

tion on the charge distribution in pyridine,²² and possible changes in the ring-current anisotropy. Examination of the values of ω_i' (Table III) shows that the effect of dissolving pyridine in water is quite small at the α position. Since some degree of solvation *via* H bonding is to be expected, and since the β and γ positions are now ~ 20 cps lower than in the neat liquid, the behavior of the α proton probably involves extensive cancellation of two or more factors. In the case of aqueous pyridinium ion, all shifts are appreciably displaced to lower field, but the γ shift is now only ~ 12 cps above the α value and, in fact, the spread of values is reduced to about half of that observed in neat pyridine.

The variation of spectral broadening of aqueous pyridine with N-decoupling and with protonation

(22) S. Mataga and N. Mataga, *Z. Physik. Chem.* (Frankfurt), **19**, 231 (1959); *Bull. Chem. Soc. Japan*, **32**, 521 (1959).

leads to some interesting conclusions. Since this broadening can be completely removed by irradiation of nitrogen, it can be inferred that the broadening is caused by a N-ring proton interaction and not chemical exchange of the N-H proton. The progressive increase of ring proton broadening with protonation, therefore, can be attributed to a decreased electric field gradient about the nitrogen.²³ This decreased gradient is provided by the addition of a proton to the nitrogen, thus making its environment more electrically symmetric.

Acknowledgments. We wish to thank the National Institutes of Health for a grant in partial support of this work.

(23) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

The Nuclear Magnetic Resonance Spectrum of 2-Butanol

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Abstract: The nmr spectra of *erythro*- and *threo*-2-butanol-3-*d* as well as 2-butanol itself have been observed both undiluted and in carbon tetrachloride solution, and these spectra have been explicitly analyzed. It has been found that the methylene protons are magnetically nonequivalent and that the extent of nonequivalence decreases with dilution. From a knowledge of the coupling constants and chemical shifts, this behavior has been interpreted in terms of an alteration of conformer populations as a consequence of hydrogen-bonding rupture on dilution.

It was recognized early in the development of proton nmr that the position of a resonance line as determined by its relationship to a reference such as TMS or another line in the same spectrum is often dependent on concentration or the nature of the solvent. In certain cases these solvent shifts are quite large, amounting to as much as several ppm. This type of solvent dependence is illustrated by the behavior of the hydroxyl proton in alcohols and phenols, the position of aromatic proton resonances when diluted with nonaromatic solvents, and the shift in line positions of nonaromatic compounds when diluted with aromatic solvents. Because the change in spectral appearance on dilution in these cases is quite dramatic, they were the subject of early investigations and theoretical treatment; consequently, it is felt that their origin is reasonably well understood.³

When the proton nmr spectra of compounds of types other than those just discussed are examined, it is often found that many of the resonance lines are likewise displaced from a reference by changes in solvent or concentration. For the majority of such compounds

and typical nmr-solvent systems, these displacements are rather small and may be, characteristically, in the range of 0.01–0.1 ppm. The origin and interpretation of solvent shifts in such compounds have not been the subject of extensive investigation since their study presents serious difficulties. First, as has already been noted, the magnitudes of these dilution shifts are often quite small, and thus careful calibration and analyses of errors are required; furthermore, not all lines in a given spectrum will be affected equally or even necessarily in the same direction. In addition, the concentration dependence associated with a given solute-solvent system may be effectively eliminated in most cases by using moderately dilute solutions; under these conditions the observed resonances do not usually differ significantly from those obtained by extrapolation to infinite dilution, and thus the existence of a small solvent dependence does not interfere with the interpretation or other information which may be sought from the spectrum.

A special case of the latter type of dilution effect involves the chemical shift difference between two magnetically nonequivalent geminal protons. Several investigators have observed that the degree of nonequivalence, as evidenced by the difference in chemical shifts between these protons, may vary with the nature of the solvent. Thus Finegold⁴ was able to increase the separation between the nonequivalent methylene

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(2) To whom all inquiries should be directed.

(3) For a discussion of early studies and theoretical interpretations of solvent dependence of this type, see 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, Chapters 15 and 16.

