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THE NMR SPECTRA OF FOUR-MEMBERED CARBOCYCLIC RING SYSTEMS

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Abstract—A summary of proton–proton coupling constant data for cyclobutanes, cyclobutanones, cyclobutenes and cyclobutenones is presented. In cyclobutanes, vicinal *cis* and *trans* coupling constants vary widely (4·6–11·5 c/s and 2·0–10·7 c/s, respectively), whereas the range of geminal coupling constants is smaller (−10·9 to −14·4 c/s. in the absence of a π-contribution). If the cyclobutane ring is incorporated into the strained bicyclo[2.1.1]-hexane system, then the geminal coupling constant is much smaller (−5·4 to −8·4 c/s) and a characteristic, large (6·7–8·1 c/s) 4σ-bond coupling between *endo* protons of the cyclobutane ring is observed. The vinylic coupling constant in cyclobutenes varies from 2·5–4·0 c/s (perhaps negative in sign) and the vicinal coupling between protons attached to adjacent sp^3 and sp^2 carbon atoms is very small (~0–1 c/s). Values of $J_{^{13}C-H}$ are tabulated. Chemical shift data indicate that protons in cyclobutanes and cyclobutenes resonate at slightly lower field than those in the larger cycloalkanes and cycloalkenes.

Proton–proton coupling constants. The desirability of a review of coupling constants in four-membered carbocyclic rings (cyclobutanes, cyclobutenes, cyclobutanones etc.) seems to be indicated. For example, the fact that spin–spin coupling between olefinic protons and adjacent methylene protons is generally very small[1] has not always been appreciated and as a result a mistaken structure assignment has been made.[2] The authors of a recent theoretical paper[3] calculated vicinal coupling constants of 5·4 c/s and 5·1 c/s (*cis* and *trans* respectively for *planar* cyclobutane), but commented that suitable experimental data for cyclobutanes are not available. Bothner-By has noted in a recent valuable review[4] of geminal and vicinal coupling constants (reported chiefly in 1962 and 1963) that for geminal couplings "data on cyclobutanes are scarce" and for vicinal couplings in four-membered rings "data are sparse and appear rather erratic". In 1964 and 1965, however, many more values appeared, and it is the purpose of this article to summarize this data.

The geminal, vincinal and long-range coupling constants measured for cyclobutane and cyclobutanone rings are summarized in Table 1. All the geminal coupling constants quoted are probably negative, but in many cases the sign has not been determined experimentally and is assumed here. In the absence of a π-contribution[28] due to an adjacent sp^2 hybridized atom, the range of geminal coupling constants (−10·9 to −14·4 c/s) is relatively small. When there is a CO group adjacent to the methylene protons then there appears to be an appreciable π-contribution[28] to J_{gem}. The ranges of vicinal *cis* (4·6–11·38 c/s) and *trans* (2·24–10·72 c/s) coupling constants

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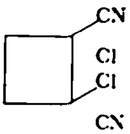
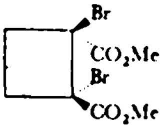
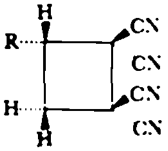
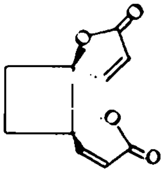
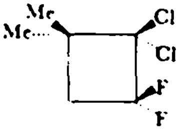
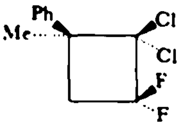
[1] E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.* **84**, 784 (1962).

[2] NMR at Work Series, Nos. 91 and 92, Varian Associates, Palo Alto, California.

[3] R. C. Fahey, G. C. Graham and R. L. Riccioni, *J. Am. Chem. Soc.* **88**, 193 (1966).

[4] A. A. Bothner-By, *Advances in Magnetic Resonance* (Edited by J. S. Waugh) pp. 195–316. Academic Press (1965).

TABLE 1. SUMMARY OF COUPLING CONSTANTS IN CYCLOBUTANE AND CYCLOBUTANONE RINGS

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
1		−13·1	9·4 (*cis*) 9·3 (*trans*) 4·5 (*trans*)		5
2		−12·0	6·2 (*cis*) 10·0 (*trans*) 8·4 (*trans*)		5
3		−14 −13·5 −13	R = OMe {9·2, 7·8} R = OEt {8·6, 7·4} R = $-C_6H_4OMe$ {11·5, 9·5}		6
4		−12·15	10·19 (*cis*) 10·72 (*trans*) 2·24 (*trans*)		7
5		−13			8
6		−13·1			9

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[5] E. Lustig, *J. Chem. Phys.* **37**, 2725 (1962).

