Relationship between the Magnitude of J_{gem} and the Spatial Orientation of α-Substituents [1]

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

An empirical relationship between ΔJ_{gem} and a relative orientation of a methylene group attached to oxygen and sulphur, and two groups, sulphonyl and sulphinyl, has been experimentally determined. The empirical curve for oxygen shows marked similarity to a theoretically derived curve relating the magnitude of J_{gem} in the rotamers of methanol about the C–O bond. All four curves bear out the predictions of the theory of geminal coupling.

MUCH use has been made of vicinal coupling constants in solving chemical problems of a structural and stereochemical nature. The use of the geminal coupling constant (J_{gem}) in such studies is not yet as widely spread. A molecular orbital theory [2] of nuclear spin coupling between geminal hydrogen atoms has predicted the effect of substituents in positions both α and β to a methylene group on the magnitude of J_{gem} for that group. This paper describes an empirical study of the effects of α-heteroatoms and groups on the magnitude of J_{gem}; in the following paper we examine empirically the effects of β-substituents.

The theory [2] predicts that J_{gem} should become more positive when an α-heteroatom can inductively withdraw σ-electrons from the symmetric ψ_1 orbital of the methylene group, or can back-donate π-electrons from its lone pair(s) into the anti-symmetric ψ_2 orbital. This latter effect should be dependent upon the dihedral angle between one of the C–H bonds and a lone pair. The shift (ΔJ_{gem}) in the geminal coupling constant of the methylene group should be a maximum when the dihedral angle $\phi = 0°$, *i.e.*, when the lone pair eclipses a C–H bond.

An improved MO treatment [3] of geminal coupling constants demonstrated the dependence of calculated values of J_{gem} upon the dihedral angle between the methylene group and an adjacent oxygen atom through 360°, using methanol as a model.

We have conducted an experimental examination of the predictions of the MO theory for the cases where the α-substituents are the atoms oxygen and sulphur, and the groups sulphinyl and sulphonyl. For each substituent we have constructed an empirical curve relating the shift in J_{gem} produced by the substituent to the dihedral angle between a C–H bond and an adjacent π-orbital (or S–O bond in the case where the substituent in the sulphonyl group).

For each compound from which we have taken a value of J_{gem} we have chosen a reference compound in order to measure the shift in J_{gem} produced by the substituent. The reason for plotting values of ΔJ_{gem} rather than J_{gem} is that this eliminates other factors that affect the magnitude of J_{gem}, such as the angle strain at the methylene carbon atom.[4] Each point on the graphs represents an average value of ΔJ_{gem}, taken from all the compounds corresponding to a particular conformation.

Model Compounds.—Compounds from which we have taken geminal coupling constants have been classified into groups according to the dihedral angle between the methylene group and the α-heteroatom. A major

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

[1] Preliminary communication, R. Davies and J. Hudec, *J.C.S. Chem. Comm.*, 1972, 124.

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

[3] G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4151.

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

criterion for our model compounds is that they must be conformationally homogeneous. Thus much of our data relating to five- and six-membered rings has been taken from compounds in which such rings are locked in a particular conformation, either by fusion to other ring systems or by the presence of one or more bulky substituents on the ring.

Most of the data we have used for the conformation $\phi = 0°$ for the case of an oxygen atom adjacent to a methylene group have been taken from compounds in which a tetrahydrofuran ring is fused to other ring systems. We recognise that considerable puckering is likely to exist in such a tetrahydrofuran ring, but models of the compounds we have used show that such puckering does not involve the $-CH_2-O-$ portion of the molecule, and that this portion substantially retains the eclipsed conformation.

No values of J_{gem} for the 2-methylene protons in 1,3-diheterocyclic compounds have been used. The couplings between the methylene protons in the two triads of compounds[5] shown in Figure 1 show that the value of ΔJ_{gem} produced by two heteroatoms is more than double that due to one.

Some of the more common types of structure which correspond to the various dihedral angles ϕ are illustrated in Figure 2.

Four-membered heterocycles are considered to correspond to the fully eclipsed conformation, this being the average of oscillations caused by ' flipping ' over a fairly small angle.

We have used data from a few model compounds corresponding to dihedral angles intermediate to those illustrated in Figure 2. In such cases the dihedral angle has been obtained from *X*-ray data, where this has been available, or has been measured from a Dreiding model of the compound with a protractor.

