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CONFORMATION AND STEREOSPECIFIC LONG-RANGE SPIN COUPLING IN CIS-3,5-DIBROMOCYCLOPENTENE

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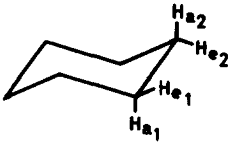
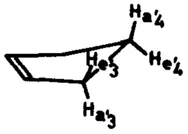
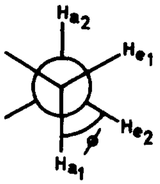
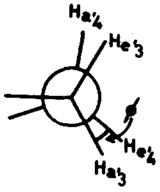
In fixed cyclohexanes the torsional or dihedral angle for vicinal cis protons is close to 60^{o} and reported values for the coupling constants J_{aa} and J_{ae}, which may be used in studies of conformational equilibria (1), usually range from 10-12.5 c/s and 3.5-4.5 c/s, respectively (1). In the series of cyclopentenes only few values have been reported for the averaged vicinal coupling constants between protons on adjacent sp^3-hybridised carbon atoms. For cyclopentene itself the average coupling constants in the CH_2—CH_2 fragment are $J_{cis} = \frac{1}{2}(J_{a'_3e'_4} + J_{e'_3a'_4}) = 7.4$ c/s, and $J_{trans} = \frac{1}{2}(J_{a'_3a'_4} + J_{e'_3e'_4}) = 4.6$ c/s (2), and the dihedral angle is ca. 20-25° (3).

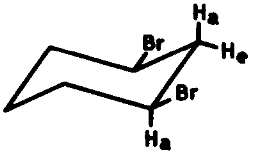




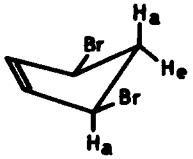




<u>Cis</u>-1,3-dibromocyclohexane exists exclusively in the e,e conformation (I) according to NMR spectra and dipole moment (4,5). It seemed worth-while to examine whether the 1,3-bromine interaction in <u>cis</u>-3,5-dibromocyclopentene would increase the dihedral angle in the $CH(Br){-}CH_2$ fragment resulting in a more buckled (cyclohexane-like) conformation (II) or if the molecule retains the more planar conformation as in cyclopentene itself.



I



II

In the NMR spectrum (6) of <u>cis</u>-3,5-dibromocyclopentene the CH_2 fragment shows up as the AB part (FIG.1) of an ABM_2 (more correctly ABMM'XX') spin system thus confirming the <u>cis</u> orientation of substituents in the isomer with m.p. 45° as reassigned by Young <u>et al</u>. (7). The lines for the high field proton in the AB part are clearly split into triplets indicating long-range coupling to the ethylenic protons (J = 0.4 c/s), while a weaker triplet splitting (J = 0.2 c/s) was observed for the lines due to the low field proton. Examples of this type of long-range coupling over four bonds $(H{-}\overset{\|}{C}{-}C{-}C{-}H)$ have recently been observed by Garbisch (8), and have also been shown to exist in cyclohexene, but not in cyclopentene (9a). Analysis (9b) of the AB part of the spectrum gave the values 6.9 c/s and 1.5 c/s for the two averaged vicinal coupling constants.

If the dihedral angle for the <u>cis</u> protons is assumed to be near 60°, a conformationally homogenous compound (e,e) (II) is expected, as the contribution from the diaxial bromine conformation will be insignificant because of the van der Waal's radius of 1.95 Å for Br (molecular model). This involves $J_{trans} = J_{aa}$ and $J_{cis} = J_{ae}$. However, as for <u>cis</u>-1,3-dibromocyclohexane (I) $J_{trans} = J_{aa} = 10.2$ c/s (1), and $J_{cis} = J_{ae} = 3.9$ c/s (4), the experimental values, 6.9

c/s and 1.5 c/s, for cis-3,5-dibromocyclopentene appear too small for J_{trans} and J_{cis}, respectively, to make the assumed e,e-conformation (II) probable.