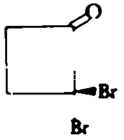
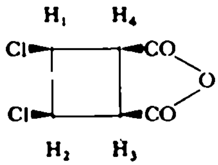
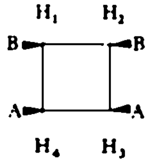
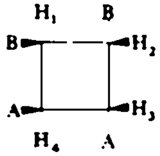
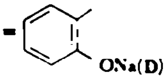
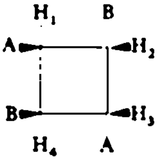
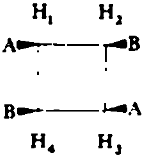
[6] J. K. Williams, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.* **84**, 2210 (1962).

[7] E. Lustig and R. M. Moriarty, *J. Am. Chem. Soc.* **87**, 3252 (1965).

[8] J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.* **87**, 3891 (1965).

[9] M. Takahashi, D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.* **84**, 2935 (1962).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
7		−15·3 ± 0·2 −10·9 ± 0·2	11·2 ± 0·2 7·7 ± 0·2		10
8			$J_{1,2}$ 6·7 $J_{3,4}$ 8·1 $J_{1,4}$ 8·8	$J_{1,3}$ 1·5	11
9			$J_{1,2}$ 9·4 ± 1·4 $J_{3,4}$ 10·0 ± 1·4 $J_{1,4}$ 10·1 ± 0·3	$J_{1,3}$ 0·6 ± 0·3	12
10		A = CO_2Na B = 	$J_{1,2}$ 4·0 ± 0·2 $J_{3,4}$ 10·7 ± 0·2 $J_{1,4}$ 10·2 ± 0·2	$J_{1,3}$ −1·1 ± 0·2	12
11			$J_{1,2}$ 7·5 ± 0·3 $J_{1,4}$ 10·6 ± 0·3		12
12			$J_{1,2}(J_{3,4})$ 9·6 ± 0·3		12

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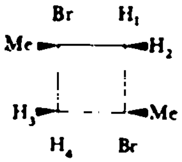
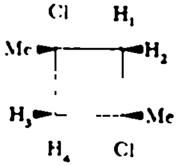
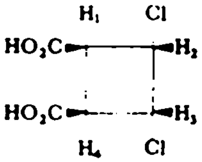
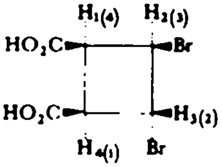
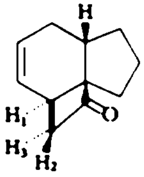
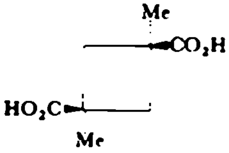
[10] K. L. Servis and J. D. Roberts, *J. Phys. Chem.* **67**, 2885 (1963).

[11] R. Steinmetz, W. Hartmann and G. O. Schenck, *Chem. Ber.* **98**, 3854 (1965).

[12] C. H. Krauch, S. Farid and G. O. Schenck, *Chem. Ber.* **99**, 625 (1966).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
13		−13		$J_{1,3}$ 2	13
14		−13		$J_{1.}$ 2	13
15			$J_{1,4}$ (or $J_{2,3}$) 6·3 $J_{2,3}$ (or $J_{1,4}$) 10·6 $J_{1,2}$ 5·9	$J_{1,3}$ −1·5	14
16			$J_{1,2}$ 8·7 $J_{2,3}$ 8·7 $J_{3,4}$ 8·7 $J_{1,4}$ 9·2	$J_{1,3}$ ± 0·5	14
17		−17·1	$J_{1,3}$ 10·3 $J_{1,2}$ 6·8		15
18		13·5			16

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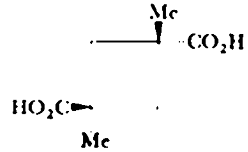
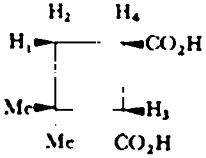
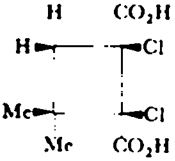
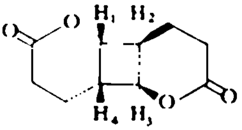
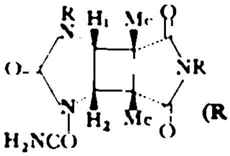
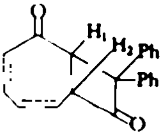
[13] K. Griesbaum, W. Naegele and G. G. Wanless, *J. Am. Chem. Soc.* **87**, 3151 (1965).

[14] V. Georgian, L. Georgian, A. V. Robertson and L. F. Johnson, *Tetrahedron* **19**, 1219 (1963).

