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GEMINAL COUPLING CONSTANTS IN METHYLENE GROUPS

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Abstract—Coupling constants between protons in CH_2 groups cover the range from +42 to −22·3 c/s. The factors that influence the coupling constant are reviewed and ranges of values are listed for various structural types of CH_2 groups, especially in cyclic compounds.

OVER the last few years we have accumulated almost a thousand geminal coupling constants, both from our own measurements and from published values. We should now like to review some of the broad trends in variation of J with the molecular environment of the CH_2 group: later papers will discuss more restricted classes of compounds in greater detail. Since the value of J is sensitive to the conformation of adjacent groups and the strain in adjacent bonds, we have paid most attention to CH_2 groups in cyclic compounds, where the molecules are rigid or of known conformation. We believe this summary will help organic chemists in the interpretation of PMR spectra of compounds containing methylene groups.*

In an important paper that appeared while this review was being written Pople and Bothner-By[1] outlined a MO treatment of coupling between protons in CH_2 groups, which justified some of the regularities we have observed and expressed more elegantly some of our interpretations. By considering the four possible transitions to triplet excited states of a CH_2 group they showed that withdrawal of electrons from orbitals symmetric to the plane at right-angles to the H—H axis (inductive effect of an electronegative substituent) should lead to a positive change in coupling constant (ΔJ), whereas withdrawal of electrons from orbitals antisymmetric between the H atoms (hyperconjugation) should produce a negative ΔJ. Supply of electrons, of course, leads to opposite results.†

Olefinic methylene groups

In olefinic hydrocarbons and natural products such as terpenes J is small and positive (ca. 2 c/s). Taking the value for ethylene (Table A, No. 7) as the norm, the largest ΔJ is produced by substitution of O for CH_2. As explained by Pople and

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* Tables A–F have been compiled from lists of published and unpublished values collected by authors, who have made no special effort to cover the literature exhaustively.

† Throughout this paper "J" refers to *geminal coupling constants* only. Since J can be positive or negative an increase in numerical value of J can represent either an increase (ΔJ + ve) or decrease (ΔJ − ve) in absolute value. There is therefore danger of confusion over qualitative descriptions of changes in J produced by variation in molecular structure. We will invariably use phrases like "increase in J", "larger J" or "higher value of J" to mean that J becomes more positive (i.e. ΔJ + ve). Equally, "small" means relatively negative in the range expected, and "large" relatively positive. Thus −15 c/s, for example, will be said to be a smaller coupling constant than −5 c/s, even when the signs have been inferred and not actually determined by experiment.

Bothner-By,[1] the very large positive J in formaldehyde (A, 1) is caused by the removal of electrons from the symmetric CH_2 orbital by the inductive effect of the electronegative oxygen atom, combined with supply of electrons to the antisymmetric orbital by overlap with the non-bonding electrons on the oxygen atom. A similar argument justifies the large positive J in the nitrogen analogues (A, 2–4). The other extremes of J probably occur in the methylene compounds with cumulated double bonds: in dimethylallene (A, 18) and even more in ketene (A, 19) electrons are removed from the antisymmetric CH_2 orbital by strong hyperconjugation[1,2] with the second double bond, producing the large negative ΔJ.

According to theory,[1] substitution of an electronegative group on ethylene withdraws electrons mainly from the antisymmetric CH_2 orbital, which should produce a negative ΔJ. In fact, some years ago Banwell and Sheppard[3] showed that this trend was followed in a series of vinyl compounds, J being roughly proportional to the electronegativity of the substituent. Some representative examples are quoted in the Table (A, 5–17).

J for CH_2 groups in π-allyl complexes of transition metals is very near zero (examples covering Mo, Mn, Fe, Co, Ni, Pd, Pt).[4]

Tetrahedral CH_2 *groups*

By removing electrons inductively from the symmetric CH_2 orbital, substitution of electronegative groups in methane* (and α-substitution in methyl compounds) causes an increase in J, as demonstrated by Bernstein and Sheppard[6] (Table B, 1–6). Substitution by a saturated hydrocarbon radical hardly affects J: for example, in 42 examples containing the group $-\underset{|}{\overset{|}{C}}-CH_2OH$ or $-\underset{|}{\overset{|}{C}}-CH_2OAc$ J varies only from $-10{\cdot}2$ to -13 c/s (cf. B, 2).

In rigid molecules β-substitution by electronegative groups generally produces an opposite (negative) ΔJ, as discussed above for ethylene. This has been illustrated in a series of 1,1-dichlorocyclopropyl compounds,[7] epoxides,[7] bicycloheptenes,[8] and other less extensive series. However, the value of ΔJ produced by a particular β-substituent, X, depends on the projected angle between the CH_2 group and the

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* The almost linear correlation of J for substituted silanes[5] with values for the equivalent substituted methanes[6] shows that J for SiH_4 is roughly five times as sensitive to α-substituents as J for CH_4. It also suggests that J for silane itself (2·75 c/s) and all its saturated derivatives is positive.

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

[2] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.* **83**, 4726 (1961); **85**, 1899 (1963); *J. Chem. Phys.* **36**, 2054 (1962); R. A. Niedrich, D. M. Grant and M. Barfield, *Ibid.* **42**, 3733 (1965).

[3] C. N. Banwell and N. Sheppard, *Mol. Phys.* **3**, 351 (1960); *Discussions Faraday Soc.* **34**, 115 (1962).

[4] H. C. Dehm and J. C. W. Chien, *J. Amer. Chem. Soc.* **82**, 4429 (1960); *Chem. & Ind.* 745 (1961); D. W. Moore, H. B. Jonassen, T. B. Joyner and A. J. Bertrand, *Ibid.* 1304 (1960); B. L. Shaw and N. Sheppard, *Ibid.* 517 (1961); W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Amer. Chem. Soc.* **83**, 1601 (1961); M. Cousins and M. L. H. Green, *J. Chem. Soc.*889 (1963).

[5] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.* **36**, 2628 (1962).

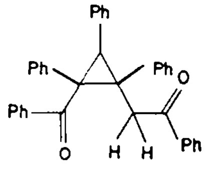
[6] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.* **37**, 3012 (1962).

[7] K. L. Williamson, C. A. Langford and C. R. Nicholson, *J. Amer. Chem. Soc.* **86**, 762 (1964).

[8] K. L. Williamson, *J. Amer. Chem. Soc.* **85**, 516 (1963).

C—X bond, and on the C—C—X bond angles and lengths, so no single set of values for ΔJ can be derived for β-substituents; this is borne out for example by the very different variation of ΔJ with electronegativity of X in the series just cited. For tetrahedral CH_2 groups (i.e. excluding those in olefins and small rings) β-substitution seems to have a relatively small effect on J, so in the summarizing tables that follow no attempt has been made to derive parameters for the nature and orientation of β-substituents. In any case, most of the values have been taken from publications primarily dealing with structural chemistry rather than spectroscopy: although experimental errors are seldom quoted they are probably often $\pm 0{\cdot}5$ c/s and occasionally even $\pm 1{\cdot}0$ c/s.[*] The finer points will be elucidated by accurate measurements on series of closely related compounds.

The largest ΔJ is produced by hyperconjugation of the CH_2 group with an α π-bond,[2] which removes electrons from the antisymmetric CH_2 orbital. For a freely rotating methyl group an adjacent π-bond produces a ΔJ of about $-2{\cdot}0$ c/s (B, 8–12), the effect being additive[2] up to the maximum possible number of four increments (B, 14).



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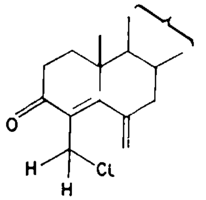

II

However, theory requires[1,2] and the cyclic methylene compounds of fixed conformation discussed below confirm that ΔJ varies with the angle between the CH_2 group and the π-system. The maximum ΔJ occurs when the HH axis of the CH_2 group is parallel to the p orbital of the α sp^2 carbon atom,[1,2] and for a molecule locked in such a conformation one might expect ΔJ of three times that in the methyl compounds, or about -6 c/s. Most acyclic methylene compounds show a more positive J than this minimum, because the population of extreme conformers is not large enough: benzyl derivatives, for illustration, have $J = -12{\cdot}5$ to -14 c/s (16 examples). An example of a molecule that does achieve the minimum ($J = -18{\cdot}6$ c/s) is the benzoyl derivative[10] (I), in which a conformation with the plane of the carbonyl group bisecting the angle between the CH bonds of the methylene group seems very reasonable. The least change in J comes when the HH axis is parallel[1] (or nearly parallel[2]) with the plane of the double bond. The chloromethyl steroid[11] (II) would be expected to adopt such a conformation, to keep the chlorine atom as far as possible from the planar dienone system. In fact, J for II is slightly more positive ($-10{\cdot}2$ c/s) than that for methyl chloride (B, 4).

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[*] In addition, the spectra have been measured in various solvents. Even in rigid molecules, not likely to change their conformations, J can vary significantly with change in solvent.[9]

[9] S. L. Smith and R. H. Cox, *J. Mol. Spec.* **16**, 216 (1965), and Refs. given there.

[10] G. R. Evanega, W. Bergmann and J. English, *J. Org. Chem.* **27**, 13 (1962).

[11] J. Fried, A. N. Nutile and G. E. Arth, *J. Org. Chem.* **26**, 976 (1961).

Cyclic methylene groups

General trends. Tables C to G summarize the values for J for methylene groups in rings, arranged in increasing size. The particular examples may contain double bonds or hetero-atoms in place of sp^3 C anywhere in the ring except at the α position, where the atoms are explicitly shown. They may include the parent compound, simple derivatives, or complex structures with many substituents. Double bonds include benzo derivatives. In most cases the sign of J has not been determined: it has then been given by analogy with similar compounds where the sign is known relative to ^{13}C—H or vicinal H—C—C—H coupling constants.

Although β and more remote substituents may play an important part in individual molecules, the broad trends in variation of J with structure can be understood in terms of four major factors: (a) ring-strain and hybridization of the C of the CH_2 group, (b) hyperconjugation of the C—H bonds with α π-bonds, (c) overlap of the C—H bonds with electron-pairs on α hetero-atoms, (d) inductive effect of α-substituents (already illustrated above).

(a) *Hybridization.* Since H—C—H angles are seldom accurately known, we focus attention on the complimentary X—CH_2—Y angles. The smaller the X—CH_2—Y angle, the greater the s character in the CH bonds and the more positive the coupling constant

CH_2 groups in cyclohexanes and cyclopentanes with no polar or bulky substituents near the CH_2 all have $J = -12$ to -13 c/s, hardly changed from the value in methane. As an example of a methylene group with a large C—CH_2—C angle we chose the tetramethylcyclohexanone (III) in which, in the crystal,[12] the angle is enlarged to about 120°. J was (—)14·7 ± 0·2 c/s in deuteriochloroform solution.

In bicyclo[2,2,1]heptane, heptene and heptadiene the C—CH_2—C angle on the [1] bridge has been reduced towards 90°,[13–15] and J has already begun to increase conspicuously: *exo*-epoxybicyclo[2,2,1]heptane[16] has $J = -9{\cdot}5$ c/s, benzobicyclo-[2,2,1]heptene[17] (A) $J = -8{\cdot}7$ c/s, bicyclo[2,2,1]heptene[17] (B) $J = -8{\cdot}2$ c/s, and benzobicyclo[2,2,1]heptadiene[17] $J = -7{\cdot}2$ c/s, the progressive shortening of the [2] bridges* coinciding with the increase in J for the CH_2 in the [1] bridge. [The rather wide range of J quoted in Table E is due to the inclusion of many examples with electronegative substituents and of polycyclic cage compounds that allow a larger C—CH_2—C angle. For example, the cyano groups in the tetracyano derivatives of A and B, above, lower J by $-3{\cdot}3$ c/s to $-12{\cdot}0$ c/s in the indene-tetracyanoethylene adduct[18] and $-11{\cdot}5$ c/s in the cyclopentadiene-tetracyanoethylene adduct.[18]]

* The effect of shortening the bond length is opposed by the increase in the preferred C═C—C bond angle, so that the net effect could be determined only by detailed calculation. Introduction of double bonds will also alter the electron distribution in other ways: for example, hyperconjugation between the C—CH_2 bonds and the double bond might also produce a positive ΔJ by removing electrons from the symmetric CH_2 orbital.

[12] L. C. G. Goaman and D. M. Grant, *Tetrahedron* **19**, 1531 (1963); *Acta Cryst.* **17**, 1604 (1964).

[13] C. F. Wilcox, *J. Amer. Chem. Soc.* **82**, 414 (1960); A. I. Kitaygorodsky, *Tetrahedron* **14**, 230 (1961).

[14] G. Ferguson, C. J. Fritchie, J. M. Robertson and G. A. Sim, *J. Chem. Soc.* 1976 (1961); D. A. Brueckner, T. A. Hamor, J. M. Robertson and G. A. Sim, *Ibid.* 799 (1962); A. C. MacDonald and J. Trotter, *Acta Cryst.* **18**, 243, 456 (1965).

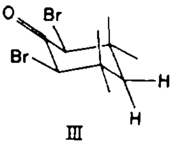
[15] H. G. Norment, *Acta Cryst.* **18**, 627 (1965).

[16] J. E. Franz, C. Osuch and M. W. Dietrich, *J. Org. Chem.* **29**, 2922 (1964).

[17] K. Tori, R. Muneyuki and H. Tanida, *Canad. J. Chem.* **41**, 3142 (1963).

[18] P. Brown, Ph.D. Thesis, Southampton (1964).

Conversely, partial relaxation of the angle in the bicyclo[3,2,1]octene derivatives IV[19] (two isomers) and V[20] allows a decrease in J towards the value for an undistorted tetrahedral CH_2 group, to −11 and −10·7 c/s respectively.



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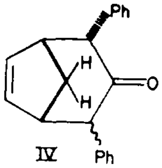

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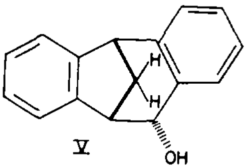

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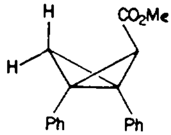

VI

Rather surprisingly, the cyclobutanes* for which there are values (D, 1) have an almost unchanged J, but as soon as the ring is bent by the ethane bridge (and the perturbing substituents are left off) in bicyclo[2,1,1]hexane[23] (C—CH_2—C angle ca. 85° [13]) J rises further to −5·4 c/s, and reaches even −3·1 c/s in tricyclopentane[24] (D, 12), about the same value as in cyclopropane. At last in the bicyclobutane[25] (VI) J = −1·7 c/s (sign assumed).

