The C atoms constituting each of the rings in the naphthalene unit lie within 0·01 Å of their respective least-squares planes, but there is evidence for slight (but statistically significant) non-planarity in the naphthalene segment as a whole, with naphthalene C atoms positioned up to 0·023 (4) Å from the least-squares plane. The evidence for the existence of steric congestion is reinforced by the magnitude of the C—Ph bond lengths, which at 1·495 (3) and 1·501 (3) Å for C(5)—C(18) and C(13)—C(24) respectively, are somewhat longer than the normal value of 1·486 Å.

The phenyl groups, which are planar within three standard deviations, and are oriented at angles of 63·2 (5)° [C(24) through C(29)], and 103·5 (5)° [C(18) through C(23)], to the naphthalene least-squares plane and 166·7° to each other, also show evidence of the effects of steric overcrowding, with internal ring angles at the C(24) and C(18) *ipso* C atoms of 118·4 (2) and 118·5 (3)° respectively.

The nine-membered ring adopts a distorted tub conformation, exhibiting strongly localized double bonds, high torsion angles about the single bonds and expansion of the internal ring angles. The tub lies on the same side of the naphthalene entity as the C(21)—C(22)—C(23)—C(18) and C(27)—C(28)—C(29)—C(24) fragments of the two phenyl rings, and the mean plane of the tub forms an angle of 45·2 (6)° with the naphthalene plane. The mirror plane which could be expected in the parent 9-annulene (at right angles to the molecular least-squares plane and along a line joining the sp^3 C with the midpoint of the opposite C—C single bond) is absent in (I), presumably due to the distorting influence of the ring annelation.

The intermolecular packing arrangement is determined by normal van der Waals contacts, with no interactions between the C atoms involving contact distances of less than 3·5 Å.

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Structure of 2-(2-Hydroxy-1,1-dimethylethyl)-5,5-dimethyl-1,3-dioxan-4-ol, $C_{10}H_{20}O_4$, a Dimer of 3-Hydroxy-2,2-dimethylpropanal. Example of an Anhydrous Acetal Hydrolysis

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Abstract. $M_r = 204·3$, monoclinic, $P2_1/c$, $a = 6·159$ (2), $b = 36·212$ (13), $c = 11·530$ (4) Å, $\beta = 116·86$ (1)°, $V = 2294·1$ Å^3, $Z = 8$, $D_x = 1·18$, $D_m = 1·06$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1·54051$ Å, $\mu = 0·75$ mm^{-1}, $F(000) = 896$, $T = 294$ K. Final $R = 0·053$ for 1405 observed reflections. There are two independent molecules per asymmetric unit, each one in a *cis* chair conformation. They lie on separate layers (*A* and *B*) in the crystal (perpendicular to **b**), with different hydrogen-bonding schemes in each layer. When melted, the dimer decomposes into the monomer, following an anhydrous acid-catalyzed acetal 'hydrolysis' mechanism. It is initiated by an *inter*molecular H-atom transfer which is assisted by a hydrogen bond in the *B* layer between the hydroxy group and a dioxane O atom on adjacent molecules. This decomposition is reversible, with the liquid monomer dimerizing on cooling. Attempts to form an orientationally disordered crystalline monomer by rapid cooling were unsuccessful.

Introduction. The title compound, hereafter referred to as $(R\text{CHO})_2$, was selected for investigation as part of our continuing study of polymorphism and orientational disorder in single crystals of pseudo-spherical molecules (Rudman, 1981; Sake Gowda & Rudman, 1982). The monomer of the title compound, hereafter

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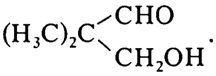
referred to as *R*CHO, has the structural formula



$(H_3C)_2C\begin{smallmatrix}CHO\\CH_2OH\end{smallmatrix}$

. *R*CHO is pseudo-spherical as are the various methylchloromethane and polyhydroxymethyl compounds which are known to form orientationally disordered (plastic) crystalline phases just below their melting points (Rudman, 1981). However, *R*CHO is unique in that there is an equilibrium between *R*CHO and $(RCHO)_2$ in solution and there is a reversible transformation between monomer and dimer on melting and refreezing: $(RCHO)_2$ exists in the crystalline state while *R*CHO is found in the molten state. In the molten state, *R*CHO can be compared to 2,2-dimethylpropanal, $(CH_3)_3CCHO$, and 3-hydroxy-2-oxopropanal, $HOH_2CCOCHO$, both of which are liquid at room temperature.

