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The Proton Magnetic Resonance Spectra of 2,3-Disubstituted *n*-Butanes

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High resolution proton magnetic resonance spectra have been obtained for the *meso*- and *dl*-forms of 2,3-dibromobutane, 2,3-dichlorobutane, 2,3-diacetoxybutane and 2,3-diphenylbutane. The spectra have been analyzed in terms of chemical shifts and coupling constants. From the magnitude of the spin-spin coupling constant between the methine protons, qualitative estimates of rotamer population have been made, and the factors controlling these populations are discussed. A dependence of 1,3-proton coupling in the system $H-C-C-CH_3$ on dihedral angle is demonstrated.

Introduction

It has been both theoretically predicted[1,2] and experimentally confirmed[3–5] that the spin–spin coupling of protons on adjacent carbons should be a smooth function of the dihedral angle describing the degree of rotation about the bond joining the carbons. The value of the coupling constant is a maximum when the dihedral angle is 180° (protons *trans* oriented), falls approximately as $\cos^2\theta$ to a value near zero at about 90°, then rises to slightly less than the maximum value at 0° (*cis* eclipsed conformation). Experiment[4,5] suggests that the coupling constants are in general somewhat higher than predicted, particularly for angles greater than 90°. Furthermore, the size of the coupling constants depends on other factors than the rotational conformation about the central bond, for example the presence of electron-donating or -withdrawing groups[4,6,7] and changes in H–C–C bond angles[1] as a result of strain or steric interference. Nevertheless the trend is sufficiently well established that one may now consider using this relation to study at least qualitatively rotational isomerism in substituted ethanes.

Anet[8] has pointed out that in compounds such as *meso*- and *dl*-2,3-dibromobutane, the methine protons are not magnetically equivalent because they are differently coupled to the terminal methyl groups, and that a complete analysis of their n.m.r. spectra will therefore yield the magnitude of the coupling constant between the methine protons. He has reported preliminary measurements on the dibromobutanes, and notes that the coupling constants differ sharply for the two isomers, reflecting a difference in the relative populations of conformers with *trans*-methine protons.

In the course of other work on the analysis of the *cis*- and *trans*-butene-2 spectra, we had developed algebraic expressions for the $X_3AA'X_3'$ case, with zero coupling of the X and X′ nuclei. These expressions are not useful for the butenes (where $J_{XX'} \approx J_{AX'}$), but are valid for the 2,3-disubstituted butanes. We have used these expressions in the analysis of the spectra of the *meso*- and *dl*-forms of the 2,3-dibromobutanes, the 2,3-dichlorobutanes, the 2,3-diacetoxybutanes and the 2,3-diphenylbutanes. Our work confirms and extends that of Anet.

Experimental

Materials.—**2,3-Dibromobutanes and 2,3-dichlorobutanes** were prepared by the addition of bromine and of chlorine to *cis*- and *trans*-butene-2, according to well established procedures.[9–11] The materials were isolated by distillation and were shown to be pure by gas-phase chromatography. The physical properties were observed.

Butane	B.p., °C. (mm.) Obsd.	B.p., °C. (mm.) Reported	n^{25}D Obsd.	n^{25}D Reported
meso-2,3-Dibromo-[9,10]	71 (45)	72.7 (50)	1.5091	1.5092
dl-2,3-Dibromo-[9,10]	75 (49)	75.6 (50)	1.5116	1.5125
meso-2,3-Dichloro-[11]	49 (80)	49.5 (80)	1.4389	1.4386
dl-2,3-Dichloro-[11]	53.5 (80)	52.5 (80)	1.4410	1.4409

2,3-Diacetoxybutanes were prepared by the acetylation[12] of the 2,3-butanediols. The *meso*-diacetate is a liquid, b.p. 190 (760 mm.) (reported[12] 66° (5.5 mm.)). The *dl*-diacetate was obtained as white leaflets, m.p. 42.8–43.6° (reported[12] 41.0–41.5°), after recrystallization from petroleum ether.

2,3-Diphenylbutanes were kindly supplied by Dr. S. Seltzer.[13]

Samples.—Samples were degassed on the vacuum line, 1% (w.w.) of tetramethylsilane was added, and they were then sealed into 5 mm. o.d. Pyrex tubes, containing sealed 1-mm. capillaries of methylene chloride or chloroform to serve as external references. Solutions were made up directly on the vacuum line, using calibrated receivers.