In cyclopropane itself it has been estimated[26] that J should be −3·0 c/s. Tetra-alkyl substituted cyclopropanes, which occur in many natural steroids and terpenoids, usually have J = −4 to −5·5 c/s. J in cyclopropanes is unusually sensitive to electronegative substituents on the ring, and J in mono-substituted 1,1-dichlorocyclopropanes has been shown[7] to vary linearly with the electronegativity of the substituent. The extreme ends of the range recorded (C, 1) refer to 1,1-dichloro-2-acetoxycyclopropane and cyclopropyl-lithium.

If the recent correlation[26] of J in three-membered rings $(CH_2)_2X$ with the electronegativity of X is applied to the ethylene-immonium cation, J in the two tetrasubstituted derivatives (C, 2) should be positive.

Values of J have been plotted against C—CH_2—C angles in Fig. 1. The angle plotted for point 4 is that for bicyclo[2,2,1]heptadiene,[22] which may be very slightly smaller (but see footnote*). While other factors no doubt play a part, especially in

* Cyclobutane ($J_{C^{13}-H}$ = 134 c/s; C—CH_2—C = 89·3°) and bicyclo[2,2,1]heptadiene ($J_{C^{13}-H}$ = 135 c/s; C—CH_2—C = 96·7°) also deviate somewhat from Foote's[21] inverse linear correlation of C^{13}—H coupling constants with C—CH_2—C angle. Assumption of a slightly smaller angle (cf. Ref. 13–15) at the [1] bridge of bicycloheptadiene than that[22] accepted by Foote would bring its point onto the line, leaving cyclobutane the only significant deviation.

[19] M. Nye, Ph.D. Thesis, Southampton (1963).

[20] A. R. Katritzky and B. Wallis, *Chem & Ind.* 2025 (1964).

[21] C. S. Foote, *Tetrahedron Letters* 579 (1963); see also K. Mislow, *Ibid.* 1415 (1964).

[22] V. Schomaker quoted by C. F. Wilcox, S. Winstein and W. G. McMillan, *J. Amer. Chem. Soc.* **82**, 5450 (1960).

[23] K. B. Wiberg, B. R. Lowry and B. J. Nist, *J. Amer. Chem. Soc.* **84**, 1594 (1962).

[24] G. L. Closs and R. B. Larrabee, *Tetrahedron Letters* 287 (1965).

[25] S. Masamune, *Tetrahedron Letters* 945 (1965).

[26] S. L. Manatt, D. D. Elleman and S. J. Brois, *J. Amer. Chem. Soc.* **87**, 2220 (1965).

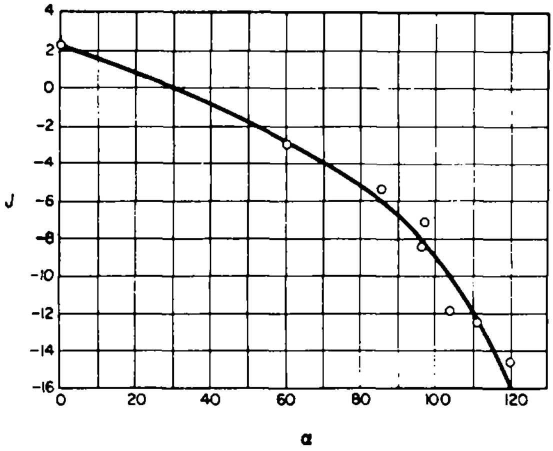

Fig. 1. Variations of J with C—CH$_2$—C angle.

No.	Structure	α[a]	J[b]	Refs.
1	Ethylene	0	+2·3	110
2	Cyclopropane	60	−3·0	26
3	Bicyclo[2,1,1]hexane (6-CH$_2$)	85	−5·4	13, 23
4	Benzo-bicyclo[2,2,1]heptadiene (7-CH$_2$)	97	−7·2	17, 22
5	exo-1,2-Diphenylbicyclo[2,2,1]heptene (7-CH$_2$)	96	−8·5	14, 175
6	2-Methyl-bicyclo[2,2,1]heptane-2 *exo*-carboxylic acid (3-CH$_2$)	104	−12·0	13–15, 218
7	Cyclohexane-d$_{11}$	111·5	−12·6	41, 55
8	*Cis*-2,6-dibromo-3,3,5,5-tetramethyl-cyclohexanone	120	−14·7	12

[a] C—CH$_2$—C angle in degrees.
[b] Geminal coupling constant in c/s.

compounds 4, 5, 6 and 8*, Fig. 1. confirms that hybridization and bond angles dominate the series.

Although the consequences of the upper part of the curve indicated in Fig. 1 are already widely known, if only from the conspicuous example of cyclopropane, the implications of the lower part do not seem to have been appreciated. Because less highly substituted structures incorporating C—CH$_2$—C groups usually give PMR spectra too complex for simple extraction of J, in practice J tends to be visible only in spectra of compounds R$_3$CCH$_2$CR$_3$ and R$_3$CCH$_2$CHCR$_2$ (AB and ABX systems). These are the very compounds in which repulsion between the R groups may splay out the C—CH$_2$—C angle. The enlarged angle is often an important factor determining J in such structures in acyclic compounds,† and in rings of six, five or even four members.

Compound III has already been mentioned. Among five-membered rings, X-ray analysis[12] reveals a very similar enlargement of the C—CH$_2$—C angle (to 121°) in the tetramethylcyclopentanedione (VII). The value of J is not known here, but the

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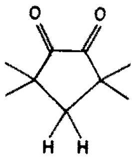
* In particular, allowance of a small negative ΔJ for the carboxylic acid group in 6 would raise the point more onto the general trend.

† In unsubstituted n-paraffins the angle is only slightly greater than tetrahedral (112–113°) [R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* **81**, 4765 (1959); D. R. Lide, *J. Chem. Phys.* **33**, 1514 (1960); N. Norman and H. Mathisen, *Acta Chem. Scand.* **18**, 353 (1964)].

large negative values for the cyclopentenes[27] VIII, R = H or Ph (J = −15·0 c/s) and the cyclopentane[28] IX (J = −15·0 c/s) owe more to enlargement of the angle than to the inductive effect of substituents. The surprisingly large negative values of J in the cyclobutanes X (R = Cl or Br,[29] J = −13: R = I,[30] J = −15 c/s) may also be partly due to increase in the angle.*

From the trend in Fig. 1 cyclobutane itself would be expected to have J = −6 to −8 c/s. Unfortunately, the value for the hydrocarbon or any simple derivative is not known: all the derivatives for which J is available carry at least four substituents and have a much more negative J (D, 1). Sensitivity to the inductive effect of 2-substituents increases in the order cyclopentane < cyclopropane < ethylene. Even if cyclobutane comes between cyclopentane and cyclopropane in this series it seems rather unlikely that the inductive effect of substituents can be blamed for all the decrease in J, if the parent hydrocarbon is assumed to have J = ca. −7 c/s. Some further negative contribution to J might be made by enlargement of the C—CH$_2$—C angle in some cases (e.g. X), but cannot be a major factor. At present it seems more likely that for some reason cyclobutane has a smaller J than expected, perhaps nearer −10 c/s.

Since the breakdown of the early correlation[31] of J with H—C—H angle and its valence-bond interpretation, there seems to have been no clear demonstration of dependance of one on the other. The rough correlation of J with C—CH$_2$—C angle in Fig. 1 would imply such a relationship, if the complimentary angles C—CH$_2$—C and H—C—H were interdependent. There are few cyclic molecules for which both J and the angle H—C—H are known.



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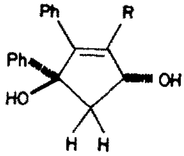

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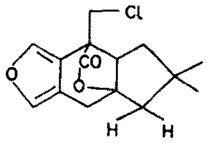

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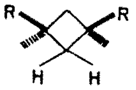

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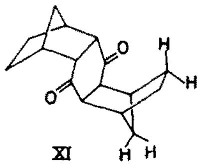

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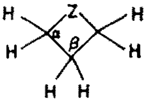

XII

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* *Note added in proof:* Perdeuteriocyclo-octane-1,1-h_2 is an interesting case, with J = (−) 14·3 c/s [F. A. L. Aner and M. S. Jacques, *J. Amer. Chem. Soc.* **88**, 2585 (1966)].

[27] P. Bladon and P. L. Pauson, personal communication.

[28] J. J. Dugan, P. de Mayo, M. Nisbet and M. Anchel, *J. Amer. Chem. Soc.* **87**, 2768 (1965), and personal communication.

[29] K. Griesbaum, W. Naegele and G. G. Wanless, *J. Amer. Chem. Soc.* **87**, 3151 (1965).

[30] W. von E. Doering and J. F. Coburn, *Tetrahedron Letters* 991 (1965).

[31] H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.* **31**, 1278 (1959).

The crystal structure of the diketone (XI), which has just been published,[15] is particularly interesting because the hydrogen atoms have been located as well as carbon and oxygen, although their positions are, of course, subject to a relatively large error. The endocyclic angle at C-7 is 96·48 ± 0·64° and the complimentary 7 H—C—H angle is 112·5 ± 1·8°: thus the expected increase in the latter is detectable. The corresponding angles at C-2 are 104·43 ± 0·74° and 108·9 ± 2·0°, so any distortion of the 2 H—C—H angle is within the error of measurement. From analogous compounds, one would expect J of about −9 c/s for the 7-CH_2 and −12 c/s for the 2-CH_2.

Table 1. Bond angles in four-membered rings (XII)

Z	$Z—C_\alpha—C_\beta$	$H—C_\alpha—H$	$C_\alpha—C_\beta—C_{\alpha'}$	$H—C_\beta—H$
CHBr[32]		108°44′	88°06′	110°44′
C=O[33]	90°42′	112°27′	87°58′	112°56′
O[34]	91°44′	110°18′	84°33′	110°44′

Accurate dimensions of the three key compounds (XII) have been measured by microwave spectroscopy.[32–34] The bond angles, which are given in Table 1, show no obvious general correlation. It is striking that the α H—C—H angle in cyclobutyl bromide in particular is actually smaller than tetrahedral. The apparent deviation of cyclobutane from the trend in Fig. 1 may possibly be due to a peculiarity of the system, and its failure to open the CH_2 angles. There seems to be no general relationship of X—CH_2—Y angles to the H—C—H angles. More determinations of CH_2 angles and coupling constants in cyclic compounds are most desirable: values of J for simple cyclobutanes are also badly needed.

The H—C—H angles in the three-membered rings of cyclopropane,[35] ethylene oxide,[36] sulphide[36] and imine[37] are all about 116·7°, and slightly smaller in cyclopropyl chloride[38] and cyanide.[38] In the extreme case of diazirine,[39] with the angle N—CH_2—N 49°, the angle H—C—H is still 117 ± 2°.

(b) *Hyperconjugation.* Barfield and Grant's theoretical curve[2] connecting the π-electron contribution (ΔJ) to the coupling constant with the dihedral angle (θ) between the methylene group and the p-orbital of the adjacent sp^2 carbon atom is reproduced in Fig. 2a. The actual value of J (neglecting all other contributions) is

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[32] W. G. Rothchild and B. P. Dailey, *J. Chem. Phys.* **36**, 2931 (1962).

[33] A. Bauder, F. Tank and H. H. Gunthard, *Helv. Chem. Acta* **46**, 1453 (1963).

[34] S. I. Chan, J. Zinn, J. Fernandez and W. D. Gwinn, *J. Chem. Phys.* **33**, 1634 (1960); **34**, 1319 (1961).

[35] H. H. Gunthard, R. C. Lord and T. K. McCuffin, *J. Chem. Phys.* **25**, 768 (1956); O. Bastiansen, F. N. Fritsch and K. Hedberg, *Acta. Cryst.* **17**, 538 (1964).

[36] G. L. Cunningham, A. W. Boyd, R. J. Myers, W. D. Gwinn and W. I. Le Van, *J. Chem. Phys.* **19**, 676 (1951).

[37] T. E. Turner, V. C. Fiora and W. M. Kendrick, *J. Chem. Phys.* **23**, 1966 (1955); M. Igarashi, *Bull. Chem. Soc. Japan* **34**, 369 (1961).

[38] J. P. Friend and B. P. Dailey, *J. Chem. Phys.* **29**, 577 (1958); but see R. H. Schwendeman, G. D. Jacobs and T. M. Krigas, *Ibid.*, **40**, 1022 (1964), who give 116·2° for cyclopropyl chloride.

[39] L. Pierce and V. Dobyns, *J. Amer. Chem. Soc.* **84**, 2651 (1962); R. Ettinger, *J. Chem. Phys.* **40**, 1693 (1964).

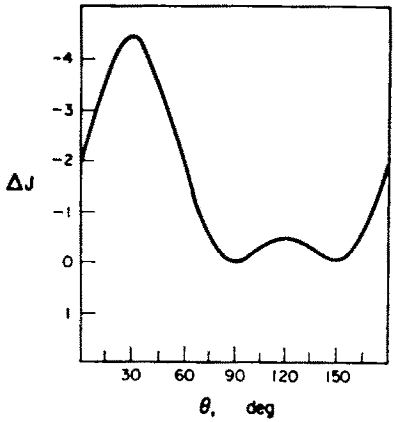

Fig. 2a. Barfield-Grant Curve.

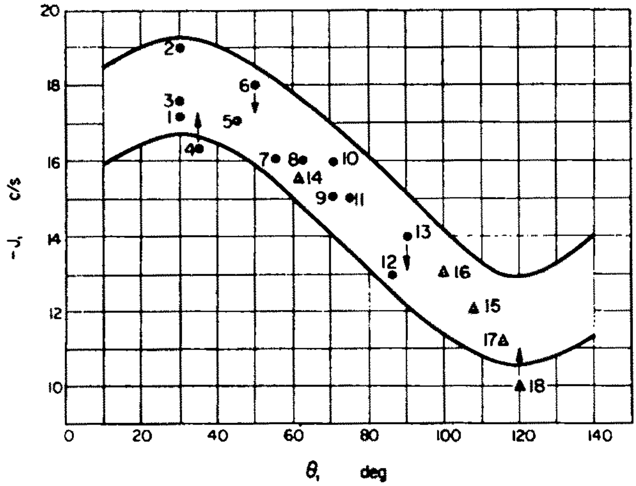

Fig. 2b. Variation of J with Projected Angle of CH_2 with Adjacent p orbital of sp^2 Carbon Atom.