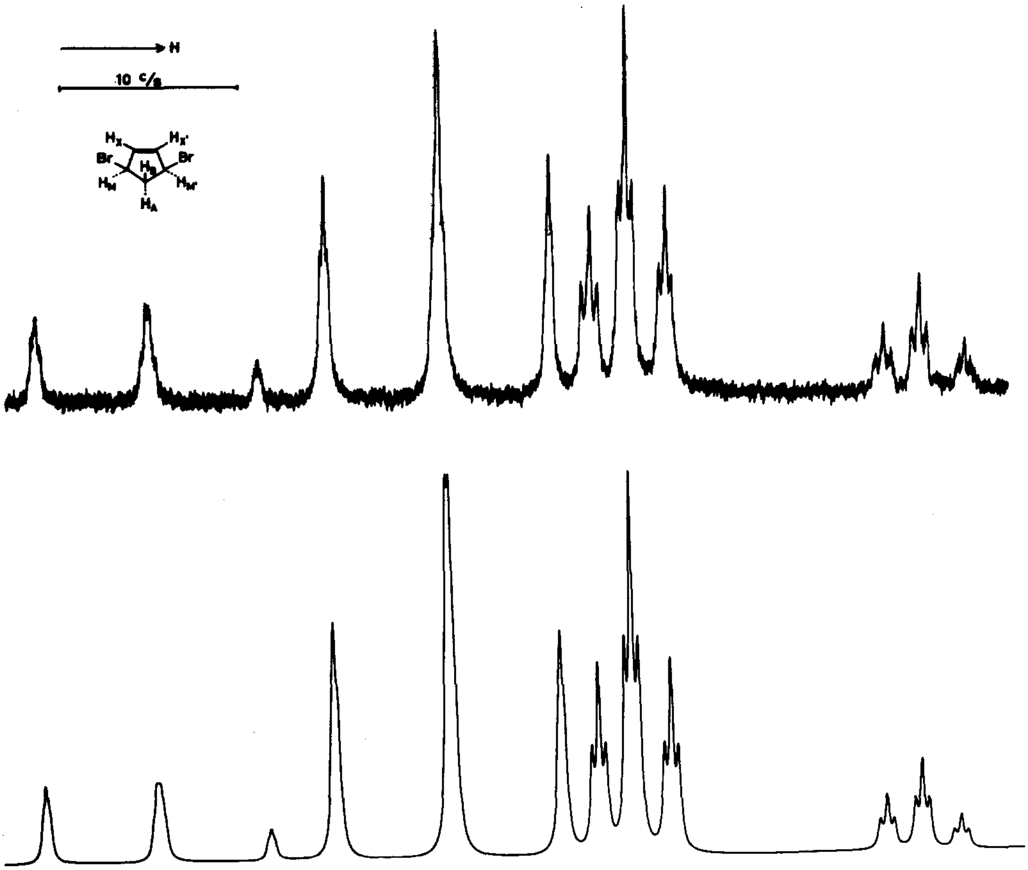


FIG.1. Experimental (above) and computed (below) 60 Mc/s spectra for the AB protons of the ABMM'XX' spin systems in cis-3,5-dibromocyclopentene. ν_A = 182.1 c/s, ν_B = 160.9 c/s, ν_M = 300.0 c/s, J_{AB} = -16.4 c/s, J_{AM} = +6.9 c/s, J_{BM} = +1.5 c/s, $|J_{BX}|$ = 0.4 c/s, $|J_{AX}|$ = 0.2 c/s.

A more planar conformation seems favoured, and as J_{cis} and J_{trans} should be roughly in the ratio 4:1 for a planar ring (10) (e.g., for cyclopentenone J_{cis} = 7.2 c/s and J_{trans} = 2.2 c/s) (10), the result of the ABM_2 analysis was interpreted as follows: $J_{cis} = J_{AM}$ = +6.9 c/s, $J_{trans} = J_{BM}$ = +1.5 c/s,

$J_{gem} = J_{AB} = -16.4$ c/s, and $\nu_A - \nu_B = +21.2$ c/s (at 60 Mc/s). The interpretation implies that proton B (the proton cis to the bromine atoms) has the strongest long-range coupling to the two ethylenic protons.

A remarkable result from this analysis is the small value obtained for J_{trans}. However, observations on six-membered rings indicate that the maximum effect of an electronegative substituent on J_{vic} coincides with trans-coplanarity of the substituent and H-vicinal (11). Furthermore it was suggested (11) that a second weaker maximum electronegativity effect may coincide with cis-coplanarity in the system R—C—C—H. This suggestion is clearly substantiated by the results from analyses of the CH_2—CHBr fragments in 4-bromocyclopent-2-enone ($J_{cis} = 6.4$ c/s and $J_{trans} = 1.8$ c/s; the computed spectrum for proton H_4 is shown in FIG.2) and in 1-bromoacenaphthene ($J_{cis} = 7.4$ c/s and $J_{trans} = 1.9$ c/s) (12). The strong decrease suffered by J_{cis} in cis-3,5-dibromocyclopentene therefore agrees with a nearly planar conformation and fully supports the cis-coplanarity rule.