Spectra.—Nuclear magnetic resonance spectra were obtained at 60 mc./sec. using the Varian VR-4300 spectrometer. Graphical interpolation between sidebands of the tetramethylsilane reference served to calibrate the spectra. Line positions reported are the averages of 10 observations.

Analysis of the Spectra.—The methods of analysis outlined by Pople, Schneider and Bernstein[14] were applied to the $X_3AA'X_3'$ case. Basis functions were formed by linear combination of nuclear spin states; for the methyl groups, the symmetrized combinations

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

[2] H. Conroy, private communication.

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

[4] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (*London*), **A252**, 506 (1959).

[5] H. Conroy, in "Advances in Organic Chemistry, Method and Results," Interscience Publishers, Inc., New York, N. Y., 1960, p. 265.

[6] R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

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

[8] F. A. L. Anet, *Proc. Chem. Soc.*, 327 (1959).

[9] H. J. Lucas, T. P. Simpson and J. M. Carter, *J. Am. Chem. Soc.*, **47**, 1465 (1925).

[10] W. G. Young, R. T. Dillon and H. J. Lucas, *ibid.*, **51**, 2531 (1929).

[11] H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

[12] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[13] Brookhaven National Laboratory, Upton, L. I., N. Y.

[14] 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, p. 103.

$$\alpha\alpha\alpha = S_{3/2}$$
$$\frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) = S_{1/2}$$
$$\frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) = A_{1/2}$$
$$\frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha) = A_{1/2}' \text{ etc.} \qquad (1)$$

were used. Setting $\nu_x = 0$ arbitrarily, the basis functions and energies were then written following well-known rules, *viz.*

(1) $S_{3/2}\,\alpha\alpha\,S_{3/2}$ $\quad \nu_A + J_{AA}/4 + 6J_{AX}/4 + 6J_{AX}'/4$
(2) $S_{3/2}\,\alpha\alpha\,S_{1/2}$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}'/4$
(3) $S_{3/2}\,\alpha\beta\,S_{3/2}$ $\quad - J_{AA}/4$
(4) $S_{3/2}\,\beta\alpha\,S_{3/2}$ $\quad - J_{AA}/4$
(5) $S_{1/2}\,\alpha\alpha\,S_{3/2}$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}/4$
(6) $S_{3/2}\,\alpha\alpha\,A_{1/2}$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}'/4$
(7) $A_{1/2}\,\alpha\alpha\,S_{3/2}$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}'/4$
(8) $S_{3/2}\,\alpha\alpha\,A_{1/2}'$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}'/4$
(9) $A_{1/2}'\,\alpha\alpha\,S_{3/2}$ $\quad \nu_A + J_{AA}/4 + 4J_{AX}/4 + 4J_{AX}'/4$
etc. (2)
(41) $S_{3/2}\,\alpha\beta\,A_{1/2}$ $\quad -J_{AA}/4 + 4J_{AX}/4 - 4J_{AX}'/4$
(42) $S_{3/2}\,\beta\alpha\,A_{1/2}$ $\quad -J_{AA}/4 - 4J_{AX}/4 + 4J_{AX}'/4$
etc.

The only off-diagonal elements connect states such as 3 and 4, or 41 and 42 and are all equal to $J_{AA}'/2$. In the general case, where $\psi_1 = \phi_m\alpha\beta\phi_n$ and $\psi_2 = \phi_m\beta\alpha\phi_n$, diagonalization gives two states

$$\omega = a_1\psi_1 + a_2\psi_2$$
$$\chi = -a_2\psi_1 + a_1\psi_2$$

where

$$a_1 = \{(R_i + id)/R_i\}^{1/2} \qquad (3)$$
$$a_2 = \{(R_i - id)/R_i\}^{1/2} \qquad (4)$$

and where

$$i = m - n \qquad (5)$$
$$d = 1/2(J_{AX} - J_{AX}') \qquad (6)$$
$$R_i = \{(J_{AA}/2)^2 + i^2d^2\}^{1/2} \qquad (7)$$

In these equations m and n are the z components of the nuclear angular momentum in the methyl groups. Transition energies and intensities are then obtained in the usual way and are given in Table I. For each kind of proton one-half of the symmetrical spectrum is given.

