Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Sodium percarbonate between 293 and 100 K

Robin Gavin Pritchard* and Emran Islam

Department of Chemistry, UMIST, PO Box 88, Manchester, England

Correspondence e-mail: robin.pritchard@umist.ac.uk

Received 12 May 2003
Accepted 10 July 2003

Sodium carbonate perhydrate, $Na_2CO_3{\cdot}1.5H_2O_2$, commonly known as sodium percarbonate, has been structurally characterized at temperatures ranging from 293 down to 100 K. As the temperature drops, there is a reversible phase change between 250 and 240 K, in which the crystallographic mirror plane of the room-temperature space group, *Cmca*, is lost, transforming it to *Pbca*. This transformation is accompanied by a reversal in the expansion coefficient of cell side *b*, which, like the other two sides, initially contracts on cooling. The two crystallographically independent hydrogen peroxide sites undergo the largest change, where the disorder seen at room temperature gradually diminishes and is almost completely absent at 100 K, thus indicating dynamic rather than static disorder. It is noteworthy that, despite *Cmca* being the preferred room-temperature space group in the current work, two previous single-crystal studies rejected this space group in favour of non-centrosymmetric *Aba*2 [Carrondo *et al.* (1977). *J. Chem. Soc. Dalton Trans.* pp. 2323–2331; Adams & Pritchard (1977). *Acta Cryst*. B**33**, 3650–3653]. A re-evaluation of these determinations indicates that they are identical to the current structure and should be re-assigned to *Cmca*.

1. Introduction

Sodium percarbonate is manufactured on an industrial scale for use as environmentally friendly bleach in household cleaning products. Knowledge of the crystal structure of sodium percarbonate is important in order to understand how it decomposes under the influence of heat and humidity as well as through interactions with other components of a formulation. In addition, as sodium percarbonate is being used increasingly for organic synthesis (McKillop & Sanderson, 2000), including in some instances as a suspension, solid-state structure and crystal morphology are again an issue.

Sodium percarbonate was studied simultaneously by two groups using X-ray single-crystal methods (Adams & Pritchard, 1977; Carrondo *et al.*, 1977). Although different techniques were used to produce the crystals in each case, the two determinations are in good agreement, with both studies assigning the crystals to orthorhombic space group *Aba*2. Two distinct crystallographic sites house disordered hydrogen peroxide in both these examples, but the extent of the disorder is different in each case. There is, however, considerable disparity in the quality of the two data collections, and it would be reasonable to ascribe at least some of the differences to this fact, *e.g.* the Adams & Pritchard structure was only subjected to isotropic refinement. It is, however, worrying that the hydrogen peroxide O—O bond lengths deviate considerably from a typical value of 1.47 Å, particularly in the high-quality Carrondo *et al.* structure [O—O = 1.42 (2), 1.52 (2) and 1.35 (3) Å].

The current study was initiated in order to address this last point, as it was hoped that, by cooling the crystal, disorder would be reduced and hence the accuracy of the H_2O_2 geometry in this industrially important material would be improved.

2. Experimental

2.1. Synthesis

The sodium percarbonate crystal whose structure is reported here was prepared by dissolving anhydrous sodium carbonate to saturation in an aqueous hydrogen peroxide solution (30% *w*/*w*). This solution was then placed in a Petri dish to a depth of ~2 mm and left overnight to crystallize.

Crystals were also prepared, for comparison purposes, using the alkaline conditions described by Adams & Pritchard (1977) and from the more dilute hydrogen peroxide solutions (10% *w*/*w*) used by Carrondo *et al.* (1977).

2.2. Data collection, structure solution and refinement

All measurements were carried out using a Nonius KappaCCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Details of cell parameters, data collection and refinement are summarized in Table 1, together with a list of software employed.[1]

Systematic absences and statistical tests clearly indicate space group *Cmca* for the 293 and 250 K structures; however, contraventions of the C-centring condition become apparent at 240 K and necessitate a change to space group *Pbca* for this and all the lower-temperature structures. Interestingly, refinement of the 293 K structure in *Aba*2, the non-centrosymmetric version of *Cmca* used by the earlier investigators (Adams & Pritchard, 1977; Carrondo *et al.*, 1977; Pritchard, 1978), led to poorer results [$wR = 0.094$ (all data), 131 parameters, $R1 = 0.033$ for 634 data with $I > 2\sigma(I)$ in *Aba*2, *cf.* $wR = 0.064$ (all data), 83 parameters, $R1 = 0.028$ for 603 data with $I > 2\sigma(I)$ for the same data in *Cmca*]. Furthermore, the hydrogen peroxide geometries in *Cmca* showed a considerable improvement over those determined previously at room temperature in *Aba*2 (Table 2).

The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based on $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976).

Treatment of the sodium and carbonate ions was straightforward at all temperatures; however, the two crystallographically independent hydrogen peroxide molecules proved to be more problematic because of disorder, as illustrated by the electron-density maps in the planes containing the peroxide O atoms (Fig. 1).

The modelling schemes used for the hydrogen peroxide sites are summarized in Fig. 2. At 293 and 250 K, site I $(0, \frac{1}{8}, \frac{3}{8})$ straddles the *Cmca* mirror plane and is therefore modelled by a semi-populated diagonal hydrogen peroxide molecule (O11, O12), whose second disordered component is reproduced by the crystallographic mirror plane.

Although *Pbca* lacks a crystallographic mirror plane, the disorder in site I at 240 K is very similar to that seen in *Cmca*, but in the latter case the second disordered component (O21, O22) is related to the first by a pseudo-mirror plane. The populations of the two molecules are free to refine but the total site occupancy is fixed to unity. As the temperature decreases, the population of hydrogen peroxide O21, O22 diminishes, and at 150 K the disorder has disappeared completely. It proved necessary to apply DFIX restraints to

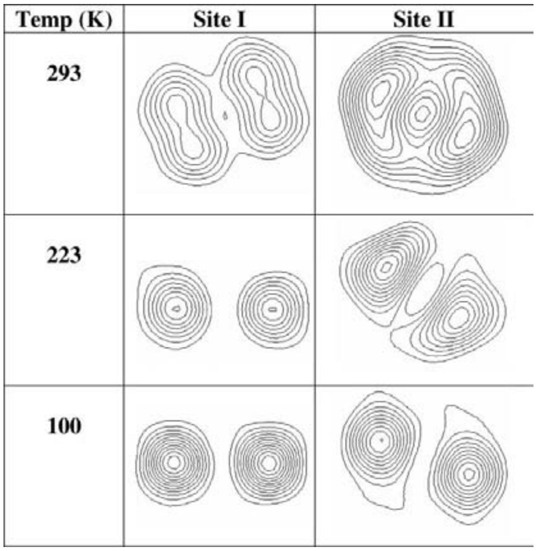


Figure 1
Variation of electron density in hydrogen peroxide sites with temperature.

