Relationship between the Magnitude of J_{gem} and the Spatial Orientation of β-Substituents

By **Roger Davies**,† Chemistry Department, The University, Southampton SO9 5NH

An empirical relationship between ΔJ_{gem} and a relative orientation of an electronegative substituent, X, situated β to a methylene group has been experimentally determined, where X is OH, OAc, Ph, NO_2, Cl, Br, NH_2, $\overset{+}{N}H_3$, and NHAc. The curves are discussed in relation to a theory of geminal coupling, and agreement is found to be good.

THE application of a molecular orbital theory[1] has resulted in the prediction of the effects of α- and β-substituents on the geminal coupling constant (J_{gem}) of a methylene group. In the preceding paper, we have described an empirical study of the effects of heteroatoms and groups on the magnitude of the J_{gem} of an adjacent methylene group, in the light of the theoretical predictions. The agreement with theory was found to be good.

We now describe the work carried out to examine empirically the effects of an electronegative β-substituent on the magnitude of J_{gem}. The substituents whose effects we have examined are OH, OAc, Ph, NO_2, Cl, Br, NH_2, $\overset{+}{N}H_3$, and NHAc.

The theory of Pople and Bothner-By[1] predicts that withdrawal of electrons from orbitals symmetric between the hydrogen atoms of a methylene group should produce a positive shift in J_{gem}, whilst withdrawal of electrons from antisymmetric orbitals should give a negative shift. The corresponding but opposite predictions were made for electron donation. An electronegative β-

---

† *Present address*: Ministry of Agriculture, Fisheries and Food, Food Science Unit, Food Research Institute, Colney Lane, Norwich NR4 7UA.

[1] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

substituent X should withdraw electrons mainly from the antisymmetric pseudo-π orbitals of the methylene group which overlap X. The shift in J_{gem} is predicted to be sensitive to the stereochemistry. In general a negative shift should occur but when the β-carbon–X bond lies perpendicular to the internuclear axis of the hydrogen atoms of the methylene group, a small positive shift is predicted.

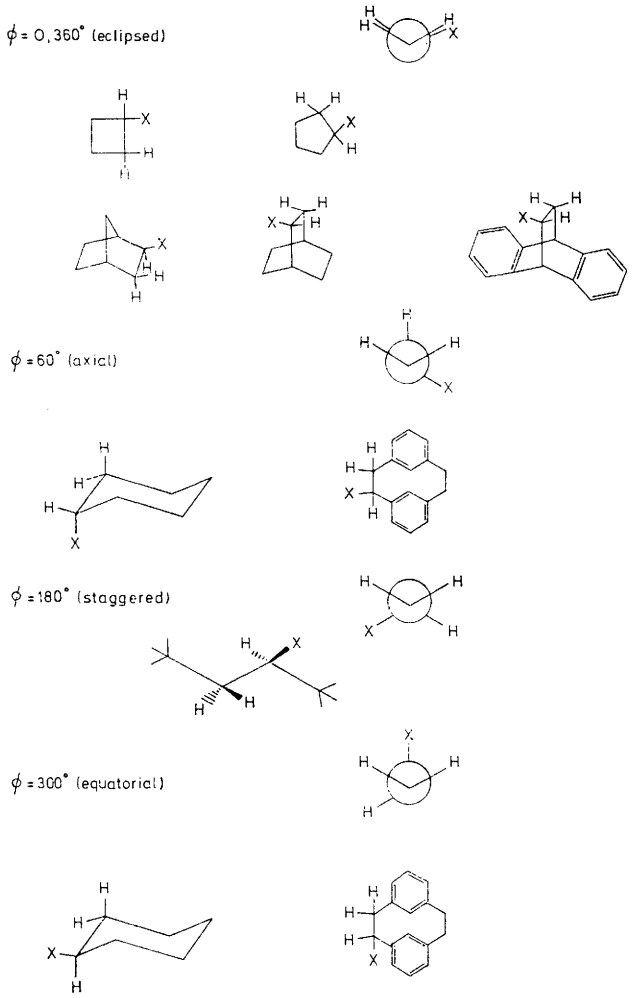


Figure 1 Common structures corresponding to the main dihedral angles

Our approach to this empirical study of the dependence of J_{gem} on the spatial orientation of an electronegative β-substituent is similar to that described for α-substituents in the preceding paper. We have defined a dihedral angle ϕ between a C–H bond of the methylene group and the β-carbon–X bond. For each substituent X we have plotted a graph relating ΔJ_{gem}, the shift in the magnitude of J_{gem} from a chosen reference value, to the dihedral angle ϕ.

The reasons for plotting ΔJ_{gem}, rather than the absolute magnitude of J_{gem}, were discussed in the previous paper. Much of our data has again been taken from the literature, and of necessity some of this relates to compounds in which the methylene group is strained. Such strain is known to affect the value of J_{gem}.[2] To eliminate these effects, we have chosen for each compound from which we have taken a value of J_{gem}, a suitable reference compound, in order to assess the shift in J_{gem} produced solely by the β-substituent. As before, each point on the graphs represents an average value of ΔJ_{gem}, taken from all the compounds corresponding to a particular conformation.

Model Compounds.—The types of compounds corresponding to the various dihedral angles ϕ are shown in Figure 1. The restrictions imposed in the preceding paper, regarding conformational homogeneity of our model compounds, again apply. In cases where we have taken data from four-membered ring compounds, we have again considered that the average of oscillations produced by flipping over a small angle gives the eclipsed conformation $\phi = 0°$.

The dihedral angles can be defined as: eclipsed, $\phi = 0, 360°$; axial, 60°; staggered, 180°; and equatorial, 300°. In a preliminary communication,[3] we considered the conformations corresponding to dihedral angles 60 and 180° to be equivalent. However, an examination of the Newman projections of these two conformations (Figure 2a), in which the second substituent, Y, on the β-carbon atom is also considered, shows that they are not equivalent. We therefore had to find new model compounds corresponding to the $\phi = 180°$ conformation.

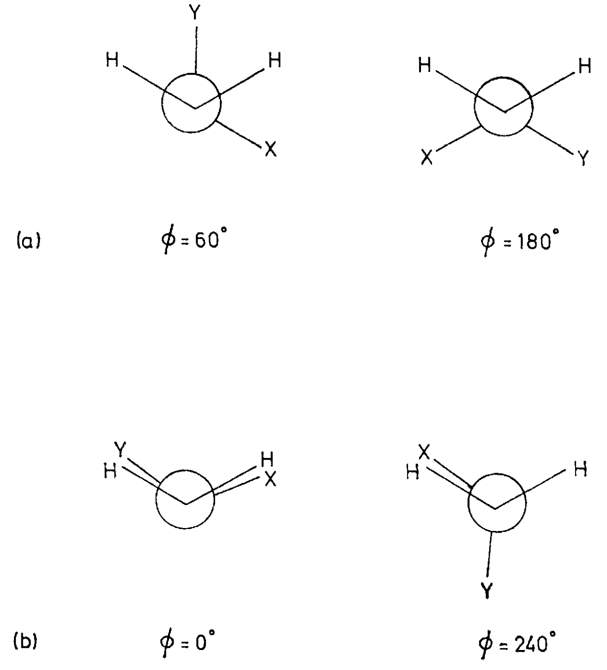


Figure 2 Newman projections of (a) conformations $\phi = 60$ and 180°, and (b) conformations $\phi = 0$ and 240°

By the same token, consideration of the second substituent, Y, on the β-carbon atom for the conformations $\phi = 0$ and 240° (Figure 2b) shows that these are also

---

[2] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, Supplement No. 7, 355.

[3] J. Hudec, *Chem. Comm.*, 1970, 242.

non-equivalent. However, we can find no suitable conformationally homogeneous model for the conformation of $\phi = 240°$, and have therefore considered it to be equivalent to the fully eclipsed $\phi = 0°$ (360°) conformation.

In most of our model compounds, the second substituent, Y, on the β-carbon atom is either a hydrogen atom or an alkyl group, and so presumably will have little effect on ΔJ_{gem}. In the cases where the second substituent, Y, is electronegative, Pople and Bothner-By[1] have predicted that its effect on the magnitude of J_{gem} will be additive to that of the group we are examining. In such cases, we have used our compilation of geminal coupling constants to obtain a correction factor for this substituent, Y, in its particular spatial orientation relative to the methylene group.

The $\phi = 0°$ Conformation.—In two cases, due to paucity of data, we have used geminal coupling constants taken from five-membered ring compounds which may differ slightly from the conformation $\phi = 0°$. One such compound is 3,3-dimethyl-1-hydroxyindane. Microwave data[4] have indicated that the cyclopentene ring is puckered with the C(4) atom bent out of plane, and a dihedral angle of 22°. In the above compound interaction between the hydroxy-group and the *syn*-methyl group will have the effect of flattening the ring, thus bringing the conformation closer to $\phi = 0°$. The other compound is 1-deuterio-3,3,4,4-tetramethylcyclopentanol. Here again interaction between the hydroxy-group and the two *syn*-methyl groups should partly flatten the puckered ring, bringing the conformation closer to $\phi = 0°$.