The most prominent features of the spectra are the two intense lines (relative intensity 192) in the methyl spectrum which are separated by $J_{AX} + J_{AX}'$ (they are, however, often mixed with the lines $R_2 - R_1$ and $R_3 - R_2$); two intense lines in the methylene (relative intensity 36) having the same separation; and two further lines of nearly the same intensity in the methylene (relative intensity $36\mu_{01}$), which are separated by $2(R_1 - R_0)$. From these lines in an observed spectrum an approximate set of coupling constants, J_{AA}', J_{AX} may be calculated assuming $J_{AX}' = 0$. Calculation of predicted spectra from arbitrary parameters was facilitated by programming the IBM 704 high-speed computer to produce a list of frequencies and intensities according to Table I. The spectrum calculated using these coupling constants sufficiently resembles that observed so that the lines may be unambiguously assigned.

TABLE I

FREQUENCIES AND INTENSITIES OF LINES IN THE $X_3AA'X_3'$ SPECTRUM WITH $J_{XX}' = 0$

For the X-nuclei

Frequency rel. to ν_X	Rel. intensity
$1/2(J_{AX} + J_{AX}')$	192
$R_1 - R_0$	$120\mu_{01}$
$R_1 + R_0$	$120\phi_{01}$
$R_2 - R_1$	$60\mu_{12}$
$R_2 + R_1$	$60\phi_{12}$
$R_3 - R_2$	$12\mu_{23}$
$R_3 + R_2$	$12\phi_{23}$

For the A-nuclei

Frequency rel. to ν_A	Rel. intensity
$3/2(J_{AX} + J_{AX}')$	4
$1/2(J_{AX} + J_{AX}')$	36
$J_{AX} + J_{AX}' + R_1 - R_0$	$12\mu_{01}$
$J_{AX} + J_{AX}' + R_1 + R_0$	$12\phi_{01}$
$J_{AX} + J_{AX}' - R_1 + R_0$	$12\mu_{01}$
$J_{AX} + J_{AX}' - R_1 - R_0$	$12\phi_{01}$
$1/2(J_{AX} + J_{AX}') + R_2 - R_0$	$12\mu_{02}$
$1/2(J_{AX} + J_{AX}') + R_2 + R_0$	$12\phi_{02}$
$1/2(J_{AX} + J_{AX}') - R_2 + R_0$	$12\mu_{02}$
$1/2(J_{AX} + J_{AX}') - R_2 - R_0$	$12\phi_{02}$
$R_3 - R_0$	$4\mu_{03}$
$R_3 + R_0$	$4\phi_{03}$
$R_1 - R_0$	$36\mu_{01}$
$R_1 + R_0$	$36\phi_{01}$

In this table

$$R_i = 1/2\{(J_{AA})^2 + i^2(J_{AX} - J_{AX}')^2\}^{1/2}$$
$$\mu_{jk} = \frac{1}{2R_jR_k}\left\{R_jR_k + jk\left(\frac{J_{AX} - J_{AX}'}{2}\right)^2 + \left(\frac{J_{AA}}{2}\right)^2\right\}$$
$$\phi_{jk} = 1 - \mu_{jk}$$

In order to obtain the best fit, it was assumed that for small changes in the input parameters, the lines would change in frequency linearly, *i.e.*, that the set of equations

$$\nu_1 + \frac{\partial\nu_1}{\partial J_{AA}}\Delta J_{AA} + \frac{\partial\nu_1}{\partial J_{AX}}\Delta J_{AX} + \frac{\partial\nu_1}{\partial J_{AX}'}\Delta J_{AX}' = \nu_1' \qquad (8)$$

$$\nu_2 + \frac{\partial\nu_2}{\partial J_{AA}}\Delta J_{AA} + \frac{\partial\nu_2}{\partial J_{AX}}\Delta J_{AX} + \frac{\partial\nu_2}{\partial J_{AX}'}\Delta J_{AX}' = \nu_2' \qquad (9)$$

would be obeyed, where ν_1 is a line position calculated with J_{AA}, J_{AX} and J_{AX}', and ν_1' is the corresponding line in the spectrum calculated with the parameters $J_{AA} + \Delta J_{AA}$, $J_{AX} + \Delta J_{AX}$, and $J_{AX}' + \Delta J_{AX}'$. The coefficients $\partial\nu_i/\partial J$ were evaluated from 3 spectra predicted changing slightly each J in turn. The best (least squares) fit is expected when the ΔJ's are adjusted so that

$$R = \sum_i (\nu_i \text{ obs.} - \nu_i')^2 \qquad (10)$$

is a minimum. In this equation ν_i obs. is the experimental line position of line i. Combining 8 and 10 one obtains

$$R = \sum_i \left[\nu_i \text{ obs.} - \nu_i - \sum_k(\partial\nu_i/\partial J_k)\Delta J_k\right]^2 \qquad (11)$$

