unspecified: No matter how exactly the π system is perturbed it responds mainly by a spin dislocation along the CC double bonds. That is, the response depends only weakly on the position of the perturbation.

It is interesting to see how the two $\pi(\text{CC})$ orbitals interact in transporting spin information through the molecule. When only orbital $\pi(\text{C1C2})$ (Fig. 2c) is passive, *i.e.* orbital $\pi(\text{C3C4})$ is frozen, the FC spin polarization in the region of C1C2 and the adjacent H atoms is similar to that shown in Fig. 2b. In the region of C3C4 and the adjacent H atoms, the FC(π) spin polarization is by about a factor of 5 smaller than in Fig. 2b but follows the same qualitative pattern. This indicates that even for orbital $\pi(\text{C3C4})$ frozen, some spin density information

from $\pi(\text{C1C2})$ is carried into the region C3C4 either by delocalization tails of $\pi(\text{C1C2})$ or with the help of the σ -orbital system.

If orbital $\pi(\text{C1C2})$ is frozen (Fig. 2d), the FC(π) spin polarization in the region C1C2 will become smaller than that in the C3C4 region for $\pi(\text{C3C4})$ frozen (Fig. 2c). In the region C3C4, the spin polarization resembles that in Fig. 2c. Fig. 2c and 2d reveal that the contributions of the π orbitals are not additive. This is confirmed by the values of the FC(π) terms of the SSCCs. For instance, the full FC(π) term for $J(\text{H5H10})$ is 0.82 Hz. For $\pi(\text{C1C2})$ or $\pi(\text{C3C4})$ passive and the other π orbital frozen, one obtains FC(π) terms of 0.14 Hz each (the values are equal for reasons of symmetry). That is, $(0.82 - 0.14 - 0.14) \text{ Hz} = 0.54 \text{ Hz}$, or nearly 70% of the total value have to be ascribed to the interaction between the two π orbitals, *i.e.* the delocalization of spin information from one π orbital to the other.

It remains to clarify the large differences between the INDO/SOS2 FC(π) contributions^{30,31} for ${}^n\text{FC}(\text{C,C})$ and ${}^n\text{FC}(\text{C,H})$ and the values obtained in this work (INDO/SOS2 values are exaggerated by factors between 1.5–4). Agreement between the two sets of data is, however, reasonable in the case of the ${}^n\text{FC}(\text{H,H})$ values (Table 2). Analysis of the differences¹⁹ reveals that the INDO/SOS2 FC(π) contributions are artificially increased when a minimal basis set is used (as done in the INDO calculations) to describe the spin polarization of the 1s(C) orbitals, which plays a role for ${}^n\text{FC}(\text{C,C})$ and ${}^n\text{FC}(\text{C,H})$ but not for ${}^n\text{FC}(\text{H,H})$. The 1s(C) contribution to FC(π) (*i.e.* the spin polarization transferred *via* 1s(C) to the π -orbital) is negative and its absolute magnitude is smaller when the s-density is less contracted to the C nucleus as in a minimal basis

¹ FC		4.5; <u>4.9</u> ; 5.1; 5.3		3 Hz	2.9; <u>3.3</u> ; <u>3.4</u> ; <u>2.8</u>	¹ FC
5 Hz		5.9; <u>6.5</u> ; 6.8; 7.0			1.0; <u>1.1</u> ; <u>1.1</u> ; <u>0.9</u>	
4 Hz		<u>3.5</u> ; 4.0		-1.1 Hz	<u>-1.1</u>	² FC
		<u>4.6</u> ; 5.3			<u>-0.4</u>	
² FC		<u>-2.4</u> ; -2.8; -2.8		-2.5 Hz	-2.4; <u>-2.7</u> ; <u>-2.8</u> ; <u>-2.3</u>	
-2.8 Hz		<u>-3.2</u> ; -3.7; -3.7			-0.8; <u>-0.9</u> ; <u>-0.9</u> ; <u>-0.8</u>	
³ FC		1.9; 2.2		0.7 Hz		<u>0.7</u>
2 Hz		<u>2.5</u> ; 2.9				<u>0.3</u>
1.8 Hz		1.8		1.7 Hz		<u>1.7</u> ; <u>1.6</u>
		2.4				<u>0.6</u> ; <u>0.5</u>
⁴ FC		-1.5		-1.3 Hz		<u>-1.3</u> ; <u>-1.2</u>
-1.5 Hz		-2.0				<u>-0.4</u> ; <u>-0.4</u>
⁵ FC		1.2				
1.2 Hz		1.6				
² FC		-1.5; <u>-1.8</u> ; -1.9		0.1		⁵ FC
-1.8 Hz		-0.2; <u>-0.2</u> ; -0.3				
³ FC		1.5; 1.5; <u>1.4</u> ; <u>1.4</u> ; 1.5; 1.4; 1.3		0.9 Hz	<u>0.9</u> ; <u>1.0</u> ; <u>0.9</u> ; 0.9; 0.9; 0.9; 0.9	
1.5 Hz		0.2; 0.2; <u>0.1</u> ; <u>0.1</u> ; 0.2; 0.1; 0.1			<u>0.1</u> ; <u>0.1</u> ; <u>0.1</u> ; 0.1; 0.1; 0.1; 0.1	
0.4 Hz		<u>0.3</u> ; 0.4		-0.3 Hz	-0.3; -0.3; -0.3; -0.3	⁶ FC
		<u>0.0</u> ; 0.0 ₃			-0.0 ₂ ; -0.0 ₂ ; -0.0 ₂ ; -0.0 ₂	
⁴ FC				0.6 Hz		⁷ FC
-0.5 Hz		<u>-0.5</u> ; <u>-0.5</u> ; -0.7; -0.6; -0.4; -0.4			0.6; 0.7; 0.6; 0.7	
		<u>-0.0</u> ₄ ; <u>-0.0</u> ₄ ; -0.0 ₆ ; -0.0 ₅ ; -0.0 ₃ ; -0.0 ₃			0.0 ₅ ; 0.0 ₆ ; 0.0 ₅ ; 0.0 ₆	

