Hydrogen Bonds

^{1}J(C,H) Couplings to the Individual Protons in a Methyl Group: Evidence of the Methyl Protons' Engagement in Hydrogen Bonds[**]

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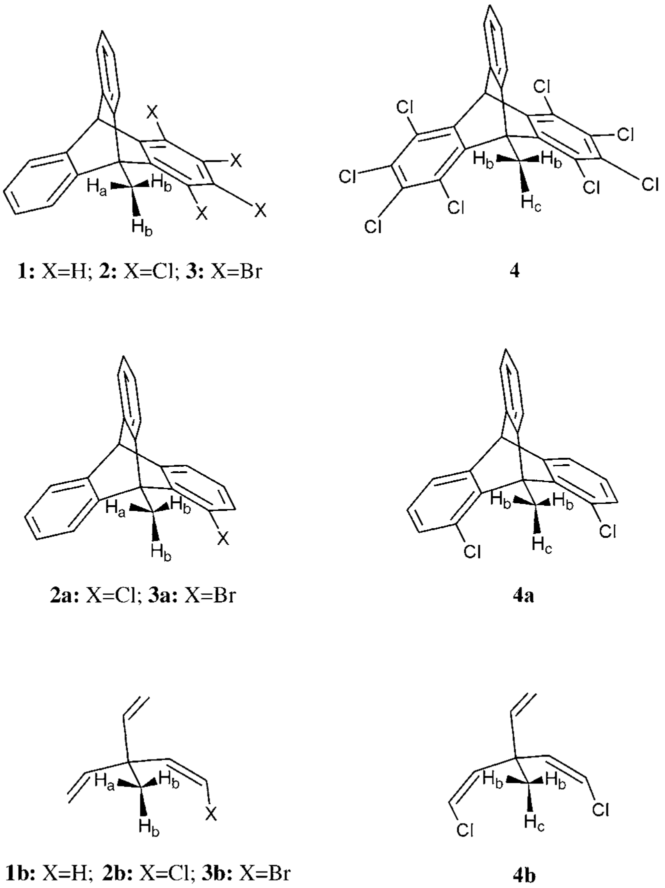
The exceptionally high torsional energy barriers, reaching 40 kJ mol^{-1}, for the methyl group in 9-methyltriptycene derivatives bearing chlorine or bromine atoms in the *peri*-positions, allow the freezing out of the stochastic motion of the methyl rotor in these compounds on the timescale of NMR spectroscopy experiments in liquids.[1–3] The measurements performed by us at ambient temperature for the parent 9-methyltriptycene (**1**) as the reference molecule and in the range of 170–200 K for 1,2,3,4-tetrachloro-9-methyltriptycene (**2**), 1,2,3,4-tetrabromo-9-methyltriptycene (**3**), and 1,2,3,4,5,6,7,8-octachloro-9-methyltriptycene (**4**; Scheme 1), yielded the ^{1}J(C,H) couplings to the individual methyl protons in all three halogeno derivatives. The protons of the methyl group in these compounds represent a first-order A_2B spin system with $^{2}J_{H,H}$ of approximately 12.5 Hz and a $|H_a$-$H_b|$ chemical shift difference of about 0.9–1.1 ppm, depending on the compound. This result allowed us to determine the ^{1}J(C,H) couplings directly from the corresponding ^{13}C satellite signals in ^{1}H spectra. The results are presented in Table 1.


1: X=H; **2:** X=Cl; **3:** X=Br

4

2a: X=Cl; **3a:** X=Br

4a

1b: X=H; **2b:** X=Cl; **3b:** X=Br

4b

Scheme 1. Top row: Structures of the 9-methyltriptycenes investigated. Middle row: model compounds for molecular geometry optimization. Bottom row: *cis* 1-halogeno-3-methyl-3-vinylpenta-1,4-dienes used as models for *J* coupling calculations.

