Tetrahedron Letters,Vol.23,No.28,pp 2845-2848,1982 0040-4039/82/282845-04$03.00/0
Printed in Great Britain

DEUTERIUM-INDUCED PERTURBATION OF HYPERCONJUGATION ?
- A CARBON-13 NMR STUDY -

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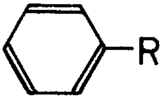
Abstract: $^{2}H/^{1}H$ isotope effects on ^{13}C chemical shifts in toluene-α-d_3 and related compounds are reported and discussed in terms of hyperconjugation

It is generally agreed upon that secondary deuterium isotope effects on reaction rates are of vibrational origin.1) On the other hand, Halevi2) has introduced a model that treats these effects in terms of inductive and hyperconjugative contributions as if they were conventional substituent effects. Notwithstanding the true physical cause of the observed phenomena, Halevi's model is attractive as it allows to rationalize the experimental findings in familiar chemical terms.

NMR isotope effects are also of vibrational origin and it seems that for those over one bond a satisfactory theoretical treatment is available.3) On the other hand, NMR isotope effects over more than one bond are still not fully understood, and it is unlikely, at least in the majority of cases encountered, that these effects can be predicted from simple considerations of shifts in the frequencies of localized vibrations. The Halevi model is thus an attractive alternative and in fact has already been used by Maciel4) in discussions of NMR isotope effects. More recently, the hyperconjugative mechanism has been advanced to explain results for carbenium ions5) and a few data for cyclophanes.6) This prompts us to report here data from a more systematic study on unsaturated neutral systems undertaken in our laboratory after the discovery of negative (downfield) $^{2}H/^{1}H$ NMR isotope effects on ^{13}C chemical shifts over three and four bonds in saturated systems.7) Clearly, the study of long-range deuterium isotope effects on ^{13}C chemical shifts is now greatly facilitated through the increased availability of superconducting high-field NMR spectrometers. For obvious reasons, these parameters are of special interest to organic chemistry and further investigations of their relation to chemical structure seem rewarding both for possible applications and a better understanding of the mechanisms involved.

In the present communication we describe data for α-deuterated toluenes (1-3), ethylbenzene-α-d_1 (4), and cumene-α-d_1 (5). ^{13}C NMR spectra were obtained at 100.6 Hz using mixtures of the deuterated (D) and the isotope-free (H) system. The spectral assignments of the parent compounds are known[4b], those for their deuterated counterparts could easily be established from the observed ^{13}C,^{2}H spin-spin splittings. In cases where these were not resolved, a second measurement with different D/H ratio was always sufficient. Further experimental details are given in Fig. 1 that shows the spectrum of toluene-α-d_1/toluene. The observed isotope effects for 1-5 are collected in Table I.



1 R = CD_3
2 R = CHD_2
3 R = CH_2D
4 R = $CHDCH_3$
5 R = $CD(CH_3)_2$

From an inspection of Table I it is immediately clear that negative isotope effects are observed for positions where hyperconjugative interactions are involved. Following Halevi[2] and others[8], the less effective electron release of the C-D as compared to the C-H bond leads to deshielding effects in the *ortho*- and *para*-position (C-2,6 and C-4, respectively). The shift in the *ortho*-position is less negative since here the "normal", mostly positive[3,7], through-bond isotope effect operates in addition to the hyperconjugative contribution. Both effects are zero in the *meta*-position (C-3,5) and it is reasonable to assume that the *para*-effect is mainly of hyperconjugative nature (see below). With interest we note