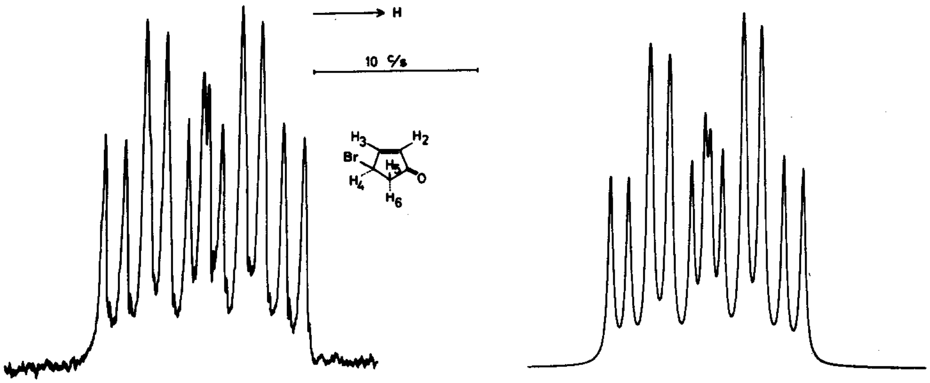
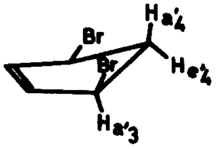
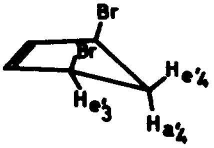


FIG.2. Observed (left) and computed (right) NMR spectra of proton H_4 in 4-bromocyclopent-2-enone in CS_2 at 60 Mc/s. $\nu_2 = 370.0$ c/s, $\nu_3 = 456.8$ c/s, $\nu_4 = 308.9$ c/s, $\nu_5 = 153.7$ c/s, $\nu_6 = 175.1$ c/s; $J_{42} = -1.2$ c/s, $J_{43} = +2.6$ c/s, $J_{45} = +1.8$ c/s, and $J_{46} = +6.4$ c/s.

Assuming the dihedral angle in cis-3,5-dibromocyclopentene to be close to that in cyclopentene (ca.20-25°) we obtain from the two possible conformations III and IV: J_{cis}(average) = x $J_{a'_3e'_4}$ + (1-x)$J_{e'_3a'_4} \approx J_{a'_3e'_4}$ as $J_{a'_3e'_4} \approx J_{e'_3a'_4}$ because of the small dihedral angle. $J_{a'_3e'_4}$ is expected to be only slightly greater than $J_{e'_3a'_4}$ due to the out of plane orientation of the electronegative substituents (11): (Br—C—C—H$_{e'_4}$) ≈100° in III, while (Br—C—C—H$_{a'_4}$) ≈140° in IV.



x
III



1-x
IV

It should be emphasized that J_{cis} for the CHBr—CH$_2$ fragments in cis-1,3-dibromocyclohexane (I) and cis-3,5-dibromocyclopentene seems to be roughly related by the equation $3.9 \approx 6.9 \cos^2\theta$ where $\theta = 60^\circ - \varphi$ is the difference in dihedral angles; a rough value of $\varphi = 19^\circ$ is obtained for the torsional angle in cis-dibromocyclopentene. Further examples from related cyclohexanes and cyclopentenes are needed to support or reject this relation, although the values for J_{cis} in cyclohexane and cyclopentene also seem to fulfil the relation. Using the likely value of 4.5 c/s for J_{ae} in cyclohexane and $J_{a'_3e'_4} = 7.4$ c/s for cyclopentene we obtain $\varphi = 21^\circ$ for the angle of buckle in cyclopentene from $4.5 \approx 7.4 \cos^2(60 - \varphi)$.

Efforts to relate the vicinal coupling constants with an equilibrium conformational distribution were prevented by the lack of reliable values for $J_{a'_3e'_4}$, $J_{e'_3a'_4}$, $J_{a'_3a'_4}$, and $J_{e'_3e'_4}$ although a method for solving the problem has been clearly outlined by Gutowsky et al. (9c).

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