(4) H. S. Finegold, *Proc. Chem. Soc.*, 283 (1960).

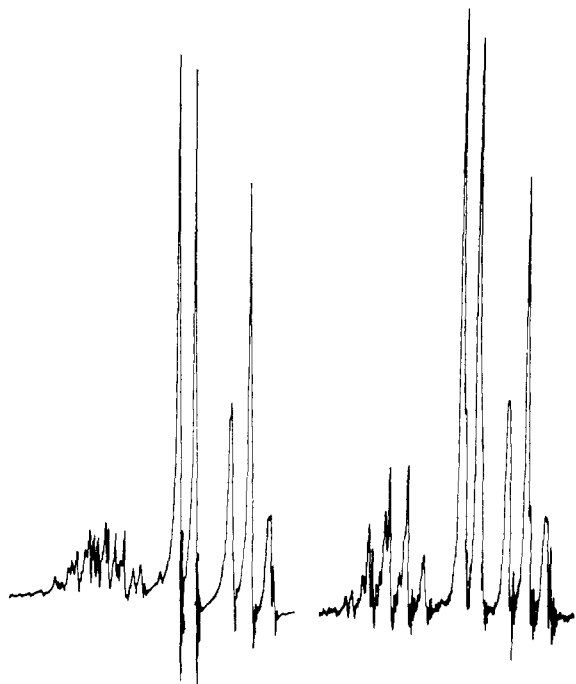
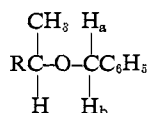


Figure 1. High-field region of 100-Mc spectrum of 2-butanol: left, undiluted; right, 3 mole % in carbon tetrachloride.

proton resonances in diethyl sulfite by the use of benzene as a solvent. Shafer and co-workers⁵ made a similar observation involving carbon tetrachloride solutions of compounds they had under investigation. Snyder⁶ was able to show a correlation between the extent of nonequivalence of certain compounds containing magnetically nonequivalent methylene protons or methyl groups and the dielectric constant of the solvent. He noted that a possible explanation could involve a change in populations of conformations as a consequence of reduced dipole-dipole repulsion in solvents of high dielectric constant. Since, however, similar behavior is displayed by certain rigid systems where no such change in conformer population is possible, it was concluded that solvent dependence of nonequivalence does not accurately reflect changes in rotational equilibria. Whitesides, Holtz, Roberts, and co-workers have studied ethers of the type shown below.^{7,8}



They observed that if R is saturated, there is essentially no change in the value of the chemical shift difference $\nu_a - \nu_b$ with solvents of differing dielectric constants. If, however, R is unsaturated then a solvent dependence does exist. These findings were interpreted as arising from an alteration of the orientation of the aromatic group with respect to the nonequivalent hydrogens, rather than from a change in conformation about the asymmetric center.

(5) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **47**, 49 (1961).

(6) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

(7) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

(8) G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *ibid.*, **87**, 1058 (1965).

It has been found^{9,10} that the resonance frequencies of certain protons bonded to carbon in molecules also containing a hydroxyl group are often sensitive to the nature of the solvent and to changes in concentration, the latter effect being as great as several tenths of a ppm in nonpolar solvents. It was felt that in these particular cases the origin of such solvent effects might lie in changes of conformational preferences, which in turn are determined by the extent of hydrogen bonding of the hydroxyl groups. It therefore appeared desirable to make a detailed study of a specific model compound. Such a compound should fulfill several requirements. First, the spectrum should be relatively simple with as few lines as possible superimposed in order that there be no ambiguity in assigning coupling constants and chemical shifts. Secondly, the structure should be such that steric and/or electrostatic effects should not be so dominant that a preferred conformation would be expected to be impressed upon the molecule irrespective of hydrogen bonding. Finally, there should be a convenient synthetic route for stereospecifically introducing deuterium into the molecule. These criteria are satisfied reasonably well by 2-butanol, and thus the present study is focused upon the behavior of this compound on dilution with carbon tetrachloride.

