A Novel Substituent Effect in Vicinal Proton–Proton Couplings

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PRESENT interpretations of vicinal proton couplings are based on the dependence of the coupling on the dihedral angle between the C–H bonds, the well known $\cos^2\phi$ law,[1] plus the variation of the couplings with the electronegativity of the substituents.[2] These two mechanisms would predict that the values of J_{cis} and J_{trans} in a planar ring would be roughly in the ratio of 4 : 1, as the dihedral angles are 0° (*cis*) and 120° (*trans*), and that the couplings should decrease with increasing electronegativity of the atom X in a $CH_2{\cdot}CH_2X$ fragment. In cyclopentenone the couplings are 7·2 and 2·2 c./sec. respectively, in good agreement with these predictions. In the cyclopentene ring only the sum of the couplings is known (14·2 c./sec.), but in dihydro-thiophen and -furan the couplings are 10·0 and 7·5 c./sec., and 10·7 and 8·3 c./sec., respectively, whilst in the Δ^2-pyrroline ring their sum is 18·4 c./sec. The individual couplings do not obey the $\cos^2\phi$ law and furthermore the couplings *increase* as the electronegativity of X increases, in direct contrast to the usual electronegativity mechanism.

In other ring systems, only the value of $J_{cis} + J_{trans}$ can always be obtained. The Table lists values of this quantity (N) for a variety of three-, four-, five-, and six-membered rings. As all the compounds considered are either planar or flipping between two mirror image conformations, if we use $J = k\cos^2\phi$ we obtain

$$N = \frac{k}{2}\left(\frac{3}{2} + \cos^2\phi\right)$$

where ϕ is the angle of buckle of the $CH_2{\cdot}CH_2$ fragment considered. For k = 10 c./sec., N decreases from 12·5 c./sec. in a planar ring to

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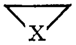
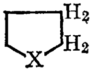
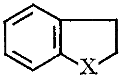
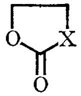
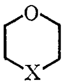
[1] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[2] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 1964, **7**, 165.

11·9 c./sec. for $\phi = 20°$ and 8·8 c./sec. for $\phi = 60°$. The electronegativity equation predicts that the average coupling will decrease from 7·0 c./sec. in a $C{\cdot}CH_2{\cdot}CH_2{\cdot}C$ fragment to 6·2 c./sec. in an $O{\cdot}CH_2{\cdot}CH_2{\cdot}O$ fragment. If all the couplings behaved in a similar fashion, this would predict a decrease of *ca.* 10% in *N* in these fragments.

The predicted dependence on the electronegativity of the atom X is closely followed in the case of the six-membered ring systems in the Table, but the five-membered ring systems show clearly the anomalous behaviour mentioned previously. In the cases of the cyclopentene analogues, the indane analogues, and the lactones, all of which will be almost planar rings the hetero-atom markedly increases the value of *N* in the series $CH_2 < S < NH < O$. In the case of the cyclopentane analogues, which would be expected to be considerably buckled (the angle of buckle in cyclopentane is *ca.* 40°[9]) and thus be intermediate between the six-membered rings and the planar rings, the values of *N* behave in a manner intermediate between the two extremes.

The three- and four-membered rings are special

TABLE. *Values of* N ($J_{cis} + J_{trans}$) *in some* $CH_2{\cdot}CH_2$ *fragments**

Compound	X	CO	CH_2	S	NH	NH_2^+	O
		—	14·6[a]	12·7[4]	10·1[4]	—	7·7[4]
		16·2[6]	15·7[b]	15·2[6]	—	—	15·2[6]
		10·5[7]	14·0[b]	12·5	13·3	14·5[e]	13·3
		9·4	14·2	17·5	18·4[c]	—	19·0
		12·8[6]	13·2[8]	—	17·0	15·6	17·7[8]
		—	13·5[8]	14·0[10]	16·0	—	15·9[5]
		—	10·8[d]	10·0[11]	9·4	9·4[e]	9·3[12]

* Values obtained in this investigation unless otherwise stated.
[a] Value for the methyl derivative (ref. 3).
[b] Value for 1,1-diethoxycarbonyl derivative.
[c] Value for 1-methyl-2-phenyl-Δ^2-pyrroline.
[d] Value for 4,4-dimethyl derivative.
[e] Value for *NN*-dimethyl derivative.

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[3] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 3218.
[4] F. S. Mortimer, *J. Mol. Spectroscopy*, 1960, **5**, 199.
[5] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.
[6] E. Lustig, private communication.
[7] F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 2316.
[8] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, N.M.R. Spectra Catalog, Varian Associates, 1962.
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[10] P. L. Corio, *Chem. Rev.*, 1960, **60**, 363.
[11] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, 1965, **69**, 579.
[12] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506.

cases, as the hybridization of the atoms is far from tetrahedral. Although these are planar systems the anomalous behaviour of the planar five-membered rings is modified considerably. The four-membered rings show an almost constant value of N but in the three-membered N decreases by almost a factor of two along the series CH_2, S, NH, and O. This suggests that the mechanism of this variation is not due entirely to the electronegativity of the atom X but that differences in hybridization play an important part. This is supported by the values of the geminal couplings in these ring systems.[13]

The anomalous behaviour of the five-membered ring systems appears to be associated with the planarity of the ring. However, planar rings without the hetero-atom show small vicinal couplings. For instance, J_{cis} and J_{trans} for the CH_2CH fragment of 1-bromoacenaphthene are 7·4 and 1·9 c./sec. respectively.[14] In a planar ring the p-orbitals of the lone pair on the hetero-atom obtain maximum overlap with the hydrogen atomic orbitals of the CH_2 protons. This overlap will decrease with increasing buckle of the ring until at 60° dihedral angle, as in the chair conformation of the six-membered rings, there will be minimum overlap. This suggests that the lone-pair orbitals on the hetero-atom are contributing towards the CH·CH coupling. Such a mechanism has not been considered previously although the influence of such lone pairs on the geminal proton coupling is now known to be considerable.[13] Support for this explanation is provided by the decrease in the value of N in going from indoline (17·0) to indoline hydrochloride (15·6) in which the lone pair is removed. Obviously this is not the only factor as the value of N in the latter is still larger than in indane (13·2) with which it is isoelectronic.

Obviously there are many other mechanisms which may affect the values of the couplings, *e.g.* the internal angles in the ring will vary considerably in these systems. It is clear, however, that vicinal proton–proton coupling constants are affected by factors which have not previously been considered theoretically, and that any comprehensive calculation of these couplings will need to take such interactions into account.

(*Received, July 20th,* 1965; *Com.* 455.)

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[13] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.
[14] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 1962, **84**, 2012.