4-(*p*-Methoxyphenyl)-2-butanone Semicarbazone.—To 1.0 g. (6.0 mmoles) of *d*-butuligenol in 5 ml. of methanol was added 10 mmoles of diazomethane[8] in 100 ml. of ether, and the resulting solution was left at room temperature overnight, during which time the solution was allowed to concentrate spontaneously. The product was dissolved in chloroform and extracted twice with 0.1 *N* sodium hydroxide. The 555-mg. residue from the chloroform layer would not crystallize, but its infrared spectrum (chloroform) no longer contained the broad hydroxyl band at 3.00 μ. To this product in 12 ml. of pyridine was added slowly a solution of 1.8 g. (18 mmoles) of chromium trioxide in 18 ml. of pyridine. The reaction mixture was stirred 2 hr., 100 ml. of ice-water was added, the resulting solution was acidified with hydrochloric acid, and the product was extracted with chloroform. The 435 mg. of oil thereby obtained afforded a crystalline semicarbazone, m.p. 170–173° (lit[1] m.p. 176°), after recrystallization from a mixture of ethanol and water.

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[8] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166, note 3.

Hydrogen Bonding in 1,4-Substituted Butane-1,4-diols[1]

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An extensive investigation of the hydrogen-bonding propensities of 2,3-substituted butane-1,4-diols demonstrated the utility of the infrared spectroscopic approach to the elucidation of conformational details.[4] This study was restricted intentionally to compounds with no substituents upon the hydroxyl-bearing carbon atoms in order to avoid expected complications: primary, secondary, and tertiary alcohols absorb at different positions in the O–H stretching region of the infrared,[5,6] and all three types of alcohols differ in their proton-donating and -accepting abilities.[6] The present report, dealing with such 1,4-substituted butane-1,4-diols, illustrates the limitations encountered.

Table I summarizes the observed spectroscopic data. The appearance of the free peak followed expectations from literature examples. Primary hydroxyl groups absorbed near 3636 cm.$^{-1}$, secondary hydroxyl groups from 3623 to 3628 cm.$^{-1}$, and tertiary hydroxyl groups from 3611 to 3619 cm.$^{-1}$, normal positions for these types of alcohols.[5,6] For compounds containing only one substitution type (*e.g.*, compounds **1**, **2**, **3**, **6**, **7**, **9**, and **10**) only one free peak was prominent. The other compounds (**4**, **5**, and **8**) showed two free peaks. It is well-known that primary alcohols are the weakest acceptors and the strongest donors, while tertiary alcohols are the strongest acceptors and the weakest donors.[6] In unsymmetrical cases such as the primary–tertiary example (**5**), the major hydrogen-bonding conformation utilizes the primary OH as proton donor and the tertiary OH as acceptor; hence, the 3636-cm.$^{-1}$ band (free primary OH) appears only as a shoulder. Analogous situations are true for compounds **4** and **8**. As suggested by Cole and Jefferies,[5a] spectral shifts (differences in frequencies between free and bonded peaks) in such situations should be measured from the lower intensity free peak.

In our previous study of 1,4-diols, spectral shifts varied from $\Delta\nu$ = 91–196 cm.$^{-1}$.[4] In Table I, despite the changes of substitution type, variations are much less ($\Delta\nu$ = 157–167 cm.$^{-1}$). This illustrates very well the compensating electronic effects of the terminal alkyl substituents on alcohol proton-donating and -accepting abilities.[6] Again, such electron-donating substituents increase the basicity of the adjacent oxygen, but decrease the acidity of the hydroxyl hydrogen. Furthermore, it appears that all of the compounds are quite similar with regard to conformational restrictions and there are no severe steric interactions. Even in the case of the two diastereoisomeric hexane-2,5-diols, very little difference was observed in either $\Delta\nu$ or in the ratio of the integrated free and bonded peak areas (A_f/A_b, Table I).

