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A COMMENT ON THE USE OF HOMOALLYLIC COUPLING CONSTANTS TO PROBE THE SOLUTION CONFORMATION OF 1,4-DIHYDROBENZENES AND 1,4-DIHYDRONAPHTHALENES

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Recent claims for a conformationally dependent "dual-path" effect for homoallylic couplings about a cyclohexa-1,4-diene ring are questioned and evidence is presented that homoallylic coupling constant ratios may allow a direct comparison of the solution geometries of 1,4-dihydrobenzenes and 1,4-dihydronaphthalenes.

Recently Marshall and his co-workers[1] have described SCF-INDO-FTP calculations for homoallylic coupling about a cyclohexa-1,4-diene ring (1). These were intended to replace earlier data,[2] based on the work of Barfield and Sternhell,[3] in which homoallylic couplings were calculated across a *cis*-but-2-ene moiety, the predicted values in this case being simply and perhaps naively doubled to allow for the dual interaction pathway in (1). The results of these two studies are compared in Figure 1, the degree of puckering of the cyclohexa-1,4-diene ring being defined by the angle α in (1)[4].

There now exists a considerable body of experimental data[1,2,5-8] which suggests that the maximum *cis*-homoallylic coupling across a cyclohexadienyl ring is *ca*. 12 Hz. This agrees quite well with our original calculations (Fig.1a), where J_{max} = *ca*. 10.5 Hz (α = *ca*. 147°). In contrast the more recent work predicts J_{max} = *ca*. 25.5 Hz (α = *ca*. 150°). Indeed, as Marshall notes,[1] his calculations consistently lead to coupling constant values about twice those found experimentally. Accordingly, in Fig.1 Marshall's data has been reduced by a factor of 2 (by changing the y-axis scale) to allow direct comparison of the two sets of curves.

Marshall[1] suggests that the excessively large couplings predicted by his calculations arise from a "dual path" effect which is additional to that arising simply from the presence of two interaction pathways. It is further proposed that the decrease of $J_{\psi a/\psi a}$ with greater ring puckering results from a lesser contribution from this special effect with decreasing α. However, the similarity of the shapes of the two sets of curves in Fig.1 reveals that this angular dependence is an inherent property of the system - indeed it simply arises because at α = *ca*. 150° the C-H σ-bonds of the pseudoaxial (ψ_a) protons at C-3 and C-6 and the p-orbitals of the π-bond are parallel, allowing maximum coupling interaction. This coupling will of course decrease again as α reduces further and overlap becomes poorer. Thus it would appear that a special "dual-path" effect is not required to explain the results obtained.

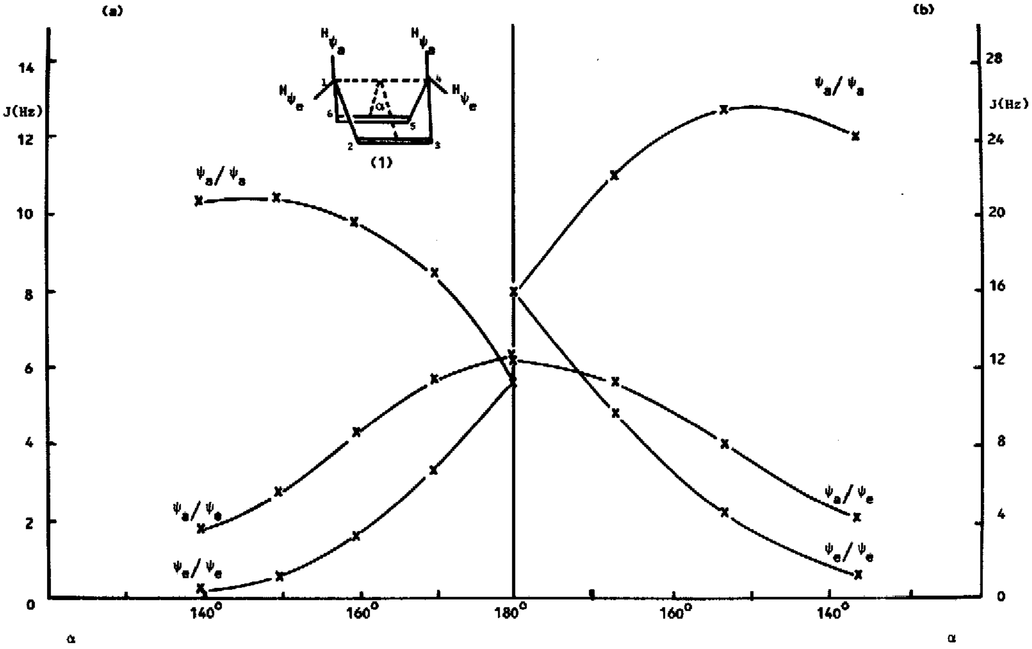
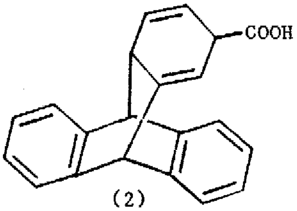
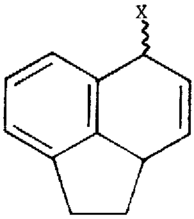


Figure 1. The conformational dependence of homoallylic coupling in cyclohexa-1,4-diene between pseudoaxial (ψa) and pseudoequatorial (ψe) protons, as predicted by: (a) Grossel and Perkins[2]; and (b) Marshall, Faehl, McDaniel, and Ledford[1], the latter being plotted on a halved scale.