The $\phi = 180°$ Conformation.—The literature provided no data for the conformation $\phi = 180°$. Therefore we had to design a suitable conformationally homogeneous system which would yield the required data. This conformation is analogous to the $\phi = 180°$ conformation for the α-substituents, and so the model we have used is similar to the one used in that case. It is an acyclic structure, with a t-butyl group placed on each of two adjacent carbon atoms, to prevent rotation about the C–C bond. Thus the model is the 3-substituted 2,2,5,5-tetramethylhexane system. We still have no J_{gem} data corresponding to dihedral angles in the range $\phi = 60$—180°.

Syntheses.—The literature yielded a substantial amount of J_{gem} data for the substituents Cl, Br, OH, and OAc for all the main conformations except those corresponding to $\phi = 120$ and 180°. There was a limited amount of data concerning J_{gem} values for compounds containing a nitro-group β to the methylene group but virtually no data for the NH_2, $\overset{+}{N}H_3$, and NHAc classes of compound.

Our requirements for synthesis were therefore β-amines, β-amine hydrochlorides, β-acetamido-compounds, and β-nitro-compounds in all conformations, and all other classes of compounds in the conformation $\phi = 180°$.

(A) *Eclipsed conformations* ($\phi = 0$, 240°) *for* β-*amines*, β-*amine hydrochlorides*, and β-*acetamido-compounds*. Wawzonek and Hallum[5] have described the synthesis of 9,10-(11-aminoethano)-9,10-dihydroanthracene in four stages, starting from anthracene and methyl acrylate. This was repeated as described, with the exception of the last step; we found that hydrolysis of the intermediate 11-ethoxycarbonylaminoethanoanthracene was accomplished far more readily in dilute aqueous alkali than in glacial acetic acid. The amine was readily converted into the two desired derivatives.

(B) *Axial* ($\phi = 60°$) *and equatorial* ($\phi = 300°$) *conformations for* β-*amines*, β-*amine hydrochlorides*, β-*acetamido-compounds, and* β-*nitro-compounds*. The model 5-substituted 1,3-dioxan system was chosen because it offered ease of synthesis and clear n.m.r. spectra, with signals well separated. There is also sufficient thermodynamic data available for this system[6] to predict that conformational homogeneity can be assured by placing a phenyl or a t-butyl group at the 2-position.

Condensation of 2-methyl-2-nitropropane-1,3-diol with benzaldehyde, in benzene, gave 5-methyl-5-nitro-2-phenyl-1,3-dioxan in good yield. The product consisted of one isomer. The n.m.r. evidence (see later) indicates that the configuration of the molecule about C(5) is that with the nitro-group axial. In a series of 5-nitrotetrahydro-1,3-oxazines, n.m.r. and dipole moment data[7,8] indicate that the nitro-group always adopts the axial position. Eliel,[9,10] in a study of the configurational preferences of 5-heterosubstituents in 2-isopropyl-1,3-dioxans, concludes that the nitro-group favours the axial position to the equatorial by roughly 0.6 kcal mol^{-1}. A methyl group at C(5) favours the equatorial position by 0.8 kcal mol^{-1}.[6] Our assignment of configuration, based on the accumulated evidence, is therefore most likely correct.

Condensation of 2-nitro-2-phenylpropane-1,3-diol with pivalaldehyde, in benzene, gave 5-nitro-5-phenyl-7-t-butyl-1,3-dioxan. Again the product consisted of one isomer and, on the basis of its n.m.r. spectrum, to be discussed later, and the above evidence, it was assigned the axial nitro-configuration. In further support, Eliel[6] has found that in 2-isopropyl-5-phenyl-1,3-dioxan, the phenyl group prefers the equatorial position to the axial by 1.0 kcal mol^{-1}.

Reaction of 2-methyl-2-nitropropane-1,3-diol and pivalaldehyde, in benzene, gave 5-methyl-5-nitro-2-t-butyl-1,3-dioxan. The product consisted of two isomers in the ratio of *ca.* 4 : 1, and these were separated by fractional crystallisation from benzene. On the basis of the n.m.r. spectra, and the above thermodynamic evidence, the major product was assigned the axial nitro-configuration at C(5) and the minor product the equatorial nitro-configuration.

Condensation of 2-nitro-2-phenylpropane-1,3-diol with benzaldehyde in benzene gave 5-nitro-2,5-diphenyl-1,3-

---

[4] G. W. Rathjens, jun., *J. Chem. Phys.*, 1962, **36**, 2401.

[5] J. V. Hallum and S. Wawzonek, *J. Org. Chem.*, 1953, **18**, 288.

[6] E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, 1968, **90**, 3444; F. W. Nader and E. L. Eliel, *ibid.*, 1970, **92**, 3050.

[7] D. Gurne and T. Urbanski, *J. Chem. Soc.*, 1959, 1912.

[8] D. Gurne, L. Stefaniak, T. Urbanski, and M. Witanowski, *Tetrahedron*, 1964, Supplement No. 6, 211.

[9] E. L. Eliel and M. K. Kaloustian, *Chem. Comm.*, 1970, 290.

[10] R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, *J. Amer. Chem. Soc.*, 1972, **94**, 1913.

dioxan. This product consisted of two isomers in ratio 6 : 1 and again they were separated by fractional crystallisation from benzene. On the basis of n.m.r. and thermodynamic evidence, the major product was assigned the axial configuration of NO_2 at C(5).

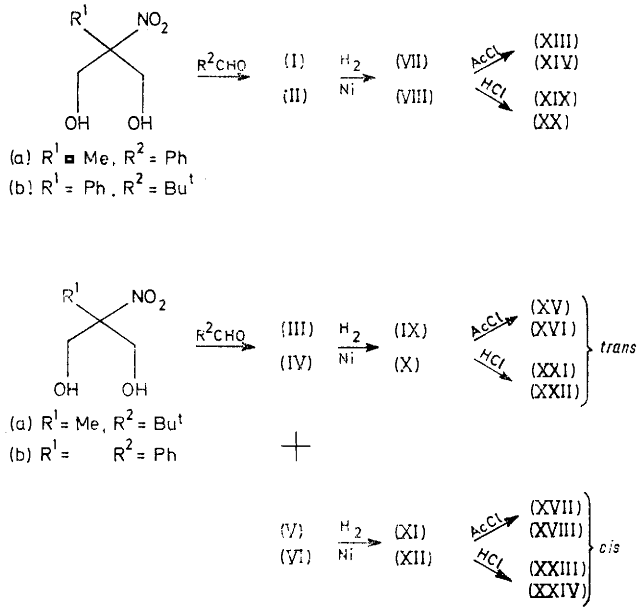


FIGURE 3 Syntheses of equatorial and axial β-nitro-compounds, β-amines, β-amine hydrochlorides, and β-acetamido-compounds; *cis* and *trans* refer to the orientations of the alkyl (and phenyl) groups in the 2- and 5-positions

Reduction of the 5-nitro-1,3-dioxans to the corresponding amines was accomplished without rearrangement or isomerisation by hydrogenation at room temperature and atmospheric pressure over an extremely active grade of Raney nickel catalyst.[11]

Conversion of the 5-amino-1,3-dioxans to the corresponding acetamido and amine hydrochloride derivatives was accomplished by avoiding excessive acid conditions, in order to prevent possible rearrangement or isomerisation.

These syntheses are summarised in Figure 3.

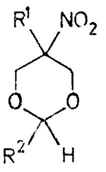
(C) *Syntheses of the* 3-*substituted*-2,2,5,5-*tetramethylhexanes: the* $\phi = 180°$ *conformation.* 2,2,5,5-Tetramethylhexan-3-ol was prepared by the method of Howard *et al.*,[12] by the Grignard reaction of methyl 3,3-dimethylbutyrate with two molar equivalents of t-butylmagnesium chloride. t-Butyl neopentyl ketone was also obtained in this reaction.

Acetylation of 2,2,5,5-tetramethylhexan-3-ol was achieved under vigorous conditions, to give 3-acetoxy-2,2,5,5-tetramethylhexane.

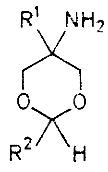
Our attempts to prepare the remaining compounds in this series were unsuccessful. The attempted preparation of 3-chloro-2,2,5,5-tetramethylhexane by reaction of the alcohol with carefully purified thionyl chloride gave a mixture of several products.

The synthesis of 3-amino-2,2,5,5-tetramethylhexane was attempted by two methods. The first was by hydrogenation of the oxime formed from neopentyl t-butyl ketone. The second attempt was by the *in situ* reduction with lithium aluminium hydride of the Grignard intermediate from neopentyl cyanide and t-butyl magnesium chloride. Neither reaction was successul.

