

sodium hydroxide, benzene, ethanol or chloroform, and only slightly soluble in hot acetone.

**Photochemical Carboxymethylation of Pyrene with Thioglycolic Acid.**—A solution of 2 g. of pyrene, m.p. 148–149°, in 30 ml. of thioglycolic acid was irradiated for 6 hours in a quartz vessel, using a General Electric BH-6 lamp. Treatment of the reaction mixture by procedure B yielded 60 mg. of crude 1-pyreneacetic acid, m.p. 209–214°. A mixture of this product with authentic 1-pyreneacetic acid, m.p. 213–219°, melted at 210–218°.

Parallel experiments with dibenzofuran yielded no water-insoluble acidic fraction. Results with dibenzofuran were also negative when a special 3 kilowatt low-pressure mercury arc delivering intense radiation at 2537 and 1930 Å. was used, and the reaction mixture was maintained at a temperature of 80–85°.

**Catalysis of Formation of Chloroacetyl polyglycolic Acids.**—To test the efficiency of various alkali metal salts as catalysts for conversion of chloroacetic acid into polyglycolic acids, 50-g. (0.529 mole) quantities of chloroacetic acid were heated for 6 hours under an air condenser with 0.058-mole quantities of the salt in question. The reaction mixture was then cooled and processed to obtain the CPGA(w) polymer. The quantities of CPGA(w) obtained in this way with different salts were as follows: lithium chloride, 7.5 g.; lithium bromide, 7.2 g.; sodium chloride, none; potassium chloride, 16.7 g.; potassium bromide, 13.2 g.; potassium carbonate, 5.0 g.

The CPGA(w) samples produced in the presence of the different salts were tested as carboxymethylation agents by heating 1-g. samples with 5 g. of naphthalene at 210° for 24 hours. All were effective except the sample obtained with potassium chloride, which did not produce a homogeneous melt with naphthalene. It did, however, produce naph-

thaleneacetic acids when 3 g. of chloroacetic acid was added to produce a homogeneous mixture.

**Carboxymethylation of Dibenzofuran by the Reaction Product of Chloroacetic Acid and Aluminum.**—Carboxymethylation of naphthalene by heating with chloroacetic acid and aluminum metal has been described.<sup>46</sup> In order to learn whether this use of aluminum salts might alter the orientation, the procedure was applied to dibenzofuran. A mixture of 17 g. (0.1 mole) of dibenzofuran, 9.5 g. (0.1 mole) of chloroacetic acid and 0.8 g. (0.03 gram atom) of granulated aluminum was heated for 12 hours under an air condenser, reaching a final reflux temperature of 237°. Evolution of hydrogen gas, causing serious foaming, was observed during the first hour of reaction, but this subsided as the initial reflux temperature of ca. 185° was reached.

When the mixture was processed by procedure B, 3.1 g. (13.8% based on chloroacetic acid) of mixed dibenzofuran-acetic acids, m.p. 115–145°, was obtained. The infrared spectrum of the mixture in Nujol was identical with that obtained by carboxymethylation with the CPGA(w) reagent. There was no evidence of alteration of the isomer distribution in the product.

**Acknowledgments.**—We are indebted to Dr. Frank O. Ellison and Dr. Lawrence C. Snyder for advice concerning molecular orbital calculations, to Dr. Gilbert J. Mains for access to equipment for performing the photochemical experiments, to Mr. Gorton Wood for the preparation of reference samples and to Dr. DeLos F. DeTar for helpful comments.

(46) Tze-Chau Kuo, *K. Hsueh Tung Pao*, 169 (1957); *C. A.*, **53**, 9160 (1959).

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## The Thorpe–Ingold Hypothesis of Valency Deviation. Intramolecular Hydrogen Bonding in 2-Substituted Propane-1,3-diols<sup>1,2</sup>

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The Thorpe–Ingold hypothesis of valency deviation has been examined by determination of the spectral shifts near 3  $\mu$  due to intramolecular hydrogen bonding in propane-1,3-diols. These spectral shifts, which varied with changes in the substituents upon the 2-position, could be correlated with the value of the C–C–C angle. The results, in agreement with more refined molecular structure determinations for analogous compounds, indicated C–C–C angles appreciably larger than 109.5° in cyclopropane-1,1-dimethanol and propane-1,3-diol and slightly spread angles in cyclobutane-1,1-dimethanol and 2-monoalkyl substituted propane-1,3-diols. The method was not applicable to 1,3-diols with bulky substituents because of adverse steric effects. The influence of alkyl groups on the rate of ring closing and opening reactions, termed the “gem-dialkyl effect,” has been attributed to a number of causes. Valency deviation may play a minor role with rings of normal size, but it may have a greater influence with reactions involving small rings.

It was noted very early that the formation of ring compounds from acyclic precursors was facilitated by the presence of alkyl substituents, especially when these were *geminal*. The reasons for this “gem-dialkyl effect” have been the subject of considerable discussion and speculation. In order to explain the many qualitative observations which had been made, Thorpe<sup>4</sup> and Ingold<sup>5</sup> de-

veloped a simple and very attractive hypothesis. It was argued that only equivalently tetrasubstituted carbon atoms would be expected to possess exactly tetrahedral angles. If, however, the angle between two of the substituents deviated from 109.5° because of incorporation into a ring structure, it was suggested that the angle between the remaining two groups would be altered by way of compensation.<sup>4</sup> Similarly, if two of the four substituents were more bulky than the others, it was predicted that angular deformation would occur in such a manner as to allow the most efficient utilization of the space available.<sup>5</sup> For example, propane would have, on this basis, a spread C–C–C angle (Ingold estimated 115.3°) and a decreased H–C<sub>2</sub>–H angle. *Geminal* groups would therefore bring the ends of a chain closer together, by virtue of the decreased angle (115.3° to 109.5°) and thus favor ring closure. Ring

(1) Paper IV of a series on hydrogen bonding; I, P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); II, P. von R. Schleyer and R. West, *ibid.*, **81**, 3164 (1959); III, P. von R. Schleyer, C. Wintner, D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 14, 1 (1959).