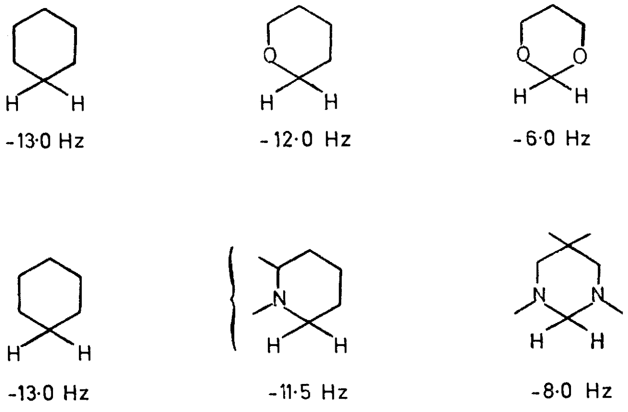

FIGURE 1 ΔJ_{gem} due to two heteroatoms is more than twice that due to one

Our survey of literature values of J_{gem} yielded no information relating to the $\phi = 180°$ conformation. We thus had to design and synthesise a conformationally homogeneous system of this type. Clearly the model system had to be acyclic, and the problem to be solved was how to prevent rotation about the carbon–heteroatom bond. Models show that this should be achieved by introducing two bulky groups into the molecule, one attached to the methylene carbon atom, the other to the heteroatom. Their steric interaction should maintain them in a *trans*-coplanar arrangement. Thus the system we used was a combination of the t-butyl neopentyl groups.

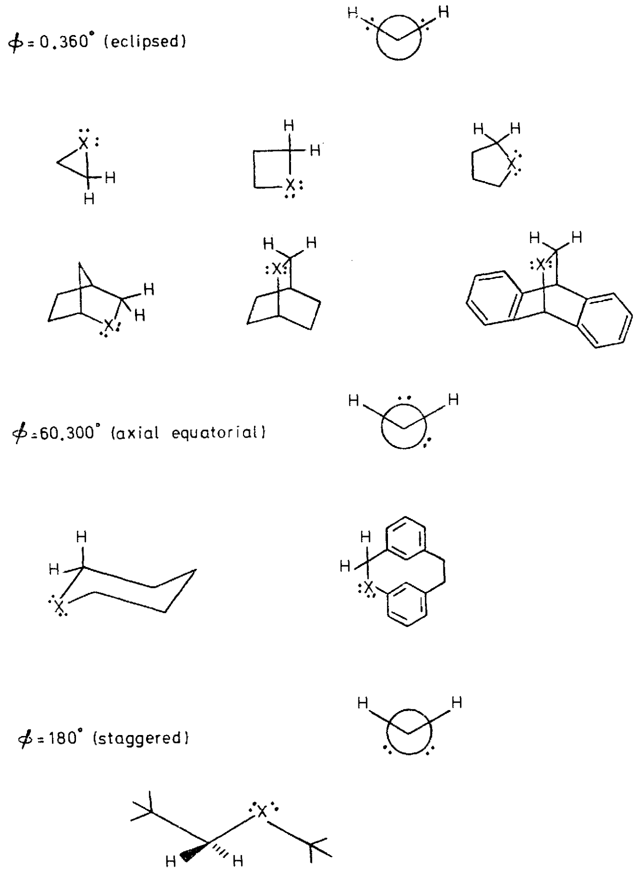

FIGURE 2 Common structures corresponding to the main dihedral angles

Syntheses.—The values of J_{gem} for all conformations except $\phi = 180°$ have been collected from the literature. The compounds for the 180° orientation were synthesised for this study. The required compounds are t-butyl neopentyl ether, sulphide, sulphoxide, and sulphone. However, since the ether, sulphide, and sulphone have a plane of symmetry bisecting the methylene group, the two methylene hydrogens will be magnetically equivalent, thus preventing the observation of coupling between them. The equivalence is removed by the introduction of one deuterium atom into the methylene group. The asymmetry of the sulphinyl group in t-butyl neopentyl sulphoxide renders the methylene protons non-equivalent and coupling between them is observed.