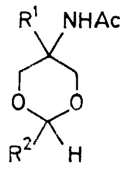
N.m.r. Spectra.—(A) 1,3-*Dioxans.* The chemical shift difference between an axial and an equatorial proton (Δae) attached to the 4- or the 6-carbon atom is a useful indication of the configuration about C(5) in a 1,3-dioxan. According to existing data on the effect of the diamagnetic anisotropy of single bonds in cyclohexane in the chair conformation,[13] an axial proton should absorb *ca.* 0.4 p.p.m. upfield relative to an equatorial proton. The diamagnetic anisotropy of the C–O bond should be smaller but of the same order of magnitude as that of the C–C bond.[8] An equatorial substituent should have no effect on the chemical shift difference (Δae) between an axial and an equatorial proton on an adjacent carbon atom, since it is symmetrically disposed to both protons. An axial substituent will affect the value of Δae, however. If it is an alkyl group, the expected effect is a substantial decrease in Δae.



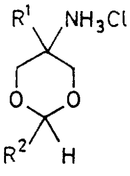
(I)-(VI)



(VII)-(XII)

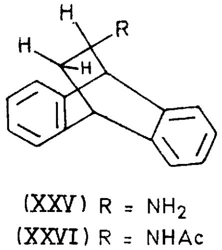


(XIII)-(XVIII)

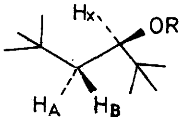


(XIX)-(XXIV)

	R^1	R^2
(I), (VII), (XIII), (XIX)	Me	Ph
(II), (VIII), (XIV), (XX)	Ph	Bu^t
(III), (IX), (XV), (XXI)	Me	Bu^t
(IV), (X), (XVI), (XXII)	Ph	Ph
(V), (XI), (XVII), (XXIII)	Me	Bu^t
(VI), (XII), (XVIII), (XXIV)	Ph	Ph



(XXV) R = NH_2
(XXVI) R = NHAc
(XXVII) R = NH_3Cl



(XXVIII) R = H
(XXIX) R = Ac

Details of the n.m.r. spectra of the 5-nitro-1,3-dioxans are given in Table 1.

The Δ4a4e values for the two mono-isomeric compounds

---

[11] R. Davies and J. Hudec, to be published.

[12] F. L. Howard, T. W. Mears, A. Fookson, and P. Pomerantz, *J. Amer. Chem. Soc.*, 1946, **68**, 2121.

[13] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon, London, 1969.

(I) and (II), and for one isomer, (III) and (IV), from each of the pairs of isomers, are fairly constant at 1.08 ± 0.08 p.p.m. Urbanski,[8] in a series of 5-nitrotetrahydro-1,3-oxazines, observed Δ6a6e values of 0.84 ± 0.04 p.p.m. between the protons of the 6-methylene group, and on this basis assigned the axial nitro-configuration in each case.

The two remaining isomers, (V) and (VI), from the pairs of isomers have Δ4a4e values of 0.20 and 0.33 p.p.m. This significant reduction is characteristic of an axial alkyl group. The four compounds with Δ4a4e values of *ca.* 1.08 p.p.m. have therefore been assigned the axial nitro-configuration, and the two with reduced Δ4a4e values the equatorial nitro-configuration.

Table 1

N.m.r. details of (I)—(VI) (solvent $CDCl_3$)

No.	R¹	R²	Chemical shifts (τ) 2-H	R¹	R²	4-H$_{ax}$	4-H$_{eq}$	Δae (p.p.m.)	J_{gem} (Hz)
(I)	Me	Ph	4.54	8.65	2.65	6.14	5.08	1.06	−12.75[a]
(II)	Ph	Bu^t	5.79	2.69	9.10	5.94	4.78	1.16	−12.00
(III)	Me	Bu^t	5.88	8.68	9.16	6.33	5.23	1.00	−12.70
(IV)	Ph	Ph	4.44	2.65	2.65	5.74	4.62	1.12	−12.35
(V)	Me	Bu^t	5.97	8.20	9.07	6.03	5.83	0.20	−10.75
(VI)	Ph	Ph	4.38	2.50	2.50	5.49	5.16	0.33	−11.75

[a] Signs assumed.

Table 2

N.m.r. details of (VII)—(XII) (solvent $CDCl_3$)

No.	R¹	R²	Chemical shifts (τ) 2-H	R¹	R²	NH_2	4-H$_{ax}$	4-H$_{eq}$	Δae (p.p.m.)	J_{gem} (Hz)
(VII)	Me	Ph	4.62	9.08	2.58	8.16	5.25	5.25	0	
(VIII)	Ph	Bu^t	5.83	2.62	9.01	8.03	6.20	6.04	0.16	−10.9[a]
(IX)	Me	Bu^t	6.00	9.12	9.08	8.09	6.45	6.45	0	[b]
(X)	Ph	Ph	4.53	2.66	2.66	7.99	6.13	5.87	0.26	−10.9
(XI)	Me	Bu^t	6.04	8.72	9.08	8.83	6.73	6.35	0.40	−10.7
(XII)	Ph	Ph	4.48	2.52	2.52	8.70	6.27	5.65	0.62	−11.3

[a] Signs assumed. [b] In pyridine solution a value of −10.4 Hz was obtained.

Table 3

N.m.r. details of (XIII)—(XVIII) (solvent $CDCl_3$)

No.	R¹	R²	Chemical shifts (τ) 2-H	R¹	R²	N*H*	COC*H*$_3$	4-H$_{ax}$	4-H$_{eq}$	Δae (p.p.m.)	J_{gem} (Hz)
(XIII)	Me	Ph	4.59	8.72	2.61	3.94	8.06	6.42	5.70	0.72	−11.5[a]
(XIV)	Ph	Bu^t	5.75	2.74	9.03	3.82	8.01	6.16	5.66	0.50	−11.2
(XV)	Me	Bu^t	5.98	8.77	9.07	4.20	8.05	6.67	5.91	0.76	−11.6
(XVI)	Ph	Ph	4.46	2.60	2.60	3.56	8.02	5.94	5.48	0.46	−11.3
(XVII)	Me	Bu^t	5.90	8.46	9.09	3.70	7.95	6.23	6.01	0.22	−10.6
(XVIII)	Ph	Ph	4.28	2.56	2.56	4.12	8.05	5.51	5.51	0	

[a] Signs assumed.

Confirmation of these assignments is provided by the positions of the methyl absorption signal in each of the three 5-methyl-1,3-dioxans. It is generally found with six-membered rings in the chair form that an axial methyl absorbs at lower field than an equatorial methyl. Here the two methyl groups to which we have assigned an equatorial configuration, (I) and (III), absorb at τ 8.65 and 8.68, whilst the methyl assigned an axial configuration, (V), absorbs at τ 8.20.

Details of the n.m.r. spectra of the 5-amino-1,3-dioxans are given in Table 2. For two compounds in this series, (VII) and (IX), the absorptions for the axial and equatorial 4-methylene protons are co-incidental in $CDCl_3$. Complete resolution of the two signals in compound (IX) was achieved in [$^2H_5$]pyridine. Complete resolution of the two signals in compound (VII) was not achieved in any of the other solvents we tried (carbon tetrachloride, [$^2H_5$]pyridine, and [$^2H_6$]dimethyl sulphoxide). However, a definite broadening of the resonance signal was observed.

The Δ4a4e values for the other two axial-amino compounds, (VIII) and (X), are 0.16 and 0.26 p.p.m. The two equatorial amino-compounds, (XI) and (XII), have Δ4a4e values of 0.40 and 0.62 p.p.m. It thus appears that the effect of the amino-group in the 5-position on the value of Δ4a4e is dominant over that of a methyl or phenyl group in the 5-position.

The position of the signal due to the protons on nitrogen is of interest. This should not be over-emphasised, since the position of this absorption signal is slightly concentration dependent, but all samples were run in the same solvent, and solutions were of similar concentration. The protons of the axial amino groups absorb in the range τ 7.99—8.16, and those of the equatorial amino groups at τ 8.70 and 8.83. This upfield shift, in the region of 0.7 p.p.m., is too large to be entirely due to concentration effects, and is therefore probably due to the changes in environment of this group.

As with the 5-methyl-5-nitro-1,3-dioxans, the 5-amino-5-methyl-1,3-dioxans show deshielding of an axial methyl group by *ca.* 0.4 p.p.m. over an equatorial methyl.

The details of the n.m.r. spectra of the 5-acetamido-1,3-dioxans are given in Table 3. The Δ4a4e values show no overall consistency. However, the two equatorial 5-methyl compounds, (XIII) and (XV), have similar values, and so do the two equatorial 5-phenyl compounds, (XIV) and (XVI), suggesting that the difference in the two sets of values could be due to a change in the preferred orientation of the acetamido-group.

TABLE 4

N.m.r. details of (XIX)—(XXIV) (solvent $[^2H_6]Me_2SO$)

			Chemical shifts (τ)						Δae	
No.	R^1	R^2	2-H	R^1	R^2	NH_3	4-H_{ax}	4-H_{eq}	(p.p.m.)	J_{gem} (Hz)
(XIX)	Me	Ph	4.42	8.75	2.54	1.60	6.07	5.85	0.32	−11.9 [a]
(XX)	Ph	Bu^t	5.60	2.53	9.04	1.20	5.88	5.74	0.14	−11.8
(XXI)	Me	Bu^t	5.84	8.84	9.09	1.44	6.31	5.97	0.34	−12.0
(XXII)	Ph	Ph	4.22	2.53	2.53	1.20	5.84	5.63	0.21	−11.25
(XXIII)	Me	Bu^t	6.00	8.71	9.13	1.20	6.45	6.27	0.18	−10.4
(XXIV)	Ph	Ph	4.31	2.40	2.40	0.83	5.58	5.42	0.16	−11.15

[a] Signs assumed.

