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DEUTERIUM ISOTOPE SHIFTS AND OFF-RESONANCE DECOUPLING AS AID IN THE ASSIGNMENT OF ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA OF 3,6-EPOXY-PENTACYCLO $[6.2.2.0^{2,7}.0^{4,10}.0^{5,9}]$ DODECANE

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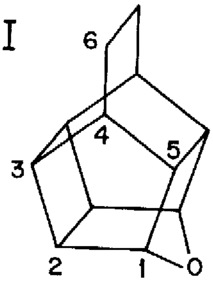
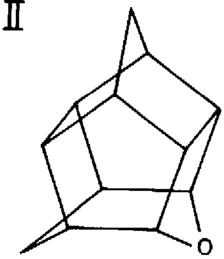
In the course of our investigations of bird-cage compounds proton and carbon-13 n.m.r. spectra of the title compound[1] I[†], its 1-d_2 derivative[2] Ia and their rearrangement products[3] II and IIa, have been recorded. Carbon-13 n.m.r. spectra showed that in compound IIa, obtained from the deuterated derivative Ia, deuterium was statistically distributed over all positions.

I



II



The carbon-13 chemical shifts for compound II are given in Table 1 below. Every carbon signal in the proton noise-decoupled spectrum of the deuterated derivative IIa consisted of two sharp singlets, one closely coinciding with the corresponding peak in the undeuterated compound II, the other shifted upfield by a β-isotope effect of - 0.11 ppm. Each pair of singlets was

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[†] The numbering system indicated on the formula is used throughout for convenience.

overlapping a triplet for the carbon atom bearing the deuterium showing the expected C-D coupling and an upfield isotope shift ($\Delta\delta_\alpha$) of - 0.34 to - 0.44 ppm. The triplets of the directly deuterated carbon atoms are weak and broad. The α-isotope shifts are consequently less accurate (± 0,03 ppm).

TABLE 1

Deuterium Isotope Shifts from ^{13}C N.M.R. Spectra* of Compounds II and IIa

Signal No.	1	2	3	4	5	6	7
δ_c (II)	82,55	53,92	52,10	44,87	44,40	41,03	29,22
$\Delta\delta_\alpha$	-0,36	-0,44	-0,38	-0,34	-0,44	-0,43	-0,42
$\Delta\delta_\beta$	-0,05	-0,11	-0,12	-0,11	-0,11	-0,11	-0,11

* ^{1}H and ^{13}C n.m.r. spectra have been recorded on a Varian XL-100-15 FT-spectrometer using concentrated solutions in CDCl$_3$. Chemical shifts are reported in ppm relative to internal TMS. The estimated precision for δ_c (II) and $\Delta\delta_\beta$ is ± 0.01 ppm, for $\Delta\delta_\alpha$ ± 0.03 ppm.