(2) Presented at the Third Delaware Valley Regional Meeting, Am. Chem. Soc., Phila., Penn., Feb., 1960, Abstracts, p. 47, and at the 137th Natl. Mtg., Am. Chem. Soc., Cleveland, O., April, 1960, Abstracts, p. 52-C.

(3) The author gratefully acknowledges support of this research by a grant from the National Science Foundation.

(4) R. M. Beesley, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915).

(5) C. K. Ingold, *ibid.*, **119**, 305 (1921).

opening, since it must involve separation of the ends, would be retarded. Cyclic compounds with *gem*-dialkyl substituents would thus be stabilized; this effect might be more marked for the small rings because of their greater Baeyer strain.

In the years between 1915 and 1930, Thorpe, Ingold and their collaborators published more than thirty papers on this subject.<sup>6,7</sup> None of these studies affords an unambiguous test of the validity of their hypothesis.<sup>7</sup> Unfortunately, many of the structures, assigned before modern physical methods became available, must be regarded at present as being highly dubious.<sup>7,8</sup> For these reasons, and others, the hypothesis fell out of popularity. The *gem*-dialkyl effect was acknowledged to be very real—other explanations were advanced to account for the data. Recently there has been a marked revival of interest in this problem,<sup>8-16</sup> a great variety of different approaches having been employed. The present paper reports an experimentally simple method of testing the Thorpe-Ingold hypothesis which is relatively free from the ambiguities of interpretation of some of the other investigations.

### Experimental

**Infrared Spectral Procedures.**—The infrared spectra of propane-1,3-diols substituted with saturated alkyl groups at the 2-position were determined in  $\text{CCl}_4$  solution in the OH stretching region, 2.7–3.0  $\mu$ . A Perkin-Elmer model 21 spectrophotometer equipped with a LiF prism was employed; the settings were for maximum resolution. The use of 1-cm. silica cells and solutions of *ca.* 0.005 *M* or less concentration made possible the observation of intramolecular hydrogen bonding free from intermolecular interferences. At least two different concentrations were employed as a

(6) For reviews of the early work, see C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, 1318 (1928); J. W. Baker, "Tautomerism," Rutledge, London, 1934, p. 179, and papers cited in refs. 7–15.

(7) For recent, critical reviews of the early work, see M. S. Newman, Ed., "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, pp. 117–120 (E. L. Eliel) and pp. 460–470 (G. S. Hammond).

(8) K. B. Wiberg and H. W. Holmquist, *J. Org. Chem.*, **24**, 578 (1959); K. D. Bhattacharyya, *Current Sci. (India)*, **21**, 312 (1952).

(9) L. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

(10) R. F. Brown and N. M. van Gulick, *J. Org. Chem.*, **21**, 1046 (1956).

(11) M. S. Newman and R. J. Harper, Jr., *J. Am. Chem. Soc.*, **80**, 6350 (1958).

(12) F. G. Bordwell, C. E. Osbourne and R. D. Chapman, *ibid.*, **81**, 2698 (1959).

(13) L. Ebersson, *Acta Chem. Scand.*, **13**, 211, 224 (1959); **14**, 641 (1960); L. Ebersson and S. Forsén, *J. Phys. Chem.*, **64**, 767 (1960); and earlier work cited therein.

(14) S. Searles, E. F. Lutz and M. Tamres, *J. Am. Chem. Soc.*, **82**, 2932 (1960).

(15) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

(15a) T. C. Bruice and U. K. Pandit, *J. Am. Chem. Soc.*, **82**, 5858 (1960).

(16) In addition to these systematic investigations there are many cases of the *gem*-dialkyl effect in preparative papers. For some examples from recent literature, see M. de Moura Campos, *J. Am. Chem. Soc.*, **76**, 4480 (1954); S. Searles, Jr., and E. F. Lutz, *ibid.*, **80**, 3168 (1958); A. T. Blomquist and F. Jaffé, *ibid.*, 3405 (1958); R. S. Edmondson and A. J. Lambie, *Chemistry & Industry*, 1048 (1959); S. Wawzonek and J. T. Loft, *J. Org. Chem.*, **24**, 641 (1959); and R. N. Boyd and R. C. Rittner, *J. Am. Chem. Soc.*, **82**, 2032 (1960). We should like to emphasize that results of this type can have many explanations (*cf.* ref. 7) and that ring closure and opening reactions do not always conform to simple expectations. For examples, see P. E. Verkade, *Rec. trav. chim.*, **40**, 192, 199 (1921); B. Conn, G. B. Kistiakowsky, R. M. Roberts and E. A. Smith, *J. Am. Chem. Soc.*, **64**, 1747 (1942), and R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **77**, 1752 (1955).