In the parent methyltriptycene **1** (in which the methyl protons are isochronous; Scheme 1) the ^{1}J(C,H) coupling of the methyl group (126.8 Hz) is similar to that in the methyl group of ethylbenzene (126.0 Hz).[4] In compounds **2** and **3** the ^{1}J(C,H) value of approximately 131 Hz for protons H_b which are close to the *peri* atom X (see Scheme 1) is considerably larger than that in **1**. For the *trans* disposed proton H_a which is remote from X, the coupling value is 124 Hz and is smaller than in **1**. In **4**, substitution of the second *peri* position with Cl causes further increase, up to the value of 135.5 Hz, of the coupling to the proton (H_c) which is close to the two chlorine atoms. In this compound, the $^{1}J(C,H_b)$ couplings to the two remaining protons which have only one halogen atom at their neighborhood each are of 128 Hz. Thus, a close contact between a halogen atom and the proton involved in a C–H coupling causes a substantial increase of the ^{1}J(C,H) value.

The results can be interpreted in terms of a C–H⋯X (X = halogen atom) interaction representing a specific, recently identified sort of hydrogen bonding.[5a] For sp^{3} carbon atoms, the distinctive feature of such a bonding is an electron-density transfer from the electron donor (X) to the σ* orbital between the carbon atom and a substituent on the carbon atom that is remote from the donor.[5a] The interaction has been termed hydrogen bonding because, as for the ordinary hydrogen bonds, it is associated with a characteristic modification of the C–H bond(s) proximate to X.[5a] However, instead of a weakening typical for an ordinary hydrogen-bond, a strengthening/contraction is observed for such bonds.[5a] Because this is reflected in a hyperchromic shift of the C–H stretching frequency, the effect is called blue-shifting hydrogen-bond.[5a] It can also cause an enhancement of the corresponding *J*(C,H) couplings.[5a–c] The occurrence of such a bond has already been postulated in many intermolecular systems.[5a–d] but its influence on the C–H coupling was usually much weaker

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Supporting information for this article (synthesis, NMR measurements, computational methods, X-ray structure of compound **2**) is available on the WWW under http://www.angewandte.org or from the author.

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(ca. 1 Hz or smaller[5c,d]) than the effects reported herein. At variance with intermolecular systems, in an intramolecular case there are no reference values for the stretching frequencies and ^{1}J(C,H) couplings of interest. Therefore, a series of indirect arguments is given below that speak in favor of the blue-shifting hydrogen bonds to occur in the systems presented.

Table 1: ^{1}J(C,H) Couplings to methyl protons in 9-methyltriptycene derivatives.

Compound	^{1}J(C,H) (exp) [Hz]			Compound	^{1}J(C,H) (calcd)[a] [Hz]		
	H_a	H_b	H_c		H_a	H_b	H_c
1	126.8	–	–	**1b**	122.2	–	–
2	124	130.5	–	**2b**	118.8	124.2	–
3	124	131.5	–	**3b**	118.3	124.7	–
4	–	128.0	135.5	**4b**	–	121.2	129.5

[a] Calculated using truncated models of series **1b**–**4b** with the geometries optimized for **1** and models of series **2a**–**4a** (see text and Scheme 1).

We consider the RB3LYP/6-31G(D,P)-optimized geometrical data[6] for **1** and for the appropriately simplified model compounds, that is, the 1-chloro- (**2a**), 1-bromo- (**3a**), and 1,5-dichloro- (**4a**) derivatives of 9-methyltriptycene, (Scheme 1, middle). The calculated C–H bond length of 1.094 Å in the methyl group of the parent compound **1** is close to the value of 1.095 Å obtained by the same method for the methyl group in ethylbenzene. In agreement with expectations for the blue-shifting hydrogen-bond model, in **2a** and **3a** the C–H_b bonds near the halogen atom are shrunk to 1.090 Å while the length of the remote C–H_a bond remains the same as in **1**. The most significant contraction of the C–H bond, down to 1.085 Å, occurs in **4a** for the methyl proton H_c which is near to two chlorine atoms (with a distance of approximately 2.70 Å to each). For the two remaining protons in **4a** (protons H_b), the corresponding values are 1.091 Å and are close to those for protons H_b in **2a** and **3a**. Note that the DFT geometry of **2a** has been validated by the X-ray structure obtained for **2** (as far as the carbon atom positions are concerned; the experimental H atom positions are insufficiently accurate).[7]