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

[16] R. T. Lalonde and R. I. Aksentijevich, *Tetrahedron Letters* 23 (1965).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
19		−13·5			16
20			$J_{1,4}$ 9·64 $J_{2,4}$ 9·64 $J_{3,4}$ 9·38	$J_{1,3}$ −0·53 $J_{2,3}$ −0·53	17
21		−13·95			17
22			$J_{1,4}$ ($J_{2,3}$) 8·3 $J_{1,2}$ ($J_{3,4}$) 4·1		18
23	 (R = H, Me, Et)		$J_{1,2}$ 9·0 ± 0·6		19
24			$J_{1,2}$ 4·6		20

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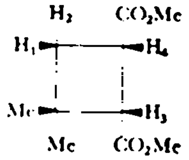
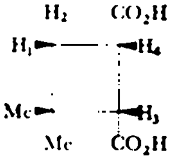
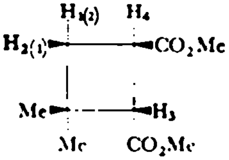
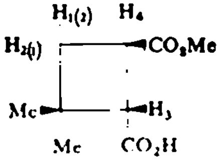
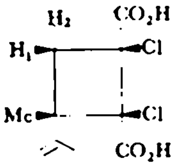
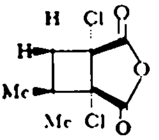
[17] H.-D. Scharf and F. Korte, *Chem. Ber.* **98**, 3672 (1965).

[18] P. E. Eaton, *J. Am. Chem. Soc.* **84**, 2344 (1962).

[19] G. M. Blackburn and R. J. H. Davies, *Chem. Comm.* 215 (1965); also G. M. Blackburn and R. J. H. Davies, private communication.

[20] Ch. Jutz, I. Rommel, I. Lengyel and J. Feeney, *Tetrahedron* **22**, 1809 (1966). The coupling constants originally reported for this compound should be multiplied by a factor of 2 (J. Feeney, private communication and *Tetrahedron* **22**, 3232 (1966).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
25		−11·19 ± 0·20	$J_{1,4}$ 9·23 ± 0·25 $J_{2,4}$ 8·82 ± 0·35 $J_{3,4}$ 9·18 ± 0·32	$J_{1,3}$ 2·23 ± 0·13 $J_{2,3}$ −0·82 ± 0·18	21
26		−11·13 ± 0·21	$J_{1,4}$ 8·90 ± 0·23 $J_{2,4}$ 8·58 ± 0·37 $J_{3,4}$ 9·77 ± 0·30	$J_{1,3}$ 2·31 ± 0·14 $J_{2,3}$ −0·4 ± 0·20	21
27			$J_{2,4}$ 9·32 $J_{1,4}$ 9·32 $J_{3,4}$ 9·02		21
28			$J_{2,4}$ 9·64 ± 0·10 $J_{1,4}$ 9·64 ± 0·10 $J_{3,4}$ 9·38 ± 0·14	$J_{1,3}$ − 0·53 ± 0·05 $J_{2,3}$ − 0·53 ± 0·05	21
29		−13·27 ± 0·3			21
30		−14·40 ± 0·3			21

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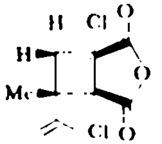
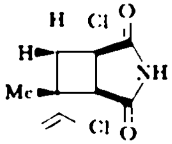
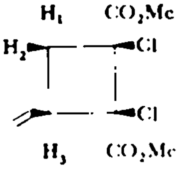
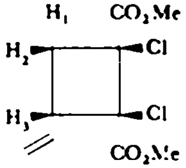
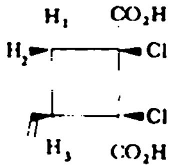
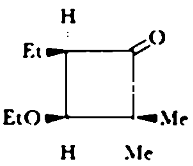
[21] H. Weitkamp and F. Korte, *Tetrahedron* Supplement, Memorial volume to Henry Stephen, 75 (1966).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
31		−13·72 ± 0·3			21
32		−13·80 ± 0·3			21
33		−11·66 ± 0·11	$J_{1,3}$ 10·81 ± 0·07 $J_{2,3}$ 7·93 ± 0·09		21
34		−12·96 ± 0·27	$J_{2,3}$ 11·38 ± 0·21 $J_{1,3}$ 9·52 ± 0·18		21
35		−11·97	$J_{1,3}$ 10·75 $J_{2,3}$ 7·68		21
36			8·0		22

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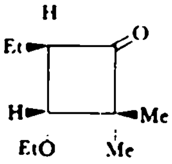
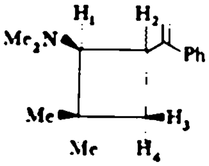
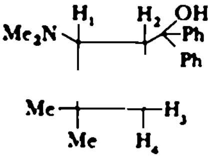
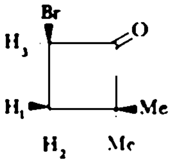
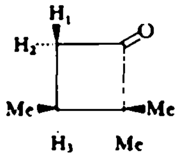
[22] J. C. Martin, V. W. Goodlett and R. D. Burpitt, *J. Org. Chem.* **30**, 4309 (1965).