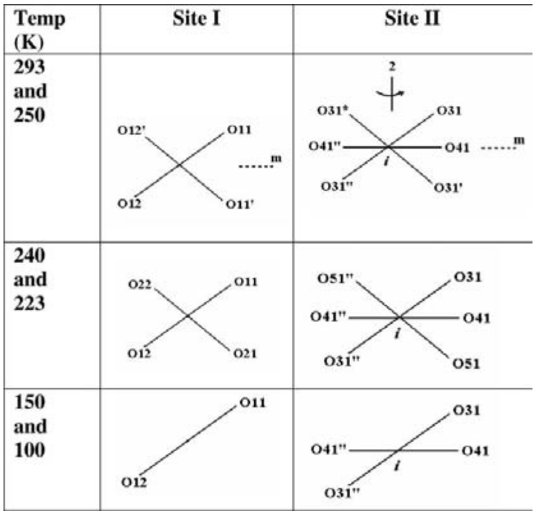


Figure 2
Modelling schemes for hydrogen peroxide O atoms.

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA5004). Services for accessing these data are described at the back of the journal.

Table 1
Experimental table.

	293 K	250 K	240 K	223 K	150 K	100 K
Crystal data						
Chemical formula	$Na_2CO_3\cdot1.5H_2O_2$	$Na_2CO_3\cdot1.5H_2O_2$	$Na_2CO_3\cdot1.5H_2O_2$	$Na_2CO_3\cdot1.5H_2O_2$	$Na_2CO_3\cdot1.5H_2O_2$	$Na_2CO_3\cdot1.5H_2O_2$
M_r	157.01	157.01	157.01	157.01	157.01	157.01
Cell setting, space group	Orthorhombic, *Cmca*	Orthorhombic, *Cmca*	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*
a, b, c (Å)	6.7138 (4), 15.7407 (11), 9.1732 (7)	6.7030 (3), 15.7388 (7), 9.1684 (4)	6.6971 (2), 15.7410 (6), 9.1635 (3)	6.6871 (2), 15.7473 (6), 9.1540 (3)	6.6592 (2), 15.7511 (8), 9.1254 (4)	6.6521 (3), 15.7579 (8), 9.1062 (4)
V (Å^3)	969.42 (12)	967.24 (7)	966.01 (6)	963.95 (6)	957.16 (7)	954.54 (8)
Z	8	8	8	8	8	8
D_x (Mg m^{-3})	2.152	2.156	2.159	2.164	2.179	2.185
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1163	2018	4111	4174	2893	2623
θ range (°)	1.0–27.5	1.0–27.5	1.0–27.5	1.0–27.5	1.0–27.5	1.0–27.5
μ (mm^{-1})	0.36	0.36	0.37	0.37	0.37	0.37
Temperature (K)	293 (2)	250 (2)	240 (2)	223 (2)	150 (2)	100 (2)
Crystal form, colour	Block, colourless	Block, colourless	Block, colourless	Block, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04	0.08 × 0.07 × 0.04
Data collection						
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan (*SORTAV*; Blessing, 1995, 1997)	Multi-scan (*SORTAV*; Blessing, 1995, 1997)	Multi-scan (*SORTAV*; Blessing, 1995, 1997)	Multi-scan (*SORTAV*; Blessing, 1995, 1997)	Multi-scan (*SORTAV*; Blessing, 1995, 1997)	Multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min}	0.993	0.992	0.987	0.991	0.93	0.992
T_{max}	1.014	1.012	1.013	1.013	0.975	1.02
No. of measured, independent and observed parameters	2341, 603, 400	3593, 599, 514	7832, 1099, 788	7217, 1097, 885	5477, 1092, 875	4463, 1091, 882
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.044	0.043	0.053	0.061	0.049	0.041
θ_{max} (°)	27.5	27.5	27.5	27.5	27.5	27.6
Range of h, k, l	$-8 \Rightarrow h \Rightarrow 7$ $-14 \Rightarrow k \Rightarrow 20$ $-11 \Rightarrow l \Rightarrow 10$	$-8 \Rightarrow h \Rightarrow 7$ $-20 \Rightarrow k \Rightarrow 17$ $-11 \Rightarrow l \Rightarrow 11$	$-8 \Rightarrow h \Rightarrow 8$ $-20 \Rightarrow k \Rightarrow 17$ $-11 \Rightarrow l \Rightarrow 11$	$-8 \Rightarrow h \Rightarrow 8$ $-20 \Rightarrow k \Rightarrow 17$ $-11 \Rightarrow l \Rightarrow 11$	$-7 \Rightarrow h \Rightarrow 8$ $-20 \Rightarrow k \Rightarrow 17$ $-10 \Rightarrow l \Rightarrow 11$	$-7 \Rightarrow h \Rightarrow 8$ $-20 \Rightarrow k \Rightarrow 17$ $-9 \Rightarrow l \Rightarrow 11$
Refinement						
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.064, 1.04	0.026, 0.065, 1.07	0.028, 0.074, 1.04	0.029, 0.075, 1.05	0.027, 0.064, 1.03	0.027, 0.068, 1.04
No. of reflections	603	599	1099	1097	1092	1091
No. of parameters	83	83	132	133	105	105
H-atom treatment	Refined independently	Refined independently	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Refined independently	Refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0137P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.119P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.0715P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.0122P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.0042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.005	0.002	0.025	0.024	0.004	0.011
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, –0.21	0.33, –0.27	0.26, –0.23	0.35, –0.27	0.23, –0.29	0.24, –0.22
Extinction method	*SHELXL*97	*SHELXL*97	*SHELXL*97	*SHELXL*97	*SHELXL*97	*SHELXL*97
Extinction coefficient	0.0081 (7)	0.0232 (17)	0.0228 (7)	0.0285 (8)	0.0150 (11)	0.0123 (11)

Computer programs: *KappaCCD Server Software* (Nonius, 1997), *COLLECT* (Nonius, 1998), *HKL DENZO* (Otwinowski & Minor 1997), *HKL SCALEPACK* (Otwinowski & Minor 1997), *SHELXS*97 (Sheldrick, 1997), *SHELXL*97 (Sheldrick, 1997), *ORTEP*-3 *for Windows* (Farrugia, 1997), *WinGX* (Farrugia, 1999).

