Conformational Analysis of Cyclohexa-1,4-dienes by Nuclear Magnetic Resonance

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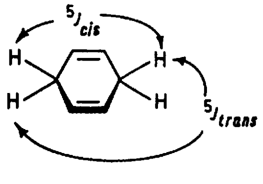
SCF–INDO–FPT calculations were performed for various geometries of the flat cyclohexa-1,4-diene molecule to obtain theoretical homoallylic coupling constants (^5J). The values of $^5J_{cis}/^5J_{trans}$ remain within the narrow range 1.22—1.29. Thus, theoretical and empirical homoallylic coupling constants for a flat cyclohexa-1,4-diene molecule agree closely, and there is no need to postulate a rapidly inverting cyclohexa-1,4-diene ring. Other anomalies in the literature can be resolved once it is recognized that for a flat cyclohexa-1,4-diene molecule $^5J_{cis}/^5J_{trans}$ is greater than 1.

It has been suggested[1,2] that, theoretically, *trans*- should be larger than *cis*-homoallylic coupling constants in the flat conformation of cyclohexa-1,4-diene [see (1)]. However, in cyclohexa-1,4-diene itself[3] and in 1-substituted cyclohexa-1,4-dienes[4] † (which from n.m.r. analysis appear to be flat) homoallylic *cis*-couplings ($^5J_{cis}$) are observed to be larger than the *trans*-couplings ($^5J_{trans}$).[3] † It has been argued[1] that, in view of this disparity, the so-called 'flat' cyclohexa-1,4-dienes could well exist as rapidly equilibrating boat conformations. Such a conclusion is surprising, because *X*-ray data,[5,6] far-i.r. data,[7] and theoretical energy studies[8] indicate cyclohexa-1,4-diene and 1-substituted cyclohexa-1,4-dienes are flat. One electron diffraction study[9] does indicate a highly puckered cyclohexa-1,4-diene, but another such study again suggests a flat conformation;[10] in any case the conclusions of the former study are in question.[7]



(1)

The contention[1] that $^5J_{trans} > {}^5J_{cis}$ for flat cyclohexa-1,4-diene is based on the fact that for *single*-path homoallylic couplings (*i.e.* for *cis*-but-2-ene) this should be the case.[11] However, it has been shown[12] that (for one set of bond lengths and angles)[9] for the *dual*-path homoallylic couplings in cyclohexa-1,4-diene, the calculated $^5J_{cis}$ is larger than $^5J_{trans}$ ($^5J_{cis}/^5J_{trans}$ is 1.29). Because of the implications of this result with regard to the previous conclusions,[1] and because of the uncertainty of the exact geometry of flat cyclohexa-1,4-diene, we have explored this phenomenon more thoroughly by performing SCF–INDO–FPT calculations[13] for various bond angles and lengths for flat cyclohexa-1,4-diene. Specifically, we have compared the geometries for the two electron diffraction studies[9,10] and that for 'standard' angles and lengths,[11] with the results given in Table 1.

TABLE 1

Calculated proton–proton coupling constants in flat cyclohexa-1,4-diene for various bond lengths and angles

Geometry	$^5J_{cis}$ [e]	$^5J_{trans}$ [e]	$^5J_{cis}/^5J_{trans}$	^3J [e]	^4J [e]
Bauer [a]	16.06	12.45	1.29	4.10	−2.30
Dallinga [b]	20.85	17.05	1.22	4.85	−2.60
'Standard' [c]	11.52	8.98	1.28	3.21	−1.93
'*cis*-But-2-ene' [d]	4.78	4.59	1.04	3.85	−2.18

[a] Ref. 8; r(C=C) 1.347 Å, r(C–C) 1.511 Å, r(C–H, olef.) 1.079 Å, r(C–H, aliph.) 1.096 Å, $\widehat{HCH}$ 109.8°. [b] Ref. 9; r(C=C) 1.334 Å, r(C–C) 1.496 Å, r(C–H, olef). 1.103 Å, r(C–H, aliph.) 1.114 Å, $\widehat{HCH}$ 103°. [c] Ref. 10; r(C=C) 1.337 Å, r(C–C) 1.540 Å, r(C–H, olef.) 1.08 Å, r(C–H, aliph.) 1.09 Å, $\widehat{HCH}$) 109.47°. [d] Geometry exactly that for Bauer's geometry; *i.e.* methylene proton bonds lie in a common plane including the terminal atoms. [e] In Hz.

Two major observations can be made. First, the specific values of ^5J are extremely sensitive to changes in the

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† The low-field methylene signal of 1,4-dihydrobenzyl alcohol, which shows the smaller homoallylic splitting, is also the most shifted by added lanthanoid; furthermore, the signal due to the homoallylic proton in *cis*-triptycenecarboxylic acid is shifted more than that of the homoallylic proton in *trans*-triptycenecarboxylic acid; this establishes that the *cis*-coupling in 1,4-dihydrobenzyl alcohol is larger than the *trans*-coupling.