TABLE 1 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
37			6·9		22
38		$J_{3,4}$ −11 ± 0·5	$J_{2,3}$ 9·0 ± 1 $J_{2,4}$ 9·0 ± 1 $J_{1,2}$ 9·0 ± 1		23
39		$J_{3,4}$ −11·5 ± 0·5	$J_{2,3}$ 9·0 ± 0·5 $J_{2,4}$ 9·0 ± 0·5 $J_{1,2}$ 9·0 ± 0·5		23
	For six alkyl, bromo, and alkylbromo cyclobutanones		J_{cis} 8·7 − 9·7		24
	For eight alkyl, bromo and alkylbromo cyclobutanones		J_{trans} 6·4 − 9·0		
40		−12·2 ± 0·1	$J_{1,3}$ 7·2 ± 0·1 $J_{2,3}$ 9·3 ± 0·1		24
41		−17·0 ± 0·1	$J_{1,3}$ 6·4 ± 0·5 $J_{2,3}$ 8·9 ± 0·3		24

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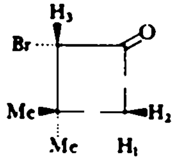
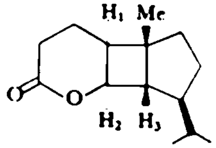
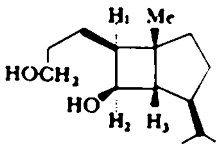
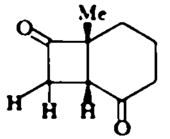
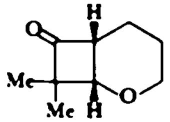
[23] I. Fleming and M. H. Karger, *J. Chem. Soc.* in press (1967).

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

TABLE 1 (*contd.*)

No.	Compound	J_{gem}(c/s)	J_{vic}(c/s)	Other	Ref.
42		-16·4 ± 0·1		$J_{1,3}$ 1·9 ± 0·1 $J_{2,3}$ 1·0 ± 0·1	24
43			$J_{1,2}$ 7·5 $J_{2,3}$ 4·0		25
44			$J_{1,2}$ 6·5 $J_{2,3}$ 2·0		25
45		−17·0	8·8 9·0		26
46			J_{vic} 6		27

are considerable. The *cis* coupling constants are usually larger than the *trans* coupling constants, but the assignment of *cis* or *trans* stereochemistry to adjacent groups in cyclobutane rings, on the basis of coupling constant evidence alone, cannot be made with any assurance.

One cause of the wide range of vicinal coupling constants is the range of conformations which the cyclobutane ring may adopt. While there is a tendency for the

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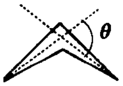
[25] J. Křepinsky, Z. Samek and F. Šorm, *Tetrahedron Letters* No. 27, 3208 (1966); however, these authors used the values of the coupling constants in the determination of the configuration.

[26] J. Yamada, H. Uda and K. Nakanishi, *Chem. Comm.* 423 (1966).

[27] A. P. Krapcho and J. H. Lesser, *J. Org. Chem.* 31, 2030 (1966).

ring to fold in order to relieve eclipsing interactions, the extent to which it folds is dependent on the substituents present.

Recent NMR studies on cyclobutane in a nematic solvent indicate that the molecule is rapidly flipping between two equivalent geometries in which the angle θ in (**47**) is 18° ± 1°,[29] in good agreement with the value (20°) obtained by electron diffraction studies.[30] Variable temperature NMR studies indicate that unsymmetrically substituted cyclobutanes are conformationally mobile, with an equilbrium between "axial" and "equatorial" conformations (**48a**) $\rightleftarrows$ (**48b**).[31] Values of θ as high as 51° are quoted for various substituted derivatives in the literature.[32] Since the position of the equilibrium between (**48a**) and (**48b**) and the extent of folding is dependent upon the nature of R, the magnitude of the vicinal coupling constants is dependent upon R.



47

48a **48b**

A hopeful example is provided by the vicinal coupling constants[7] for anemonin (**4**), in which the angle θ in the crystalline state is known to be 28° from X-ray data.[33] On the reasonable assumption that only one conformer (such as **4b** which is indicated by the X-ray data) is present in solution, it is possible to use the difference between the *trans* coupling constants to calculate the angle of folding of the cyclobutane ring. The treatment leads to a result which is in good agreement with the X-ray data. This agreement may be fortuitous since the method also assumes that the two conformers (**4a**) and (**4b**) would have equal *trans* coupling constants (i.e., it assumes that $J_{aa'}$ and $J_{bb'}$ are both governed by the same equation $J = A \cos \alpha$, where α is the dihedral angle between the vicinal protons). However, since vicinal coupling constants appear to be dependent on the configuration of an electronegative substituent (as well as the dihedral angle) in those cases where experimental evidence is available,[34–37] the assumption is not necessarily valid. Indeed, it has recently been shown[38] that the electronegativity of R in the system —(R)CH—CH_a—$CH_{a'}$— does influence the magnitude of $J_{aa'}$.

A second cause of the wide range of observed vicinal coupling constants lies in the well-known decrease in $J_{aa'}$ on increasing the electronegativity of a substituent R in

[28] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[29] For a brief summary of this work, by Dr. S. Meiboom and D.r L. C. Snyder, see *Chem. and Eng. News* **44**, 51 (1966).