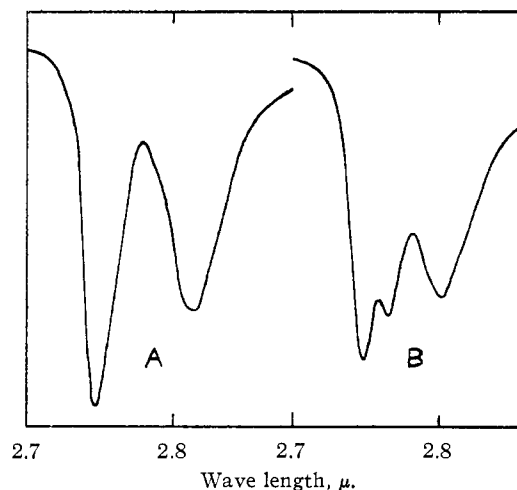


Fig. 1.—Infrared spectra in the hydroxyl region for 1,3-diols; concentrations about 0.005 *M* in  $\text{CCl}_4$  solution: A, cyclobutane-1,1-dimethanol (48); B, cyclopropane-1,1-dimethanol (47).

further check. The solvent, A.R. grade  $\text{CCl}_4$ , was decanted from  $\text{P}_2\text{O}_5$  before use. The calibration of the instrument was checked against indigenous water vapor in the standard way several times during the course of a day's run. The data quoted were corrected. The samples were run at room temperature,  $23 \pm 2^\circ$ .

Two distinct peaks were observed in each spectrum.<sup>17</sup> The first, sharp,<sup>17</sup> was the free hydroxyl band and it is found within a comparatively narrow range, 3636–3643  $\text{cm}^{-1}$ . The position of this peak could be determined with an estimated accuracy of  $\pm 1 \text{ cm}^{-1}$ . The second broader peak was due to intramolecular hydrogen bonding, and could be estimated with an accuracy of  $\pm 2 \text{ cm}^{-1}$ . The separation of the two peaks,  $\Delta\nu \text{ cm}^{-1}$ , could be measured to an accuracy of  $\pm 1 \text{ cm}^{-1}$  since the difference was dependent upon the relative and not the absolute positions of the individual bands. Reproducibility was checked by running the same sample on different days and by the use of samples of the same compounds from different sources. Examples of the reproducibility are given in Table I. Agreement was good. The positions of the peaks were estimated by determining the band envelopes at many points, and averaging. The positions were estimated to the nearest 0.00025  $\mu$  and converted to  $\text{cm}^{-1}$ . The results are given in Table I. The spectra of two of the compounds are reproduced in Fig. 1. That of cyclobutane-1,1-dimethanol is typical of all but one of the compounds examined. The exception, cyclopropane-1,1-dimethanol, also shown in Fig. 1, gave a third peak which we interpret as hydrogen bonding to the cyclopropane ring.<sup>18</sup> The ratios of the free and bonded peak heights in optical density units also are included in Table I.

**Sources of Compounds.**—Compounds 1, 18, 32 and 34 were commercial materials, redistilled or recrystallized before use. Compounds 50 and 51 were provided through the courtesy of Dr. Donald L. Heywood of the Union Carbide Chemicals Co. Compounds 47 and 48 were prepared by lithium aluminum hydride reduction of diethyl cyclopropane-1,1-dicarboxylate<sup>19a</sup> and diethyl cyclobutane-1,1-dicarboxylate<sup>19b</sup> by Mr. Claude Wintner.<sup>20</sup> The remaining forty-

(17) Primary alcohols under high resolution display a small shoulder or asymmetry upon the low frequency side of the free band. The separation is about 13  $\text{cm}^{-1}$ . The alcohols in this study behaved similarly in this regard, but the shoulders were partially obscured by the tails of the broad bonded peaks. This complication in the spectra is not of importance with regard to the present study. See R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959); M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 950, 955, 1135 (1959); T. D. Flynn, R. L. Werner and B. M. Graham, *Austral. J. Chem.*, **12**, 575 (1959); C. R. Eddy and J. Showell, private communication; D. S. Trifan and P. von R. Schleyer, unpublished observations.

(18) Reference 1, paper I.

(19) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **47**, 801 (1887); (b) J. Cason and C. F. H. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(20) C. Wintner, A. B. Thesis, Princeton University, 1959.

three compounds were prepared and characterized by Dr. F. M. Berger and Dr. B. J. Ludwig and their associates, Wallace Laboratories, Carter Products, Inc., New Brunswick, N. J. The samples, very kindly donated, were of analytical purity, and the physical constants of compounds previously reported agreed with those in the literature.