The values of θ were measured from Dreiding models. Compounds marked Δ taken from Table 3 were corrected for the contribution of one double bond only, using $J = -13$ c/s as a standard, and assuming that the contribution of one double bond is half that of two. The length and direction of the arrows indicates the correction for C—CH_2—C angle distortion, α, taken from Fig. 1. α was estimated by calculation or experimental figures from X-ray analysis of closely related structures (4, 12), or, more roughly, by examination of models (6, 18).

obtained, of course, by adding ΔJ to −12·5 c/s, the value for methane[40] or cyclohexane[41] taken as the ideal in the absence of hyperconjugation. We have plotted J (published data as well as our own measurements) against θ for a large number of substances containing methylene groups in five-, six- and rigid seven-membered rings flanked by one π-bond. Values of the dihedral angle between the CH bond and the

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[40] M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.* **27**, 597 (1957).

[41] N. Muller and P. J. Schultz, *J. Phys. Chem.* **68**, 2026 (1964).

p-orbital of the adjacent atom θ (either calculated[42,43] or, usually, measured from Dreiding models) covered the whole range from 30° to 120° with no gap greater than 10°. The approximate empirical trend that emerged is shown in Fig. 2b, which includes points for some representative compounds. If structures likely to introduce other significant contributions to J are avoided, the most serious errors occur in estimating values of θ, which in some cases may be accurate only to $\pm 10°$. Evidently J does depend on θ in the general way predicted by Barfield and Grant,[2] although there is no sign of the minor minimum at 120°. Significant deviations are mentioned later.

In undistorted cyclohexanones[42] with $\theta = 86°$, $J = -12$ to -13 c/s. The effect of θ on J is well illustrated by the 12-methylene group in 11-keto-steroids. In normal steroids (XIII, R = H), where ring C is only slightly distorted from an ideal chair cyclohexanone[42] by the *trans* fusion to ring D, $J = -12$ to $-12{\cdot}5$ c/s (6 examples).[44,45] The small decrease in J to -13 to -14 c/s (8 examples)[46] produced by substitution at C-9 (XIII, R = Me or Br) can be explained by a small downward rotation of the C=O group (slightly decreasing θ) that moves the substituent R away from the 12α- and 14α-H atoms. Cyclization of the C-10 methyl group onto C-9 as a cyclopropane, giving a *cis*-fusion of rings B and C continues this distortion of ring C, and J reaches -15 c/s (3 examples).[45,47] Then, in the 9β,14α-dimethyl compounds with a *cis*-junction of rings B and C (XIV) J falls to -16 c/s (3 examples).[48] Here a chair conformation for ring C suffers more angle-strain than a boat and brings the 14α-methyl group very near to the 10α-H atom: the boat conformation brings the two β-methyl groups very close. A balance can be struck, when the C=O group more nearly bisects the CH_2 angle. Finally, in the $\Delta^{8,9}$-11-ketone,[46] when ring C is held almost in the conformation for maximum hyperconjugation (θ = ca. 35°) $J = -16$ c/s.*

The smaller J ($-16{\cdot}2$[49] and -15 c/s[50]) for the two bicyclic ketones (XV, Z = NMe and O) than in normal cyclohexanones may be caused by repulsion[49] between the carbonyl group and the opposite axial proton on the other ring, which bends out the CO group, reducing θ to, say, about 60°. A similar effect explains the rather small J ($-13{\cdot}8$ to $-14{\cdot}5$[51] c/s) for the 1-methylene group in *cis*-2-decalones. Again, the small but distinct fall in J ($-13{\cdot}5$[44] c/s) for the 1-methylene group in the diketone (XVI) is probably to be attributed to a slight torsion of the 1-methylene group, increasing the separation of the 1β-hydrogen and the 11-oxygen atom from the close approach (ca. 2 Å) shown by an undistorted model. Substitution of CN for H in

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* This value is about 2 c/s more positive than expected. The 14-hydrogen atom may have epimerized to the β configuration, in which θ would be larger, producing the more positive J.

[42] E. J. Corey, quoted by W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Amer. Chem. Soc.* **83**, 4013 (1961); see also W. D. Cotterill and M. J. T. Robinson, *Tetrahedron* **20**, 777 (1964).

[43] R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.* 1366 (1965).

[44] N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry.* Holden-Day, London (1964).

[45] H. Wehrli, M. S. Heller, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **44**, 2162 (1961).

[46] E. R. H. Jones and D. A. Wilson, *J. Chem. Soc.* 2933 (1965).

[47] D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.* **85**, 2861 (1963).

[48] D. Lavie, B. S. Benjaminov and Y. Shvo, *J. Chem. Soc.* 3545 (1964).

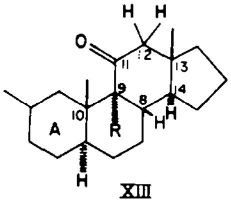
[49] C.-Y. Chen and R. J. W. Le Fèvre, *Chem & Ind.* 306 (1965).

[50] F. Bohlmann, H. J. Schulz and J. Riemann, *Tetrahedron Letters* 1705 (1964).

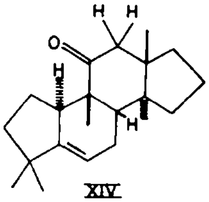
[51] D. R. Elliott and M. J. T. Robinson, *Tetrahedron Letters* 1693 (1965).

XVII lowers J from -13 (R = H) to -15[52] c/s (R = CN). The inductive effect of CN would be expected to lower J by 0·5 c/s or less: the further drop is probably from repulsion of the two dipoles, which twists the CO group in the β direction, reducing θ.

The CH_2 α to the double bond in undistorted chair methylene-cyclohexanes has J = ca. -14 c/s (F, 11), like the cyclohexanones. For half-chair cyclohexene θ has been calculated[43] as 0° (or 60°), although a Dreiding model indicates about 17° (or 43°). A model of the boat conformation, on the other hand, has θ = ca. 80°. The large negative J's typical of cyclohexenes are unchanged by 4,5-*cis*-fusion to a six-membered ring, for example in the Diels-Alder adducts[53] (XVIII) with J = -17 to -19 c/s, but *cis*-fusion to a five-membered ring, as in the anhydrides (F, 7) turns the cyclohexene into a boat with a resultant increase in J to -15 c/s.



XIII



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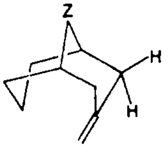

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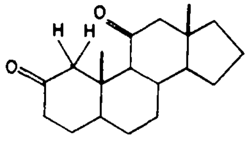

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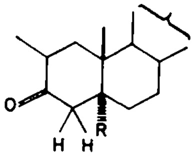
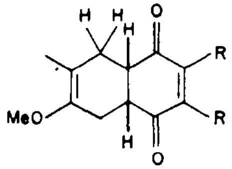
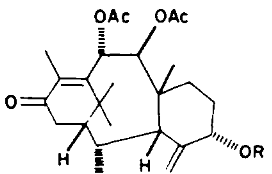


XVII



XVIII



XIX

The four ring-atoms, C_α—CO—O—C_δ in a δ-lactone are kept approximately planar by conjugation, but the shorter distance between C_α and C_δ than between C_3 and C_6 in a cyclohexene means that the preferred conformation for a δ-lactone is a half boat, rather than the half chair in cyclohexene.[54] The shorter distance also causes a slight flattening in the boat, reflected in the rather smaller value of J in the δ-lactones (F, 5: J = $-16·3$ to -17 c/s) than in the boat cyclohexenes (F, 7: J = -15 c/s).

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[52] A. D. Cross and I. T. Harrison, *J. Amer. Chem. Soc.* **85**, 3223 (1963).

[53] M. F. Ansell, J. W. Lown, D. W. Turner and D. A. Wilson, *J. Chem. Soc.* 3036 (1963).

[54] A. M. Mathieson, *Tetrahedron Letters* 81 (1963).

A model of cyclohex-2-enone indicates θ = ca. 50° for the 6-CH_2 and ca. 70° for the 4-CH_2. The range of J found for both types of CH_2 ($J_6 = -16$ to $-20{\cdot}5$ c/s and $J_4 = -18$ to $-19{\cdot}7$ c/s respectively) is thus unexpectedly negative. Twisting the ring without significantly altering the bond angles reduces θ_6 only at the expense of increasing θ_4, and *vice versa*. The fact that, in the examples available (none of which, admittedly, include J_4 and J_6 in the same molecule), *both* J_4 *and* J_6 are smaller than expected, suggests that the cyclohexenone ring is flatter than shown by the models, allowing both θ_4 and θ_6 to approach 30°, the condition for maximum hyperconjugation. Any enlarged C—CH_2—C angle would, of course, add a slight further negative ΔJ. In agreement with this suggestion, 4,5-fusion of a cyclopropane ring to the cyclohex-2-enone, which markedly flattens the ring in a model, has no effect on J ($-18{\cdot}5$ c/s).[55] Perhaps significantly, the smallest J_6 ($-20{\cdot}5$ c/s[56]) is given by taxinine (XIX)[57] in which the 3,5 bridge on the cyclohexenone ring holds the CO group about 40° out of the plane of the C═C double bond, twisting it from the undistorted conformation towards (in a model, even past) the plane bisecting the CH_2 group ($\theta = 30°$).

CH_2 groups α to a double bond in planar five-membered rings ($\theta = 30°$) all have J = ca. $-17{\cdot}5$ to -19 c/s. More positive values of J indicate twisting of the ring (or occasionally, perhaps, incorrect spectral analysis). In fact almost the only compounds that deviate from this range of J are a few 2-substituted indanes: if the first order analysis is adequate, then the high values of J (up to $-15{\cdot}4$ c/s) are consistent with the authors' suggestion,[58] based on the vicinal coupling, that C_2 is bent out of the plane of the other atoms in the ring. (In two compounds where the cyclopentene ring is kept strictly planar by 3,4-fusion to a three-membered ring[10,59] $J = -18{\cdot}2$ and $-18{\cdot}4$ c/s) 3,4-*trans*-Fusion of a cyclohexane ring to a cyclopentanone also increases J for the 2-methylene group[60] by twisting the five-membered ring (local C_2 symmetry about the CO group).

Any discussion of the effect of α trigonal atoms on J in CH_2 groups in four-membered rings is made ambiguous by lack of information on substituent effects as well as ignorance of the values of J for the parent systems, cyclobutane, cyclobutene,* and cyclobutanone. If one simply accepts the range of values of J for the miscellaneous examples available (Table D) as typical, then a single trigonal carbon atom in a four-membered ring still seems to cause the usual negative ΔJ on the adjacent CH_2 group. But the three cyclobutenes (3-bromo-3-methyl-,†[62] 1,3-diphenyl-,[25] and benzo-[63])

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* The spectrum of cyclobutene[61] is insensitive to the value of J_{gem}.

† The value $-13{\cdot}6 \pm 0{\cdot}3$ c/s was measured from a photographic enlargement of the curve given in Ref. 62.

[55] V. A. Atkinson and O. Hassel, *Acta Chem. Scand.* **13**, 1373 (1959); M. Davis and O. Hassel, *Ibid.* **17**, 1181 (1963).

[56] K. Nakanishi, M. Kurono and N. S. Bhacca, *Tetrahedron Letters* 2161 (1963).

[57] M. Kurono, Y. Maki, K. Nakanishi, M. Ohashi, K. Ueda, S. Uyeo, M. C. Woods and Y. Yamamoto, *Tetrahedron Letters* 1917 (1965); M. Shiro, T. Sato, H. Koyama, Y. Maki, K. Nakanishi and S. Uyeo, *Chem. Comm.* 97 (1966).

[58] W. E. Rosen, L. Dorfman and M. P. Linfield, *J. Org. Chem.* **29**, 1723 (1964).

[59] D. D. Elleman, S. L. Manatt and C. D. Pearce, *J. Chem. Phys.* **42**, 650 (1965).

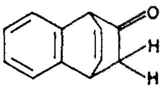
[60] D. H. Williams and N. S. Bhacca, *Chem. & Ind.* 506 (1965).

[61] S. Borcic and J. D. Roberts, *J. Amer. Chem. Soc.* **87**, 1056 (1965).

[62] E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.* **84**, 784 (1962).

[63] G. Fraenkel, Y. Asahi, M. J. Mitchell and M. P. Cava, *Tetrahedron* **20**, 1179 (1964).

TABLE 2.



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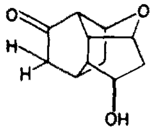

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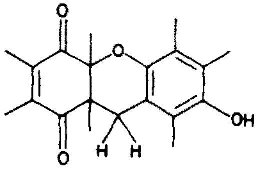

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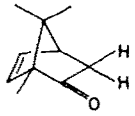

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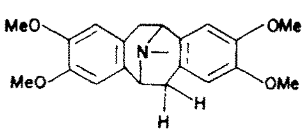

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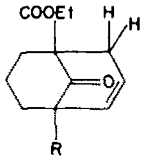

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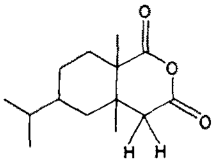

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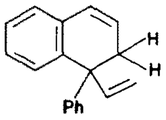

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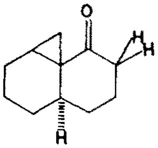

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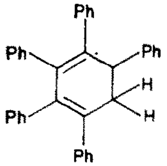

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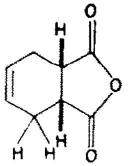

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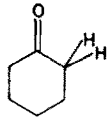

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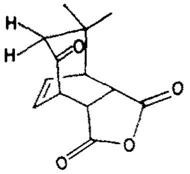

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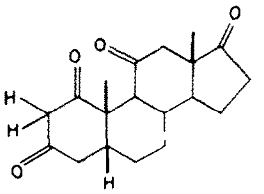
14[a] = 3,4
17 = 3,9

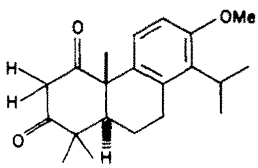
15 = 3,5
18 = 3,12

16 = 3,6

[a] Points 14 to 18 refer to compounds from Table 3.



XXI



XX

have values (−12·3 to −14·6 c/s) in the same range as the cyclobutanes (D, 1). On the other hand, for a C—CH_2—C angle[64] of 86° $J_{C^{13}-H}$ of 140 c/s[61] in cyclobutene falls almost exactly onto Foote's linear relation.[21] The 3° reduction in C—CH_2—C angle from that in cyclobutane to that in cyclobutene should not be enough to cancel the effect of hyperconjugation on J (Fig. 2). Some indication that hyperconjugation may be reduced in cyclobutene comes from the allylic 1,3-proton coupling, which is of opposite sign* (+1·55 c/s[61]) to that in cyclopentene (−1·4 c/s), cyclohexene (−1·4 c/s) and cycloheptene (−1·0 c/s).[65] If the coupling through the four σ bonds (which can be of either sign[66]) is of similar magnitude in all the olefins, the positive coupling in cyclobutene may come from failure of the π-contribution (which is necessarily negative over four bonds[67]). Further discussion must be deferred until we have obtained data on simpler compounds that will allow valid comparisons to be made.