[30] J. D. Dunitz and V. Schomaker, *J. Chem. Phys.* **20**, 1703 (1952).

[31] J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.* **87**, 3884 (1965).

[32] For a summary, see literature cited in Ref. 31.

[33] R. M. Moriarty, C. R. Romain, I. L. Karle and J. Karle, *J. Am. Chem. Soc.* **87**, 3251 (1965).

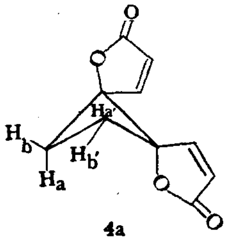
[34] F. A. L. Anet, *J. Am. Chem. Soc.* **84**, 1053 (1962).

[35] D. H. Williams and N. S. Bhacca, *J. Am. Chem. Soc.* **86**, 2742 (1964).

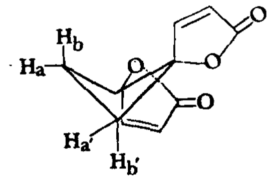
[36] H. Booth, *Tetrahedron Letters* 411 (1965).

[37] J. Fishman, *J. Am. Chem. Soc.* **87**, 3455 (1965).

[38] A. D. Cohen and T. Schaefer, *Mol. Phys.* **10**, 209 (1966).



4a

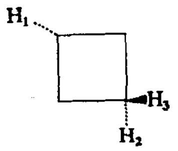


4b

$J_{ab'}$ $(J_{a'b})$ = 10·19 (*cis*)
$J_{aa'}$ = 10·72 (*trans*)
$J_{bb'}$ = 2·24 (*trans*)

the system —HCH_a—$CH_{a'}(R)$—.[39] Conformational and electronegativity effects cannot be securely separated using the data accumulated in Table 1.

Of the two possible long-range proton–proton couplings which can occur through 4 σ-bonds in a cyclobutane ring, the *trans* coupling constant ($J_{1,3}$ in **49**) varies from 0·4–2·0 c/s in magnitude, and is usually negative in those cases where sign determinations have been carried out. A similar range of values (0·5–2·3 c/s) has been observed for the *cis* coupling constant ($J_{1,2}$ in **49**).



49

Coupling constants observed for some cyclobutenes and cyclobutenones are summarized in Table 2. The vinylic coupling constants in such systems vary from 2·5–4·0 c/s. A complete analysis of the spectrum of cyclobutene has been made with the aid of the ^{13}C satellite spectra and of deuterium labelling.[40] The low values of the vinylic coupling constant are not unreasonable in the light of the trend of vinylic coupling constants with decreasing ring size.[43,55,56] The vicinal coupling between protons attached to adjacent sp^2 and sp^3 carbon atoms in cyclobutene rings varies from approximately 0–1 c/s in the cases reported, i.e., the values are very small.[57] The value obtained by extrapolation of data from other cyclo-olefins is +1·5 c/s for this coupling,[55] in fair agreement with the experimental data. In the one case where a sign determination has been made for this vinylic–allylic coupling (in cyclobutene itself),[40] the coupling constant is positive. The vicinal couplings between protons attached to sp^3 hybridized carbon atoms vary from 1·0–6·1 c/s, while the long-range vinyl–allylic coupling in cyclobutene (**50**) (through 4 bonds) is −0·35 c/s, and the corresponding

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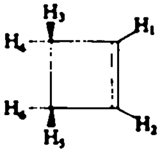
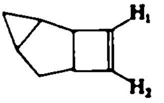
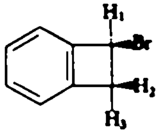
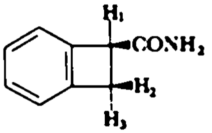
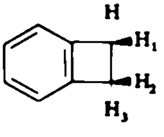
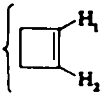
[39] See, for example, K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

TABLE 2. SUMMARY OF COUPLING CONSTANTS IN CYCLOBUTENE AND CYCLOBUTENONE RINGS

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
50		(−12·0)	$J_{1,2}$ + 2·85 $J_{1,3}$ + 1·00 $J_{3,5}$ = + 4·65 $J_{3,6}$ ≈ + 1·75	$J_{1,4}$ −0·35	40
51			$J_{1,2}$ 2·9		41
52		−14·6	$J_{1,2}$ 1·95 $J_{1,3}$ 4·76		42
53			$J_{1,2}$ 4·00 $J_{1,3}$ 4·06		42
54			$J_{1,2}$ 5·00 $J_{1,3}$ 3·5		42
55	Eight Cyclobutenes 		$J_{1,2}$ 2·5 to 3·7		43

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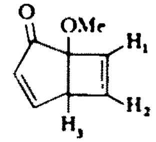
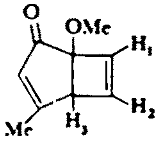
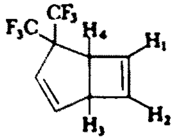
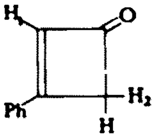
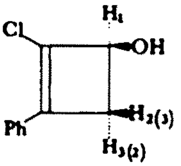
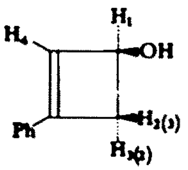
[40] S. Borcic and J. D. Roberts, *J. Am. Chem. Soc.* **87**, 1056 (1965); the J_{gem} value was chosen by analogy to other cases. The values given in Table 2 are revised parameters obtained by E. A. Hill and J. D. Roberts, *J. Am. Chem. Soc.* submitted for publication.

