Structures of Two Forms of Sodium Acetate, $Na^+.C_2H_3O_2^-$

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Abstract. $M_r = 82.02$. Form I, orthorhombic, *Pcca*, $a = 17.850$ (15), $b = 9.982$ (7), $c = 6.068$ (4) Å, $V = 1081.2$ (15) Å^3, $Z = 12$, $D_x = 1.512$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.243$ mm^{-1}, $F(000) = 504$, $T = 298$ K, $R = 0.061$ for 556 observed reflections. The structure has Na^+–carboxylate layers alternating with layers of methyl-group contacts, with the C–C bonds along **b**. Form II, orthorhombic, $a = 5.951$ (2), $b = 20.213$ (7), $c = 5.902$ (3) Å, $V = 709.9$ (5) Å^3, $Z = 8$, $D_x = 1.535$ Mgm^{-3}, μ(Mo $K\alpha$) = 0.247 mm^{-1}, $F(000) = 336$, $T = 298$ K, $R = 0.074$ for 427 observed reflections. The structure is characterized by stacking faults in the molecular layers perpendicular to **b**, giving rise to domains belonging to *Pcca*, with halved *b* axis, and *Icab* (standard *Ibca*). The cells of the two forms are related by $a_{II} \simeq a_I/3$, $b_{II} \simeq 2b_I$, $c_{II} \simeq c_I$.

Introduction. The low-temperature heat capacity of sodium acetate has recently been measured by Franzosini, Plautz & Westrum (1983). A heat capacity maximum at the surprisingly low temperature of 21 K, previously reported by Strelkov (1955), was found by Franzosini *et al.*, but the magnitude of the peak measured by them was much greater than previously reported. This crystallographic study was undertaken in the hope of contributing toward the understanding of this phase transition.

Experimental. Crystals obtained as trihydrate from aqueous solution at room temperature; anhydrous form obtained by crystallization above 331 K, the decomposition temperature of the trihydrate (Green, 1908). Two samples of sodium acetate, both crystallized from aqueous solution at 337 ± 2 K over periods of 7–10 d were kindly provided by Professor E. F. Westrum. The crystals from the first and second batch were found to belong to different forms, here labeled I and II. The lath-shaped crystals of I cleave extremely easily into fibers extended in the *c* direction. Owing to the easy fraying and bending of the crystals, acquisition of good X-ray specimens proved difficult, and the quality of the X-ray data suffered. The crystals of form II are prisms, elongated in the *b* direction, and cleave perpendicular to that direction. The form II crystals are softer than those of form I. Additional crystals were grown from methanol solution by slow evaporation at room

temperature. These crystals were examined on the precession camera and found to be identical to form II.

X-ray data for I and II collected on a Syntex $P2_1$ diffractometer, cell dimensions determined by least-squares fit to 15 reflections, well distributed in reciprocal space, 2θ range 20–25°, intensity data collected in the 2θ:θ scan mode, corrected for Lorentz and polarization effects, but not for absorption or secondary extinction.

Form I: 1426 reflections measured, $2\theta \leq 55°$, crystal approximately $0.6 \times 0.3 \times 0.05$ mm, 556 with $I > 2.33 \sigma(I)$ were used in the structure determination and refinement, space group *Pcca* uniquely determined by the observed systematic absences, 12 molecules per cell, 8 in general positions and 4 in twofold special positions, structure solved by *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), full-matrix least squares with anisotropic thermal parameters minimized $\sum w(|F_o| - |F_c|)^2$ with $w = (\sigma^2 + kF_o^2)^{-1}$, where $k = 0.0012$ was chosen to make $w(\Delta F)^2$ uniformly distributed in $|F_o|$; difference Fourier synthesis gave the coordinates of the three hydrogen atoms on the methyl group in general position, these were included with isotropic $B = 7.5$ Å^2; disordered hydrogens on the methyl group in twofold positions, found unresolved in the difference Fourier, were included as six half-hydrogens in calculated positions, with $B = 12.0$ Å^2, no hydrogen parameters were refined, $R = 0.061$ for 556 reflections.*

Form II: data sets collected at room temperature from two crystals: one, $0.5 \times 0.3 \times 0.06$ mm, was grown from the aqueous medium at 338 K the other, $0.9 \times 0.6 \times 0.05$ mm, was grown from methanol solution at room temperature; each set had 1046 reflections in the $2\theta \leq 60°$ range, the two sets contained, respectively, 427 and 416 reflections with $I \geq 2.33\sigma(I)$, partial data sets were collected from several other crystals.