The relatively positive values of J for the 3-methylene groups in 2,2-dibromo- and 2-bromo-4,4-dimethyl-cyclobutanone (J = −10·9[68] and −12·2 c/s[69] respectively) indicate no significant hyperconjugation diagonally across the ring, as in ketene (A, 19) where the $H_2C \ldots C{=}O$ distance is less.

There are many examples in which the CH_2 group is flanked on both sides by a double bond: the two contributions of hyperconjugation to J then seem to be roughly additive, although the likely error in predicting the total ΔJ is larger. For example, consider the 1,3-diketones in the *trans* (XX)[70] and *cis* series (XXI).[55] In the latter (XXI) θ is about 80° for both CO groups and ΔJ from hyperconjugation is therefore very small, in accord with the measured J of −14 c/s. An undistorted chair conformation of ring A in the *trans*-isomer (XX) would, of course, give the same J for the 3-CH_2 group, rather than the observed value of −18 c/s. However, the repulsion between the axial methyl groups at C_{10} and C_4 can be relieved by inverting ring A into a twisted boat in which θ for the CH_2 group with the 3-CO group is ca. 80° and with the 1-CO group ca. 40°, in good agreement with J.

It is more instructive to examine the few compounds in which the contributions from the two π-bonds are identical, ideally those where the CH_2 group is in a plane of symmetry or where a dyad axis bisects the CH_2 angle. Some compounds that strictly fall into this class are listed in Table 3, with some others that do so more loosely (Nos. 2, 6, 7 and 9). The dihedral angle from the adjacent p-orbital,[8] θ, estimated from Dreiding models, and the value of J in c/s are given under the structural formulae (as usual, for simplicity experimental errors are not indicated). The most negative J is almost what would be expected from two maximum hyperconjugative contributions to J [$-12{\cdot}5 + 2(-6) = -24{\cdot}5$ c/s]. The CH_2 angle in fluorene (No. 1) is not known but the C—CH_2—C angle (in the crystal[71]) is slightly reduced below the tetrahedral value (105·6°). Allowing ΔJ of, say, +1 c/s (Fig. 2) for that, brings the estimated value

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* An alternative possibility is that the assignment of the two olefinic-methylene couplings should be reversed from that given in Ref. 61: the 1,3-allylic coupling would then be normal at −0·8 c/s.

[64] E. Goldish, K. Hedberg and V. Schomaker, *J. Amer. Chem. Soc.* **78**, 2714 (1956).

[65] G. V. Smith and H. Kriloff, *J. Amer. Chem. Soc.* **85**, 2016 (1963).

[66] M. Barfield, *J. Chem. Phys.* **41**, 3825 (1964).

[67] M. Karplus, *J. Amer. Chem. Soc.* **82**, 4431 (1960); *J. Chem. Phys.* **33**, 1842 (1960).

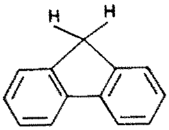
[68] K. L. Servis and J. D. Roberts, *J. Phys. Chem.* **67**, 2885 (1963).

[69] B. Braillon, J. Salaun, J. Gore and J-M. Conia, *Bull. Soc. Chim. Fr.* 1981 (1964)

[70] L. Mangoni and M. Belardine, *Tetrahedron Letters* 2643 (1964).

[71] D. M. Burns and J. Iball, *Proc. Roy. Soc.* **227A**, 200 (1955).

TABLE 3.

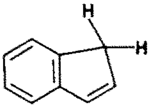


122

1

− 22·3 c/s

30°

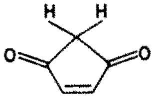


209

2

− 20·8

30°

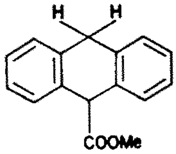


2

3

− 21·5

30°



122

4

− 18·2

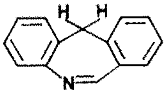
62°

210

5

− 12·4*

108°

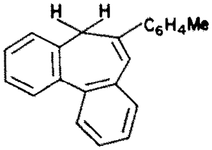


213

6

− 13·4

100°

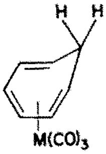


132

7

− 14

100°



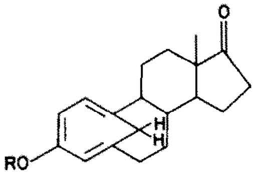
214

8

M = Mo M = Cr

− 12 − 12.6

100° ?

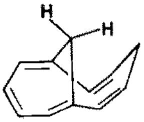


215

9

− 10

115°

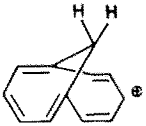


216

10

− 11

115°



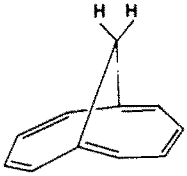
216

216

11

− 10

120°



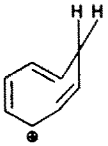
217

217

12

− 6.9

120



75

75

13

− 6.5

?

to only about 1 c/s from the experimental one. If the difference in value for indene is outside the experimental error, the larger J (No. 2) can probably be ascribed to the smaller C—CH_2—C angle.[72]

The effect of the 1,6-bridge on J for the 7-CH_2 group in derivatives of cycloheptatriene (Nos. 6–12) is particularly informative. As expected, the unbridged compounds in which the pseudo-equatorial C—H bond is nearly in the plane of the two α-double bonds, show very little π-contribution to J. (The C—CH_2—C bond angles in 6 and 7 are unknown, but in the molybdenum tricarbonyl complex, No. 8, it barely deviates from tetrahedral.[73]) 1,6-Bridging of the ring with five (No. 10) and then four atoms (No. 9) markedly increases J as θ moves towards the symmetrical 120° angle. Assuming the difference to be outside the experimental error, conversion of the tetrahedral atom in the bridge (No. 10) into the trigonal form (No. 11) causes a further slight increase in J. Finally, in the symmetrical aromatic[74] cyclodecapentaene (No. 12) J rises to $-6{\cdot}9$ c/s. Unfortunately the C—CH_2—C angle is not known for any of these compounds,* so that we cannot estimate the importance of its reduction by the pinching of the 1,6-bonds, which would also increase J. Nevertheless, the relatively positive values of J even in No. 9, for example, do support the molecular orbital treatment[1] of coupling in allylic CH_2 groups rather than the Valence Bond[2] in the critical region of $\theta = 90$ to 120°, where their predictions differ. (The M.O. treatment predicts a positive π-contribution to J between 90 and 120°, because the α π-orbital is overlapping the symmetric CH_2 orbital, whereas the V.B. treatment, assuming independent hyperconjugation from each CH bond, predicts a negative ΔJ.)

Winstein *et al.*[75] have just reported J for the ion (No. 13) formed by protonation of cyclo-octatetraene. A full 2–8 σ-bond, putting the CH_2 in a cyclopropane ring, would be expected to give $J = -4$ to -5 c/s. A rough model with no 2–8 bond and a tetrahedral CH_2 carbon atom above the plane of the other seven carbon atoms shows that $\theta =$ ca. 90°. The π-contribution to J would then be very small, giving J = ca. -12 c/s. The actual value of $(-)6{\cdot}5$ c/s (sign assumed), suggests no negative π-contribution to J but a small C—CH_2—C angle and thus substantial 2–8 bonding, as proposed by the original authors on other grounds.†

(c) *α-Hetero atoms.* The different way that J varies with ring size for O—CH_2—C in cyclic ethers than for C—CH_2—C in cyclic hydrocarbons is very significant. The increase in J from ca. -12 c/s in tetrahydropyrans (F, 12) to ca. -8 c/s in tetrahydrofurans (E, 14) cannot come from change in bond angle at carbon, especially since there is only a very slight further increase in going to the oxetans (D,6: J = ca. -7 c/s). Clearly a new factor must be involved, connected with the pairs of electrons on oxygen. In the staggered conformation of methanol and in the chair conformation

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* Since this was written M. Dobler and J. D. Dunitz [*Helv. Chim. Acta*, **48**, 1429 (1965)] have given 99·6° for the C—CH_2—C angle in crystals of 12-carboxylic acid. This has been used to correct point 18 in Fig. 2b (vertical arrow).

† The argument hinges on the ion's forming a complex with $Mo(CO)_3$ rather than $Mo(CO)_4$, requiring 6 π-electrons, and on the similarity of the PMR spectra of the free ion and its complex.

[72] cf. 102·8° in cyclopentadiene: V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.* **61**, 1769 (1939); G. Liebling and R. E. Marsh, *Acta Cryst.* **19**, 202 (1965); L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.* **43**, 2765 (1965).

[73] J. D. Dunitz and P. Pauling, *Helv. Chim. Acta* **43**, 2188 (1960).

[74] E. Vogel and H. D. Roth, *Angew. Chem.* **76**, 145 (1964); E. Vogel and W. A. Boll, *Ibid.* p. 784.

[75] S. Winstein, H. D. Kaesz, C. G. Kreiter and E. C. Friedrich, *J. Amer. Chem. Soc.* **87**, 3267 (1965).

of tetrahydropyran the axial-equatorial arrangement of the C—H bonds and the oxygen's p-electrons does not affect J. But in the planar (or nearly planar) tetrahydrofuran the CH bonds eclipse the oxygen's electron-pairs, which then effectively overlap the CH_2 orbital. This supply of electrons to the antisymmetric orbital causes[1] the increase in J. (A contribution to J is expected also when a lone pair orbital is parallel to the H—H axis.) The conformational origin of the effect is born out by the similar increased values of J (ca. −9 c/s) in oxa-bicyclo[2,2,2]octanes (F, 13), where (even in a six-membered ring) the CH_2 group also approximately eclipses the oxygen's electron-pairs. The further increase in J to −7 c/s (the same value as in the oxetans) in an oxa-bicyclo[2,2,2]octene that has just been reported[76] can be attributed to the rigidity caused by the double bond, which eliminates the slight twist possible in the saturated system. No doubt J varies continuously with the projected angle between the CH_2 group and the oxygen orbitals, analogous to the curve in Fig 2 but with a periodicity of 360° rather than 90°.

The oxetans and other heterocyclic four-membered rings (Table D) are anomalous, like cyclobutane, in not showing the increase in J expected from the reduced C—CH_2—X angle.

The second oxygen atom in the 1,3-dioxolans (E, 17) causes a slightly larger increase in J even than the first (cf. E, 14 and E, 15), and no doubt mainly for the same reason. Where J is not zero in the 1,3-dioxolans its sign has not been determined. If all the increase in J in going from the six- (F, 18) to the five-membered ring (E, 17) in the ethers is attributed to eclipsing of the CH_2 and the oxygen p-electrons, then one would expect roughly -6 (i.e. $J_{F,18}$) $+ 2 \times 3{\cdot}5$ (i.e. $J_{E,14} - J_{F,12}$) $=$ ca. 0 to $+2$ c/s for J in the 1,3-dioxolans (neglecting slight differences in the geometry of the ring produced by the second oxygen, and assuming each interaction to be independent of the other).

Although the substitution of one oxygen for carbon in cyclohexane causes only a very small increase in J, the second (F, 18) suddenly raises it to −6 c/s. That might lead one to suppose (wrongly) that the effect of eclipsing the oxygen orbitals was already apparent, and that the 1,3-dioxans therefore all adopt a boat or twist conformation. This explanation is unlikely because of other features of the spectra and because acyclic and larger-ring methylenedioxy compounds still have the same value of J. In fact, the effect of electronegative α substituents is not always additive, even when there is no possibility of conformational isomerism: J for methanol and methyl chloride are the same[6] (−10·8 c/s), so that dihydroxymethane in the absence of such complications should have about the same J as dichloromethane[6] (−7·1 c/s). This agrees well with the value actually observed[77a] for the open-chain compound $Ph{\cdot}CHMe{\cdot}O{\cdot}CH_2{\cdot}OMe$ for which $J = -6{\cdot}6$ c/s. There is therefore no reason to propose any special effect in the 1,3-dioxans. (Any small further increase in J beyond the expected value can be explained by a slight flattening of the ring, as in 1,4-dioxan.[78])

An α-nitrogen atom with its single pair of electrons produces similar but significantly smaller changes in J. The much larger range of values in different examples of the same ring-system than for the oxygen analogues is not surprising in view of the easy deformability of tertiary nitrogen. Quaternization of the nitrogen atom usually

[76] B. A. Parkin and G. W. Hedrick, *J. Org. Chem.* **30**, 2356 (1965).

[77a] T. A. Crabb, unpublished results; [b] T. A. Crabb and R. Newton, unpublished results.

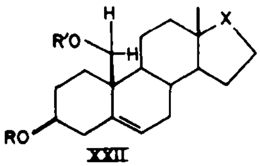
[78] M. Davis and O. Hassel, *Acta. Chem. Scand.* **17**, 1181 (1963).

lowers J slightly in CH_2—N groups, probably from a combination of increased induction and removal of the unshared electrons.

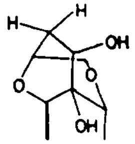
The lower J in the γ-lactones (E, 15) than in the tetrahydrofurans (E, 14) is caused by the reduced electron-density on oxygen, or, put differently, the partial CO—O double bond, and the further decrease in J in the δ-lactones (F, 12) by the lack of orbital overlap in the boat[54] conformation. The failure of the ether oxygen atom in 4- and 5-methyl-3-oxacyclopentanone (E, 6) to increase J significantly from the value in the cyclopentanones (E, 2) suggests that the ring is not planar: a twist or envelope conformation to partially stagger the 4 and 5 substituents would reduce the eclipsing of the oxygen electron-pairs and the CH_2 bonds, without changing the orientation of the CO to the CH_2, which it bisects (θ = ca. 30°). The rather surprising equality of J in the cyclopentenones (E, 3 and E, 7) and the unsaturated lactones (E, 9) must reflect the relatively small effect of ester oxygen already commented on.

Exceptions. Where the value of J reported is well outside the usual range for the structural type of CH_2 the explanation must be sought from one of the following possibilities, in order of decreasing likelihood: (a) wrong analysis of the spectrum, (b) wrong structure for the compound, (c) manifestation of a new effect. In such cases it is most desirable that J should be checked, because the existence of unexplained exceptions obviously tends to reduce the value of empirical correlations of physical constants with structure. To get as wide a range of compounds as possible many values we have included in the Tables are taken from papers dealing primarily with synthetic or structural chemistry rather than spectroscopy, and the PMR spectra are mentioned only incidentally. Estimates of likely experimental errors are seldom given, but sometimes probably reach ± 1 c/s. For isolated AB systems J can, of course, be read directly from the spectrum, but methylene groups often occur as ABX or more complicated systems where J can be extracted only by complete analysis or multiple irradiation.