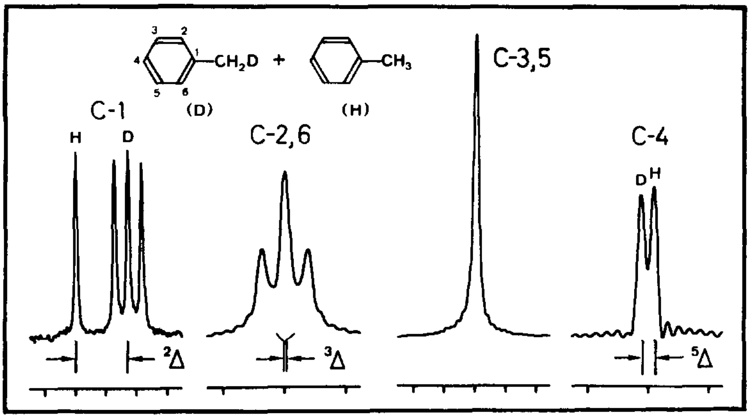


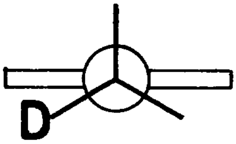
Fig. 1. 100.61 MHz ^{13}C-FT-NMR spectrum of the aromatic carbons of a mixture of toluene-α-d_1 and toluene (3:1, 1:1 for C-4) in $CDCl_3$ (1 molar) with isotope effects $^{n}\Delta$ over n bonds; scale 2 Hz/division; H broadband decoupling; digital resolution >0.02 Hz (FT-NMR spectrometer Bruker WH 400). The resonance of C-4 was resolved with Gaussian multiplication, $^{3}\Delta$ at C-2,6 was determined from the frequency difference between the center of the outer lines and the center line at various ratios of the two compounds.

Table I. $^{2}H/^{1}H$ Isotope Effects on ^{13}C Chemical Shifts in Toluene, Ethylbenzene, and Cumene (in parts per billion, ppb); exp. error ±0.4 ppb or less, positive values are shielding effects

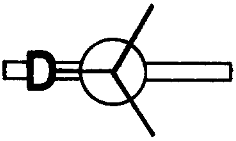
Ø-R	C-1	C-2,6	C-3,5	C-4	C-α	C-ß
R = $-CD_3$	+104.9	- 1.6	0	-12.1	+825.5	---
= $-CHD_2$	+ 69.2	- 1.1	0	- 8.0	+550.8	---
= $-CH_2D$	+ 34.1	- 0.2	0	- 3.9	+275.5	---
= $-CHDCH_3$	+ 29.3	+ 2.0	0	- 2.1	+349.1	+ 81.1
= $-CD(CH_3)_2$	+ 29.6	+14.3	0	0	+434.4	+109.4

that Maciel[9)] was able to detect a small downfield isotope effect of similar magnitude (-10 ppb) as that for C-4 in 1 on the ^{19}F resonance of *p*-fluorotoluene-α-d_3, which he attributed to an isotope-induced perturbation of hyperconjugation. It is further important that all isotope effects in 1-3, including the negative ones, are within exp. error strictly cumulative with respect to the number of deuterons involved.[10)]

Turning now to the methyl-substituted systems 3 and 4, the *ortho*-effect becomes increasingly positive and the *para*-effect is diminished and finally vanishes. Even without detailed knowledge of the population of the different rotational isomers present we can assume that the C_α-D bond in the series 3/4/5 increasingly occupies a position less favorable for hyperconjugation as indicated by the Newman projections A and B. The observed changes of the isotope effects in *ortho*- and *para*-position are thus best explained as being of conformational origin: hyperconjugation is reduced and the normal through-bond effect remains. This view is supported by the experimental finding that for cumene conformation B (D=H) is preferred.[11)]

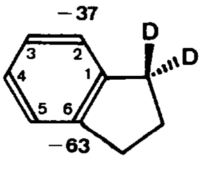


A



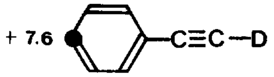
B

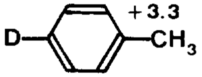
Further support for the dual mechanism proposed for NMR isotope effects comes from data for rigid systems observed in our laboratory.[12a)] For indane-α,α-d_2 we measured the following isotope effects (in ppb):

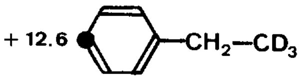


The larger negative shift at position 6 is understood as the sum of the hyperconjugative contribution and the negative through-bond effect found for cyclopentane[7)]: -37 + 2 x (-12) = -61, in excellent agreement with the observed value.

Finally, we would like to point out that long-range isotope effects are also observed for situations where hyperconjugation is not involved. The data (in ppb) for phenylacetylene-β-d_1, toluene-4-d_1, and ethylbenzene-β-d_3 selected from unpublished results derived in our laboratory may serve to illustrate this point:[12b)]







In our opinion it seems, therefore, at present too early to propose $^2H/^1H$ isotope effects on ^{13}C chemical shifts as probes for hyperconjugation, but further investigations along these lines are certainly encouraged.

Acknowledgements. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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10) *Maciel et al. (Ref. 4b) were the first who tried to measure* $^2H/^1H$-^{13}C *isotope effects for 1, 4, and 5 in order to establish a hyperconjugative mechanism. At that time, however, the experimental equipment and the field strength available did not allow to detect such small shifts.*

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12) *a) M.-E.Günther, R.Aydin, and H.Günther, unpublished; b) J.Wesener and H.Günther, unpublished; Dr.S.Berger, University of Marburg, has informed us that he has made similar observations.*

(Received in Germany 2 April 1982)