Synthesis of $[^2H_1]$neopentyl t-butyl ether was attempted by treatment with sodium t-butoxide of $[^2H_1]$-neopentyl tosylate. The single product obtained in low yield was identified not as the required ether but as dideuteriated dineopentyl ether. Presumably the mechan-

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[5] R. C. Cookson and T. A. Crabb, *Tetrahedron*, 1968, **24**, 2385.

ism involves initial attack of the t-butoxide anion at sulphur rather than at the methylene carbon atom of $[^2H_1]$neopentyl tosylate and is followed by S–O bond scission. The resulting $[^2H_1]$neopentyl oxide anion can then attack another molecule of $[^2H_1]$neopentyl tosylate, this time attack taking place at the methylene carbon atom, and the ensuing C–O bond scission gives the observed product.

A Dreiding model of dineopentyl ether indicates that steric interaction between the t-butyl groups is likely to be significant and that the molecule will adopt the $\phi = 180^\circ$ conformation. This conclusion is supported by n.m.r. evidence presented in the next section.

$[^2H_1]$Neopentyl t-butyl sulphide was prepared without difficulty by treatment with sodium t-thiobutoxide of $[^2H_1]$neopentyl tosylate. Oxidation with potassium permanganate gave the sulphone. Undeuteriated neopentyl t-butyl sulphide was oxidised to the sulphoxide with ozone.

N.m.r. Spectra.—Details of the n.m.r. spectra of the four compounds we have prepared are given in the Table.

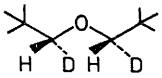
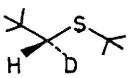
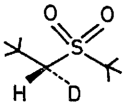
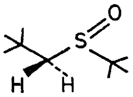
The chemical shift of the methylene protons of a neopentyl group adjacent to oxygen has been the subject of some attention.[6] It has been estimated from a study of the chemical shifts of neopentyl ether hydrogen atoms that a lone pair of electrons on the oxygen atom in a *gauche*-relationship to a hydrogen on the α-carbon atom deshields that hydrogen by 1.7 p.p.m. Taking τ 8.8 as the normal methylene proton resonance, a hydrogen atom *gauche* to one oxygen lone pair will thus appear at τ 7.1, whilst a hydrogen situated *gauche* to two oxygen lone pairs will appear at τ 5.4.

Considering the three possible staggered conformations of a neopentyl ether (Figure 3) it is simply calculated that if there is free rotation about the C–O bond, the methylene protons will absorb at an average value of τ 6.53. This value agrees well with the observed methylene resonances in unhindered open-chain alcohols and ethers. However, if steric hindrance in conformations B and C favours conformation A, the methylene protons might be expected to absorb at τ 7.1.

The Table shows that the methylene protons in dineopentyl ether absorb at τ 7.02. This then is additional evidence that the compound exists in conformation A, corresponding to $\phi = 180^\circ$.

Strom *et al.*[7] in a study of acyclic sulphoxides have assigned individual methylene protons α to the sulphinyl group on the basis of differential solvent shifts, on changing from a non-polar solvent to benzene. Assuming that the benzene molecule will position itself as far as possible from the negative end of a dipole, it should solvate a sulphoxide molecule *trans* to the oxygen atom. The hydrogen atom which suffers the largest shift on changing solvent will therefore be that which is *trans* to the S–O bond. In CCl_4 the methylene protons of t-butyl neopentyl sulphoxide absorb at τ 7.48 and 7.78. In C_6D_6 they absorb at τ 7.80 and 7.90. Applying Strom's reasoning, the low-field absorption suffers the largest shift, and should thus be assigned to the proton *trans* to the S–O bond.

N.m.r. spectra[a] of compounds corresponding to the $\phi = 180^\circ$ conformation

Compound	Methylene protons		t-Butyl protons	
	τ	J_{gem} (Hz)	τ	
	7.02	−7.55[b]		9.10
	7.64	−11.4	8.74	9.04
	7.19	−11.6	8.62	8.76
	7.48 & 7.78	−13.3	8.76	8.86

[a] Solvent $CDCl_3$. [b] Signs assumed.

In the deuteriated compounds, geminal J_{H-H} couplings have been obtained from the measurable J_{H-D} couplings using the relationship $J_{H-H} = 6.51 J_{H-D}$.[8]

The value of 6.51 is the ratio of the gyromagnetic constants of hydrogen and deuterium. Fraser[9] has recently indicated inaccuracies in this method, arising from changes in electron distribution resulting from the isotopic substitution. He suggests that a more accurate value of J_{gem} is obtained by employing a chiral shift reagent to induce coupling between the equivalent methylene protons.