Fig. 1 ⁿFC coupling constants ordered according to associated structural units. The coupling nuclei are indicated by the appropriate atomic symbol. Underlined values were obtained for *trans*-1,3-butadiene, those preceding the underlined values for ethylene, those following the underlined values for *trans,trans*-1,3,5-hexatriene. Values in normal print are in Hz, those in italics in SI units. CP-DFT/B3LYP/[7s,6p,2d/4s,2p] calculations. The bold numbers are average values for the respective ⁿFC term.

set. The same is true for the negative $\sigma(\text{CH})$ contribution to $\text{FC}(\pi)$ so that the relatively large positive $\sigma(\text{CC})$ contribution to $\text{FC}(\pi)$ is not sufficiently reduced. The passive π -contribution calculated with semiempirical methods or a small basis set at the CP-DFT level of theory is artificially exaggerated for ⁿFC(C,C) and ⁿFC(C,H) whereas larger basis sets with more functions in the core regions as used in this work lead to reasonable values.

3.2. Passive σ orbital contributions and $\pi \leftrightarrow \sigma$ interactions in butadiene

It is well-known that a zigzag arrangement of the single bonds of a hydrocarbons supports long-range FC spin coupling.²⁶ Barfield and others have shown that the back lobes of the bond

orbitals interact through-space, which helps to transport FC spin density some distance along the atom chain. This σ -mechanism depends sensitively on the all-*trans* arrangement of bonds where bond angles close to the tetrahedral are preferred.

In polyenes, the double bonds are separated by formal single bonds. Table 2 reveals that the formal single bond in butadiene does not interrupt the transfer of spin information through the π system. For instance, the ⁵*J*(H,H) SSCCs in butadiene have all $\text{FC}(\pi)$ terms with absolute values of 0.9–1 Hz as compared to 1.4 Hz for the SSCC ³*J*(H–C=C–H) (see Tables 1 and 2). This suggests that there is an efficient mechanism to transport the $\text{FC}(\pi)$ spin density information through the formal single bond. This transport may proceed either by a through-space interaction between the π orbitals or *via* the