Results

Figure 1 shows the high-field portion of the nmr spectrum of 2-butanol at 100 Mc for both a neat sample and a dilute solution in carbon tetrachloride. A cursory examination reveals that that region of the spectrum associated with the methylene protons undergoes a marked change on dilution. It is thus obvious that dilution must alter the chemical shifts or coupling constants associated with these protons, or both. Since it was the original premise that this change in appearance of the spectrum might be attributed to a lesser degree of hydrogen bonding in dilute solutions, the dilution curve for the hydroxyl proton of 2-butanol was obtained and is shown in Figure 2. Becker, Liddel, and Shoolery¹¹ have carried out a detailed study of ethanol in carbon tetrachloride and have shown that at concentrations below that corresponding to the reversal of curvature (*cf.* Figure 2, *ca.* 0.03 mole fraction) the equilibrium involved is almost entirely between monomer and dimer. In the present study it was necessary to use solutions containing the maximum fraction of monomeric 2-butanol, *i.e.*, in the range 0.0–0.03 mole fraction of butanol, the minimum value being determined by the superposition of the hydroxyl and methylene proton signals and the signal-to-noise ratio below which accurate analyses of the spectra were no longer possible. Consequently, the dilute solutions employed contained approximately 3 mole % of the alcohol.

The methylene protons of 2-butanol are magnetically nonequivalent,¹² and their absorption is the AB region of an ABC_3X system. The direct, explicit analysis of

(9) N. Mori, S. Omura, O. Yamamoto, T. Suzuki, and Y. Tsuzuki, *Bull. Chem. Soc. Japan*, **36**, 1401 (1963).

(10) N. S. Bowman, unpublished data.

(11) E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectry.*, **2**, 1 (1958).

(12) For one of the earlier references dealing with this type of nonequivalence, see P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

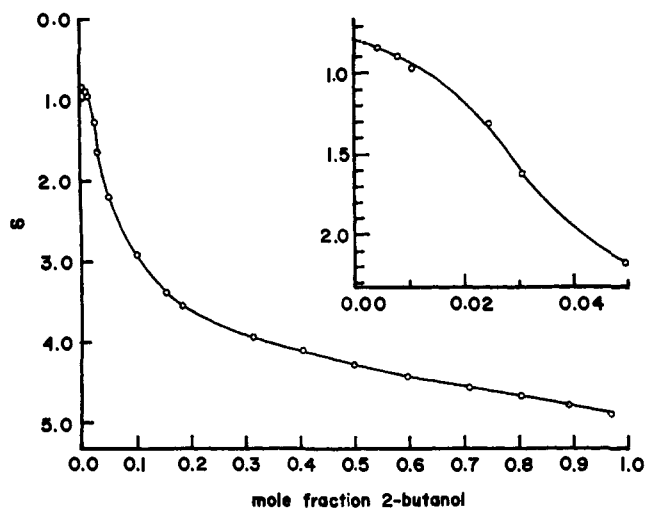


Figure 2. Chemical shift of hydroxyl proton of 2-butanol as a function of concentration in carbon tetrachloride.

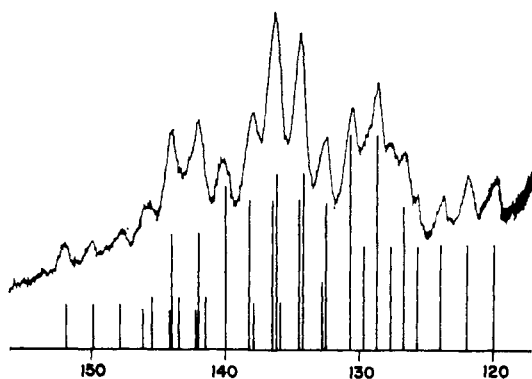
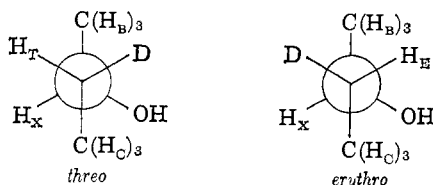


Figure 3. Observed and computed methylene proton region of 100-Mc spectrum of undiluted *threo*-2-butanol-3-*d*.

such a system is extremely difficult, and, even if such an analysis were to be carried out, there would remain the stereochemical uncertainty as to which proton should be designated A and which B. To circumvent this latter problem and at the same time simplify the analyses, *erythro*- and *threo*-2-butanol-3-*d* were prepared and their spectra obtained at 100 Mc both neat and as dilute solutions in carbon tetrachloride. These molecules are shown below in one of their conformations and included is the symbolism which will be employed to distinguish the various protons.



