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# INVESTIGATIONS INTO THE CONFORMATIONS OF NON-AROMATIC RING COMPOUNDS(1) V. THE NMR SPECTRA OF DIHALOGENOCYCLOHEXANES(2)

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In the course of a study on the 1,3 cis- and trans dihalogenocyclohexanes(3) it was deemed interesting to obtain additional information on the conformational relationships of these compounds by comparing their nmr spectra with those of the other, better known isomers. Most spectra were recorded at 35° C with the aid of a Varian A-60 Analytical NMR Spectrometer, using tetramethylsilane as the internal standard. In addition trans 1,3 dichloro-, 1,3 dibromo-, cis 1,3 dichloro-, 1,3 dibromo-, and cis 1,4 bromochlorocyclohexane were measured at lower temperatures(4). The concentrations of the solutions in $CCl_4$ did not exceed 10% (by weight).

In Table 1 some of our data are presented.

In dimethylcyclohexanes Brownstein and Miller found a correlation between the width of the absorption line due to the ring protons and the conformation of the molecules(5). However, in the case of the dihalogenocyclohexanes the differences in peak width can only give an indication of the conformation(6). The width of the -CHX absorption line is expected to increase in the order axial-axial (halogen), equatorial-axial,

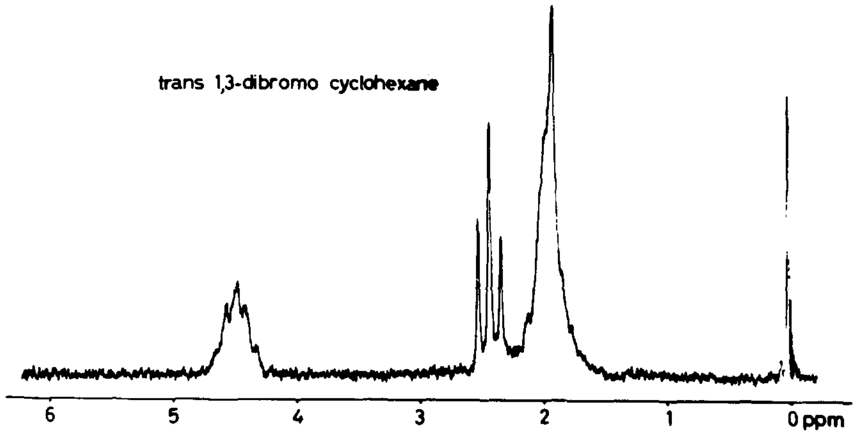
## TABLE 1

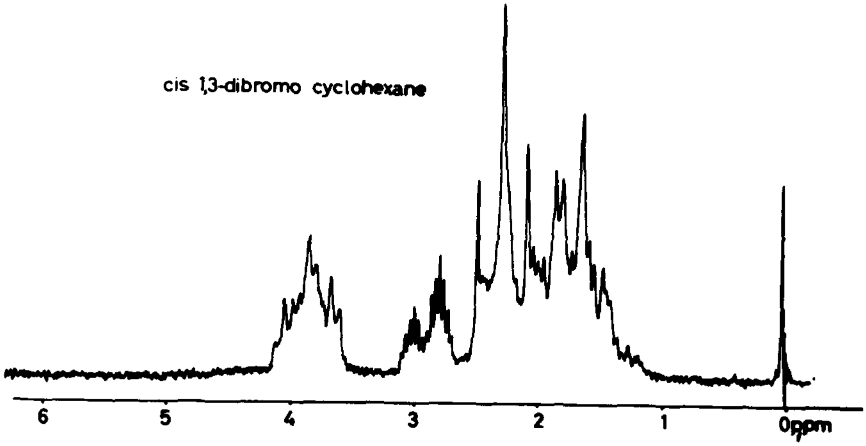
### Chemical Shifts and Peak Widths

| | -CHX Absorption | |
|---|---|---|
| Compounds | Peak Position(*) | Peak Width(**) |
| cis 1,2 dichlorocyclohexane | 253 | 11-12 |
| cis 1,2 bromochlorocyclohexane | 240-270 | 30 |
| cis 1,2 dibromocyclohexane | 263 | 11 |
| trans 1,2 dichlorocyclohexane | 241 | 9-10 |
| trans 1,2 bromochlorocyclohexane | 255 | 9-10 |
| trans 1,2 dibromocyclohexane | 268 | 8-9 |
| cis 1,3 dichlorocyclohexane | ~ 230 | > 25 |
| cis 1,3 bromochlorocyclohexane | ~ 225 | > 25 |
| cis 1,3 dibromocyclohexane | ~ 228 | ~ 25 |
| trans 1,3 dichlorocyclohexane | 260 | 13 |
| trans 1,3 bromochlorocyclohexane | 265 | 19 |
| trans 1,3 dibromocyclohexane | 270 | ~ 13 |
| cis 1,4 dichlorocyclohexane | 243 | 12 |
| cis 1,4 bromochlorocyclohexane | 246 | 16-17 |
| cis 1,4 dibromocyclohexane | 255 | 13-14 |
| trans 1,4 dichlorocyclohexane | 250 | ~ 14 |
| trans 1,4 bromochlorocyclohexane | 232-270 | 20 |
| trans 1,4 dibromocyclohexane | 257 | 13-15 |

(*) in cps from t.m.s.; mean value; the positions are slightly concentration dependent.

(**) in cps; measured at half the peak height.


trans 1,3-dibromo cyclohexane
6
5
4
3
2
1
0 ppm


cis 1,3-dibromo cyclohexane
6
5
4
3
2
1
0ppm

equatorial-equatorial. In general Ja-a > Ja-e ≥ Je-e.

A study of the newly investigated compounds at lower temperatures and in different solvents seems necessary to make definite conclusions possible. In the bromochloro compounds the -CHX peak width is considerably larger resulting from the increased number of unequivalent protons, and the different shifts caused by different substituents.