TABLE 5

N.m.r. details of (XXV)—(XXVII)

R	(XXV) NH_2 (solvent $CDCl_3$)	(XXVI) $NHCOCH_3$ (solvent $CDCl_3$)	(XXVII) NH_3Cl (solvent $[^2H_6]Me_2SO$)
1-H	6.05 [a] (2) [b]	5.72br	5.37 (2)
4-H	5.92 (3)	5.84 (3)	5.68br
7-H	6.85 (3.3)	4.94 (3,3)	6.38
8-H	7.86 (2,3,2)	7.73 (2,3,2)	7.91 (2,3,2)
8-H′	9.00 (-,4)	8.85 (3,3)	8.61 (4,4)
Other	8.90 (NH_2)	8.20, 8.02 (CH_3CO) 1.16 (NH)	1.92 (NH_3)
$J_{1.7}$	2.8 [c]	2.6	2.5
$J_{4.8}$	2.9	3.2	2.7
$J_{7.8}$	9.2	9.9	9.6
$J_{7.8'}$	3.7	3.0	5.0
$J_{8.8'}$	−12.3 [d]	−12.3	−12.7

[a] Chemical shifts in τ values. [b] Integral numbers in parentheses indicate the multiplicity of the splitting pattern, *e.g.* (2) indicates a doublet, (3,3) two triplets. [c] Coupling constants in Hz. [d] Signs assumed.

TABLE 6

N.m.r. details of (XXVIII) and (XXIX)

		Chemical shifts (τ)					Coupling constants (Hz)		
No.	R	Bu^t	H_A	H_B	H_X	Other	J_{AX}	J_{BX}	J_{AB}
(XXVIII)	H	9.05 9.13	8.49	8.84	6.66	8.75 (OH)	1.0	8.8	−14.75 [a]
(XXIX)	Ac	9.11 9.14	8.56 [b] 8.60		5.16	8.02 (CH_3CO)	1.9	8.2	−15.0

[a] Signs assumed. [b] Approximate value from calculated spectrum.

The axial and equatorial 4- and 6-H in the equatorial acetamido compound (XVIII) are equivalent in $CDCl_3$. Line broadening was observed in a number of different solvents, but complete resolution of the signals was not achieved.

The 5-methyl group is deshielded by *ca.* 0.3 p.p.m. in going from equatorial to axial.

The n.m.r. data for the 5-amine hydrochloride substituted 1,3-dioxans are given in Table 4. They show few features of note.

(B) *Dibenzobicyclo*[2.2.2]*octadienes*. The n.m.r. data for these three compounds are given in Table 5.

The protons at positions 7 and 8 were analysed as an AMX splitting pattern. The splitting is complicated by further coupling of 7- with 1-H, and of 8- with 4-H.

Cristol[14] had assigned the high-field absorption in compound (XXV) to the proton at position 8 *cis* to the electronegative substituent. A comparison of the values of *trans*-$J_{7.8}$ and *cis*-$J_{7,8}$ in each of the three compounds appears to confirm this.

The signal due to the acetamido methyl group in compound (XXVI) appears as two singlets of equal intensity. This presumably is due to hindered rotation about the C–N bond, because of its partial double-bond character.

(C) 3-*Substituted* 2,2,5,5-*tetramethylhexanes*. The details of the n.m.r. spectra of these two compounds are given in Table 6. The protons at positions 3 and 4 in both (XXVIII) and (XXIX) were analysed as an ABX splitting pattern.[15] The spectrum of the alcohol (XXVIII) was straightforward. From a consideration of the vicinal coupling constants, J_{AX} and J_{BX}, in relation to the Karplus equation,[16] we conclude that H_B, which absorbs at higher field than H_A, lies *cis* to the hydroxy-group.

The spectrum of the 3-acetoxy-compound (XXIX) was complicated by the superimposition of signals in the AB part of the spectrum, which hindered calculation of the coupling constants. Resolution of the AB signals was

---

[14] S. J. Cristol, T. W. Russell, J. H. Mohrig, and D. E. Plorde *J. Org. Chem.*, 1966, **31**, 581.

[15] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Canad. J. Chem.*, 1957, **35**, 65.

[16] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

achieved by addition of the shift reagent $Eu(dpm)_3$ (*ca.* 0.2 mol) which shifted the spectrum to such an extent that the coupling constants could be measured directly from the spectrum.[15]

As a check on the values obtained, they were used to make an approximate calculation of the X part of the spectrum. This was carried out using an iterative procedure, starting with a value of $\delta = 1$ Hz, for the chemical shift difference between H_A and H_B, and successively adding increments of 1 Hz, until the X part of the observed spectrum was satisfactorily reproduced. This was accomplished when $\delta = 5$ Hz.

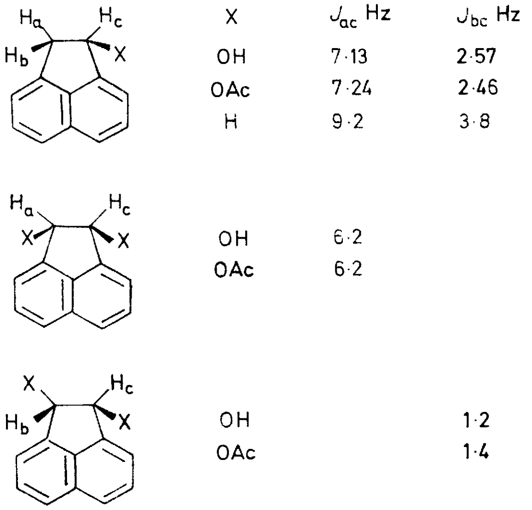
This value was then used, together with the coupling constants measured from the spectrum, to calculate the intensities of the signals in the AB region. Expressions for the intensities of the signals are given by Bernstein *et al.*[15] The intensities so calculated satisfactorily reproduced the observed intensities.

A comparison of J_{AX} and J_{BX} leads to the conclusion that H_B lies *cis* to the acetoxy-group.[16] However, it is not possible to decide whether or not H_B absorbs at higher field than H_A, since the possibility exists that in the shifted spectrum, the absorption positions of the two protons are inverted, relative to their positions in the unshifted spectrum.

Conformational studies in the 2,2,5,5-*tetramethylhexane system.* The magnitude of J_{gem} in the two compounds (XXVIII) and (XXIX) was a little surprising, and the possibility had to be considered of these two compounds existing in a conformation other than that corresponding to the assumed $\phi = 180°$, and of there being an enlargement of the $\widehat{\mathrm{Bu^tCH_2C}}$ angle in the two compounds. The C(3)–C(4) vicinal coupling constants, J_{trans} 8—9 and J_{cis} 1—2 Hz, may appear to be at variance with the conformation $\phi = 180°$ but we do not think that this is necessarily the case. Kingsbury *et al.*[17] have stated that for such a conformation J_{trans} should be 10 Hz or greater. However the introduction of an electronegative substituent into an ethano-fragment can produce significant changes in the values of the vicinal coupling constants. One notes in particular the coupling constants [18a,b] of the compounds illustrated in Figure 4. The introduction of one electronegative substituent makes $J_{eclipsed}$ more negative by *ca* 2 Hz, and a second such substituent decreases J by a further *ca.* 1 Hz. It should therefore not be surprising for an electronegative substituent to exert a comparable effect on the magnitude of J_{trans} for the $\phi = 180°$ conformation, so that a value of 8—9 Hz need not indicate a significant deviation from this conformation.

Comparisons of the C(3)–C(4) vicinal coupling constants for the $\phi = 180°$ conformation in compound (XXVIII) with the C(1)–C(2) vicinal couplings in cyclohexanol are not valid. This is demonstrated by an examination of the Newman projections of the relevant conformations (Figure 5). Although $H_{e'}$ and H_a in conformation A are in the same orientations relative to OH as are H_x and H_a in conformation C, $J_{ae'}$ in A cannot be considered equivalent to J_{ax} in C because of the differing arrangements of the remaining atoms in the two fragments. For similar reasons $J_{aa'}$ in conformation B cannot be considered equivalent to J_{bx} in conformation C. The justification of such reasoning is demonstrated by the difference in magnitude between $J_{ee'}$ in conformation A and $J_{ea'}$ in conformation B, despite the fact that in both conformations the two protons have the same orientations relative to OH.[18c]

On the basis of this accumulated evidence, we believe that the vicinal coupling constants for compounds (XXVIII) and (XXIX) do not necessarily indicate any significant deviation from the assumed conformation $\phi = 180°$. It is perhaps more likely that an enlargement of the $\widehat{\mathrm{Bu^tCH_2C}}$ angle in both compounds might account for part of the negative shift in the geminal coupling constants. With these molecules in the $\phi = 180°$ conformation there are three methyl–hydrogen and one methyl–OR 1,3-interactions. The latter interaction is probably the strongest and could produce enlargement of the $\widehat{\mathrm{Bu^tCH_2C}}$ angle. Partial relief might be obtained by rotation about the C(3)–C(4) bond so as to increase ϕ. Such rotation would probably be small however since relief from the methyl–OR 1,3-interaction will be offset by an increase in the interaction between the two t-butyl groups.