Our initial intention was twofold: to freeze molten *R*CHO quickly in an attempt to observe and study polymorphic transformations of the crystalline monomer, and to determine the structure of the dimer. We succeeded in the latter, but were unsuccessful in the former. Santoro & Chiavarini (1978), hereafter S & C, used IR and NMR spectroscopy to deduce the structure of $(RCHO)_2$.

Experimental. Synthesis: *R*CHO and $(RCHO)_2$ were prepared following the aldol condensation described by S & C, except that the reaction vessel was left in the refrigerator for three days, after which time the white precipitate that had formed was filtered, washed with water, and dried *in vacuo* for 1 h. The precipitate was recrystallized three times from ether; m.p. 364–365 K (S & C reported 362–363·5 K). The IR and NMR spectra agreed with those reported by S & C.

Differential scanning calorimetry (DSC): A Perkin–Elmer DSC-1B, equipped with a low-temperature adapter, was used for the DSC measurements employing techniques that have been described elsewhere (Silver & Rudman, 1970). The initial investigation of the thermal behavior of the *R*CHO–$(RCHO)_2$ system was carried out in a standard commercial melting-point apparatus, where it was observed that $(RCHO)_2$ forms a colorless liquid (*R*CHO) on melting. It remains a liquid as it is cooled to room temperature, and only slowly reverts to a white solid; this process is reversible.

The visual observations were confirmed with DSC: if the sample is melted, cooled to room temperature, and immediately reheated, no melting point is observed during the reheating. In an attempt to detect the monomer-to-dimer transition, the sample was melted, cooled to 303 K, and studied in an isothermal mode (at constant temperature with the recorder running). An exothermic displacement of the baseline indicated that dimerization had occurred. The original melting point was observed if the sample was heated following this baseline shift, but not if it were heated prior to the shift. The parameters governing the dimerization were not determined, with time periods of between $1\frac{1}{2}$ and 46 h required before dimerization occurred when different samples were used and the temperature was fixed at 303 K. However, the dimerization is temperature-dependent, since it occurs more rapidly at lower temperatures for a given sample.

The liquid monomer was cooled rapidly, in the DSC using liquid nitrogen, in an attempt to crystallize the monomeric form. These attempts were unsuccessful. In all cases, as the monomer was cooled to 153 K one or more small exothermic peaks (at unpredictable temperatures) appeared. If the sample were reheated immediately after these peaks appeared the $(RCHO)_2$ m.p. was observed.

It is concluded that, under the conditions obtained in the DSC, monomeric liquid *R*CHO dimerizes to $(RCHO)_2$ rather than freezing to crystalline *R*CHO. However, quick-freezing techniques, such as are used to form amorphous materials (Wenzel, 1976), might succeed in stabilizing a rigid monomer.

