Observation of 1,3-Coupling.—Though the values obtained for J_{AX}' are small, some of them are definitely non-zero. Comparison of J_{AA}' and J_{AX}' shows a correlation. When J_{AA}' is large, indicating that the methine protons are mostly oriented *trans* to each other, and therefore *gauche* to the more remote methyl groups, the J_{AX}' values bunch around -0.30 c.p.s., while if J_{AA}' is small, J_{AX}' is near zero. This suggests that in substituted ethanes the H–C–C–CH_3 coupling depends on dihedral angle, ϕ, and is about 0.0 c.p.s. for $\phi = 180°$ and about -0.5 c.p.s. for $\phi = 60°$. The reported examples of Roberts[21] are consonant with this hypothesis.

Chemical Shifts.—The chemical shifts of the methine and methyl protons in the bromo, chloro and acetoxyl compounds are unexceptional and in agreement with previously reported values for similar compounds.[22,23] The small shifts observed between *meso-* and *dl*-compounds in the chloro and bromo series are not readily interpretable. In the phenyl series, there is a definite downfield shift of the methyl signal in the *dl*-compound, which can be explained on the basis that the benzene rings are so oriented in the preferred conformations RA and RB that the magnetic anisotropy associated with them causes the shift.[24] Molecular models indicate that this is a reasonable explanation.

Acknowledgments.—We are indebted to Mrs. Anne R. Wise and to Dr. Erich Hackel for laboratory assistance, to Dr. H. Conroy for drawing our attention to the method of conjugate gradients and for supplying a computer program for this method, to Dr. S. Seltzer for supplying samples of *meso* and *dl*-2,3-diphenylbutane, and to Dr. F. A. L. Anet for helpful correspondence. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under contract No. AF 49(638)980. Computing was done with the partial support of the National Science Foundation.

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[21] D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

[22] A. A. Bothner-By and C. Naar-Colin, *ibid.*, **80**, 1728 (1958).

[23] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

[24] Reference 14, p. 180.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OTTAWA, OTTAWA, ONT., CANADA]

The N.m.r. Spectra of Cyclic and Acylic 2,3-Disubstituted Butanes[1]

BY F. A. L. ANET

RECEIVED OCTOBER 13, 1961

High-resolution proton nuclear magnetic resonance spectra have been determined for the *meso-* and *dl*-isomers of 2,3-dibromobutane, the cyclic carbonate of 2,3-butanediol and the acetonide of 2,3-butanediol (2,2,4,5-tetramethyl-1,3-dioxolane). Coupling constants are obtained by comparison of the spectra with those expected from $X_3AA'X_3'$ systems (with $J_{XX}' = 0$). Variations in J_{AA}' are discussed in terms of the conformation(s) of the compounds. Except for *dl*-2,3-dibromobutane, J_{AX}' has a definite, although very small, value, which is of opposite sign to J_{AX}.

Introduction

The high-resolution proton nuclear magnetic resonance (n.m.r.) spectra of substituted ethanes have attracted much attention recently. In part, this interest stems from the discovery[2,3] of an angular dependence in the coupling constants of protons on adjacent carbon atoms. Theoretical work[4,5] has supported this dependence and suggested that large coupling constants (8–11 c.p.s.) occur for dihedral angles of the CH bonds of 0° and 180°. The constants decrease gradually for other angles, reaching about zero for a dihedral angle of around 90°. Recent experimental work[5–7] lends support to these calculations. The size of coupling constants is also dependent on the presence of strong electron-withdrawing or donating groups[8] and very probably also on angle distortion.

In simple symmetrically substituted ethanes, Sheppard[6] and his co-workers have made use of the C^{13}-satellites to determine coupling constants that cannot be obtained directly. Although this method is extremely useful, the intensity of the satellite lines is not very high with C^{13} in natural abundance (1.1%). It therefore becomes difficult, or even impossible, to observe these bands in dilute solutions, or when they are extensively split by spin–spin interactions.

Another method which has been used with symmetrical molecules is to replace some of the hydrogen atoms by deuterium atoms. This approach,[9] although also very useful, gives less accurate values for the coupling constants, and the synthesis of the required deuterated isomers is not always easy.

The difficulties just discussed do not exist in unsymmetrical molecules, but here the spectra are often too complex for analysis.

In certain symmetrical compounds, such as *meso-* and *dl*-2,3-dibromobutanes, the coupling

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[1] This work was supported by a grant from the National Research Council of Canada and was presented in part at the Annual Conference of the Chemical Institute of Canada, Ottawa, Ont., June, 1960.

[2] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957).

[3] J. A. Pople, W. G. Schneider and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

[4] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[5] H. Conroy, quoted in "Advances in Organic Chemistry: Method and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 311.