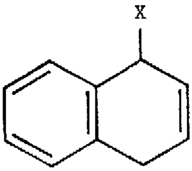


(2)



(3) X = COOH

(6) X = $Me_2C(OH)$



(4) X = COOH

(5) X = $Me_2C(OH)$

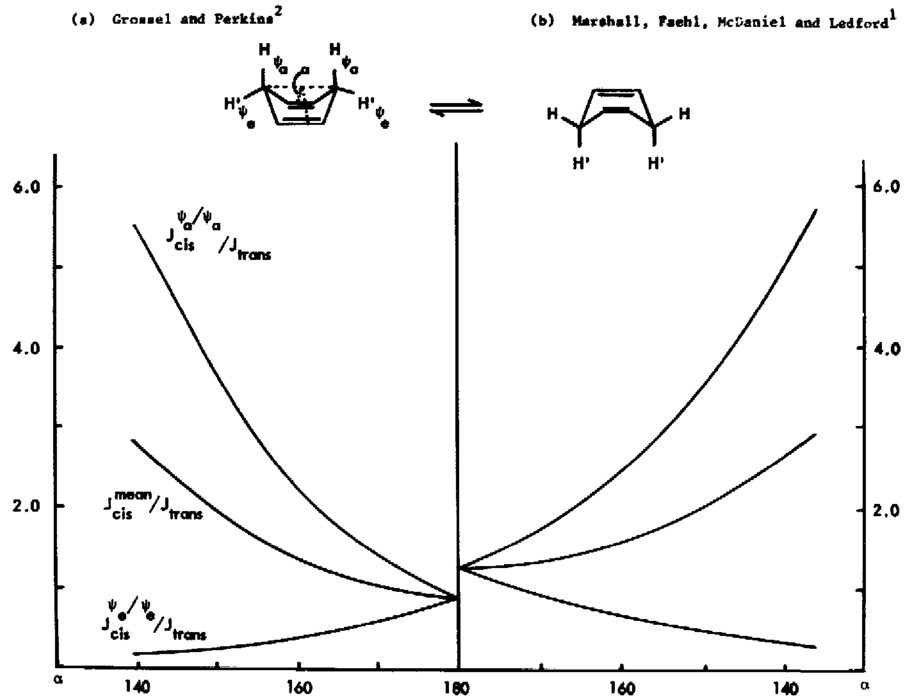


Figure 2. Theoretical variation of homoallylic coupling constant ratios with cyclohexa-1,4-diene geometry.

There remains the question of whether $^5J_{cis} > {}^5J_{trans}$ in a planar dihydrobenzene ring. No unambiguous data as yet exist relating to a conformationally rigid and planar dihydrobenzene, but recent results[9] support the view suggested by Marshall's SCF-INDO-FTP calculations[1] that $^5J_{cis}/{}^5J_{trans}$ is slightly greater than unity when $\alpha = 180^\circ$. In contrast the earlier work[2] predicted $^5J_{trans} > {}^5J_{cis}$ across a planar ring. If due allowance is made for this discrepancy between the two theoretical approaches it will be seen (Fig.2) that each predicts a very similar variation for $^5J_{cis}/{}^5J_{trans}$ with conformation. Indeed there is evidence that such ratios may provide a much more reliable probe into the solution conformations of dihydroaromatic systems than the coupling constant magnitudes themselves.[10,11] cis-Homoallylic coupling can occur in either a dipseudoaxial or dipseudoequatorial sense. For the former case there is a rapid rise in the magnitude of $^5J_{cis}/{}^5J_{trans}$ with increasing ring puckering. Thus in 2,4a-dihydrotriptycene 2-carboxylic acid (2), for which models suggest α = ca. 145°, $^5J_{cis}/{}^5J_{trans} = 2.6$ [$^5J_{cis} = 12.0$; $^5J_{trans} = 4.3$ Hz].[7] A similar value is found in 2a,5-dihydroacenaphthoic acid (3) [$^5J_{cis} = 8.54$; $^5J_{trans} = 3.3$ Hz][5,12] for which X-ray crystallography has shown that the dihydronaphthalene ring is puckered with $\alpha = 146^\circ$ [6]. Intuitively the close agreement between these coupling constant ratios in dihydrobenzenes and dihydronaphthalenes is not surprising and warrants further examination when more data become available.

