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LONG RANGE SECONDARY ^{2}H ISOTOPE EFFECTS IN THE ^{13}C-NMR SPECTRA OF NAPHTHALENE AND AZULENE

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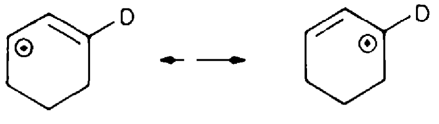
Abstract — 2,3-d_2-Naphthalene **2**, 2-d_1-azulene **3**, 6-d_1-azulene **4** and 1,3-d_2-azulene **5** have been synthesized. The 100.6 MHz ^{13}C-NMR spectra of these compounds show long range isotope effects compared with the unlabelled materials over up to six bonds. Semiempirical MO calculations fail to account for the deuterium isotope effects.

Deuterium isotope effects on NMR chemical shifts have been known for a long time,[1] however the true cause for downfield and upfield long range deuterium isotope effects is under intensive current discussion.[2-10] The observation of a γ-downfield isotope effect of 0.17 ppm in the ^{13}C-NMR spectrum of the cyclohexenyl cation **1** was interpreted by Saunders as "isotopic perturbation of resonance".[2]



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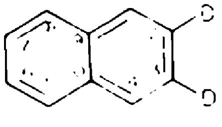
Since then, γ- and δ-downfield isotope effects have been found by Günther[3] in cyclopentane and cycloheptane, where clearly a resonance perturbation can not exist. Other explanations of downfield isotope effects include isotopic perturbation of equilibrium,[4] different ability of hydrogen bonding for OD- and OH groups,[5] and conformational effects.[6]

A further discussed reason for downfield deuterium isotope effects is the less efficient hyperconjugative electron release of deuterium atoms located in beta position to a resonance system.[7,8] Very recently even through space deuterium isotope effects in paracyclophanes have been proposed.[9] Although all these different mechanisms may be valid in certain cases, we would like to show, that similar effects can be found in compounds where all these explanations can not be correct.[10]



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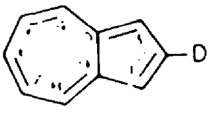

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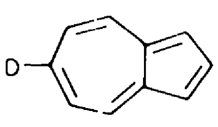

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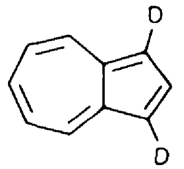

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RESULTS AND DISCUSSION

We have therefore synthesized 2,3-d_2-naphthalene **2** and a series of deuterated azulenes **3-5**, all compounds in which conformational effects or equilibrium isotope effects as well as intermolecular interactions are negligible. Since the deuterium atoms are bounded directly to the aromatic ring system the isotope effects can not be understood in terms of hyperconjugation.

The results of the ^{13}C-NMR measurements are given in the Table 1 for the compounds **2-5**, these have been obtained by mixing unequal amounts of labelled and unlabelled material in d_6-acetone to facilitate the relative assignment of the isotopically splitted resonances. Positive sign of the values given in parts per billion (ppb) indicates a downfield deuterium isotope effect.

The α- and β-effects are in the same order as previously reported for similar compounds.[11] In naphthalene **2** the carbon atoms at the γ- and the δ-position with respect to the deuteration show no isotope splitting. Surprisingly, however, the signals of the carbon atoms 6 and 7 do display a small isotope effect of −10 ppb. In the azulenes **3** and **4** both γ-isotope effects are positive, furthermore we find in both molecules upfield isotope effects over six bonds.[12] Hence in both molecules the isotope effect is first of negative sign, changes its sign at the γ-position and changes again at the ϵ-position. In **5** we find only negative isotope effects as in **2**.

