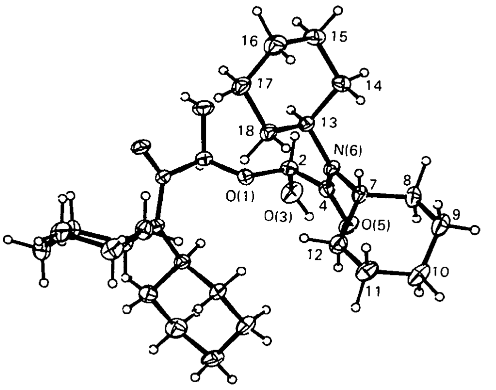

Fig. 1. *ORTEP* drawing of *N,N,N′,N′*-tetracyclohexyloxydiglycolamide hemihydrate. Thermal ellipsoids are drawn at the 35% probability level.

and O(3)–H(3)···O(5″) = 157 (3)°. H(3) may be considered as participating in an asymmetric bifurcated hydrogen bond.

In the solid state there are close intramolecular contacts between O(5)–H(12ax) and O(5)–H(13ax) of 2·515 (2) and 1·736 (2) Å, respectively. If the two cyclohexyl groups were equivalent in solution the ^{13}C spectrum should contain 8 resonances. Of the 11 lines observed the 166·58, 85·76, 56·30, and 56·22 p.p.m. resonances can be assigned to C(4), C(2) and the two cyclohexyl carbons attached to the nitrogen atoms. The remaining 7 resonances indicate there are two additional nonequivalent carbon atoms in each cyclohexyl group, which is consistent with the types of interactions observed in the solid state.

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2,3,5,6-Tetramethyl-1,4-dioxane-2,5-diol, $C_8H_{16}O_4$

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Abstract. $M_r = 176{\cdot}21$, triclinic, $P\bar{1}$, $a = 7{\cdot}430\,(4)$, $b = 6{\cdot}834\,(3)$, $c = 9{\cdot}282\,(3)$ Å, $\alpha = 91{\cdot}00\,(3)$, $\beta = 94{\cdot}50\,(4)$, $\gamma = 97{\cdot}14\,(4)°$, $V = 466{\cdot}0\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}256$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 192$. Final $R = 0{\cdot}041$ for 712 observed data. The molecules are centrosymmetric and packed in hydrogen-bonded layers parallel to the (011) plane.

Introduction. Crystals of the title compound, which is a dimer of 3-hydroxy-2-butanone, were formed inadvertently from the hydrolytic decomposition of 2,4,5-trimethyl-1,3,2-dioxaborole. The latter was prepared by heating 3-hydroxy-2-butanone and trimethylborane for 8 h (Longcor, 1983), and was purified by removal of volatiles on a vacuum line at 77 K followed by trap-to-trap distillation. After storage in a sealed container at 273 K for several weeks a crystalline product was observed. A crystallographic investigation of this product was undertaken in the expectation that it was a new, boron-containing compound. The identity of these crystals was proven by solution of the crystal structure. The title compound was subsequently shown to be a hydrolysis product of the borole.

Experimental. Crystal 0·3 × 0·2 × 0·05 mm, random orientation on a Nicolet *P*3 diffractometer, orientation matrix and unit-cell dimensions from 15 carefully centered reflections with $2\theta < 22°$; intensities measured

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for $2\theta < 55°$ ($h_{\max} = 9$, $|k_{\max}| = 8$, $|l_{\max}| = 11$), intensities of three standard reflections measured every 97 reflections showed no significant change during the entire data-collection process; total of 712 independent reflections with $F_o > 3\sigma(F_o)$ used in structure solution and refinement, no correction for absorption, extinction or anomalous dispersion; structure determined by direct methods and refined by least squares on F (Busing, Martin & Levy, 1962), scattering factors from *International Tables for X-ray Crystallography* (1974); signs of 99 reflections with $E \geq 1{\cdot}3$ determined by reiterative application of Sayre's equation (Long, 1965), an electron density map calculated using these signs used to locate and identify all non-H atoms; refinement completed with anisotropic temperature factors and inclusion of H atoms at fixed positions (Zalkin, 1974) with $B = 5{\cdot}0$ Å^2, H atoms relocated after each cycle of refinement, with C—H and O—H distances of 1·0 Å; total of 109 parameters refined, $R_w = 0{\cdot}045$, largest positional-parameter and temperature-factor shifts in final cycle of refinement 0·51 and 0·61 σ respectively, largest peak in final difference map 0·18 e Å^{-3}.

