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# AN INDO-LMO AND $^{13}C$ NMR SPECTROSCOPIC STUDY OF THE C–H BONDS IN TETRACYCLO[3.2.0.0$^{2,7}$.0$^{4,6}$]HEPTANE (QUADRICYCLANE) AND TRICYCLO[3.1.0.0$^{2,4}$]HEXANE

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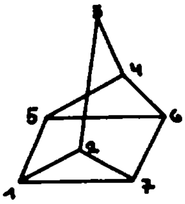
**Abstract**—Using an INDO approximation to Von Niessen's charge density localization method, the percent s character of the C atom hybrid orbitals engaged in C–H bonds is computed for a series of open-chain and cyclic saturated and unsaturated hydrocarbons. A semi-empirical linear relationship is found between these quantities and the experimental nuclear spin-spin coupling constants $J_{CH}$ (standard deviation 4·98 Hz). The experimental values of $J_{CH}$ were measured for quadricyclane (1) and tricyclo[3.1.0.0$^{2,4}$]hexane (2) and were shown to be in fair agreement with the theoretical predictions. An analogous relationship is also established between the percent s character of the involved C atom hybrid orbital and the C–H bond distance, the standard deviation being 0·0040 Å. This relation is used in order to predict the different C–H bond lengths in the vibrational ground state of 1 and 2, for which equal CH distances were assumed in the analysis of electron diffraction experiments. The results indicate that molecular geometries can be refined with the use of semi-empirical correlations of the above mentioned type.

## INTRODUCTION

No accurate experimental molecular geometry has been reported hitherto for the highly strained molecules tetracyclo[3.2.0.0$^{2,7}$.0$^{4,6}$]heptane (1) or quadricyclane and tricyclo[3.1.0.0$^{2,4}$]hexane (2).



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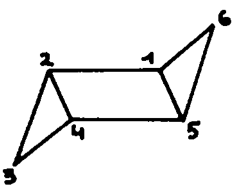

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Kutchitsu *et al.*[1] described the results of a gas phase electron diffraction experiment on quadricyclane. The experimental radial distribution curve was analysed with the help of several assumptions, one of them being that all C–H distances were equal. Assuming further either the $r_g$ ($C_1$–$C_2$) distance equal to that of cyclopropane (Method A), or $r_g$ ($C_2$–$C_3$) equal to that of norbornane (Method B), the authors proposed two different sets of geometrical parameters. A similar procedure was followed by Geise *et al.*[2] in their electron diffraction investigations on tricyclo[3.1.0.0$^{2,4}$]hexane. Here too, several restrictions were imposed on the molecular geometry; once more, all C–H distances were set equal.

In this paper, we will try to provide supplementary information on the nature of these C–H bonds with an experimental study of the $J_{CH}$ coupling constants and a theoretical investigation of these molecules using the localized molecular orbital (LMO) approach. The LMO's were obtained by the approximate localization theory we described recently[3] and which is essentially an INDO approach to the indirect intrinsic[5] localization method of Von Niessen[4]; the localization criterion we imposed is the maximalisation of the sum of the intra-orbital charge density overlap integrals. No LMO or complete $^{13}C$ NMR spectroscopic study had as yet been performed on these molecules and only partial information for 1 on the C–H nuclear spin-spin coupling constants was available[6].

## RESULTS AND DISCUSSION

### *Correlation of the percent s character of the carbon atom hybrid orbital in C–H bonds with experimental data*

Empirical correlations between the percent s character of the C atom hybrid orbital engaged in the C–H bond and the J($^{13}C$–$^{1}H$) nuclear spin-spin coupling constant have been proposed some time ago independently by Shoolery[7a] and by Müller and Pritchard[7b]. Considering the "Fermi contact" term[8] as being the predominant contribution for the indirect nuclear spin-spin interactions[9,10] and assuming that the ground state wave function describing the C–H bond is perfectly localized, they obtained a linear relationship between these two quantities.