The terms in the square brackets of eq. 11 are individual members of an over-determined set of linear simultaneous equations in the ΔJ's. The optimum value for the ΔJ's may be found by the conjugate gradient method.[15] This method has been programmed by Dr. H. Conroy for the IBM 7070 high speed electronic computer and was readily adaptable to this problem. The optimum parameters found by this method were used to recalculate predicted spectra. In each case these spectra gave a very good fit—usually well within the experimental error of line position measurement. Figure 1 illustrates an average case, that of neat *meso*-2,3-dibromobutane. Observed and predicted spectra agree with a root-mean-square deviation of 0.07 c.p.s. Table II gives calculated and observed lines positions for this sample.

TABLE II

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

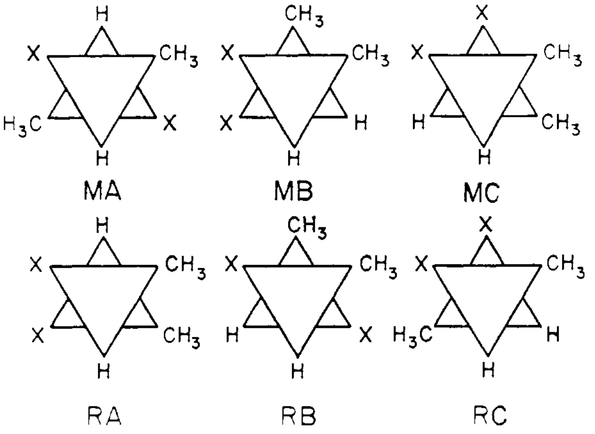
Frequencies of lines in calcd. spectrum All lines	Condensed[a]	Frequencies in obsd. spectrum	Deviation
	Methyl		
1.28	1.28	1.26	+0.02
2.78, 3.09, 3.15	3.04	3.14	− .10
9.15	9.15	9.03	+ .12
13.09	13.09	...[b]	....
18.86	18.86	...[b]	....
	Methine		
0.79, 1.28	1.17	1.18	−0.01
2.84, 3.15	3.14	3.12	+ .01
5.03	5.03	5.05	− .02
7.04, 7.10, 7.59	7.32	7.35	− .03
8.66, 9.15, 9.46	9.13	9.16	− .03
14.91, 14.97, 15.46	15.08	15.22	− .14

[a] Unresolved lines combined. Frequency given is that of the center of gravity of combined lines ($\Sigma\nu_i I_i/\Sigma I_i$), where ν_i and I_1 are the frequency and intensity of the predicted lines. [b] Too weak to be observed.

Results.—All of the data obtained are presented in Table III.

Discussion

The *meso*-forms of the 2,3-disubstituted butanes most probably[16] consist of rapidly interconverting mixtures of the three rotamers MA, MB and MC, while the *dl*-forms consist of the three rotamers RA, RB and RC (and their mirror images)



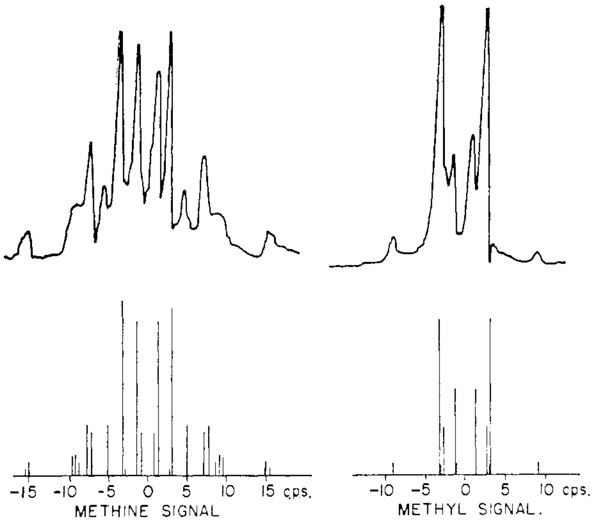


Fig. 1.—Observed and calculated spectra for neat *meso*-2,3-dibromobutane.

