Substituent effects on the through-space nuclear magnetic spin-spin coupling in van der Waals dimers

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Abstract

We have investigated the effect of substituents on the donor (benzene) and acceptor (C-H) moieties of CH/π interacting model systems **1-6** on the through-space nuclear spin-spin coupling J_{CH} and J_{HH}. These couplings were recently predicted by ab-initio and DFT calculations to be of the order of 0.2-0.3 Hz at the equilibrium separation. Electronic effects due to the substitution are found not to increase significantly, and often to decrease, the calculated coupling, since they involve mainly π orbitals, while the coupling is mainly transmitted through σ orbitals.

Keywords: Through-space coupling, scalar coupling, CH/π interaction, DFT calculations

Introduction

Recently [1,2] we have investigated several model van der Waals system dimers showing the so-called CH/π interaction, where a C-H bond is directed, more or less perpendicularly, towards a π system, typically an aromatic ring. The model systems were comprised of a benzene ring or an ethylene molecule, as the electron density donors in the CH/π interaction, while the CH bond acceptors were represented by methane, ethylene, and benzene, respectively. For the smaller dimers, we ran a series of calculations at the ab-initio (RASSCF, Restricted Active Space Self Consistent Field and SOPPA, Second Order Polarization Propagator Approach) and DFT (Density Functional Theory) levels of theory. Nuclear spin-spin J_{CH} coupling was calculated between the hydrogen of the acceptor CH bond and the carbon atoms of the donor π system, which belong to two different molecules. The calculations consistently predicted a through-space J_{CH} spin-spin coupling in the CH/π interacting dimers on the order of 0.2-0.3 Hz, which is well above the limit of resolution of modern NMR spectrometers [3]. These results prompted us to extend the study to compounds known to have stable, long-lived, CH/π interactions, unlike the

small model dimers, so that the NMR splittings may be detected within the lifetime of the compound.

The results of DFT calculations on some compounds stabilized by CH/π interaction indicate a relatively short through-space distance between a hydrogen and a carbon atom that otherwise are separated by a large number of bonds, in agreement with the corresponding results obtained for the model system dimers. They confirm that, also in these cases, the J_{CH} spin coupling must occur through space.

The cases we have studied, however, only involved unsubstituted moieties. In this paper, we present preliminary results concerning the effects of substituents, both on the aromatic donor part as well as on the acceptor CH bond of the CH/π interacting system.

Results

For this study we have selected the model dimers shown in Figure 1. All the monomers were optimized at the HF/6-31G* level of theory by using the *Gaussian 98* software package [4]. The distance R between the carbon of the CH bond and the center of the aromatic ring was set to 3.80 Å, which is in the minimum potential well for interaction of the corresponding unsubstituted complexes [1,2].
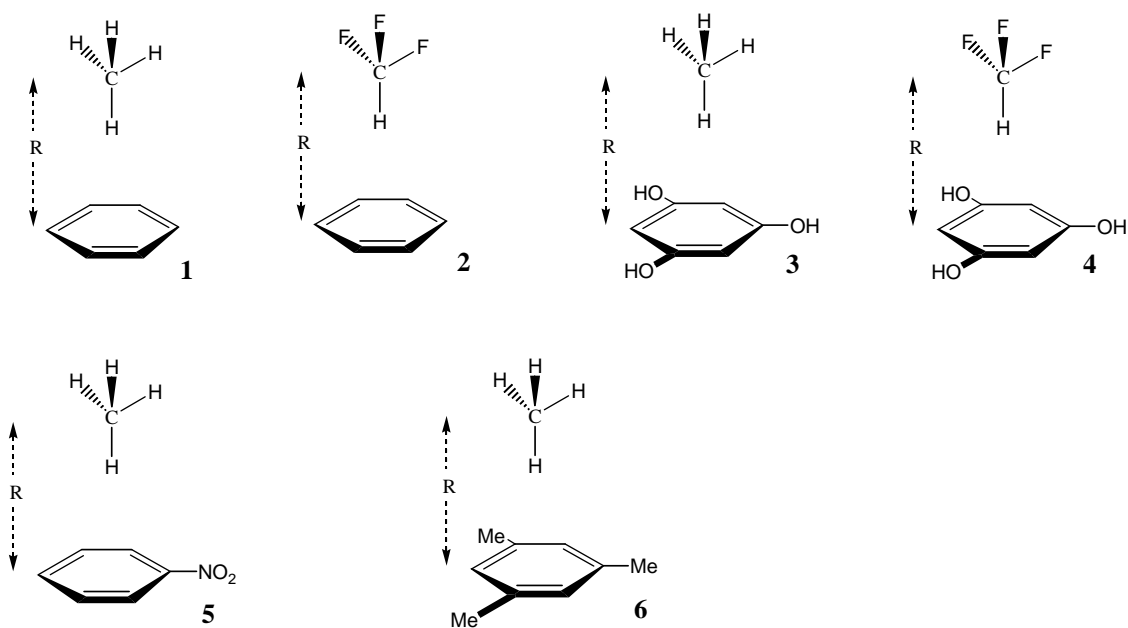
Figure 1. Schematic representation of the model dimers studied in this work.