This relationship was discussed in terms of "maximum overlap" hybrids[11] by Maksic *et al.*[12–14] and in terms of CNDO-LMO's by Trindle and Sinanoğlu.[15] However, the maximum overlap theory does not give satisfactory results for highly strained cyclopropane ring compounds and no general LMO study of the evolution of the C atom hybridization through a large series of strained hydrocarbons has as yet been realized. This is done in this work, starting from INDO canonical molecular orbitals.[16] The C–H LMO's were obtained by the localization procedure outlined in[3], truncated (i.e. contributions from atoms other than those forming the C–H bond are removed) and renormalized.

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The percent s character of the C hybrid in the LMO

$$\Psi_{CH} = a\,.\,1s\ (H) + b_1\,.\,2s\ (C) + b_2\,.\,2p_x\ (C) + b_3\,.\,2p_y\ (C) + b_4\,.\,2p_z\,(C) \qquad (1)$$

is then defined as

$$(\%\,s) = b_1^2 \Big/ \sum_{i=1}^{4} b_i^2. \qquad (2)$$

Using a set of 11 cyclic and acyclic, saturated and unsaturated hydrocarbons with $J_{CH}$ values ranging from 125 to 226 Hz we obtain, via a least-squares analysis, a linear relationship (Fig. 1) between the experimental $J_{CH}$ values and the calculated %s character:

$$J_{CH}(\mathrm{Hz}) = 6{\cdot}93\,(\%s) - 51{\cdot}06 \qquad (3)$$

with a standard deviation of 4·98 Hz†.

It is interesting to note (Table 1) the effect of ring strain on the C atom hybridizations of the smaller rings; the expected enhancement of the s-character of the carbon orbital involved in the bonding to the H atom with decreasing ring size is well reproduced. The difference in $^{13}C$–$^{1}H$ coupling constant for the *exo*- and *endo*-H atoms

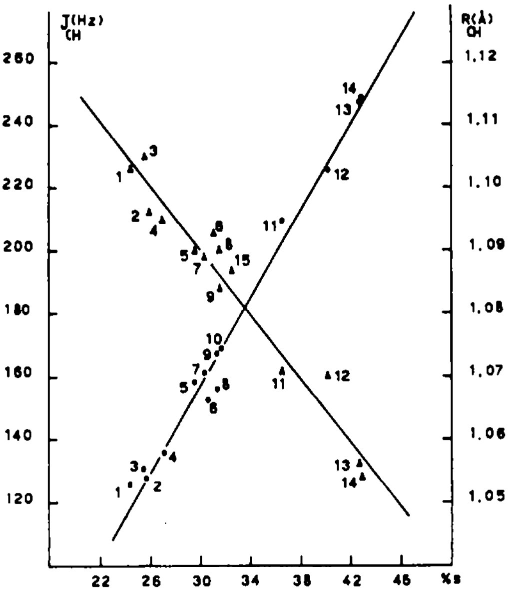


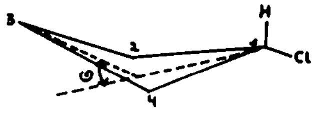
Fig. 1. Experimental nuclear spin-spin coupling constants $J_{CH}$(●) and C–H distances $R_{CH}$ (Δ) vs the per cent s character of the C hybrid in the CH localized orbital obtained from INDO-density localization of INDO-CMO's. The straight lines are the least squares fits given in eqns (3) and (4). The numbering of the points is given in Table 1. For bicyclobutane (point No. 6) the average value of the %s character of the endo- and exo-CH bonds has been taken; point No. 15 corresponds to the methylene CH bonds of cyclopropene.

Table 1. Comparison of the calculated %s character of the carbon atom hybrid orbital forming the C–H bonds with the J($^{13}$C–$^{1}$H) coupling constants and $R_{CH}$ bond lengths