Discussion. Final atomic parameters for all non-H atoms are given in Table 1.* The atom-numbering scheme is illustrated in Fig. 1. The first digit identifies half the centrosymmetric molecule while the second digit refers to the atom positions as indicated on the drawing. Bond distances and angles and their estimated standard deviations (Busing, Martin & Levy, 1964) are given in Table 2. Packing of the molecules (Johnson, 1965) is illustrated in Fig. 2.

Table 1. *Final atomic positional coordinates* (×10^4) *and equivalent isotropic thermal parameters for the non-*H *atoms*

Numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis.

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j \text{ (Hamilton, 1959).}$$

	x	y	z	$B_{\rm eq}$(Å^2)
O(11)	4708 (4)	6871 (4)	4557 (3)	2·75
O(12)	4556 (4)	3273 (4)	2960 (3)	3·57
C(11)	3198 (5)	5315 (6)	4525 (4)	2·89
C(12)	3868 (5)	3319 (5)	4310 (4)	2·75
C(13)	1828 (6)	5801 (6)	3335 (5)	4·56
C(14)	2418 (6)	1594 (6)	4510 (4)	3·66
O(21)	5705 (4)	11954 (4)	−120 (3)	2·99
O(22)	5524 (4)	9479 (4)	2333 (3)	3·32
C(21)	6917 (5)	10510 (6)	199 (4)	2·91
C(22)	5926 (6)	8777 (6)	965 (4)	2·84
C(23)	8542 (6)	11617 (7)	1075 (5)	4·38
C(24)	7001 (6)	7033 (6)	1096 (5)	4·03

Table 2. *Interatomic distances* (Å) *and angles* (°)

The primed numbers denote the atom related by the center of symmetry of the molecule.

O(11)–C(11)	1·445 (4)	O(21)–C(21)	1·436 (5)
C(11)–C(12)	1·525 (6)	C(21)–C(22)	1·532 (6)
C(11)–C(13)	1·512 (6)	C(21)–C(23)	1·513 (6)
C(12)- O(12)	1·391 (5)	C(22) O(22)	1·416 (5)
C(12)–C(14)	1·520 (5)	C(22)–C(24)	1·516 (6)
C(12)–O(11′)	1·451 (5)	C(22)–O(21′)	1·422 (5)
C(11)–O(11)–C(12′)	113·7 (3)	C(21)–O(21)–C(22′)	114·6 (3)
O(11)–C(11)–C(12)	110·0 (3)	O(21)–C(21)–C(22)	109·8 (3)
C(11)–C(12)–O(11′)	108·0 (3)	C(21)–C(22)–O(21′)	109·1 (3)
C(11)–C(12)–O(12)	108·2 (3)	C(21)–C(22)–O(22)	107·8 (3)
C(11)–C(12)–C(14)	112·9 (3)	C(21)–C(22)–C(24)	112·8 (4)
O(12)–C(12)–C(14)	112·7 (3)	O(22)–C(22)–C(24)	111·9 (3)
O(12)–C(12)–O(11′)	110·3 (3)	O(22)–C(22)–O(21′)	110·4 (3)
C(14)–C(12)–O(11′)	104·7 (3)	C(24)–C(22)–O(21′)	104·8 (3)
O(11)–C(11)–C(13)	106·3 (3)	O(21)–C(21)–C(23)	105·2 (3)
C(12)–C(11) C(13)	113·8 (3)	C(22) C(21) C(23)	114·8 (3)

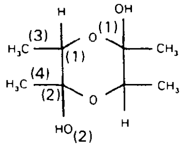

Fig. 1. A schematic view of the molecule showing numbering of the atoms.

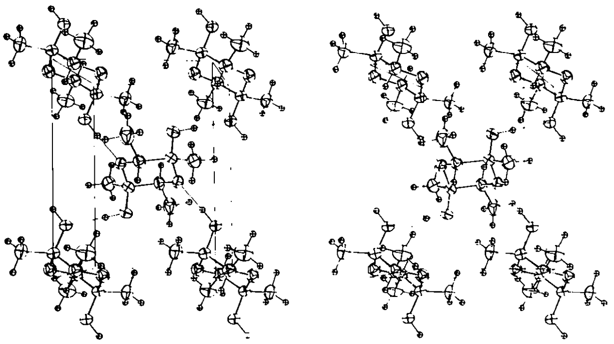

Fig. 2. Packing of the molecules as viewed down **a**. The *b* axis is across the page. Atoms are drawn with 50% probability thermal ellipsoids.