[41] W. R. Roth and B. Peltzer, *Liebigs Ann.* **685**, 56 (1965).

[42] G. Fraenkel, Y. Asaki, M. J. Mitchell and M. P. Cava, *Tetrahedron* **20**, 1179 (1964). This paper is correct in its Table but has reversed assignments in the text, see Ref. 54.

[43] O. L. Chapman, *J. Am. Chem. Soc.* **85**, 2014 (1963).

TABLE 2 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
56			$J_{1,2}$ 4·0 $J_{2,3} < 0·2$		44
57			$J_{1,2}$ 3·0 $J_{2,3} \sim 1$		44
58			$J_{1,2}$ 2·5 $J_{2,3} \sim 0$ $J_{3,4} \sim 0$ $J_{1,4} \sim 0$		45
59				$J_{1,3}$ 0·44	46
60		−11·39	$J_{1,2}$ 1·6 $J_{1,3}$ 4·1		46
61		−12·95	$J_{1,2}$ 1·2 $J_{1,3}$ 3·81	$J_{2,4}$ 1·2 $J_{3,4}$ 0·81	46

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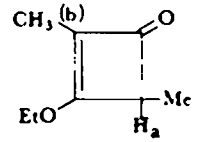
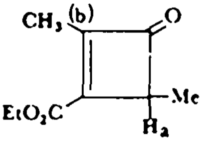
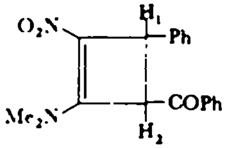
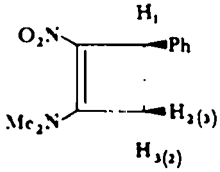
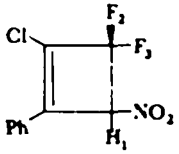
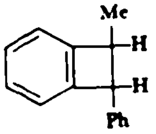
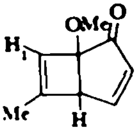
[44] W. G. Dauben, K. Koch, S. L. Smith and O. L. Chapman, *J. Am. Chem. Soc.* **85**, 2617 (1963).

[45] D. M. Gale, W. J. Middleton and C. G. Krespan, *J. Am. Chem. Soc.* **87**, 657 (1965).

[46] S. L. Manatt, M. Vogel, D. Knutson and J. D. Roberts, *J. Am. Chem. Soc.* **86**, 2645 (1964).

TABLE 2 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
62				$J_{a,b}$ 2·5	47
63				$J_{a,b}$ 2·5	48
64			$J_{1,2}$ 1·8		49
65		−13	$J_{1,2}$ 2 $J_{1,3}$ 6		49
66			$J_{1,2}$ 0·9 $J_{1,3}$ 2·2		49
67			6·1 (*cis*) 3·2 (*trans*)		50
68				$J_{1,3}$ 1–2	51

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[47] D. G. Farnum, M. A. T. Heybey and B. Webster, *J. Am. Chem. Soc.* **86**, 673 (1964).

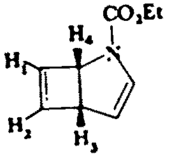
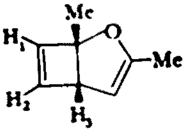
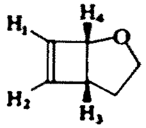
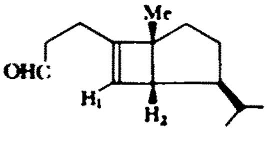
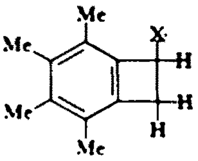
[48] D. G. Farnum, J. R. Johnston, R. E. Hess, T. B. Marshall and B. Webster, *J. Am. Chem. Soc.* **87**, 5191 (1965).

[49] R. Breslow, D. Kivelivitch, M. T. Mitchell, W. Fabian and K. Wendel, *J. Am. Chem. Soc.* **87**, 5132 (1965).

[50] A. T. Blomquist and C. G. Bottomley, *Liebigs Ann.* **653**, 67 (1962).

[51] *NMR Spectra Catalog* spectrum No. 531. Varian Associates, Palo Alto, California.

