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GEMINAL COUPLING CONSTANTS IN METHYLENE GROUPS—II[1]

J IN CH_2 GROUPS α TO HETEROATOMS

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Abstract—Further values of geminal coupling constants (*J*) in CH_2 groups α to heteroatoms confirm established trends in the variation of *J* with molecular environment; in addition, *J* is quoted for new systems not described in Part I, and the exceptions to the general trends are discussed.

SINCE our previous extensive study[1] of *J*, many values for new systems have appeared in the literature and from our research. The majority of the coupling constants shown in Tables A, B and C* are consistent with the MO treatment[1-64] of *J* in CH_2 groups and with our original discussion[1] of factors affecting *J*. However, many apparent exceptions to the correlations between *J* and molecular structure are now evident,† and it is the purpose of this paper to discuss those compounds exhibiting unusual values of *J* as well as those which illustrate the utility of *J* in conformational studies.

The most important factors affecting *J*‡ in CH_2 groups α to heteroatoms are the inductive removal of electrons and the back donation of lone pair electrons into the CH_2 group, both processes causing *J* to become more positive.[1-64] Of particular importance in conformational studies is the dependence of *J* on the dihedral angle between the lone pair orbitals and the CH_2 group, the contribution to *J* from a lone pair of electrons being minimal when the lone pair bisects the CH_2 group.§

J in 6-membered ring heterocyclic systems (Table A). *J* for N—CH_2 protons in 6-membered rings is normally in the range −12·5 to −13·5 c/s. An interesting exception to this is observed in the isomeric hydroxyskytanthines I and II[18] where *J* for the 1-methylene group is −9 c/s. *J* for the 3-methylene group is unexceptional (−11 to −12 c/s). Although this may be a result of distortion of the 6-membered ring by the *cis*-fusion to the 5-membered ring, resulting in a greater overlap of the

* The tables of coupling constants have been compiled from published and unpublished values. The literature has been scanned from 1966–1968, but no special effort was made to cover it exhaustively.

† One cannot discount the possibility that some of the apparent exceptions are due to inaccurate measurement of spectra, especially where they are measured only incidentally.

‡ Throughout this paper *J* is assumed to be negative. Lone pairs of electrons have been treated in terms of the simple hybridization model, but as Lehn[1-65] has emphasized, this is an approximation since lone pairs may be extensively delocalized. However the simple treatment, more readily appreciated from Dreiding models, is used here, but the approximations must not be forgotten.

§ The phrase "bisects the CH_2 group" is used rather loosely in this and the following paper to mean "bisects the H—H internuclear axis of the CH_2 group".

N lone pair* with the C1 methylene than with the C3 methylene, it is not evident from the examination of models.

The N,N'-dimethylbispidine III also shows a rather positive value for J of $-10{\cdot}2$ c/s. A flattened chair–chair conformation for this compound[2] is probably the reason for the increase in J over that normally observed in 6-membered rings. J for the N—CH_2 protons in quinolizidine is also slightly more positive (-11 c/s) than in monocyclic systems. A more negative value (-13 c/s) is found[2] for J in CH_2 groups α to positively charged N. J for CH_2 protons adjacent to N—Ac is also rather negative (-13 to -14 c/s)[156, 14] due to withdrawal of the N lone pair of electrons by the C=O function. Very negative values of J are observed for CH_2 groups situated between N and an sp^2 hybridized atom (Table A), and these values are all explicable in terms of removal of electrons from the antisymmetric CH_2 orbital by hyperconjugation (Barfield-Grant $J^\pi - \theta$ relationship[166]).

The "normal" J for hexahydropyrimidines is ca. $-8{\cdot}5$ c/s. If one of the substituents on N is H, J decreases; for example, compound IV[7] shows $J = -11{\cdot}9$ c/s. In the hexahydro-1,3,5-triazines (V)[6] J remains remarkably constant at -10 to $-10{\cdot}2$ c/s for the compounds V, R = Me, Et, $CHMe_2$ and CMe_3. The rather negative value of J for these compounds suggests the presence of a proportion of conformers with an axial alkyl substituent.

Tetrahydro-1,3-oxazines existing in a chair conformation with the N lone pair axially orientated as in VI show a J for the C2 methylene group very close to -8 c/s. As was noted in the case of the hexahydropyrimidines, replacement of the N alkyl group by H[25] causes J to become more negative. The use of J in studying the preferred conformation of 3-oxa-1-azabicyclo [4.4.0] decanes (VII) has been demonstrated.[161] Because of the presence of the conformationally unstable N atom this compound can exist in either *trans* fused ring conformations (VIIa) or *cis* fused ring conformations (e.g. VIIb). The unsubstituted compound is found to exist predominantly in the conformation VIIa (J for C2 methylene $-8{\cdot}0$ c/s) whereas the *trans* 6H, 10H-10-Me derivative VIII shows for the C2 methylene a J of $-10{\cdot}0$ c/s, and must therefore exist in conformation VIIb since here the N lone pair bisects the C2 methylene and does not contribute to J. Recently it has been shown[165] that 8-oxa-1-azabicyclo [3.3.1] nonane (IX) has a J of $-10{\cdot}5$ close to that observed for VIII. Both compounds have similar N—CH_2—O geometries. The interesting alkaloid lythramine (X)[20] shows a J for the N—CH_2—O protons of -11 c/s leading us to conclude that this compound exists with the AB rings *cis*-fused as in conformation VIIb.

J for the CH_2 protons α to the O atom in tetrahydropyrans is normally in the range -11 to $-12{\cdot}5$ c/s. J in tetrahydropyran itself has been found to be -12 c/s.[50] Interesting examples of J in tetrahydropyrans including deviations from the normal range are shown in Table 1.

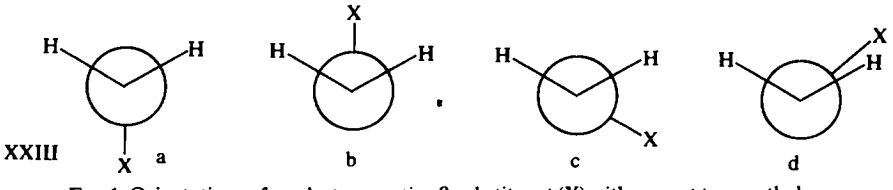


FIG. 1. Orientations of an electronegative β substituent (X) with respect to a methylene group.