All data sets showed systematic absences for $0kl$ when k odd and when l odd, for $h0l$ when l odd, and for $hk0$ when h odd, and, except for the very weak 210,

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when k odd. These are consistent with $Pcca$, $Pbca$, $Pbc2_1$, $Pb2_1a$, $P2_1ca$, $Pcc2$, and possibly $Pbcb$ and $Pccb$. Precession photographs showed some diffuseness and streaking in the k direction of reflections with $h + l$ odd.

The diffracted intensities from different crystals showed an unusual variation in relative scale. Reflections with both $h + l$ and k even gave consistent scale factors for all crystals. When the intensities from two crystals were scaled together using these reflections, the reflections with $h + l$ odd were off scale by factors dependent on the crystal specimen, and apparently also on the parity of k. For the two complete data sets, scaled with the $h + l$ even, k even reflections, the intensities of reflections with $h + l$ odd were off scale by a factor of 1·9, in this case independent of the parity of k. The intensities from the crystal grown from the aqueous medium were the higher ones, but this observation cannot be consistently ascribed to the solvent used.

A structure of form II, closely similar to that of form I (Fig. 1) was indicated by the unit-cell parameter relationship between the two forms, namely $a_{II} \simeq a_I/3$, $b_{II} \simeq 2b_I$ and $c_{II} \simeq c_I$. Models based on several of the possible space groups, and embodying various kinds of molecular disorder, were explored in a long series of attempted least-squares refinements. A uniquely consistent description of the structure in terms of a minimum number of parameters was arrived at as follows.

The 'well-behaved' reflections, *i.e.* those with $h + l$ even and k even, are accounted for by a structure in space group $Bmam$ (No. 67, standard setting $Cmma$). Refinement of one scale factor, six independent positional and 15 anisotropic thermal parameters gave $R = 0·041$ for 271 observed reflections. The oxygen atoms are disordered, and the acetate ions occupy sites of $mm2$ symmetry. Two cells of this substructure are shown in Fig. 2(a). Shown in Figs. 2(b) and (c) are two ordered structures, each with the acetate ion situated on

a twofold axis. Both structures give the substructure (Fig. 2a) when disorder is imposed on the oxygen atoms, and both make identical contributions to the reflections with $h + l$ even and k even. The first of these belongs to space group $Pcca$, and its b axis is halved. Two units cells are shown in Fig. 2(b). When indexed on the true cell, this structure only contributes to reflections with k even. The second structure (Fig. 2c) belongs to space group $Icab$ (No. 73, standard setting $Ibca$). It only contributes to reflections with $h + k + l$ even. It follows that when k is odd and $h + k + l$ is odd, *i.e.* when k is odd and $h + l$ is even, neither structure contributes to the observed intensity. In the two complete data sets there are only four and eleven, respectively, weakly observed reflections in this category; only one, 210, with intensities $5·5\sigma(I)$ and $3·9\sigma(I)$, is observed in both sets. Thus a structure consisting of domains of these two structures is essentially capable of accounting for the entire diffraction pattern.

From Figs. 2(b) and (c) it can be seen that the two structures are related to one another by an $(\mathbf{a} + \mathbf{c})/2$ translation of the central layer of acetate and sodium ions, relative to the top and bottom layers, and that this translation leaves the interlayer methyl–methyl contacts unaffected. Thus, the packing energy of the two structures is nearly the same, and a structure composed of alternating domains of the two is energetically favorable.