TABLE I  
SUMMARY OF SPECTRAL DATA FOR PROPANE-1,3-DIOLS,  
RR'C(CH<sub>2</sub>OH)<sub>2</sub>

Cmpd.	Substituents R	R'	$\nu_{\text{free}}$ , cm. <sup>-1</sup>	$\nu_{\text{bonded}}$ , cm. <sup>-1</sup>	$\Delta\nu$ , cm. <sup>-1</sup>	In- tensity ratio <sup>a</sup>
1 <sup>b</sup>	H	H	3637.0	3559.3	77.7	2.03
			3639.0	3560.0	79.0	1.95
2	H	CH <sub>3</sub>	3638.7	3554.0	84.7	1.94
3	H	C <sub>2</sub> H <sub>5</sub>	3638.7	3553.7	85.0	1.86
4	H	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3639.0	3553.7	85.3	1.83
5	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3638.7	3553.7	85.0	1.85
6	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	3638.3	3553.5	84.8	1.90
7	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	3638.3	3553.0	85.3	1.84
8	H	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	3637.4	3552.1	85.3	..
			3639.0	3553.7	85.3	1.85
9	H	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	3638.3	3552.7	85.6	1.84
10	H	<i>i</i> -C <sub>5</sub> H <sub>11</sub>	3638.3	3553.0	85.3	1.90
11	H	2-C <sub>3</sub> H <sub>7</sub>	3637.0	3552.4	84.6	1.78
12	H	2-C <sub>4</sub> H <sub>9</sub>	3637.7	3552.4	85.3	1.83
13	H	2-C <sub>5</sub> H <sub>11</sub>	3637.7	3553.7	84.0	1.66
14	H	3-C <sub>5</sub> H <sub>11</sub>	3637.7	3553.7	84.0	1.85
15	H	C <sub>6</sub> H <sub>11</sub> <sup>c</sup>	3638.3	3553.0	85.3	1.81
16	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	3636.4	3551.7	84.7	1.54
			3638.0	3552.7	85.3	1.58
17	H	<i>t</i> -C <sub>5</sub> H <sub>11</sub>	3636.4	3551.7	84.7	1.60
			3637.9	3552.4	85.5	1.66
18	CH <sub>3</sub>	CH <sub>3</sub>	3641.7	3553.7	88.0	2.20
19	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	3641.0	3553.0	88.0	2.02
20	CH <sub>3</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3639.0	3550.4	88.6	1.97
21	CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3638.0	3550.4	87.6	2.29
			3639.3	3551.7	87.6	2.17
22	CH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	3640.0	3550.7	89.3	1.91
23	CH <sub>3</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	3638.3	3549.9	88.4	2.00
24	CH <sub>3</sub>	<i>i</i> -C <sub>5</sub> H <sub>11</sub>	3639.6	3551.1	88.5	2.12
25	CH <sub>3</sub>	2-C <sub>3</sub> H <sub>7</sub>	3639.0	3553.7	85.3	1.68
			3637.7	3551.1	86.6	1.83
26	CH <sub>3</sub>	2-C <sub>4</sub> H <sub>9</sub>	3638.0	3552.0	86.0	1.80
27	CH <sub>3</sub>	2-C <sub>5</sub> H <sub>11</sub>	3639.3	3552.7	86.6	1.69
28	CH <sub>3</sub>	3-C <sub>5</sub> H <sub>11</sub>	3637.7	3550.8	86.9	1.75
29	CH <sub>3</sub>	C <sub>6</sub> H <sub>11</sub> <sup>c</sup>	3637.7	3551.1	86.6	1.70
30	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	3641.7	3558.4	83.4	2.16
31	CH <sub>3</sub>	<i>t</i> -C <sub>5</sub> H <sub>11</sub>	3642.7	3558.7	84.0	1.92
32	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	3643.0	3553.0	90.0	2.06
33	C <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3641.7	3551.7	90.0	2.00
34	C <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3640.0	3550.2	89.8	2.00
35	C <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	3640.3	3551.1	89.2	1.97
36	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	3639.0	3549.2	89.8	2.01
37	C <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>5</sub> H <sub>11</sub>	3637.7	3546.7	91.0	2.00
			3639.0	3549.9	89.1	2.03
38	C <sub>2</sub> H <sub>5</sub>	2-C <sub>3</sub> H <sub>7</sub>	3640.3	3554.0	86.3	1.67
39	C <sub>2</sub> H <sub>5</sub>	2-C <sub>4</sub> H <sub>9</sub>	3641.4	3555.9	85.5	1.68
40	C <sub>2</sub> H <sub>5</sub>	2-C <sub>5</sub> H <sub>11</sub>	3638.0	3552.1	85.9	1.59
			3638.7	3553.7	85.0	1.76
41	C <sub>2</sub> H <sub>5</sub>	3-C <sub>5</sub> H <sub>11</sub>	3638.3	3552.4	85.9	1.62
42	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>11</sub>	3637.7	3551.7	86.0	1.63
43	C <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	3643.0	3567.6	75.4	1.80
44	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3639.0	3548.6	90.4	2.09
45	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3639.0	3548.6	90.4	2.25
			3639.3	3550.5	88.8	2.06
46	2-C <sub>3</sub> H <sub>7</sub>	2-C <sub>3</sub> H <sub>7</sub>	3641.3	3556.5	84.8	2.11

47	Cyclopropane- 1,1-dimethanol	3635.7	3614.3 <sup>d</sup>	21.4 <sup>d</sup>	1.28 <sup>d</sup>	
			3566.9	68.8	1.38	
48	Cyclobutane-1,1- dimethanol	3638.3	3653.0	85.3	1.60	
			3637.7	3552.7	85.0	1.59
49	Cyclopentane- 1,1-dimethanol	3638.3	3550.2	88.1	1.74	
50	Cyclohexane-1,1- dimethanol	3640.3	3550.8	89.5	1.85	
51	Norbornane-2,2- dimethanol	3638.3	3550.4	87.9	1.47	

<sup>a</sup> Extinction coefficient (peak height) free peak/bonded peak. <sup>b</sup> Kuhn (ref. 9) reported 3636 free, 3558 bonded, 78  $\Delta\nu$ . <sup>c</sup> Cyclohexyl. <sup>d</sup> Bonding to the cyclopropyl ring, see ref. 18.

