TABLE I

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

| No. | Compound | Configuration | M.p. or b.p. (mm.), °C. | Lit. ref. | $\nu$ free | $\nu$ 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]<br>3627[f] | 3469 | 167 | 0.75 |
| **5** | 4-Methylpentane-1,4-diol | | 92 (1.0) | *g* | 3635 sh[e]<br>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]<br>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).

TABLE I

POTASSIUM SALTS OF TERMINAL DINITROMETHYL COMPOUNDS[a]

| Potassium salt of | Yield, % | Potassium | | Carbon | | Hydrogen | | Nitrogen | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| 1,1-Dinitropropane | | 22.70 | 22.92 | 20.92 | 21.12 | 2.93 | 3.18 | 16.28 | 16.23 |
| | | | 22.62 | | 20.85 | | 3.10 | | 16.17 |
| 1,1-Dinitropentane | 70 | 19.53 | 19.65 | 30.00 | 30.06 | 4.53 | 4.40 | 14.00 | 14.15 |
| | | | 19.83 | | 30.25 | | 4.66 | | 14.18 |
| 4,4-Dinitrobutyric acid[b] | 67 | 28.71 | 28.88 | 17.64 | 17.32 | 2.22 | 2.30 | 10.29 | 10.54 |
| | | | 28.71 | | 17.84 | | 2.30 | | 10.67 |

[a] See ref. 5 for spectral data. [b] Dipotassium salt, monohydrate.

fied to produce pure samples of the potassium dinitromethyl compounds for elemental analysis and for spectral determinations. Glover and Kamlet[2] have reported previously a method for preparing potassium salts of dinitromethyl compounds using potassium iodide. Where side reactions are possible (such as saponification), the iodide procedure is preferred.[3] For example, methyl 4,4,4-trinitrobutyrate readily gave the potassium salt of methyl 4,4-dinitrobutyrate with iodide, but with hydroperoxide a mixture of dipotassium 4,4-dinitrobutyrate and dipotassium 4,4-dinitrobutenoate was formed (see Table I for potassium salts of terminal dinitromethyl compounds).

Like iodide ion, hydroperoxide ion did not give 2,2-dinitroethanol from 2,2,2-trinitroethanol, but produced potassium nitroform, probably by deformylation.

## Experimental[4]

**Reduction Procedure.**—To 0.01 mole of trinitromethyl compound in 25 ml. of methanol was added 5 ml. of 30% hydrogen peroxide. The solution was mixed and cooled in an ice bath to about 5–10°. Methanol (20 ml.) containing 4 g. of potassium hydroxide (0.07 mole) was cooled and added slowly with swirling. The solution became yellow immediately and a yellow solid began to precipitate. After all the potassium hydroxide was added, the solid was filtered cold with suction and washed with three 10-ml. portions of methanol.

The solid was then taken up in no more than 5 ml. of water and the mixture warmed gently to effect solution. If all of the peroxide was not washed out, this solution frothed until all the colorless gas was expelled. Two to three pellets of potassium hydroxide were then added and dissolved. Then methanol was added, if necessary, to cause precipitation to start. After about 5 min. the solid was filtered, washed with methanol, and dried at room temperature in a vacuum desiccator.

**Attempted Preparation of Methyl Potassium 4,4-Dinitrobutyrate.**—Methyl 4,4,4-trinitrobutyrate, 2.65 g. (0.0112 mole), was dissolved in 25 ml. of methanol in a 250-ml. erlenmeyer flask, and 5 ml. of 30% hydrogen peroxide was added at 25°. Potassium hydroxide, 2.2 g. (0.039 mole), in 10 ml. of methanol was added slowly with stirring. The solution became deep red and the temperature rose to 40–50°. The solution was cooled in an ice bath and a sticky solid precipitated. The liquid was decanted and methanol was added to the solid, which then became crystalline. The yellow-orange solid (I) was filtered and 2 g. of solid potassium hydroxide was added to the filtrate and dissolved, causing further precipitation. The solid which precipitated was filtered off and combined with the first batch (I) in methanol. The solid did not all dissolve when this mixture was warmed. After cooling the solution in an ice bath, the yellow-orange solid was filtered and dried in a vacuum desiccator. One gram of product was obtained.

The filtrate from the second batch of I, when evaporated by heating to one-fourth its volume (now 10 ml.), became quite red. The solution was cooled in an ice bath and a red solid (II) precipitated. The precipitate was filtered, and slurried with boiling methanol, and this mixture was cooled and filtered. While methanol-wet, the solid was quite red, but appeared to become yellowish when dry. After drying, the solid (II) weighed 0.15 g. The ultraviolet spectra showed $\lambda_{max}$ water 381 m$\mu$ for I and 409 m$\mu$[5] for II.

*Anal.* Calcd. for $C_4H_4K_2N_2O_6$ (I, dipotassium 4,4-dinitrobutyrate): K, 30.72. Found: K, 30.97.

*Anal.* Calcd. for $C_4H_2K_2N_2O_6$ (II, dipotassium 4,4-dinitrobutenoate): K, 30.98. Found: K, 29.43.

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[2] D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

[3] For the reaction of 1,1,1,3-tetranitropropane with hydroperoxide, see M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961).

[4] *Caution:* As these compounds are explosive, they should be handled with appropriate precautions.

[5] M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962), give 410 m$\mu$ (log $\epsilon$ 3.92) for this long wave-length peak.

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# The Twist-Boat Form of Cyclohexane

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In a number of recent discussions by organic chemists[2] of the twist-boat ($C_2$) form of cyclohexane, it has been stated or implied that the torsional or dihedral angles ($\omega_1$ and $\omega_2$ in I) of this molecule are 30 and 60°, a conclusion apparently arrived at by considering that these angles arise *halfway* through a pseudorotation cycle from one boat form to the next in which the relevant dihedral angles change from 0 to 60° and 60 to 60°, respectively. In fact, these angles are 33.2 and 70.6°; they may be computed from the equations given by Hazebroek and Osterhoff[3] in their earlier development of the flexible cyclohexanes (although these authors did not actually compute them) or more simply from the general equations for distances between points in space derived by the present author.[4]

These equations easily can be simplified for those cases with all bonds of equal length ($d$) and all bond angles tetrahedral ($\tau$), the distances between atoms 1 and 4 ($r_{14}$) and between 1 and 5 ($r_{15}$), for example, being

$$r_{14}^2 = d^2(41-16 \cos \omega)/9$$

$$r_{15}^2 = 16d^2 [11-4 (\cos \omega_1 + \cos \omega_2) - \cos \omega_1 \cos \omega_2 + 3 \sin \omega_1 \sin \omega_2]/27$$

In the twist-boat form of cyclohexane (I), $l_1^2 = l_2^2 = 8/3$ (as a function of the intercepted tetrahedral angle) if the C–C bond length, $d$, is taken as unity. Since $l_1^2 = f_{15}(\omega_1,\omega_1)$, a solution of the second equation yields

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[1] Alfred P. Sloan Foundation Fellow.

[2] *Cf.*, W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960); K. E. Howlett, *J. Chem. Soc.*, 4353 (1957); N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959); R. D. Stolow, *ibid.*, **81**, 5806 (1959).

[3] P. Hazebroek and L. J. Osterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

[4] J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).