* Overlap of the N lone pair with the CH_2 group implies overlap with the antisymmetric CH_2 MO.

The pair of compounds XI and XII show a marked difference in J for the O—CH_2 protons in the dioxan ring. According to Pople and Bothner-By's MO theory of geminal coupling,[164] CH_2 protons which are a *gauche-trans* pair relative to a vicinal electronegative substituent should show a smaller (more negative) J than those in a CH_2 group which has both protons in a *gauche* relationship to the substituent (see Fig. 1, c and b respectively). In the former case the substituent must be axial, and in the latter equatorial. Thus 4,6-O-benzylidene-1,2,dideoxy-D-xylo-hex-1-enopyranose XII and its 3-OAc derivative, both of which, in effect, have an axial electronegative substituent vicinal to the CH_2 group, exhibit a geminal coupling of $-12{\cdot}5$ c/s for this group. In 4,6-O-benzylidene-1,2,dideoxy-D-ribo-hex-1-enopyranose XI, with the *ribo* configuration and an effective equatorial substituent β to the CH_2 group, J is much larger, i.e. $-10{\cdot}0$ c/s in the parent XI, and $-9{\cdot}6$ c/s in its 3-OAc derivative. Presumably there is also a slight change in orientation of the O lone pairs with respect to the CH_2 bonds, brought about by differences in geometry at the ring fusion to the dihydropyran ring.

J_{5a5e} in pyranosides appears to be dependent on the configuration at the anomeric C atom. For example, in some ribopyranose derivatives[37] the values of J_{5a5e} vary between $-10{\cdot}8$ and $-10{\cdot}9$ c/s for the α-halides (e.g. XVI), whereas the values for the β-halides are appreciably smaller ($-13{\cdot}4$ to $-14{\cdot}0$ c/s, e.g. XV, XVII). These differences can be correlated with the conformational preferences of the α- and β-anomers. Theoretically, pyranosides may adopt 8 distinct unstrained conformations, 2 chairs, Cl and 1C, and 6 boats, the former being thermodynamically more stable (boat conformers are excluded in the following discussion). As noted previously, J depends on the relative orientation of an electronegative substituent β to the CH_2 group in question; J is more negative when this substituent is axial and hence *gauche* to only one of the geminal protons, than when it is equatorial and hence in a *gauche* relationship to both these protons (XXIIIb). Taking the specific case of the C4 OBz group as the β-substituent, it can be seen that the β-halides, which exhibit the more negative J for the C5 protons, require the C4 OBz group to be axial and hence adopt the IC conformation XXVII rather than the Cl conformation XXVI, whereas the α-halides require the C4 OBz to be equatorial and exist in the Cl conformation XXIV in preference to IC conformation XXV. (See Table 2).

J for the β-CN, β-OBz and β-OMe groups is slightly more positive than for the β-halides; if the spectrum is a time-averaged spectrum of both conformers, a small proportion of the rapidly equilibrating less favoured conformer will have only a small effect on J.

Similar considerations apply to the α- and β-chloro 2,3,4-tri-O-acetyl-D-xylopyranosides[60] (XIII and XIV). One would predict the β-anomer XIII ($J = -12{\cdot}9$ c/s) to exist predominantly in the IC conformation, XXVIII, whereas in the α-anomer XIV ($J = -11{\cdot}4$ c/s) the CI conformation will be favoured.

In general, the operation or non-operation of the anomeric effect is the decisive factor in determining whether the CI or IC conformation predominates. In XXVIII with the axial halogen substituent the O and Cl dipole interaction has a substantial antiparallel component giving rise to dipolar stabilization, whereas in XXIX the interaction between the almost coplanar dipoles is destabilizing. In adopting the IC conformation, the β-anomer XXVIII is subjected to the destabilizing influence of four axial groups and two *syn*-diaxial interactions. Presumably this is more than

counteracted by the dipolar stabilization resulting from the axial orientation of the halogen substituent in the IC conformation, since a substantial proportion of this conformation is present in the equilibrium mixture.

The corresponding α and β methyl tri-O-acetyl-D-xylopyranosides[66] exhibit $J_{5a5e} = -10{\cdot}7$, and $-11{\cdot}8$ c/s respectively; this is in accord with the β anomer existing partially in the less favoured CI conformation, as it is to be expected since the magnitude of the anomeric effect for a CI Me group will be less than in the case of CI halogen.

To summarize, the magnitude of the anomeric effect determines which chair form predominates in the conformational equilibrium and hence the axial/equatorial nature of the C4 substituent, which in turn influences the magnitude of J_{5a5e}. In pyranoses with a C4 OAc substituent, for example, we therefore expect to find a correlation between J_{5a5e} and the axial or equatorial orientation of the C4 OAc substituent, C5 CH_2 protons vicinal to an axial C4 OAc substituent XXXI (*gauche* and *trans* orientation) exhibiting a more negative J than methylene hydrogens vicinal to an equatorial C4 OAc XXX (both hydrogens *gauche*). This is observed in practice. (Table 3).

In the nucleoside XXII $J_{55'}$ is unusually positive (-8 c/s) for a tetrahydropyran ring. A detailed NMR study of this compound has been made and on the basis of the value of vicinal couplings a distorted chair conformation for the compound has been proposed. In particular it is considered that the C5 CH_2 group approaches coplanarity with the ring O atom and the C4′ carbon. Such a conformation would cause an increase in J due to a more effective transference of the O lone pair of electrons into the antisymmetric C5 CH_2 MO, perhaps assisted by increase in the C—CH_2—O angle. Similarly the marked difference in J (C5 methylene) for XVIII (-12 c/s) and XX (-9 c/s) must be due to a deformation of the chair in the latter compound. In support of this is the considerable difference in the value of J_{45} for XVIII and XX. The J of -13 c/s is as expected in XIX, but one would predict J to be more positive in XXI if the conformation is as shown with an equatorial C4 substituent.