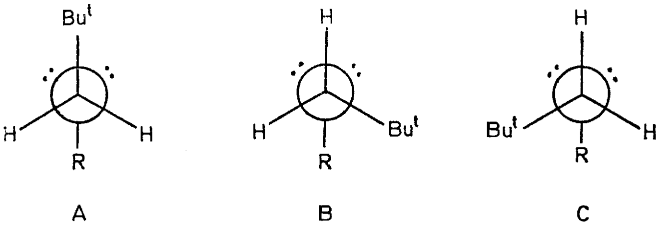


FIGURE 3 Staggered conformations of a neopentyl ether

DISCUSSION

The curves describing the empirical relationship between the shift in J_{gem} and the spatial orientation of the

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[6] C. C. Price, *Tetrahedron Letters*, 1971, 4527 and references therein.

[7] E. T. Strom, B. S. Snowden, jun., and P. A. Toldan, *Chem. Comm.*, 1969, 50.

[8] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, 1962, **37**, 3012.

[9] R. R. Fraser, M. A. Petit, and M. Miskow, *J. Amer. Chem. Soc.*, 1972, **94**, 3253.

lone pairs on adjacent oxygen and sulphur atoms are shown in Figures 5 and 6 * (curves A and C respectively). The empirical relationship between ΔJ_{gem} and an adjacent sulphonyl group is described by curve D (Figure 6) and that between ΔJ_{gem} and an adjacent sulphinyl group is shown in Figure 7 (curve E)

Curves A, C, and D (Figures 5 and 6) are all symmetrical about 180°, but curve E (Figure 7) is not, due to the asymmetry of the sulphinyl group. We have chosen the direction of rotation for the sulphinyl group such that $\phi = 60°$ when the lone pair bisects the methylene protons (Figure 4).

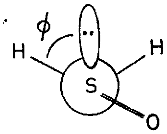


FIGURE 4 The $\phi = 60°$ conformation for a sulphinyl group adjacent to a methylene group

Empirical Curves for Oxygen and Sulphur.—Photoelectron spectroscopic studies of organic oxygen- and sulphur-containing compounds [10] have shown that the lone pairs on the heteroatom cannot be considered as being equivalent. The ionisation potential of one lone pair is considerably higher than that of the other, showing that it possesses considerable bonding character. This has been interpreted as implying that hybridisation on oxygen and sulphur approximates to sp^2, each atom containing a filled non-bonding p-orbital. Thus curves A and C can be considered to describe the variation of ΔJ_{gem} with the spatial orientation of the filled non-bonding p-orbital on the adjacent oxygen and sulphur atoms respectively.

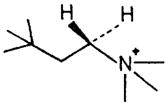
The situation is the equivalent but opposite case to that calculated by Barfield and Grant [11] for the effect of an adjacent π-bond on the magnitude of J_{gem}. Whereas Barfield and Grant were describing a hyperconjugative electron withdrawal (π-withdrawal) from the methylene group, and thus predicted a negative shift in J_{gem}, we expect the lone pair on oxygen and sulphur to back donate (π-donate) into the methylene group, thus producing a positive shift. By analogy with the Barfield and Grant curve, we would expect curves A and C to have a periodicity of 180° due to the symmetry of the filled non-bonding p-orbital.

The shape of curves A and C (Figures 5 and 6) does indicate a periodicity of 180°. The geminal coupling constants of dineopentyl ether and neopentyl t-butyl sulphide indicate that the magnitude of ΔJ_{gem} corresponding to $\phi = 180°$ is comparable to that produced by the $\phi = 0°$ conformation. This provides the experimental verification of the prediction of Pople and Bothner-By [2] that the largest shift in J_{gem} produced by an adjacent π-orbital will occur when this orbital is parallel to the H–H internuclear axis of the methylene group.

Curve A shows that ΔJ_{gem} at conformations $\phi = 90$ and 270° is virtually zero. This suggests that the effect of the inductive σ withdrawal of electrons from ψ_1 on the magnitude of J_{gem} is small, and that the dominant factor is the π-donation of lone-pair electrons into ψ_2. This conclusion is supported by values of J_{gem} adjacent to a quaternary nitrogen atom in compounds (I) [12] and (II).[13] These values show little difference from values for suitable reference compounds, [$^2H_2$]neopentane (J_{gem} −12.55 Hz [14]) and cyclohexane (J_{gem} −13.0 Hz [15]).