The rotamers MB and MC are mirror images of each other, and in solution in symmetric media are of equal energy. The rotamers RA, RB and RC may all differ in energy. Factors which effect the relative energies include steric and electrostatic interactions of the groups CH_3, X and H. In attempting to estimate rotamer populations, use is made of the size of J_{AA}, the coupling constant between the methine protons. In rotamer MA, the methine protons are *trans*, and should have a large coupling constant, J_t. In MB and MC they are *gauche* and should have small and equal coupling constants J_g. Representing the population of rotamer MA by p_{MA} and of MB and MC by $^1/_2(1 - p_{MA})$, the relation (12) is obtained. Strictly

$$p_{MA} = \frac{J_{AA} - J_g}{J_t - J_g} \tag{12}$$

speaking, it is not permissible to apply eq. 12 to the *dl*-case, since the rotamers RB and RC may differ both in energy and in *gauche* coupling constant. We will here make the assumption that they are equal, and we will further assume that the coupling constants in MA and RA are equal, as well as in MB, MC, RB and RC.

The presence of electron-withdrawing groups in the molecule also affects the magnitude of the coupling constants. Previous reports suggest that substitution with O, Cl or Br has very nearly the same effect on coupling constants, and this argument is strengthened by the small differences noted in the magnitude of J_{AX} in the six cases at hand. We will therefore assume also that J_{AA}' in forms MA and RA of the bromides, chlorides and acetates is identical, and similarly for forms MB, MC, RB and RC. We recognize that this renders further deduction of a qualitative nature, but suggest that *relative* rotamer populations based on these assumptions is probably quite good. From Sheppard's work,[4,7] reasonable estimates for J_g and J_t in the chlorides, bromides and acetates are 1 and 11 c.p.s. In the case of the diphenylbutanes these may be raised to 3 and 13 c.p.s.

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(15) M. R. Hestenes and E. Stiegel, *J. Research Natl. Bur. Standards*, **49**, 409 (1952).

(16) S. I. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954; numerous further references are contained in this book.

TABLE III

DATA OBTAINED FROM THE ANALYSIS OF THE N.M.R. SPECTRA OF 2,3-DISUBSTITUTED BUTANES

Butane	State	External ref.[a] position	τ_{CH_3},[c] p.p.m.	τ_{CH},[c] p.p.m.	$J_{AA'}$,[d] c.p.s.	J_{AX},[d] c.p.s.	$J_{AX'}$,[d] c.p.s.
meso-Dibromo-	Neat	177.0	8.16	5.785	7.87	6.57	−0.26
meso-Dibromo-	10.1% in CS_2	167.8	8.148	5.930	8.81	6.54	− .28
dl-Dibromo-	Neat	178.1	8.267	5.568	3.03	6.75	+ .02
dl-Dibromo-	10.3% in CS_2	167.8	8.265	5.620	3.11	6.74	+ .02
meso-Dichloro-	Neat	160.2	8.427	5.938	6.26	6.48	− .13
meso-Dichloro-	10.1% in CS_2	165.9	8.400	6.088	7.39	6.45	− .12
dl-Dichloro-	Neat	161.0	8.465	5.802	3.28	6.57	− .01
dl-Dichloro-	10.3% in CS_2	166.2	8.473	5.868	3.45	6.47	− .08
meso-Diacetoxy-	Neat	143.8	8.828	5.070	3.53	6.63	+ .03
meso-Diacetoxy-	9.9% in CS_2	164.0	8.868	5.173	3.59	6.66	+ .02
meso-Diacetoxy-	9.9% in $(CD_3)_2CO$	121.5	8.817	5.060	3.51	6.57	− .01
meso-Diacetoxy-	10.4% in $HCON(CH_3)_2$	253.4[b]	8.813	5.053	3.64	6.59	− .04
dl-Diacetoxy-	35.2% in CS_2	156.8	8.872	5.155	5.12	6.51	− .08
dl-Diacetoxy-	13.6% in CS_2	279.6[b]	8.885	5.194	5.08	6.50	− .05
meso-Diphenyl-	9.9% in CS_2	164.5	9.035	7.192	9.91	6.97	− .29
dl-Diphenyl-	43.7% in CS_2	273.1[b]	8.807	7.168	7.02	7.76	− .34
dl-Diphenyl-	9.9% in CS_2	165.3	8.782	7.158	7.00	7.61	− .20

[a] $CHCl_3$ (except as noted) position given in c.p.s. with $Si(CH_3)_4$ at +600.00 c.p.s. [b] CH_2Cl_2 used as external reference. [c] Parts/million, with $Si(CH_3)_4$ at +10.00 p.p.m. field increasing with larger numbers. [d] J_{AA} and J_{AX} assumed positive, $J_{AX'}$ then requires sign as shown.