X-ray analysis: $(RCHO)_2$ synthesized and crystallized as described above. D_m measured in xylene–carbon tetrachloride mixture. Crystal size 0·08 × 0·09 × 0·20 mm. Syntex $P2_1$-F diffractometer, Ni-filtered Cu $K\alpha_1$. Lattice parameters from 20 reflections ($13 < 2\theta < 45°$); ω-scan FWHM 0·15°. 4394 total reflections ($h, \pm k, \pm l$ with $2\theta \leq 65°$, $h, k, \pm l$ with $65 < 2\theta \leq 115°$, $h_{\max} = 6$, $|k_{\max}| = 39$, $|l_{\max}| = 12$). θ–2θ scan with automatic recentering every 633 reflections. Three standard reflections ($0\bar{4}0$, $0\bar{1}2$, $1\bar{4}0$) every 102 reflections (45% decay in intensities). 3142 independent ($R_{\rm int}$, after merging equivalent reflections and after decay correction, 2·4%), 1405 with $F > 3\sigma(F)$. Lp correction, decay correction. Structure solved by direct methods (*MULTAN*, Declercq, Germain, Main & Woolfson, 1973; 217 $E > 1{\cdot}75$, $53\psi_o$, $E < 0{\cdot}12$ using Syntex *XTL* version on data *un*-corrected for decay, all non-H atoms located from *E* map and subsequent Δ*F* map). Full-matrix anisotropic least-squares refinement on Burroughs 7600 computer using decay-corrected intensity data based on *F*. H from Δ*F* synthesis and calculations, *B* fixed at *B* of atom to which it is attached. Each molecule refined separately on alternate cycles (188 parameters *each* cycle: scale factor, extinction factor, nine parameters per C and O, three parameters per H). *R* and R_w (defined in Sake Gowda & Rudman, 1982): 0·053 and 0·058, $S = 1{\cdot}44$; $w^{-1} = \sigma^2(F) + (0{\cdot}04F)^2$, $\sigma(F) = \sigma(F^2)/(2F)$, $\sigma(F^2)$ based on counting statistics. Final Δ*F* map featureless (maximum height 0·33 e Å^{-3}). Extinction coefficient 1·09 (24) mm^{-1}, smallest extinction factor 0·84. Local versions of standard programs used in calculations; Syntex *XTL* version of *ORTEP* (Johnson, 1976) used for diagrams. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) (Table 2.2A for C,O; Table 2.2C for H).

Discussion. The final fractional coordinates and isotropic thermal parameters are listed in Table 1 following the atom-numbering scheme shown in Fig. 1 (only H atoms involved in hydrogen bonding are drawn).*

This crystal-structure analysis confirms the conclusions arrived at by S & C (from their NMR and IR analyses): (*a*) The dimer is a substituted 1,3-dioxane compound rather than an eight-membered-ring compound. (*b*) The preferred conformation in the crystalline state is the chair form with the groups in the 2 and 4 ring positions oriented equatorially and lying on the same side of the ring (*i.e.* a *cis* chair conformation, *cf.* S & C). The formation of molecules related by a center of inversion is in accordance with the well known rule of stereochemistry, *viz.* the synthesis of a chiral compound from achiral starting materials results in a racemic mixture (March, 1977).

Bond lengths for all non-H atoms and H atoms involved in the hydrogen-bonding scheme are found in Table 2, while all other data have been placed on deposit.* In the 1,3-dioxane rings, the observed bond lengths and angles agree with those found in similar