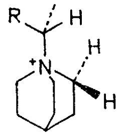
We have no data relating to conformations $\phi = 90$ and 270° on curve C (Figure 6) for sulphur. However, a smooth curve drawn through the available points indicates that a sulphur atom in such a conformation will produce a slight negative shift in J_{gem}. Thus for both curves A and C, the points at 90 and 270° are minima, in agreement with theoretical predictions.

The theoretical curve derived for methanol by Pople *et al.*[3] is also reproduced in Figure 5, curve B. We have anchored this curve to our experimental curve for oxygen, curve A, at $\phi = 0°$. This point on curve A has been chosen since it represents ΔJ_{gem} derived from the greatest number of compounds. The theoretical curve B is seen to be qualitatively similar to our experimental curve A. However Pople's curve is more negative than curve A in the region of $\phi = 180°$. This may reflect a difference in the contribution to J_{gem} of the O–H bond in an alcohol compared with that of the O–C bond in an ether.



(I)

-12·5 ± 0·1 Hz



(II)

R = Ph -12·5 Hz

R = CO$_2$Et -12·5 Hz

A comparison of curves A and C (Figures 5 and 6) shows that the maxima in curve C are not as positive as those in curve A. Three possible reasons can be suggested for this. (i) The smaller separation between the energy of a C–H bond and the energy level of an oxygen lone-pair, by comparison with that of a sulphur lone-pair, enables greater back donation to take place into ψ_2 from oxygen. (ii) The C–O bond, being shorter than the C–S bond, permits more efficient overlap of the oxygen lone-pair with ψ_2. (iii) The vacant 3d orbitals on sulphur can accept electrons from ψ_2 thus producing a negative shift in J_{gem}.

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* Footnotes to Figures 5—7 which give details of the compounds studied and the corresponding reference compounds from which ΔJ_{gem} values have been calculated are in Supplementary Publication No. SUP 21421 (6 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.

[10] S. D. Worley, *Chem. Rev.*, 1971, **71**, 295 and references therein.

[11] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

[12] R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961.

[13] J. McKenna, J. M. McKenna, and B. A. Wesby, *Chem. Comm.*, 1970, 867.

[14] M. J. Lacey, C. G. MacDonald, A. Pross, J. S. Shannon, and S. Sternhell, *Austral. J. Chem.*, 1970, **23**, 1421.

[15] E. W. Garbisch, jun. and M. G. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 6543.

Empirical Curve for the Sulphonyl Group.—The curve for sulphone (Figure 6, curve D) is qualitatively similar to those for oxygen and sulphur. Consideration of the theory of geminal coupling constants [2] leads to the prediction that the sulphone curve should suffer a negative shift relative to the oxygen and sulphur curves, since there is no lone-pair available for back-donation into ψ_2.

Curve D shows that in certain orientations, ΔJ_{gem} is negative, suggesting withdrawal of electrons from ψ_2 into the sulphonyl group. This could be accomplished using a combination of the partially vacant orthogonal π-orbital on sulphur, or the σ^*-orbital of the S–O bond.

The curve has a maximum at $\phi = 180°$, at which point ΔJ_{gem} is positive. Thus it is possible that in this conformation, there is some back donation from the electron-rich oxygen atoms into ψ_2.

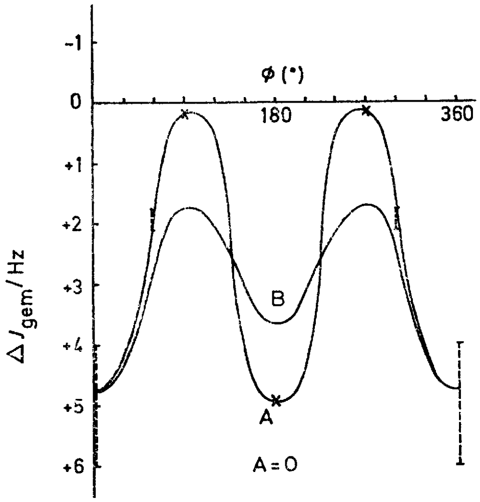

FIGURE 5 A, Empirical relationship between ΔJ_{gem} and dihedral angle ϕ for oxygen adjacent to a methylene group. B, Theoretical relationship for the rotamers of methanol

Empirical Curve for the Sulphinyl Group.—The empirical curves A, C, and D (Figures 5 and 6) are all symmetrical about $\phi = 180°$. The asymmetry of the sulphinyl group is apparent in curve E (Figure 7) which has no symmetry about $\phi = 180°$. The sulphinyl group exerts two effects which will influence the magnitude of J_{gem}, and both are dependent on stereochemistry. The lone-pair of electrons can back-donate into ψ_2, and the S–O bond can either accept electrons from ψ_2 or back donate them, possibly from the electron-rich oxygen atom as has been discussed for curve D for the sulphonyl group.