### Interpretation of Experimental Results

Kuhn<sup>9</sup> and other workers<sup>21,22</sup> have reported observations similar to the above on a very large number of 1,2-diols. The  $\Delta\nu$  values have been shown to be very sensitive to configurational and conformational changes. These spectral shifts ranged from  $\Delta\nu = 0$  cm.<sup>-1</sup>, for compounds such as *trans*-1,2-cyclopentanediol which have the hydroxyl groups held too far apart to permit intramolecular interaction, to  $\Delta\nu = 170$  cm.<sup>-1</sup> for 1,1,2,2-tetra-*t*-butylethane-1,2-diol, the maximum which can be expected from a ROH...ORH hydrogen bond in the aliphatic series. The magnitude of the latter value, which differed enormously from  $\Delta\nu = 32$  cm.<sup>-1</sup> for ethylene glycol, was accounted for by application of the Thorpe-Ingold hypothesis.<sup>9</sup> Substituents less bulky than the *t*-butyl group gave lower, but still abnormally large  $\Delta\nu$  values. Along with the behavior of the dissociation constants of dibasic acids,<sup>18</sup> and the molecular structure work discussed below, these spectral observations provide some of the best available experimental evidence in support of the Thorpe-Ingold hypothesis. Although it is quite probable that angle deformation is the main reason for the enhanced  $\Delta\nu$ 's in 1,2-diols with bulky substituents, this interpretation is not unambiguous.<sup>9</sup> The substituents may affect the azimuthal angle between the hydroxyl groups or may result in a "bent" central bond.<sup>9</sup> In addition, the changes in substitution were made directly upon the carbon atoms bearing the hydroxyl groups thus creating the possibility of alterations in the proton acceptor abilities of the oxygen atoms or in the hydrogen bond acidities of the hydroxyl hydrogens. Further, strain due to congestion at the carbon atom may cause rehybridization of the C-O bond.

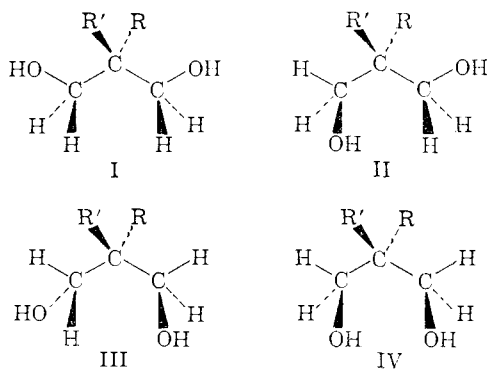
These ambiguities in interpretation of the 1,2-diol behavior have been eliminated in the present study, in which hydroxyl groups are attached to primary carbon atoms throughout and substitution changes are made upon a different carbon atom.

(21) H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954); H. Kwart and C. Gatos, *ibid.*, **80**, 881 (1958).

(22) E. L. Eliel and C. Pillar, *ibid.*, **77**, 3600 (1955); P. Hirsjarvi, *Ann. Acad. Sci. Fenn., AII*, No. 84 (1957); E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957); *J. Am. Chem. Soc.*, **81**, 6472 (1959); J. S. Brimacombe, A. B. Foster, M. Stacey and D. N. Whiffen, *Tetrahedron*, **4**, 351 (1958); M. E. Ali and L. N. Owen, *J. Chem. Soc.*, 1066, 2119 (1958); S. J. Anygal and R. J. Young, *J. Am. Chem. Soc.*, **81**, 5251, 5467 (1959); R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959); A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956).

Two new difficulties might be anticipated. First, because of the larger hydrogen bonding ring size involved, the spectral shifts are larger with 1,3-diols than with normal vicinal diols. The sensitivity of the spectroscopic method to small structural alterations may be insignificant. However, the  $\Delta\nu$  of 1,3-propanediol, 78  $\text{cm}^{-1}$ , is only about half of the maximum possible value (cf. 1,4-butanediol,  $\Delta\nu = 156 \text{ cm}^{-1}$ ).<sup>9</sup> Furthermore, the spectral shifts for the few 1,3-diols reported in the literature show large differences, from  $\Delta\nu = 52 \text{ cm}^{-1}$  for *cis-cis*-1,6-dihydroxyspiro[4.4]nonane<sup>23</sup> to  $\Delta\nu = 113 \text{ cm}^{-1}$  for cyclohexano-2,3-dicyclo-[3.3.1]nonane-2-*cis*-9-*syn*-diol.<sup>24</sup> The comparatively small range of values observed in the present study, from 69 to 90  $\text{cm}^{-1}$ , is quite significant for the purposes of this investigation.

The second potential difficulty is the basic assumption made in this work that changes in substituents upon the 2-position of propane-1,3-diols will affect only the C-C-C angle and none of the other molecular parameters. Conformational principles and an examination of molecular models indicate that there are four distinct conformations, I-IV, of minimum energy that can be assumed by the 1,3-diols. The hydroxyl groups in only one of these, IV, are close enough to permit intramolecular hydrogen bonding. The OH...O distance in conformations II and III, 3.43 Å., is too great for internal interaction.<sup>9</sup>



Without further argument, we shall adopt the following assumption as a working hypothesis: the only conformation permitting internal hydrogen bonding in 1,3-diols is IV; changes in R and R' alter the value of the C-C-C angle but do not otherwise change the geometry of the molecule. We shall cite evidence below to support the validity of this suggestion.

Adopting IV as a model with standard structural parameters (C-C = 1.54 Å., C-O = 1.43 Å., O-H = 0.96 Å.,  $\angle \text{CCO} = 109.5^\circ$ ,  $\angle \text{COH} = 108^\circ$ ,<sup>25</sup> the angle between the C-C-C and the CO-CO planes is  $120^\circ$ ), the OH...O distances were

(23) T. Bürer, E. Maecher and H. H. Günthard, *Helv. Chim. Acta*, **40**, 1823 (1957); E. Hardegger, E. Marder, H. M. Semarne and D. J. Cram, *J. Am. Chem. Soc.*, **81**, 2729 (1959).

(24) S. Julia and D. Varech, *Compt. rend.*, **246**, 1559 (1958); *Bull. soc. chim. France*, 1127 (1959). For other 1,3-diols having intermediate values see refs. 9 and 21 and R. West, J. J. Korst and W. S. Johnson, *J. Org. Chem.*, **25**, 1976 (1960); S. Julia, D. Varech, T. Bürer and H. H. Günthard, *Helv. chim. acta*, **43**, 1823 (1960).