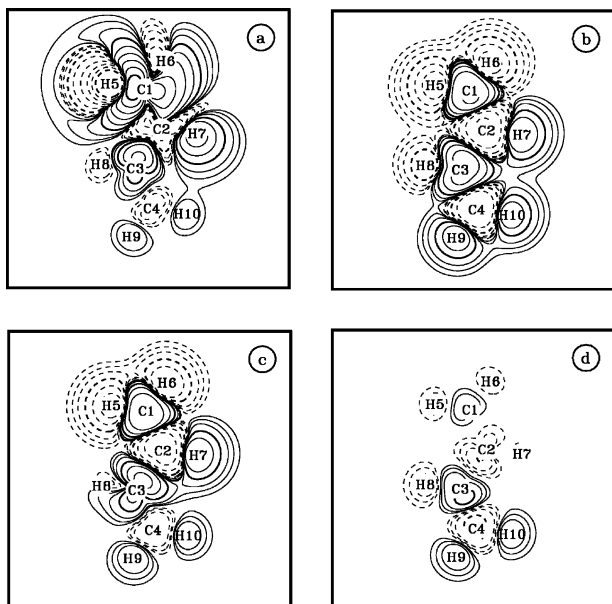


Fig. 2 The FC and FC(π) spin density distribution of butadiene plotted in the molecular plane. Contour levels were chosen in geometric progression with a ratio of $100^{1/5}$ between neighboring levels. For the purpose of facilitating a comparison of levels, the contours for 0.1 and 10 were printed in boldface. Solid (dashed) lines represent positive (negative) values of the FC spin density distribution. Calculations were done at the B3LYP/[7s,6p,2d/4s,2p] level of theory. The perturbing nucleus is H5. (a) The total FC spin density distribution. (b) The total FC(π) spin density distribution (scaling factor: 10). (c) The FC(π) spin density for the frozen π (C3C4) orbital (scaling factor: 100). (d) The FC(π) spin density for the frozen π (C1C2) orbital (scaling factor: 100).

σ (C–C) orbital in the formal single bond. Since we work with localized orbitals a through-space interaction between π -orbitals corresponds to the π -delocalization of canonical orbitals. Hence, the passive π -contributions to FC(π) clarify the role of π -delocalization for long-range coupling. For the purpose of determining the contribution of each of the possible mechanisms to the total spin density transformation, we calculated FC[$\pi \leftrightarrow \sigma$ (C2C3)] according to eqn. (11) and the corresponding spin polarization density. The results are shown in Table 3.

One finds that FC[$\pi \leftrightarrow \sigma$ (C2C3)] is 1.8 Hz for 1J (C1C2) and -1.7 Hz for 2J (C1C3), whereas the influence of the σ (C2–C3) orbital on 3J (C1C4) is less than 0.01 Hz. The results can be rationalized by considering that contributions to FC(π) may be generated either by FC spin density transport (transport mechanism caused by Pauli coupling) through the π orbitals or by echo effects of the π orbital at the perturbing or responding nucleus. For 1J (C1C2) and 2J (C1C3), there is spin density transport through the π (C1C2) orbital, whereas both π (C1C2) and π (C3C4) may give rise to echo effects. For 3J (C1C4), the two π (CC) orbitals are involved in spin density transport but not in echo effects. The values for the two-orbital contribution

Table 3 The role of the formal single bond in the π -network polarisation for the FC component of the SSCCs nJ (CC) of *trans*-1,3-butadiene^a

Nuclei	FC	FC(σ)	FC(π)	FC($\sigma \rightarrow \pi$)
C1C2	80.0	-16.4	4.9	1.8
C2C3	56.6	95.5	3.5	3.4
C1C3	1.0	1.0	-2.4	-1.7
C1C4	7.5	0.8	1.9	0.0

^a For nuclei numbering see Scheme 1. All SSCCs are expressed in Hz and were calculated using CP-B3LYP with the (11s,7p,2d/6s,2p) [7s,6p,2d/4s,2p] basis. In each pair of nuclei the perturbed nucleus is given first.

FC[$\pi \leftrightarrow \sigma$ (C2C3)] thus indicate that the σ (C2–C3) orbital has an influence on the echo effects of π (CC) bonds but not on the transport of π spin density. In this framework, it is also understandable that FC[$\pi \leftrightarrow \sigma$ (C2C3)] is approximately opposite for 1J (C1C2) and 2J (C1C3): In both cases, the π (C3C4) orbital gives rise to echo effects. For 2J (C1C3), the echo of π (C3C4) affects the FC[$\pi \leftrightarrow \sigma$ (C2C3)] term directly through the 1s and σ orbitals present at C3 whereas for 1J (C1C2) it has to be mediated to C2 by the orbital σ (C2–C3), which according to the Dirac vector model results in a sign change.

The transport mechanism for 3J (C1C4) becomes clear when inspecting Fig. 3a and 3b, which depict the FC(π) spin densities of the two π (CC) orbitals at a height of 0.6 Å above the molecular plane. The contour plots reveal that there are effective through-space interactions between the two orbitals: The π (C1C2) FC spin density has a positive lobe at C4, the π (C3C4) orbital, a negative one at C1. In this way, the FC spin densities of π (C1C2) and π (C3C4) stabilize each other by an effective 1,4-through space mechanism. At positions C1 and C4 interactions are optimized by having for both π contributions the same sign. In the C2–C3 region, where the two contributions have opposite spin, the spin densities are slightly bent in the direction of H7 for the passive π (C1C2) FC spin density (Fig. 3a) and in the direction of H8 for the passive π (C3C4) FC spin density (Fig. 3). Consequently, the opposite-spin region becomes as small as possible.