X	J_{ac} Hz	J_{bc} Hz
OH	7·13	2·57
OAc	7·24	2·46
H	9·2	3·8
OH	6·2	
OAc	6·2	
OH		1·2
OAc		1·4

FIGURE 4 Effect of electronegative substituents on the vicinal coupling constants in acenaphthene derivatives

We therefore believe that these two molecules do exist in the $\phi = 180°$ conformation or very close to it. It is quite possible however that the interactions discussed above could produce an enlargement of the $\widehat{\mathrm{Bu^tCH_2C}}$ angle, which would account for part of the observed negative shift in J_{gem}. Such interactions could be partly relieved, with correspondingly less enlargement of the $\widehat{\mathrm{Bu^tCH_2C}}$ angle, by a small rotation about the C(3)–

---

[17] D. C. Best, G. Underwood, and C. A. Kingsbury, *Chem. Comm.*, 1969, 627.

[18] (*a*) C. K. Fay, J. B. Grutzner, L. F. Johnson, S. Sternhell, and P. W. Westerman, *J. Org. Chem.*, 1973, **38**, 3122; (*b*) S. Sternhell and P. W. Westerman, *ibid.*, 1974, **39**, 3794; (*c*) F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.

C(4) bond so as to increase ϕ. This change in the dihedral angle ϕ would produce only a minimal change in the shapes of curves A and B of Figure 9.

Empirical Curves for the β-Substituents.—The empirical curves A—I describing the effects of the spatial orientation of the electronegative substituents OH, OAc, Ph, NO_2, Cl, Br, NH_2, NH_3Cl, and NHAc on the magnitude of J_{gem} are shown in Figures 9—12.*

General Features.—The only two curves for which we have a point at $\phi = 180°$ are A and B (Figure 9) for the groups OH and OAc respectively. These are therefore the only curves which have been described through the whole range of ϕ from 0 to 360°.

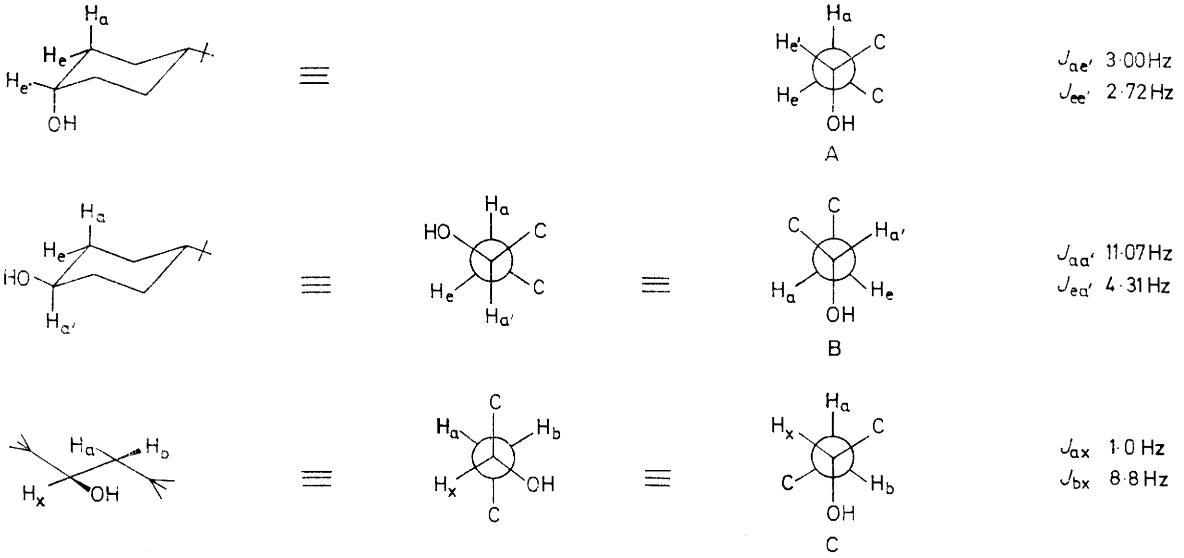


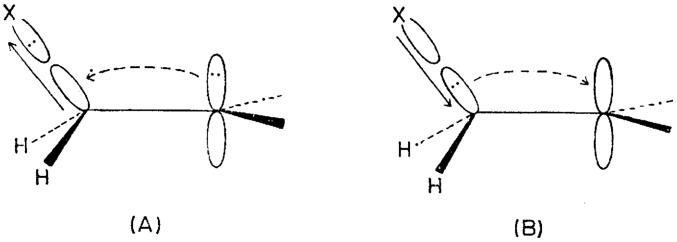
FIGURE 5 Newman projections of the C(1)–C(2) bond in axial and equatorial cyclohexanol and of the C(3)–C(4) bond in compound (XXVIII)

By analogy with curves A and B, C—I are expected to have a minimum value of ΔJ_{gem} in the region of ϕ between 120 and 180°. All curves have a maximum at $\phi = 300°$.

The theory of Pople and Bothner-By[1] predicts that, in general, a β-electronegative substituent will produce a negative shift in J_{gem}, except when the β-carbon-substituent bond lies perpendicular to the internuclear axis of the methylene group hydrogens, in which case a small positive shift will be produced. The shape of the curves thus bears out the theoretical predictions. Although curves E and F do not show a positive value of ΔJ_{gem} at $\phi = 300°$, this point does correspond to the maximum value of J_{gem} on each curve.

Curves A and B (Figure 9) have no symmetry for ϕ 0—360°. The Newman projections of the various conformations in this range (*e.g.* see Figure 2a and b) indicate their non-equivalence. Thus curves C—I are also expected to have a periodicity of 360°.

Factors influencing the Magnitude of J_{gem}.—The negative ΔJ_{gem} produced by an electronegative β-substituent, as shown in curves A—I, suggests that electrons are being withdrawn from the anti-symmetric molecular orbital of the methylene group. Hoffman *et al.*[19] have carried out MO calculations on a model of a methyl group interacting with a neighbouring p-orbital, and have examined the changes produced by substituting a methyl hydrogen by a group X, depending on whether X is more or less electronegative than H. One of their conclusions is that a polar C–X bond is at its carbon end a better π-acceptor than C–H [see Figure 6 (A)], provided X is more electronegative than H, whereas if X is less electronegative than H, the C–X bond will be a better π-donor [Figure 6 (B)]. Both cases lead to increased π-bonding opportunities.



(A) (B)

FIGURE 6 Hyperconjugative interactions between the C–X bond and a neighbouring p-orbital

The case which applies to our study is that represented by (A) in Figure 6. In our situation, the p-orbital is replaced by the filled ψ_2 orbital of the methylene group. The hyperconjugative interaction predicted by Hoffman[19] will lead to removal of electrons from ψ_2, and this, according to the rules of Pople and Bothner-By,[1] should produce a negative ΔJ_{gem}. The extent of the hyperconjugation will vary with rotation about the C–C bond,

---

* Footnotes to Figure 9—12 giving details of the compounds studied and the corresponding reference compounds from which ΔJ_{gem} values have been calculated are given in Supplementary Publication No. SUP 21422 (7 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

[19] R. Hoffmann, L. Radom, J. A. Pople, P. von R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 6221.

and this accounts, at least in part, for the dependence of the magnitude of ΔJ_{gem} on the spatial orientation of the β-substituent in relation to the methylene group.

In the two curves A and B, the value of ΔJ_{gem} corresponding to $\phi = 180°$ is more negative than that corresponding to $\phi = 60°$. Figure 7 shows that in both these conformations the C–X bond is *trans*-coplanar with a C–H bond of the methylene group. The influence of the C–X bond on the magnitude of ΔJ_{gem} should therefore be equal for the two conformations.

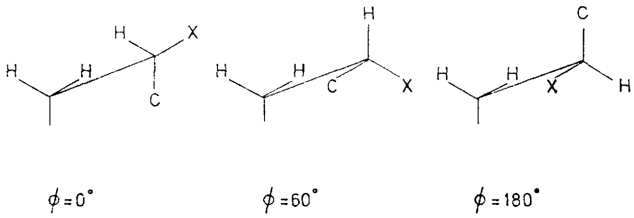


FIGURE 7 Conformations showing the stereochemical relationship between a β-C–C bond and a methylene group

This suggests that another factor is also influencing the magnitude of ΔJ_{gem}. It is possible that in certain orientations, the β-C–C σ-bond can back-donate electrons into the anti-symmetric orbital of the methylene group, thus giving a positive contribution to J_{gem}. Such back-donation is analogous to that of one lone-pair, the conformational dependence of which has been described by Crabb,[20] for a nitrogen atom. Hence the positive shift in J_{gem}, in opposition to the negative shift caused by the C–X bond, should have a minimum value when the β-C–C bond bisects the methylene H–H internuclear axis, *i.e.* when $\phi = 180°$ (Figure 7). The maximum negative shift in curves A and B corresponds to this conformation. However, there should be a significant positive shift when the β-C–C bond is *trans*-coplanar with a C–H bond of the methylene group, at $\phi = 60°$. This agrees with the value of ΔJ_{gem} corresponding to $\phi = 60°$ being more positive than that corresponding to $\phi = 180°$.