It has been argued[13] that deuterium isotope effects could arise in addition to the mechanisms mentioned above from an "inductive" isotope effect. Due to the lower zero point motion of the heavier isotope and the unharmonic vibrational potential the deuterium atom is at the average closer to the carbon atom than hydrogen. Neutron diffraction studies found a CD distance in deuterated naphthalene of 1.073 Å[14] compared with the average CH distance in aromatic compounds of 1.085 Å.[15] The closer CD distance would lead to an inductive effect, which in π-systems could be transmitted even to carbon atoms rather far apart from the side of deuteration. If the observed splittings are due to such an "inductive isotope effect" one would expect that the signs of the substituent increments of an inductive group such as the methyl group would correlate with the signs of the isotope splittings. This, however, is not the case, as shown by a comparison with the ^{13}C-NMR spectra of methyl substituted azulenes[16] and naphthalenes.[17]

Table 1. Deuterium isotope effects in the ^{13}C-NMR spectra of the compounds 2–5

Compound	Carbon atoms									
	1	2	3	4	5	6	7	8	9	10
2	-115	-386	-386	-115	-	-12	-12	-	-	-
3	-108	-246	-108	-	-10	-9	-10	-	+13	+13
4	-7	-15	-7	+27	-96	-322	-96	+27	+9	+9
5	-270	-222	-270	-39	-30	-16	-30	-39	-113	-113

Values given in ppb, negative sign indicates upfield deuterium isotope effect.

To get further insight into the nature of these isotope effects, we have carried out some semiempirical MO-calculations on the INDO,[18] the CNDO/2 and the MNDOC[19] level. For this purpose the geometries of naphthalene and azulene were optimized with the MNDOC program. The deuterium label was then simulated by shortening the C–H distance at the substitution site from 1.09 to 1.07 Å in 0.05 Å steps. The SFC accuracy was good enough to give a consistent change in the electron density for all carbon atoms. The changes in σ- and π-electron density were taken as a measure of the isotope effect. The INDO and CNDO/2 programs correctly reproduce the α-isotope effects giving about 2 millielectron higher electron density at the α-carbon atoms. This is expected as judged from the well known relationship of about 160 ppm per electron.[20] However, already the β-effect was predicted by all programs to be of opposite sign compared with the α-effect, whereas experimentally all α- and β-deuterium isotope effects are negative. The programs predict that σ-electron change is dominating at the α-position, whereas π-electron changes cause the sign reversal at the β-position. At longer distance π-electron changes become of equal magnitude as the σ-electron changes. The calculated differences in electron densities between the normal and the deuteriated compounds, however, do not correlate with the experimental results.

The IR-spectra of azulene and of deuteriated derivatives of azulene have been extensively investigated.[21,22] The authors discuss the possibility of Fermi resonance between the CH vibrations, especially for the 2 and 6 positions.[22] Therefore, on deuteriation of one CH group the vibrational behaviour of even distant CH groups can be affected. The very small deuterium isotope effects observed by ^{13}C-NMR could possibly be viewed at as a NMR-detection of the different vibrational situation of the deuteriated compound. To make quantitative predictions which are based on this model, however, is not possible at the moment.

CONCLUSION

We have shown that long range deuterium isotope effects can be observed in molecules where the mechanisms discussed in the literature are not valid. Semiempirical MO calculations fail to reproduce the experimental results. Further investigations for an appropriate model, which explains the data in deuteriated aromatic compounds are necessary.

EXPERIMENTAL

2,3-d_2-Naphthalene 2 was prepared by the deuteriodebromination procedure[11] from 2,3-dibromo-naphthalene.[23] The compound was purified by GLC. MS analysis showed a deuterium distribution of 3% d_0, 26% d_1, 58% d_2 and 13% d_3. This, however, did not affect the results of the ^{13}C-NMR measurements. 2-d-Azulene 3 was prepared according to the procedure given by Alder.[24] 6-d-Azulene 4 was prepared using the single pot version of the Hafner azulene synthesis[25] starting from 4-d-pyridine.[26] 1,3-d_2-Azulene was obtained by H/D exchange of azulene.[27] The 100.6 MHz ^{13}C-NMR spectra were taken on a Bruker WH-400 spectrometer in d_6-acetone solutions. The measurements have been repeated several times, first with the pure deuteriated compounds and then after subsequent addition of small amounts of the unlabelled material. The spectral width was set to 1000 Hz for naphthalene and to 3000 Hz for azulene. 64 K spectra were taken to allow a digital resolution of better than 0.1 Hz/point after the Fourier Transform. Gaussian multiplication[28] of the FID was used to increase the resolution.

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