Fig. 3c, 3d and 3e show the FC[$\pi \leftrightarrow \sigma$ (C2C3)] spin densities for the two π orbitals (in a plane 0.6 Å above the molecular plane) and for the σ (C2C3) orbital (in the molecular plane). Effects are much smaller than for the total passive π spin polarization and therefore contour lines are scaled by a factor of ten relative to those in Fig. 3a and 3b (scaling factor is 100 for the latter). As Fig. 3e reveals, the σ – π interaction results in an additional polarization of σ (C2C3) along the C2–C3 axis. The π orbitals react differently on the $\pi \leftrightarrow \sigma$ interaction, which accounts for the different response of the σ system in the regions C1C2 and C3C4. These differences are second order effects and have one aspect in common: The π (C1C2) orbital does not undergo a substantial change of its spin polarization at C4 and the π (C1C2) orbital not at C1. This implies that the interaction with σ (C2C3) essentially plays no role for the transport of spin information from π (C1C2) into π (C3C4), in other words, the spin information is carried *via* a formal σ bond by a through-space interaction of the adjacent π orbitals. This confirms that π -delocalization (note that the through-space interactions between the localized π -orbitals indicate π -delocalization in the canonical orbital description) dominates the long-range coupling mechanism. This result may sound trivial, however a priori there was no reason to exclude any contribution from σ (C2C3), which could not be determined in the previous investigations. Here, we show for the first time that the σ -orbitals of the formal CC single bonds of a polyene do not play any role in long-range spin–spin coupling, probably because spin-polarization of π -orbitals is much easier than that of σ -orbitals.

3.3. The π spin–spin coupling mechanism in 1,3,5-hexatriene

In Table 4, nine SSCCs nJ (C,C) and 22 SSCCs nJ (H,H) of *trans,trans*-1,3,5-hexatriene are listed together with their FC and FC(π) contributions. The latter are ordered according to structural units in Fig. 1 (entries after the underlined butadiene values). This summary is the basis for a number of observations:

(1) The FC(π) contributions are primarily typical of the structural unit defining the coupling path rather than the molecule considered. There is a slight increase of the magnitude of the FC(π) contributions for SSCCs nJ (C,C) and nJ (C,H) with the same value of n , when the length of the

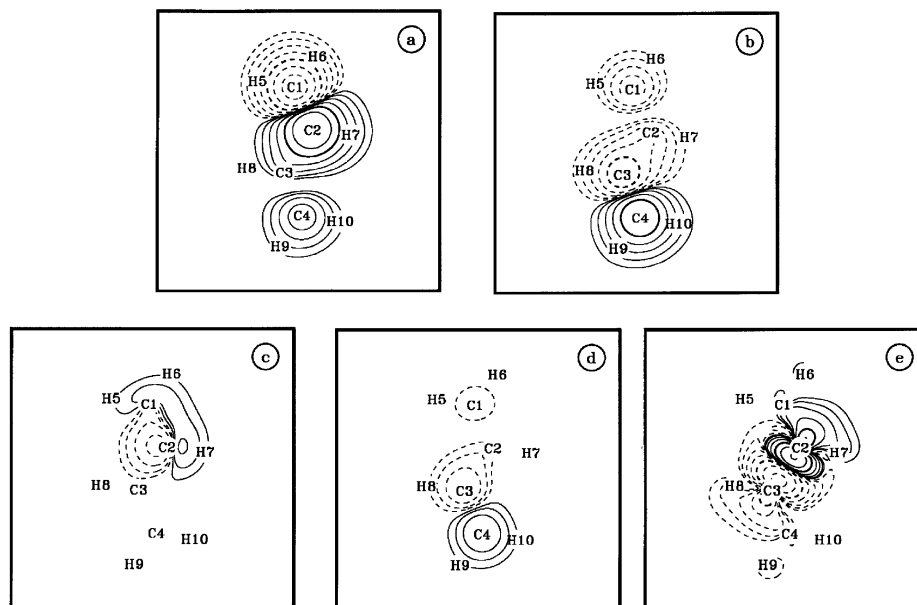


Fig. 3 The FC(π) and FC[$\pi \leftrightarrow \sigma$ (C2C3)] spin polarization for *trans*-1,3-butadiene. The drawing plane is 0.6 Å above the molecular plane (3a to 3d) or identical to the molecular plane (3e). For the choice of contour levels, see caption to Fig. 2. CP-DFT/B3LYP/[7s,6p,2d/4s,2p] calculations. The perturbing nucleus is C1. (a) The contribution of the π (C1C2) orbital to the FC(π) spin density (scaling factor: 100). (b) The contribution of the π (C1C2) orbital to the FC(π) spin density (scaling factor: 1000). (c) The contribution of the π (C1C2) orbital to the FC[$\pi \leftrightarrow \sigma$ (C2C3)] spin density (scaling factor: 1000). (d) The contribution of the π (C3C4) orbital to the FC[$\pi \leftrightarrow \sigma$ (C2C3)] spin density (scaling factor: 1000). (e) The FC[$\pi \leftrightarrow \sigma$ (C2C3)] spin density (scaling factor: 1000).