1-Substituted flexible 1,4-dihydronaphthalenes should favour a boat conformation in which the substituent is placed pseudoxial[2,13,14]. In this case $^5J_{cis}$ will be dipseudoequatorial and thus $^5J_{cis}/{}^5J_{trans}$ should fall relatively slowly as α decreases (Fig.2). This is reflected in the experimental data. Thus 1,4-dihydronaphthoic acid (4) has $^5J_{cis}/^5J_{trans}$ = 0.86 [$^5J_{cis}$ = 3.8; $^5J_{trans}$ = 4.4 Hz][15] and is thought to be slightly puckered in solution[13,14]. This is supported by an X-ray crystallographic study which shows α = 170.5°.[16] Puckering is further increased for 1-(2-hydroxypropyl)-1,4-dihydronaphthalene (5) for which $^5J_{cis}/^5J_{trans}$ = 0.6 [$^5J_{cis}$ = 1.8; $^5J_{trans}$ = 3.0 Hz].[16] $^5J_{trans}$ here is very close to the to the values reported for the related dihydroacenaphthenes (3)[12] and (6)[14] suggesting that all are similarly puckered.

I have now prepared 1,4-dihydrooctadeuteronaphthalene (as a mixture of stereoisomers) and find[18] that $^5J_{cis}$ = 7.15 Hz and $^5J_{trans}$ = 4.55 Hz (i.e. $^5J_{cis}/^5J_{trans}$ = 1.57). The interpretation of these data is complicated by the possibility of boat-boat equilibration leading to a time-averaged value for $^5J_{cis}$. It is, however, clear (Fig.2) that for a *ca.* 50:50 population of boat conformers, $^5J_{cis}/^5J_{trans}$ should increase as the extreme boat geometrics become more puckered. These couplings thus appear to provide the first clear evidence for a boat geometry here and a comparison of $^5J_{trans}$ suggests a time-averaged conformation similar to that of 1,4-dihydronaphthoic acid (4).[19]

References and notes

1. J.L. Marshall, L.G. Faehl, C.R. McDaniel,Jr., and N.D. Ledford, J. Amer. Chem. Soc., 99, 321, (1977)
2. M.C. Grossel, and M.J. Perkins, J.C.S., Perkin II, 1544, (1975).
3. M. Barfield, and S. Sternhell, J. Amer. Chem. Soc., 94, 1905, (1972).
4. Conventionally the angle α in (1) (numbered as a 1,4-dihydrobenzene) and its derivatives is that between the C(1)-C(2)-C(3)-C(4) and C(4)-C(5)-C(6)-C(1) planes. However, Marshall[1] defines the ring geometry by a different angle (also referred to as α) which is that between the C(2)-C(3)-C(5)-C(6) and C(6)-C(1)-C(2) planes. Care should be taken not to confuse these angles.
5. M.C. Grossel, and R.C. Hayward, J.C.S., Perkin II, 851, (1976).
6. A.K. Cheetham, J.M. Newsam, M.C. Grossel, and R.C. Hayward, J.C.S., Perkin II, 1153, (1977).
7. P.W. Rabideau, J.W. Paschal, and L.E. Patterson, J. Amer. Chem. Soc., 97, 5700, (1975).
8. M. Barfield, A.M. Dan, C.J. Fallick, R.J. Spear, S. Sternhell, and P.W. Westerman, J. Amer. Chem. Soc., 97, 1482, (1975).
9. M.C. Grossel, and M.J. Perkins, Nouveau J. Chem., 3, 285, (1979).
10. M.C. Grossel, A.K. Cheetham, D. James, and J.M. Newsam, J.C.S., Perkin II, in press
11. P.W. Radideau, J.W. Paschal, and J.L. Marshall, J.C.S., Perkin II, 842, (1977).
12. This work. Reduction of 5-acenaphthoic acid with Na/NH_3, quenched with water leads mainly to the formation of thermodynamically more stable *trans*-(3).
13. P.W. Rabideau, Acc. Chem. Research, 11, 141, (1978).
14. P.W. Rabideau, E.G. Burkholder, M.J. Yates, and J.W. Paschal, J. Amer. Chem. Soc., 99, 3596, (1977).
15. J.L. Marshall, A.M. Ihrig, and P.N. Jenkins, J. Org. Chem., 37, 1863, (1972).
16. M.C. Grossel, A.K. Cheetham, and D.James, in preparation.
17. The solid-state geometry of (4) need not be identical to its time-averaged solution conformation. However, good agreement has been found for those flexible dihydrobenzoic acids so far studied.[10]
18. c.f. E.W. Garbisch, Jr., and M.G. Griffith, J. Amer. Chem. Soc., 90, 3590, (1968).
19. Steric isotope effects have been neglected.

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