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geometrical parameters. Comparison of these geometrical parameters (footnotes of Table 1) with the ^5J values suggests that the most important factor is the C–C single bond length, *i.e.* how close the methylene proton bonds are to the π-bonds. Secondly, notwithstanding the wide variation of the individual ^5J values, $^5J_{cis}$ is always larger than $^5J_{trans}$; in fact $^5J_{cis}/^5J_{trans}$ remains within a very narrow range (1.22—1.29).

Empirical values of $^5J_{cis}/^5J_{trans}$ for simple cyclohexa-1,4-dienes include 1.20 for cyclohexa-1,4-diene itself,[3] 1.22 for 1,4-dihydrobenzoic acid,[12] and 1.2 for dihydrobenzyl alcohol.[4b] Thus, theoretical $^5J_{cis}/^5J_{trans}$ values for flat cyclohexa-1,4-diene and empirical $^5J_{cis}/^5J_{trans}$ values for simple cyclohexa-1,4-dienes agree within a few percent. Clearly, there is no need to resort to equilibrating boat conformations for simple cyclohexa-1,4-dienes.

The fact that $^5J_{cis}/^5J_{trans}$ is not the same for single-path (*cis*-but-2-ene) and dual-path (cyclohexa-1,4-diene) couplings is of no particular surprise for two reasons. First, the two systems are of different symmetry. (The former system has C_{2v} and the latter D_{2h} symmetry, and the magnitudes of homoallylic couplings are critically dependent upon symmetry properties.[14]) Secondly, the geometry of the homoallylic system changes as one progresses from *cis*-but-2-ene to cyclohexa-1,4-diene, *viz.* in cyclohexa-1,4-diene the methylene hydrogen atoms lie in the same plane as the homoallylic carbon atoms, whereas in *cis*-2-butene the homoallylic hydrogen atoms are not so constrained. To ascertain the consequence of this latter effect, calculations were performed for *cis*-2-butene with cyclohexa-1,4-diene geometry. Table 1 shows the results: $^5J_{cis}/^5J_{trans}$ is now 1.04, whereas for normal *cis*-but-2-ene the calculated result [14] is 0.9. Thus, geometrical considerations do influence the $^5J_{cis}/^5J_{trans}$ ratio.

The geometry in Table 1 that gives the most satisfactory results for individual values of homoallylic coupling constants is the 'standard' one. This observation prompts inspection of the other theoretical values and comparison with the experimental ones. Thus, theoretical values of ^3J and ^4J (3.2 and −1.9, respectively) are to be compared with the respective experimental values of 3.1 and (−)1.5.[4a] Hence for these non-homoallylic coupling constants also, agreement is better for the 'standard' geometry than for the electron diffraction geometry.[12] In the 'standard' geometry the significant difference appears to be the C–C single bond length, as noted above. However, *X*-ray data [5,6] support the shorter C–C bond length. Thus it seems that the calculated coupling constants are overestimates rather than that the published bond lengths are too small. In any case, the calculated homoallylic couplings are consistently larger than the observed values, consistent with previous observations that in the present computational scheme the hyperconjugative σ–π contribution is overestimated.[12,15] Nevertheless, it has been shown [12] that the ratio of the calculated coupling constants is quite meaningful, and apparently $^5J_{cis}$ and $^5J_{trans}$ are 'overestimated' to the same extent.

Now that the experimental homoallylic data have been reconciled with theoretical considerations, it is possible to explore some 'anomalies' in the literature. In this analysis, it must be remembered that as a conformationally free cyclohexa-1,4-diene becomes more puckered, (*a*) both $^5J_{cis}$ and $^5J_{trans}$ decrease, and (*b*) $^5J_{cis}/^5J_{trans}$ generally decreases from *ca.* 1.2 for a flat system to <0.5 for a highly puckered system.[12]

In an effort to determine the steric effects of 2- and 6-substitution, Grossel and Perkins [1] prepared 2,6-dimethoxy- (2) and 2,6-dimethyl-1,4-dihydrobenzoic acid (3). They concluded that these substituents have little effect on the conformation and that the structures of these molecules are essentially planar. The lower values of the homoallylic coupling constants were attributed to a 'substituent' effect. We have determined the *J* values for 3,5-dimethyl-1,4-dihydrobenzyl alcohol (5) [see Table 2; compounds (6) and (7) are included for comparison].

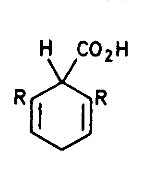
TABLE 2

Homoallylic proton–proton coupling constants (Hz) for compounds (2)—(7)

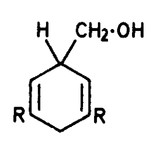
Compound	Ref.	^5J *cis*	^5J *trans*	$^5J_{cis}/^5J_{trans}$
(2)	*a*	6.3	6.8 [f]	0.93 [g]
(3)	*a*	6.0	6.25 [f]	0.96 [h]
(4)	*b*	9.19	7.56	1.22
(5) [i]	*c*	8.1	7.1	1.14
(6)	*d*	8.6	7.4	1.16
(7)	*e*	9.63	8.04	1.20

[a] Ref. 1. [b] Ref. 12. [c] Present study. [d] Ref. 4*a*. [e] Ref. 3. [f] Assignments suggested but uncertain (ref. 1). [g] Reverse assignments would give a value of 1.08. [h] Reverse assignments would give a value of 1.04. [i] Other *J* values for (5): ^2J −23.6, ^3J 3.6, ^4J (−)1.7. Measurements were made in the presence of Eu(fod)$_3$ with spin decoupling as previously described (ref. 4*b*).