The spectra of the cis 1,3 dihalogeno- and the trans 1,3 dihalogeno compounds deserve special attention. At 35° C the spectra of the cis 1,3 compounds consist of a rather broad line at low field, two septuplets at higher field and a complex part at high field. The width of the -CHX peak (25cps) supports the conclusion(3) that the e-e (halogen) conformation is the only one occurring. A possible interpretation of the multiplets due to the $-CH_2$ protons on C2 is, that these protons give rise to an AB quadruplet ($J_{gem}$= 13cps), the lower part of which is distinguishable in the spectrum. The lines of this lower part are split into a triplet (J= 3.9cps) by an equatorial-axial coupling to the protons at C1 and C3 (the equatorial proton on C2 probably absorbs at lower field). The triplets again are split, possibly by a pair of equivalent protons at C4 and C6; one has to assume then a long range coupling with J= 1.9cps.

The spectra of the trans 1,3 compounds show a smaller peak width for the -CHX absorption (13cps), a reasonable value in view of the a-e conformation. As a result of time averaging due to rapid interconversion of the two energetically equivalent chairforms the protons on C2 give rise to a "triplet". The coupling (J= 5.5cps) is half the sum of the two vicinal coupling constants(7). This value is close to that recently found for cyclohexane-1,3-diols(8).

TABLE 2

Chemical Shifts and Coupling Constants

| | $-C(2)H_2$ Peak | | | |
|---|---|---|---|---|
| Cyclohexane Compound | Position | Multiplicity | J "triplet" | J "sept" |
| cis 1,3 dichloro- | 167;180 | 7;7 | - | 1.9 |
| cis 1,3 bromochloro- | 161;174 | 7;7 | - | 1.9 |
| cis 1,3 dibromo- | 167;180 | 7;7 | - | 1.9 |
| trans 1,3 dichloro- | 134 | 3 | 5.5 | - |
| trans 1,3 bromochloro- | 139 | 3 | 5.5 | - |
| trans 1,3 dibromo- | 145 | 3 | 5.5 | - |

Measurements at Low Temperatures

Solutions of cis and trans 1,3 dibromo- and the cis and trans 1,3 dichlorocyclohexanes in $CS_2$ were measured at temperatures down to -104°C on a 40mc Varian nmr spectrometer(4). The spectra of the cis 1,3 isomers showed to be temperature independent, which confirms that only the e-e (halogen) conformation plays a role. The spectra of the trans 1,3 compounds did change at lowering the temperature. The "coalescence" temperature was found to be about -79°C for both compounds. Calculation of $G^*$ gave $k=31.1$ $sec^{-1}$; $dG^*=9.9$ Kcal for the trans dibromo- and $k=40.0$ $sec^{-1}$; $dG^*=9.8$ Kcal for the trans dichloro compound.

According to Atkinson and Lunde(9) cis 1,4 bromochlorocyclohexane is existing in the a-bromo-e-chloro conformation only. However, the spectrum at $-55^{\circ}$C is essentially different from that at $35^{\circ}$C, indicating an equilibrium of two conformations at room temperature.

Comparison of the infrared spectrum of this compound with those of the other dihalogenocyclohexanes leads to the same conclusion.

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