The coupling constant between the two 19-methylene protons in the steroid (XXII; $R = R' = H$, $X = CO$) has been reported[79] to change remarkably with solvent: in deuteriochloroform $J = (-)11{\cdot}2$ c/s, a typical value for a hydroxymethyl group, but in pyridine $J = (-)7{\cdot}0$. If the facts were accepted, the only explanation seemed to be that in the latter solvent the hydroxymethyl group adopted a conformation in which the two CH bonds eclipsed the oxygen's electron pairs (Section c) and the OH bond eclipsed the quaternary 10-carbon atom. It might have been due to strong hydrogen-bonding to the 5,6-double bond in pyridine but *not* in chloroform solution. This seemed so unlikely that we decided to check the observation.



XXII



XXIII

The similar primary alcohol (XXII; $R = Ac$, $R' = H$, $X = CH{\cdot}COCH_3$-β), kindly given by Dr. M. Akhtar of the Department of Physiology and Biochemistry, was examined in pyridine solution. The CH_2 protons appeared as the well resolved

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[79] J. Tadanier, *J. Org. Chem.* **28**, 1744 (1963).

AB part of an ABX system, the X proton (OH) overlapping the olefinic 6-proton at about 4·35 τ. J_{AB} had the quite normal value of (−)11·3 c/s. Since the different substitution at C-17 in the two compounds is most unlikely to have a significant effect, we conclude that the original report[79] arose from a mistaken reading of the spectrum in pyridine, the two outer pairs of lines perhaps having been overlooked. (The spectrum: $\delta_A = 3{\cdot}78$, $\delta_B = 4{\cdot}1$, $\delta_X =$ ca. 5·65, $J_{AB} = -11{\cdot}3$, $J_{AX} = 4{\cdot}6$, $J_{BX} = 6{\cdot}0$ c/s: did exhibit one interesting feature, the unequal coupling of the OH proton to the two methylene protons. That implies[80] that in the most highly populated conformations the planes H—O—C and O—C—C do not exactly coincide.) In deuteriochloroform the pair of AB doublets had J = (−)11·3 c/s also, and in pyridine the diacetate (XXII; R = R′ = Ac, X = CH·COCH$_3$-β) J = (−)12·0 c/s. In both solvents the values of J agreed within the experimental error with those of corresponding compounds with the cholestane side-chain, which were also measured.

One of the relatively few compounds with a CH$_2$ group in a five or six-membered ring between two tetrahedral carbon atoms with J less than −14 c/s is the dioxabicyclo[2,2,2]octane[81] (XXIII). The unusually low value of (−)14·9 c/s has been quoted[1] as an example of the theoretically predicted dependance of J on the angle of β substituents. However, the protons of the methylene group are part of the complex system CH—CH$_2$—CH in which all the protons are coupled except perhaps the first and last. The authors stated that the J values were "read from the first-order splittings": to equate these with actual coupling constants might well involve errors of up to 2 c/s.

Other CH$_2$ groups between tetrahedral carbon atoms in five- and six-membered rings with unusually large negative J's, some of which may turn out to be exaggerated by incomplete spectral analysis, are now briefly mentioned: The bromo-nitrocamphane (XXIV) (C—CH$_2$—C angle in the crystal[14] = 103°) is reported[82] to have J = (−)16·3 c/s.* The phosphite (XXV, Z = two electrons) shows the normal J = (−)13·5 c/s but the phosphates (XXVI and XXV, Z = O) J = (−)15·2 and (−)15·5 c/s.[83] The diazirine[84] (XXVII) has J = −15·2 c/s, although XXVIII has J = −12 c/s. A possible reason here is the serious repulsion between the nitrogen and the ethane bridge in XXVII (or the sulphur atom in the boat conformation), which can be relieved only by bending the thiacyclohexane ring with consequent enlargement of the C—CH$_2$—C angle (cf. Fig. 1). If it is a true coupling constant, the small value (−15 c/s) for the 1-methylene group in the 2,3-epoxy-steroid[44] (XXIX) may also include a significant contribution from opening of the C—CH$_2$—C angle, for electron diffraction[85a] indicates 116° for the corresponding angle in cyclohexene epoxide itself.

Securinine (XXX) hydrobromide in the crystalline state[85b] has a C—CH$_2$—C

* This has recently been checked by Mr. M. J. Bulman, who finds J = (−)15·5 c/s.

[80] M. Karplus, *J. Amer. Chem. Soc.* **85**, 2870 (1963).

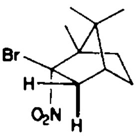
[81] J. S. Webb, R. W. Boschard, D. B. Cosulich, J. H. Mowat and J. E. Lancaster, *J. Amer. Chem. Soc.* **84**, 3183 (1962).

[82] Y. Brunel, H. Lemaire and A. Rassat, *Bull. Soc. Chim. Fr.* 1895 (1964).

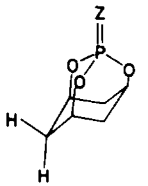
[83] K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier and J. G. Verkade, *Tetrahedron* **20**, 323 (1964).

[84] J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.* **86**, 4618 (1964).

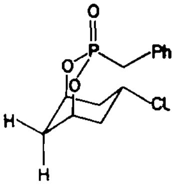
[85a] B. Ottar, *Acta Chem. Scand.* **1**, 283 (1947); [b] S. Imado, M. Shiro and Z. Horii, *Chem. Pharm. Bull. Japan* **13**, 643 (1965); [c] F. H. Westheimer in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) Wiley, New York (1956); J. B. Hendrickson, *J. Amer. Chem. Soc.* **83**, 4537 (1961); [d] J. Parello, A. Melera and R. Goutarel, *Bull. Soc. Chim. Fr.* 898 (1963).



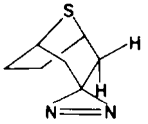
XXIV



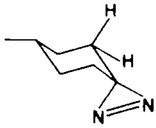
XXV



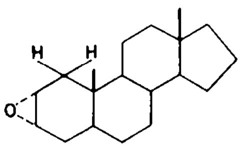
XXVI



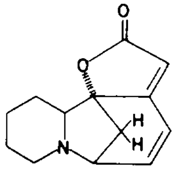
XXVII



XXVIII



XXIX



XXX

angle of 99 ± 2°. If the same angle is assumed for the free base as for the salt and possible distortion by intermolecular forces is neglected,* the J of (—)9·5 c/s for the free base [85c] then falls nicely onto the trend of Fig. 1. The striking drop in J to (—)13 c/s produced by protonation of the nitrogen atom[85c] must be at least partly due to the favourable orientation[1] of the N^+ for interaction with the CH_2 group.

Treatment of the tosyl ester of chaparrol (XXXI) with alcoholic alkali gives an anhydro-chaparrol apparently still containing a hydroxyl group, which Geissman and Ellestad,[86a] reasonably enough at the time, considered to be the product with a cyclopropane CH_2 bridging C-8 and C-9. J, however, is rather low (—7·5 c/s) for a cyclopropane. If there were no skeletal rearrangement, alkylation of an enolate from XXXI might occur on C-11, 12 or 13, as well as C-9. J is too high for a cyclobutane (C-11 or 13), but just right for a bicyclo[2,2,1]heptane (C-12). The chemical shifts of the two protons (7·92 and 8·49 τ) are also more consistent with a bicyclo[2,2,1]heptane than a cyclopropane.

The larger J for CH_2—O groups in tetrahydrofuran rings than in acyclic esters or in lactones is sometimes useful in deciding between alternative structures. For example, the glaucanol oxidation product, formulated[86b] as (XXXII, R = Ac), has J = (—)13·5 c/s, as expected for a neopentyl acetate. The value for the free diol, (—)9 c/s, is suspiciously large for the structure assumed (XXXII, R = H), and

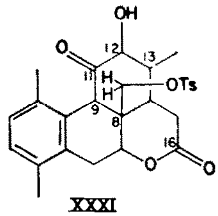
* Since bending one C—CH_2—C angle 10° takes only about 1·9 kcal/mole,[85d] bond angles in molecules in crystals and in solution may differ by several degrees even in relatively rigid bridged rings. Compare, for example, the shapes of the bicyclo[2,2,1]heptane rings in the two crystallographically different sites in crystals of 10-bromo-2-chloro-2-nitrosocamphane.[14]

[86a] T. A. Geissman and G. A. Ellestad, *Tetrahedron Letters* 1083 (1962); [b] J. Polonsky, C. Fouquey and A. Gaudemer, *Bull. Soc. Chim. Fr.* 169 (1963); 1818 (1964); [c] J. Polonsky and J.-L. Fourrey, *Tetrahedron Letters* 3983 (1964).

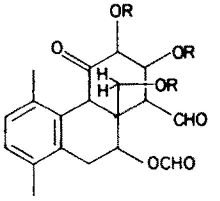
suggests that the compound exists as the γ-lactol, where the primary hydroxyl group has added either to the ketol or the aldehyde carbonyl group. A correction in the opposite sense is required in another case: glaucanol triacetate[86b] has $J = (-)13$ c/s, confirming the presence of the neopentyl acetate group (XXXIII), but isoglaucanol-A triacetate[86b] with $J = (-)12$ c/s cannot be merely the isomeric γ-lactol triacetate as supposed, which would have $J = -8$ to -9 c/s (E, 14) as indeed do several analogous γ-lactols[86c] with a non-aromatic ring A. The simplest change[87] consistent with the value of J would be to involve the primary hydroxyl group in a new δ-lactone with C-16 (cf. F, 12).

Although XXXIV[79] (Z = dioxolan) has $J = (-)7{\cdot}2$ c/s, as expected, a substance claimed[88] to be the analogue XXXIV ($Z = CH{\cdot}C_8H_{17}$-β) has $J = (-)12$ c/s: the structure or the spectrum of the latter needs revision.

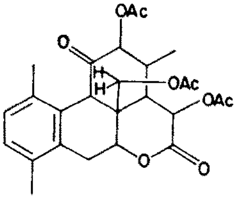
The J of (−)4 c/s reported[89] for the CH$_2$ group in the oxetan ring of verrucarol and its derivatives immediately aroused our suspicions about the structure proposed, which would have required J = ca. −7 c/s. The recently revised[90] structure (XXXV; R = OH, Y = H$_2$, Z = β-OH) which places the CH$_2$ in an epoxide ring is quite satisfactory (cf. C, 4).



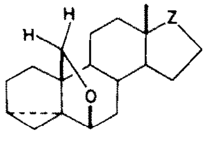
XXXI



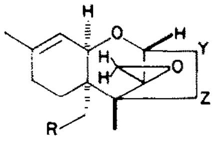
XXXII



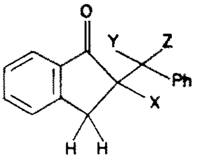
XXXIII



XXXIV



XXXV



XXXVI

The related ketone (XXXV; R = OAc, OMs, or OH; Y = O; Z = H$_2$) has an isolated AB system of protons at Z, which show the expected $J = (-)19$ c/s.[91] It is incredible that dehydrororidin-C[91] (XXXV; R = H, Y = H$_2$, Z = O) (= dehydrotrichodermol), in which the CH$_2$ and CO groups in the cyclopentane ring have been interchanged, really has $J = (-)11$ c/s: the coupling to the third proton (on the bridge-head) must have caused a wrong analysis of the resulting ABX spectrum.

The expected $J = (-)18$ c/s is reported[92] for the 3-methylene protons of the four

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[87] cf. T. A. Davidson, T. R. Hollands and P. de Mayo, *Tetrahedron Letters* 1089 (1962).

[88] R. M. Moriarty and T. D. D'Silva, *J. Org. Chem.* **28**, 2445 (1963).

[89] J. Gutzwiller and C. Tamm, *Helv. Chim. Acta* **46**, 1786 (1963).

[90a] J. Gutzwiller, R. Mauli, H. P. Sigg and C. Tamm, *Helv. Chim. Acta* **47**, 2234 (1964); [b] S. Abrahamson and B. Nilsson, *Proc. Chem. Soc.* 188 (1964); W. O. Godfredsen and S. Vangedal, *Ibid.* A. T. McPhail and G. A. Sim, *Chem. Com.* 350 (1965).

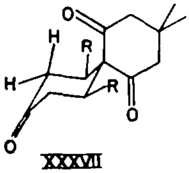
[91] H. P. Sigg, R. Mauli, E. Flury and D. Hauser, *Helv. Chim. Acta* **48**, 962 (1965).

[92] D. N. Kevill, G. Coppens, M. Coppens and N. H. Cromwell, *J. Org. Chem.* **29**, 382 (1964).

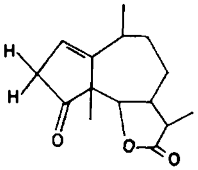
2-benzyl-1-indanones (XXXVI; X = D or Br, Y = Z = D, or Y = H and Z = Halogen), but inexplicably J = (−)14 c/s for a fifth (XXXVI; X = Br, Y = Z = H). The error seems to have arisen from the use of a different solvent. The dideuterio compound (XXXVI; X = Br, Y = Z = D) was recorded unambiguously as having J = (−)18 c/s, δ = 6·33 and 6·45 τ, *in deuteriochloroform*. The normal compound (XXXV; X = Br, Y = Z = H) had δ = 6·40 and 6·59 τ with J = (−)14 c/s, and a singlet from two protons at 6·51 τ, *in carbon tetrachloride*. The AB system was assumed to come from the 3-methylene group and the singlet from the benzyl CH_2. However, change of solvent is most unlikely to alter J to that extent in such a rigid system, whereas a change in δ by 0·15 ppm or so is quite usual. No doubt, then, the AB system should be assigned to the non-equivalent protons in the benzyl CH_2 group, for which J = −14 c/s is typical,* and the singlet to the two 3-methylene protons, which happen to have the same δ in carbon tetrachloride solution. In deuteriochloroform they would, of course, show the identical AB system with J = −18 c/s as reported for the dideuterio-compound.