This possibility was explored by least-squares refinement of the model shown in Fig. 2(d), which is a superposition of the $Pcca$ and $Icab$ structures. This model belongs to $Pcca$ and has the full unit cell. The two independent acetate ions lie on twofold axes; one of them is disordered between two positions with occupancies reflecting the relative amounts of the two domain structures present. Refinement was carried out with both data sets, systematically varying the oxygen occupancies. For each data set the best agreement was obtained with the oxygens equally or very nearly equally, distributed among the two positions, implying essentially equal contributions from the two domain structures. These refinements gave $R = 0·059$ for the 427 observed reflections from the crystal from the aqueous medium, and $R = 0·092$ for the 416 observed reflections from the methanol-grown crystal. These refinements were full matrix, minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = (\sigma^2 + kF_o^2)^{-1}$, where $k = 0·0008$ was chosen to make $w(\Delta F)^2$ uniformly distributed in $|F_o|$.

The preceding refinements do not account for the observed variation in relative scale of $h + l = $ odd reflections in the two data sets. By employing separate scale factors for the substructure reflections, with $h + l$ even and k even, and the rest of the reflections, the refinements gave $R = 0·051$ and $0·060$, respectively, with the scale factors assuming values consistent with the above-mentioned relative intensity variation in the two crystals. We interpret this scale variation as a
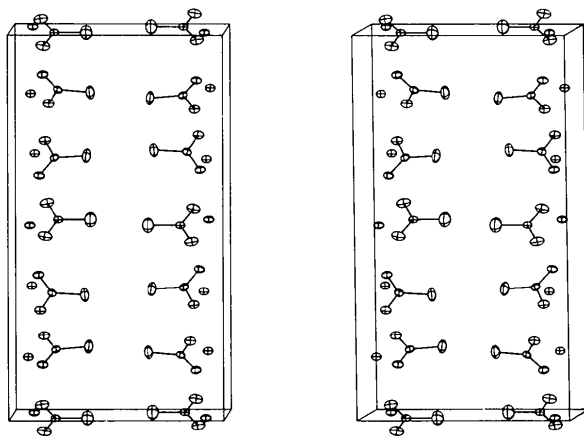

