

## Structure of Sodium *tert*-Butoxide: a Re-refinement

BY J. E. DAVIES

Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

AND J. KOPF AND E. WEISS

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6,  
2 Hamburg 13, Federal Republic of Germany

(Received 19 October 1981; accepted 18 March 1982)

**Abstract.**  $C_4H_9NaO$ ,  $M_r = 96.10$ , trigonal,  $R3c$ ,  $a = 19.388$  (14),  $c = 43.335$  (30) Å,  $U = 14107$  Å<sup>3</sup>,  $Z = 90$ ,  $D_c = 1.02$  Mg m<sup>-3</sup>,  $F(000) = 4680$ . This structure has been reported [Greiser & Weiss (1977). *Chem. Ber.* **110**, 3388–3396] as monoclinic, space group  $Cc$ . The original  $Cc$  reflexion data have been transformed to a trigonal setting and the structure has been successfully refined in the true space group  $R3c$  ( $R = 0.170$ ,  $R' = 0.142$  for 1730 reflexions). Bond lengths and angles in the  $R3c$  structure do not differ significantly from those reported earlier for the  $Cc$  structure. The  $R3c$  cell contains six hexameric and six nonameric  $C_4H_9ONa$  units; the centre of each unit lies on a triad axis. There is considerable rotational disorder associated with the *tert*-butoxy groups.

**Introduction.** The X-ray structure of the title compound was reported by Greiser & Weiss (1977) as monoclinic, space group  $Cc$ ,  $a = 30.995$ ,  $b = 19.378$ ,  $c = 18.269$  Å,  $\beta = 121.01^\circ$ ,  $Z = 60$ . The  $[101]$  zone axis of this  $Cc$  cell is, however, the unique  $c$  axis of a trigonal cell with  $a = 19.388$ ,\*  $c = 43.335$  Å,  $Z = 90$ . The Laue symmetry and the systematic absences are consistent with space groups  $R3c$  and  $\bar{R}3c$ . The  $Cc$  structure contains no centre of symmetry and the correct space group is therefore  $R3c$ . Atomic coordinates in the trigonal structure ( $x/a'$ ,  $y/b'$ ,  $z/c'$ ) are related to atomic coordinates in the  $Cc$  structure ( $x/a$ ,  $y/b$ ,  $z/c$ ) by the equation

$$\begin{pmatrix} x/a' \\ y/b' \\ z/c' \end{pmatrix} = \begin{pmatrix} \frac{1}{3} & 1 & \frac{1}{3} \\ \frac{2}{3} & 0 & \frac{2}{3} \\ \frac{2}{3} & 0 & -\frac{1}{3} \end{pmatrix} \begin{pmatrix} x/a \\ y/b \\ z/c \end{pmatrix} + \begin{pmatrix} -\frac{1}{6} \\ -\frac{5}{6} \\ \frac{1}{6} \end{pmatrix}.$$

This equation was used to obtain a set of atomic coordinates for the five  $C_4H_9NaO$  units which define the asymmetric unit of the trigonal ( $R3c$ ) structure. The

\* Average of the three axes  $[010] = 19.378$ ,  $[\frac{1}{3}\frac{1}{3}1] = 19.393$  and  $[\frac{1}{3}\frac{1}{3}\bar{1}] = 19.393$  Å in the  $Cc$  lattice.

original  $Cc$  reflexion data were transformed to the  $R3c$  setting and equivalents were averaged to give 1730 reflexions with  $F > 3\sigma(F)$ . Three cycles of least-squares refinement in space group  $R3c$  were sufficient to demonstrate that the structure is indeed  $R3c$  and that the *tert*-butoxy groups are rotationally disordered about the O–C bonds. This disorder presented considerable problems during subsequent refinement cycles. The structure was finally refined by full-matrix least squares with complex neutral-atom scattering

Table 1. Atomic coordinates and isotropic thermal parameters

The first digit of each atom label indicates either hexamer(6) or nonamer(9). Atom O(xy) is bound to atom C(xy). Methyl C atoms C(xyn) ( $n = 1, 2, 3$ ) are bound to carbon atom C(xy).