The α-keto-methylene groups indicated in XXXVII (R = Ph) have J = (−)13·6 c/s,[93] as expected for a simple chair cyclohexanone slightly flattened by the substituents. Nevertheless, the analogues where R = α-furyl and α-thienyl are reported[93] to show the surprisingly small J of (−)15·5 and (−)15·2 c/s. Substitution of one aryl group for another is unlikely to alter the conformation of the cyclohexanone ring noticeably, so the apparent difference in J may perhaps come from the spectral analysis.† (This was done by direct measurement of splittings when $(\nu_A - \nu_B)/J$ was greater than 2 and by ABX analysis when this ratio was less than 2. In fact this figure is too small to be taken as the dividing line.[94] As a result, J_{AB} from ABX was not always equal to J_{AM} from AMX analysis, although that is the only parameter that should not differ.†)

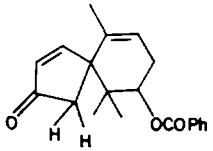
Amongst molecules with allylic CH_2 groups with an impossibly positive J is the



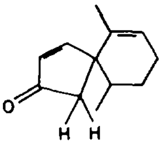
XXXVII



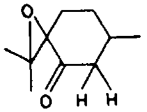
XXXVIII



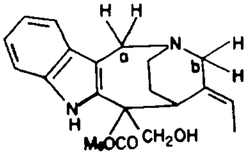
XXXIX



XL



XLI



XLII

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* All twelve examples of $PhCH_2C$ we have collected show J = −13·0 to −14·0 c/s.

† Mr. M. J. Bulman has remeasured the three coupling constants of the ABX systems of XXXVII by double irradiation, finding values substantially in agreement with those reported.

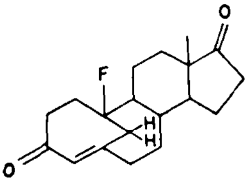
[93] H. A. P. De Jongh and H. Wynberg, *Tetrahedron* **21**, 515 (1965).

[94] K. B. Wiberg and B. J. Nist, *Interpretation of NMR Spectra* p. 21. Benjamin, New York (1962).

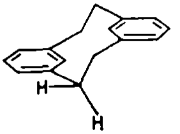
sesquiterpene[95] (XXXVIII), stated to have J = (−)5 c/s. Actually the spectrum, consisting of a triplet and two doublets, is of the simple ABX type, from which J_{AB} cannot be determined (or perhaps some weak lines were overlooked). J should be about −20 c/s or less. J = (−)11·5 c/s cannot be correct for the cyclopentenone[96] (XXXIX) nor J = (−)4 c/s for XL,[97] for both of which ca. −18 c/s is expected: either the structure or the analysis of the spectrum needs revision. A wrong spectral assignment is indicated also for XLI, J = (−)9 c/s.[98]

A more subtle point is illustrated by the spectrum of vallesamine,[99] which has been assigned structure (XLII). A pair of doublets at ca. 5·3 and 5·9 τ with J = (−)17 c/s were attributed to CH_2-a and an unresolved singlet at ca. 7·4 τ to CH_2-b. A model reveals, however, that in either possible boat conformation for the eight-membered ring the H—H axis of CH_2-a is nearly parallel with the plane of the indole ring (θ = ca. 115°), so that J should be not less than about −12 c/s. The spectrum shows that the ring is either inverting rapidly or is fixed entirely in one conformation, the latter being much more likely. If the structure XLII is accepted, the only possible solution is to reverse the spectral assignments: the pair of doublets with J = (−)17 c/s must come from CH_2-b and the singlet from CH_2-a. After allowing for the effects of the indole ring and the ethylidene double bond the chemical shifts are reasonable only if the indole ring is in the conformation where it is over the ethane bridge rather than over CH_2-b, whose resonance would then be moved to higher rather than lower fields. The piperidine ring is fairly flexible in this arrangement. In the conformation that places the ethylidene group furthest from the quaternary carbon centre the plane of the ethylidene double bond approximately bisects the H—C—H angle of CH_2-b, and the coupling constant of (−)17 c/s becomes quite acceptable.*

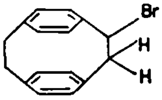
J for the allylic CH_2 group indicated in the rearranged fluoro-steroid (XLIII)



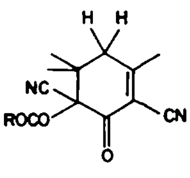
XLIII



XLIV



XLV



XLVI

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* The assignment of the AB system with J = (−)18 c/s at 5·73 and 5·53 τ in the spectrum of apparicine (to which is attributed structure XLII with $MeOCO{\cdot}C{\cdot}CH_2OH$ replaced by $C{=}CH_2$) needs revision for similar reasons (J. A. Joule, H. Monteiro, L. J. Durham, B. Gilbert and C. Djerassi, *J. Chem. Soc.* 4773 (1965)).

[95] W. Herz, H. Watanabe, M. Miyazaki and Y. Kishida, *J. Amer. Chem. Soc.* **84**, 2601 (1962).

[96] P. J. Kropp, *J. Amer. Chem. Soc.* **85**, 3779 (1963).

[97] P. J. Kropp, *J. Amer. Chem. Soc.* **87**, 3914 (1965).

[98] W. Reusch and C. K. Johnson, *J. Org. Chem.* **28**, 2557 (1963).

[99] A. Walser and C. Djerassi, *Helv. Chim. Acta* **47**, 2072 (1964).

would be interesting, for θ is near 120°. But the value suggested,[100] (—)5 c/s, is unreasonable. The two protons and the fluorine nucleus constitute an ABX system, of which only two peaks of total intensity equivalent to one half of a proton can be observed. It seems likely that the difference between these two peaks (5 c/s) is not J_{AB}, but J_{AX}, one of the H—F^{19} coupling constants, if it is a true coupling constant. (Only exceptionally is J_{AB} not the difference between alternate peaks of the AB part of the spectrum.)

In [2,2]metacyclophane (XLIV) the C—CH_2—C angle (in the crystal[101]) hardly deviates from tetrahedral. In a Dreiding model each pseudo-equatorial C—H bond is in the plane of the α-benzene ring ($\theta = 90°$), but in the real molecule[101] repulsion between the benzene rings causes rotation so that θ is nearly 120°. (This was overlooked in an earlier discussion.[1]) The large J of −12·0 c/s[102] is therefore quite understandable. J for bromo-[2,2]paracyclophane (XLV) is, then, at first sight unexpectedly small (−14·05 c/s).[103] In the crystalline parent hydrocarbon the C—CH_2—C angle is reported[104] as 114°37′, and $\theta = 120°$. Most of the decrease in J for XLV can be ascribed to the enlarged C—CH_2—C angle and to the inductive effect of the bromine atom. In addition, the eclipsing of the bromine atom with the *cis*-hydrogen on the adjacent CH_2 group and especially with the *o*-hydrogen atom on the benzene ring can be relieved by movement so that the benzene rings remain parallel but no longer one directly above the other. θ may then drop below 120°. The almost equal vicinal coupling constants (7·40 and 8·85 c/s)[103] also are unusual for eclipsed groups.

J for the allylic CH_2 groups in the two cyclohexenones (XLVI, R = Me and Et) had been reported[105] to have the improbably large numerical value of (—)26·3 c/s. Dr. J. K. Williams kindly gave us a generous supply of the precursor of the two esters so that we could make fresh samples for measurement. J was (—)19·4 c/s for the methyl ester, and (—)19·7 c/s for the ethyl ester, small values but still in the range for other cyclohexenones (F, 4 and F, 8).

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[100] L. H. Knox, E. Velarde, S. Berger, D. Cuadriello and A. D. Cross, *Tetrahedron Letters* 1249 (1962).

[101] C. J. Brown, *J. Chem. Soc.* 3278 (1953).

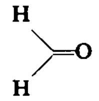
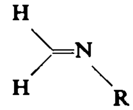
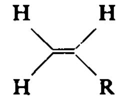
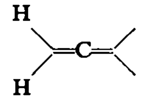
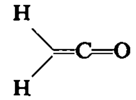
[102] H. S. Gutowsky and C. Juan, *J. Chem. Phys.* **37**, 120 (1962).

[103] E. B. Whipple and Y. Chiang, *J. Chem. Phys.* **40**, 713 (1964).

[104] C. J. Brown, *J. Chem. Soc.* 3265 (1953).

[105] J. K. Williams, *J. Org. Chem.* **28**, 1054 (1963).

TABLE A. OLEFINIC METHYLENE GROUPS

No.	Compound		J (c/s)	Ref.
1			+41	1, 106
2		$R = CMe_3$	+16·5	1, 107
3		$R = NH{\cdot}C_6H_3(NO_2)_2$	+11·6	107
4		$R = OH$	+8	107
5		$R = MgBr$	+7·4	108
6		$R = Li$	+7·1	109
7		$R = H$	+2·3	110
8		$R = Me$	+2·1	111
9		$R = CH_2Ph$	+1·9	112
10		$R = Ph$	+1·3	113
11		$R = CH_2Cl$	+1·3	112
12		$R = CH_2CN$	+0·8	2
13		$R = SMe$	−0·3	114
14		$R = Cl$	−1·4	115, 116
15		$R = Br$	−1·8	116
16		$R = OMe$	−2·1	114, 117
17		$R = F$	−3·2	116, 118
18			−9·0	1, 119
19			−15·8	1, 119

[106] B. L. Shapiro, R. M. Kopchik and S. J. Ebersole, *J. Chem. Phys.* **39**, 3154 (1963).

[107] B. L. Shapiro, S. J. Ebersole and R. M. Kopchik, *J. Mol. Spec.* **11**, 326 (1962).

[108] G. Fraenkel, D. G. Adams and J. Williams, *Tetrahedron Letters* 767 (1963).

[109] C. S. Johnson, M. A. Weiner, J. S. Waugh and D. Seyferth, *J. Amer. Chem. Soc.* **83**, 1306 (1961).

[110] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* **269A**, 385 (1962); G. S. Reddy and J. H. Goldstein, *J. Mol. Spec.* **8**, 475 (1962); D. M. Graham and C. E. Holloway, *Canad. J. Chem.* **41**, 2114 (1963).

[111] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.* **83**, 231 (1961).

[112] A. A. Bothner-By and H. Gunther, *Discussions Faraday Soc.* **34**, 127 (1962).

[113] T. Yoshino, Y. Manabe and Y. Kikuchi, *J. Amer. Chem. Soc.* **86**, 4670 (1964).

[114] R. T. Hobgood, G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.* **67**, 110 (1963).

[115] C. N. Banwell, N. Sheppard and J. J. Turner, *Spectrochim. Acta* **16**, 794 (1960).

[116] H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.* **31**, 1278 (1959).

[117] J. Feeney, A. Ledwith and L. H. Sutcliffe, *J. Chem. Soc.* 2021 (1962).

[118] H. S. Gutowsky, quoted in Ref. 116.

[119] E. L. Allred, D. M. Grant and W. Goodlett, *J. Amer. Chem. Soc.* **87**, 673 (1965).

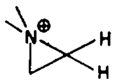
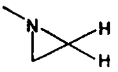
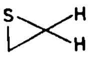
TABLE B. SUBSTITUTED METHANES

No.	Compound	J	Ref.
1	CH_4	−12·4	40
2	CH_3OH	−10·8	6
3	CH_3F	−9·6	6
4	CH_3Cl	−10·8	6
5	CH_3Br	−10·2	6
6	CH_3I	−9·2	6
7	CH_3CCl_3	−13·0	6, 40
8	CH_3COCH_3	−14·9	2
9	CH_3CO_2H	−14·5	2
10	CH_3CO_2Na	−14·2	2
11	CH_3Ph	−14·5	2, 120
12	γ-$CH_3C_5H_4N$	−14·5	121
13	CH_3CN	−16·9	2
14	$CH_2(CN)_2$	−20·3	2

[120] C. G. MacDonald, J. S. Shannon and S. Sternhell, *Aust. J. Chem.* **17**, 38 (1964).

[121] D. P. Biddiscombe, E. F. G. Herington, I. J. Lawrenson and J. F. Martin, *J. Chem. Soc.* 444 (1963).

TABLE C. THREE-MEMBERED RINGS

No.	Ring system	J	No. of examples	Ref.
1		−0·5 to −9·1	82	7, 26, 122–124*a*
2		(+)5	2	125
3		0 to +0·87	2	26, 126, 127
4		+4·0 to +6·3	30*	7, 9, 26, 31, 90*a*, 128–129
5		0 to −1·4	4	26, 128

* 29 further examples of disubstituted epoxides with J = +4 c/s are given in Ref. 91.

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[122] J. J. Frankel Ph.D. Thesis, Southampton (1965).

[123] H. M. Hutton and T. Schaefer, *Canad. J. Chem.* **41**, 684 (1963); D. J. Patel, M. E. H. Howden and J. D. Roberts, *J. Amer. Chem. Soc.* **85**, 3218 (1963); J. D. Graham and M. T. Rogers, *Ibid.* **84**, 2249 (1962); K. B. Wiberg and B. J. Nist, *Ibid.* **85**, 2788 (1963); E. Arnal, A. A. Pavia and J. Wylde,

Bull. Soc. Chim. Fr. 460 (1964); E. B. Whipple and Y. Chiang, *J. Chem. Phys.* **40**, 713 (1964); U. Schöllkopf and H. Küpgers, *Tetrahedron Letters* 105 (1963); A. M. von Leusen, R. J. Mulder and J. Strating, *Ibid.* 543 (1964); T. Stone, T. Morikawa, A. Oku and R. Oda, *Ibid.* 791 (1964); W. C. Howell, M. Ktenas and I. M. MacDonald, *Ibid.* 1719 (1964); W. I. Awad, A. K. Fateen and M. A. Zayed, *Tetrahedron* **20**, 891 (1964); H. Weitkamp and F. Korte, *Ibid.* **20**, 2125 (1964); U. Schöllkopf, A. Lerch and J. Paust, *Chem. Ber.* **96**, 2266 (1963); J-M. Conia and J. Salaun, *Bull. Soc. Chim. Fr.* 1957 (1964); H. M. Hutton and T. Schaefer, *Canad. J. Chem.* **41**, 1623, 1857, 2429, 2774 (1963); C. L. Bumgardner, *J. Org. Chem.* **29**, 767 (1964); L. Skattebøl, *Ibid.* **29**, 2951 (1964); W. M. Jones, M. H. Grasley and W. S. Brey, *J. Amer. Chem. Soc.* **85**, 2754 (1963).