In all curves, the shift, ΔJ_{gem}, corresponding to $\phi = 0°$ is more positive than that corresponding to $\phi = 60°$ (Figure 7). If our suggestion that the β-C–C bond can act as an electron donor is correct, it should have little effect on ΔJ_{gem} in the conformation $\phi = 0°$, by analogy with the nitrogen lone pair. The change in ΔJ_{gem} may therefore be due to the change in orientation of the C–X bond in relation to the methylene group. Possibly, the hyperconjugative interaction between the C–X bond and the ψ_2 MO of the methylene group is greater in the conformation $\phi = 60°$ than it is in the conformation $\phi = 0°$.

Additional Influences on the Magnitude of J_{gem}.—It is possible that effects other than those due to the C–X and C–C bonds may affect the magnitude of J_{gem}. Hoffmann[21] has made a theoretical study of orbital interactions through a number of intervening σ-bonds. Thus it is possible that an orbital belonging to the substituent group could interact with the σ-orbital of the CH_2–C bond, provided that the mutual orientation of the two orbitals is favourable, and that the orbitals are sufficiently close to one another energetically. For maximum interaction, the most favourable orientation of the orbitals would presumably be *trans*-coplanar with one another (Figure 8).

Such an interaction could affect the electron density of the symmetric (ψ_1) molecular orbital of the methylene group, and thus influence the magnitude of J_{gem}.

If the interacting substituent orbital is filled, as with the lone pair(s) on substituents NH_2, NHAc, OH, OAc, Cl, and Br, then, given a favourable orientation, back donation into the symmetric methylene group MOs might be expected, giving a negative ΔJ_{gem}. If this orbital is vacant, as with the π* orbitals on substituents NO_2 and Ph, then electron withdrawal from ψ_1 giving a positive ΔJ_{gem} might be expected. Such effects, if operative, should be independent of the conformational angle, ϕ, of the molecule.

Of the lone pair substituents, curves G and I in Figure 12 for NH_2 and NHAc are of small amplitude, showing only a small negative shift in J_{gem}. Curves A and B in Figure 9 for OH and OAc do show a significant negative shift in J_{gem}, but are no larger in amplitude than curves C and D in Figure 10 for Ph and NO_2. Thus with these four substituents, this additional influence on the magnitude of J_{gem} is negligible, but this may be due to the failure of the orbitals to adopt a favourable orientation for interaction to take place.

Curves E and F (Figure 11) for Cl and Br, show the greatest amplitude of all, and do not produce the predicted positive shift in J_{gem} at $\phi = 300°$. It is therefore possible that such an effect as described above, involving the substituent lone pairs, does operate, giving an additional negative shift to J_{gem}.

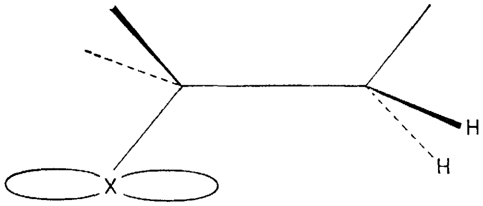


FIGURE 8 *trans*-Coplanar relationship between an orbital on the substituent X and the CH_2–C σ-bond

Curves C and D, due to Ph and NO_2, would be expected to be of small amplitude if the above effect involving the substituent π* orbital is operative. However, both curves show a significant negative shift in J_{gem} implying that the effect is not in operation. Again, this could be due to a non-favourable orientation of the two orbitals, or to too great a difference in energy for interaction to occur.

The Amplitudes of the Curves.—The amplitudes of curves E and F, due to Cl and Br respectively, have been discussed above in terms of a possible effect regarding the filled non-bonding orbital on the substituent. There is, however, a significant difference in the amplitudes of the two curves and this may reflect a difference in the degree of hyperconjugative interaction between the ψ_2

---

[20] P. J. Chivers and T. A. Crabb, *Tetrahedron*, 1970, **26**, 3389.

[21] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

orbital of the methylene group and the C–Br bond, as compared with the C–Cl bond.

In general, the amplitude of each curve is probably determined by the balance of electron-withdrawing and -donating orbital interactions, such as have been discussed above. It is not possible to state precisely to what extent such interactions are in operation for a particular substituent. This is an area where more theoretical studies need to be carried out, to determine the exact nature of these interactions, and their stereochemical dependence.

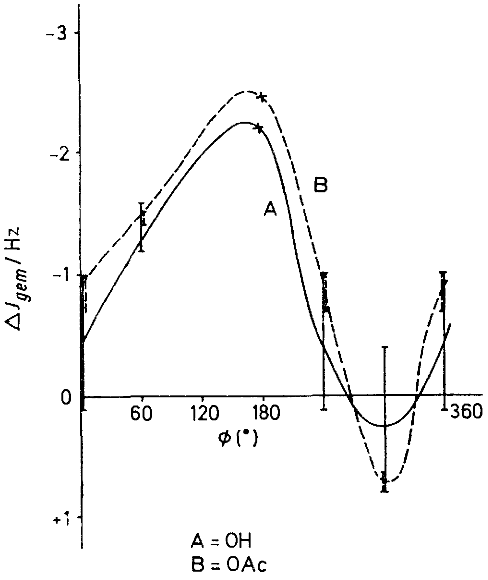


FIGURE 9 Empirical relationship between ΔJ_{gem} and dihedral angle, ϕ, for OH (A) and OAc (B) β to a methylene group

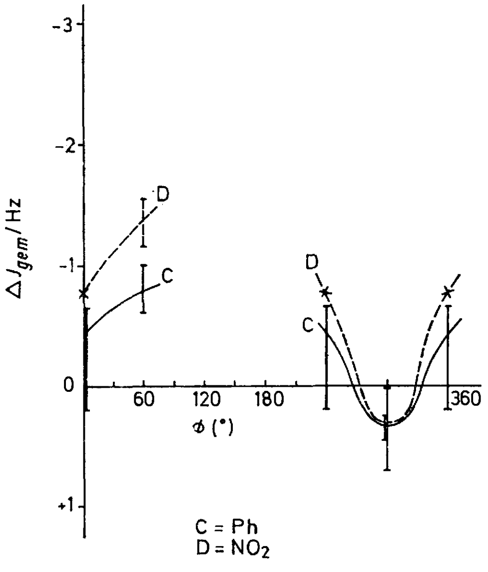


FIGURE 10 Empirical relationship between ΔJ_{gem} and dihedral angle, ϕ, for Ph (C) and NO_2 (D) β to a methylene group

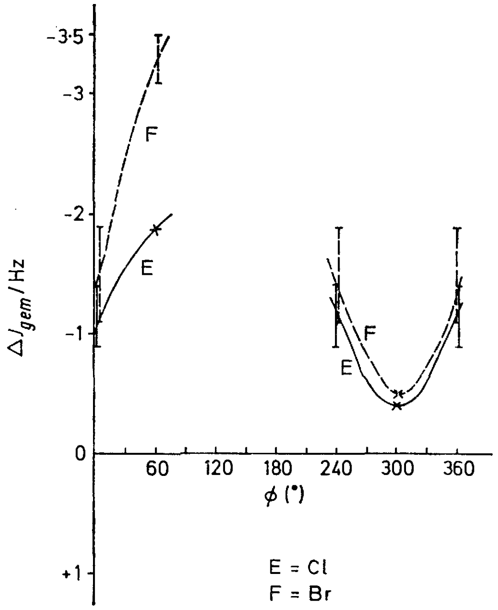


FIGURE 11 Empirical relationship between ΔJ_{gem} and dihedral angle, ϕ, for Cl (E) and Br (F) β to a methylene group

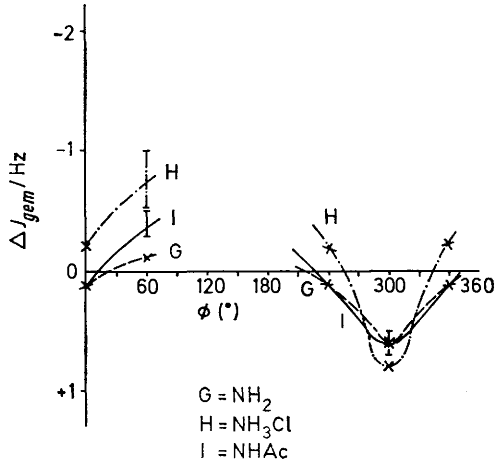


FIGURE 12 Empirical relationship between ΔJ_{gem} and dihedral angle, ϕ, for NH_2 (G), NH_3Cl (H), and NHAc (I) β to a methylene group

EXPERIMENTAL

General conditions are given in the preceding paper. Full n.m.r. details are given in Tables 1 to 6.