Table 2
Comparison of hydrogen peroxide sites at various temperatures.

			Selected hydrogen peroxide parameters					
			Site I			Site II		
Study	Temp (K)	Space group	Symmetry	O—O (Å)	% occupancy	Symmetry	O—O (Å)	% occupancy
Carrondo *et al.* (*R* = 0.029)	293	*Aba*2	General Pseudo *m*	1.42 (2) 1.52 (2)	50 50	2 Pseudo 2/*m*	1.35 (3)	50 × 2 (disorder)
Adams & Pritchard (*R* = 0.114)	293	*Aba*2	General	1.51 (6)	100	2 Pseudo 2/*m*	1.49 (7)	50 × 2 (disorder)
This work	293	*Cmca*	*m*	1.4771 (18) (O11—O12)	50 × 2 (disorder)	2/*m*	1.492 (4) (O31—O31) 1.475 (6) (O41—O41)	30.7 (1) × 2 38.6 (3)
This work	250	*Cmca*	*m*	1.4814(14) (O11—O12)	50 × 2 (disorder)	2/*m*	1.490 (4) (O31—O31) 1.456 (4) (O41—O41)	26.8 (1) × 2 46.4 (2)
This work	240	*Pbca*	General	1.4820 (5) (O11—O12) 1.4741 (12)† (O21—O22)	72.18 (3) 27.82 (3)	*i*	1.4775 (12) (O31—O31) 1.4805 (11)‡ (O41—O41) 1.482 (3) (O51—O51)	39.07 (5) 44.51 (6) 18.02 (6)
This work	223	*Pbca*	General	1.4804 (4) (O11—O12) 1.497 (2)† (O21—O22)	87.87 (3) 12.13 (3)	*i*	1.4807 (10) (O31—O31) 1.4792 (11)‡ (O41—O41) 1.478 (3) (O51—O51)	45.34 (5) 46.16 (5) 10.38 (6)
This work	150	*Pbca*	General	1.4785 (8) (O11—O12)	100	*i*	1.4773 (17) (O31—O31) 1.480 (5)§ (O41—O41)	72.4 (2) 27.6 (2)
This work	100	*Pbca*	General	1.4823 (8) (O11—O12)	100	*i*	1.4808 (15) (O31—O31) 1.498 (10)§ (O41—O41)	84.9 (2) 15.1 (2)

† DFIX O11—O12, O21—O22. ‡ DFIX O31—O31, O41—O41, O51—O51. § DFIX O31—O31, O41—O41.

the two site I O—O bonds at 240 and 223 K, and also to generate the H atoms of the minor component by applying constraints based on the pseudo-mirror operation.

In contrast to the bimodal hydrogen peroxide distribution at 293 K in site I, electron density is smeared over arcs centred on crystallographic inversion points in site II (0, 0, 0). As this site has crystallographic 2/*m* symmetry, it is possible to model the hydrogen peroxide using two fractional O atoms, O31 and O41. Atom O41 sits on the mirror plane, so that atoms O31 and O41 generate a total of three hydrogen peroxide orientations on application of the site symmetry. As in site I, the total H_2O_2 population in site II is constrained to one, and a semi-populated H-atom site, H31, lying off the mirror plane is shared by both O31 and O41.

Site II's symmetry is reduced to *i* in space group *Pbca*, and a third O atom, O51, related to atom O31 by a pseudo-mirror plane, has to be used. This greater freedom requires the three O—O bond lengths to be tied together *via* a DFIX instruction. In addition, another H-atom site, H51, has to be added and subjected to constraints based on the pseudo-mirror plane. As the temperature drops the population of atom O31 climbs at the expense of atom O51 and, at 100 K, site O51 is completely unoccupied.

3. Results and discussion

3.1. Crystallization characteristics

Sodium percarbonate crystallizes as colourless flattened needles when sodium carbonate dissolved in aqueous hydrogen peroxide (30% *w*/*w*) is allowed to evaporate to dryness. Once formed, the crystals are susceptible to the effect of humidity and must be used immediately or stored in a refrigerator.

Crystals formed in this way are identical in appearance to those grown using the alkaline conditions described by Adams & Pritchard (1977) or from the more dilute hydrogen peroxide solutions (10% *w*/*w*) used by Carrondo *et al.* (1977). Subsequent single-crystal measurements showed that crystals grown by all three methods are identical in structure.

3.2. Supramolecular structures

The crystal packing of sodium percarbonate at 100 K, shown in Fig. 3, is almost identical in appearance to the higher-temperature structures, except for the degree of H_2O_2 disorder. The sodium and carbonate ions form corrugated sheets parallel to the *ac* plane *via* coordinate bonds, which are, on average, at least 0.1 Å shorter than the corresponding bonds to hydrogen peroxide (Fig. 4). These sheets are cross-linked in the *b* direction by hydrogen peroxide solvate molecules, which exert a disproportionate influence on this axis when they become ordered on cooling. The variation in unit-cell dimensions with temperature is illustrated in Fig. 5 and shows that, although all three axes initially contract, *b* expands below the *Cmca*-to-*Pbca* transition temperature.

Each disordered hydrogen peroxide configuration is able to participate in two hydrogen and four coordinate bonds, as shown in Figs. 6(*a*) and 6(*b*) for the 240 K structure. The distribution of hydrogen peroxide between the various disorder sites is summarized in Table 2. Initially, on cooling, there is a decrease in the oxygen vibrational amplitudes, accompanied by a population drop in the peripheral O31 positions in site II. Once the transition from *Cmca* to *Pbca* has occurred, the hydrogen peroxide distribution in both sites becomes increasingly asymmetric as the temperature falls; however, site II lags behind site I.