Fig. 1. The structure of sodium acetate, form I, viewed along c. The a axis is vertical, b horizontal.
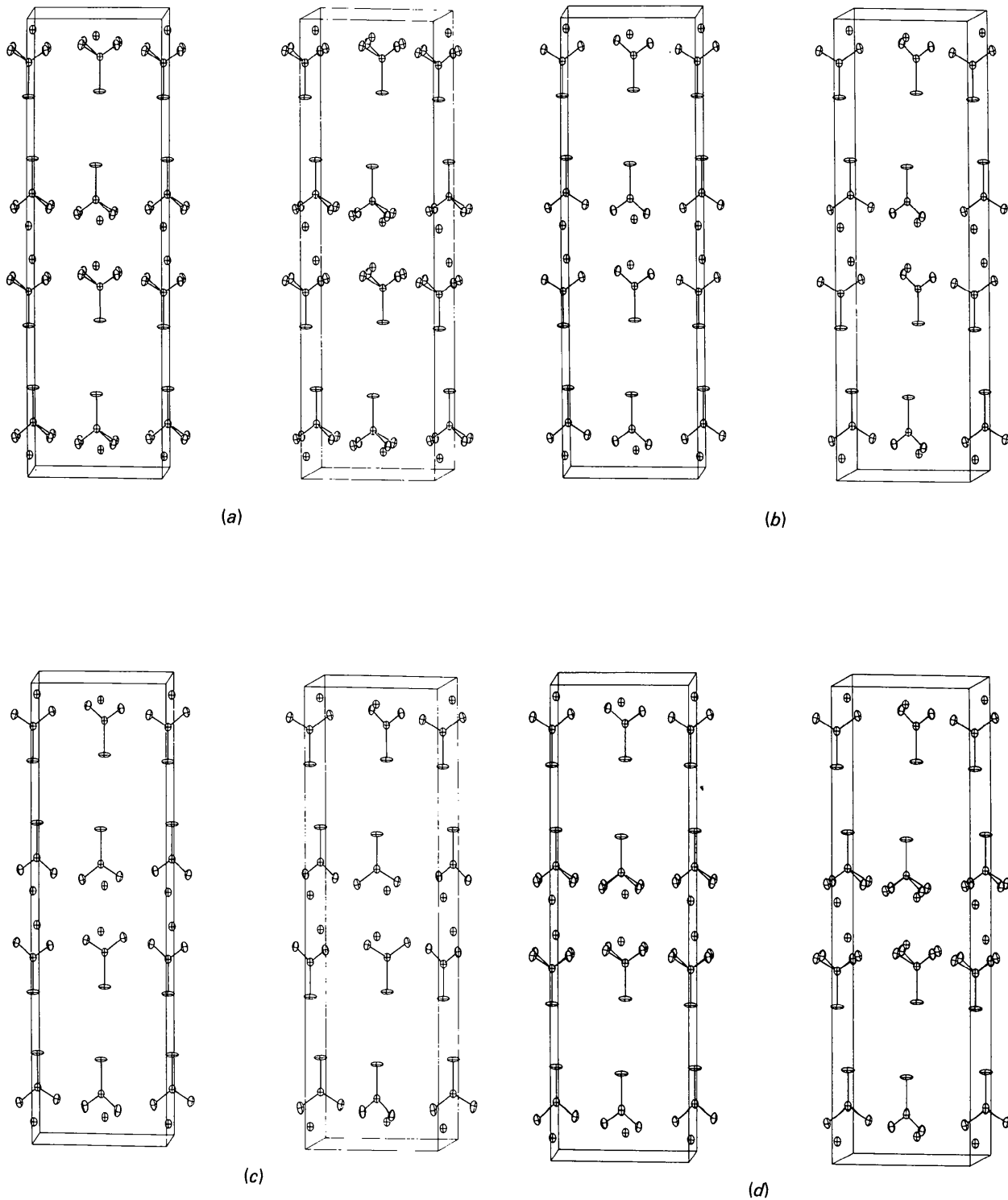
Fig. 2. Models of sodium acetate, form II, viewed along **c**. The *a* axis is horizontal, *b* vertical. (*a*) Two cells of the substructure in space group *Bmam*. (*b*) Two cells of one domain type, in *Pcca*. (*c*) One cell of the other domain type, in *Icab*. (*d*) One cell of the composite structure, in space group *Pcca*.

manifestation of a varying randomness in the domain structure, with relatively strong superstructure reflections occurring in crystals with large domains, and *vice versa*.

The coordinates and thermal parameters resulting from the two refinements showed no significant differences. Those resulting from the crystal grown from aqueous medium were judged the more accurate, as they stemmed from a crystal of more favorable size and shape, and gave the lower R value. These parameters and data were used in the following.

The full-cell *Pcca* structure employed in the above-described least-squares refinement contains 15 positional and 42 anisotropic thermal parameters and two scale factors, while the composite of the halved-cell *Pcca* structure (Fig. 2*b*) and the *Icab* structure (Fig. 2*c*), which are assumed to constitute the domains of the crystal, contains only six positional and 18 anisotropic thermal parameters, and two scale factors. The latter parameter set was obtained from the former by appropriate averaging of the least-squares parameters of the $R = 0.051$ structure. Following a slight adjustment of the two scale factors, the final R value was 0.074.*

Discussion. The coordinates and thermal parameters of forms I and II are given in Table 1. The data given for form II pertain to space group *Pcca*, but the values have been averaged so as to obey the constraints implied by the two contributing structures, as explained in the preceding section. Estimated standard deviations are shown for the independent parameters only. The values of the e.s.d.'s are taken as the means of the full-matrix least-squares e.s.d.'s of the parameter in question, or as one half the difference between the two least-squares values, whichever is larger.

