THE STEREOCHEMICAL DEPENDENCE OF ONE-BOND CARBON-CARBON COUPLING CONSTANTS

Jennifer C.J. Barna and Michael J.T. Robinson

Dyson Perrins Laboratory, University of Oxford

South Parks Road, Oxford OX1 3QY, England

Abstract.   Spin-spin coupling constants for carbon-carbon single bonds vary with
the orientation of lone pairs on adjacent nitrogen atoms and of adjacent carbonyl groups.

IT IS WELL known that carbon-hydrogen bonds and hence nuclear spin-spin coupling constants
($^1J_{CH}$) are sensitive to the orientation of nearby non-bonding electrons and unsaturation.
In particular it has been observed that $^1J_{CH}$ is smaller for axial than for equatorial C-H
bonds adjacent to atoms with non-bonding electrons in six-membered ring compounds (1) or
adjacent to a carbonyl group in 2(or 6)-halogenocyclohexanones (2).

In contrast, no important stereochemical effects on one-bond carbon-carbon coupling
constants ($^1J_{CC}$) have been reported. Hansen, Poulsen, and Berg found that $^1J_{CC}$ for a
carbonyl carbon atom directly bonded to an aromatic ring is insensitive to steric hindrance
to resonance caused by _ortho_ substituents (3) and most measurements of $^1J_{CC}$ have been made
on compounds in which stereospecific effects, if present, cannot be readily separated from
other factors. We have now sought and observed substantial stereochemical effects on $^1J_{CC}$
using six-membered ring compounds having a methyl group enriched in carbon-13. The coupling
constants were measured from proton decoupled spectra by observing the natural abundance
signals, split by coupling to the enriched methyl group, of the C-2 carbon atoms in the pairs
of stereoisomers 1-5 (see Table on the following page).

The differences ΔJ (cis-trans) for the piperidinium salts 1 and 3 show that when there
are no non-bonding electrons or unsaturation stereochemical effects on $^1J_{CC}$ for single C-C
bonds are small and indeed insignificant at the level of precision of the present data. In
contrast, ΔJ for 2, 4, and 5 are substantial and in all three pairs $^1J_{CC}$ is larger when the
C-methyl group is equatorial. A similar trend found for axial and equatorial C-H bonds in,
eg, derivatives of tetrahydropyran and 1,3-dioxane (1) has been rationalised in terms of
overlap of non-bonding electrons with anti-bonding orbitals of the C-H bonds (4). This
overlap was predicted to increase $^1J_{CH}$ when the non-bonding electron orbital and C-H bond
are _cis_ or gauche but to decrease it when the latter are _trans_. It is probable that similar
interactions occur with C-C bonds and the observed differences ΔJ may be rationalised
qualitatively on this basis using the known or predictable conformations of the compounds 1-5.

First it should be noticed that inductive effects appear to be small for $^1J_{CC}$ (compare
1 or 3 with 6; the most important difference should be the change from Ṅ to C). In the

TABLE. One bond carbon-carbon coupling constants for C(2)-C(Me) in diastereomeric pairs of anancomeric derivatives of piperidine (1-4) and cyclohexanone (5).

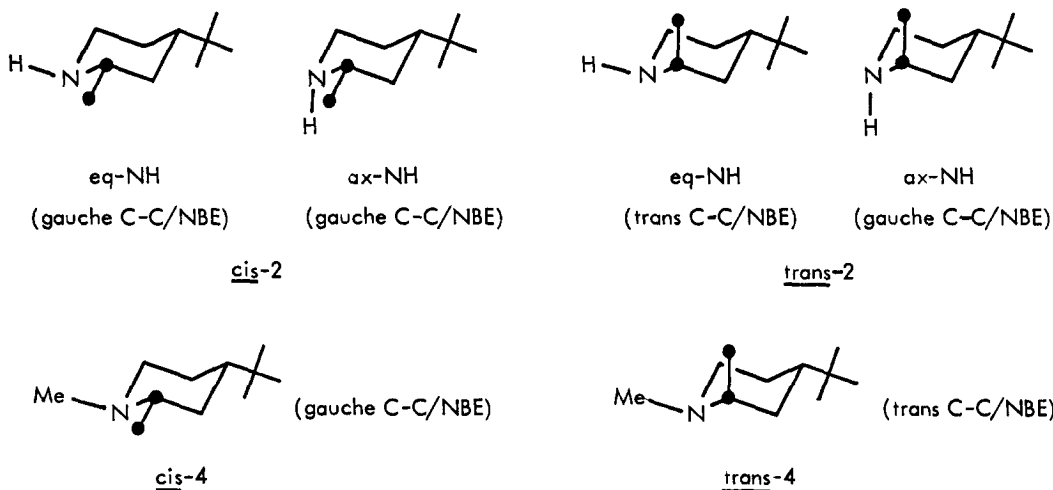| Compound	Solvent	$^1J_{CC}$ (Hz)[a]		ΔJ (Hz)
		cis(ea-Me)	trans(ax-Me)	(cis-trans)
1:	CF_2CO_2H	36.4	36.6	-0.2
2:	$CDCl_3$	38.4	36.5	+1.9
3:	CF_3CO_2H	36.8	37.3[b]	-0.5
4:	$CDCl_3$	39.3	35.3	+4.0
5:	$CDCl_3$	37.6	33.8	+3.8
6:	(No solvent)	35.6[c]]		

[a] ± 0.1 Hz.   [b] ± 0.5 Hz: the uncertainty is mainly caused by interference from overlapping lines.