[6] C. N. Banwell, A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 266 (1959); N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (*London*), **A252**, 506 (1959).

[7] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

[8] R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956); C. N. Banwell, N. Sheppard and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960).

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

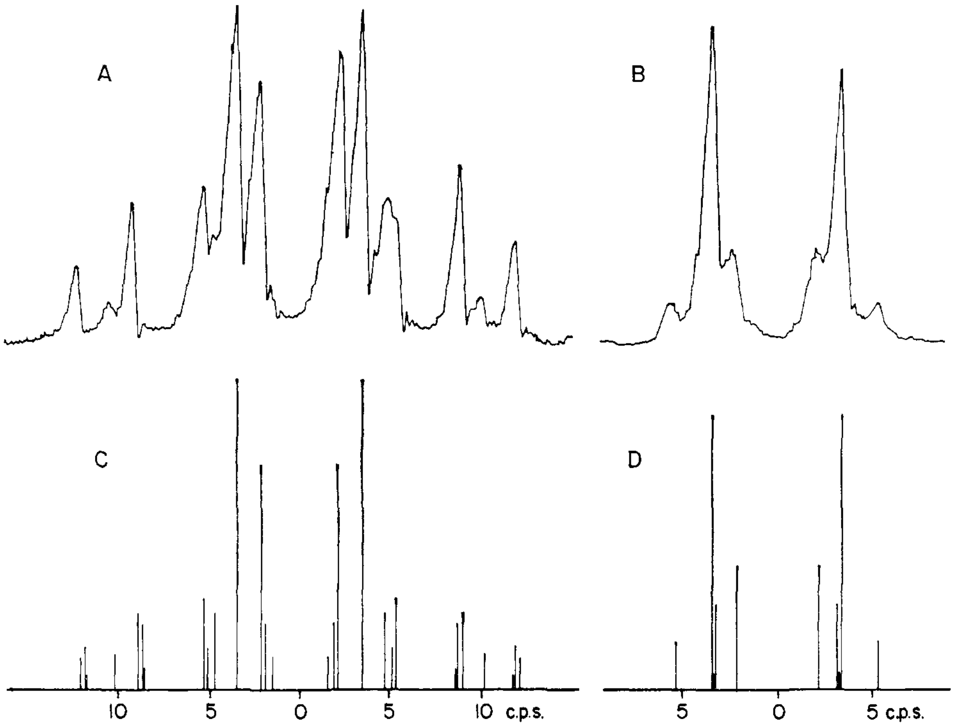

Fig. 1.—Observed spectrum of *dl*-2,3-dibromobutane: A, methine protons; B, methyl protons. Calculated spectrum with $J_{AA'} = 3.15$, $J_{AX} = 6.70$, $J_{AX'} = +0.05$ cps: C, methine protons; D, methyl protons. The intensity scales are different for A and B, and for C and D.

constants between H2 and H3 can be obtained from a direct analysis of the spectra, in spite of the fact that these protons have the same chemical shifts.[10] This is so because, in general, H2 and H3 are differently coupled to either methyl group and are thus not magnetically equivalent.[11] This type of situation was first found in 1,1-difluoroethylene,[12] where all the coupling constants have been obtained by direct analysis. In the present instance such an analysis should be very suitable, because of the great difference between 1,2-coupling constants (6–7 c.p.s.) and 1,3-coupling constants (< 1 c.p.s.) involving the protons of a methyl group and another proton in saturated systems.[13] It is the purpose of the present work to obtain coupling constants for a number of cyclic and acyclic 2,3-disubstituted butanes and to correlate these constants with the conformation(s) of these molecules.

Experimental

Materials.—The 2,3-dibromobutanes[14] were prepared by Miss J. Budzik from *trans*- and *cis*-2-butene during the course of another investigation. The *meso*-isomer had b.p. 40.5° (11.4 mm.) and the *dl*-isomer had b.p. 44–44.5° (10.6 mm.).

The acetonides[15] (dioxolanes) were prepared from the 2,3-butanediols. The *meso* isomer of the diol was obtained by recrystallization of commercial 2,3-butanediol from diisopropyl ether. The *dl*-diol was prepared from *cis*-2-butene *via* the chlorohydrin and epoxide.[16] *trans*-2,2,4,5-Tetramethyldioxolane, which is the *dl*-isomer, had b.p. 110°. The *meso* isomer, *cis*-2,2,4,5-tetramethyldioxolane, had b.p. 118°.

The cyclic carbonates were prepared by ester exchange[17] between the 2,3-butanediols and diethyl carbonate in the presence of a small amount of sodium. The *cis* isomer[17] had b.p. 116–117° (5 mm.). The *trans* isomer, which does not seem to have been described previously, was a solid, m.p. 37°, after recrystallization from petroleum ether and sublimation *in vacuo*.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.89; H, 7.21.

