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THE DEUTERIUM ISOTOPE AS A POLAR SUBSTITUENT?

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Abstract Long range deuterium isotope effects on ^{13}C chemical shifts of several biphenyl derivatives are presented and discussed in terms of polar substituent effects.

Secondary deuterium isotope effects on chemical equilibria and reaction rates have been interpreted in terms of inductive and mesomeric substituent effects[1]. Although this point of view may be criticized as contradictory to the Born-Oppenheimer approximation it has found widespread application in the rationalization of deuterium isotope effects on the ^{13}C NMR spectra of neutral aromatic molecules[2]. Recently shifts to lower field of the signals of ortho and para ring carbons in side chain α-deuterated benzene derivatives were shown to correlate with π-bond orders[3] and long range spin-spin coupling constants[4], substantiating the idea of isotopic perturbation of hyperconjugation on a more quantitative level.

According to this substituent-model a deuteron directly attached to the aromatic nucleus should give rise to isotope effects, mainly by polar mechanisms. Indeed such long range effects have been reported for polyenic molecules[5,6].

A correlation between isotope effects and ρ_I- and ρ_R-parameters as obtained from a dual substituent parameter (DSP) analysis of substituent chemical shifts (SCS) would strongly support this concept. We have therefore chosen to investigate a series of substituted biphenyls 1 (Tab.1) where ρ_I and ρ_R values for all carbon atoms are known from a DSP analysis[7].

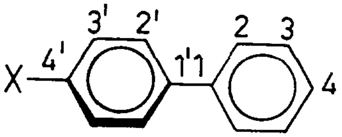

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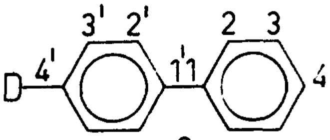
Table 1 Deuterium Isotope Effects on ^{13}C Chemical Shifts of Biphenyl Derivatives[a)] and $\rho_{I/R}$ Values from SCS Analysis[7].

C	4′	3′	2′	1′	1	2	3	4	α-C	β-C
2	277	109	b)	0	−10	0	0	4		
3	277	109	8	0	−10	0	0	6		
4	280	109	10	3	−10	0	0	2		
5	101	7	0	−8	−8	0	0	3	823	
6	100	0	6	−10	−10	0	0	0	823	
7	−25	0	0	24	−13	0	0	9	679	1110
ρ_I	–	–	2.87	5.77	−2.86	0.53	0.37	1.94		
ρ_R	–	–	−1.21	15.05	−1.25	1.02	0.32	2.13		

a) Values given in ppb; a positive sign means that the signal of the deuterated compound occurs at higher field. Spectra recorded at 100.6 MHz on a Bruker WH-400 spectrometer in acetone-d_6 solutions. All solutions contained unequal amounts of deuterated and parent compounds. Errors amount to 0.75 ppb.
b) not observed.



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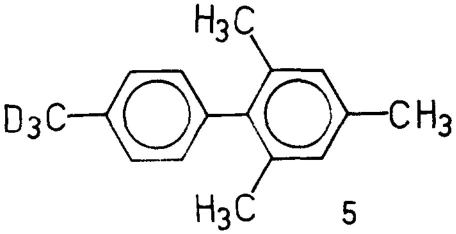

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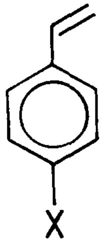

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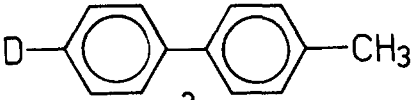

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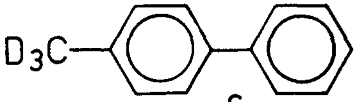

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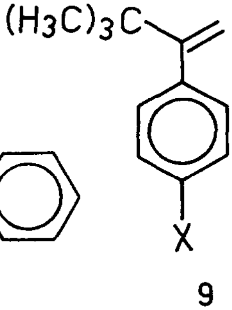