A Dreiding model of compound XXXII[149] shows axial-equatorial relationship of the O lone pairs to the C12 methylene group which does not explain the rather negative J of -14 c/s reported for this compound.

Compounds XXXIII and XXXIV[34] form an interesting pair. In XXXIII (J O—CH_2 $= -14$ c/s) the dihydropyran ring must be in the half-chair conformation since the contribution to J from the adjacent π-bond of about -2 c/s is that expected[1] for a dihedral angle (θ) of 60° between the CH_2 and the adjacent π orbital. In support of this, J for the C—CH_2—C=C protons is -17 c/s, expected for a θ of 30°. In XXXIV, J is slightly more positive (-13 c/s) and examination of models shows that in order to relieve non-bonded interactions between the dihydropyran ring and the bicyclooctene substituents θ has to be increased from 60° with the result of increasing J. The J of 16 c/s for XXXV[57] is explicable in terms of the Barfield-Grant relationship since in the preferred conformation the plane of the phenyl ring almost bisects the CH_2. In XXXVI[32] the J of $-15{\cdot}4$ c/s is slightly too negative for the θ of 50° suggested by Dreiding models and presumably here the extra negative contribution to J arises from a reduced overlap of the O lone pairs with the antisymmetric CH_2MO's, brought about by bending the benzofuran group away from a pseudo-axial conformation.

The J of $-17{\cdot}6$ c/s for the benzylic methylene group confirms this conformation (θ = ca. 30°).

The J of -17 to -18 c/s observed[97] for the morpholinones XXXVII has been interpreted in terms of a half-chair conformation for the ring (XXXVIII). The half-chair conformation is also consistent with the J of $-10{\cdot}6$ to $-11{\cdot}4$ c/s observed for the series of compounds XXXIX.

In 6-membered ring sulphoxides, the differences in J observed for the methylene protons vicinal to the sulphoxide centre appear to be related to the chirality of the sulphoxide group.[24] In some equatorial sulphoxides,[77] in which the S lone pair is axial, J is $-11{\cdot}3$ to $-12{\cdot}8$ c/s (XL), whereas in the corresponding axial sulphoxides, J is considerably smaller, viz. $-13{\cdot}8$ to $-15{\cdot}5$ c/s. (XLI).

J *in 5-membered ring heterocyclic systems* (Table B). As has been discussed previously[167] J in a 5-membered ring heterocyclic compound is more positive than in the 6-membered ring analogue due to the increased possibilities of transfer of lone pair electrons into the antisymmetric CH_2 MO. This arises because many 5-membered rings exist in conformations such that the lone pairs of electrons on the heteroatoms actually eclipse the adjacent CH bonds. Since this is the most important effect operating in the systems under discussion most of this section will be concerned with the efficiency of this electron donating process, and in general compounds with the most positive values of J will be those with eclipsing lone pair $-CH_2$ geometries, and those with unusually negative J values must exist with 5-membered rings in conformations such that this favourable geometry is lost. In addition it is found that compounds in which eclipsing of the small lobe of the lone pair orbital with adjacent CH bonds occurs also possess rather more positive values of J—this being an alternative way of describing the "parallelity effect" of Anteunis.[171] Values of J α to N cover a wider range of values, even in apparently closely related structures, than in any other type of CH_2 group. This is presumably because of the very easy deformability of bonds to nitrogen, and the consequent changes in hybridization and overlap with the CH_2 orbitals.

J (C7 methylene) in 4,7,7-trimethyl-2-chloro-2-azabicyclo [2.2.1] heptane (XLII) is $-10{\cdot}2$ c/s. This is a key value since here the lone pair must bisect the C7 methylene protons and the influence of the N on J in this compound must be due to the inductive effect alone of the N atom. The value of $-10{\cdot}2$ c/s is in the range observed for bicyclo-[2.2.1]-heptadienes. J for the NCH_2 protons in pyrrolizidine (XLIII) has recently been found[176] to be $-9{\cdot}75$ c/s. Protonation of the N causes a decrease in J to $-11{\cdot}50$ c/s. J is also rather negative (-11 c/s) in XLIV,[83,84,91] once again a structure with the N at a bridgehead, so that the electron pair bisects the CH_2.

Some values of J for CH_2 groups α to nitrogen come from work on pyrrolizidine alkaloids.[168,169] J (C5 methylene) is unusually positive ($-8{\cdot}6$ c/s) in retronecine (XLV) and rather negative ($-11{\cdot}2$ c/s) in heliotridine (XLVI). Culvenor has produced good evidence for an *exo*-buckled conformation XLVII for retronecine and has shown that heliotridine is, at room temperature, a rapidly interconverting mixture of the *exo* and *endo* buckled conformations XLVII and XLVIII. It has been suggested that the value of $-8{\cdot}6$ c/s for J in XLV is due to abnormal bond angles but it is much more likely to be a result of transfer of the N lone pair electrons into the antisymmetric MO since in XLVII there is a near parallel arrangement of the lone pair and the C5Hβ bond which does not exist in the *endo* buckled conformation XLVIII.

1-methoxymethyl-1,2-epoxypyrrolizidine (XLIX)[170] shows the much more negative value of J (C3 methylene) of -14 c/s compared to that in heliotridine and J in L is recorded as being -15 c/s.

J for the N—CH_2—O protons in oxazolidines vary between $-0{\cdot}7$ and $-5{\cdot}0$ c/s, the very positive values being observed for the *trans* fused ring 8-oxa-1-azabicylo [4.3.0] nonanes LI. The values of J for the related oxa-thia (LII, X = S) and oxa-aza (LII, X = NR) compound are all more positive for the *trans* fused conformation LII than for the *cis* fused ring compounds LIII. This has been discussed in detail elsewhere; it is interesting to note here the near parallel arrangement of N lone pair and an adjacent CH bond in the *trans* fused ring conformations LI and LII.