Table 1. *Positional parameters of* $(R\mathrm{CHO})_2$ *in fractional coordinates* ($\times 10^4$ *for* C, O; $\times 10^3$ *for* H) *with e.s.d.'s in parentheses and isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}/ B_{iso}(Å^2)
Molecule *A*				
O(1*A*)	3386 (7)	49 (1)	6253 (3)	3·45
O(2*A*)	5057 (6)	−245 (1)	8260 (3)	3·00
O(3*A*)	4659 (7)	−861 (1)	8494 (3)	3·53
O(4*A*)	7953 (8)	757 (1)	10158 (4)	4·29
C(1*A*)	2894 (11)	−620 (1)	6319 (5)	3·19
C(2*A*)	3199 (13)	−290 (2)	5575 (6)	3·81
C(3*A*)	4982 (12)	−599 (1)	7685 (6)	3·07
C(4*A*)	5321 (12)	46 (2)	7505 (6)	2·88
C(5*A*)	3070 (16)	−977 (2)	5666 (8)	5·25
C(6*A*)	453 (13)	−593 (2)	6361 (6)	4·57
C(7*A*)	5396 (10)	418 (1)	8162 (5)	2·70
C(8*A*)	7514 (12)	404 (2)	9527 (6)	3·43
C(9*A*)	3038 (13)	484 (2)	8223 (6)	4·06
C(10*A*)	5826 (14)	716 (2)	7356 (7)	4·13
H(O3*A*)	602 (11)	−98 (2)	900 (5)	3·46
H(O4*A*)	722 (12)	79 (2)	1060 (6)	4·29
Molecule *B*				
O(1*B*)	11091 (7)	2321 (1)	7749 (3)	4·86
O(2*B*)	12346 (7)	2323 (1)	9951 (3)	4·48
O(3*B*)	13397 (11)	2837 (1)	11137 (6)	9·68
O(4*B*)	11240 (7)	1190 (1)	9971 (4)	4·58
C(1*B*)	12080 (13)	2910 (1)	8874 (7)	5·14
C(2*B*)	10440 (16)	2706 (2)	7632 (7)	6·27
C(3*B*)	11701 (15)	2710 (2)	9930 (6)	5·74
C(4*B*)	10797 (12)	2152 (2)	8774 (6)	4·16
C(5*B*)	14719 (18)	2895 (2)	9096 (8)	7·63
C(6*B*)	11280 (24)	3305 (2)	8783 (12)	9·82
C(7*B*)	11404 (10)	1746 (1)	8843 (5)	3·16
C(8*B*)	10895 (12)	1581 (2)	9919 (6)	4·20
C(9*B*)	14032 (13)	1683 (2)	9142 (6)	5·09
C(10*B*)	9647 (14)	1574 (2)	7538 (7)	5·78
H(O3*B*)	1289 (10)	277 (1)	1191 (5)	4·33
H(O4*B*)	1008 (11)	110 (2)	1000 (6)	4·33

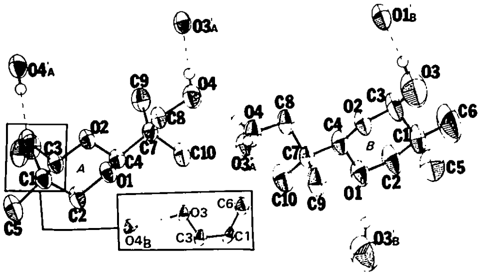


Fig. 1. The two molecules of $(R\mathrm{CHO})_2$ in the asymmetric unit are shown together with the atoms hydrogen-bonded to these molecules. The *A* molecule is on the left and the *B* molecule on the right. The overlapping atoms in the box are shown in detail in the inset. H atoms are labeled according to the O atoms to which they are attached.

Table 2. *Bond lengths* (Å) *and hydrogen-bonded distances* (Å) *and angles* (°) *for* $(R\mathrm{CHO})_2$ *with e.s.d.'s in parentheses*

Distances in brackets are calculated using a riding correction (Busing & Levy, 1964).

(*a*) Bond lengths

	X = *A*	*X* = *B*
O(1*X*)–C(2*X*)	1·431 (7)	1·439 (7)
O(1*X*)–C(4*X*)	1·396 (6)	1·414 (9)
O(2*X*)–C(3*X*)	1·435 (6)	1·454 (7)
O(2*X*)–C(4*X*)	1·423 (8)	1·401 (6)
O(3*X*)–C(3*X*)	1·406 (8)	1·388 (8)
	[1·411 (8)]	[1·409 (10)]
O(4*X*)–C(8*X*)	1·434 (7)	1·430 (7)
	[1·442 (8)]	[1·431 (8)]
C(1*X*)–C(2*X*)	1·532 (9)	1·521 (9)
C(1*X*)–C(3*X*)	1·520 (7)	1·523 (12)
C(1*X*)–C(5*X*	1·525 (10)	1·528 (14)
	[1·549 (10)]	[1·551 (15)]
C(1*X*)–C(6*X*)	1·529 (12)	1·501 (10)
	[1·544 (12)]	[1·555 (13)]
C(4*X*)–C(7*X*)	1·535 (8)	1·511 (7)
C(7*X*)–C(8*X*)	1·525 (7)	1·532 (10)
	[1·531 (8)]	[1·541 (11)]
C(7*X*)–C(9*X*)	1·505 (11)	1·513 (10)
	[1·520 (11)]	[1·532 (11)]
C(7*X*)–C(10*X*)	1·524 (10)	1·534 (7)
	[1·537 (10)]	[1·563 (9)]