Further evidence of the occurrence of the C–H···X interaction is obtained from an analysis of the DFT *J* couplings calculated for the model *cis* and *trans* 1-halogeno-3-methyl-3-vinylpenta-1,4-dienes, (**2b**–**4b**, *cis* compounds shown in Scheme 1, bottom).[8,9] The trends observed in the experimental *J* values are well reproduced by the couplings calculated for compounds of the *cis* configuration (Table 1). The couplings in *trans* compounds where the C–H···X interaction is not possible are very close to the DFT *J* coupling in the parent compound **1b** (122 Hz or slightly smaller). In all the cases the Fermi contact contribution is the main factor determining the coupling values (> 98 %) as well the changes occurring in them. The dia- and paramagnetic orbital dipole terms are small and their magnitudes remain constant through the whole series of the compounds studied.

For such 9-methyltriptycene derivatives where the *peri* substituents do not have electron-donating properties, examples of the methyl group dynamics being frozen on the timescale of liquid-phase NMR spectroscopy are not known.[2] Therefore, the strong steric repulsion alone, experienced by the methyl group in the transition state, is not enough to hinder the methyl rotation. When, as in the compounds investigated, the potential electron donors are present at a suitable distance, the ground torsional state can gain an extra stabilization through the hydrogen bonds engaging the methyl protons. This situation would explain the ease with which the methyl group rotation can be stopped, because in the transition state a similar stabilization could not be effected for geometrical reasons.

The most direct evidence of the occurrence of the C–H···X hydrogen bonds stems from the natural bond orbital (NBO) analysis.[10] In **2a**, an electron-density transfer from one of the three lone pairs of Cl to the remote σ* orbital on the methyl carbon atom,[5a] that is, to the σ* orbital of the C–H_a bond situated *trans* to *peri*-Cl, does take place. (Note that, for the blue-shifting hydrogen-bond to be formed, the accepting orbital on carbon need not involve a C–H bond; in general, it can involve any properly situated C–Y bond[5a] (see also the Supporting Information).) The corresponding NBO stabilization energy[10] is 4.5 kJ mol^{-1}, this value can be used as a rough measure of the strength of the intramolecular hydrogen bond concerned. It seems likely that the decrease of the ^{1}J(C,H_a) coupling below the value in the parent system **1** is a response to this electron transfer.

The foregoing discussion sheds new light on the nature of factors that shape up the torsional potential of the methyl groups in the triptycenes investigated. Following the discovery of a novel dynamic effect, most clearly exhibited by strongly hindered methyl groups, the so called damped quantum rotation,[3,11] a renewed interest in NMR spectroscopy studies of such systems can be expected.

Finally, effects similar to those described above were also found in 1,2,3,4-tetrachloro-9,10-dimethyltriptycene (**5**) and 1,2,3,4-tetrabromo-9,10-dimethyltriptycene (**6**). In 1,2,3,4-tetrafluoro-9-methyltriptycene (**7**) the torsional energy barrier is not high enough to allow direct observation of the ^{1}J(C,H) couplings of the individual methyl protons. For the CH···F grouping the NBO stabilization energy of only 2.5 kJmol^{-1} was calculated for **7a**. Accordingly, the difference between the calculated ^{1}J(C,H) couplings in **7b**, ^{1}J(C,H_b)$-$$^{1}J$(C,$H_a$) = 4.5 Hz, is noticeably smaller than the corresponding quantity for **2b** (5.4 Hz, see Table 1). This result is in a qualitative agreement with the relationship between the respective NBO stabilization energies. (For more details concerning compounds **5**–**7** see the Supporting Information.)

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