Values of J for N—CH_2—N protons in a series of substituted *syn* and *anti* perhydrodipyrido [1.2-*c*, 2'.1'-*e*] imidazoles range from $-3{\cdot}5$ to $-4{\cdot}0$ c/s for those compounds adopting the *trans trans* conformations LIV and LV. The *trans* 1H, 11b H 1-methyl *syn* compound was assigned the conformation LVI, since, *inter alia*, it possessed a J of $-8{\cdot}0$ c/s. The more negative J for this conformation than for conformation LIV is expected since in LVI the *cis* B:C ring junction places the N lone pair almost in a position to bisect the C6 methylene H—H internuclear axis. The very negative J of $-11{\cdot}5$ c/s observed for LVII has been discussed previously[167] and here both N lone pairs bisect the CH_2 group (cf. XLII).

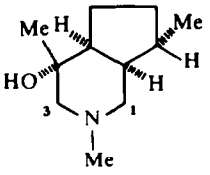
J for O—CH_2 protons in tetrahydrofurans is usually in the range $-8{\cdot}0$ to $-9{\cdot}0$ c/s. Table 4 shows compounds exhibiting rather positive (ca. $-6{\cdot}0$ c/s) or unusually negative ($-10{\cdot}0$ to $-11{\cdot}8$ c/s) values for this coupling constant. The not too dissimilar pair of compounds LVIII and LXVI exhibit the two ends of the range and presumably in LVIII we have a conformation permitting eclipsing of the O lone pairs and the adjacent CH_2 whereas in LXVI this geometry cannot be present, as must be the case in LX to LXVII. Models of LIX show clearly the eclipsing of the CH_2 bonds by both O lone pair orbitals accounting for the very positive value of $J = -6{\cdot}0$ c/s. Work is in progress on coupling constants in the tetrahydrofuran system.

J *in 3-membered ring compounds* (Table D). J in aziridines is normally in the range 0 to + 1 c/s. Exceptions to this range are shown by the N-chloroaziridine LXVIII with a J of $|2{\cdot}4|$ and LXIX with a J of $|2{\cdot}1|$. 3-Phenyl-1-azabicyclo [1.1.0] butane shows a J of $|2{\cdot}75|$,[193] and very surprisingly 1-aziridine-propionitrile a J of 6 c/s.[180]

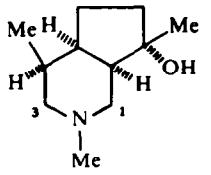
J *in acyclic compounds* (Table E). Numerous values of J in these systems appear in the literature and only a selection are shown in Table E. The J of $-12{\cdot}5$ c/s observed for the sulphoxide LXX has been interpreted in terms of the conformation shown, and the corresponding selenium compound LXXII shows a slightly more positive J ($-11{\cdot}3$ c/s). J in protonated formaldehyde (LXXI) is $+22{\cdot}2$ c/s, closer to that in the isoelectronic imines than to the value of +41 c/s for formaldehyde itself. J for the OCH_2 protons in the acyclic compounds LXXIII ($J = -9{\cdot}56$) and LXXIV ($J = -8{\cdot}79$ c/s) are more positive than in tetrahydropyrans indicating the presence of conformations with eclipsing of the O lone pairs and the adjacent CH bonds. A linear correlation of the geminal coupling constants of the $PhCH_2$-protons with the Hammet σ constant of the aromatic substituent in a series of benzyl tetrahydropyranyl ethers has been obtained.[125]

J *in cyclic compounds with ring size greater than 6-membered.* J for CH_2 groups in large ring compounds is shown in Table 5. These values of J are all interpretable in

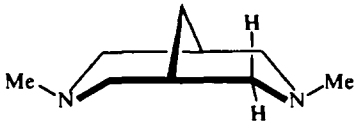
terms of either lone pair orbital overlap or the effect of an adjacent π bond, and require no special comment.



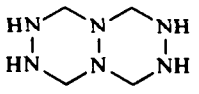
I[18]



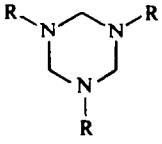
II[18]



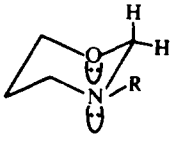
III[2]



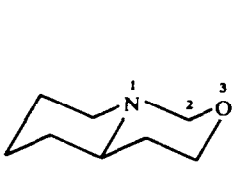
IV[7]



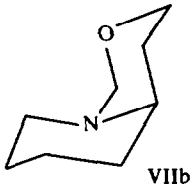
V[6]



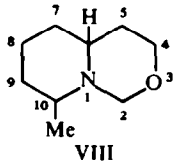
VI



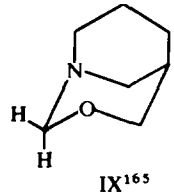
VIIa[161]



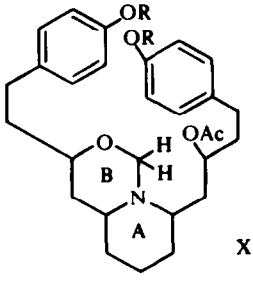
VIIb



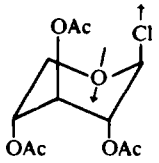
VIII



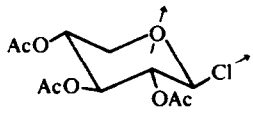
IX[165]



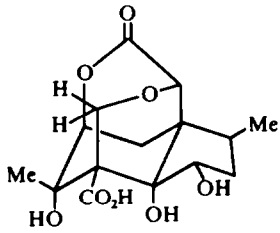
X[20]



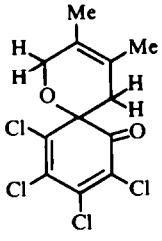
XXVIII



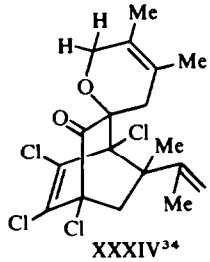
XXIX



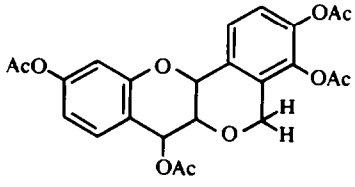
XXXII[149]