[124a] W. G. Dauben and P. Laug, *Tetrahedron* **20**, 1259 (1964); E. Vogel, W. Wiedermann, H. Kiefer and W. H. Harrison, *Tetrahedron Letters* 673 (1963); A. H. Kapadi and S. Dev, *Ibid.* 1171 (1964); J. Tadanier and W. Cole, *Ibid.* 1345 (1964); G. Berti, F. Bottani, B. Macchia, A. Marsiel, G. Ourisson and H. Piotowska, *Bull. Soc. Chim. Fr.* 2359 (1964); M. S. Heller, H. Wehrli, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **45**, 1261 (1962); R. Darms, T. Threlfall, M. Pesaro and A. Eschenmoser, *Ibid.* **46**, 2893 (1963); J. J. Bonet, H. Wehrli and K. Schaffer, *Ibid.* **45**, 2615 (1962); K. S. Brown and S. M. Kupchan, *J. Amer. Chem. Soc.* **84**, 4590 (1962); L. H. Knox, E. Velarde and A. D. Cross, *Ibid.* **85**, 2533 (1963); [b] T. Schaefer, F. Hruska and G. Kotowycz, *Canad. J. Chem.* **43**, 75 (1965),

[125] N. J. Leonard, K. Jann, J. V. Paukstelis and C. K. Steinhardt, *J. Org. Chem.* **28**, 1499 (1963).

[126] See also F. S. Mortimer, *J. Mol. Spec.* **5**, 199 (1962).

[127] B. Halton, unpublished results.

[128] R. J. Abraham, L. D. Hall, L. Hough and K. A. McLaughlan, *J. Chem. Soc.* 3699 (1962); J. I. Musher and R. G. Gordon, *J. Chem. Phys.* **36**, 3097 (1962).

[129] C. A. Reilly and J. D. Swalen, *J. Chem. Phys.* **32**, 1378 (1960); **35**, 1522 (1961); D. Bertin and L. Nedelec, *Bull. Soc. Chim. Fr.* 2140 (1964); S. Munavalli and G. Ourisson, *Ibid.* 729 (1964); K. L. Reinhart, J. R. Beck, W. W. Epstein and L. D. Spicer, *J. Amer. Chem. Soc.* **85**, 4035 (1963); D. D. Elleman and S. L. Manatt, *J. Mol. Spec.* **9**, 477 (1962); N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* **252A**, 506 (1959).

TABLE D. FOUR-MEMBERED RINGS.

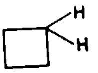
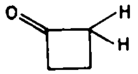
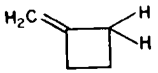
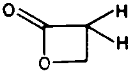
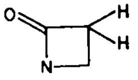
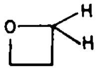
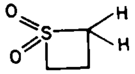
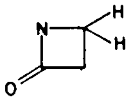
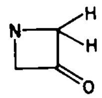
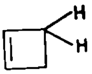
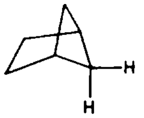
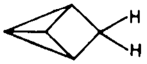
No.	Ring System	J	No. of examples	Ref.	No. of exceptions	Ref.
1		−12·0 to −15·0	17	29, 30, 69, 127, 130	1	68
2		−15·3 to −18·0	6	68, 69, 131, 132	—	—
3		−15·6	1	133	—	—
4		−16·6	1	31	—	—
5		−14·2 to −15·0	4	134	—	—

Table D. (*contd.*)

No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
6		−6·2 to −7·3	5	135	—	—
7		−12·5	1	136	—	—
8		−5·5 to −5·6	3	134	—	—
9		−17·0 to −17·5	6	137, 138	—	—
10		−12·3 to −14·6	3	25, 62, 63	—	—
11		−5·4 to −8·4	22	23	— —	— —
12		−3·1	1	24	—	—

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[130] M. Takahashi, D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.* **84**, 2935 (1962); J. B. Lambert and J. D. Roberts, *Ibid.* **87**, 3891 (1965); J. K. Williams, D. W. Wiley and B. C. McKusick, *Ibid.* **84**, 2210 (1962); E. Lustig, *J. Chem. Phys.* **37**, 2725 (1962); E. Lusitg and R. M. Moriarty, *J. Amer. Chem. Soc.* **87**, 3252 (1965); R. T. LaLonde and R. I. Aksentijevich, *Tetrahedron Letters* 23 (1965); H. Gilman and W. H. Atwell, *J. Amer. Chem. Soc.* **87**, 2678 (1965).

[131] D. Bays, Ph.D. Thesis, Southampton (1964) and unpublished results.

[132] H. O. House, S. G. Boots and V. K. Jones, *J. Org. Chem.* **30**, 2519 (1965).

[133] G. E. Usher, unpublished results

[134] K. D. Barrow and T. M. Spottiswood, *Tetrahedron Letters* 3325 (1965).

[135] P. Yates and A. G. Szabo, *Tetrahedron Letters* 485 (1965); R. B. LaCount and C. E. Griffin, *Ibid.* 1549 (1965); F. Piozzi, A. Quilico, T. Ajello, V. Spiro and A. Melera, *Ibid.* 1829 (1965).

[136] G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.* **84**, 313 (1962).

[137] J. A. Moore, F. J. Marascia, R. W. Medeiros and R. L. Wineholt, *J. Org. Chem.* in press, and personal communication.

[138] J. A. Moore, F. J. Marascia, R. W. Medeiros and E. Wyss, *J. Amer. Chem. Soc.* **84**, 3022 (1962); T. Yamanchi and J. A. Moore, *J. Org. Chem.* in press, and personal communication.

TABLE E. FIVE-MEMBERED RINGS

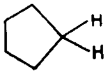
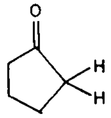
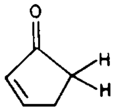
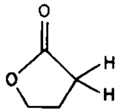
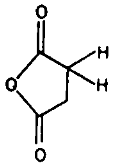
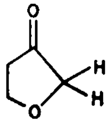
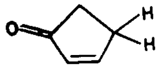
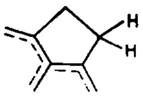
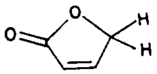
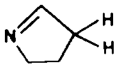
No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
1		−12·0 to −15·0	18	27, 139, 140, 141, 142, 143	—	—
2		−19·0 to −19·5	5	91, 144*a*, 144*b*	1	144*c*
3		−18·0 to −19·0	17	27, 97, 145, 146, 147, 148	2	96, 97
4		−17·0 to −18·9	12	77*a*, 140, 148, 149, 150	—	—
5		−18·2 to −19·8	3	151	—	—
6		−17·0	2	146	—	—
7		−17·0 to −18·8	8	58, 92, 152	3	92, 152
8		−17·5 to −18·8	4	144*a*, 153	—	—
9		−18·0	2	44, 153	—	—
10		−15·3 to −18·4	14	10, 58, 59, 154, 155, 156	—	—
11		−15·5	1	157	—	—

Table E. (*contd.*)

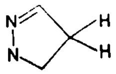
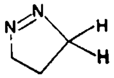
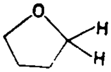
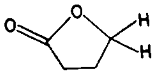
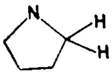
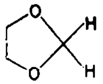
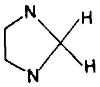
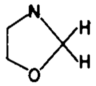
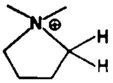
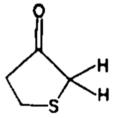
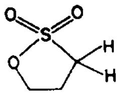
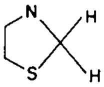
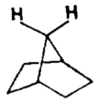
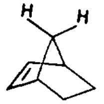
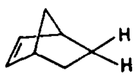
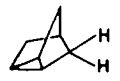
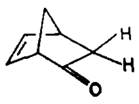
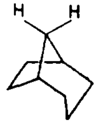
No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
12		−17·5 to −18·8	3	144, 158	—	—
13		−16·5 to −19·6	6	122, 137, 159	—	—
14		−6·7 to −9·9	42	77*a*, 79, 86*c*, 144, 160, 161, 162, 163, 164	2	86*b*, 88
15		−8·8 to −10·5	10	91, 140, 143, 165	2	165
16		−9·0 to −12·1	25	77*a*, 141, 166, 167, 168	1	157
17		0 to ±2·0	17	153, 169	—	—
18		−3·4 to −7·0	3	77*a*, 163	—	—
19		−0·7 to −7·0	29	77*a*, 77*b*, 163	—	—
20		−12·5 to −14·0	3	141, 170	—	—
21		−15·5	1	77*a*	—	—
22		−14·0	1	142	—	—
23		−9·4	1	77*a*	—	—

Table E. (*contd.*)

No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
24		−9·5 to −13·0	16	16, 18, 19, 171, 172	—	—
25		−8·0 to −12·0	32	17, 18, 19, 122, 173, 174, 175	—	—
26		−10·4 to −13·2	32	8, 131, 147, 173, 174, 176	1	82
27		−10·5 to −11·5	3	177	—	—
28		−16·2 to −16·4	3	131	—	—
29		−10·0 to −12·0	8	19, 85*d*, 178	—	—

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[139] I. W. Elliot, E. S. McCaskill, M. S. Robertson and C. H. Kirksey, *Tetrahedron Letters* 291 (1962); N. Yoda and P. Yates, *Tetrahedron* **19**, 849 (1963); R. Creigee, J. Dekker and H. A. Brure, *Chem. Ber.* **96**, 2368 (1963); C. G. Overberger, N. Weinshenker and J. P. Anselme, *J. Amer. Chem. Soc.* **86**, 5364 (1964); R. M. Creswell, W. R. D. Smith and H. C. S. Wood, *J. Chem. Soc.* 4882 (1961).

[140] J. B. Lowry and N. V. Riggs, *Tetrahedron Letters* 2911 (1964).

[141] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.* 3739 (1964).

[142] R. W. Ohline, A. L. Allred and F. G. Bordwell, *J. Amer. Chem. Soc.* **86**, 4641 (1964).

[143] J. J. Dugan, P. de Mayo, M. Nisbet and M. Anchel, *J. Amer. Chem. Soc.* **87**, 2768 (1965).

[144a] P. Bosshard, S. Fumagalli, R. Good, W. Trueb, W. v. Philipsborn and C. H. Eugster, *Helv. Chim. Acta* **47**, 769 (1964); [b] P. K. Grant and N. R. Hill, *Aust. J. Chem.* **17**, 66 (1964); [c] P. K. Grant and R. M. Carman, *J. Chem. Soc.* 3740 (1962).

[145] C. Gauter, R. Warszawski, H. Wehrli, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **46**, 320 (1963); R. Breslow, W. Vitale and K. Wendel, *Tetrahedron Letters* 365 (1965); P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.* **85**, 2456 (1963); W. L. Meyer and B. S. Bielaski, *J. Org. Chem.* **28**, 2896 (1963).

[146] Varian NMR Spectra Catalogue.

[147] D. C. Warrell, unpublished results.

[148] N. Dutter, C. Gauter, H. Ryf, E. C. Utsinger, K. Weinberg, K. Schaffner, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **45**, 2346, 2403 (1962).

[149] P. J. Kropp, *J. Amer. Chem. Soc.* **86**, 4053 (1964).

[150] H. O. House, R. G. Carlson, H. Muller, A. W. Noltis and C. D. Slater, *J. Amer. Chem. Soc.* **84**, 2614 (1962); G. W. Perold and K. Pachlar, *Proc. Chem. Soc.* 62 (1964); K. S. Brown and C. Djerassi, *J. Amer. Chem. Soc.* **86**, 2451 (1964).

[151] L. E. Erikson, *J. Amer. Chem. Soc.* **87**, 1867 (1965).

[152] D. J. Goldsmith and J. A. Hartman, *J. Org. Chem.* **29**, 3520 (1964).

[153] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.* **85**, 2704 (1963); S. McLean and M-S. Lin, *Tetrahedron Letters* 3819 (1964); Varian Advert. in *J. Amer. Chem. Soc.* No. 85.

[154] C. J. Craig, A. R. Naik, R. Pratt, E. Johnson and N. S. Bhacca, *J. Org. Chem.* **30**, 1573 (1965).

[155] H. Prinzbach and E. Druckrey, *Tetrahedron Letters* 2959 (1965).

[156] S. Vary, unpublished results.

[157] M.-M. Janst, X. Lusincki and R. Goutarel, *Bull. Soc. Chim. Fr.* 1566 (1964).

[158] H. J. Shine, L. T. Faug, H. E. Mallory, N. F. Chamberlain and F. Stehling, *J. Org. Chem.* **28**, 2326 (1963).

[159] T. V. van Auken and K. L. Rinehart, *J. Amer. Chem. Soc.* **84**, 3736 (1962).

[160] D. Hauser, K. Hensler, J. Kalvoda, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **47**, 1961 (1964).

[161] U. Scheidegger, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **45**, 400 (1962); J. Zylber and J. Polonsky, *Bull. Soc. Chim. Fr.* 2016 (1964); M. E. Wolff, J. F. Kerwin, F. F. Owings, B. B. Lewis and B. Blank, *J. Org. Chem.* **28**, 2729 (1963); R. Criegee, U. Zirngible, H. Turner, D. Seebach and G. Freund, *Chem. Ber.* **97**, 2942 (1964); R. R. Frazer, R. U. Lemieux and J. D. Stevens, *J. Amer. Chem Soc.* **83**, 3901 (1961); J. M. Lehn and A. Vystrčil, *Tetrahedron* **19**, 1733 (1963); R. Henderson, R. McCrindle, K. H. Overton and A. Melera, *Tetrahedron Letters* 3969 (1964); L. F. Fieser, J. Goto and B. K. Bhattacharyya, *J. Amer. Chem. Soc.* **82**, 1700 (1960); J. Fried, J. W. Brown and L. Borkenhagen, *Tetrahedron Letters* 2499 (1965); R. J. Abraham, *J. Chem. Soc.* 256 (1965).

[162] R. C. Cookson, A. Melera and A. Morrison, *Tetrahedron* **18**, 1321 (1962).

[163] A. Cerutti and H. Schmid, *Helv. Chim. Acta* **45**, 1992 (1962); **47**, 203 (1964).

[164] D. L. Dreyer, *Tetrahedron* **21**, 75 (1965).

[165] T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, M. Takuhushi, H. Irie, A. Numata, T. Fujita, T. Okamoto, N. Natsume, Y. Kawazoe and K. Sudo, *Tetrahedron Letters* 1243 (1964).

[166] C. F. Murphy and W. C. Wildman, *Tetrahedron Letters* 3863 (1964).

[167] Q. Khuong-Hu, J. Yani and R. Goutarel, *Bull. Soc. Chim. Fr.* 2486 (1963); C. Mormeret, F-X. Jarreau, Q. Khuong-Huu and R. Goutarel, *Ibid.* 2167, 2169 (1964); Y. Inubushi, Y. Sasaki, Y. Tsuda, B. Yasui, T. Konita, J. Matsunoto, E. Katarao and J. Nakano, *Tetrahedron* **20**, 2007 (1964); R. G. Hiskey and S. J. Dominianni, *J. Org. Chem.* **28**, 1506 (1965); H. O. House and R. W. Magin, *Ibid.* **28**, 647 (1963); P. L. Southwick, B. McGrew, R. R. Engel, G. E. Milliman and R. J. Owellon, *Ibid.* **28**, 3058 (1963).