It is useful, at this point, to recall some qualitative considerations on the effect of substituents on the energetics of the CH/π dimers [5]. If we consider the CH/π interacti on as a donor/acceptor interaction with a partial charge transfer from the HOMO of the donor (aromatic

ring) to the LUMO of the acceptor (CH bond), then substituents on the donor which increase the energy of the HOMO (electron-donating substituents) and/or substituents on the acceptor which decrease the energy of the LUMO (electron-withdrawing substituents) will increase the stability of the dimer. This is because more electron density is "pushed" onto the aromatic ring and/or more electron density is also "pulled" onto the CH bond. Therefore we expect the dimer **4** to be the most stable and the unsubstituted dimer **1** the least stable. However, it is by no means clear how these substituents can affect the through-space coupling. Therefore we have calculated J_{CH}, as well as J_{HH}, between the hydrogen of the CH bond and the carbon and hydrogen atoms of the aromatic ring. We have used the *deMon-NMR* software package [6] to calculate the spin-spin couplings at the VWN/IGLO-III level of theory, as in our previous studies [1,2]. The *deMon-NMR* code allows for the calculations of the main contributions to the spin-spin couplings, namely the Fermi contact term (FC) and the diamagnetic (DSO) and paramagnetic (PSO) spin-orbit contributions. The results of such calculations are reported in Table 1.

Table 1. Through-space spin-spin couplings (Hz) for the dimers investigated

		FC	PSO	DSO	Total
1	J_{CH}	0.09	-0.28	0.38	0.19
	J_{HH}	0.00	-0.15	0.15	0.00
2	J_{CH}	0.05	-0.38	0.53	0.21
	J_{HH}	0.00	-0.42	0.57	0.16
3	$J_{CH}^{(a)}$	0.04	-0.45	0.52	0.11
	$J_{CH}^{(b)}$	0.11	-0.39	0.45	0.16
	J_{HH}	0.01	-0.30	0.30	0.01
4	$J_{CH}^{(a)}$	0.03	-0.55	0.68	0.15
	$J_{CH}^{(b)}$	0.06	-0.49	0.60	0.17
	J_{HH}	0.01	-0.57	0.73	0.17
5	$J_{CH}^{(a)}$	0.08	-0.46	0.52	0.15
	$J_{CH}^{(d)}$	0.11	-0.33	0.44	0.21
	$J_{CH}^{(e)}$	0.09	-0.31	0.41	0.19
	$J_{CH}^{(f)}$	0.10	-0.30	0.40	0.20
	J_{HH}	0.00	-0.30	0.30	0.00
6	$J_{CH}^{(a)}$	0.07	-0.36	0.46	0.17
	$J_{CH}^{(b)}$	0.09	-0.36	0.44	0.17
	J_{HH}	0.00	-0.30	0.30	0.00

[a] Substituted Carbons. [b] Unsubstituted carbons. [c] Ortho carbons. [d] Meta carbons. [e] Para carbon.

First of all let us consider the unsubstituted dimer **1**. In this case, as already found in our previous work [1,2], the through-space J_{CH} spin-spin coupling is of the order of 0.2 Hz and stems equally from a non negligible FC term (0.09 Hz) and from a non exact cancellation of the spin-orbit contributions (0.10 Hz). The J_{HH} spin-spin coupling, instead, is essentially zero, because the FC term is zero, and because of an exact compensation of the spin-orbit contributions.

The substitution of the hydrogen on the CH bond with fluorine atoms leads to dimer **2**. Here, we observe a slight increase in the total J_{CH}, up to 0.21 Hz and a large increase of the J_{HH} spin-spin coupling to 0.16 Hz. However, the increase is entirely due to the spin-orbit contribution; in fact the FC term of the J_{CH} coupling is strongly decreased by 50%, while the FC term of J_{HH} remains zero. For dimer **3**, the results differ according to the substitution on the carbon atoms of the donor aromatic moiety. For both types of carbons, a decrease of J_{CH} is observed compared to model dimer **1**. This decrease is due to (i) a decrease in the value of the FC term for the substituted carbons and (ii) to a decrease in the spin orbit contribution for the unsubstituted carbons. Once again, the J_{HH} values are unaltered, the FC term remains zero, and the spin-orbit contributions exactly cancel each other.

The results of model dimer **4** show the same trend compared with **3**, as observed when going from dimer **1** to dimer **2**. In fact, there is a slight increase in the total through-space spin-spin coupling, which is due entirely to the spin-orbit contribution. The FC term is reduced by about 50% compared to dimer **3**, but an increase in the spin-orbit contributions compensate for this reduction, particularly for the J_{HH} coupling, which rises to a value of 0.17 Hz.

In dimer **5**, the benzene ring bears an electron-withdrawing substituent, $-NO_2$. The effect of this substitution appears to be almost irrelevant. Compared to the unsubstituted dimer **1**, the presence of the nitro group slightly alters the various contributions to the total through-space coupling, but no major changes in either J_{CH} or in J_{HH} can be detected.

Finally, the mesitylene-methane dimer **6** does not show any relevant difference compared to the unsubstituted model dimer **1**.