(25) K. Kimura and M. Kubo, *J. Chem. Phys.*, **30**, 151 (1959), and refs. therein cited.

calculated for various values of the C-C-C angle (Table II). It is well established that there is some relationship between spectral shifts and the distances separating functional groups participating in hydrogen bonding.<sup>26</sup> The closer the groups, the larger is  $\Delta\nu$ . In order to correlate the OH...O distance with  $\Delta\nu$  for intramolecular hydrogen bonds, Kuhn<sup>2</sup> derived an empirical formula

$$\Delta\nu \text{ (in cm}^{-1}\text{)} = 250/\text{OH}\dots\text{O (in Å.)} - 74$$

TABLE II  
THE RELATIONSHIP BETWEEN THE C-C-C ANGLE, THE OH...O DISTANCE AND  $\Delta\nu$

$\angle$ C-C-C, deg.	OH...O, Å.	$\Delta\nu$ , $\text{cm}^{-1}$	$\angle$ C-C-C, deg.	OH...O, Å.	$\Delta\nu$ , $\text{cm}^{-1}$
120.0	2.085	46.0	109.5	1.629	79.5
112.5	1.760	68.0	108.5	1.585	83.7
111.5	1.717	71.6	107.5	1.541	88.2
110.5	1.673	75.4	106.5	1.497	93.0

Although there are serious misgivings about the accuracy of this equation,<sup>27</sup> it is adopted here for illustrative purposes. The calculated  $\Delta\nu$  values (Table II) show that, on the average, a change of  $1^\circ$  in the size of the C-C-C angle results in a difference of 4  $\text{cm}^{-1}$  in  $\Delta\nu$ . It is this estimate which is of importance for the interpretation of the 1,3-diol results, and not the absolute values of Table II. A modified Kuhn formula would give somewhat different  $\text{cm}^{-1}/\text{deg.}$  values, but it is to be emphasized that the magnitude of the influence of changes in the C-C-C angle is satisfactorily established by the original equation.

Data for 1,3-diols of similar substitution type has been summarized in Table III. The results show considerable support for the Thorpe-Ingold hypothesis. A difference of 7  $\text{cm}^{-1}$  in  $\Delta\nu$  or  $2^\circ$  in the C-C-C angle is observed between the parent compound, propane-1,3-diol, and its 2-mono-substituted derivatives. The more bulky 2-alkyl substituents do not affect  $\Delta\nu$  for the monosubstituted series since the preferred conformation would have the hydroxyl groups on the opposite side of the molecule (IV, R' = H, R = alkyl) and steric interactions would be minimal. The intensity ratio shows a progression, easily explicable on steric grounds. As the size of the substituent increases from H to primary, secondary and tertiary alkyl there is a decrease in the intensity ratio, indicating that a greater percentage of the molecules are present in the hydrogen bonding form (IV, R' = H, R = alkyl). An increased size of the alkyl group causes a decreased population of the conformations in which intramolecular hydrogen bonding is impossible (I-III).

2,2-Disubstituted trimethylene glycols show a further  $\Delta\nu$  increase, provided that the alkyl groups are not bulky. The average spectral shift values suggest a further decrease in the C-C-C angle by about  $1^\circ$ . The foregoing observations are in

(26) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapt. 3, p. 67 ff.

(27) Kuhn himself pointed out limitations of the formula, which gives internuclear distances which are too short when calculated from the larger spectral shifts.<sup>9</sup> Two of the points used to derive the relationship were based on the erroneous assumption of a planar cyclopentane ring (see ref. 21). For criticisms of this formula, see J. L. Mateos and D. J. Cram, *J. Am. Chem. Soc.*, **81**, 2756 (1959); H. Krieger, *Suomen Kemi.*, **B31**, B48 (1958).

TABLE III  
SUMMARY OF HYDROGEN BONDING IN PROPANE-1,3-DIOLS,  
RR'C(CH<sub>2</sub>OH)<sub>2</sub>

R'	R	No. cmpds. studied	Av. $\Delta\nu$ , cm. <sup>-1</sup>	Intensity ratio, ave.
H	H	1	78.4 ± 0.7	1.99 ± 0.04
H	Prim. alkyl	9	85.1 ± .3	1.87 ± .03
H	Sec. alkyl	5	84.6 ± .5	1.80 ± .04
H	Tert. alkyl	2	85.1 ± .1	1.60 ± .04
H	All alkyl <sup>b</sup>	16	85.0 ± .3	(1.81 ± .06)
CH <sub>3</sub>	Prim. alkyl	7	88.3 ± .4	2.06 ± .10
CH <sub>3</sub>	Sec. alkyl	5	86.4 ± .3	1.74 ± .04
CH <sub>3</sub>	Tert. alkyl	2	83.7 ± .3	2.04 ± .12
C <sub>2</sub> H <sub>5</sub>	Prim. alkyl <sup>a</sup>	8	89.9 ± .3	2.04 ± .05
CH <sub>3</sub> or C <sub>2</sub> H <sub>5</sub>	Prim. alkyl <sup>a</sup>	15	89.2 ± .8	2.05 ± .07
C <sub>2</sub> H <sub>5</sub>	Sec. alkyl	5	85.8 ± .3	1.64 ± .02
C <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>3</sub> H <sub>11</sub> (43)	1	75.4	1.80
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub> (46)	1	84.8	2.11
Cyclopropane-1,1-dimethanol (47)		1	68.8	1.38
Cyclobutane-1,1-dimethanol (48)		1	85.2 ± .2	1.60 ± .01
Cyclopentane-1,1-dimethanol (49)		1	88.1	1.74
Cyclohexane-1,1-dimethanol (50)		1	89.5	1.85
Norbornane-2,2-dimethanol (51)		1	87.9	1.47

<sup>a</sup> Including compounds 44 and 45. <sup>b</sup> All alkyl combined.

accord with the Thorpe-Ingold hypothesis and with the assumption that 2-substituents will not alter the geometry of propane-1,3-diol except for the C-C-C angle. Noteworthy is the close agreement of the data for compounds within a given substitution type (Table III).