	$x$	$y$	$z$	$U$ (Å <sup>2</sup> )
Na(91)	0.8893 (8)	-0.1156 (9)	0.2931	0.092 (5)
Na(92)	0.9986 (8)	0.1079 (7)	0.2092 (3)	0.076 (4)
Na(93)	0.8185 (6)	-0.0450 (6)	0.2519 (4)	0.088 (3)
Na(61)	0.9027 (8)	0.0317 (8)	0.0250 (4)	0.079 (4)
Na(62)	0.8836 (9)	-0.0881 (9)	-0.0215 (5)	0.114 (6)
O(91)	0.8773 (11)	-0.0059 (11)	0.2981 (5)	0.061 (6)
O(92)	0.8786 (12)	-0.0020 (12)	0.2057 (6)	0.073 (7)
O(93)	0.8203 (10)	-0.1673 (10)	0.2520 (7)	0.090 (6)
O(61)	0.9703 (12)	-0.1262 (11)	-0.0282 (5)	0.068 (7)
O(62)	0.8700 (14)	-0.0959 (14)	0.0300 (6)	0.101 (9)
C(91)	0.8375 (18)	0.0015 (18)	0.3252 (7)	0.123 (14)
C(911)	0.7574 (22)	-0.0101 (24)	0.3125 (10)	0.180 (19)
C(912)	0.8159 (22)	-0.0693 (19)	0.3465 (9)	0.143 (17)
C(913)	0.8865 (19)	0.0781 (17)	0.3439 (8)	0.134 (15)
C(92)	0.8315 (16)	0.0103 (17)	0.1826 (7)	0.106 (14)
C(921)	0.7733 (19)	0.0331 (19)	0.1975 (9)	0.120 (13)
C(922)	0.8830 (21)	0.0787 (20)	0.1595 (10)	0.157 (19)
C(923)	0.7858 (16)	-0.0691 (15)	0.1650 (7)	0.076 (9)
C(93)	0.7574 (15)	-0.2503 (12)	0.2531 (7)	0.101 (9)
C(931)	0.7709 (20)	-0.3165 (18)	0.2424 (8)	0.136 (13)
C(932)	0.7069 (32)	-0.2356 (37)	0.2301 (11)	0.336 (34)
C(933)	0.7207 (17)	-0.2765 (17)	0.2851 (7)	0.096 (10)
C(61)	0.9441 (15)	-0.1967 (13)	-0.0472 (6)	0.057 (9)
C(611)	0.9461 (18)	-0.2649 (17)	-0.0302 (8)	0.108 (13)
C(612)	0.9996 (23)	-0.1700 (23)	-0.0751 (9)	0.189 (19)
C(613)	0.8563 (18)	-0.2280 (29)	-0.0551 (11)	0.224 (25)
C(62)	0.8063 (19)	-0.1485 (19)	0.0508 (8)	0.180 (21)
C(621)	0.7417 (26)	-0.1998 (26)	0.0263 (10)	0.206 (22)
C(622)	0.7852 (21)	-0.0959 (19)	0.0694 (8)	0.123 (13)
C(623)	0.8299 (21)	-0.2017 (21)	0.0669 (9)	0.137 (16)

Table 2. Selected bond lengths (Å) and angles (°)

Numbers in parentheses are e.s.d.'s associated with the least significant digits. A prime denotes an atom generated by the triad.

Na(61)—O(62)	2.24 (3)	Na(92)—O(93')	2.25 (3)
Na(61)—O(62')	2.32 (3)	Na(92)—O(92)	2.24 (2)
Na(61)—O(61')	2.31 (3)	Na(92)—O(92')	2.23 (2)
Na(62)—O(62)	2.24 (3)	Na(93)—O(91)	2.24 (2)
Na(62)—O(61)	2.17 (2)	Na(93)—O(93)	2.39 (2)
Na(62)—O(61')	2.14 (2)	Na(93)—O(92)	2.26 (2)
Na(91)—O(91)	2.26 (2)	O(xy)—C(xy)	1.45 (1)*
Na(91)—O(91')	2.28 (2)	C(xy)—C(xyn)	1.54 (5)*
Na(91)—O(93)	2.15 (3)		
O(91)—Na(91)—O(91')	125 (1)	Na(91)—O(93)—Na(92')	111 (1)
O(91)—Na(91)—O(93)	101 (1)	Na(91)—O(93)—Na(93)	82 (1)
O(91')—Na(91)—O(93)	118 (1)	Na(92')—O(93)—Na(93)	79 (1)
O(92)—Na(92)—O(92')	130 (1)	O(62)—Na(61)—O(62')	119 (1)
O(92')—Na(92)—O(93')	101 (1)	O(62')—Na(61)—O(61')	95 (1)
O(92)—Na(92)—O(93')	113 (1)	O(61')—Na(62)—O(61')	126 (1)
O(91)—Na(93)—O(92)	126 (1)	O(61')—Na(62)—O(62)	99 (1)
O(91)—Na(93)—O(93)	94 (1)	O(61)—Na(62)—O(62)	101 (1)
O(92)—Na(93)—O(93)	96 (1)	Na(62')—O(61)—Na(62)	110 (1)
Na(93)—O(91)—Na(91)	83 (1)	Na(62')—O(61)—Na(61')	83 (1)
Na(93)—O(91)—Na(91')	110 (1)	Na(62)—O(61)—Na(61')	82 (1)
Na(91)—O(91)—Na(91')	114 (1)	Na(61)—O(62)—Na(62)	83 (1)
Na(92')—O(92)—Na(92)	109 (1)	Na(61)—O(62)—Na(61')	119 (1)
Na(92')—O(92)—Na(93)	83 (1)	Na(62)—O(62)—Na(61')	81 (1)
Na(92)—O(92)—Na(93)	113 (1)		