The above substitution of deuterium for protium converts the C_3 -proton portion of the spectrum into the A region of an AB_3X system. This considerably simplifies the problem since the A part of such a system consists of only 12 lines¹³ and is readily analyzed in these particular cases by the use of subspectral

(13) In the molecules in question, 36 lines are to be expected, however, since each of the 12 lines is tripled as a consequence of approximately a 2-cps coupling between H_T (or H_B) and deuterium; this tripling is readily discernible in Figures 3-6.

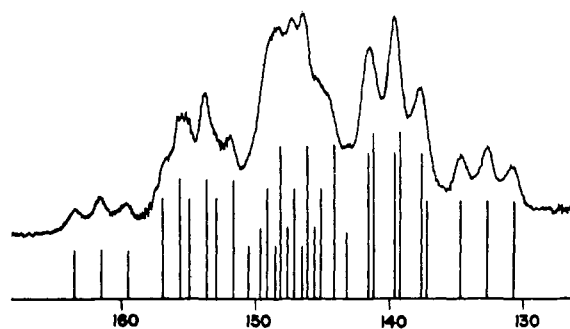


Figure 4. Observed and computed methylene proton region of 100-Mc spectrum of undiluted *erythro*-2-butanol-3-*d*.

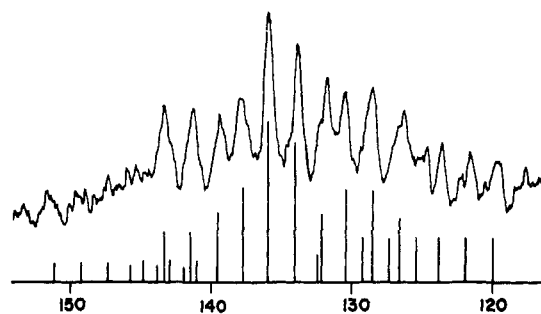


Figure 5. Observed and computed methylene proton region of 100-Mc spectrum of a 3 mole % carbon tetrachloride solution of *threo*-2-butanol-3-*d*.

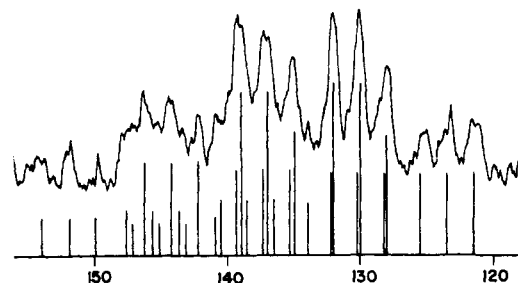


Figure 6. Observed and computed methylene proton region of 100-Mc spectrum of a 3 mole % carbon tetrachloride solution of *erythro*-2-butanol-3-*d*.

analysis.¹⁴ The values obtained by these analyses are summarized in Table I, and the agreement between the observed and calculated region of the spectrum involving the C_3 protons is shown in Figures 3-6.¹⁵

The data obtained from the analyses of the deuterated butanols furnish the information necessary to account for the change in appearance on dilution of the methylene region of the spectrum if the additional assumption is made that the same values of chemical shifts and coupling constants hold at comparable concentrations for both the deuterated and nondeuterated species. In order to test this assumption and at the same time to see if the values obtained from the deu-

(14) For a partial list of references dealing with the concept that complex spectra can often be treated as superpositions of simpler subspectra, see J. A. Pople and T. Schaefer, *Mol. Phys.*, 3, 547 (1960); P. Diehl and J. A. Pople, *ibid.*, 3, 557 (1960); P. Diehl, R. G. Jones, and H. J. Bernstein, *Can. J. Chem.*, 43, 81 (1965).