Details of hydrogen peroxide interactions at various temperatures are presented in Table 3. Although each hydrogen peroxide orientation facilitates two hydrogen and four coordinate bonds, there is a considerable difference in the lengths of the two Na—O bonds to O31 (and O51). However, this asymmetry is reduced when O31 becomes the preferred site at lower temperatures, as shown by a plot of the Na1—O31 bond lengths against temperature (Fig. 7).

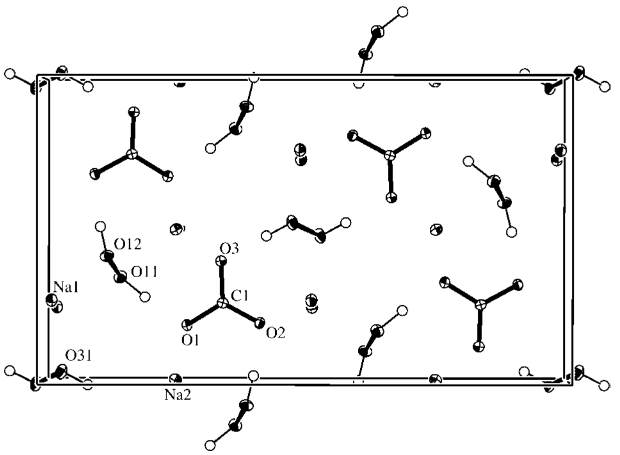


Figure 3
Crystal packing of one half of the unit cell (*a*/2) of sodium percarbonate at 100 K, viewed along *a*. The minor H_2O_2 site, O41, has been omitted for clarity.

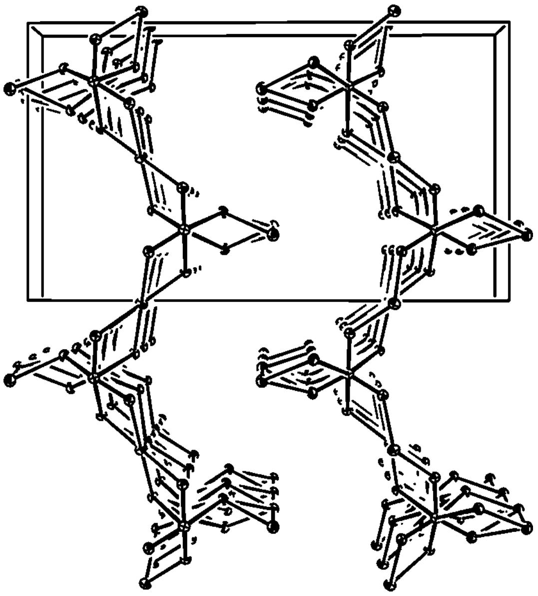


Figure 4
View along cell axis *a*, showing the corrugated sodium carbonate sheets lying parallel to the *ac* plane.

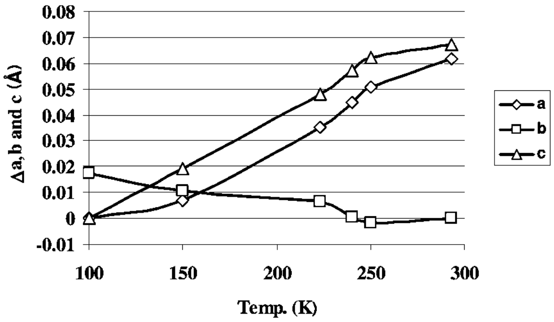


Figure 5
Variation of the unit-cell dimensions with temperature.

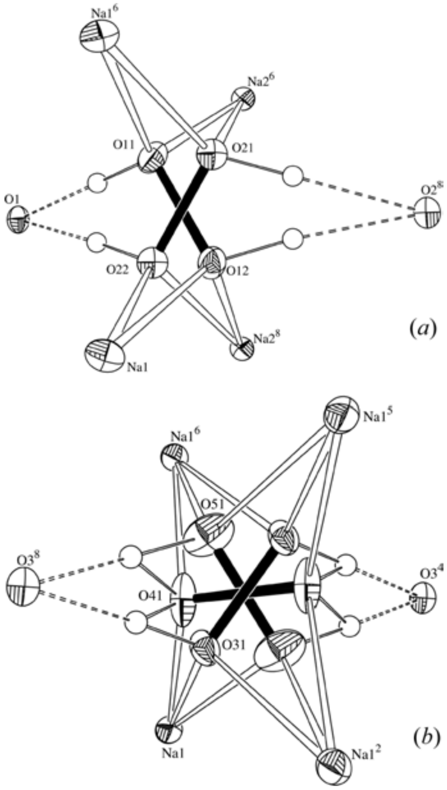


Figure 6
Hydrogen peroxide environment at 240 K in (*a*) site I and (*b*) site II. [Symmetry codes: (2) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (4) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (5) $-x, -y, -z$; (6) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (8) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.]

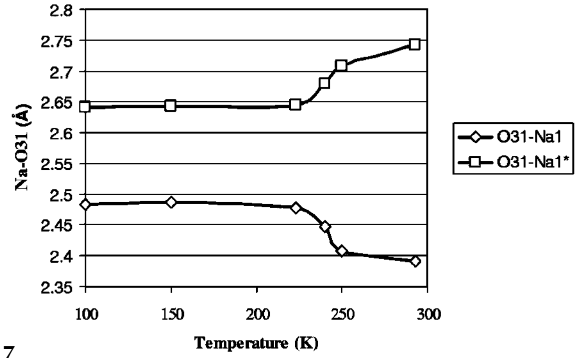


Figure 7
Variation of the two Na1—O31 bond lengths with temperature, where the asterisk (*) signifies ($\frac{1}{2}-x, -y, z-\frac{1}{2}$) in *Cmca* and ($\frac{1}{2}-x, -y, \frac{1}{2}+z$) in *Pbca*.

Table 3

(*a*) Hydrogen bonds at 293 and 250 K (Å, °) in space group *Cmca*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
293 K				
O11—H11···O1	0.962 (18)	1.652 (18)	2.5973 (18)	166.8 (18)
O12—H12···O2^1	1.002 (19)	1.626 (19)	2.6141 (18)	167.5 (17)
O31—H31···O3^2	1.031 (19)	1.556 (19)	2.571 (3)	167.2 (18)
O41—H31···O3^2	1.088 (19)	1.556 (19)	2.540 (3)	147.4 (15)
250 K				
O11—H11···O1	0.954 (17)	1.658 (17)	2.6013 (12)	169.1 (17)
O12—H12···O2^1	0.953 (14)	1.663 (14)	2.6081 (11)	170.7 (14)
O31—H31···O3^2	0.969 (16)	1.625 (16)	2.5690 (18)	163.6 (14)
O41—H31···O3^2	1.021 (16)	1.625 (16)	2.5503 (19)	148.3 (15)

Symmetry transformations used to generate equivalent atoms in *Cmca*: (1) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (2) $-x, -y+\frac{1}{2}, z-\frac{1}{2}$.