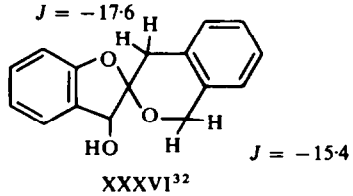
XXXIII[34]



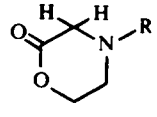
XXXIV[34]



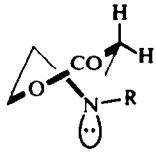
XXXV



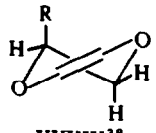
XXXVI[32]



XXXVII[97]

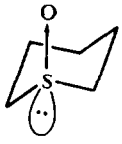


XXXVIII

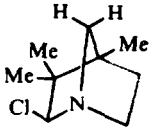


XXXIX[38]

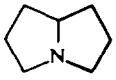
$J = -11{\cdot}3$ to $-12{\cdot}8$[77]
"equatorial" sulphoxides



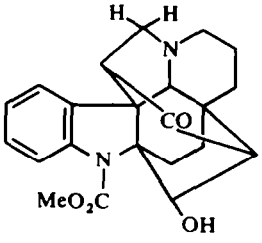
$J = -13{\cdot}8$ to $-15{\cdot}5$[77]
"axial" sulphoxides



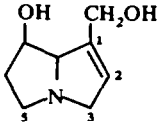
XLII[98]



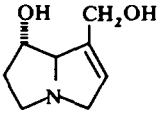
XLIII[176]



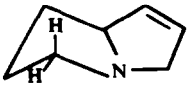
XLIV[83,84,91]



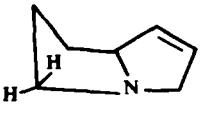
XLV[89]



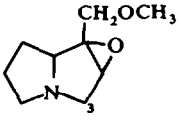
XLVI



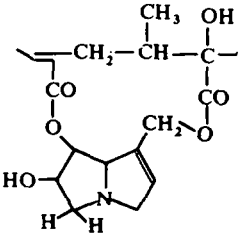
XLVII



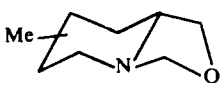
XLVIII



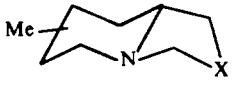
XLIX



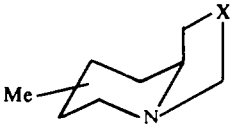
L[89]



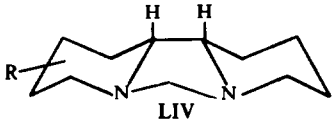
LI



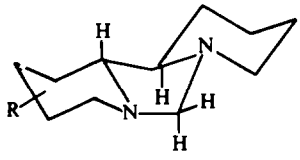
LII



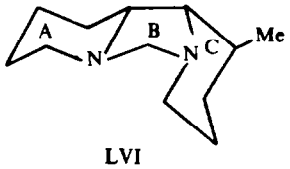
LIII



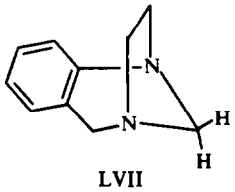
LIV



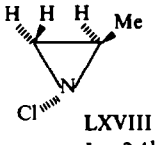
LV



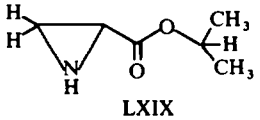
LVI



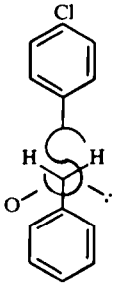
LVII



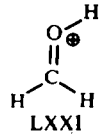
LXVIII
$J = 2{\cdot}4$[179]



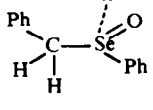
LXIX
$J = 2{\cdot}1$[155]



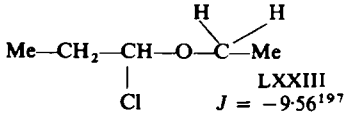
LXX
$J = -12{\cdot}5$[200]



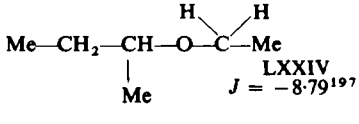
LXXI
$J = .22{\cdot}2$[199]



LXXII
$J = -11{\cdot}3$[198]



LXXIII
$J = -9{\cdot}56$[197]



LXXIV
$J = -8{\cdot}79$[197]

TABLE A. J IN 6-MEMBERED RINGS CONTAINING HETEROATOMS α TO THE CH_2 GROUP

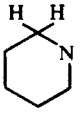
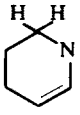
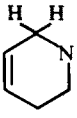
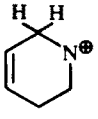
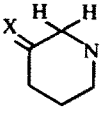
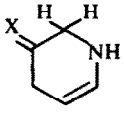
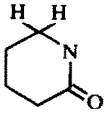
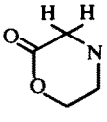
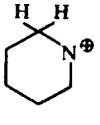
Ring system	$-J$	References
	9·0, 9·0, 10·2, 11·0, 11·0, 12·0 to 12·5 (5 examples) 13·0 (10 examples) 14·0 (2 examples)	2, 5, 9, 10, 14, 18 99, 146, 156
	11·0	16
	15·5 (3 examples) 16·0 (4 examples) 16·3 to 16·5 (3 examples) 17·0 (12 examples) 17·5 (2 examples)	8, 11, 12, 13, 17, 21, 177
	16·0	12
	14·0	15
	16·0	4
	12·5, 13·0	3, 146
	17·0–18·0 (10 examples)	97
	13·0	2