TABLE 2 (*contd.*)

No.	Compound	J_{gem} (c/s)	J_{vic} (c/s)	Other	Ref.
69			$J_{1,2}$ 2·6 $J_{2,3} \sim 0$ $J_{3,4}$ 2·6	$J_{1,3} < 0·4$	25
70			$J_{1,2}$ 2·8 $J_{2,3} \sim 0$	$J_{1,3}$ 1·5	52
71			$J_{1,2}$ 2·8	$J_{3,4}$ 2·8 $J_{1,3}$ 1·5	53
72				$J_{1,2}$ 0·8	25
73		X = OH −13·5 X = Br −14	$J_{cis(trans)}$ 4 $J_{trans(cis)} < 1$ $J_{cis(trans)}$ 4 $J_{trans(cis)} < 1$		54

value in the cyclobutenone (59) is 0·44 c/s. The 5-bond homoallylic couplings in (62) and (63) are relatively large (2·5 c/s). The π-bond contribution to J_{gem} is surprisingly small, but otherwise the range of values (−11·39–−14·6 c/s) is unexceptional.

[52] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.* **88**, 1718 (1966).

[53] L. A. Paquette, J. H. Barrett, R. P. Spitz and R. Pitcher, *J. Am. Chem. Soc.* **87**, 3417 (1965).

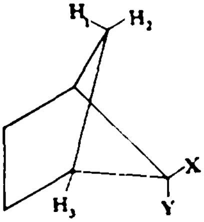
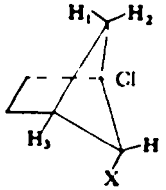
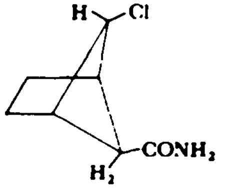
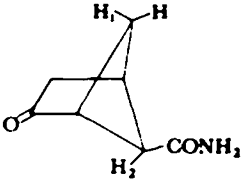
[54] H. Hart, J. A. Hartlage, R. W. Fish and R. R. Rafos, *J. Org. Chem.* **31**, 2244 (1966).

[55] G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.* **85**, 2017 (1963).

[56] P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.* **85**, 2017 (1963).

[57] See also L. M. Jackman, *Nuclear Magnetic Resonance Spectroscopy* p. 86. Pergamon Press, London (1959).

TABLE 3. SUMMARY OF COUPLING CONSTANTS IN CYCLOBUTANE RINGS INCORPORATED IN THE BICYCLO[2.1.1]HEXANE SKELETON

No.	Compound	J_{gem} (c/s)			J_{vic} (c/s)		Other	Ref.
		X	Y	$J_{1,2}$	$J_{2,3}$	$J_{1,3}$	$J_{1,4}$ (Y = H_4)	
74		H	H	−5·4			6·7	58, 4
		H	CH_2OH	−6·0				
		H	Br	−6·0				
		H	CO_2Me	−6·3	2·9			
		H	CH_2Br	−6·6				
		H	CH_2OAc	−6·6				
		H	$CONMe_2$	−6·6	3·0			
		H	COCl	−6·6				
		H	COMe	−6·6	3·8			
		OH	H	−6·8	2·8		6·8	
		OTos	H	−7·1			8·1	
		(−O)		−7·2				
		H	OH	−7·6	2·9			
		H	OAc	−7·8	2·6			
		H	OTos	−7·8	2·7			
		Br	H	−8·1			8·1	
		H	CF_3CO_2	−8·4	2·7			
75		X						58, 4
		CO_2Me		−6·4	3·3			
		COCl		−6·6				
		CO_2H		−6·6				
76							$J_{1,2}$ 7	59
77							$J_{1,2}$ 7·5	60

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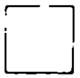
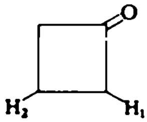
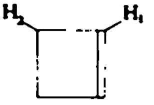
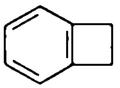
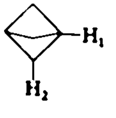
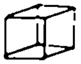
[58] K. B. Wiberg, B. R. Lowry and B. J. Nist, *J. Am. Chem. Soc.* **84**, 1594 (1962).

[59] J. Meinwald and A. Lewis, *J. Am. Chem. Soc.* **83**, 2679 (1961).

[60] J. Meinwald and J. K. Crandell, *J. Am. Chem. Soc.* **88**, 1292 (1966).

If the cyclobutane ring is part of a bicyclo[2.1.1]hexane system (Table 3), then the geminal coupling constant is greatly reduced in magnitude, and, in 20 compounds referred to in Table 3, lies between 5·4 and 8·4 c/s (all values are almost certainly negative, but the sign is assumed in Table 3). $J_{2,3}$ in the series of compounds (74) and (75) corresponds to a vicinal *cis* coupling constant in a cyclobutane ring. The effect of the ethylene bridge is to greatly reduce this coupling constant ($J_{2,3}$ = 2·6–3·8 c/s) relative to the values (4·6–11·38 c/s) observed in the absence of the bridge. There is

TABLE 4. ^{13}C—H COUPLING CONSTANTS

No.	Compound	$J_{^{13}C-H}$ (c/s)	Ref.
78		136 134	61, 62
79		H_1 131 H_2 136	62
50		H_1 170 H_2 140	40
54		138	42
80		H_1 164 H_2 144	63
81		160 ± 5	64

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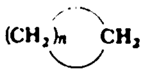
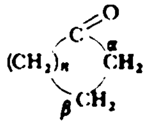
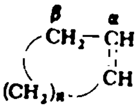
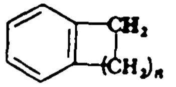
[61] J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.* **86**, 1870 (1964).