Spectra.—The n.m.r. spectra were measured at 60 mc./sec. with a Varian V-4302 spectrometer. In some cases the samples were mixed with small amounts of tetramethylsilane as an internal standard. Calibrations of the spectra were carried out either by interpolation between sidebands of the tetramethylsilane, or by sweeping over a band and both low and high sidebands. Spectra were obtained with both increasing and decreasing magnetic fields, and line positions were obtained by averaging the results of 6 to 10 determinations. The sideband frequencies were measured on a Hewlett-Packard frequency counter to 0.1 c.p.s.

Analysis of the Spectra.—The analysis of the $X_3AA'X_3'$ system,[11] present in the compounds investigated, can be carried out quite simply, provided that $J_{XX'} = 0$. In saturated compounds, 1,4-coupling constants appear to be negligible, although this is certainly not true for unsaturated compounds, such as the 2-butenes. The presence of appreciable $J_{XX'}$ greatly increases the complexity of the analy-

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(10) The analysis of such spectra was briefly reported in a preliminary communication, F. A. L. Anet, *Proc. Chem. Soc.*, 327 (1959). The coupling constants in that paper are not quite as accurate as those given in the present paper. In line 23, second paragraph $J_{12} + J_{13}$ should read $J_{12} - J_{13}$. The *meso* isomer of 2,3-dibromobutane has 6 lines corresponding to the methyl groups and not 4 as stated.

(11) For a discussion of this and related terms see P. L. Corio, *Chem. Revs.*, **60**, 385 (1960).

(12) H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

(13) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959), p. 85.

(14) W. G. Young, R. T. Dillon and H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 2528 (1929).

(15) A. C. Neish and F. J. Macdonald, *Can. J. Res.*, **25B**, 70 (1947); H. J. Backer, *Rec. trav. chim.*, **55**, 1036 (1936).

(16) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2396 (1936).

(17) P. Chabrier, H. Najer and R. Gindicelli, *Compt. rend.*, **238**, 108 (1954).

sis. When $J_{XX'} = 0$, the transition energies and intensities can be obtained[10] without recourse to the usual procedures of analysis,[18] which are somewhat lengthy for an 8-spin system.

Since the chemical shift between A and X is very large (by definition) and the protons of X_3 (and likewise X_3') are equally coupled to any other proton in the system, we can speak about the *total spin*[19] of each of the methyl groups, provided that $J_{XX'} = 0$. The total spin can have the values of $-3/2$, $-1/2$, $+1/2$, $+3/2$ with statistical weights of 1,3,3,1, respectively.[18] These are simply the possible combinations of 3 protons of spin 1/2. In the system of interest there are two methyl groups present and the above values have to be taken in pairs in all possible combinations. It is easily seen that the sets of spin (3/2, 3/2), (3,2, 1/2), (1/2, 1/2), etc., have statistical weights of 1, 3, 9, etc. We can now obtain the transition energies and intensities of the AA′ protons. If one considers the molecules with methyl groups of spin state, say (3/2, 3/2), the effect of coupling with A and A′ is *equivalent* to a chemical shift of $3/2\ J_{AX} + 3/2\ J_{AX'}$ in both[20] the A and A′ protons. If the first number in bracket refers to X_3 and the second to X_3', the spin state (3/2, 1/2) similarly "induces" a chemical shift in A of $3/2\ J_{AX} + 1/2\ J_{AX'}$ and in A′ of $1/2\ J_{AX} + 3/2\ J_{AX'}$. Thus, the AA′ protons give rise to an A_2 system[18] when the methyl groups have the same total spin, but to an AB system[18] when their total spins are different. In the former case, and for the spin state (3/2, 3/2), a single line (of intensity, say, 1) is obtained at $3/2(J_{AX} + J_{AX'})$ from the position of the AA′ protons in the absence of any coupling. In the latter case, the AB system is centered on $J_{AX} + J_{AX'}$, with a chemical shift of $J_{AX} - J_{AX'}$, and a coupling constant of $J_{AA'}$. The solution[18] of the AB system gives four lines at $\pm 1/2[(J_{AX} - J_{AX'})^2 + J_{AA'}{}^2]^{1/2} \pm 1/2\ J_{AA'}$. The total intensity of the four lines is 3 and the intensity of each line can easily be calculated.[18] The entire AA′ spectrum can thus be obtained and consists of a super-position of AB or degenerate AB (*i.e.*, A_2) systems.