Interatomic distances and bond angles of form I are listed in Table 2. The acetate-ion bond distances and angles are in reasonable agreement with the more accurately determined values in sodium acetate trihydrate (Wei & Ward, 1977). Each of the two independent Na^+ ions is surrounded by six oxygens at distances of 2.35 (1) to 2.67 (1) Å. In each coordination sphere two of the six oxygens belong to the same acetate ion, while the other four oxygens belong to four different acetate ions. The first two oxygens then form an O—Na—O angle which is much smaller than the rest, 50.6 (2) and 48.6 (2)°, respectively. The structure of form I, shown in Fig. 1, consists of layers of coordinated Na^+ ions alternating with layers of methyl—methyl contacts. The extreme cleavage of the crystals is well accounted for by this structure.

Bond distances and angles in form II are C—C = 1.52 (14), C—O = 1.26 (5) Å, O—C—O = 123 (3) and O—C—C = 118 (2)°. Within their relatively low ac-

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* See previous footnote regarding deposition of structure factor tables.

Table 1. *Atomic parameters for sodium acetate, forms* I *and* II

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

		x	y	z	$B_{eq}(\text{Å}^2)$
Form I					
C(1)	8(*f*)	0.1687 (4)	−0.2007 (6)	0.4471 (9)	2.9 (3)
C(2)	8(*f*)	0.1742 (5)	−0.3499 (8)	0.4086 (14)	6.4 (6)
C(3)	4(*c*)	0	0.2076 (9)	0.25	2.4 (5)
C(4)	4(*c*)	0	0.3551 (13)	0.25	10.1 (9)
O(1)	8(*f*)	0.1266 (2)	−0.1333 (5)	0.3267 (6)	3.5 (3)
O(2)	8(*f*)	0.2092 (2)	−0.1509 (5)	0.5949 (6)	3.6 (3)
O(3)	8(*f*)	0.0383 (3)	0.1497 (6)	0.3886 (7)	5.2 (5)
Na(1)	8(*f*)	0.1649 (1)	0.0905 (3)	0.4585 (4)	3.0 (2)
Na(2)	4(*c*)	0	0.0909 (4)	0.75	3.1 (2)
Form II					
C(1)	4(*c*)	0	0.1012 (20)	0.25	2.1 (7)
C(2)	4(*c*)	0	0.1767 (69)	0.25	4.8 (11)
C(3)	4(*c*)	0	0.6012	0.25	2.1
C(4)	4(*c*)	0	0.6767	0.25	4.8
O(1)	8(*f*)	0.1311 (7)	0.0717 (3)	0.1161 (18)	2.8 (3)
O(2)	8(*f*)*	0.1311	0.5717	0.1161	2.8
O(3)	8(*f*)*	0.1311	0.5717	0.3839	2.8
Na(1)	4(*c*)	0.5	0.0429 (6)	0.25	2.2 (3)
Na(2)	4(*c*)	0.5	0.5429	0.25	2.2

* Occupancy 0.50 (2).

Table 2. *Bond distances* (Å) *and angles* (°) *in sodium acetate, form* I

C(1)—C(2)	1.511 (10)	O(1)—C(1)—O(2)	123.6 (6)
C(1)—O(1)	1.245 (8)	O(1)—C(1)—C(2)	118.7 (6)
C(1)—O(2)	1.255 (8)	O(2)—C(1)—C(2)	117.7 (6)
C(3)—C(4)	1.472 (19)	O(3)—C(3)—O(3')	123.9 (9)
C(3)—O(3)	1.228 (7)	O(3)—C(3)—C(4)	118.1 (5)

curacy these values are chemically reasonable, and as such support the essential correctness of the structural model.

As noted earlier, four weak reflections observed with intensities greater than $2.33\sigma(I)$ are not accounted for. These are 210, 212, 351 and 3,19,1. Aside from experimental inaccuracy, the reason for this could lie in the restrictions imposed on the two contributing structures, especially the assumption that the acetate and sodium ions lie on twofold axes. Relaxing this constraint would greatly increase the number of least-squares parameters; given the quality of the available crystals and X-ray data exploration of more general models was considered unwarranted.