Discussion

Apparently, none of the attempted substitutions, either in the donor π system or in the acceptor CH bond, was capable of producing an increase in the strength of the through-space spin-spin coupling. Even more surprisingly, the FC contribution appeared to be unaltered by substituents or, more often, strongly diminished. This result may appear to be counter-intuitive, since the Fermi contact term is proportional to the amount of delocalization of the electrons between the nuclei involved in the coupling. In this respect, **3** certainly displays larger charge transfer character, from the 1,3,5-trihydroxybenzene HOMO to the trifluoromethane LUMO, than does (unsubstituted) **1**. However, we should recall that the FC contribution is transmitted by σ-type orbitals, since it requires the probability, and therefore the wave function of the electron, to be non-zero at the nucleus. On the other hand, the mesomeric electronic effects on the benzene ring

only involve the aromatic π system, which has a nodal plane on the carbon atoms. These effects, therefore, should not be invoked to explain the results.

If we concentrate on σ-type orbitals it is not surprising that substitution with more electronegative atoms produce a reduction of the Fermi contact contribution. The more electronegative atom (e.g., oxygen in **3**) attracts the *s* electron density of the carbon, thereby reducing the already small overlap with the *s* electron density of the hydrogen of the CH bond. Therefore, the coupling with the substituted carbon atom of **3** decreases to 0.04 Hz. Substitution of hydrogens by fluorine on the CH bond has exactly the same effect, thereby polarizing the *s* electron density far away from the internuclear region, thus decreasing even more the FC term associated with all carbon atoms of 1,3,5-trihydroxybenzene in **4**.

Despite the opposite mesomeric effect, already mentioned, of the nitro group with respect to the hydroxy group, nitro substitution in **5** produces the same effect as the other substitutions. Thus, the nitro group polarizes the *s* electron density towards the periphery of the dimer and reduces the overlap which is responsible for the small through-space FC contribution to the coupling.

Since all substitutions with a more electronegative atom on the aromatic ring and on the CH bond lead to a decrease of the FC term, and often a decrease of the overall coupling, we also investigated the effect of alkyl substitution, as in **6**. However, this produced no significant changes in the through-space coupling. The inductive effect, which may be expected to be effective in this case, seems not to be large enough to induce an increase in the coupling.

At this juncture, it is instructive to visualize the "small" overlap between the *s* orbitals of the hydrogen of the CH bond and the adjacent carbon atom in the aromatic ring. In Figure 2 we show a molecular orbital obtained as a linear combination of the 1*s*, 2*s* and 3*s* basis function of the carbon atoms of the aromatic ring and the 1*s* and 2*s* orbitals of the hydrogen of the CH bond, for the dimer **2**.
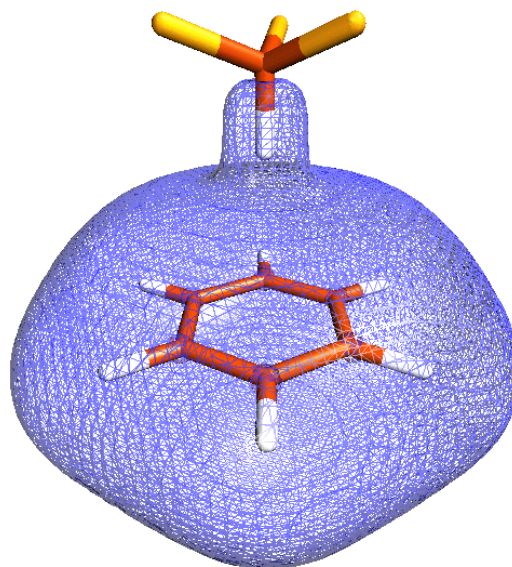
Figure 2. Molecular orbital of model dimer **2**. Contour level is 0.002; HF/6-31G* level of theory.

   The contour value in Figure 2 is set to 0.002, which indicates the small overlap that exists between the two *s* electron densities, one from the donor and one from the acceptor. However, when present, this small overlap is responsible for the observed Fermi contact contribution.

   The trends observed in the spin-orbit contribution are more difficult to rationalize. It is interesting to notice that the substitution of the CH bond with fluorine produces an increase in the otherwise negligible J_{HH} coupling.

Conclusions

We have investigated substituent effects on the through-space spin-spin coupling on the donor and acceptor moieties of a series of CH/π interacting dimers. The results of DFT calculations can be interpreted qualitatively, limited to the Fermi contact contribution, by considering the difference in electronegativity of the substituent ligands rather then their electronic mesomeric effects. Therefore, we do not observe any difference between "activating" and "deactivating" substituents with respect to the benzene ring. In contrast, because in all cases the substituent ligand is more electronegative than hydrogen, the effect of the substituent is to reduce the Fermi contact contribution to the coupling. This reduction may be offset by an increase in spin-orbit contribution. However, no significant increase in the overall coupling can be induced by the kind of substitution we have considered. These results suggest that a larger value of the coupling, in particular an increase in the Fermi contact contribution, could be present in systems where the

hydrogen and carbon atoms are bonded to an electropositive element, as, e.g., in organometallic compounds.

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