Since the ABX_3 system[21] has been solved, the lines of the methyl protons can be obtained by considerations similar to the above applied to the X_3AA' portion of the $X_3AA'X_3'$ system. Thus, when X_3' has a total spin of 3/2, the rest of the system is effectively an ABX_3 system with a chemical shift between A and B of $3/2\ (J_{AX} - J_{AX'})$. By taking all the spin states of X_3', the transition energies and relative intensities of the X_3 protons can be calculated. These results also apply to the X_3' protons and therefore to the X_3X_3' protons as a whole.

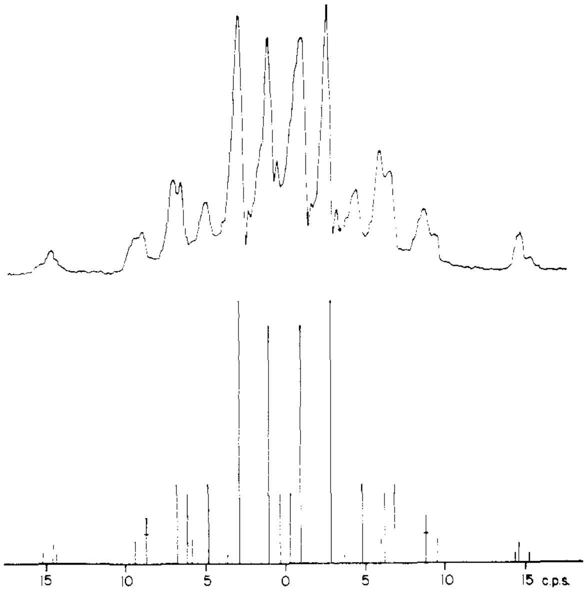

Fig. 2.—Observed and calculated ($J_{AA'} = 8.35$, $J_{AX} = 5.90$, $J_{AX'} = -0.15$ c.p.s.) spectra for the methine protons of *trans*-2,2,4,5-tetramethyldioxolane. Where two calculated lines are virtually coincident they are placed on top of one another and separated by a small horizontal line.

It is also possible to calculate the methyl portion of the spectrum without recourse to the results obtained in the ABX_3 case. Thus, when A and A′ both have the same spin (*i.e.*, the total spin of AA′ is + 1 or − 1), it is easily seen[22] that there are two lines, separated by $J_{AX} + J_{AX'}$, which account for half the total intensity of the methyl group. The other half of the intensity corresponds to the states when A and A′ have opposite spin. The situation here is more difficult as the AA′ spin states (+ 1/2, − 1/2) and (− 1/2, + 1/2) have the same total spin and mix. The extent of the mixing, however, depends on the spin states of the methyl groups. These transitions of the methyl group will therefore depend on $J_{AA'}$. They can be obtained, though not very simply, by setting up the appropriate energy levels as described by Pople and Schaeffer.[19]

The transition energies and intensities of the complete $X_3AA'X_3'$, with $J_{XX'} = 0$ are given[23] in Table I. Whilst the AA′ spectrum varies rather widely in the way the lines are distributed (Figs. 1 and 2), the spectrum of the methyl group is always roughly a doublet. This is because the two lines at $\pm 1/2\ (J_{AX} + J_{AX'})$, which are independent of $J_{AA'}$, account for half the intensity of the methyl group. These lines are usually strengthened by the close proximity of the lines at $\pm 1/2\ (B - A)$ and $\pm 1/2\ (C - B)$. The other four lines of appreciable intensity in the methyl group are identical with an AB system of chemical shift $J_{AX} - J_{AX'}$ and coupling constant $J_{AA'}$. Except when $J_{AA'}$ is very small, these lines are well resolved, although if $J_{AA'}$ is very large the outer lines are quite weak. Thus one can obtain approximate values of J_{AX}, $J_{AX'}$ and $J_{AA'}$ just from the methyl band. The lines at $\pm 1/2(A + B)$ and $\pm 1/2(B + C)$ have zero intensities when the ratio $J_{AA'}/(J_{AX} - J_{AX'})$ is either zero or infinity. For other values of this ratio the intensities are still extremely small. The more intense pair ($\pm 1/2(A + B)$) has maximum intensity when the above ratio has the value 2, when each line has an intensity of about 0.14.

The AA′ spectrum has four lines that are independent of $J_{AA'}$. Two of these, at $\pm 3/2(J_{AX} + J_{AX'})$, are quite weak and are often not resolved from other lines. The other two, at $\pm 1/2(J_{AX} + J_{AX'})$, are usually the strongest lines and account for 9/32 of the intensity of the AA′ spec-

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[18] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, chapter 6.