(*b*) Hydrogen bonds at 240, 223, 150 and 100 K (Å, °) in space group *Pbca*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
240 K				
O11—H11···O1	0.928 (5)	1.679 (5)	2.6007 (4)	171.5 (5)
O12—H12···O2^3	0.985 (5)	1.628 (5)	2.6011 (4)	168.8 (5)
O21—H21···O2^3	0.983 (5)	1.646 (5)	2.6207 (8)	170.6 (5)
O22—H22···O1	0.939 (5)	1.680 (5)	2.6108 (9)	170.6 (5)
O31—H31···O3^4	0.925 (6)	1.670 (6)	2.5713 (6)	163.8 (5)
O41—H31···O3^4	0.949 (6)	1.670 (6)	2.5453 (6)	151.7 (5)
O51—H51···O3^4	1.042 (12)	1.546 (12)	2.5721 (14)	167.1 (11)
223 K				
O11—H11···O1	0.931 (5)	1.679 (5)	2.6008 (3)	170.4 (4)
O12—H12···O2^3	0.905 (4)	1.703 (4)	2.5994 (3)	170.0 (4)
O21—H21···O2^3	0.905 (5)	1.719 (4)	2.6158 (18)	170.6 (5)
O22—H22···O1	0.929 (5)	1.693 (4)	2.6157 (18)	171.9 (4)
O31—H31···O3^4	1.001 (3)	1.588 (3)	2.5700 (5)	165.6 (4)
O41—H31···O3^4	0.993 (3)	1.588 (3)	2.5467 (6)	160.6 (3)
O51—H51···O3^4	0.997 (4)	1.942 (9)	2.657 (2)	126.3 (3)
150 K				
O11—H11···O1	1.012 (12)	1.601 (12)	2.6020 (8)	169.2 (10)
O12—H12···O2^5	0.970 (12)	1.644 (13)	2.5957 (9)	165.7 (9)
O31—H31···O3^6	0.961 (12)	1.622 (13)	2.5579 (11)	163.6 (10)
O41—H31···O3^6	0.954 (13)	1.622 (13)	2.554 (3)	164.3 (11)
100 K				
O11—H11···O1	1.035 (12)	1.577 (12)	2.6022 (8)	170.2 (11)
O12—H12···O2^5	0.966 (13)	1.642 (13)	2.5952 (8)	168.5 (10)
O31—H31···O3^6	0.949 (12)	1.619 (12)	2.5569 (10)	169.1 (10)
O41—H31···O3^6	0.990 (13)	1.619 (12)	2.558 (5)	156.6 (11)

Symmetry transformations used to generate equivalent atoms in *Pbca*: (3) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (4) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (5) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (6) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

(*c*) Na—O coordination bonds involving hydrogen peroxide (Å).

Cmca	293 K	250 K
Na1—O11	2.4104 (16)	2.4025 (10)
Na2—O11^7	2.5233 (16)	2.5217 (10)
O12—Na1^8	2.4175 (15)	2.4191 (10)
O12—Na2^9	2.5271 (15)	2.5208 (10)
Na1—O31	2.392 (3)	2.407 (2)
O31—Na1^{10}	2.742 (3)	2.708 (2)
Na1—O41	2.493 (2)	2.4868 (14)
O41—Na1^8	2.493 (2)	2.4868 (14)

Table 3 (continued)

Pbca	240 K	223 K	150 K	100 K
O11—Na1^{11}	2.4091 (4)	2.4133 (3)	2.4139 (6)	2.4159 (7)
Na2—O11^{12}	2.5217 (3)	2.5235 (3)	2.5215 (6)	2.5189 (7)
O12—Na1	2.4015 (3)	2.3877 (3)	2.3771 (6)	2.3709 (7)
Na2—O12^{13}	2.5168 (3)	2.5114 (3)	2.4973 (6)	2.4916 (7)
O21—Na1^{11}	2.4321 (8)	2.4581 (18)		
Na2—O21^{12}	2.5264 (8)	2.5102 (18)		
O22—Na1	2.4014 (9)	2.4011 (18)		
Na2—O22^{13}	2.5133 (8)	2.4942 (18)		
O31—Na1	2.4464 (6)	2.4775 (5)	2.4871 (10)	2.4825 (8)
Na1—O31^{14}	2.6800 (6)	2.6457 (5)	2.6440 (10)	2.6422 (9)
O41—Na1	2.4698 (6)	2.4588 (6)	2.470 (3)	2.472 (5)
Na1—O41^{12}	2.5038 (6)	2.5306 (6)	2.483 (3)	2.441 (5)
Na1—O51^{15}	2.7391 (14)	2.709 (2)		
O51—Na1^{11}	2.3642 (13)	2.319 (2)		

Symmetry transformations used to generate equivalent atoms in *Cmca*: (7) $-x+\frac{1}{2}, y, -z+\frac{1}{2}$; (8) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (9) $-x, -y+\frac{1}{2}, z+\frac{1}{2}$; (10) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$. Symmetry transformations used to generate equivalent atoms in *Pbca*: (11) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (12) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (13) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (14) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (15) $-x, -y, -z$.

As there are no direct interactions between neighbouring hydrogen peroxide molecules, the development of asymmetry throughout the crystal must also involve the carbonate and sodium ions, which bridge adjacent hydrogen peroxide molecules, as shown in Fig. 8 for the 100 K structure. At 293 and 250 K, the disordered hydrogen peroxide molecules have a mirror-symmetric distribution with respect to the carbonate plane; however, as the temperature drops, small but significant distortions of the sodium carbonate sheets accompany ordering of the hydrogen peroxide molecules. These distortions take the form of a carbonate tilt (Fig. 9) and correlated distortions of the sodium columns (Figs. 10 and 11). Thus, on cooling, a clear preference emerges for particular hydrogen peroxide orientations from what were initially energetically equivalent sites.