2,3-Dibromobutanes.—Applying eq. 12, one obtains for the pure *meso* compound the composition 70% MA, 15% MB, 15% MC. In dilute solution in CS_2 the proportion of MA is raised to ~80%. Form MA is favored in the *meso* compound, since in this form the halogen atoms are *trans* oriented. Both steric repulsion and electric dipole repulsion between the bromines favor this conformation. In addition, the methyl groups are *trans* oriented and only two *gauche* interactions between bulky groups $(Br)(CH_3)$ are present as opposed to three in forms MB and MC. The effect of solution in CS_2 is consistent with the effect of changes in solvent dielectric constant on the relative energies of non-polar (MA) and polar (MB, MC) molecules.[17]

In the case of the *dl*-compound, application of eq. 12 gives 20% RA. Since the form RC also contains *gauche* halogen atoms, but *three gauche* interactions, as opposed to *two* in RA, it is difficult to see how it could have a lower energy than RA. The composition would thus be 20% RA, 60^+% RB, 20^-% RC. On the other hand, RB should not be favored over RA by more than MA is favored over MB, since on going from MA to MB the number of *gauche* interactions is *increased* from two to three, while on going from RB to RA the number of *gauche* interactions is *decreased* from three to two, so that the ratio 70% MA to 15% MB is reasonable compared to the ratio 60% RB to 20% RA. The effect of solvent on J_{AA} in the *dl*-case is small (within probable error), and this is reasonable since the population of RA is small anyway.

2,3-Dichlorobutanes.—The behavior observed in the dichlorobutanes parallels that in the dibromobutanes, except that the Cl–Cl *gauche* conformations are not as highly discriminated against.[18,19] The compositions calculated for the neat *meso*- and *dl*-forms are: 52% MA, 24% MB, 24% MC and 33% RA, 33^+% RB, 33^-% RC. The effect of solvent is again to increase the proportion of MA by about 10%. The relative behavior of chlorine and bromine substituents in these cases is in harmony with the findings of Mizushima.[20]

2,3-Diacetoxybutanes.—Applying eq. 12 yields the analyses: *meso* = 26% MA, 37% MB, 37% MC and *dl* = 41% RA, 59% RB + RC. These results indicate that the conformations with *gauche* acetoxyl substituents possess a *lower* energy than those with a *trans* arrangement. It is possible that the acetoxyl groups may attract each other through an electrostatic interaction between the dipoles residing in the ester groups. While the lack of influence of solvent dielectric constant on J_{AA} would seem to argue against this explanation, it does not rule it out completely, since the possibilities for rotation about the ester oxygen bonds may confer a dipole moment on form MA which is fortuitously equal to the dipole moment in the more stable forms.

2,3-Diphenylbutanes.—Using slightly higher values for $J_g + J_t$ to allow for the absence of electron-withdrawing substituents,[7] the analyses obtained for the *meso*- and *dl*-forms are: *meso* = 70% MA, 15% MB, 15% MC and *dl* = 40% RA, 60% RB + RC. In this case, the steric requirements of the phenyl are rather larger than those of the methyl. Rotamer MA is highly favored both because the bulky phenyl groups are *trans* oriented, and because only two *gauche* interactions are present. In the *dl*-compound RB should be highly favored over RC, but the number of *gauche* interactions on going from RB to RA is reduced, and hence the proportion of RA is raised. Reasonable values are 40% RA, 40^+% RB, 20^-% RC.

Be it again noted that these estimates of rotamer population are qualitative, and should be used only for comparing *trends* in the rotamer population.

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(17) Reference 16, p. 42 ff.

(18) O. H. Rank, R. E. Kagarise and D. W. E. Axford, *J. Chem. Phys.*, **17**, (1949).

(19) H. Gerding and P. G. Meerman, *Rec. trav. chim.*, **61**, 523 (1942).

(20) Reference 16, p. 41.

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.

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

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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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