[19] That is the total spin (actually the component in the *z*-direction[18]) is a good quantum number. Subsequent to our original paper,[10] J. A. Pople and T. Schaefer, *Mol. Phys.*, **3**, 547 (1960), and P. Diehl and J. A. Pople, *ibid.*, 557 (1960), have used the same general procedure to analyze more general systems such as X_nABR_m. These authors give a detailed justification of the method in terms of the high-resolution spin Hamiltonian. The method used by Sheppard[6] for the analysis of C^{13}-satellites is actually an extreme, though simple, example of these principles. The satellites of Hg^{199}, Pb^{207} have similarly been analyzed by P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **31**, 1431 (1959); **34**, 1049 (1961).

[20] By symmetry, it follows that $J_{A'X'} = J_{AX}$ and $J_{A'X} = J_{AX'}$.

[21] R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 994 (1960). Some weak transitions (*e.g.*, 8–25, 9–24, etc.) of the methyl group are not mentioned in Table III of this paper. All allowed transitions have been included in the present calculations.

[22] This is also true when $J_{XX'} \neq 0$, since for the spin states +1 and −1 of AA′, the methyl groups behave as though they were equally coupled (by ${}^1/_2(J_{AX} + J_{AX'})$) to both the A and A′ protons. These are precisely the conditions required for the two methyl groups to be magnetically equivalent and therefore all the methyl transitions for these spin states of AA′ are independent of $J_{XX'}$. Thus one may calculate these transitions with $J_{XX'} = 0$. This is a useful result, as the two lines at $\pm{}^1/_2(J_{AX} + J_{AX'})$ are the most intense lines of the methyl spectrum. The rather small J_{AX} reported for *cis*- and *trans*-2-butenes (ref. 18, p. 242) are thus understandable, as these values actually correspond to $J_{AX} + J_{AX'}$ and these two constants are generally of opposite signs in olefins. Much less can be said about the AA′ spectrum when $J_{XX'} \neq 0$. The lines at $\pm{}^3/_2(J_{AX} + J_{AX'})$, which correspond to all the protons of both methyl groups with the same spins, are the only ones which are completely unchanged when $J_{XX'}$ is no longer zero. Unfortunately, these lines have less than 3% of the total intensity of the AA′ spectrum.

[23] Exactly the same results, although stated in somewhat different terms, have been obtained by A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962), by means of the usual method[11] of analysis.

TABLE I

THEORETICAL SPECTRUM FOR THE $X_3AA'X_3'$ SYSTEM WITH $J_{XX'} = 0$, $\nu_{AX} \gg J_{AX}$ AND $J_{AX'}$[a]

AA′ Spectrum

Frequency relative to ν_A	Rel. intensity (total 64)
$\pm 1/2(J_{AX} + J_{AX'})$	18
$\pm 3/2(J_{AX} + J_{AX'})$	2
$\pm 1/2(A - J_{AA'})$	$9(1 + J_{AA'}/A)$
$\pm 1/2(A + J_{AA'})$	$9(1 - J_{AA'}/A)$
$\pm[1/2(A - J_{AA'}) \pm (J_{AX} + J_{AX'})]$	$3(1 + J_{AA'}/A)$
$\pm[1/2(A + J_{AA'}) \pm (J_{AX} + J_{AX'})]$	$3(1 - J_{AA'}/A)$
$\pm 1/2[B - J_{AA'} \pm (J_{AX} + J_{AX'})]$	$3(1 + J_{AA'}/B)$
$\pm 1/2[B + J_{AA'} \pm (J_{AX} + J_{AX'})]$	$3(1 - J_{AA'}/B)$
$\pm 1/2(C - J_{AA'})$	$1 + J/_{AA'}C$
$\pm 1/2(C + J_{AA'})$	$1 - J_{AA'}/C$

X_3X_3' Spectrum

Frequency relative to ν_X	Rel. intensity (total 32)
$\pm 1/2(J_{AX} + J_{AX'})$	16
$\pm 1/2(A - J_{AA'})$	$5(1 + J_{AA'}/A)$
$\pm 1/2(A + J_{AA'})$	$5(1 - J_{AA'}/A)$
$\pm 1/2(B - A)$	$5 \cos^2(\theta_A - \theta_B)$
$\pm 1/2(B + A)$	$5 \sin^2(\theta_A - \theta_B)$
$\pm 1/2(C - B)$	$\cos^2(\theta_B - \theta_C)$
$\pm 1/2(C + B)$	$\sin^2(\theta_B - \theta_B)$

[a] In Table I, $A = [(J_{AX} - J_{AX'})^2 + J^2_{AA'}]^{1/2}$, $B = [(2J_{AX} - 2J_{AX'})^2 + J^2_{AA'}]^{1/2}$, $C = [(3J_{AX} - 3J_{AX'})^2 + J^2_{AA'}]^{1/2}$ $\sin 2\theta_A = J_{AA'}/A$, $\sin 2\theta_B = J_{AA'}/B$, $\sin 2\theta_C = J_{AA'}/C$.

trum. Two other prominent lines are those at ± $1/2(A - J_{AA'})$ which, except for unlikely combinations of coupling constants, lie inside those at $\pm 1/2(J_{AX} + J_{AX'})$.