3.3. Conformations and dimensions

The carbonate geometries presented in Table 4 show excellent agreement with published results, deviating only

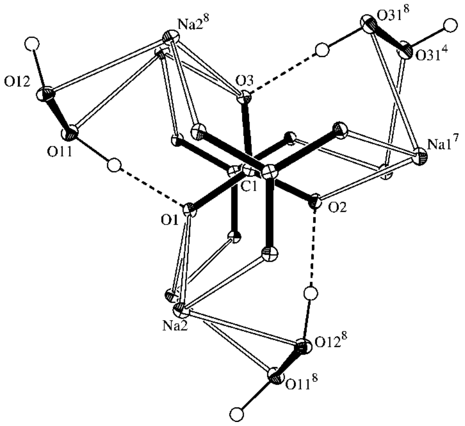


Figure 8
Carbonate environment at 100 K. The minor H_2O_2 site, O41, has been omitted for clarity. [Symmetry codes: (4) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$, (7) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (8) $x, \frac{1}{2}-y, z-\frac{1}{2}$.]

slightly from idealized D_{3h} geometry. In each case, atom O3 has been pushed away from atom O2 towards atom O1 by approximately 0.7°. This angular distortion does not have strong temperature dependence, in contrast to the O—C bond lengths, which vary as shown in Fig. 12.

Surprisingly, C1—O3 is consistently the shortest carbonate bond despite coordination and hydrogen bonds to atom O3 being no longer than those to atoms O1 and O2. The main difference between atom O3 and the other carbonate O atoms is that it hydrogen bonds exclusively to site II hydrogen peroxide, whereas the others interact only with site I.

No hydrogen peroxide atoms from site I coincide with the carbonate plane; however, atom O41 is located in this plane, and it is thus possible that the above angular distortion results from repulsion between atom O41 and the lone pairs on atom O3. This interaction would also discourage negative charge build up on atom O3 and hence explain the shorter C—O bond. This view is further supported by a peaking of the difference between C1—O3 and the other C—O bond lengths at around 250 K, when the peroxide oxygen population coincident with the carbonate plane is at a maximum. Technically, O41 population is high at 250, 240 and 223 K, but actual peroxo-oxygen population in the carbonate plane is reduced at 240 and 223 K because site O41 gradually drifts away from this plane when the space group changes at 240 K. This behaviour suggests that the above clash may indeed be the trigger for space-group change.

No temperature dependence could be detected in the hydrogen peroxide O—O bond length, but temperature dependence may have been masked by high thermal motion/disorder in both site I and site II. Despite the disorder, the O—O bond lengths fall in a remarkably narrow range, site I O—O bond lengths ranging from 1.474 (1) to 1.497 (2) Å (mean 1.482 Å) and site II bonds ranging from 1.456 (4) to

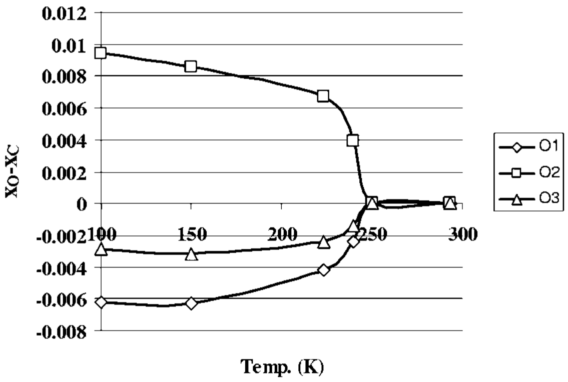
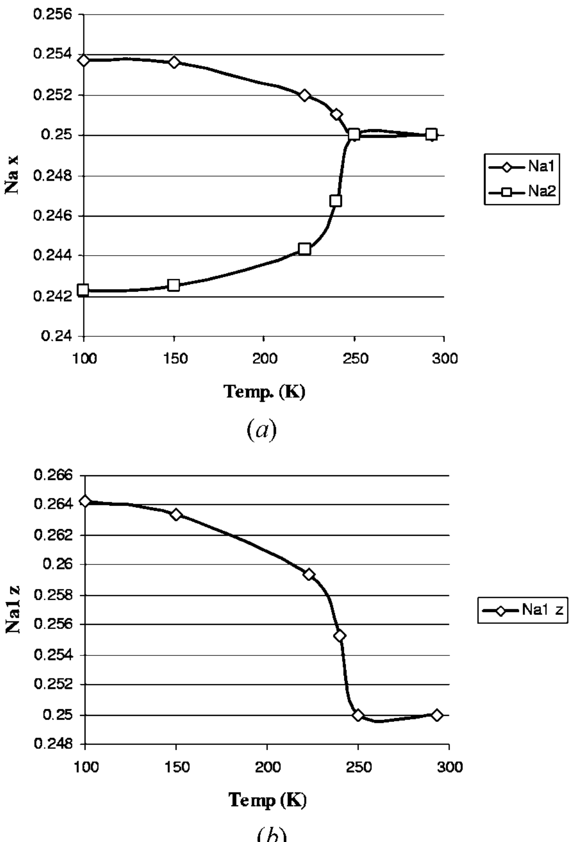


Figure 9
Effect of temperature on the carbonate tilt as measured by the three $x_{\rm oxygen}$–$x_{\rm carbon}$ distances.



(*a*)

(*b*)

Figure 10
The most significant changes in sodium positions on cooling: (*a*) $x_{\rm Na1}$ and $x_{\rm Na2}$; (*b*) $z_{\rm Na1}$.

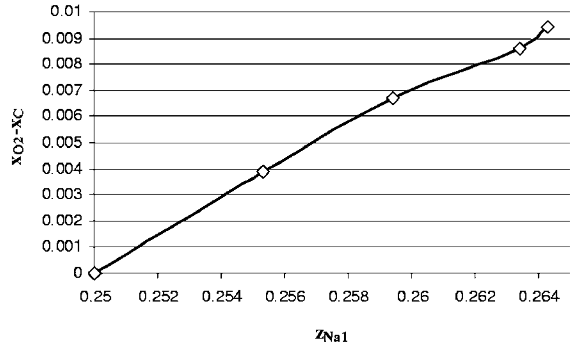


Figure 11
Correlation of the carbonate tilt ($x_{\rm O2}$–$x_{\rm C}$) with the Na1 z shift ($z_{\rm Na1}$).