(15) In actual practice the coupling constants and chemical shifts found by subspectral analysis were used as input parameters for a computer program described later. The calculated spectra in Figures 3-6 are those obtained by the NMRIT(0) program using these parameters.

Table I. Spectral Parameters (in cps) for Deuterium-Substituted 2-Butanol at 100 Mc

Compound	Mole fraction of 2-butanol-3-d	ν_X^a	ν_E	ν_T	ν_C	J_{EX}	J_{TX}	J_{ED}/J_{TD}	J_{EC}	J_{TC}
<i>threo</i> -2-Butanol-3-d	1.00	361.5		135.1	87.7		5.8	1.9		7.5
<i>erythro</i> -2-Butanol-3-d	1.00	362.0	146.4		87.8	6.6		1.9	7.5	
<i>threo</i> -2-Butanol-3-d	0.03 ^b	358.8		134.7	88.1		5.5	1.9		7.4
<i>erythro</i> -2-Butanol-3-d	0.03 ^b	358.7	136.9		88.2	6.9		2.0	7.3	

^a All chemical shifts are relative to internal TMS. ^b Carbon tetrachloride solvent.

Table II. Spectral Parameters (in cps) Obtained for 2-Butanol at 100 Mc by Iteration

Mole fraction of 2-butanol	ν_X^a	ν_E	ν_T	ν_C	J_{LX}	J_{TX}	J_{ET}	J_{EC}	J_{TC}
1.00	361.8	148.1	137.1	87.7	6.45	5.85	-13.24	7.32	7.50
0.03 ^b	359.3	140.6	137.8	88.0	7.07	5.43	-13.00	7.63	7.09

^a All chemical shifts are relative to internal TMS. ^b Carbon tetrachloride solvent.

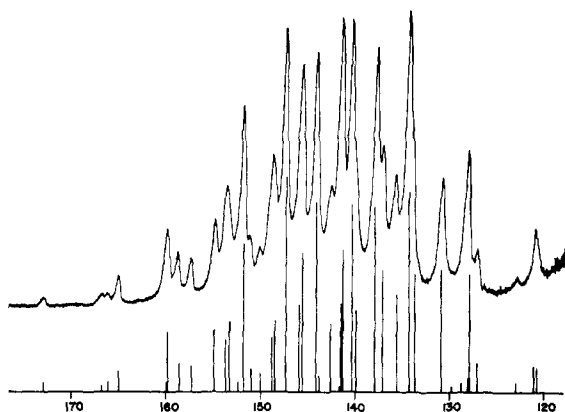


Figure 7. Observed and computed methylene proton region of 100-Mc spectrum of undiluted 2-butanol.

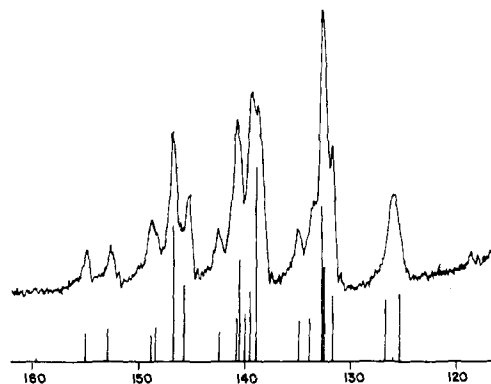


Figure 8. Observed and computed methylene proton region of 100-Mc spectrum of a 3 mole % carbon tetrachloride solution of 2-butanol.

terated compounds would indeed reproduce spectra in general agreement with those observed for the undeuterated compound, the calculated spectra associated with 2-butanol itself were generated with the aid of a computer. This was done using the program of Ferguson and Marquardt¹⁶ which is a modification of an earlier program developed by Swalen and Reilly.¹⁷ In the iterative portion of this program the values of ν_E , ν_T , J_{TC} , J_{EC} , J_{TX} , and J_{EX} obtained from the deuterated spectra, the values of ν_X and ν_C observed for 2-butanol itself, and an assumed value of J_{TE} were used as a part of the input data. Twenty iterations were carried out, and the chemical shifts and coupling constants rapidly converged to those given in Table II. This was done for both the neat and dilute cases, and the agreement between the observed and computed methylene region of the spectra is shown in Figures 7 and 8.