2-*Nitro*-2-*phenylpropane*-1,3-*diol*.—This was prepared by the method of Fieser and Gates,[22] from phenylnitromethane (36 g) and 37% formalin solution (45 g) (yield 22 g, 43%), m.p. 97—98.5° (lit.,[22] 97.5—98.5°).

2-*Methyl*-2-*nitropropane*-1,3-*diol*.—Prepared by the method of Vanderbilt and Hass,[23] from nitroethane (30 g) and 37.5% formalin solution (64 g) (yield 16 g, 30%), m.p. 152—153° (lit.,[23] 149—150°).

General Procedure for the Preparation of 5-*Nitro*-1,3-*dioxans*.—The 2-nitropropane-1,3-diol and the aldehyde (1.1 mol. equiv.) were dissolved in benzene containing a catalytic amount of toluene-*p*-sulphonic acid. The mixture

---

[22] L. F. Fieser and M. Gates, *J. Amer. Chem. Soc.*, 1946, **68**, 2249.

[23] B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, 1940, **32**, 34.

was refluxed for 14 h under a Dean and Stark water separator, until no more water separated. On cooling benzene was evaporated, and the residue taken up in ether. The ethereal solution was washed twice with dilute NaOH solution and then with water until neutral, and finally dried (Na_2SO_4). Ether was evaporated and the residue recrystallised. *N.B.* The terms *cis* and *trans* refer to the orientations of the alkyl and phenyl groups in the 2- and 5-positions.

trans-5-*Methyl*-5-*nitro*-2-*phenyl*-1,3-*dioxan* (I).—This was prepared from 2-methyl-2-nitropropane-1,3-diol (9 g) and benzaldehyde (7.8 g) and recrystallised from light petroleum (b.p. 60—80°)–benzene (yield 12.1 g, 81.5%), m.p. 116.5—118°, M^+ 223, $\nu_{max.}$ (Nujol) 699s, 750s, 870m, 980s, 1 010s, 1 098s, 1 293s, 1 358s, 1 400s, 1 555s, and 2 900s cm^{-1}.

trans-5-*Nitro*-5-*phenyl*-2-*t*-*butyl*-1,3-*dioxan* (II).—This was prepared from 2-nitro-2-phenylpropane-1,3-diol (7.05 g) and pivalaldehyde (3.4 g) and recrystallised from light petroleum (b.p. 60—80°) (yield 4.08 g, 43%), m.p. 118—119°, M^+ 265, $\nu_{max.}$ (Nujol) 698s, 710s, 761m, 850m, 980s, 1 045s, 1 110s, 1 150s, 1 350s, 1 550s, and 2 900s cm^{-1}.

cis- *and* trans-5-*Nitro*-2,5-*diphenyl*-1,3-*dioxan* (IV) *and* (VI).—These were prepared from 2-nitro-2-phenylpropane-1,3-diol (6.6 g) and benzaldehyde (3.9 g) and recrystallised from light petroleum (b.p. 60—80°)–benzene. The first and second crops of crystals were *trans*-5-nitro-2,5-diphenyl-1,3-dioxan (IV), needles (5.9 g, 61.5%), m.p. 132—133°, M^+ 285, $\nu_{max.}$ (Nujol) 701s, 719m, 760s, 922s, 985s, 1 098s, 1 145s, 1 380s, 1 542s, and 2 880s cm^{-1}. The third crop was *cis*-5-nitro-2,5-diphenyl-1,3-dioxan (VI), prisms (1.0 g, 10.5%), m.p. 117.5—118.5°, M^+ 285, $\nu_{max.}$ (Nujol) 693m, 709m, 735m, 753s, 1 103s, 1 118s, 1 378s, 1 545s, and 2 850s cm^{-1}.

cis- *and* trans-5-*Methyl*-5-*nitro*-2-*t*-*butyl*-1,3-*dioxan* (III) *and* (V).—These were prepared from 2-methyl-2-nitropropane-1,3-diol (4.9 g) and pivalaldehyde (3.5 g) and recrystallised from light petroleum (b.p. 60—80°)–benzene. The first and second crops of crystals were *trans*-5-methyl-5-nitro-2-t-butyl-1,3-dioxan (III) needles (4.8 g, 65%), m.p. 145.5—147°, M^+ 203, $\nu_{max.}$ (Nujol) 853m, 885m, 955s, 1 005s, 1 045s, 1 115s, 1 185s, 1 295s, 1 350s, 1 545s, and 2 850s cm^{-1}. The third crop was *cis*-5-methyl-5-nitro-2-t-butyl-1,3-dioxan (V), prisms (1.15 g, 15.5%), m.p. 90—92°, M^+ 203, $\nu_{max.}$ (Nujol) 760s, 953s, 991s, 1 045s, 1 110s, 1 195m, 1 358s, 1 405m, 1 550s, and 2 900 cm^{-1}.

General Procedure for the Preparations of 5-*Amino*-1,3-*dioxans*.—The 5-nitro-1,3-dioxan was dissolved in ethanol, and freshly prepared, highly active Raney nickel [11] was added. Hydrogenation was carried out at room temperature and atmospheric pressure. Absorption of hydrogen ceased after the uptake of 3 mol. equiv. Raney nickel was filtered off, the solvent evaporated, and the residue recrystallised.

trans-5-*Amino*-5-*methyl*-2-*phenyl*-1,3-*dioxan* (VII).—This was prepared from (I) (3 g), Raney nickel (20 ml), and hydrogen (900 ml). The calculated uptake of H_2 was 905 ml. Recrystallisation was from light petroleum (b.p. 60—80°) (yield 1.5 g, 58%), m.p. 82—84°, M^+ 193, $\nu_{max.}$ (Nujol) 698s, 746s, 1 025s, 1 110s, 1 390s, 1 593s, 2 870s, 3 350w, and 3 420w cm^{-1}.

trans-5-*Amino*-5-*phenyl*-2-*t*-*butyl*-1,3-*dioxan* (VIII).—This was prepared from (II) (0.83 g), Raney nickel (10 ml), and hydrogen (225 ml). The calculated uptake of H_2 was 210 ml. Recrystallisation was from light petroleum (b.p. 60—80°) (yield 0.4 g, 54.5%), m.p. 84—84.5°, M^+ 235, $\nu_{max.}$ (Nujol) 705s, 760s, 880s, 1 020s, 1 115s, 1 160m, 1 405m, 1 605s, 2 900s, 3 350w, and 3 410w cm^{-1}.

trans-5-*Amino*-2,5-*diphenyl*-1,3-*dioxan* (X).—This was prepared from (IV) (1.68 g), Raney nickel (10 ml), and hydrogen (400 ml). The calculated uptake of H_2 was 396 ml. Recrystallisation was from light petroleum (b.p. 60—80°) (yield 1.26 g, 84%), m.p. 85—86.5°, M^+ 255, $\nu_{max.}$ (Nujol) 710s, 765s, 945m, 995s, 1 021s, 1 109s, 1 577s, 2 950s, 3 350w, and 3 420w cm^{-1}.

cis-5-*Amino*-2,5-*diphenyl*-1,3-*dioxan* (XII).—This was prepared from (VI) (0.18 g), Raney nickel (5 ml), and hydrogen (41 ml). The calculated uptake of H_2 was 42.5 ml. Recrystallisation from light petroleum (b.p. 60—80°) (yield 90 mg, 56%), m.p. 110—112°, M^+ 255, $\nu_{max.}$ (Nujol) 698s, 760s, 990s, 1 030s, 1 065s, 1 375s, 1 605w, 2 850s, 3 150w, and 3 250w cm^{-1}.

trans-5-*Amino*-5-*methyl*-2-*t*-*butyl*-1,3-*dioxan* (IX).—This was prepared from (III) (2.49 g), Raney nickel (20 ml), and hydrogen (840 ml). The calculated uptake of H_2 was 825 ml. Recrystallisation was from light petroleum (b.p. 60—80°) (yield 1.25 g, 59%), m.p. 82—84°, M^+ 173, $\nu_{max.}$ (Nujol) 820s, 955s, 995s, 1 045s, 1 115s, 1 400m, 1 587m, 2 830s, 3 250w, and 3 320w cm^{-1}.

cis-5-*Amino*-5-*methyl*-2-*t*-*butyl*-1,3-*dioxan* (XI).—This was prepared from (V) (1.27 g), Raney nickel (10 ml), and hydrogen (435 ml). The calculated uptake of hydrogen was 420 ml. Recrystallisation was from light petroleum (b.p. 60—80°) (yield 0.51 g, 47%) M^+ 173, $\nu_{max.}$ (Nujol) 985m, 1 047s, 1 087m, 1 127s, 1 370m, 1 615m, 2 850s, 3 250w, and 3 350w cm^{-1}.