[168] W. Koch and H. Zollinger, *Helv. Chim. Acta* **46**, 2697 (1963).

[169] J. S. Brimacombe, A. B. Foster, B. D. Jones and J. J. Willard, *Chem. Comm.* 174 (1965); R. Wallace, A. L. Porte and R. Hodges, *J. Chem. Soc.* 1445 (1963); T. A. Crabb and R. C. Cookson, *Tetrahedron Letters* 679 (1964).

[170] N. J. Leonard, J. V. Paukstelis and L. E. Brady, *J. Org. Chem.* **29**, 3383 (1964); *Ibid.* **30**, 817 (1965).

[171] P. Carter, R. Howe and S. Winstein, *J. Amer. Chem. Soc.* **87**, 914 (1965).

[172] R. C. De Selms and C. M. Combs, *J. Org. Chem.* **28**, 2206 (1963).

[173] J. C. Davis and T. V. Van Auken, *J. Amer. Chem. Soc.* **87**, 3900 (1965).

[174] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.* **86**, 1171 (1964).

[175] H. E. Simmons, *J. Amer. Chem. Soc.* **83**, 1657 (1961); P. M. Subramanian, M. T. Emerson and N. A. Le Bel, *J. Org. Chem.* **30**, 2624 (1965); J. Dance, N. S. Isaacs, G. Subrahmanyam and R. O. Williams, unpublished results.

[176] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.* **85**, 2709 (1963); C. T. Watts, unpublished; L. Besford, unpublished results.

[177] H. G. Kuivila and C. R. Warner, *J. Org. Chem.* **29**, 2845 (1964); R. A. Finnegan and R. S. McNees, *Ibid.* **29**, 3234 (1964).

[178] B. V. Drake, unpublished results; T. N. Margulis, L. Schiff and M. Rosenblum, *J. Amer. Chem. Soc.* **87**, 3269 (1965).

TABLE F. SIX-MEMBERED RINGS

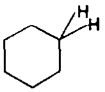
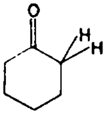
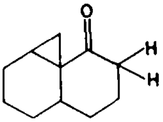
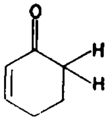
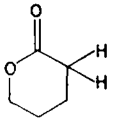
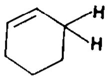
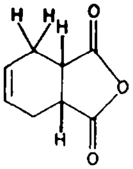
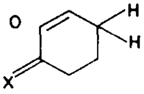
No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
1		−11·6 to −15·0	60	10, 41, 44, 49, 51, 81, 84, 93, 179, 180, 181, 182.	6	44, 84, 93, 182, 183.
2		−12·0 to −16·0	38	44, 45, 46, 48, 49, 50, 51, 52, 93, 180, 184, 185.	2	98, 186
3		−15·0	3	44, 45	—	—
4		−16·0 to −20·0	9	44, 46, 56, 90*a*, 186	—	—
5		−16·0 to −17·0	5	146, 164, 180, 187	—	—
6		−17·0 to −19·0	7	139, 188	—	—
7		−15·0 to −15·1	3	189	—	—
8	X = NH or O 	−17·0 to −19·7	5	93, 122, 190	—	—

Table F (*contd*).

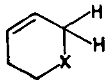
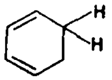
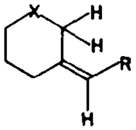
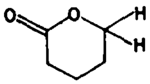
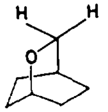
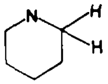
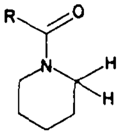
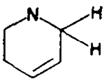
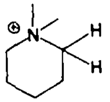
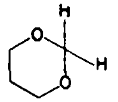
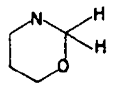
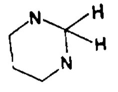
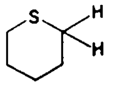
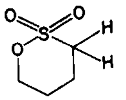
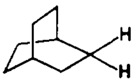
No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
9	X=CH$_2$ or O 	−15·0 to −16·0	3	86*b*, 166, 170	—	—
10		−16·0	2	147,191	—	—
11	X = CH$_2$ or N 	−13·0 to −15·0	7	192	2	99, 193
12		−11·0 to −13·4	33	77*a*, 91, 154, 162, 164, 181, 194, 195	2	77*a*
13		−9·0 to −10·0	3	91, 160	—	—
14		−11·0 to −14·0	18	77*a*, 77*b*, 196	—	—
15		−13·0 to −14·5	7	99, 196, 197	—	—
16		−16·4 to −18·0	9	77*a*, 99, 193, 198	—	–
17		−12·8 to −14·0	4	77*a*, 199	—	—

Table F (contd.)

No.	Ring system	J	No. of examples	Ref.	No. of exceptions	Ref.
18		−5·8 to −6·3	13	77*a*, 181, 194, 200	—	—
19		−8·0 to −10·0	14	77*a*, 77*b*, 204	—	—
20		−8·0 to −11·2	10	77*a*, 77*b*	—	—
21		−13·4 to −15·0	7	201	—	—
22		−13·9	1	202	—	—
23		−13·6 to −13·8	4	203	—	—

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[179] F. Korte, V. Claussen and G. Snatzke, *Tetrahedron* **20**, 1477 (1964); P. W. K. Woo, H. W. Dion and L. F. Johnson, *J. Amer. Chem. Soc.* **84**, 1066 (1962); H. Dunothan, I. W. Elliott and P. Yates, *Tetrahedron Letters* 781 (1961); J. M. Lehn and G. Ourisson, *Bull. Soc. Chim. Fr.* 1113 (1963); P. Laszlo and J. I. Musher, *Ibid.* 2558 (1964); B. D. N. Rao, J. D. Baldeschwieler and J. I. Musher, *J. Chem. Phys.* **37**, 2480 (1962); R. U. Lemieux and R. J. Cushley, *Canad. J. Chem.* **41**, 858 (1963); L. Oliver, J. Levy, J. LeMeu, M-M. Janot, C. Djerassi, N. Budzikiewicz, J. M. Wilson and L. J. Durham, *Bull. Soc. Chim. Fr.* 646 (1963); R. U. Lemieux and S. Levine, *Canad. J. Chem.* **42**, 1473 (1964); A. Rosenthal and D. Abson, *Ibid.* **42**, 1811 (1964); J. F. Trager, F. F. Vincenzi and A. C. Huitric, *J. Org. Chem.* **27**, 3006 (1962); W. Holfheinz, H. Grisebach and H. Friebolin, *Tetrahedron* **18**, 1265 (1962); J. W. Elliott and H. C. Dunothan, *Ibid.* **19**, 833 (1963); W. F. Trager, B. J. Nist and A. C. Huitric, *Tetrahedron Letters* 267 (1965); G. Claeson, G. M. Androes and M. Calvin, *J. Amer. Chem. Soc.* **82**, 4428 (1960).

[180] M. Kingsland, Ph.D. Thesis, Southampton (1965).

[181] C. Barbier, J. Delmau and J. Ranft, *Tetrahedron Letters* 3339 (1964).

[182] R. U. Lemieux and J. W. Lown, *Canad. J. Chem.* **42**, 893 (1964).

[183] K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier and J. G. Verkade, *Tetrahedron* **20**, 323 (1964).

[184] D. Lavie, E. Glotter and Y. Shvo, *Tetrahedron* **19**, 1377 (1963).

[185] G. H. Cooper, unpublished results; A. Lablanche-Combier and J. Levisalles, *Bull. Soc. Chim. Fr.* 2236 (1964); S. Masamune and N. T. Castelluci, *Chem. & Ind.* 184 (1965).

[186] G. Anguilar-Santos, *Chem. & Ind.* 1074 (1965); J. D. Edwards and N. Ichikawa, *J. Org. Chem.* **29**, 503 (1964); G. W. Kirby and H. P. Tiwari, *J. Chem. Soc.* 4655 (1964); T. Rüll, *Bull. Soc. Chim. Fr.* 586 (1963).

[187] S. K. Balasubrahmanian, D. H. R. Barton and L. M. Jackman, *J. Chem. Soc.* 4816 (1962); T. R. Govindachari, B. R. Pai, K. K. Puroshothaman and S. Rajadurai, *Tetrahedron* **12,** 105 (1961).

[188] L. D. Hall, *J. Org. Chem.* **29,** 297 (1964); J. W. van Dyke and H. R. Snyder, *Ibid.* **27,** 3888 (1962); G. F. H. Green, J. E. Page and S. E. Staniforth, *J. Chem. Soc.* 1595 (1965).

[189] B. D. N. Rao and J. D. Baldeschwieler, *J. Mol. Spec.* **11,** 440 (1963); V. N. Gogte, unpublished results.

[190] M. R. S. Weir and J. B. Hyne, *Canad. J. Chem.* **43,** 772 (1965); M. Tomita, T. Ibuka, Y. Inubushi, Y. Watanabe and M. Matsui, *Tetrahedron Letters* 2937 (1964).

[191] W. Herz and G. Caple, *J. Amer. Chem. Soc.* **84,** 3517 (1962).

[192] C. W. Shoppee, F. P. Johnson, R. E. Lack and S. Sternhell, *J. Chem. Soc.* 2489 (1965); M. Ohashi, J. A. Joule and C. Djerassi, *Tetrahedron Letters* 3899 (1964); J. D. Connolly, R. McCrindle and K. H. Overton, *Chem. Comm.* 162 (1965); V. M. Hesse, W. v. Philipsborn, D. Schumann, G. Spiteller, M. Spiteller-Friedmann, W. I. Taylor, H. Schmid and P. Karrer, *Helv. Chim. Acta* **47,** 878 (1964).

[193] J. A. Joule, H. Monteiro, L. J. Durham, B. Gilbert and C. Djerassi, *J. Chem. Soc.* 4773 (1965).

[194] R. U. Lemieux and J. Howard, *Canad. J. Chem.* **41,** 308 (1963).

[195] P. De Mayo and A. N. Starratt, *Canad. J. Chem.* **40,** 1632 (1962); D. Lavie, E. Glotter and Y. Shvo, *Tetrahedron* **19,** 1377 (1963); E. J. Grubbs and D. J. Lee, *J. Org. Chem.* **29,** 3105 (1964); R. U. Lemieux and R. Nagarajan, *Canad. J. Chem*, **42,** 1270 (1964); R. U. Lemieux and J. Howard, *Canad. J. Chem.* **41,** 393 (1963); B. A. Arbusov, Yu. Saitov and R. M. Mamina, *Proc. Akad. Sci. USSR* 186 (1962) (Engl. transl.); F. A. L. Anet, *Canad. J. Chem.* **41,** 883 (1963); D. D. Perrin and D. R. Perrin, *J. Amer. Chem. Soc.* **84,** 1922 (1962); D. Hauser, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **47,** 1883 (1964); P. Jerkeman and B. Lindberg, *Acta Chem. Scand.* **18,** 1477 (1964); F. Bohlmann and C. Arndt, *Chem. Ber.* **98,** 1416 (1965); J. G. Verkade, T. J. Huttemann, M. K. Fung and R. W. King, *Inorg. Chem.* **4,** 83 (1965).

[196] W. Koch and H. Zollinger, *Helv. Chim. Acta* **46,** 2697 (1963).

[197] S. Chiavarelli and G. Settiny, *J. Org. Chem.* **30,** 1969 (1965); J. A. Moore and L. J. Pandya, *J. Org. Chem.* **29,** 336 (1964).

[198] T. Miyadera and Y. Kishida, *Tetrahedron Letters* 905 (1965); U. Renner and H. Fritz, *Helv. Chim. Acta* **48,** 308 (1965); A. L. Burlingame, H. M. Fales and R. J. Highet, *J. Amer. Chem. Soc.* **86,** 4976 (1964); H. A. Lloyd, E. A. Kielar, R. J. Highet, S. Uyeo, H. M. Fales and W. C. Wildman, *Tetrahedron Letters* **3,** 105 (1961); H. Hauth and D. Stauffacher, *Helv. Chim. Acta* **46,** 810 (1963).

[199] H. O. House and H. C. Muller, *J. Org. Chem.* **27,** 4436 (1962); R. Lygo, J. McKenna and I. O. Sutherland, *Chem. Comm.* 356 (1965).

[200] C. Barbier, M. Davidson and J. Delmau, *Bull. Soc. Chim. Fr.* 1046 (1964).

[201] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.* 335 (1965); W. Schroth, *Tetrahedron Letters* 195 (1965).

[202] Samples kindly provided by Dr. G. Opitz.

[203] K. Tori, Y. Takano and K. Kitahonoki, *Chem. Ber.* **97,** 2798 (1964).

[204] Samples kindly provided by Dr. F. J. Murray.

[205] J. Gutzwiller, Ch. Tamm and H. P. Sigg, *Tetrahedron Letters* 4495 (1965).

[206] R. F. H. Manske, Kju Hi Shin, A. R. Battersby and D. F. Shaw, *Canad. J. Chem.* **43,** 2183 (1965).

[207] E. W. Colwin and W. Parker, *J. Chem. Soc.* 5764 (1965).

[208] The value of J used is an average computed from compounds in Table F, 2, expected to have the undistorted $\theta = 85^\circ$.

[209] G. Bergson, *Acta Chem. Scand.* **18,** 2003 (1964).

[210] K. G. Untch and R. K. Kurland, *J. Mol. Spec.* **14,** 156 (1964).

[211] A. S. Lindsey, *J. Chem. Soc.* 1685 (1965); H. Erdtman, F. Haglid and R. Ryhage, *Acta Chem. Scand.* **18,** 1249 (1964).

[212] F. Hunziker, F. Künzle, O. Schindler and J. Schmutz, *Helv. Chim. Acta* **47,** 1163 (1964).

[213] M. B. Rubin, *J. Org. Chem.* **29,** 3333 (1964).

[214] M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.* 2037 (1961).

[215] L. H. Knox, E. Verlarde and D. A. Cross, *J. Amer. Chem. Soc.* **85,** 2533 (1963); **87,** 3727 (1965).

[216] W. Grimme, H. Hoffmann and E. Vogel, *Angew. Chem.* **77,** 348 (1965).

[217] H. Günther, *Angew. Chem.* **77,** 726 (1965).

[218] R. R. Fraser, *Canad. J. Chem.* **40,** 78 (1962).