TABLE A—*continued*

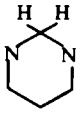
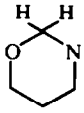
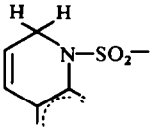
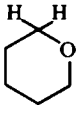
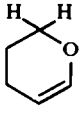
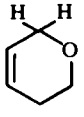
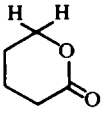
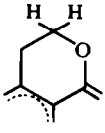
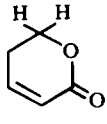
Ring system	$-J$	References
	8·9, 10·2, 11·9, 13·0	6, 7, 22
	7·0 to 8·0 (11 examples) 8·9 9·2 to 11·4 (11 examples)	20, 25, 52, 161, 162 178, 217
	17·0	152
	8·0 9·0 to 10·0 (16 examples) 10·1 to 11·0 (17 examples) 11·1 to 12·5 (42 examples) 12·6 to 13·5 (11 examples) 13·8, 14·0	69 19, 27, 28, 29, 33, 35, 42, 43, 45, 46, 47, 48, 50, 51, 58, 60, 61, 63, 66, 67, 70, 71, 73, 148, 217, 219 37
	10·6 to 11·5 (20 examples) 12·0 to 13·0 (10 examples)	26, 30, 31, 34, 36, 38, 44, 49, 56, 59, 62, 64, 68, 150
	13·0, 14·0, 15·4, 16·0 16·6.	32, 34, 57
	11·4 12·0 to 13·0 (4 examples) 13·5	39, 40, 65, 72, 148, 218
	11·0, 11·7	41
	10·0, 11·0, 11·0, 12·0	40, 53, 54, 55

TABLE A—*continued*

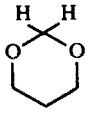
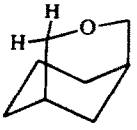
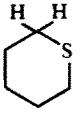
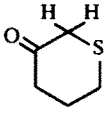
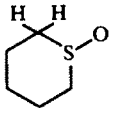
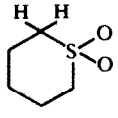
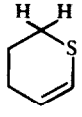
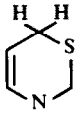
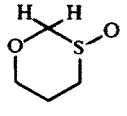
Ring system	$-J$	References
	6·0	51
	14·0	149
	13·0 to 13·5 (7 examples) 13·6 to 14·0 (5 examples) 14·1, 14·2	75, 77, 78, 79
	13·0	74
	11·3 to 14·1 (12 examples) 13·8 to 15·5 (8 examples)	76, 77, 79, 80
	13·8, 14·5	79, 80
	12·6, 12·8, 12·9, 13·0	81
	18·5 (3 examples) 19·0	153
	11·0	82

TABLE A—*continued*

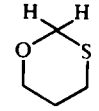
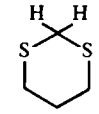
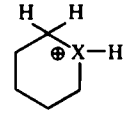
Ring system	$-J$	References
	11·1	24
	14·0	24
	X = S 15·0 X = Se 13·0 X = Te 13·5	216

TABLE B. J IN 5-MEMBERED RINGS CONTAINING HETEROATOMS α TO THE CH_2 GROUP

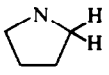
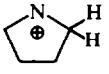
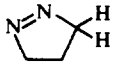
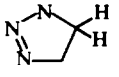
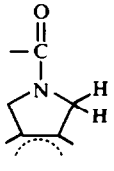
Ring system	$-J$	References
	8·6, 9·5, 9·5, 9·6, 9·75 10·0 (5 examples) 10·2, 10·5, 11·0 15·0	7, 83, 84, 86, 89, 91, 98, 168, 169, 170, 173, 176
	11·50	176
	16·8 to 19·6 (6 examples)	87, 88, 90, 95, 141
	9·65	92
	12·1 to 12·7 (4 examples)	96

TABLE B—*continued*

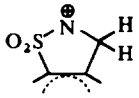
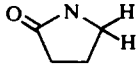
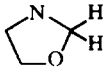
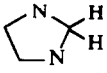
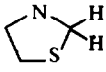
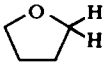
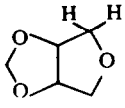
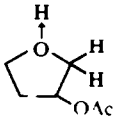
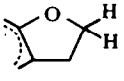
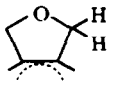
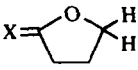
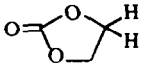
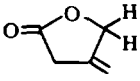
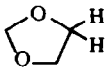
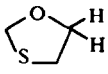
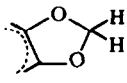
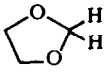
Ring system	$-J$	References
	15·0	85
	15·0	163
	0·7 to 5·0 (9 examples)	93, 144, 160
	3·4 to 3·8 (5 examples) 4·0 to 4·8 (11 examples) 5·7, 5·9, 6·5 8·0, 10·0	22, 157, 158, 159
	6·0 (4 examples) 6·25, 8·5, 9·0, 9·0	23
	6, 6·7, 6·9 7·0 to 8·0 (12 examples) 8·1 to 9·0 (12 examples) 9·5 10·0 to 10·5 (6 examples) 11·3	101, 103, 104, 106, 110 111, 117, 118, 118, 121 122, 123, 128, 133, 139, 147, 174, 175 132
	11·8, 11·8	105
	11·0	108, 114
	8·0, 8·5	102

TABLE B—*continued*

Ring system	$-J$	References
	14·0	112
	8·8 9·0 to 9·9 (6 examples) 10·0 to 12·0 (15 examples)	73, 100, 120, 126, 134, 143 151
	8·64	142
	13·0 (4 examples)	134, 220
	18·0	109
	7·0 to 9·0 (28 examples)	113, 115, 116, 124, 130, 131, 132, 145
	8·57 to 9·79 (11 examples)	107
	1·0	127
	Ca. 1 (2 examples)	140

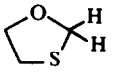
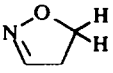
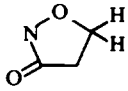
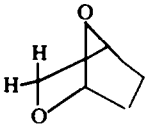
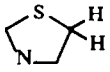
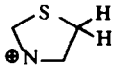
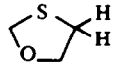
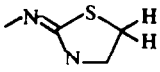
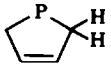
Ring system	$-J$	References
	5·2, 5·2	24
	8·1, 9·8, 9·4	129
	8·5, 8·6	129
	5·4 (2 examples) 5·8 6·0 (3 examples)	94
	11·5, 12·0	135, 136
	13·8	136
	9·0 to 11·24 (13 examples)	107, 138
	11·5, 11·9, 12·0 (2 examples)	137
	Ca. 15·5	154