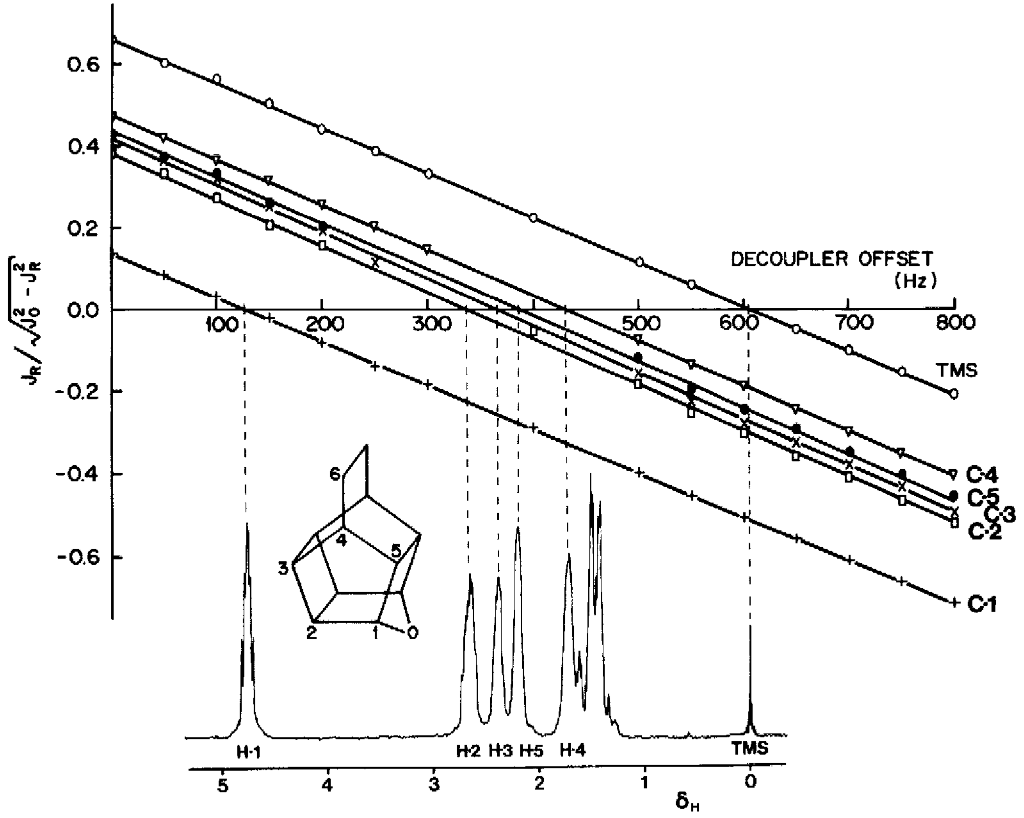
The isotope shifts, in particular the β-effect, in this type of compound are very consistent The two singlet resonances of signal 1, assigned to carbon-1 are not completely resolved though a shoulder at higher field is discernible. The smaller β-isotope shift of carbon-1 as compared to other β-effects in this molecule is due to the electronegative oxygen atom attached to carbon-1. This is in agreement with the general observation that electronegative substituents reduce the magnitude of the β-effect.[4] The consistency of the isotope effects lends confidence to our assignments of the carbon-13 resonances of compound I. The chemical shifts of the title compound and its 1-d$_2$ derivative are given below (Table 2):

TABLE 2

Carbon-13 Chemical Shifts for Compounds I and Ia

Signal No.	Multiplicity	Assignment	δ_c (I) (ppm from internal TMS)	δ_c (Ia)	Δδ
1	D	1	84.54	84.19	-0.35
2	D	5	45.07	44.96	-0.11
3	D	2	44.63	44.52	-0.11
4	D	3	37.05	37.05	0.00
5	D	4	31.26	31.26	0.00
6	T	6	17.80	17.80	0.00

Assignment of the low-field resonance to carbon-1 is obvious from its chemical shift and the methylene carbons are characterised by the triplet structure in the proton-coupled spectrum. The carbon-1 signal disappears in the 1-d_2 derivative and a characteristic weak triplet for the C- group is observed in the proton-noise-decoupled spectrum. The β-isotope effect of -0.11 ppm distinguishes the signals of carbons 2 and 5 from those of 3 and 4. Final assignments of these pairs as given in Table 2 are based on further n.m.r. experiments which will be reported soon.



Correlation between $^{13}C - \{^1H\}$ off-resonance decoupling data and ^1H chemical shifts for compound I.

Carbon-13 spectra are usually assigned by correlating proton with carbon-13 resonances by double resonance experiments. In the particular case of compound I the proton spectrum consisted of broad unresolved peaks for the methine protons (see Figure). Only the H-1 protons and the methylene AA'BB'-type pattern could be assigned directly. Off-resonance decoupled $^{13}C-\{^1H\}$ spectra gave linear relations between $J_R/\sqrt{J_o^2-J_R^2}$ (J_R = residual splitting) and $\Delta\nu$, the frequency offset in the proton range[5] (see Figure) and lead to an unambiguous correlation of carbons to the directly bound protons. This allowed an assignment of the resonances for protons 2 to 5 in a reversal of the usual assignment procedure. The straight lines in the Figure have been obtained from a least squares fit of the experimental data. Correlation coefficients were better than 0.999 in all cases. The standard deviations for the proton chemical shifts varied from 0.01 to 0.06 ppm. The proton chemical shifts obtained from the carbon-13 spectra agreed to within 0.02 ppm (2Hz) with those measured directly from 100 MHz ^1H n.m.r. spectra.

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2 The synthesis of Ia was carried out according to the same procedure followed for I (ref. 1), using $LiAlD_4$ instead of $LiAlH_4$ as reducing agent.

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