\* Constrained bond lengths; these are average values and the e.s.d. is a measure of the deviation of the individual lengths from the average. (The labelling scheme is defined in Table 1.)

factors, weights proportional to  $1/\sigma^2(F)$ , individual isotropic temperature factors and the following constraints. The fifteen distances  $[C(xy)-C(xyn)]^*$  were fixed at 1.54 Å; the two sets of distances  $[O(xy)-C(xy); \text{five distances}]$  and  $[C(xy1)-C(xy2), C(xy2)-C(xy3), C(xy3)-C(xy1); 15 \text{ distances}]$  were each assigned common variable distances  $d_1$  and  $d_2$  respectively. These three constraints effectively average the geometries of all five independent *tert*-butoxy groups in the structure. This refinement converged with  $R = 0.170$ ,  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.142$ ,  $d_1 = 1.45 (1)$ ,  $d_2 = 2.51 (2)$  Å. Final coordinates and the resulting bond lengths are in Tables 1 and 2.† All calculations were performed with *SHELX 76* (Sheldrick, 1976).

**Discussion.** The crystal and molecular structure are illustrated in Figs. 1 and 2. There are no significant differences between bond lengths and angles in the *R3c* and *Cc* structures. In *R3c*,  $\cdots$ nonamer-hexamer-nonamer $\cdots$  chains run parallel to the crystal *c* axis; the centre of each discrete nonameric and hexameric unit lies on a triad axis. The high *R* factor (0.170) is actually slightly better than that achieved for the *Cc* structure (0.203 with isotropic temperature factors)

\* The atom labelling scheme is defined in Table 1.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36807 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

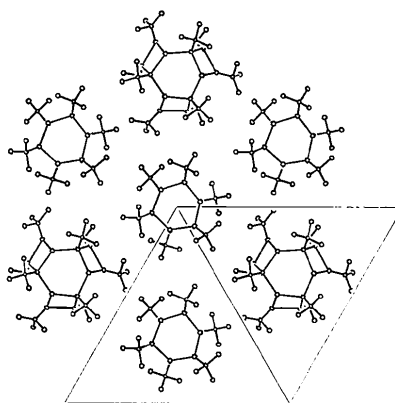


Fig. 1. Part of the crystal structure of sodium *tert*-butoxide projected onto the *ab* plane. Each of the four hexameric and three nonameric units depicted here is part of a  $\cdots$ nonamer-hexamer-nonamer $\cdots$  chain running perpendicular to the page. The unit cell is outlined. In this diagram, O and Na atoms overlie each other (see Fig. 2).

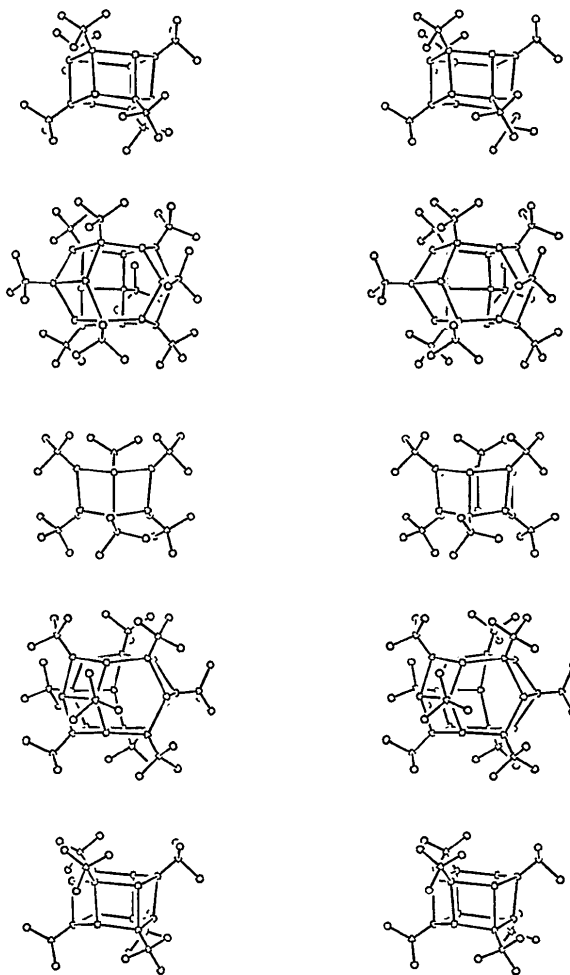


Fig. 2. Stereoscopic view of one  $\cdots$ nonamer-hexamer-nonamer $\cdots$  chain. The trigonal *c* axis (43.335 Å) runs from the centre of the bottom hexamer to the centre of the top hexamer.