Besides $\Delta\nu$, the second feature of hydrogen-bonding spectra ordinarily amenable to analysis is the relative areas of the free and bonded peaks. For diols of the same type, these areas should be indicative of the extent of intramolecular association. In the present instance, although only 1,4-diols were examined, the substitution type varied. Therefore, direct comparisons are hazardous, since primary, secondary, and tertiary hydroxyl stretching peaks are known to have different integrated intensities,[5b] in general decreasing with increased substitution. This factor alone should result in a decreased A_f/A_b ratio, provided the bonded peak intensity does not vary similarly with substitution type. In addition, the "*gem*-dialkyl" effect, the increased tendency toward ring formation induced by alkyl substituents,[4] also would be expected to reduce the A_f/A_b ratio (compare compounds **1**, **2**, and **3**). The actual data (Table I) are not particularly revealing. All of the alkyl-substituted diols show A_f/A_b values less than that of the parent, butane-1,4-diol, but in the case of compounds **4** through **10** the cause of this behavior cannot be interpreted with certainty. Even the diastereoisomers (**6** and **7**) show no appreciable difference, despite the fact that the *dl*-compound must have one quasiaxial methyl group on the hydrogen-bonding ring, whatever the conformation of this ring may be.[4]

The hydroxyl stretching peaks for four commercially available 2-butyne-1,4-diols, which compounds served as synthetic precursors for some of the saturated diols, are also given in Table I (**11** to **14**). The spectrum of butyne-1,4-diol, examined previously,[4] showed only one major peak at the abnormal position for primary alcohols, 3610 cm.$^{-1}$. The shift from the usual region was attributed to hydrogen bonding with the π-electrons of the triple bond.[4,7] Compounds **11** to **14** also absorbed from 3610 to 3615 cm.$^{-1}$, but in these instances it is impossible to say with certainty whether these peaks are π-bonded or free. There is very little shift

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[1] Paper XII of a series on hydrogen bonding; paper XI, ref. 4. Taken from the Ph.D. thesis of W. F. B., Princeton University, 1964.

[2] American Cyanamid Junior Research Fellow, 1960–1962; National Institutes of Health Fellow, 1962–1963.

[3] Alfred P. Sloan Research Fellow.

[4] L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, and L. Eberson, *J. Am. Chem. Soc.*, **86**, 650 (1964).

[5] (a) A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956); (b) T. D. Flynn, R. L. Werner, and B. M. Graham, *Australian J. Chem.*, **12**, 575 (1959); (c) C. S. Cook and I. H. Reese, *ibid.*, **14**, 211 (1961).

[6] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

[7] P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *ibid.*, **80**, 6691 (1958).

TABLE I

PHYSICAL AND SPECTROSCOPIC PROPERTIES OF SUBSTITUTED BUTANE-1,4-DIOLS

No.	Compound	Configuration	M.p. or b.p. (mm.), °C.	Lit. ref.	ν free	ν bonded	$\Delta\nu$	A_f/A_b[a]
1	Butane-1,4-diol			*b*	3636	3477	159	1.0
2	2-Methylbutane-1,4-diol	*dl*		*b*	3636	3477	159[c]	0.59
3	2,2-Dimethylbutane-1,4-diol			*b*	3636	3477	159[c]	0.35
4	Pentane-1,4-diol	*dl*	94 (0.45)	*d*	3636 sh[e] 3627[f]	3469	167	0.75
5	4-Methylpentane-1,4-diol		92 (1.0)	*g*	3635 sh[e] 3619[h]	3468	167	0.97
6	2,5-Hexanediol	*dl*	*i*	*j*	3627	3466	161	0.66
7	2,5-Hexanediol	*meso*	*i*	*j*	3628	3470	158	0.58
8	2-Methylhexane-2,5-diol	*dl*	88 (1.5)	*k*	3623 sh[f] 3617[h]	3466	157	0.71
9	2,5-Dimethylhexane-2,5-diol		89.6–90.5	*l*	3617	3459	158	0.85
10	1,1′-Ethylenedicyclohexanol		129.8–131.0	*m*	3611	3451	160	0.52
11	4-Methyl-2-pentyne-1,4-diol		*n*	*l, p*	3615[o,s]			
12	2,5-Dimethylhexyne-2,5-diol		95–97	*l, q*	3613[o]			
13	3,6-Dimethyl-4-octyne-3,6-diol		58–59.4	*l, r*	3615[o]			
14	1,1-Ethynylenedicyclohexanol		103.6–105	*l, q*	3610[o]			