Although the number of lines in the entire spectrum is the same whether $J_{AX'}$ is zero or not, the *relative* positions of several lines are fairly sensitive to $J_{AX'}$, so that even a very small value of this coupling constant is discernible.

The best fits of the calculated with the observed spectra were obtained by trial and error. In this procedure it is not necessary to calculate the positions of all the bands. The intensities do not change appreciably for small changes of coupling constants and do not need to be calculated except finally.

The final calculated spectra agreed very closely with the observed spectra. Deviations in line positions were not more than 0.15 c.p.s. and usually much less. As an example of the fit achieved, a spectrum of *dl*-2,3-dibromobutane is compared with the calculated spectrum in Fig. 1. A comparison of the calculated line positions with the observed line positions (averaged over a number of spectra) is shown in Table II. The changes in the AA′ bands in passing from a small $J_{AA'}$ to a large $J_{AA'}$ are readily apparent from Figs. 1 and 2.

The C^{13} satellites of the AA′ protons were observed for a number of compounds studied and were analyzed by simple first-order treatment. These spectra were readily recognizable as doublets of quartets. Even in the undiluted compounds and when thin-wall sample tubes were used, the signal-to-noise ratio was only barely sufficient to observe the weakest lines of the satellites. As a result, coupling constants so obtained were less accurate than those calculated by the direct procedure.

Results

Chemical shifts and coupling constants for the compounds investigated are shown in Table III.

Discussion

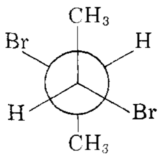
meso- **and** *dl*-**2,3-dibromobutane** have been studied in the gas phase by electron diffraction.[24] The conclusion was reached that the bromine atoms were *trans* in both cases, but that considerable torsional oscillation occurred about the mean position. Owing to the early nature of this work, the presence of appreciable concentrations of molecules with gauche bromine atoms cannot be excluded. In the liquid state the concentration of such molecules should be larger because of the greater dielectric constant. The coupling constants (Table III) found for these compounds are entirely consistent with these conclusions.

TABLE II

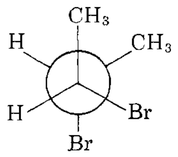
CALCULATED AND OBSERVED LINE POSITIONS FOR *dl*-2,3-DIBROMOBUTANE

Methyl protons			Methine protons		
Position		Calcd. rel. intensity (total = 32)	Position		Calcd. rel. intensity (total = 64)
Obsd.	Calcd.		Obsd.	Calcd.	
2.20	2.11	7.2	2.13	1.51	1.7
3.35	3.16	4.95		1.88	3.7
	3.26	1.0		2.11	12.9
	3.37	16.0	3.45	3.37	18.0
5.38	5.26	2.8	4.98	4.66	4.3
Not obsd.	10.57	0.05		5.04	2.3
	16.93	<0.01		5.26	5.1
			8.78	8.52	0.8
				8.64	3.7
				8.86	4.3
			10.10	10.12	2.0
			11.93	11.67	1.2
				11.78	2.3
				12.01	1.7

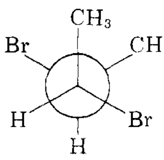
The *meso* isomer has effectively two conformations, the *trans* (I) and gauche (II) with the latter existing in two mirror-image forms, only one of which is shown. The *dl*-isomer is of course a mixture of distinct *d*- and *l*-molecules. Each enantiomer can exist in three different conformations, III, IV, V (or mirror-image forms depending on the enantiomer). The methine protons are gauche in III and IV, and *trans* in V. In I and V the coupling constant $J_{AA'}$ should be large by analogy with the compounds studied by Sheppard and from the theoretical work previously mentioned. A value of 10 to 12 c.p.s. is reasonable. Similarly, II, III and IV should have a low $J_{AA'}$, say in the range of 1 to 3 c.p.s.



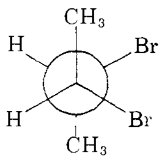
I



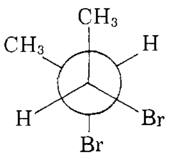
II



III



IV



V

The comparatively large value, namely, 7.85 c.p.s., observed for $J_{AA'}$ in the *meso* isomer shows that conformation I must predominate in agreement with the electron diffraction studies. However, this value is not as large as would be expected if structure I were essentially the only conformation present. That appreciable amounts of II and its mirror-image are present, was shown by

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(24) D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3173 (1939).