[62] C. S. Foote, *Tetrahedron Letters* 579 (1963).

[63] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler and J. Lavanish, *Tetrahedron* **21**, 2749 (1965)

[64] P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.* **86**, 962 (1964).

TABLE 5. CHEMICAL SHIFT VALUES FOR CYCLOBUTANES AND CYCLOBUTENES COMPARED TO THE VALUES FOR OTHER RING SIZES

No.	Compound	δ (ppm downfield from TMS)		Ref.
82		n = 3	1·96	66
		n = 4	1·51	
		n = 5	1·44	
83		α n = 1	3·03	66
		n = 2	2·06	
		n = 3	2·22	
		β n = 1	1·96	
		n = 2	2·02	
		n = 3	1·79	
	α-C—H of other cyclobutanones containing only distant anisotropic functional groups		2·63	15
			2·62	
			3·12	
84		α n = 1	5·95	66
		n = 2	5·60	
		n = 3	5·59	
		β n = 1	2·57	
		n = 2	2·28	
		n = 3	1·96	
	Olefinic C—H of other cyclobutenes containing none or only distant anisotropic functional groups		5·75	67
			5·96	68
			6·1	69
			6·15	70
			6·05	41
			5·94	41
			6·04	71
85		n = 1	3·14	42
		n = 2	2·91	72
		n = 3	2·76	73

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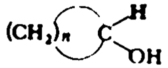
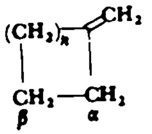
[65] P. Laszlo, *Bull Soc. Chim. Fr.* 558 (1966).
[66] K. Wiberg and B. J. Nist, *J. Am. Chem. Soc.* 83, 1226 (1961).
[67] W. H. Schuller, R. N. Moore, J. E. Hawkins and R. V. Lawrence, *J. Org. Chem.* 27, 1178 (1962).
[68] W. G. Dauben and R. L. Cargill, *J. Org. Chem.* 27, 1910 (1962).
[69] L. A. Paquette, *J. Am. Chem. Soc.* 86, 500 (1964).
[70] O. L. Chapman and E. D. Hoganson, *J. Am. Chem. Soc.* 86, 489 (1964).
[71] K. M. Shumate, P. N. Neumann and G. J. Fonken, *J. Am. Chem. Soc.* 87, 3996 (1965).
[72] *NMR Spectra Catalogue*, spectrum no. 527. Varian Associates, Palo Alto, California.
[73] *NMR Spectra Catalogue*, spectrum no. 557. Varian Associates, Palo Alto, California.

TABLE 5 (*contd.*)

No.	Compound	δ (ppm downfield from TMS)	Ref.
86		n = 3 4·15 ± 0·05	74
		n = 4 4·20 ± 0·05	75
		n = 5 3·60 ± 0·05	75
87		α n = 1 2·7	76
		n = 2 2·22	77
		n = 3 ~2·20	78
		β n = 1 1·92	76
		n = 2 1·65	77
		n = 3 ~1·50	78

also a remarkable long-range 4 σ-bond coupling between the *endo* protons of the two C_1 bridges ($J = 6·7–8·1$ c/s), which has been very useful in making stereochemical assignments in bicyclo[2.1.1]hexane systems.

^{13}C—H coupling constants are given in Table 4; in the absence of further strain the values fall within the range 131 to 140 c/s for hydrogens bound to sp^3 hybridised carbon. The effect of ring size on ^{13}C—H coupling has been reported by Foote[63] for cycloalkanes and by Laszlo[65] for cycloalkenes.

Chemical shift values

It can be seen from Table 5 that in general protons in simple cyclobutanes and cyclobutenes show resonance at slightly lower field than protons in the larger cycloalkanes and cycloalkenes. Beyond this generalization little can be said because in the many compounds for which chemical shift values have been reported anisotropy effects make comparisons between the values for different ring sizes worthless.

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[74] K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964).

[75] I. Fleming, unpublished result; $CDCl_3$ solution. W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963), give equatorial C—H at δ 3·87 and axial C—H at δ 3·27 for cyclohexanol.

[76] *NMR Spectra Catalogue*, spectrum no. 109. Varian Associates, Palo Alto, California.

[77] *NMR Spectra Catalogue*, spectrum no. 132. Varian Associates, Palo Alto, California.

[78] *NMR Spectra Catalogue*, spectrum no. 180. Varian Associates, Palo Alto, California.