Contrary to this regular behavior are the results with 2,2-disubstituted compounds when one of the substituents is secondary or tertiary. With increasing bulk of the substituent,  $\Delta\nu$  decreases instead of increasing. This effect is more pronounced in the ethyl than the methyl series. The extreme example, 2-ethyl-2-*t*-amyl-1,3-propanediol (43), gives a value even less than that of 1,3-propanediol itself. The constricted nature of the highly substituted compounds can cause conformational changes due to non-bonded interactions which result in greater OH...O distances and decreased  $\Delta\nu$  values. For example, a bulky R group in IV coupled with a R' substituent may force the hydroxyls apart by causing rotations about the C-O bonds.

Steric effects in a series of compounds with primary, secondary and tertiary substituents often do not show a quantitatively regular behavior, but the tertiary compounds exhibit more pronounced effects.<sup>23</sup> Unlike the other groups, rotation of a tertiary substituent cannot give a conformation with reduced steric hindrance.<sup>23</sup> Operation of this effect is noted most particularly here in the intensity ratios and in  $\Delta\nu$  for the ethyl series.

The intensity ratio is about the same for the propane-1,3-diols 2,2-disubstituted with primary alkyl substituents as for the unsubstituted com-

pound, but the reasons for this are not clear. When the two alkyl substituents have different effective sizes, the intensity ratio decreases, just as it did with the monosubstituted compounds. However, the trend reverses when one group is tertiary because of the adverse steric effects noted above.

The results with the homologous 1,1-dihydroxymethylcycloalkanes are particularly interesting. The cyclobutyl compound showed a significantly decreased  $\Delta\nu$ , while the spectral shift for cyclopropane-1,1-dimethanol was the lowest for any compound studied.<sup>29</sup> The other cyclic compounds had normal values. The Thorpe-Ingold hypothesis,<sup>4</sup> suitably modified by more modern ideas concerning non-planar rings, explains these data admirably well. The intensity ratio also follows a regular progression, due to the greater effective steric hindrance afforded by the adjacent methylene groups of the larger rings. Competitive hydrogen bonding to the cyclopropane ring<sup>18</sup> contributes to the low ratio for compound 47. Steric requirements of the norbornane ring evidently favor the hydrogen bonding conformation, and the intensity ratio is low for compound 51.

In summary, the experimental evidence supports the interpretation that the C-C-C angle of the conformation IV, permitting intramolecular hydrogen bonding, can be altered by substituents upon the 2-position. The total difference in the compounds studied corresponds to a range of about 5° (Table IV). The method is not applicable to bulky substituents, since they alter not only the C-C-C angle but change other aspects of the molecular geometry as well. Despite the fact that  $\Delta\nu$  is related to  $\Delta H$  for the hydrogen bond,<sup>26</sup> there is no correlation of  $\Delta\nu$  with the intensity ratio. The latter is more sensitive to conformational and steric strain effects.

TABLE IV  
MOLECULAR STRUCTURE OF 1,3-DIOLS, RR'C(CH<sub>2</sub>OH)<sub>2</sub>

R	R'	Av. $\Delta\nu$ , cm. <sup>-1</sup>	< C-C-C, deg. <sup>a</sup>
H	H	78.4	112.2
H	Alkyl	85.1	110.5
Prim. alkyl	Prim. alkyl	89.2	109.5
Cyclopropane-1,1-dimethanol		68.8	114.6
Cyclobutane-1,1-dimethanol		85.2	110.5

<sup>a</sup> Estimated assuming tetrahedral angles in the nearly equivalently substituted 2,2-di-*prim*-alkylpropane-1,3-diols. Deviations from this angle were calculated using  $\Delta\nu$  differences from 89.2 cm.<sup>-1</sup> and 4 cm.<sup>-1</sup>/deg. as the correlation.

### Discussion

Refined modern physical methods of molecular structure determination have made possible the measurement of intramolecular distances and angles with considerable accuracy. Some of the recent data pertinent to the present study are summarized in Table V. Elegant confirmation of aspects of the Thorpe-Ingold hypothesis is pro-

(29) J. D. Roberts and V. C. Chambers (*J. Am. Chem. Soc.*, **73**, 5030 (1951)) have demonstrated that the cyclopropyl ring has electron-attracting properties. The low  $\Delta\nu$  observed for compound 47 is probably not due to this cause. Other propane-1,3-diols, substituted on the 2-position with electron-attracting substituents, displayed *larger* rather than *smaller*  $\Delta\nu$  values than normal. For example, the 2-methyl-2-phenyl compound had  $\Delta\nu$  = 93 and the 2,2-diphenyl derivative,  $\Delta\nu$  = 101. These compounds will be reported subsequently

(28) H. C. Brown, *J. Chem. Ed.*, **36**, 424 (1959).