[c] For C(1)-equatorial methyl: measured at $-90°$; previously reported to be 36.0 Hz (13).

second place the inductive and/or steric effects of N-methyl groups in the ions (see note 5) are barely significant (compare 1 with 3). The effect of N-methylation in the cis-amines (compare cis-2 with cis-4) may be due to one or more of a number of factors, eg:

    a. A difference between >NH and >NMe (in eq-cis-2 and cis-4: the N-methyl group in the latter is expected to be predominantly equatorial (5));

    b. Differences between apparently similar gauche relationships for non-bonding electrons (NBE) and C-H bonds in eq- and ax-cis-2;

    c. Effects of differing steric strains (ie, NH...CMe in cis-2 and NMe...CMe in cis-4), which are unlikely to be closely comparable in the ions and in the amines (6).

Whatever the relative importance of such factors, however, the large differences between diastereomeric amines compared with the small or negligible differences between diastereomeric

eq-NH   ax-NH   eq-NH   ax-NH

(gauche C-C/NBE)   (gauche C-C/NBE)   (trans C-C/NBE)   (gauche C-C/NBE)

cis-2   trans-2

(gauche C-C/NBE)   (trans C-C/NBE)

cis-4   trans-4

ions strongly suggest that the differences in interactions between non-bonding electrons (NBE) and C-C bonds in trans and in gauche relationships are much more important. Only one conformer, with an equatorial methyl group, is expected to be present in cis- and in trans-4 (5) with gauche and trans relationships for the NBE and C-C respectively. In cis- and trans-2 the conformational equilibrium at nitrogen (7) tends to diminish the difference in $^1J_{CC}$ between the diasteromers because ax-trans-2 has a gauche relationship between the NBE and C-C, as in both conformers of cis-2. Depending on the assumptions one makes about factors such as (a)-(c) above the value of $^1J_{CC}$ for trans-2 is consistent with K(trans-2) = ∿ 0.5-1, in agreement with most recent evidence for this controversial equilibrium (7), but can not be readily reconciled with Lambert's claim that K for piperidine is considerably greater than unity (8).

cis-5   trans-5

The difference ΔJ for cis- and trans-5 is qualitatively similar to differences in $^1J_{CH}$ observed for 2(6)-halocyclohexanones (2) and cyclohexane itself (9) but it is proportionately considerably larger, as well as being strikingly different from ΔJ for each of the pairs of ions 1 and 3. The low value of $^1J_{CC}$ in trans-5 compared with $^1J_{CC}$ in methylcyclohexane may be attributable to hyperconjugative withdrawal of electrons from the C-Me bond by the C=O. The cause of the high value of $^1J_{CC}$ for cis-5 (in which the C(2)-Me bond is approximately in the nodal plane of the C=O π orbital) compared with methylcyclohexane

is not obvious because purely inductive effects do not appear to be large for $^1J_{CC}$.

In the present work $^1J_{CC}$ values have been measured with a precision of ±0.1 Hz (except for trans-3; see Table) using spectra with a digital resolution of 0.5 or 1 Hz plotted on a large scale. In future work we hope to greatly improve the precision by using curve fitting either to the real part of transformed spectra or to the original free induction decays (note 11), for compounds doubly labelled with carbon-13, so that conformational equilibria about C-C bonds adjacent to atoms carrying non-bonding electrons or adjacent to unsaturation may be studied using the temperature dependence of $^1J_{CC}$. Although the stereochemical effects on $^1J_{CC}$ are no larger than those observed for $^3J_{CC}$ the large magnitude of $^1J_{CC}$ values make them much easier to measure with accuracy even at low temperatures when viscosity broadening could become a serious obstacle to the measurement of $^3J_{CC}$. The use of doubly labelled compounds will eliminate the problems caused by coincidental overlap of lines as well as overcoming the serious problems of sensitivity experienced when measuring coupling constants in singly enriched compounds.

REFERENCES AND NOTES

1. See, eg, K. Bock and C. Pedersen, J. Chem. Soc. Perkin II, 1974, 293, and earlier papers by Bock and his co-workers.

2. J. Cantacuzene, R. Jantzen, M. Tordeux, and C. Chachaty, Org. Mag. Res., 1975, 7, 407.

3. P.E. Hansen, O.K. Poulsen, and A. Berg, Org. Mag. Res., 1977, 9, 649.

4. V.M.S. Gil and J.J.C. Teixeira-Dias, Mol. Phys., 1968, 15, 47.

5. The N-methyl group in N-methylpiperidine is almost exclusively equatorial (6). The solutions of the ions cis- and trans-4 were obtained by dissolving crystalline salts in trifluoracetic acid and contain exclusively ions with equatorial N-methyl groups.

6. P.J. Crowley, M.J.T. Robinson, and M.G. Ward, Tetrahedron, 1977, 33, 915.

7. E.L. Eliel, C-Y. Yen, G. Juaristi, and W.R. Kenan, Tetrahedron Letters, 1977, 2931.

8. P.J. Crowley, G.A. Morris, and M.J.T. Robinson, Tetrahedron Letters, 1976, 3575, and references therein; F.A.L. Anet and I. Yavari, J. Amer. Chem. Soc., 1977, 99, 2794.

9. J.D. Lambert and S.I. Featherman, Chem. Rev., 1975, 75, 611.

10. V.A. Chertkov and N.M. Sergeyev, J. Amer. Chem. Soc., 1977, 99, 6750.

11. Both methods have been tried for a number of very simple carbon-13 spectra (12) and work particularly effectively for well spaced lines such as may be obtained with couplings of 30-40 Hz.

12. A.N. Hunt, D.J. Loomes, and M.J.T. Robinson, unpublished work.

13. O.A. Subbotin and N.M. Sergeyev, J.C.S. Chem. Comm., 1976, 141; H. Booth and J.R. Everett, Ibid, 278.