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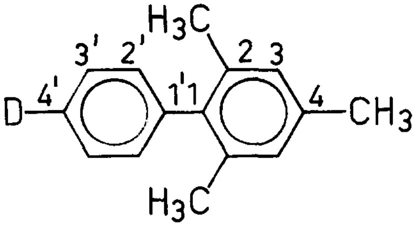

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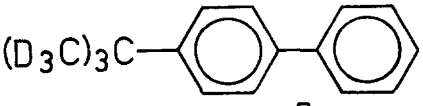

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The negative signs of ρ_I and ρ_R for C-1 and positive signs of ρ_I and ρ_R for C-4 indicate π-polarization of the second ring by substituents in 4′-position. Electropositive substituents consequently yield shielding of C-4 and deshielding of C-1. This is indeed in a qualitative manner the pattern of long range deuterium isotope effects observed for compound 2 and all other biphenyls studied here.

Furthermore, due to the torsional angle of ca 80° caused by the two ortho methyl groups in 4[8], the behaviour of the deuterium isotope effects parallels that of the SCS values for a comparable example. Thus, compounds 3 and 4 exhibit no difference in their isotope effects at C-1. The value at C-4, however, reduces from 6 ppb in 3 to 2 ppb in 4 and an additional difference in the shift at C-1′ arises in 4. From these data one may conclude that π-polarization of the second ring in biphenyl derivatives consists of two components, the extended and the direct[7,9]. The latter should be responsible for nearly all the polarization in the second ring of 4 and a corresponding part in 3. Steric inhibition of extended π-polarization in 4 causes the difference in chemical shift of 3 ppb at C-1′. Interestingly summation of the isotope effects of C-1′ and C-4 of 4 reproduces the value of C-4 in 3 (torsional angle ca 20°). Similar angle dependence of SCS values exists in the 4-substituted styrene derivatives 8 and 9[10]. The t.butyl group prevents coplanar arrangement of the vinyl group and the aromatic ring in the series of compounds 9. As a consequence reduced π-polarization of the vinyl group is observed which mainly affects the shifts of the β-position of the double bond, while the effects at the α-carbon remain almost constant in both series.

Each mesityl ring in 4 and 5 is polarized to the same extent. Due to the torsion these effects cannot originate from hyperconjugation in 5 leaving the difference in polar character between the CD_3- and CH_3-group in 4′-position as the sole plausible explanation. Again, these isotope effects in 5 should reflect the direct component of π-polarization, whereas the negative values in the first ring at C-1′ of 5 and 6 are due to isotopic perturbation of hyperconjugation similar to that in toluene[2]. Steric inhibition of extended π-polarization confined to the first ring of 5, changes the negative splitting of this carbon atom as compared to the less twisted counterpart 6. In the latter molecule neither hyperconjugation nor extended π-polarization are sterically inhibited. Both effects therefore cancel at C-4 in the second ring.

The photoelectron spectra of a series of alkyl-benzenes have been interpreted using CC-hyperconjugation between the t.butyl group and the aromatic π-system[11]. Deuterium isotope effects should be well suited to contribute to the discussion of CC-hyperconjugation. In comparison to a CD_3-group a perdeuterated t.butyl group effects a reversed hyperconjugative interaction with the adjacent ring, because electron density between the α- and β-carbons of the t.butyl group is inductively enhanced by deuteration of the β-carbon atoms[12]. The predicted shielding at C-1′ of 7 is experimentally borne out by an isotope effect of 24 ppb. The two signal splittings in the second ring again can be accounted for by the difference in polar and mesomeric character of the two isotopomeric t.butyl groups, the polar effect predominating at C-1.

It has to be emphasized that the correspondence between substituent induced shifts and deuterium isotope effects as delineated above is only qualitative. A satisfacory correlation between the isotope effects and ϱ_I and ϱ_R values could not be obtained, perhaps due to the small number of data available for one particular class of compounds.

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