| | | J($^{13}$C–$^{1}$H) (Hz) | | | %s | $R_{CH}$ (Å) | | |
|---|---|---|---|---|---|---|---|---|
| No. | Molecule | exp. | | theor. | calc. | exp. | | theor. |
| 1 | Cyclohexane | 125·0 | (19) | 119·1 | 24·56* | 1·103 | (23) | 1·104 |
| 2 | Ethane | 126 | (19) | 128·3 | 25·88 | 1·096 | (24) | 1·101 |
| 3 | Propyne (methyl) | 131 | (19) | 126·8 | 25·66 | 1·105 | (25) | 1·102 |
| 4 | Cyclobutane | 136 | (19) | 136·6 | 27·08† | 1·095 | (26)<br>(27) | 1·098 |
| 5 | Benzene | 159 | (19) | 154·7 | 29·69 | 1·084 | (28) | 1·091 |
| 6 | Bicyclobutane (exo) | 153 | (20) | 161·5 | 30·67 | 1·093 | (29) | 1·089 |
| 7 | Cyclopropane | 160·5 | (19) | 159·8 | 30·43 | 1·089 | (30) | 1·089 |
| 8 | Ethylene | 156·2 | (19) | 167·2 | 31·50 | 1·090 | (31) | 1·087 |
| 9 | Allene | 168 | (19) | 167·9 | 31·60 | 1·084 | (32) | 1·086 |
| 10 | Bicyclobutane (endo) | 169 | (20) | 169·3 | 31·80 | 1·093 | (29) | 1·086 |
| 11 | Bicyclobutane (bridgehead) | 205 | (20) | 201·9 | 36·50 | 1·071 | (29) | 1·074 |
| 12 | Cyclopropene (vinyl) | 226 | (21) | 228·3 | 40·32 | 1·070 | (33) | 1·064 |
| 13 | Propyne (ethynyl) | 247·6 | (19) | 244·9 | 42·70 | 1·056 | (25) | 1·058 |
| 14 | Acetylene | 248·7 | (19) | 246·7 | 42·97 | 1·054 | (34)<br>(35) | 1·058 |

*Average value for axial and equatorial CH bonds.

†The input geometry is based on the structure proposed by Wright and Salem[26] with a puckering angle θ of 35°; the $C_4\hat{C}_1C_2$ angle was taken equal to that in cyclobutylchloride[27] (90°50). We give here the average value of the %s character obtained for the different CH bonds.



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†While this work was in progress, a comparable study has been published by M. D. Newton *et al.*[17] who localized INDO-CMO's by the unapproximated but time-consuming Edmiston–Rüdenberg procedure.[18] The resulting linear relation has a standard deviation of 5·7 Hz.

in bicyclobutane is seen to result for a great deal from the different hybridizations of the carbon orbitals forming these bonds, confirming the relative assignments of Wüthrich *et al.*[19]

It has also been commonly assumed that the internuclear distance $R_{CH}$ is essentially determined by the hybridization of the C atom involved[22] and in the original work of Müller and Pritchard, a dependence of J($^{13}$C–$^1$H) values upon C–H bond lengths was suggested. In recent years, several accurate determinations of $R_{CH}$ distances were reported in the literature and it was interesting to discuss some of these results in terms of the electronic structure of the corresponding LMO's. The bond lengths we used are those which approach the most closely the average C–H distance in the vibrational ground state of the molecule (Table 1). As shown in Fig. 1, a linear relation is obtained between $R_{CH}$ and the percent s character of the C atom hybrid orbital involved; the least-squares equation which results from these data is:

$$R_{CH}(\text{Å}) = 1{\cdot}1669 - 0{\cdot}0025\,(\%s_C) \qquad (4)$$

with a standard deviation of 0·0040 Å†.

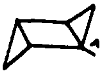
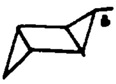
*Nature of the* C–H *bonds in quadricyclane and tricyclohexane*

In view of the preceding results, it was particularly interesting to perform a similar INDO-LMO and $^{13}$C-NMR study on quadricyclane (1) and tricyclohexane (2). Both of these compounds contain indeed two cyclopropane rings fused to the opposite C–C bonds of a 4-membered ring, and since shorter bond lengths were observed for the bridgehead C–H bonds in bicyclobutane[29] (1·071 Å) and bicyclo[2.1.0]pentane[38] (1·085 Å) relative to the mean value of the cyclopropane and cyclobutane methylene bonds in these molecules (1·093 Å and 1·095 Å, respectively), the question arose to which extent the C–H bonds in 1 and 2 were really equivalent.