Table 4 The extent of the π contribution to the transmission of the SSCCs *via* the FC term in 1,3,5-hexatriene^a

Nuclei	# Bonds	FC	FC(π)	Total	Exp.
C–C					
1-2	1	79.9	5.1	74.5	
2-3	1	59.8	4.0	58.2	
3-4	1	80.7	5.3	75.7	
1-3	2	0.8	–2.8	–1.2	
2-4	2	1.7	–2.8	0.2	
1-4	3	7.8	2.2	11.8	
2-5	3	8.1	1.8	8.8	
1-5	4	–1.1	–1.5	–2.2	
1-6	5	1.3	1.2	3.3	
H–H					
7-8	2	1.0	–1.9	1.7	
7-9	3	10.4	1.5	10.1	
7-10	4	–0.9	–0.7	–1.0	
7-11	5	0.8	0.9	0.8	
7-12	6	–0.3	–0.3	–0.3	
7-13	7	0.6	0.6	0.5	
7-14	7	0.7	0.7	0.9	
8-9	3	16.5	1.4	16.4	
8-10	4	–0.9	–0.6	–1.0	–1.0 ^b
8-11	5	0.8	0.9	1.0	0.8 ^c
8-12	6	–0.2	–0.3	–0.3	–0.1 ^c
8-13	7	0.6	0.6	0.7	
8-14	7	0.6	0.6	0.5	
9-10	3	10.8	0.4	10.7	
9-11	4	–0.8	–0.4	–0.8	
9-12	5	0.2	0.1	0.2	
9-13	6	–0.2	–0.3	–0.3	
9-14	6	–0.3	–0.3	–0.3	
10-11	3	14.6	1.3	14.5	
10-12	4	–0.8	–0.4	–0.8	
10-13	5	0.8	0.9	1.0	
10-14	5	0.8	0.9	0.8	

^a For nuclei numbering see Scheme 1. All SSCCs are expressed in Hz and were calculated using CP-B3LYP with the (11s,7p,2d/6s,2p) [7s,6p,2d/4s,2p] basis. In each pair of nuclei the perturbed nucleus is given first. ^b Ref. 47. ^c Ref. 40.

polyene increases and by this also the polarizability of the π -density, however this increase is a second-order effect.

(2) The magnitude of a FC(π) contribution depends on whether the coupling nuclei are directly connected by double bonds in a conjugated system (ⁿFC(C,C) is relatively large), are connected by single bonds, which are part of a conjugated system (ⁿFC(C,C) values are reduced by about 1 Hz; see first and second entry in Fig. 1), are connected by CH and CC bonds where of course only the latter are part of a conjugated system (ⁿFC(C,H) is smaller), are connected by C–H bonds that are on the periphery of the conjugated system (ⁿFC(H,H) is relatively small). In this connection it is advisable to compare *K* values in SI units (values in italics in Fig. 1) rather than *J* values in Hz to separate the π -electron effects from those of the gyromagnetic ratios.

(3) The value of the FC(π) contribution depends on the position of the π bonds relative to the spin–spin coupling path. However, it does not depend on the configuration at the π bonds, *i.e.* *cis* and *trans* SSCCs have about the same FC(π) contribution as is documented by the summary in Fig. 1. Especially for ⁿFC(H,H) terms, the π contributions are independent of the configuration of the connecting bond path.

(4) Within the group of ⁿFC(C,C) values, the π contributions change their sign regularly with increasing *n*. For odd *n* values positive, for even *n* values negative FC(π) contributions result. This holds also for the ⁿFC(C,H) and ⁿFC(H,H) terms (Fig. 1), *i.e.* contrary to SSCCs *J* and their total FC terms, the FC(π) contributions strictly follow the rules predicted by a Dirac vector model. This indicates that the π -mechanism of FC spin–spin coupling is more uniform and simpler than, *e.g.*, the σ -mechanism.