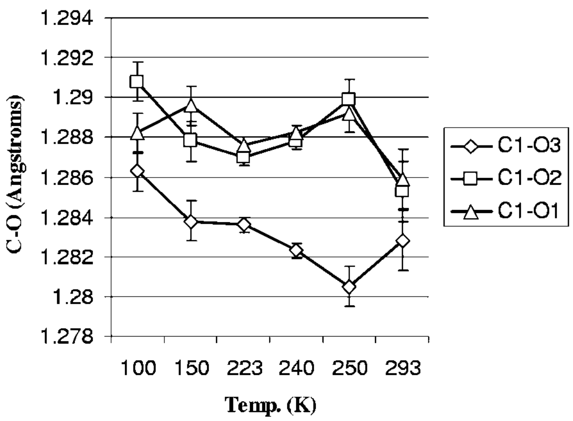


Figure 12
Variation of carbonate bond lengths (Å) with temperature (K).

Table 4
Carbonate and hydrogen peroxide geometry (Å, °) at various temperatures.

	293 K	250 K	240 K	223 K	150 K	100 K
Carbonate						
C1—O3	1.2828 (15)	1.2805 (10)	1.2823 (4)	1.2836 (4)	1.2838 (10)	1.2863 (10)
C1—O2	1.2853 (16)	1.2899 (11)	1.2878 (4)	1.2870 (4)	1.2878 (10)	1.2908 (11)
C1—O1	1.2859 (16)	1.2892 (11)	1.2882 (4)	1.2876 (4)	1.2896 (10)	1.2882 (10)
O3—C1—O2	120.80 (12)	120.82 (8)	120.71 (3)	120.72 (3)	120.76 (8)	120.72 (8)
O3—C1—O1	119.23 (12)	119.44 (8)	119.37 (3)	119.29 (3)	119.34 (8)	119.42 (8)
O2—C1—O1	119.96 (12)	119.74 (8)	119.92 (3)	119.99 (3)	119.90 (8)	119.87 (7)
Hydrogen peroxide						
O11—O12	1.4771 (18)	1.4814 (14)	1.4820 (5)	1.4804 (4)	1.4785 (8)	1.4823 (8)
O11—H11	0.962 (18)	0.954 (17)	0.928 (5)	0.931 (5)	1.012 (12)	1.035 (12)
O12—H12	1.002 (19)	0.953 (14)	0.985 (5)	0.905 (4)	0.970 (12)	0.966 (13)
O21—O22			1.4741 (12)	1.497 (2)		
O21—H21			0.983 (5)	0.905 (5)		
O22—H22			0.939 (5)	0.929 (5)		
O31—O31^{16}	1.492 (4)	1.490 (4)	1.4775 (12)	1.4807 (10)	1.4773 (17)	1.4808 (15)
O31—H31	1.031 (19)	0.969 (16)	0.925 (6)	1.001 (3)	0.961 (12)	0.949 (12)
O41—O41^{16}	1.475 (6)	1.456 (4)	1.4805 (11)	1.4792 (11)	1.480 (5)	1.498 (10)
O41—H31	1.088 (19)	1.021 (16)	0.949 (6)	0.993 (3)	0.954 (13)	0.990 (13)
O41—H51			1.133 (12)	0.995 (4)		
O51—O51^{16}			1.482 (3)	1.478 (3)		
O51—H51			1.042 (12)	0.997 (4)		
O12—O11—H11	101.7 (13)	102.9 (13)	103.5 (3)	99.7 (3)	98.6 (6)	98.8 (6)
O11—O12—H12	104.4 (10)	105.1 (9)	103.0 (3)	100.5 (3)	98.8 (6)	100.4 (6)
O22—O21—H21			103.9 (3)	98.0 (3)		
O21—O22—H22			102.5 (3)	100.6 (3)		
O41^{16}—O41—H31	97.5 (10)	96.7 (8)	98.2 (4)	94.4 (2)	95.0 (8)	90.7 (8)
O41^{16}—O41—H51			98.2 (6)	103.9 (5)		
O51^{16}—O51—H51			100.8 (6)	103.8 (3)		
O31^{16}—O31—H31	101.9 (10)	100.1 (10)	100.4 (4)	93.7 (2)	94.5 (6)	94.5 (6)
H11—O11—O12—H12	−150.1 (13)	−147.4 (13)	146.6 (3)	142.7 (3)	143.7 (6)	143.5 (6)
H21—O21—O22—H22			−146.6 (3)	−144.2 (3)		
H31—O31—O31^{16}—H31^{16}	180	180	180	180	180	180
H31—O41—O41^{16}—H31^{16}	180	180	180	180	180	180
H51—O51—O51^{16}—H51^{16}			180	180		

Symmetry transformations used to generate equivalent atoms in *Cmca* and *Pbca*: (16) −*x*, −*y*, −*z*.

1.498 (10) Å (mean 1.481 Å); these values can be compared with the range 1.439 (15)–1.509 (7) Å for the alkali metal oxalate monoperhydrates [$M_2C_2O_2$]·H_2O_2 (M = Li, Na, K and Rb; Pedersen & Pedersen, 1964; Pedersen, 1969; Adams *et al.*, 1980*a*,*b*; Pedersen & Kvick, 1989, 1990), which, like sodium percarbonate, contain H_2O_2 that participates in two hydrogen and four coordination bonds.

Site II facilitates 180° torsion angles at all temperatures and all levels of disorder. Site I torsion values, however, show a slight temperature dependence, with the room-temperature angle of −150 (1) closing to 143 (1)° at lower temperatures. All values are within the range established for the oxalate perhydrates [180–100 (1)°] and avoid the high-energy *cis* conformation (Hunt *et al.*, 1965).

The O—H bonds in sodium percarbonate fall in the range 0.905 (4)–1.088 (19) Å, which makes them slightly longer than the analogous bonds in the oxalate perhydrates [0.83 (10)–1.0117 (5) Å].[2] In addition, at 90.7 (8)–105.1 (9)°, the O—O—H angles show reasonable agreement with the oxalate values of 97 (3)−104 (5)° so that, overall, the hydrogen peroxide geometry, despite the disorder, is chemically reasonable at all temperatures.