The INDO-LMO's of these two molecules were calculated[3,16] assuming for each of them equal CH bond lengths (1·103 Å for 1[1] and 1·085 Å for 2[2]). The results are listed in Table 2; for 1, the C atom hybridizations were calculated for the two possible geometries (Methods A and B) given by Kuchitsu *et al.*[1] J($^{13}$C–$^1$H)- and $R_{CH}$-values were then obtained using eqns (3) and (4). It is interesting to note that although equal C–H bond lengths were used as initial structural parameters, different $R_{CH}$-values are obtained, indicating that the method can be used in an iterative way in order to refine molecular geometries.

A subsequent iteration for the two molecules was performed using the computed $R_{CH}$-values quoted in

Table 2. Experimental and calculated $J_{CH}$ and $R_{CH}$ values for the C–H bonds in quadricyclane, tricyclohexane and bicyclopentane

| Molecule and bond | % s | J($^{13}$C-$^1$H) (Hz)<br>calculated | experimental | $R_{CH}$ (Å)<br>calculated |
|---|---|---|---|---|
|  | 26·13 (A)<br>26·58 (B) | 130·0 (A)<br>133·1 (B) | 133 | 1·100 (A)<br>1·099 (B) |
|  | 30·05 (A)<br>30·21 (B) | 157·2 (A)<br>158·3 (B) | 166 | 1·090 (A)<br>1·090 (B) |
|  | 33·49 (A)<br>33·33 (B) | 181·0 (A)<br>179·9 (B) | 185 | 1·082 (A)<br>1·082 (B) |
|  | 32·57 | 174·7 | 179 | 1·084 |
|  | 31·03 | 164·0 | 165 | 1·088 |
|  | 29·96 | 156·6 | 152 | 1·091 |
|  | 32·92 | 177·1 | 178·1 [39] | 1·083 |
|  | 26·82 | 134·8 | | 1·099 |
|  | 26·58 | 133·1 | | 1·100 |
|  | 30·99 | 163·7 | | 1·089 |
|  | 30·21 | 158·3 | | 1·090 |

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†Recently, Maksic *et al.*,[36,37] using hybrids evaluated according to the maximum overlap approximation, obtained a linear relation between the calculated C–H bond overlaps and the corresponding experimental bond lengths; deviations as large as $10^{-2}$ Å may, however, occur.

Table 2 as input CH-distances. The % s-character of the carbon hybrid in the CH-LMO's so obtained lead, via eqn (4) to new bond lengths which differed at most by $1\cdot10^{-3}$ Å from the input-values, indicating that self-consistency is reached very rapidly by this procedure.

Table 2 also contains the experimental values of the different $J(^{13}C–^{1}H)$ coupling constants (Experimental); due to the approximations involved in the establishment of the molecular geometries, we may say that the agreement with the theoretical predictions is satisfactory. The calculated values are only slightly affected by the use of the iterative procedure (maximum difference 1 Hz). Experimental assignment of the different $\delta$ $^{13}C$ resonances is straightforward in these molecules as it is based on the relative intensity and multiplicity of the signals. In the case of tricyclohexane, the $^{1}H$ NMR spectrum has been analyzed by Schipperijn and Lukas[42] and the methylene- *exo*- and *endo*-proton resonance frequencies attributed with the use of a Karplus-plot. Our attempts to assign the two measured $J(^{13}C–^{1}H)$ coupling constants to the *exo*- and *endo*-bonds by selective decoupling experiments were unsuccesful; their value was obtained by computer analysis[41] of the corresponding ABX system, using a value of −4 Hz for $J(H_AH_B)$ (gem) and 13·5 Hz (0·15 ppm) for $\Delta\nu_{AB}$[40,42]. The largest $^{13}C–^{1}H$ coupling constant in this system is attributed by comparison with the theoretically predicted values to the *endo* C–H bond. This situation has been shown experimentally to occur also in bicyclo[1.1.0]butane[20] and is supported by our calculations (Table 1).