(5) The FC(π) contributions decrease exponentially with increasing coupling path length *n*, however this decrease is much slower than that for the FC(σ) contributions as is reflected by the fact that the ⁿFC terms for *n* = 4, 5, 6, 7 are predominantly or even exclusively determined by the corresponding FC(π) contributions (see Tables 2 and 4). Long-range coupling is mediated by the π -mechanism as was anticipated by many experimentalists.^{4,5,25–27}

(6) Especially for the ⁿFC(H,H) terms, it becomes obvious that the negative π -contributions (*n* even) possess smaller

magnitudes than those calculated for the positive π -contributions (n odd; see Fig. 1). This is simply a result of the fact that coupling paths in a linear polyene with an even number of connecting bonds involve at least on one side two subsequent single bonds, which weaken the transmittance of FC spin polarization.

(7) A corollary of observation 6) is that long-range proton-proton coupling should be observable in polyenes (depending of course on the resolution in the NMR experiment) for $n = 5, 7, 9, \dots$ more easily than for $n = 6, 8, \dots$

The few SSCCs measured for hexatriene are in agreement with the calculated values: ${}^4J(\text{H8H10}) = -1.0 \text{ Hz}$ ⁴⁷ (calculated value of -1.0 Hz); ${}^5J(\text{H8H11}) = 0.8 \text{ Hz}$ ⁴⁰ (calculated value of 1.0 Hz); ${}^6J(\text{H8H12}) = -0.1 \text{ Hz}$ ⁴⁰ (calculated value of -0.3 Hz). Hence, the computational methods used prove again to be reliable and should provide a reasonable account of the FC(π) contributions and the π spin-spin coupling mechanism in polyenes.

The long-range effect of the π -mechanism is a result of the stronger delocalization of a π -orbital and its spin polarization as compared to that of a σ system. Also, π -orbitals are easier to polarize than σ -orbitals. This in turn depends on the excitation energies $\pi \rightarrow \pi^*$, which are much smaller than the excitation energies $\sigma \rightarrow \sigma^*$. With increasing length of the polyene, the excitation energies $\pi \rightarrow \pi^*$ decrease, which helps somewhat to compensate the decay of the spin polarization with increasing path length.

3.4. The limit of long-range coupling in polyenes

The CP-DFT/B3LYP calculations of the polyene SSCCs and their analysis at the J -OC-PSP level of theory has led to a number of interesting quantitative results characterizing the spin-spin coupling in polyenes. However, it remains to answer the question how long-ranging long-range coupling can be in a conjugated system. For answering this question we investigated the FC spin coupling in *trans,trans,trans*-1,3,5,7-octatetraene (see Fig. 4).

The FC values in Fig. 4 confirm that for large n the FC(π) term is identical to the full FC term (CC: $n \geq 7$; CH: $n \geq 7$ or 8; HH: $n \geq 7$ or 8), which in turn dominates the J value. With increasing n the magnitude of the ${}^n\text{FC}(\pi)$ terms decreases exponentially as was already indicated by the calculated

${}^n\text{FC}(\pi)$ terms for the smaller polyenes. Using the values summarized in Figs. 1 and 4 and assuming that SSCCs smaller than 0.1 Hz are difficult to measure we can predict that in a polyene ${}^nJ(\text{C,C})$, ${}^nJ(\text{C,H})$, and ${}^nJ(\text{H,H})$ are measurable up to $n = 17, 16$ and 17 , respectively. This confirms again that for the three types of SSCCs the π -mechanism is almost uniform. With NMR measurements for long polyenes in solution, conformation flexibility has to be taken into consideration. However, for a non-polar solvent such as pentane the conformational fluctuations of polyenes are expected to be small. For instance, (1,3)-butadiene has a rotational barrier of about 7 kcal mol^{-1} , which occurs at $\tau(\text{C}=\text{C}-\text{C}=\text{C}) \approx 150^\circ$. At room temperature, one can thus expect fluctuations of the conformational angles by about $\pm 10^\circ$, which should pose no problem for the NMR measurements. The *cis* conformer of (1,3)-butadiene is about 3 kcal mol^{-1} higher in energy than the *trans*-conformer. At room temperature this conformer is populated to about 0.7% and makes thus no sizeable contribution to the NMR signal. Alternatively, one may consider to perform the NMR measurements for nematic phases, where the conformational flexibility is suppressed.

The transport mechanism through the polyene chain from one end to the other is exclusively based on spin polarization of a delocalized π -system where all π -orbitals act passively. SSCCs with a smaller n than the maximal one are enhanced by echo effects of the spin polarization involving the π -orbitals.