Two aspects of the results obtained from this iterative technique require further comment. First, it will be noted from a comparison of Tables I and II that the values of ν_T and ν_E are found at about 2-3 cps higher fields in the deuterated compound than in

the undeuterated one of comparable concentration. This behavior has been noted earlier by other workers^{18,19} and has been interpreted [by Tiers²⁰ as a consequence of a greater electron-donating power for deuterium than for hydrogen. Gutowsky²¹ has further treated this isotopic shift in terms of an electrostatic model. Secondly, the data computed for dilute 2-butanol would appear to be slightly less satisfactory than those obtained for the undiluted alcohol. This result is inherent in the nature of the problem and the method of computer solution.

In order to carry out the iterative stage of the program as was done for 2-butanol, it is necessary to determine a set of "experimental" energy levels which are then used to generate an improved set of diagonal matrix elements for the Hamiltonian. Consequently, it is first necessary to assign in the experimentally observed spectrum as many lines as possible as arising from transitions between definite energy levels. As a consequence of magnetic equivalence factoring, a general ABC_3X system has only 48 energy levels.

(18) G. V. D. Tiers, *ibid.*, **29**, 963 (1958).

(19) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(20) G. V. D. Tiers, *J. Am. Chem. Soc.*, **79**, 5585 (1957).

(21) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959).

(16) R. Ferguson and D. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).
(17) J. D. Swalen and C. A. Reilly, *ibid.*, **37**, 21 (1962).

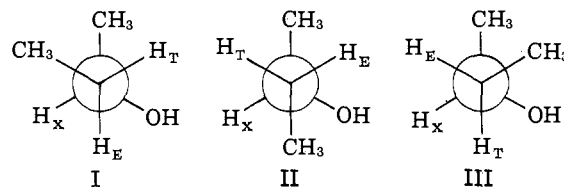
The initial stage of the solution in effect then becomes one of solving 48 independent simultaneous equations.²² Since the computation of these "experimental" energy levels involves a least-squares fit, it is obvious that, in general, agreement between the observed and calculated spectra will improve both with an increase in the number of assignable transitions and with the accuracy in determining the frequencies associated with these transitions. An identical argument holds for the reliability of the chemical shifts and coupling constants obtained from this analysis. As can be seen in Figure 7, there are numerous sharp lines in the methylene region of the spectrum alone; consequently in computing the "experimental" energy levels, the system was readily overdetermined, and the results for undiluted 2-butanol obtained by iteration appear to be quite satisfactory. In the case of dilute 2-butanol however, the experimental spectrum is characterized by a paucity of sharp lines as is indicated in Figure 8, and it was thus difficult to make even the minimum of 46 assignments with confidence. Since this would suggest that not all data in Tables I and II are equally reliable, it is desirable to remark on the accuracy of these data before discussing their significance.

Line positions in the experimental spectra were determined to the nearest 0.1 cps, and it is believed that this figure is representative of the accuracy of the coupling constants in Table I. The *absolute* values recorded for the chemical shifts are probably less accurate than 1 cps; however, the internal consistency among the six spectra is considerably better than this. If the effect of deuterium on protons other than those geminal is ignored, and if it is then further assumed that under conditions of comparable concentration the values of ν_B , ν_C , and ν_X are identical for each of the three compounds studied, it is possible to estimate the internal accuracy of the chemical shifts. Such a comparison shows an average deviation of 0.2 cps for both the dilute and undiluted cases and a maximum deviation of 0.4–0.5 cps. This then is indicative of the reliability of the various chemical shifts recorded in Table I. It is more difficult to evaluate the parameters associated with the methylene protons in Table II. Exclusive of ν_T and ν_E , the values for the undiluted alcohol are within 0.2 cps of those which would be expected from a consideration of Table I; at the same time the average deviation between observed and computed line positions is less than 0.1 cps. It is thus probable that the data for undiluted 2-butanol are as satisfactory as those obtained for the deuterated compounds. In the case of dilute 2-butanol numerous other spectra were calculated using different sets of spectral parameters, but the best agreement was obtained by iteration. A comparison of Tables I and II would indicate an agreement in coupling constants within 0.3 cps for the dilute alcohol. The error in computed chemical shifts may be several times this, however. Thus the chemical shift difference, $\nu_E - \nu_T$, obtained from the deuterated compounds is 2.2 cps while that found in Table II is 2.8 cps. Other indications which support a lower accuracy in the values of ν_T and ν_E calculated for the dilute alcohol are the

magnitude of the displacement of these values on deuteration, and an average deviation of 0.2 cps between observed and computed line positions.