Several observations can be made. (*a*) Comparison of compounds (5) and (6) shows little effect of the methyl groups. Thus, the effect of the methyl groups in (3) is not a 'substituent' one. (*b*) Both $^5J_{cis}$ and $^5J_{trans}$ values are lower for (2) and (3) than for (4)—(7). This indicates [12] that (2) and (3) are more puckered than are (4)—(7). (*c*) The $^5J_{cis}/^5J_{trans}$ values for (2) and (3) are lower than for (4)—(7) [no matter what the assignments are for the homoallylic protons in (2) and (3)], again



(2) R = OMe
(3) R = Me
(4) R = H



(5) R = Me
(6) R = H

(7)

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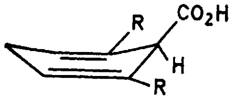
indicating that (2) and (3) are more highly puckered than are (4)—(7). We conclude that the effect of the methyl groups in (3) and the methoxy-groups in (2) is a steric effect. However, we do not suggest that (2) and (3) are highly puckered, but rather believe that the effect involves only modest deviation from planarity. The $^5J_{cis}/^5J_{trans}$ value for (2) and (3) (either *ca.* 0.95 or *ca.* 1.05) is larger than for 1,4-dihydro-1-naphthoic acid (0.88),[12] and we believe the extent of puckering of (2) and (3) is intermediate between that of the molecules (4)—(7) and that of puckered 1,4-dihydro-1-naphthoic acid.[12]



(2) or (3)

Another anomaly in the literature is that for 1,4-dihydro-1-naphthoic acid the non-homoallylic couplings indicate a puckered structure, whereas (with the faulty assumption that $^5J_{trans} > {}^5J_{cis}$) the homoallylic couplings indicate ' oscillation about an approximately planar geometry.' [1] Our interpretation, however, makes it clear that $^5J_{cis}/^5J_{trans}$ is not the same for simple cyclohexa-1,4-dienes and 1,4-dihydro-1-naphthoic acid (*cf.* 1.22 with 0.88),[12] and that the expected value of $^5J_{cis}/^5J_{trans}$' for flat cyclohexa-1,4-diene is precisely what is observed for simple cyclohexa-1,4-dienes but is different for 1,4-dihydro-1-naphthoic acid. Clearly, 1,4-dihydro-1-naphthoic acid is puckered, although perhaps less so than the 9,10-dihydroanthracene system.[12]

We believe our interpretation explains another puzzling feature from the conformational analysis of cyclohexa-1,4-dienes by n.m.r. It is now clear that $^5J_{cis}/^5J_{trans}$ can remain ' close to 1 ' throughout a significant range of puckering: $^5J_{cis} > {}^5J_{trans}$ for flat cyclohexa-1,4-diene, and as the ring becomes more puckered, then gradually $^5J_{trans} < {}^5J_{cis}$.[12] Thus, the extent of ring puckering cannot be ' inferred from the near equality of the *cis*- and *trans*-coupling constants.' [1]

The new interpretation further removes the necessity of resorting to a situation where cyclohexa-1,4-diene vibrates rapidly about a planar minimum and yet must spend most of its time in a highly puckered conformation to explain why $^5J_{cis} > {}^5J_{trans}$.[1] Although such a situation is physically possible, the preferred interpretation [7] is that cyclohexa-1,4-diene is essentially planar.

EXPERIMENTAL

3,5-*Dimethyl*-1,4-*dihydrobenzyl Alcohol*.—Sodium (2.3 g, 0.1 mol) was added to 3,5-dimethylbenzoic acid (5 g, 0.033 mol) in liquid anhydrous ammonia (250 ml) containing absolute ethanol (40 ml). After the blue colour had disappeared, saturated ammonium chloride solution was added and the ammonia was allowed to boil off. The remaining solution was acidified at 0 °C with hydrochloric acid, and the product extracted with ether. Without further purification, the acid was dissolved in anhydrous ether (ice-bath), and lithium aluminium hydride (5 g) was added to the stirred solution. The mixture was then brought to reflux for 1 h, cooled, and quenched cautiously with water. Extraction and removal of the ether produced an oil which was distilled to afford 3.0 g pure 3,5-*dimethyl*-1,4-*dihydrobenzyl alcohol* (3.0 g), b.p. 85 °C at 5 mmHg; δ($CDCl_3$) 5.4 (2 H, m), 3.6 (2 H, d), 2.9 (1 H, m), 2.5br (2 H, d), 1.8 (6 H, s), and 1.5br (1 H, s) (Found: C, 78.45; H, 10.1. $C_9H_{14}O$ requires C, 78.2; H, 10.2%).

N.m.r. spectra were recorded with a Varian HA-100 instrument in the internal lock frequency sweep mode.

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