TABLE III

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE 2,3-DISUBSTITUTED BUTANES

Compound	State	Chemical shifts[a]		Coupling constants[b]		
		τ_{CH_3}	τ_{CH}	$J_{AA'}$	J_{AX}	$J_{AX'}$
meso-2,3-Dibromobutane	Neat	(2.38)[c]		7.85 (7.6)[d]	6.60	−0.20
dl-2,3-Dibromobutane	Neat	(2.68)[c]		3.15 (3.25)[e]	6.70	+ .05
meso-2,3-Butanediol cyclic carbonate (*cis*)	39% in CCl_4	8.626	4.160	7.35	6.55	− .15
dl-2,3-Butanediol cyclic carbonate (*trans*)	39% in CCl_4	8.587	4.340	7.20	6.10	− .10
cis-2,2,4,5-Tetramethyldioxolane	Neat	8.95 (8.67, 8.78)[f]	5.85	5.85	6.30	− .25
trans-2,2,4,5-Tetramethyldioxolane	Neat	8.85 (8.72)[f]	6.62	8.35	5.90	− .15

[a] In p.p.m. increasing to high field with tetramethylsilane at 10.00 p.p.m. [b] $J_{AA'}$ and J_{AX} taken arbitrarily as positive; units are c.p.s. [c] Chemical shift between CH_3 and CH in p.p.m. [d] From C^{13}-satellite, $J_{C^{13},H}$ = 144 c.p.s. [e] From C^{13}-satellite, $J_{C^{13},H}$ = 154 c.p.s. [f] *gem*-Dimethyl group, J_{CH_3,CH_3} = 0.55 c.p.s. in *cis* isomer.

preliminary measurements of the *meso* compound dissolved in non-polar solvents such as carbon tetrachloride, which has a lower dielectric constant than the pure dibromobutane. Although accurate coupling constants were not obtained in these cases, inspection of the spectra showed that $J_{AA'}$ was larger by about 1 c.p.s. from that found in the pure liquid. Changes in coupling constants resulting from a changing equilibrium between two conformations of different dipole moments on varying the polarity of the solvent has already been found by Sheppard.[6]

The above observations also show that, as expected,[25] there is a rapid interconversion between the different conformations as otherwise the spectrum would be much more complicated than is observed. It is difficult from the present results to give accurate values for the population of the different conformations. This would be much easier if $J_{AA'}$ for conformations I and II were known[26] from experiment.

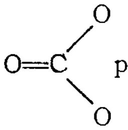
The observed value of $J_{AA'}$, when interconversion is rapid, is given by the expression

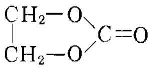
$$J_{AA'} = 1/100[xJ_{AA'}(\mathrm{I}) + (100 - x)J_{AA'}(\mathrm{II})]$$

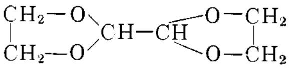
where x is the percentage of conformation I. With the J-values given previously, $x = 66 \pm 10\%$ for the pure liquid *meso*-2,3-dibromobutane at room temperature.

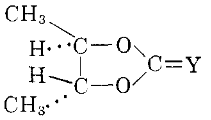
The low value (3.15 c.p.s.) of $J_{AA'}$ found for the *dl*-isomer shows that conformation V must be a minor one. The two gauche conformations III and IV are different in this case. For simplification, one can ignore conformation IV, which not only has a small $J_{AA'}$, but which also has the unfavorable gauche bromine–bromine interaction of V, and therefore should only occur in small concentration. Calculations then show 14 ± 10% of V, with the rest mainly III and presumably a small amount of IV.

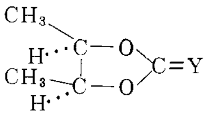
Cyclic 2,3-Disubstituted Butanes.—Two conformations have been suggested for non-planar five-membered rings, *e.g.*, cyclopentane and derivatives. These are the half-chair[27] or C_2[28] and the envelope[27] or C_s[28] conformations.

A careful X-ray diffraction study of the structure[29] of ethylene carbonate (VI) shows that the molecules possess the half-chair or C_2 conformation with the C–C bond forming an angle of 20° with the  plane.


VI


VII


X, Y = O
XI, Y = $(CH_3)_2$


VIII, Y = O
IX, Y = $(CH_3)_2$

Whilst no accurate structure determination has been carried out on 1,3-dioxolane itself, the compound VII has been studied[30] by X-ray diffraction. The five-membered rings have a slightly distorted envelope conformation, with one of the CH_2 groups 0.6 Å. above the general plane of the ring. With both this compound and ethylene carbonate the least accurately known distances are those in a direction at right angles to the general plane of the rings. This is unfortunate, as these distances are very important from the conformational point of view. Because of this and the fact that the structures are those in the solid states, only rough conclusions can be drawn about the conformations in solution. The conclusion that these compounds are non-planar in solution would appear safe. It is interesting that in both compounds mentioned above the OCC bond angles are in the range of 102–104°, which is indicative of appreciable strain. The conformations observed for the solid state are those which minimize the eclipsing of CH_2 groups.