We predict the same behaviour for the cyclopropyl methylene group in bicyclo[2.1.0]pentane[*] (Table 2), so that it may be stated as a general rule that in fused cyclopropane ring systems, the C atom hybrid oribtal engaged in the *endo* C–H bond has more s character than the *exo*-hybrid.

Inspection of the experimental $J(^{13}C–^{1}H)$ values listed in Table 2 reveals that both quadricyclane and tricyclohexane possess C–H bonds with a rather different electronic structure, and this conclusion is supported by our theoretical results. Both theory and experiment indicate a very high per cent s character in the C–H bonds starting from the bridgehead C atoms which are part of both the 3- and 4-membered rings; the calculated values for $J(^{13}C–^{1}H)$ and $R_{CH}$ in this position in bicyclo[2.1.0]pentane are very close to the experimental ones (177·1 Hz vs 178·1 Hz, 1·083 Å vs 1·085 Å, this last value being not optimized in the experimental study[38]), showing that the proposed $R_{CH}$-values quoted in the last column of Table 2 are quite reliable. The bridgehead $C_1$–H bond in quadricyclane should accordingly be very short (1·082 Å), which is acceptable when considering that $C_1$ in this molecule is part of a 3-, a 4- and a 5-membered ring. From this result, a second general rule can be derived; if a bridgehead C atom which is part of different small fused rings is noted as $C[n + m + \ldots]$, then it is easily seen from Table 3 that the per cent s character in this C–H bond increases with increasing ring-strain at the C atom involved.

An analogous investigation of the electronic structure of the C–C single bonds in small fused rings in order to obtain a more complete insight into the factors responsible for their molecular geometry is now in progress.

Table 3. Variation of the percent *s*-character of the carbon hybrid in the CH localized orbital with the ring-strain at the carbon atom involved

| Molecule | Type of C atom | %s in C–H hybrid |
|---|---|---|
| Cyclopropane | [3] | 30·43 |
| Bicyclo[1.1.0]butane | | 30·67 (exo)<br>31·80 (endo) |
| Bicyclo[2.1.0]pentane | | 30·21 (exo)<br>30·99 (endo) |
| Quadricyclane ($C_4$) | [3 + 5] | 30·05 (A)<br>30·21 (B) |
| Tricyclohexane ($C_1$) | [3 + 4] | 32·57 |
| Bicyclopentane ($C_1$) | | 32·92 |
| Quadricyclane ($C_1$) | [3 + 4 + 5] | 33·49 (A)<br>33·33 (B) |
| Bicyclobutane | [3 + 3] | 36·50 |

## EXPERIMENTAL

Quadricyclane was prepared by acetophenone sensitized irradiation of norbornadiene[43] during 5 hr with a HANAU TQ 150 medium pressure mercury lamp and was purified by fractional distillation on a Perkin Elmer 251 spinning band column (b.p. 121°/760 mm Hg).

Tricyclo[3.1.0.0$^{2,4}$]hexane was obtained from Prof. J. E. Baldwin of the University of Oregon in the frame-work of a common research program with Prof. H. Geise of the University of Antwerp (U.I.A.) on the structure and geometry of this molecule.

The $^{13}C$ NMR spectra were recorded on a Brücker HX90 high resolution spectrometer operating at 22·63 MHz with the field locked on the $^{19}F$ resonance of $C_6F_6$ at 84·6 MHz. The sample tube (10 mm) was fitted with a coaxial cell containing $C_6F_6$. The spectra were obtained by the pulse Fourier transform mode (8 K).

For 1: pure liquid, 2950 Hz spectral window, 10,000 scans. $\delta_{C_1} = 15\cdot05$ ppm, $\delta_{C_2} = 23\cdot15$ ppm, $\delta_{C_3} = 32\cdot22$ ppm from TMS, in fair agreement with the values reported by J. D. Roberts *et al.*[44] ($\delta$ $CS_2$ from TMS = 192·24 ppm).

For 2: $CS_2$ solution 10% w/v, 2200 Hz spectral window, 23,000 scans. $\delta_{C_1} = 18\cdot56$ ppm, $\delta_{C_3} = 24\cdot09$ ppm from TMS.

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