We have made an attempt to simulate, in a simple manner, the effect of a sulphinyl group on J_{gem} by adding two curves describing the influence on J_{gem} of the two effects present in the sulphinyl group. Thus curve G (Figure 7), obtained for a bromine atom attached to a carbon atom adjacent to the methylene group [16] should be qualitatively similar to that for an ' isolated ' S–O bond. The curve describing the effect of an adjacent lone-pair on J_{gem} has been determined by Crabb [17] and resembles a reflection of the bromine curve in the ϕ-axis. Thus the bromine curve is set at $\phi = 0°$, and its reflection (curve H) is set at $\phi = 120°$ to account for the spatial orientation of the lone pair and of the ' S–O ' bond in the sulphinyl group. The addition of the two curves (curve F) is seen to resemble qualitatively curve E, the empirical curve for the sulphinyl group.

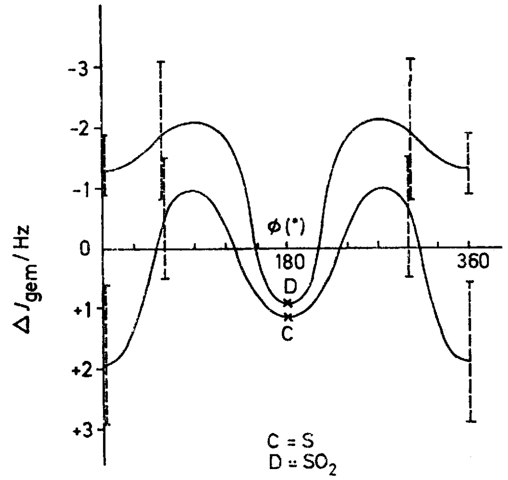

FIGURE 6 Empirical relationship between ΔJ_{gem} and dihedral angle ϕ C, for sulphur and D, for sulphone adjacent to a methylene group

It should be admitted however, that this is an over-simplified approach, since it neglects completely any interaction between the lone pair and the S–O bond in the sulphinyl group.

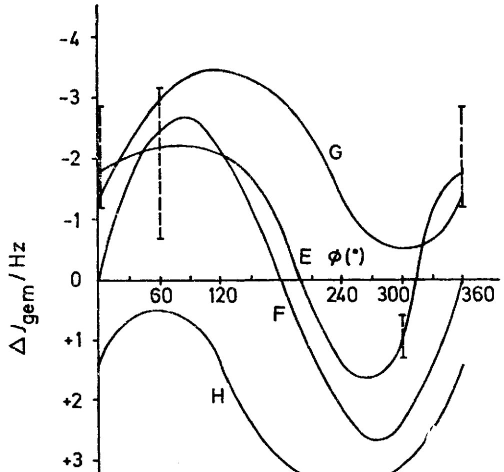

FIGURE 7 E, Empirical relationship between ΔJ_{gem} and dihedral angle ϕ for sulphoxide adjacent to a methylene group. Curve F is a simulated curve for sulphoxide, formed by adding curve G, representing the S–O bond, to curve H, representing the lone pair

EXPERIMENTAL

M.p.s were determined on a Kofler micro hot-stage apparatus and are corrected. I.r. spectra were recorded on a Unicam SP 200 spectrophotometer. Mass spectra were

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

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

recorded on an A.E.I. MS12 instrument at 70 and 15 eV. N.m.r. spectra were recorded on a Varian HA-100 instrument, using tetramethylsilane as internal reference. Full details are given in the Table. Geminal coupling constants were measured from expansions to between 50 and 10 Hz sweep width using an external frequency oscillator, sweeps being carried out in both directions. R_F Values are given to characterise liquids which were prepared in small quantities, and not distilled. The values refer to t.l.c. on alumina plates, the solvent being as stated.