What is the relationship of our two crystal forms to the powdered sodium acetate used in the heat capacity study of Franzosini, Plautz & Westrum (1982)? We have examined powder X-ray patterns of this material and of our forms I and II. The comparison conclusively showed the heat capacity powder to be form II. Franzosini *et al.* detected no phase transitions in sodium acetate between 21 and 350 K, the upper limit of their measurements. This implies, paradoxically, that form II, rather than the more ordered form I, is the thermodynamically stable form under ordinary pressure, at temperatures up to 350 K. The complications encountered in characterizing form II crystallographically cast doubt on any structural in-

terpretation of the 21 K phase transition; methyl hydrogen ordering is a possibility, if the acetate ions lie on twofold axes. On the other hand, the reported variability in the magnitude of the 21 K C_p-curve peak may well be related to the variability in diffraction pattern and domain size, found by us.

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Sodium–Hydrogen and Boron–Hydrogen Interactions in the Cubane Structure of Tetrasodium Tetra-μ_3-hydrido-tetrakis(trimethylborate) Diethyl Ether Solvate, [NaB(CH₃)₃H]₄.(C₂H₅)₂O

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Abstract. $M_r = 393.8$, monoclinic, space group $P2_1/m$, $a = 10.046$ (4), $b = 10.81$ (3), $c = 12.842$ (6) Å, $\beta = 99.54$ (2)°, $U = 1375.3$ Å³, $Z = 2$, $D_m = 0.93$ (2), $D_x = 0.95$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.54184$ Å, $\mu = 0.868$ mm⁻¹, $F(000) = 436$, $T = 133$ K, $R = 0.105$ for 1252 observed reflections. The compound contains the tetrameric unit [NaB(CH₃)₃H]₄, as did the ether-free compound in benzene solution. The molecule is situated on a mirror plane giving a cubane structure of Na and H atoms. The structure thus consists of two interpenetrating tetrahedra of Na and hydridic H atoms at alternate corners of the very distorted cube. One of the Na atoms which lies on the mirror plane is coordinated to an ether molecule. Each hydridic H is bonded to the B of one trimethylboron group, thus forming a larger tetrahedron of B atoms. The tetrameric units are stacked along the *b* direction *via* interactions between the two Na atoms on the mirror plane and methyl H atoms of trimethylboron units in neighbouring tetramers. These chains are loosely held together in a two-dimensional network.

Introduction. Hydrides of the type MBR_3 H (M = alkali metal, R = alkyl) are readily prepared from MH and R_3B (*e.g.* Brown & Krishnamurthy, 1978; Brown,

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Khuri & Kim, 1977; Honeycutt & Riddle, 1961) or from *tert*-BuLi and R_3B (Brown, Kramer, Hubbard & Krishnamurthy, 1980) and some are now commercially available ['Superhydride', R = Et, M = Li (Brown & Krishnamurthy, 1973); 'L- and K-Selectride', R = *sec*-Bu, M = Li, K (Brown & Krishnamurthy, 1972; Brown, 1973)]. These highly attractive reducing agents for organic synthesis are capable of achieving stereo- and regio-selective transformations unequalled by any other reagents currently available (Brown, Kim & Krishnamurthy, 1980; Ireland & Thompson, 1979; Walker, 1976). However, little is known about the nature of such reagents which have probably been assumed to contain the pseudotetrahedral hydrido-trialkylborate anion. We therefore examined the crystal structure of sodium hydridotrimethylborate. A preliminary report of this structure has appeared (Bell, Shearer & Spencer, 1980).

Experimental. Obtained from sodium hydride and trimethylboron in diethyl ether as reported earlier (Binger, Benedikt, Rotermund & Köster, 1968), re-crystallized from hexane solution as colourless needles; drying in high vacuum gives solvent-free NaB(CH₃)₃H, which is tetrameric in benzene solution (Bell, Coates & Heslop, unpublished); crystalline needles, elongated along **b**, picked from hexane solution in a glove-box under an atmosphere of nitrogen without subjecting the crystals to high-vacuum drying and then individually sealed in thin-walled quartz capillary tubes in an atmosphere of dry nitrogen; X-ray analysis showed