3.5. Passive σ contributions in the case of PSO and SD coupling

In view of the importance of the passive π contributions for the FC spin-spin coupling mechanism in conjugated systems, we have also investigated the possibility of passive σ contributions in the case of PSO and SD coupling. For ethylene, the passive σ contributions PSO(σ) (calculated as difference PSO(total σ)-PSO(active σ)) are negligible, taking only in the case of ${}^1J(\text{C,C})$ a value of -0.1 Hz . This is in line with the fact that both SO coupling mechanisms are mediated by orbital currents involving the p_σ and p_π orbitals, which generate a magnetic field at the responding nucleus. This new magnetic field could generate an additional orbital current involving the $s\sigma$ electrons. The resulting new currents are definitely too weak

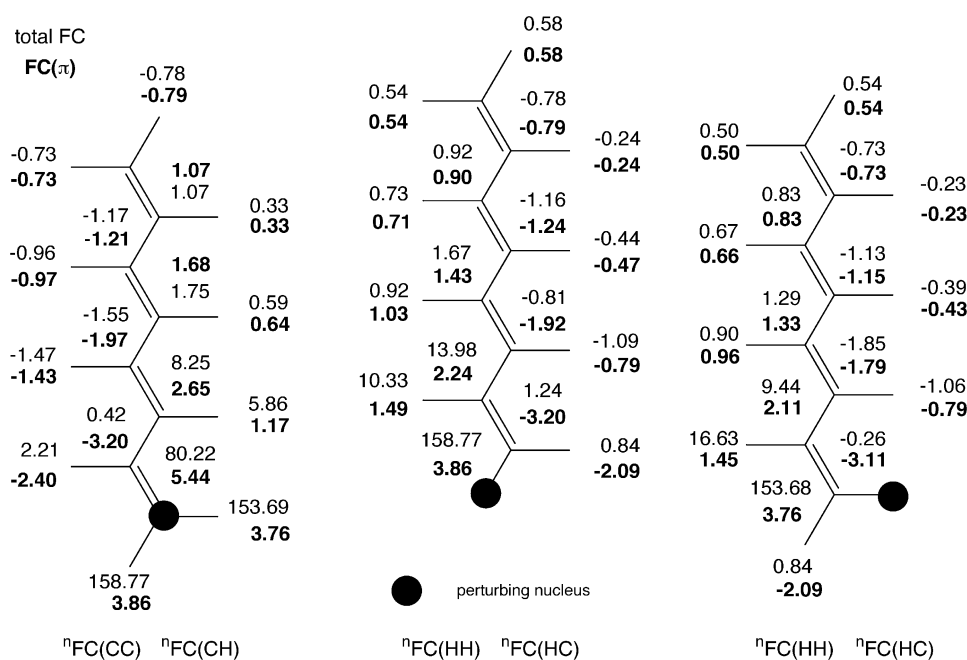


Fig. 4 ${}^n\text{FC}$ coupling terms (normal print) and FC(π) contributions (bold print) given in Hz for *trans,trans,trans*-1,3,5,7-octatetraene. The perturbing nucleus is indicated by a black ball. CP-DFT/B3LYP/[7s,6p,2d/4s,2p] calculations.

(considering the larger excitation energies) to have any significant impact on the SO terms.

In the case of the SD coupling mechanism, a passive SD(σ) contribution of 0.4 Hz is found for SSCC $^1J(\text{CC})$, which cancels partially an active contribution of -1.3 Hz. Since the SD coupling mechanism is based on the spin polarization caused by the external magnetic dipole field of the nuclear spin moment, a passive contribution implies an induction of spin polarization of the s-electrons, which is then felt by the responding nucleus. Clearly, the passive contribution must be of opposite sign compared to the active orbital contribution. The calculated data reveal that the passive SD contribution is also too small to be of any relevance for the interpretation of the spin-spin coupling mechanism. In view of the results for ethylene, we have refrained from calculating passive PSO/SD(σ) contributions for butadiene or hexatriene. However, it can not be excluded that for SSCCs with a relatively large SD term a σ -mechanism plays a significant role for the SD coupling mechanism.

4. Chemical relevance of results and conclusions

For the practical use of the observations made in this work, one has to consider the limits of measurement using modern NMR equipment. Although it is possible to measure small SSCCs, one has to keep in mind that the number of long-range SSCCs also increases with increasing length of the polyene and, therefore, it will be difficult to identify specific long-range SSCCs. Isotope substitution can simplify this task and provide the basis for making long-range coupling in polyenes a similar useful tool for structural analysis as it is already the case in saturated systems (indicating their zigzag conformation). A field of useful applications would be nano structures composed of benzenoid or cyclopolyene units. Considering both the exponential decay and the alternating signs of the long-range $^nJ(\text{C,C})$ coupling constants, NMR could be used to identify defined positions in nano structures. Alternatively, the measurement of specific long-range couplings can be facilitated by fluorine substitution. Provasi *et al.*⁴¹ performed a computational study of long-range $J(\text{F,F})$ in F-substituted polyenes and polyynes and found *e.g.* $^3J(\text{F,F}) = 12.3$ Hz for all-*trans*-(1,7)-difluoro-(1,3,5,7)-heptatetraene, corresponding to a F-F distance of 10.9 Å.