(*b*) Hydrogen bonding

X–H···*Y*	*X*···*Y*	*X*–H	H···*Y*	*X*–H···*Y*
O(4*A*)–H(O4*A*)···O($3A^{i}$)	2·721 (7)	0·83 (9)	1·89 (9)	176 (5)
O(3*A*)–H(O3*A*)···O($4B^{ii}$)	2·622 (5)	0·88 (5)	1·74 (5)	178 (5)
O(3*B*)–H(O3*B*)···O($1B^{iii}$)	2·860 (9)	1·10 (7)	1·79 (7)	161 (4)
O(4*B*)–H(O4*B*)···O(4*A*)	2·642 (7)	0·79 (8)	1·87 (7)	162 (6)

Symmetry code: (i) $1-x$, $-y$, $2-z$; (ii) $2-x$, $-y$, $2-z$; (iii) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

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* Lists of structure factors, anisotropic thermal parameters, bond angles, H-atom positional parameters, bond lengths and angles involving H, torsion angles, least-squares planes and interplanar angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38580 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

compounds. The average values were calculated for the two independent $(RCHO)_2$ molecules and the five structures reported by Kobayashi & Iitaka (1977), Shoja & White (1979) and Delmas, Gorrichon, Gaset, Roques, Declercq & Germain (1981). In all cases, the average C—O distances involving the C atom lying between the two O atoms (the dioxane ring position 2) are significantly shorter (1·407 Å) than the other C—O distances (1·432 Å) and the C—C distances are normal (1·523 Å), while the C—C—C angles (107·0°) are significantly smaller than the angles involving O atoms (O—C—O 110·8, C—O—C 110·7, O—C—C 110·3°).

In $(RCHO)_2$, the average C—H bond length is 1·01 Å, with 35 of the 36 distances lying between 0·93 and 1·15 Å. The C(4)—C(7) and C(3)—O(3) bonds are in the equatorial positions, with the C(8)—O(4) bonds parallel to the C(4)—C(7) direction. The rings of both molecules have the chair conformation, which can be resolved into three planes: (I) C(4)—O(1)—O(2), (II) O(1)—C(2)—C(3)—O(2), (III) C(1)—C(2)—C(3). The angles between these planes are: (I)–(II) 53·2, 55·7; (II)–(III) 48·8, 53·2; (I)–(III) 175·6, 177·4°, for molecules *A* and *B* respectively.The C(1) and C(4) atoms are approximately 0·7 Å above and below plane (II) in each molecule.*

As a consequence of their different hydrogen-bonding schemes, the thermal motions of the two molecules differ, with molecule *B* having the larger anisotropic temperature factors. In particular, O(3*B*) and C(6*B*) have β_{ii} nearly three times those of O(3*A*) and C(6*A*) (Fig. 1); the riding corrections (Table 2) are largest for distances involving these atoms.

The long axis [C(5) to O(4)] of each molecule lies parallel to the *b* axis, which is approximately four molecules long. The crystal is composed of alternating layers of *A* and *B* molecules, with the *A* layers at $y = 0,\frac{1}{2}$ and the *B* layers at $y = \frac{1}{4},\frac{3}{4}$ (Fig. 2).

The hydrogen-bonding scheme within each layer is different. The *A* molecules are hydrogen-bonded in head-to-tail centrosymmetrically related pairs, while in the *B* layer the molecules form chains due to the hydrogen bonds between O(3*B*)—H(O3*B*)···O(1*B*) on adjacent molecules, also arranged in a head-to-tail pattern. The three-dimensional hydrogen-bonded network is completed by two types of interlayer bonds: O(4*B*)—H(O4*B*)···O(4*A*) and O(3*A*)—H(O3*A*)···O(4*B*), with O(4*B*) acting as a hydrogen-bond donor to one *A* molecule and as an acceptor from another *A* molecule. As a result, each adjacent pair of $(RCHO)_2$ *A* and *B* molecules is hydrogen-bonded to five other molecules (Fig. 1). The O(3*B*) hydrogen group serves only as a hydrogen-bond donor to the O(1*B*) atom on an adjacent dioxane ring, while all the other hydroxy O atoms act as both donors and acceptors.