[^{2}H]*Neopentyl Alcohol.*—This was prepared by the method of Nystrom and Brown,[18] by the reduction of pivalaldehyde (10 ml) with lithium aluminium deuteride (2.5 g) (yield 4.9 g, 92.5%), b.p. 112—113° (lit.,[19] 110—111°), M^+ 89.

[^{2}H]*Neopentyl Tosylate.*—This was prepared from [^{2}H]neopentyl alcohol (1.2 g) and tosyl chloride (3.05 g) in pyridine. The product was recrystallised from ether–light petroleum (b.p. 40—60°) (yield 3.04 g, 92.5%), m.p. 45–46.5° (lit.,[20] 46—46.5°), M^+ 243.

[^{2}H]*Neopentyl Iodide.*—This was prepared by the method of Landauer and Rydon [21] from [^{2}H]neopentyl alcohol (4.8 g), triphenyl phosphite (16.7 g), and methyl iodide (10.7 g). The work-up was carried out according to the method of Kornblum and Iffland [22] (yield 5.4 g, 50%), b.p. 74—78° at 110 mmHg (lit.,[21] 71° at 100 mmHg), M^+ 199.

Di[^{2}H]*neopentyl Ether.*—Potassium t-butoxide (1.4 g) was refluxed, with stirring, with a solution of [^{2}H]neopentyl tosylate (2.15 g) in diglyme (20 ml) for 48 h. Elution from an alumina column (100—200 mesh; grade H; Laporte) with ether–light petroleum (b.p. 40—60°) gave a liquid (0.26 g, 18.5%), R_F 0.13 [light petroleum (b.p. 40—60°)], M^+ 160, $\nu_{max.}$ (liquid film) 816m, 1 078s, 1 113m, 1 258s, 1 378s, 1 467s, 2 180w, and 2 980s cm^{-1}.

[^{2}H]*Neopentyl t-Butyl Sulphide.*—Freshly sliced sodium (0.24 g) was dissolved in absolute alcohol (6.5 ml). 2-Methylpropane-2-thiol (1.9 g) was added and the mixture refluxed for 2 h. [^{2}H]Neopentyl tosylate (2.5 g) was added, and the whole was refluxed for a further 6 h. The crude product obtained from normal work-up was distilled and the fraction boiling at 69—71° and 30 mmHg was collected. This was further purified by elution from an alumina column (100—200 mesh; grade H; Laporte) with light petroleum (b.p. 40—60°), giving a liquid (0.89 g, 53%), R_F 0.90 (ether), M^+ 161, $\nu_{max.}$ (liquid film) 785w, 925m, 945m, 1 118m, 1 160s, 1 369s, 1 400m, 1 465s, 2 150m, and 2 950s cm^{-1}.

Neopentyl t-Butyl Sulphoxide.—Ozone was bubbled for 1 h into a solution of neopentyl t-butyl sulphide (1.0 g) in methanol (100 ml) cooled to −70° in a dry ice–acetone bath. The mixture was left at room temperature overnight. Solvent was fractionated off. Elution of the residue from an alumina column with methylene chloride gave the product, which slowly crystallised as needles (0.71 g, 64.5%), m.p. 68—71°, M^+ 176, $\nu_{max.}$ (Nujol) 655m, 750s, 1 020s, 1 040s, 1 120s, 1 275m, 1 300m, 1 395m, and 2 990s cm^{-1}.

[^{2}H]*Neopentyl t-Butyl Sulphone.*—A 3% aqueous solution of potassium permanganate (15 ml) was added in portions with shaking to a solution of [^{2}H]neopentyl t-butyl sulphide (0.3 g) in glacial acetic acid (4 ml). The mixture was then stirred at room temperature for 48 h. Sufficient sodium hydrogen sulphite solution was added to decolourise the solution. The solution was basified with dilute NaOH solution and normal work-up carried out. The crude product was chromatographed on a column of silica (100—200 mesh; Grace). Elution with methanol gave the product, which crystallised slowly as needles (0.32 g, 89%), m.p. 55—57°, M^+ 193, $\nu_{max.}$ (Nujol) 660s, 1 025m, 1 047s, 1 115s, 1 155s, 1 250m, 1 285m, 1 380s, and 2 950s cm.$^{-1}$

[4/1631 *Received, 5th August,* 1974]

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