In view of the FC mechanism of long-range coupling, which is strongly based on the transport of spin polarization in a delocalized π -system, it is easy to predict that long-range coupling should be stronger in polyacetylenes and cumulenes, which is experimentally confirmed.^{4,5,25-27} Also it is easy to predict that long-range coupling is largely cut off by a 90° rotation at the single bond of a polyene as the through-space transport mechanism (indicating π -delocalization) can no longer function and echo effects are not strong enough to connect the two perpendicular π -systems effectively. If such a rotation is possible at the temperature of the NMR experiment and a polyene such as butadiene possesses global and local conformational minima (*e.g.*, for *trans* and *gauche* conformation), the measured long-range SSCCs are rotationally averaged values. Considering however that the *gauche* minimum for butadiene is already 3 kcal mol⁻¹ above the *trans* minimum, the population of the *gauche* conformer is too small to play any role for the long-range SSCCs. If long-range coupling is tested with an extra methyl group, then rotational averaging has to be considered. In aromatic and polyaromatic compounds, long-range coupling will be complicated by multipath coupling²² which can lead to a reduction of the SSCC, especially in the case of $J(\text{H,H})$ when paths with odd or even n are possible.

Clearly, further studies on long-range coupling are needed. However, these studies can be based on the results obtained in this work, which are summarized in the following:

(1) The FC(π) values calculated in this work for $^nJ(\text{C,C})$ and $^nJ(\text{C,H})$ (0.7 to 5.3 Hz, Fig. 1) are much smaller than those obtained on the basis of semiempirical calculations²⁸⁻³¹ and empirical estimates.⁴ The large values found in the semiempirical investigation are an artifact caused by the minimal basis set used in the semiempirical calculations, which are unable to describe the core and inner valence region of a heavy atom correctly. For SSCCs $^nJ(\text{H,H})$, for which the basis set problem is no longer as serious as for $^nJ(\text{C,C})$ and $^nJ(\text{C,H})$, better agreement between INDO/SOS2 and CP-DFT results is found.

(2) The π -mechanism of FC spin-spin coupling is largest for SSCCs $^nJ(\text{C,C})$, smaller for SSCCs $^nJ(\text{C,H})$, and smallest for SSCCs $^nJ(\text{H,H})$. It is rather uniform, follows strictly the Dirac vector model predictions concerning the sign of the ^nFC term, does only depend on the position of the π -units in or outside the coupling path, and decreases exponentially in magnitude with the coupling path length n . It is possible to assign typical FC(π) values to a given structural unit of a polyene (see Fig. 1) and to predict the π contributions to the FC terms of the SSCCs of a polyene.

(3) Long-range coupling in polyenes is due to the FC (π)-mechanism: The long-range passive σ contributions decrease more rapidly than the long-range passive π contributions, which results from the fact that π electrons delocalize much better than σ electrons and that due to the lower excitation energies π electrons can be spin-polarized more easily than σ electrons. With increasing path length n , the total SSCC is dominated more by the FC term, which in turn becomes equal to the FC(π) contribution.

(4) Long-range SSCCs $^nJ(\text{H,H})$ for n being odd are larger in magnitude than for n being even because the FC(π) part is larger in the first case. This can be easily explained considering the fact that for n being even, a formal CC single bond is next to one of the CH bonds in the coupling path.

(5) Formal single bonds in polyenes do not interrupt the transfer of spin information through the molecule. The gap between the two π systems at each side of the formal single bond is bridged by through-space interactions between the π orbitals, which corresponds to π -delocalization in the canonical description. The $\pi \leftrightarrow \sigma$ (C-C) interactions involving the $\sigma(\text{CC})$ orbital of the single bond contribute to the FC terms by echo effects in the order of a couple of Hz for those SSCCs involving one or both of the singly bonded C nuclei. If however the latter play only a passive role, the $\pi \leftrightarrow \sigma$ (C-C) interaction contributes less than 0.1 Hz. The σ -orbitals of the formal CC single bonds play no significant role in the long-range coupling mechanism because it is much easier to spin-polarize π -rather than σ -orbitals.

Improved knowledge resulting from this and follow-up investigations will make long-range SSCCs structural descriptors, which they largely failed to be in the past.

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