TABLE B—*continued*

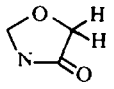
Ring system	$-J$	References
	13·0	146

TABLE C. J IN 4-MEMBERED RINGS CONTAINING HETEROATOMS α TO THE CH_2 GROUP

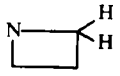
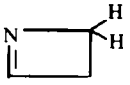
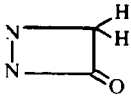
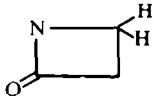
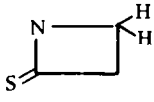
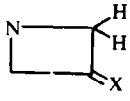
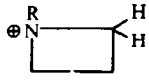
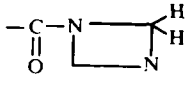
Ring system	$-J$	References
	6·5	194
	9·0 10·0	191
	13·0 13·5 (3 examples) 14·0 (2 examples)	192
	5·2 5·6 5·7 (2 examples)	191
	6·9 (2 examples) 7·0 7·2 (2 examples)	191
	16·0 17·0, 17·2, 17·3 17·5 (2 examples)	141, 189, 190
	3·0	99
	9·6	178

TABLE C—*continued*

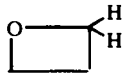
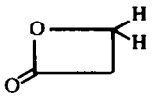
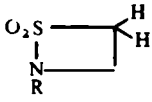
Ring system	$-J$	References
	9·5	195
	7·0 (4 examples)	148, 149
	14·0	196

TABLE D. J IN 3-MEMBERED RINGS CONTAINING HETEROATOMS

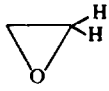
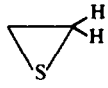
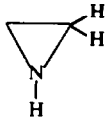
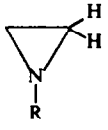
Ring system	J	References
	−5·0 (3 examples) −5·5 −5·66 −6·0	142, 186, 187, 188
	−1·38	142
	0 0·9 (3 examples) 2·1	155, 180, 181, 185
	0 (3 examples) $\leqslant \pm 0{\cdot}4$ 1·07 to 1·96 (8 examples) 2·3, 2·4, 3·3, 2·7, 2·75 $6 \pm 1, 6 \pm 1$	182, 184, 185 222 183 179, 185, 193 180

TABLE E. J IN ACYCLIC SYSTEMS CONTAINING HETEROATOMS α TO THE CH_2 GROUP

System	$-J$	References
—N—CH_2—	14·2, 14·0	204
—N—CH_2—C=	14·0 to 15·0 (9 examples) 15·5, 15·5, 15·6, 16·0	209, 223, 224, 225, 231

TABLE E—*continued*

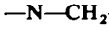
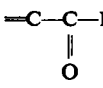
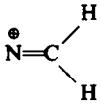
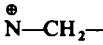
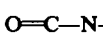
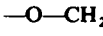
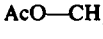
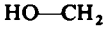
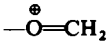
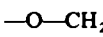
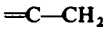
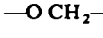
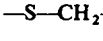
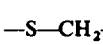
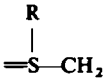
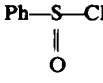
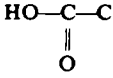
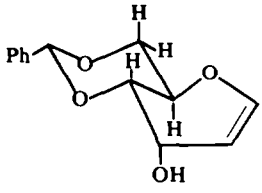
	−J	References
	17·0 (4 examples) 18·0	207, 209
	13·3 to 13·5 (5 examples)	228
	7·5	229
	13·5	230
	10·5 (3 examples)	178
	9·4, 9·56, 8·79 9·9, 11·3, 11·6, 11·6, 11·7 12·0, 12·5	197, 203, 205, 226
	11·0, 12·0, 12·0	233, 236
	11·0, 11·5	238
	22·2 (positive)	199
	11·0	202
	13·5 to 14·0	153
	12·0	237
	15·3 to 15·9 (3 examples) 13·6	210 206
	14·0	201
	12·0 (4 examples)	227
	12·5	200
	14·5 to 15·0	208

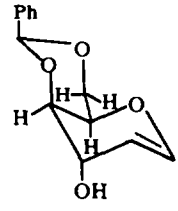
TABLE E—*continued*

	−J	References
Ph—Se(=O)—CH_2—Ph	11·3	198
Cl—CH_2—	12·0, 13·0, 13·0	232, 234
Br—CH_2—	12·0, 12·0	234
Cl—CH_2—C=	10·0	235

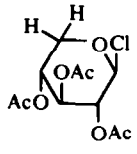
TABLE 1



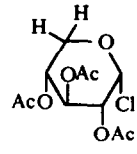
XI
$J = -10{\cdot}0$[66]



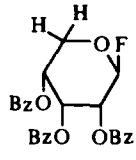
XII
$J = -12{\cdot}5$[66]



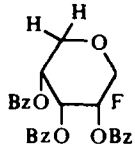
XIII
$J = -12{\cdot}9$[60]



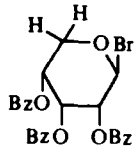
XIV
$J = -11{\cdot}4$[60]



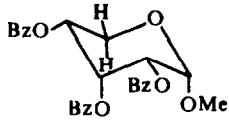
XV
$J = -13{\cdot}5$[37]



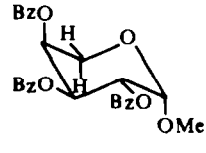
XVI
$J = -10{\cdot}9$[37]



XVII
$J = -13{\cdot}8$[37]

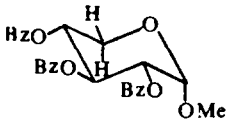


XVIII
$J = -12{\cdot}0$[48]