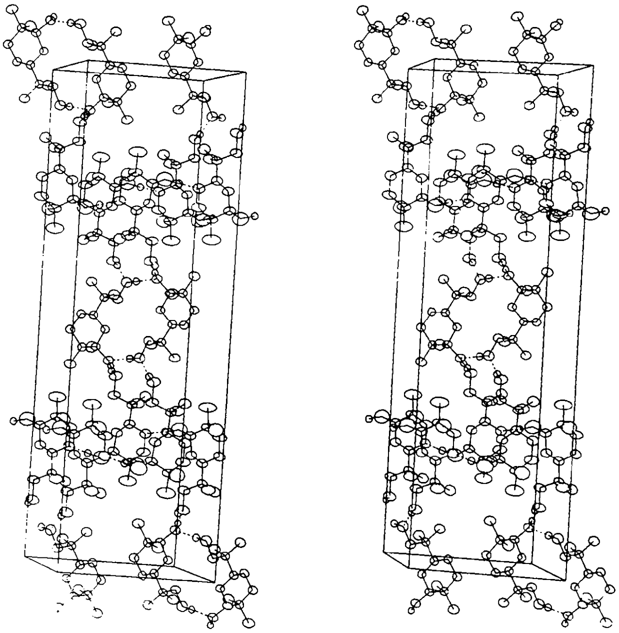

Fig. 2. A stereoview of the $(RCHO)_2$ unit cell.

Monomer–dimer conversion. The intermolecular H(O3*B*)···O(1*B*) hydrogen bond appears to be the key to the $(RCHO)_2 \rightarrow RCHO$ conversion on melting. Reversible addition reactions between alcohols and aldehydes have been extensively studied (March, 1977). In general, the product of addition of one mole of alcohol to an aldehyde is referred to as a hemiacetal, while dehydration and addition of a second mole of alcohol results in an acetal, with the general formula $R_2C(OR')_2$. *R*CHO contains both aldehyde and alcohol groups and even though water is not lost during dimerization, $(RCHO)_2$ is an acetal with the O*R*′ groups forming the 1,3-dioxane ring and one of the *R* groups being H. The mechanisms for acetal formation and hydrolysis have been worked out in detail for reactions in solution and have been shown to be acid-catalyzed by an attack of an H atom on the O of the —O*R*′ groups. In $(RCHO)_2$, we find an anhydrous acid-catalyzed acetal ‘hydrolysis’ which occurs when the compound is melted. The reaction is initiated by the intermolecular transfer of H(O3*B*) to O(1*B*), resulting in O(3*B*) becoming an aldehydic O atom and O(1*B*) becoming part of the hydroxy group. Once initiated the reaction continues with the O(1)—C(4) and O(2)—C(3) bonds on both the *A* and *B* molecules splitting to form four *R*CHO molecules, in accordance with the standard mechanism. It is interesting to note that the observed bond length for O(3*B*)—H(O3*B*) is substantially longer than the other O—H bonds in this compound (Table 2) and the H(O3*B*)···O(1*B*)—C(2*B*) angle is 109·6 (17)°. These structural features indicate that H(O3*B*) is lined up with the lone-pair electrons on O(1*B*) and an

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* Least-squares planes for plane II, molecules *A*, *B*, have been deposited. See deposition footnote.

intermolecular H-atom transfer from O(3*B*) to O(1*B*) is easily accomplished.