TABLE V  
PRECISE MOLECULAR STRUCTURE DATA

Compound	Angle	Value, deg.	Method <sup>a</sup>	Ref.
Propane	C-C-C	112.4	MW	30
<i>n</i> -Butane	C-C-C	112.4	ED	31
		112.2	ED	32
<i>n</i> -Alkanes	C-C-C	112.4	ED	31
		112.2	XR	
Isobutane	C-C-C	111.15	MW	33
Neopentane	C-C-C	109.5	ED	34
Cyclopropyl chloride	H-C-H	114.6	MW	35
Cyclopropyl cyanide	H-C-H	115.6	MW	35
Cyclobutane	H-C-H	(114 ± 8)	ED	35

<sup>a</sup> MW = microwave spectroscopy, ED = electron diffraction, XR = X-ray crystallography.

vided. A comparison of data of Tables IV and V indicates excellent agreement for compounds of similar substitution types. Propane-1,3-diol (Table IV) corresponds to propane, butane and the *n*-alkanes (Table V), etc. While the excellence of the agreement is fortuitous, confidence in the hydrogen bonding method and the assumptions made here is provided. It will be interesting to compare the C-C-C angle values of Table IV with results of molecular structure determinations as yet unreported on isobutane,<sup>33</sup> 1,1-dimethylcyclopropane and 1,1-dimethylcyclobutane. The present results suggest that the exocyclic angle in cyclobutane compounds may not be distorted as much as is generally assumed, but no precise structural determinations are available.<sup>35</sup> The existence of a greatly spread exocyclic cyclopropane angle<sup>35</sup> is confirmed here.

Of the recent papers on the *gem*-dialkyl effect,<sup>9-16</sup> discussion of three is particularly pertinent in the light of the hydrogen bonding results. Allinger and Zalkow<sup>15</sup> have presented a thermodynamic basis for the *gem*-dialkyl effect. The enthalpy term was attributed to a decrease in the number of skew interactions during ring closure, while the entropy term was suggested to be due mainly to the increased internal rotation barrier heights with chain branching. The conclusions of the present paper suggest that Thorpe-Ingold angle deformation probably also contributes to a minor degree. For example, a given C-C-C angle in *n*-hexane has the value 112.4°. <sup>31b</sup> For ring closure to cyclohexane to occur, this angle must be distorted to 109.5° in the cyclic derivative. Employing the usual C-C-C bending force constant,  $E = 0.0175\theta^2$  kcal./mole, where  $\theta$  is angle distortion in degrees,<sup>36</sup> the strain involved in ring closure for each C-C-C angle is calculated to be 0.16 kcal./mole. If one

of the positions of *n*-hexane carries a *gem*-dimethyl group, the C-C-C angle at that position would be 109.5° and no distortion would be necessary for ring closure. The Thorpe-Ingold contribution to the *gem* dialkyl effect, 0.16 kcal./mole, is small compared to the other conformational and thermodynamic influences. An additional example will show that this is not always the case. A given C-C-C angle in *n*-butane will be distorted 22.4° to form cyclobutane; this represents a strain of 8.8 kcal./mole for this angle.<sup>37</sup> To form 1,1-dimethylcyclobutane from 2,2-dimethylbutane, a distortion of only 19.5°, corresponding to a strain of 6.65 kcal./mole, is required for the C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> angle. In this case the Thorpe-Ingold contribution is about 1 kcal.<sup>37</sup> This suggests a preferential operation of the *gem*-dialkyl effect in small ring compounds, but thermodynamic data on such compounds are not yet available.

Brown and van Gulick<sup>10</sup> have demonstrated that substituents have a marked effect upon the rate of ring closure of 4-bromobutylamines. The rates relative to the unsubstituted compound (1.0) were: 2,2-(CH<sub>3</sub>)<sub>2</sub> = 158; 2,2-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> = 594; 2,2-(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> = 9190. Rather similar results for a ring-opening reaction were observed by Newman and Harper,<sup>11</sup> who studied the rates of hydrolysis of a number of cyclic ketals formed from propane-1,3-diols. The ketal from cyclohexanone and 2,2-dimethylpropane-1,3-diol was 15 times more resistant to acid-catalyzed hydrolysis than the ketal from the same ketone and propane-1,3-diol itself. Additional but smaller effects were noted with the similar 2,2-diethyl and 2,2-diisopropyl derivatives. The very same diols used in this latter research have been examined in the present investigation. The hydrogen bonding results indicate that the contribution of valency deviation to the rate differences can be significant only in going from the parent compounds to their *gem*-dialkyl derivatives and not within the latter group. The  $\Delta\nu$  values of compounds 18 (dimethyl), 32 (diethyl) and 46 (diisopropyl) are all about the same. It is admitted, however, that this conclusion is less secure with regard to the diisopropyl compound. In any event, conformational effects are undoubtedly of much greater importance than valency deviation in these instances.

Hydrogen bonding results with 1,3-diols which have competitive bonding sites, such as aryl groups, or are substituted upon the 1- or 3-positions, with 1,4-diols<sup>38</sup> and with 1,5-diols, reveal other aspects of the *gem*-dialkyl effect. These studies will be presented subsequently.

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(37) Westheimer<sup>36</sup> has pointed out that the bending force constant used in obtaining this figure gives strain values 20-50% too high for large values of  $\theta$ .

(38) In collaboration with L. P. Kuhn and L. Ebersohn.

(30) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

(31) (a) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959); (b) R. A. Bonham, L. S. Bartell and D. A. Kohl, *ibid.*, **81**, 4765 (1959); see this latter reference for a literature summary.

(32) K. Kuchitsu, *Bull. Chem. Soc. Japan*, **32**, 748 (1959).

(33) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958). The refined molecular structure was reported while this paper was in press: D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960).

(34) R. L. Livingston, C. Lurie and C. N. R. Rao, *Nature*, **185**, 458 (1960).

(35) Data on small ring compounds have been reviewed by E. Goldish, *J. Chem. Ed.*, **36**, 408 (1959).

(36) F. H. Westheimer in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 12, p. 523.