[a] The planimeter area of the free peak over the area of the bonded peak. [b] Data from ref. 4. [c] These compounds gave unsymmetrical bonded peaks; see ref. 4. The compounds **4–10**, reported here, gave only symmetrical bonded peaks. [d] O. Philipow, *J. prakt. Chem.* [2] **93,** 162 (1916). [e] Primary free OH. [f] Secondary free OH. [g] A. Franke and A. Kohn, *Monatsh. Chem.*, **28,** 1006 (1904). [h] Tertiary free OH. [i] Samples collected from alumina chromatography could not be crystallized; lit. [j] m.p. 24.5–25.5° (*dl*-), 40–41° (*meso*-). The samples collected were, however, separated by ten fractions containing no material, and isomer separation obviously was realized. [j] K. Serck-Hanssen, S. Ställberg-Stenhagen, and E. Stenhagen, *Arkiv Kemi*, **5,** 220 (1953). [k] M. S. Losanitsch, *Compt. rend.*, **154,** 392 (1911). [l] Commercially available from Air Reduction Chemical Co. [m] *Anal.* Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.33; H, 11.78. [n] Liquid, boiling point of this sample not determined. [o] May be bonded to triple bond, but it is impossible to distinguish this from the tertiary free OH in these instances (see text). [p] E. T. Roe, J. M. Stutzman, J. T. Scanlan, and D. Swern, *J. Am. Oil Chemists' Soc.*, **29,** 18 (1952). [q] G. H. Whitfield (to I. C. I., Ltd.), British Patent 735,118; *Chem. Abstr.*, **50,** 8721 (1956). [r] V. I. Nikitin and S. D. Savrauskaya, *Zh. Obshch. Khim.*, **25,** 1106 (1955). [s] Peak unsymmetrical on high frequency side (see text).

from the free peak positions of corresponding saturated compounds; compare **9** (3617 cm.$^{-1}$) with **12** (3613 cm.$^{-1}$), and **10** (3611 cm.$^{-1}$) with **14** (3610 cm.$^{-1}$). Compound **11** does show asymmetry as a shoulder on the high frequency side of the OH absorption, but this can reasonably be attributed to the presence of both secondary and tertiary alcohol groups in this molecule. The important and obvious feature of the spectra of these molecules is the complete absence of intramolecular OH. . .O interactions; the minimum O. . .O (5.1 Å.) and OH. . .O (4.6 Å.) distances are clearly much too great to permit such intramolecular associations.

We conclude that the spectroscopic data of all these compounds fit expectations reasonably well, but that very little additional conformational information can readily be obtained from an analysis of the hydrogen-bonding interactions of these molecules.

Experimental

Source and Preparation of Diols.—Compounds 1, 2, and 3 (Table I) had been included in the previous investigation.[4] Pentane-1,4-diol (4) was obtained by lithium aluminum hydride reduction of 3-acetylpropanol (Aldrich Chemical Co.). 4-Methylpentane-1,4-diol (5) and 1,1′-ethylene dicyclohexanol (10) were prepared by catalytic hydrogenation in methanol with platinum oxide catalyst of 4-methyl-2-pentyne-1,4-diol (11) and 1,1′-ethynylenedicyclohexanol (14), both available from Air Reduction Chemical Co. 2-Methylhexane-2,5-diol (8) was prepared by the addition of 3 moles of methylmagnesium iodide to ethyl 3-formylpropionate (Union Carbide Chemical Co.), followed by work-up in the usual fashion. Compounds **9, 12,** and **13** were furnished by Air Reduction Chemical Co.

The isomeric 2,5-hexanediols (6 and 7) were obtained by chromatographic separation on an alumina column of an isomeric mixture (Aldrich Chemical Co.). Two distinct fractions were collected, the first on elution with ether containing 0.5% methanol, and the latter. after ten fractions containing no material, on elution with a mixture of 90% ether and 10% methanol. All attempts to induce crystallization of the two liquid fractions failed. In view of the clean separation, we feel these are the two diastereoisomers. Infrared spectra were determined on the materials as obtained from the column.

Physical constants and literature citations for the compounds studied appear in Table I. Melting points are corrected but boiling points are not. The infrared curves were determined in the same fashion as outlined previously.[4] All determinations were made in *ca.* 0.002 *M* concentration in carbon tetrachloride solution using 1-cm. silica cells and a Perkin-Elmer Model 421 grating spectrometer, equipped with scale expansion. For the purpose of this investigation, the integrated intensities of the free and bonded peaks were determined with the use of a planimeter and were used to interpret the results. The estimated accuracy of this area data is 10%.

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Reaction of Trinitromethyl Compounds with Hydroperoxide Ion

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Alkaline hydrogen peroxide rapidly and quantitatively reduces trinitromethyl compounds, except esters of trinitroethanol, to the corresponding 1,1-dinitro anions.[1] This general analytical prodedure was modi-

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(1) D. J. Glover, *Tetrahedron*, **19**, Suppl. 1, 219 (1963).