

Conformations of the Bicyclo[3,2,2]non-2-ene Skeleton

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THE nuclear magnetic resonance spectra of 3-bromobicyclo[3,2,2]non-2-ene (I) and its 4-hydroxy-derivative (II) display surprising differences.¹ The signal due to the vinyl proton of (I) appears as a doublet of triplets, in contrast to the

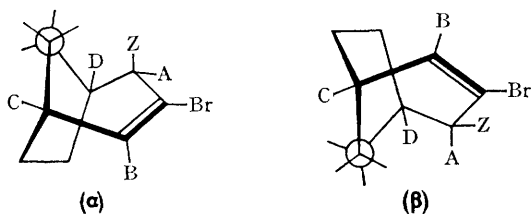
vinyl resonance of (II) which shows as a clean-cut doublet. Furthermore, the allylic resonance of (I) appears as a broadened doublet and that of (II) appears as a doublet of doublets² (Fig. 1).

The coupling constants for the vinyl and allylic

¹ C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Amer. Chem. Soc.*, 1965, **87**, 2183.

² The spectra were determined in *ca.* 10% carbon tetrachloride solution at about 30° and at 60 Mc./sec. on a Varian Associates model A-60 spectrometer. Tetramethylsilane was used as an internal standard.

protons of (I) and (II) were established by application of the double resonance method³ (Table). The vinyl proton (B) of 3-bromobicyclo[3,2,2]-non-2-ene (I) not only couples with the bridgehead proton (C), but also to an equal extent with *both* allylic protons (A and Z). The residual unresolvable broadening of the single allylic signal is due to further coupling with the protons of the ethane bridge. The magnetic equivalence of the allylic protons (A and Z) may be due to rapid dynamic interconversion between the enantiomeric⁴ twist conformations (α and β). Another, but less attractive, possibility is that (I) is held in a symmetrical conformation midway between (α) and (β).⁵



(I) Z = H (II) Z = OH
(A - D designate hydrogen atoms)

The vinyl proton (B) in 3-bromo-4-hydroxybicyclo[3,2,2]non-2-ene (II) shows only coupling with the bridgehead proton (C), whereas the allylic proton (A), in addition to coupling with the bridgehead proton (D), interacts with just

TABLE

Coupling constants of the vinyl and allylic protons of (I) and (II)

Compound (I)	Compound (II)
$J_{BC} = 8.9$ c./sec.	$J_{BC} = 9.5$ c./sec.
$J_{AD} = J_{ZD} \sim 5.0$	$J_{AD} = 4.5$
$J_{AB} = J_{ZB} = 1.7$	$^4J_{\text{due to A}} = 0.7$

one of the protons of the ethane bridge. Consequently, (II) may be represented by either of the diastereomeric⁴ static conformations (α) or (β).

The absence of vinyl-allylic coupling in (II) strongly favours conformation (α). In this con-

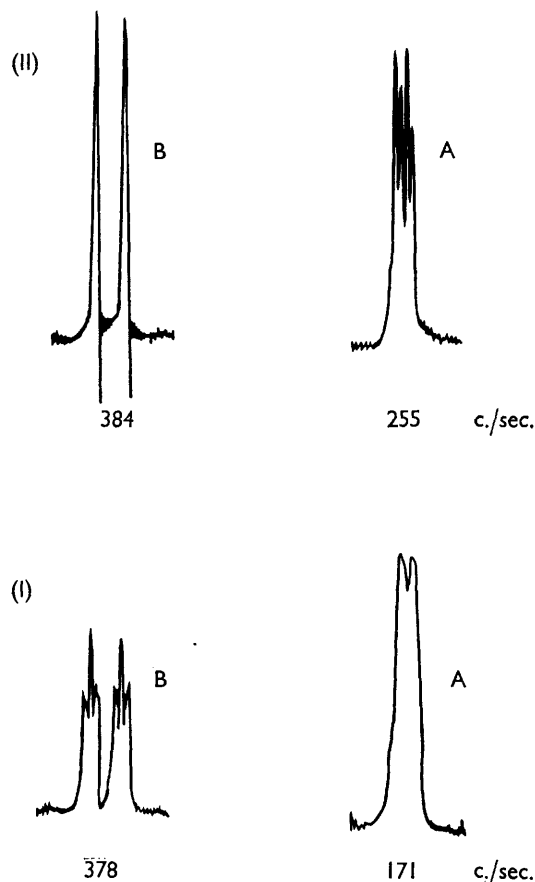


FIGURE 1.

formation, the C_4 -A bond is inclined at an angle of about 30° to the plane described by the C_2 - C_3 - C_4 atoms and accordingly, $^4J_\sigma$ and $^4J_\pi$ contributions to vinyl-allylic coupling are expected to cancel each other.⁶

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³ Our procedure has been described previously (C. W. Jefford, B. Waegell, and K. C. Ramey, *J. Amer. Chem. Soc.*, 1965, **87**, 2191).

⁴ For a definition of these terms see K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, Inc., New York, 1965, Ch. 2.

⁵ The same considerations have been entertained with regard to the possible conformation adopted by the radical anion derived from bicyclo[3,2,2]nonane-2,3-dione (G. A. Russell, K. Y. Chang, and C. W. Jefford, *J. Amer. Chem. Soc.*, 1965, **87**, 4383).

⁶ E. W. Garbisch, *J. Amer. Chem. Soc.*, 1964, **86**, 5561.