and reflects the considerable disorder associated with the *tert*-butoxy groups. Molecular motion of *tert*-butoxy groups has previously been observed (Weiss, Alsdorf, Kühr & Grützmaier, 1968) in a  $^1\text{H}$  wide-line NMR study of the compound  $[(\text{CH}_3)_3\text{COK}]_4$ . In this case, the NMR results above 243 K indicate that rotation of the *tert*-butoxy group as a whole is coupled with rotation of individual methyl groups.

*Acta Cryst.* (1982). B38, 2253–2256

## Chloro[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C,N*]-[4-(dimethylamino)pyridine]palladium(II)

BY GEORGE FERGUSON,\* ALAN J. MCALEES, ROBERT MCCRINDLE AND BARBARA L. RUHL

*Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

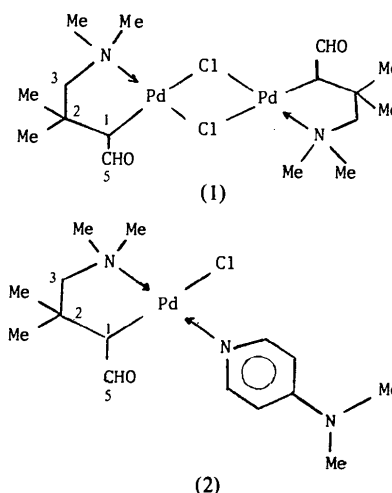
(Received 21 January 1982; accepted 19 March 1982)

**Abstract.**  $\text{Pd}(\text{C}_7\text{H}_{10}\text{N}_2)(\text{C}_8\text{H}_{16}\text{NO})\text{Cl}$ ,  $\text{C}_{15}\text{H}_{26}\text{ClN}_3\text{OPd}$ ,  $M_r = 406.2$ , monoclinic,  $P2_1/n$ ,  $a = 10.762$  (1),  $b = 23.994$  (5),  $c = 6.989$  (1) Å,  $\beta = 98.46$  (2)°,  $U = 1785.2$  Å $^3$ ,  $D_c = 1.51$  g cm $^{-3}$ ,  $Z = 4$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo K}\alpha) = 29.0$  cm $^{-1}$ ,  $F(000) = 832$ , space group determined uniquely from systematic absences:  $h0l$ ,  $h + l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ .  $R = 0.028$  for 2449 reflections [with  $I > 3\sigma(I)$ ] measured by diffractometer. The palladium atom has a slightly distorted square-planar configuration in a five-membered chelate ring that has an envelope conformation. Principal bond lengths are Pd–Cl(*trans* to C) 2.413 (1), Pd–C(1) 2.052 (4), Pd–N(1) 2.086 (3), and Pd–N(2) 2.038 (3) Å. The X-ray data establish that there is a significant interaction between the palladium and aldehyde carbon C(5), Pd...C(5) 2.664 (4) Å, C(5)–C(1)–Pd 97.3 (2)°. The Pd–C(1)–C(5)–O torsion angle is 96.0 (5)°.

**Introduction.** We have previously reported (Alyea, Dias, Ferguson, McAlees, McCrindle & Roberts, 1977) the synthesis and X-ray structure analysis of di- $\mu$ -chloro-bis[1-formyl-2,2-dimethyl-3-(dimethylamino)-propyl-*C,N*]dipalladium(II) (1), in which there appears to be a direct interaction between the palladium atom and the carbon atom of the formyl group. Interactions of this type have been discussed (Green, 1968; Pannell, Cassias, Crawford & Flores, 1976) in

- References**
- GREISER, T. & WEISS, E. (1977). *Chem. Ber.* **110**, 3388–3396.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WEISS, E., ALSDORF, H., KÜHR, H. & GRÜTZMÄCHER, H.-J. (1968). *Chem. Ber.* **101**, 3777–3786.

terms of a direct overlap of metal *d* orbitals with  $\pi$  orbitals of the carbonyl function. Alternatively, a  $\sigma$ - $\pi$  conjugative interaction of the Pd–C bond with the carbonyl group could be invoked to explain the properties of such systems. The latter description has been widely applied in the rationalization of the spectral properties and reactivities of organometallic derivatives of non-transition metals (Meyer, Gorrichon-Guigon & Maroni, 1980). In the course of an investigation (McCrindle & McAlees, 1982) of the influence of changes in the palladium coordination sphere on this interaction, a series of compounds related to (1), and including the title compound (2), has now been



\* To whom correspondence should be addressed.