The Nuclear Magnetic Resonance Spectra of 5-Substituted Bicyclo[2,2,1]hept-2-enes

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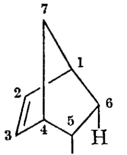
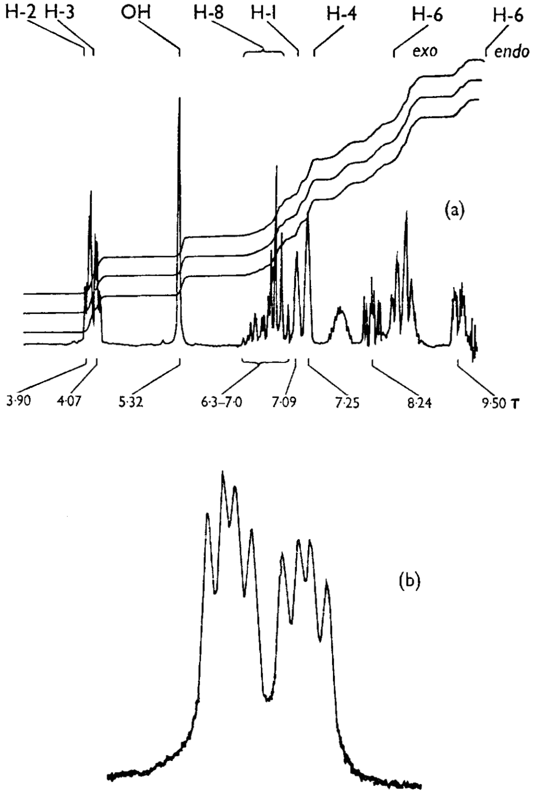
THE nuclear magnetic resonance (n.m.r.) spectra of bicyclo[2,2,1]hept-2-ene and related compounds have been the subject of numerous publications.[1] We have recently examined the Diels–Alder adducts of known[2] structure (I) made from cyclopentadiene and allyl compounds; these adducts (I) have a (substituted) methyl substituent at the 5-position, the effect of which on the n.m.r. spectrum is noteworthy. From the n.m.r. spectra of the carefully redistilled products it was clear that the *endo*-substituted bicycloheptenes were contaminated with a small amount of the corresponding *exo*-isomer. To date our attempts to separate the isomers [distillation, g.l.c., and repeated recrystallisation of the diterephthalate of (Ia)] have failed to provide an absolutely pure sample of one of the *endo*-isomers.



(I)

(a: X = OH)
(b: X = H)
(c: X = OAc)
(d: X = Br)

(II)



FIGURE

(a) *N.m.r. spectrum of* endo-2-*hydroxymethylbicyclo*[2,2,1]*hept*-2-*ene in carbon tetrachloride at* 100 *Mc./sec.*

(*b*) *Expansion of multiplet at* τ 9·50.

The spectrum of (Ia) is presented in the Figure together with an expansion of one of the bands. The unusual feature of the spectrum is the multiplet at τ 9·50 (intensity equivalent to 1 proton.) This occurs at an exceptionally high field for a compound containing no cyclopropane ring. The cyclopropane analogue of (Ib) shows two multiplets at τ 9·46 and 9·66.[3] On hydrogenation of the double bond over Pd–C to (IIa) this high-field multiplet moves to τ 9·37, a much higher field than the corresponding multiplet in the bicyclo[2,2,1]-heptane spectrum.

We assign this multiplet to the (C-6)-*endo* proton on the following grounds.

(i) The multiplicity can be explained by a main coupling to the (C-6)-*exo* proton ($J = 11{\cdot}5$ c./sec.) giving basically half of an AB spectrum, each component of which is split by further coupling to the (C-5)-*exo* ($J = 4{\cdot}0$ c./sec.) and to the (C-7)-*anti* ($J = 2{\cdot}5$ c./sec.) protons.[1]

(ii) On hydrogenation of the double bond of compound (I) the resonance moves downfield.[4]

Fraser[4] has measured the spectra of compounds similar to ours and has also assigned a multiplet in the region of τ 9·1 to the (C-6)-*endo* proton. The chemical shifts of the high-field multiplet in the spectra of compounds (Ia—d) and (IIa—d) together with those reported for bicyclo[2,2,1]hept-2-ene and bicyclo[2,2,1]heptane[1] are listed in the Table.

TABLE

Chemical shifts (τ) *of the* (*C*-6)-endo *protons measured in* CCl_4 *solution*

X	Compounds (I)	Compounds (II)
OH	9·50	9·37
H	9·54	9·36
OAc	9·43	9·31
Br	9·40	9·30
Bicyclo[2,2,1]hept-2-ene[1]	9·06	
Bicyclo[2,2,1]heptane[1]		8·8

Our explanation of the unusually high-field position of this resonance is that in compounds (I) the (C-6)-*endo* hydrogen nucleus is subjected to *two* positive shielding influences due to the diamagnetic anisotropy of the double bond and also of the (C-5)–(C-8) carbon–carbon single bond. The positive shift due to the double bond is calculated to be $\simeq 0{\cdot}1$ p.p.m. by subtracting the values quoted in the Table for compounds (II) from the values for the corresponding compounds (I). The positive shielding influence of the (C-5)–(C-8) single bond can be roughly estimated to be of the order of 0·5 p.p.m. by comparison of the values for (Ia—d) in the Table with that quoted for bicyclo[2,2,1]hept-2-ene or of the values for (IIa—d) with that for bicyclo[2,2,1]heptane. The influence of the group X attached to the C-8 atom on the magnetic field at the (C-6)-*endo* hydrogen nucleus must be accounted for in more accurate calculations. Since the (C-6)-*endo* H multiplet is well separated from the rest of the spectrum, these molecules provide excellent models for calculations of the carbon–carbon single and double bond anisotropies according to the methods of Musher[5] and Zürcher.[6]

The Figure shows that the two bridgehead protons give rise to separate resonances. Decoupling experiments involving the resonances due to the olefinic, the bridgehead, and the (C-6)-*exo* protons establish that the bridgehead resonance at high field is due to the C-1 proton and the lower field olefinic resonance to the proton attached to C-2.

The resonance due to the protons attached to C-8 consists of two sets of multiplets. The multiplet at higher field arises from the (C-5) *endo*-isomer and the one at lower field from the corresponding *exo*-isomer present as impurity. Each multiplet can be interpreted as being the AB part of an ABX pattern.

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