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Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. VIII.[*] Structures of the Tris(hydroxymethyl)aminomethane Hydrogenhalides,[†] $(HOH_2C)_3CNH_3^+.X^-$ (X=F,Cl,Br,I)

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Abstract. Three of the title compounds, TrisH$^+$.X^- (X = F,Cl,Br), are isostructural: rhombohedral, $R\bar{3}$ (H), $Z = 6$. At 294 K the crystal data are: TrisH$^+$.F$^-$: $M_r = 141{\cdot}2$, $a = 7{\cdot}123$ (6), $c = 22{\cdot}47$ (2) Å, $V = 987{\cdot}3$ Å^3, $D_x = 1{\cdot}425$, $D_m = 1{\cdot}418$ Mg m^{-3}, μ(Cu $K\alpha$) = $1{\cdot}21$ mm^{-1} (only crystal data were obtained for this compound). TrisH$^+$.Cl$^-$: $M_r = 157{\cdot}6$, $a = 7{\cdot}569$ (1), $c = 24{\cdot}694$ (4) Å, $V = 1225{\cdot}2$ Å^3, $D_x = 1{\cdot}278$, $D_m = 1{\cdot}275$ Mg m^{-3}, μ(Cu $K\alpha$) = $3{\cdot}78$ mm^{-1}, $F(000) = 504$; final $R = 0{\cdot}072$ for 266 unique reflections. TrisH$^+$.Br$^-$: $M_r = 202{\cdot}1$, $a = 7{\cdot}701$ (2), $c = 25{\cdot}447$ (8) Å, $V = 1306{\cdot}9$ Å^3, $D_x = 1{\cdot}540$, $D_m = 1{\cdot}537$ Mg m^{-3}, μ(Cu $K\alpha$) = $6{\cdot}74$ mm^{-1}, $F(000) = 612$; final $R = 0{\cdot}032$ for 508 unique reflections. The fourth title compound, TrisH$^+$.I$^-$, $M_r = 249{\cdot}1$, is cubic, $I2_13$, $a = 11{\cdot}627$ (3) Å, $V = 1571{\cdot}8$ Å^3, $Z = 8$, $D_x = 2{\cdot}105$, $D_m = 2{\cdot}089$ Mg m^{-3}, μ(Cu $K\alpha$) = $32{\cdot}28$ mm^{-1} at 294 K, $F(000) = 960$; final $R = 0{\cdot}056$ for 210 unique reflections. All data were collected with Ni-filtered Cu K radiation ($\lambda_{K_{\alpha_1}} = 1{\cdot}54051$ Å). In the chloride and bromide structures, the halide anions lie on both sides of a hydrogen-bonded double layer of TrisH$^+$ cations formed with the $-NH_3^+$ moieties facing toward each other, such that the $X \cdots$N distances are greater than the X$\cdots$C(C) (central carbon) distances. The resulting anion–anion repulsion explains the unusually low density and high cleavability of these crystals. The iodide structure has a normal density with $X \cdots$N less than $X \cdots$C(C), but is distinguished by crystallizing in a space group rarely found for an organic compound.

Introduction. Many compounds with approximately spherical molecules undergo solid–solid phase transitions, with the phase stable just below the melting point referred to as the orientationally disordered, or plastic, crystalline state. As part of our continuing effort to define the sphericity of the molecular envelope needed for the formation of the plastic state, a series of poly(hydroxymethyl) compounds is being investigated. The variation of the hydrogen-bonding schemes in these compounds, as a function of molecular substituents, is also of interest.

The structures of the ordered and plastic phases of tris(hydroxymethyl)aminomethane were reported previously (Eilerman & Rudman, 1980). This compound is a widely used buffering agent, commonly known as Tris. The possibility that the Tris–hydrogen-halide (TrisH$^+$.X^-) salts also form orientationally disordered phases (in a manner analogous to NH_4Cl) was investigated and is reported here. A preliminary report on TrisH$^+$.Cl$^-$ was reported earlier (Rudman, Lippman & Eilerman, 1979).

Experimental. Single crystals of the TrisH$^+$.X^- compounds were prepared by crystallizing them (by slow

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[*] Part VII: Eilerman, Lippman & Rudman (1983).

[†] (1,3-Dihydroxy-2-hydroxymethyl-2-propyl)ammonium halides.

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