The carbonate and dioxolane derived from *meso*-2,3-butanediol have the *cis* structures (VIII and IX, respectively). The corresponding deriva-

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(25) Reference 17, Chapter 13.

(26) At sufficiently low temperatures it may be possible to slow down the interconversion of I and II and so to obtain these coupling constants. A study of this is planned.

(27) F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

(28) K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959), and previous papers.

(29) C. J. Brown, *Acta Cryst.*, **7**, 92 (1954).

(30) S. Furberg and O. Hassel, *Acta Chem. Scand.*, **4**, 1584 (1950).

tives of *dl*-2,3-butanediol have the *trans* structures (X and XI, respectively). The *cis* isomers have essentially one conformation whereas the *trans* isomers can exist in two possible conformations. for the methine hydrogen atoms, and likewise the methyl groups, can be in either the quasi-equatorial or quasi-axial positions. The difference in energy between these two conformations should not be large, especially for the carbonate, since there are no 1:3 diaxial interactions. Even in the dioxolanes the quasi-axial methyl group would be expected to interact only weakly with the *gem*-dimethyl groups as the latter are in bisectional positions.

In comparison with the dioxolanes, the cyclic carbonates should be somewhat flatter because of the presence of the resonance-stabilized carbonate group. This is borne out by the values of $J_{AA'}$ listed in Table III; $J_{AA'}$ is larger (7.35 c.p.s.) for the *cis*-carbonate than for the *cis*-dioxolane (5.85 c.p.s.). On the basis of the theoretical calculations of Karplus[4] and Conroy[5] these values indicate the very reasonable dihedral angles of a little less than 20° and a little more than 30°, respectively.

However, the values of $J_{AA'}$ for the *trans* isomer cannot be so easily explained as, for the reasons discussed above, the observed $J_{AA'}$ depends on the $J_{AA'}$ of two conformations and the population of these conformations. In the diaxial (for the methine hydrogens) conformation rather large coupling constants would be expected, *e.g.*, 6.5–7.5 c.p.s. for the carbonate and 8–9.5 c.p.s. for the dioxolane. These values actually fit quite well with the observed ones of 7.20 and 8.35 c.p.s., respectively. Unfortunately, there is no reason to discard the alternate conformations whose contribution to $J_{AA'}$ is almost zero. Thus the final calculated values turn out to be too small. That this conclusion is correct is shown by the results obtained by Sheppard for 1,3-dioxolane, where two large coupling constants (6.0 and 7.3 c.p.s.) were found. In that case the coupling constant of the stereochemically *trans*-hydrogens is exactly the average of the coupling constants of the axial-axial and the equatorial-equatorial protons. Preliminary calculations of the C^{13}-satellites of ethylene carbonate show that there are two large coupling constants (*ca.* 7.2 and 8.8 c.p.s.) between the vicinal protons.

Some large coupling constants have been reported previously for the five-membered ring compound 2,3-dihydrofuran by Jackman.[31] The average of the vicinal coupling constants between the methylene groups in that compound is 9.1 c.p.s. In cyclopentanone rather large coupling constants also occur.[32] These results show that caution is needed in applying the results of Karplus to determine[33,34] the conformations of five-membered rings. On the other hand, the coupling constants in several camphane derivative[7] fit very well with the theoretical calculations. It is obvious that more data will be required before a satisfactory picture of coupling constants in five-membered rings can be obtained.

1,3-Coupling Constants.—In all the compounds, except *dl*-2,3-dibromobutane, the 1,3-coupling constant $J_{AX'}$ has an appreciable value and is of opposite sign to the 1,2-coupling constant J_{AX}. Although $J_{AX'}$ is always quite small, there is little doubt that the results are meaningful. Appreciable 1,3-coupling constants have been found in a few cases in saturated systems.[7,35] In the present series 1,3-coupling also occurs between the *gem*-methyl group of *cis*-2,2,4,5-tetramethyldioxolane for which $J = 0.55$ c.p.s.

Chemical Shifts.—The chemical shifts for the various groups of protons are normal.[36] The small shifts between diastereoisomers cannot be readily explained, especially as the spectra were not all measured under the same conditions.

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(31) Reference 13, p. 87.

(32) F. A. L. Anet, *Can. J. Chem.*, **39**, 2316 (1961).

(33) C. D. Jardetsky, *J. Am. Chem. Soc.*, **82**, 229 (1960); **83**, 2919 (1961).

(34) R. U. Lemieux, *Can. J. Chem.*, **39**, 116 (1961).

(35) D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

(36) L. M. Jackman, ref. 13, chapter 4.