General Procedure for the Preparation of 5-*Acetamido*-1,3-*dioxans*.—Triethylamine was added to an ethereal solution of the 5-amino-1,3-dioxan. The mixture was cooled in an ice-bath and acetyl chloride was added with stirring. Ether, and excess of triethylamine and acetyl chloride were evaporated. Water was added to the residue, and work-up carried out as usual.

trans-5-*Acetamido*-5-*methyl*-2-*phenyl*-1,3-*dioxan* (XIII).—This was prepared from (VII) (0.3 g), triethylamine (0.18 g), and acetyl chloride (0.14 g) and recrystallised from carbon tetrachloride (yield 0.33 g, 91%), m.p. 115—116°, M^+ 235, $\nu_{max.}$ (Nujol) 700m, 760s, 1 009s, 1 098s, 1 295m, 1 385s, 1 465m, 1 653s, 2 840s, and 3 250m cm^{-1}.

trans-5-*Acetamido*-5-*phenyl*-2-*t*-*butyl*-1,3-*dioxan* (XIV).—This was prepared from (VIII) (0.45 g), triethylamine (0.21 g), and acetyl chloride (0.17 g) and recrystallised from light petroleum (b.p. 60—80°) (yield 0.49 g, 92.8%), m.p. 120—121°, $\nu_{max.}$ (Nujol) 698m, 760m, 1 045m, 1 115s, 1 165m, 1 555s, 1 650s, 2 850s, and 3 250m cm^{-1}.

trans-5-*Acetamido*-2,5-*diphenyl*-1,3-*dioxan* (XVI).—This was prepared from (X) (0.35 g), triethylamine (0.15 g), and acetyl chloride (0.12 g) and recrystallised from carbon tetrachloride (yield 0.35 g, 86%), m.p. 161—162.5°, M^+ 297, $\nu_{max.}$ (Nujol) 695s, 778m, 978m, 1 106s, 1 296m, 1 380s, 1 400m, 1 535m, 1 670s, 2 810s, and 3 300m cm^{-1}.

cis-5-*Acetamido*-2,5-*diphenyl*-1,3-*dioxan* (XVIII).—This was prepared from (XII) (150 mg), triethylamine (65 mg), and acetyl chloride (50 mg) and recrystallised from carbon tetrachloride (yield 160 mg, 91.8%), m.p. 148—150°, M^+ 297. $\nu_{max.}$ (Nujol) 700s, 763m, 1 002s, 1 089s, 1 140s 1 295m, 1 385m, 1 533s, 1 663s, 3 050m, and 3 250m cm^{-1}.

trans-5-*Acetamido*-5-*methyl*-2-*t*-*butyl*-1,3-*dioxan* (XV).—This was prepared from (IX) (0.4 g), triethylamine (0.26 g), and acetyl chloride (0.20 g) and recrystallised from light petroleum (b.p. 60—80°) (yield 0.45 g, 90.5%), m.p. 113—

113.5°, M^+ 215, $\nu_{\text{max.}}$ (Nujol) 663m, 761m, 960m, 1 010m, 1 040s, 1 106s, 1 320s, 1 565s, 1 653s, 2 850s, and 3 280m cm^{-1}.

cis-5-*Acetamido-5-methyl-2-t-butyl*-1,3-*dioxan* (XVII).—This was prepared from (XI) (100 mg), triethylamine (65 mg), and acetyl chloride (50 mg) and recrystallised from light petroleum (b.p. 60—80°) (yield 105 mg, 85%), m.p. 105—107°, M^+ 215, $\nu_{\text{max.}}$ (Nujol) 940m, 989s, 1 050s, 1 135s, 1 375s, 1 540m, 1 635s, 2 850s, and 3 280w cm^{-1}.

General Procedure for the Preparation of 5-*Amino*-1,3-*dioxan Hydrochlorides*.—The 5-amino-1,3-dioxan (0.2 g) was dissolved in dry ether (5 ml). Anhydrous HCl was bubbled in for *ca.* 10 s. The precipitated amine hydrochloride was quickly filtered off under reduced pressure in a dry atmosphere and washed with ether.

trans-5-Amino-2-phenyl-1,3-dioxan hydrochloride (XIX) had $\nu_{\text{max.}}$ (Nujol) 700m, 765s, 970m, 1 005s, 1 100s, 1 385m, 1 510s, 2 900s, and 3 080w cm^{-1}. *trans*-5-Amino-5-phenyl-2-t-butyl-1,3-dioxan hydrochloride (XX) had $\nu_{\text{max.}}$ (Nujol) 665m, 699m, 760m, 970m, 1 025s, 1 109s, 1 164s, 1 490m, 2 850s, and 3 050w cm^{-1}. *trans*-5-Amino-2,5-diphenyl-1,3-dioxan hydrochloride (XXII) had $\nu_{\text{max.}}$ (Nujol) 700s, 760s, 923m, 980m, 1 030m, 1 100s, 1 160m, 1 510m, 2 850s, and 3 050w cm^{-1}. *cis*-5-Amino-2,5-diphenyl-1,3-dioxan hydrochloride (XXIV) had $\nu_{\text{max.}}$ (Nujol) 695s, 750s, 965m, 1 030s, 1 125s, 1 145m, 1 510m, 2 850s, and 3 050w cm^{-1}. *trans*-5-Amino-5-methyl-2-t-butyl-1,3-dioxan hydrochloride (XXI) had $\nu_{\text{max.}}$ (Nujol) 949m, 1 006s, 1 032s, 1 110s, 1 375m, 1 395m, 1 515s, 2 850s, and 3 100w cm^{-1}. *cis*-5-Amino-5-methyl-2-t-butyl-1,3-dioxan hydrochloride (XXIII) had $\nu_{\text{max.}}$ (Nujol) 950m, 1 005s, 10 33m, 1 051m, 1 112s, 1 410s, 1 510s, 2 850s, and 3 150w cm^{-1}.

9,10-(11-Aminoethano)-9,10-dihydroanthracene (XXV).—This was prepared in four stages as described by Wawzonek and Hallum,[5] apart from the last stage which was carried out as follows.

9,10-(11-Ethoxycarbonylaminoethano)-9,10-dihydroanthracene (0.5 g) was dissolved in ethanol (10 ml). A 30% sodium hydroxide solution (50 ml) was added and the mixture refluxed with stirring for 48 h. Work-up was as usual. The product was recrystallised from light petroleum (b.p. 60—80°) (yield 0.3 g, 79.5%), m.p. 104—105.5° (lit.,[5] 104.5—105°).

9,10-(11-*Aminoethano*)-9,10-*dihydroanthracene Hydrochloride* (XXVII).—Compound (XXV) (0.2 g) was dissolved in ether (5 ml). Anhydrous HCl was bubbled into the solution. The precipitated product was quickly filtered off under reduced pressure in a dry atmosphere, and washed with ether, $\nu_{\text{max.}}$ (Nujol) 667m, 724s, 759s, 809m, 1 029m, 1 260m, 1 603m, 2 900s, and 3 150w cm^{-1}.

9,10-(11-*Acetamidoethano*)-9,10-*dihydroanthracene* (XXVI).—Compound (XXV) (0.3 g) was heated under reflux with a mixture of glacial acetic acid (2 ml) and acetic anhydride (2 ml) for 1 h. The mixture was allowed to cool and poured into ice–water. The product crystallised out, was filtered off, and recrystallised from light petroleum (b.p. 60—80°)–benzene (yield 0.22 g, 62%), m.p. 189—191°, M^+ 263, $\nu_{\text{max.}}$ (Nujol) 739m, 758s, 1 110m, 1 148m, 1 280m, 1 550s, 1 565s, 1 630s, 2 850s, and 3 250m cm^{-1}.

2,2,5,5-*Tetramethylhexan*-3-*ol* (XXVIII).—This was prepared by the method of Howard *et al.*[12] from t-butylmagnesium chloride, prepared from magnesium turnings (3.7 g) and t-butyl chloride (21 ml), and methyl 3,3-dimethylbutyrate (5 g). Elution from an alumina column (100—200 mesh; Grade H; Laporte) with light petroleum (b.p. 40—60°) gave starting material (1.4 g) and 2,2,5,5-*tetramethylhexan*-3-*one* (1.3 g). Further elution with light petroleum (b.p. 40—60°)–ether gave (XXVIII) (0.57 g, 13%), m.p. 51—52.5°.

3-*Acetoxy*-2,2,5,5-*tetramethylhexane* (XXIX).—Compound (XXVIII) (0.3 g) was refluxed in acetic anhydride (5 ml) containing sodium acetate (0.1 g) for 14 h. Work-up was as usual. The crude product was chromatographed on an alumina column (100—200 mesh; grade H; Laporte). Elution with light petroleum (b.p. 40—60°) gave (XXIX) as a liquid (0.25 g, 66%), R_F 0.34 [alumina; light petroleum (b.p. 40—60°) as eluant], M^+ 200, $\nu_{\text{max.}}$ (liquid film) 915m, 975m, 1 025m, 1 050m, 1 250s, 1 380s, 1 485s, 1 730s, and 2 950s cm^{-1}.

[4/1632 *Received, 5th August*, 1974]