Discussion

The three conformations of 2-butanol most commonly accepted are shown by structures I–III. Bernstein and Pedersen²³ studied the rotation of dilute



solutions of optically active 2-butanol in various non-polar solvents including carbon tetrachloride. By assuming that conformations I and II were equally populated, they calculated that the equilibrium ratio (%) of rotamers was 42.35:42.35:15.3 at 20°, and 43.0:43.0:14.0 at 70°. Buc²⁴ pointed out that for I and II to be present in equal amounts, it was necessary that they have the same energy and entropy. He felt that this was most unlikely and implied that, by analogy with butane and the cyclohexanols, II is probably the preferred conformation. The present study would tend to support the conclusions of Buc.

Inspection of Tables I and II shows that J_{EX} is greater than J_{TX} . Since *trans* coupling constants are larger than *gauche*, these data indicate that conformation II is populated to a greater extent than I for both dilute and undiluted 2-butanol. A consideration of these coupling constants gives no direct information on the extent to which III is populated. However, in agreement with arguments developed by Bernstein and Pedersen²³ and also by Buc,²⁴ with steric considerations which will be developed later and with the absolute magnitudes of the coupling constants, it seems probable that I and II are the predominant conformers under the conditions of this study.

On dilution of 2-butanol, there are two significant changes in the spectral parameters. The values of both the coupling constants and the chemical shifts associated with the methylene protons are altered, and it is this latter factor which is primarily responsible for the change in spectral appearance on dilution. Each of these effects will now be considered in turn.

Diluting the alcohol results in a decrease of J_{TX} which is simultaneously accompanied by an increase in J_{EX} . This is precisely the behavior that would be expected if the population of II were increasing at the expense of I. Such a shift in the position of rotational equilibrium may reasonably be interpreted by a consideration of the steric factors involved. In the concentrated alcohol, the hydroxyl group is extensively involved in hydrogen bonding. This has the effect of making that group a much larger moiety than is suggested by structures I–III. As a consequence of the interaction between the C₄-methyl group and the species bonded to the hydroxyl group, it would be expected that I would be populated to a greater extent and II to a lesser extent than would otherwise be the case.

(22) In reality only 46 equations are theoretically required since each trace relation $\sum_n E_n = 0$ serves as one such equation.

(23) H. J. Bernstein and E. E. Pedersen, *J. Chem. Phys.*, **17**, 885 (1949).

(24) H. Buc, *Ann. Chim. (Paris)*, **8**, 409 (1963).

Extension of this argument leads to the conclusion that conformation III is least favorable of all since it involves interactions between the C₄-methyl and both the hydroxyl and C₁-methyl groups. On dilution there is a lesser degree of hydrogen bonding which effectively decreases the size of the hydroxyl group resulting in a displacement of the equilibrium I \rightleftharpoons II to the right. It is also probable that there is an accompanying increase in the population of III, although this cannot be directly demonstrated by the data. However, if the original contention that III is not highly populated in the undiluted alcohol is correct, then it follows that on dilution this situation cannot be significantly changed, for otherwise a decrease in both J_{TX} and J_{EX} would be expected.