The molecules are located on crystallographic centers of symmetry and are arranged in hydrogen-bonded layers parallel to the (011) plane. The dioxane moiety is in the chair configuration and the interatomic distances within the dioxane moiety are comparable to those found in dioxane complexes (Barnes & Weakley, 1976, and references therein; Cobbledick & Small, 1973; Bjornvatten, 1969; Hassel & Rømming, 1960). The shortest intermolecular distance between a C atom and an H atom is 2·705 Å. The hydrogen-bonded O atoms are at distances of 2·804 (4) and 2·838 (4) Å, and the shortest intermolecular H···H distance is 2·379 Å.

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* Lists of structure factors, final H-atom positions and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38230 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of *N*-Acetyldibenz[*b*,*f*]azepine, $C_{16}H_{13}NO$, and its Photodimer, $C_{32}H_{26}N_2O_2$, and of *N*-(Bromoacetyl)dibenz[*b*,*f*]azepine, $C_{16}H_{12}BrNO$

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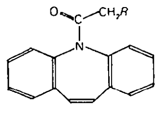
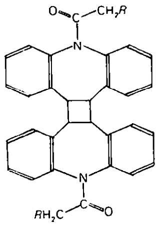
Abstract. $C_{16}H_{13}NO$ (I): $M_r = 235{\cdot}1$, $R\bar{3}$, $a = 36{\cdot}00\,(6)$, $c = 5{\cdot}43\,(1)$ Å, $V = 6094$ Å^3, $Z = 18$, $D_x = 1{\cdot}15$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 4{\cdot}96$ cm^{-1}, $F(000) = 2232$, final $R = 0{\cdot}081$ for 623 observed reflections. $C_{16}H_{12}BrNO$ (II): $M_r = 314$, *Pbca*, $a = 13{\cdot}867\,(4)$, $b = 7{\cdot}231\,(3)$, $c = 27{\cdot}867\,(10)$ Å, $V = 2794{\cdot}3$ Å^3, $Z = 8$, $D_x = 1{\cdot}49$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 28{\cdot}5$ cm^{-1}, $F(000) = 1264$, final $R = 0{\cdot}079$ for 823 observed reflections. $C_{32}H_{26}N_2O_2$ (III): $M_r = 470{\cdot}2$, $R\bar{3}$, $a = 28{\cdot}08\,(1)$, $c = 8{\cdot}926\,(4)$ Å, $V = 6095{\cdot}1$ Å^3, $Z = 9$, $D_x = 1{\cdot}15$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}40$ cm^{-1}, $F(000) = 2232$, final $R = 0{\cdot}086$ for 733 observed reflections, $R_w = 0{\cdot}090$. In all three compounds the seven-membered azepine ring has a boat conformation, and bond lengths and torsion angles suggest very little π-electron delocalization. The dimer (III) has molecular geometry $\bar{1}$ (i) with stereochemistry *endo,trans,endo* at the central cyclobutane ring.

Introduction. Photodimerization, using benzophenone as sensitizer, of the *N*-substituted dibenzazepine (I) (in benzene) gives a dimer (III); this type of reaction may be used for controlled chain extension in polymers (Âlimoğlu, Bamford, Ledwith & Mullik, 1977). The stereochemistry of the resulting dimer, previously unknown, is established here, together with details of the monomer (I) which has pharmacological activity (Kricka & Ledwith, 1973), and its bromo derivative (II).



(I) R = H
(II) R = Br



(III) R = H

Experimental. (I), (II) and (III) were prepared by Mr D. B. Sykes and Dr A. K. Âlimoğlu using methods described by Kricka & Ledwith (1973,1974); (II) was crystallized from dichloromethane and *n*-hexane, (I) and (III) by vapour diffusion of petroleum ether into a solution of each compound in dichloromethane. Weissenberg photographs of (I) for the layers *hk*0 to *hk*3 were taken from a hexagonal needle crystal of length 0·65 mm and thickness 0·08 mm; they were measured by the SERC Microdensitometer Service to give 630 unique reflections; approximate interlayer scale factors were derived from exposure times and subsequently refined (in the early rounds of least

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