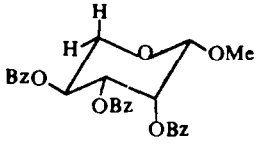


XIX
$J = -13{\cdot}0$[48]

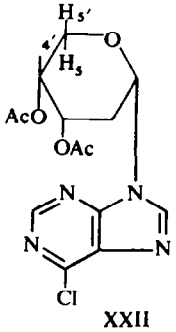
TABLE 1—*continued*



XX
$J = -9{\cdot}0$[48]

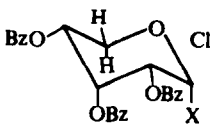


XXI
$J = -13{\cdot}0$[48]

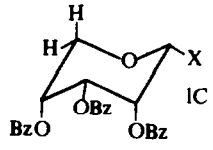


XXII
$J = -8{\cdot}0 \pm 0{\cdot}1$[69]

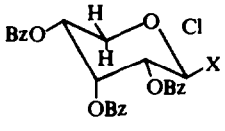
TABLE 2



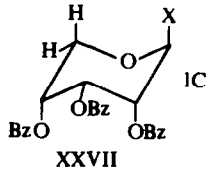
XXIV



XXV



XXVI



XXVII

TABLE 3

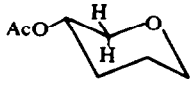
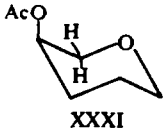
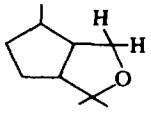
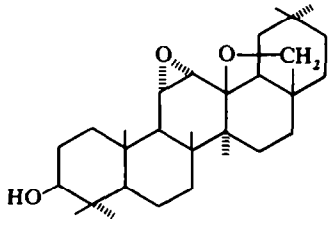
	$-J$	References
 XXX	11·7 to 12·0	27
	12·0	67
	11·0	71
	11·4	60
	10·7 (2 examples)	66
 XXXI	12·2 to 12·6	27
	12·5	35
	12·4, 12·5	43
	12·9	60
	11·8, 12·3	66

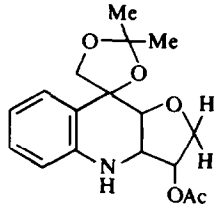
TABLE 4



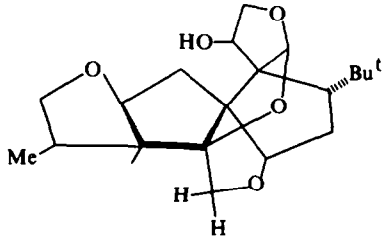
LVIII
$J = -6{\cdot}7$[133]



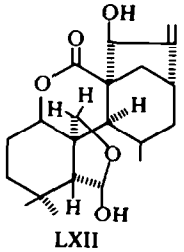
LIX
$J = -6{\cdot}0$[106]



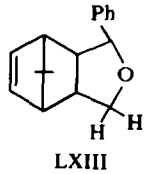
LX
$J = -11{\cdot}3$[132]



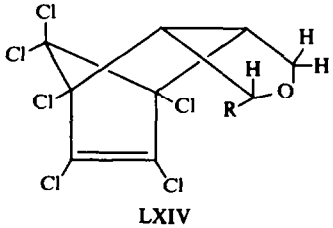
LXI
$J = -10{\cdot}5$[128]



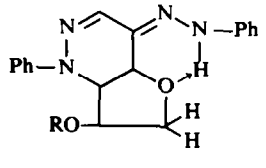
LXII
$J = -10{\cdot}0$[110]



LXIII
$J = -10{\cdot}5$[111]

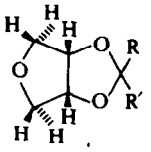


LXIV
$J = -10{\cdot}3$ to $-10{\cdot}4$[123]



LXV
$J = -11{\cdot}0$[108,114]

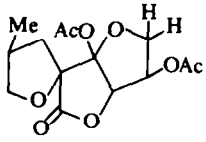
TABLE 4—*continued*



LXVI[105]

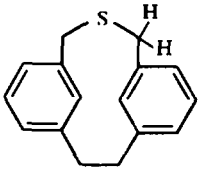
R = CF_3, R′ = OH
R = OH, R′ = CF_3

} $J = -11{\cdot}8$ for both isomers

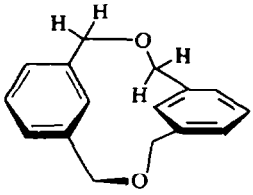


LXVII
$J = -10{\cdot}6$[172]

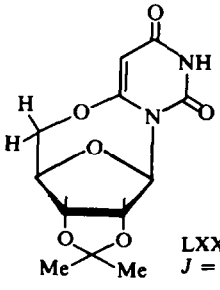
TABLE 5



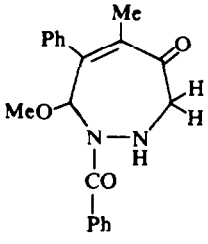
LXXV
$J = -13{\cdot}4$[215]



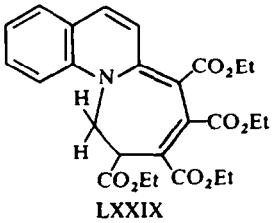
LXXVI
$J = -11{\cdot}3$[214]



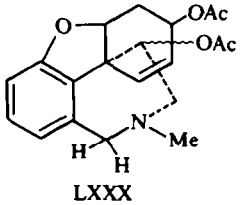
LXXVII
$J = -13{\cdot}0$[213]



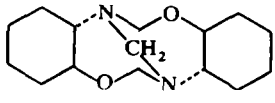
LXXVIII
$J = 18{\cdot}0$[212]



LXXIX
$J = -9{\cdot}2$[211]

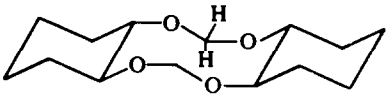


LXXX
$J = -16{\cdot}0$[221]



LXXXI
$J = -11{\cdot}6$[144]

TABLE 5 —*continued*



LXXXII
$J = -7.0^{140}$

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