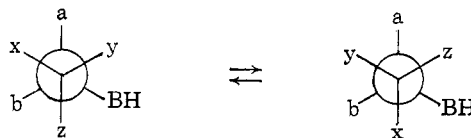
Perhaps the most interesting feature of the data in Tables I and II is the behavior of the magnetically nonequivalent protons in which the chemical shift of only one of these is appreciably affected by a change in concentration. In view of the present state of knowledge of the various factors which determine the absolute magnitudes of chemical shifts, this result could not be predicted. It is of interest to note, however, that if only the long-range shielding associated with the anisotropy of the C_{1,2} bond is considered, the results actually obtained are those to be expected. In I, H_E is deshielded by this bond while H_T is shielded; in II, both H_E and H_T are shielded. This conclusion follows from studies of alkylcyclohexanols²⁵ from which it is found that a vicinal diaxial relation between a methyl group and a ring proton is associated with a deshielding of 0.2 ppm whereas axial-equatorial, equatorial-axial, or diequatorial relations result in a shielding of \sim 0.4 ppm. Since dilution results in an increase in the fraction of molecules in conformation II and a decrease in those in I, it would be expected that H_E would be displaced to higher fields while H_T would be unaffected. This is in agreement with the observed results. The above explanation, however, is probably too simple as it ignores the influence of the hydroxyl group. The shielding effect of a hydroxyl group appears to be associated with its electric dipole rather than its diamagnetic anisotropy,²⁶ and, as the orientation of the dipole is an unknown variable, the sign and magnitude of this contribution cannot be predicted.

Finally, it may be noted that a similar shift in equilibrium produced by dilution is to be expected for many molecules where the preferred conformation is predominately determined by steric rather than electrostatic interactions. For the general case given below, it assumed that BH is a group capable of entering into

(25) E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 741 (1962).

(26) R. F. Zürcher in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press Inc., New York, N. Y., 1965, p 45.

hydrogen bonding, and that sterically $a > BH$, b and $x > y$, z in an isolated molecule. It is furthermore assumed that there is a significant interaction between a and x . While all of the various interactions will, of course, be involved in determining the position of equilibrium, a maximum dilution effect is to be expected in those cases where $BH \gg a$ when hydrogen bonded and $BH \ll a$ in the monomer.



Experimental Section

The spectra used in preparing the dilution curve were obtained on a Varian A-60; all other spectra were taken on a HA-100 spectrometer. Spectral calculations were carried out using an IBM 7040 computer.

cis- and *trans*-2,3-Epoxybutane were prepared from the corresponding Matheson CP grade *cis*- and *trans*-2-butene. The olefin was passed into a gas trap immersed in a Dry Ice-acetone bath until 14 g had been collected. The condensed butene was then slowly allowed to evaporate over a 2-hr period into a reaction vessel containing 70 ml of 40% peracetic acid and 5 g of NaOAc and fitted with a gas-inlet tube, mechanical stirrer, and Dry Ice-acetone cold finger mounted on a condenser. During the addition, the reaction temperature was kept below 10°. The reaction mixture was then slowly allowed to come to room temperature and stirring continued until no unreacted 2-butene remained. Sufficient 25% sodium hydroxide was then added with cooling to make the solution strongly basic. The reaction flask was then set for downward distillation and the product obtained in 80–85% yield by distilling from a water bath. After drying over anhydrous magnesium sulfate, the epoxybutanes were further purified by distillation.

erythro- and *threo*-2-Butanol-3-*d* were prepared by the lithium aluminum deuteride reduction of the appropriate epoxide according to the method of Helmkamp, Joel, and Sharman.²⁷

All alcohols were further purified before obtaining their spectra by preparative gas chromatography using a 20-ft column of supported diethylene glycol adipate.

Acknowledgments. This research was in part supported by funds made available through the National Science Foundation. The authors are grateful to Drs. W. Goodlett and W. Patton of the Tennessee Eastman Corp., Kingsport, Tenn., for obtaining the 100-Mc spectra. We also wish to acknowledge E. E. Holmes and Associates and Northern Scientific/Inc. for the use of a digital memory oscilloscope employed in obtaining spectra of 2-butanol at very low concentrations and which constituted a part of the dilution curve data. Finally we especially wish to acknowledge the contribution of Dr. A. F. Saturno of this department for setting up the computer program used in this study and his assistance and many helpful discussions on the application of this program to the problem at hand.

(27) G. K. Helmkamp, C. D. Joel, and H. Sharman, *J. Org. Chem.*, **21**, 844 (1956).