4. Conclusions

Although the current study clearly establishes that sodium percarbonate has *Cmca* symmetry at room temperature and that this transforms to *Pbca* below 250 K, the question remains whether the original room-temperature studies in *Aba*2 pertain to different polymorphs or whether these structures could also be fitted with the current *Cmca* model.

It has been estimated that 3% of all structures have not been published in the optimal space group (Baur & Tillmanns, 1986).

Site I has pseudo-mirror symmetry in the Carrondo *et al.* (1977; CGJS) structure and is almost identical to the arrangement about the crystallographic mirror plane in the current room-temperature structure. Although site I is not disordered in the Adams & Pritchard (1977; AP) structure, several factors indicate that this result should be treated with caution. In addition to having a high *R*-factor of 0.111, this

---

[2] Determined using neutrons.

Table 5
Some details of the refinement of the current *Cmca* model using F_o data from the published AP and CGJS crystal structures.

Refinement	AP (1977)	AP data, *Cmca* model	CGJS (1977)	CGJS data, *Aba*2 model	CGJS data, *Cmca* model
Space group	*Aba*2	*Cmca*	*Aba*2	*Aba*2	*Cmca*
No. of reflections	279	272	486	486	486
No. of restraints	0	18	0	7	4
No. of parameters	40	79	108	110	79
*wR*2	–	0.1586	–	0.0858	0.0865
*R*1 or *R*	0.114	0.0638	0.029	0.0317	0.0377
Site I O—O (Å)	1.51 (6)	1.494 (6)	1.42 (2), 1.52 (2)	1.447 (12), 1.510 (12)	1.471 (3)
Site II O—O (Å)	1.49 (7)	1.441 (11), 1.495 (16)	1.35 (3)	1.368 (8)	1.459 (9), 1.508 (8)

determination was carried out using film methods, which severely limited the resolution perpendicular to the mirror plane (only levels 0–4 were collected about the 6.7 Å axis). This limited resolution was compounded by miss-modelling of site II with an asymmetric distribution of hydrogen peroxide around the (pseudo-) mirror plane (see below). The original AP F_o data was therefore used to re-refine the current 293 K *Cmca* model. The limited data made it necessary to apply ISOR restraints to one site II O atom and DFIX restrictions to H-atom positions, but the resulting structure shows considerable improvement over the original refinement in terms of residuals and hydrogen peroxide O—O bond lengths (Table 5), thus indicating strongly that the AP structure is identical to the current 293 K structure and should be re-assigned to *Cmca*.

Site II has twofold rotation symmetry in *Aba*2 and looks the same in both the AP and the CGJS refinement. Furthermore, both research groups considered this site to be problematic and, in the AP case, the possibility of partial water substitution was considered. In the higher-accuracy CGJS study, the authors commented that it was the displacement of the disordered hydrogen peroxide away from the *Cmca* mirror plane in this site that was the primary reason for using *Aba*2. However, comparison of the previous studies with the current work shows that the most likely explanation for the asymmetry is that, by modelling the electron density with two hydrogen peroxide orientations and not the three used in the current work, the CGJS and AP studies have based their O atoms on O31 and a combination of O41 and O31′ (Fig. 13). This model draws the centre of the combined atom site near to the mirror plane and hence leads to an asymmetric distribution relative to this plane, a view supported by the extremely small vibrational amplitude of the O atom nearest the plane in the AP structure [0.005 (6) Å^2] and by the narrow elongated vibrational ellipsoid of this atom in the CGJS refinement (0.002, 0.013 and 0.168 Å^2)

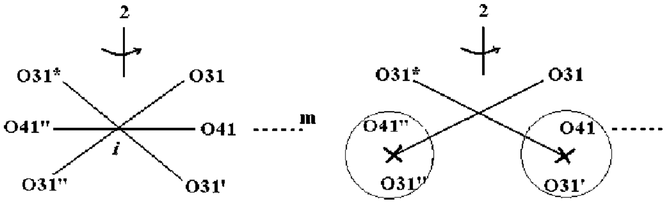


Figure 13
Comparison of room-temperature site II model used in current study with the Carrondo *et al.* (1977) and Adams & Pritchard (1977) models.

This site has already been remodelled successfully for the AP structure and, despite the excellent residuals achieved in the CGJS refinement, the current *Cmca* model was re-refined using the CGJS structure factors. Details of the refinement are presented in Table 5, which also includes, for comparison, the results from refining the CGJS model using *SHELXL*97 (Sheldrick, 1997).

The *Cmca* refinement has a slightly elevated *R*1 value compared with the refinement in *Aba*2, but this result would be expected, as 31 fewer parameters are being refined. It is highly significant that the O—O bond lengths in site II have now increased from 1.368 (8) Å to chemically sensible values of 1.459 (9) and 1.508 (8) Å.

Both the AP and the CGJS studies should therefore be re-assigned to *Cmca*, thus making them identical to the current 293 K structure.

It has to be concluded that sodium percarbonate, despite its disorder, does not appear to be predisposed to forming polymorphs, certainly not under the conditions used in this and previous crystallographic studies.

It should also be noted that, despite hydrogen peroxide's ability to flip between energetically equivalent sites in the zigzag channels between the sodium carbonate columns, the columns would not form in the first place without the templating influence of hydrogen peroxide. These columns are a unique feature of the sodium percarbonate structure and are not found in any of the sodium carbonate polymorphs, hydrates or hydrogen carbonates.

We would like to thank the EPSRC for purchasing the Nonius KappaCCD diffractometer.

References

Adams, J. M. & Pritchard, R. G. (1977). *Acta Cryst.* B**33**, 3650–3653.
Adams, J. M., Ramdas, V. & Hewat, A. W. (1980*a*). *Acta Cryst.* B**36**, 570–574.
Adams, J. M., Ramdas, V. & Hewat, A. W. (1980*b*). *Acta Cryst.* B**36**, 1096–1098.
Baur, W. H. & Tillmanns, E. (1986). *Acta Cryst.* B**42**, 95–111.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Carrondo, M. A. A. F. de C. T., Griffith, W. P., Jones, D. P. & Skapski, A. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2323–2331.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hunt, R. H., Leacock, A., Peters, C. W. & Hecht, K. T. (1965). *J. Chem. Phys.* **42**, 1931–1946.
McKillop, A. & Sanderson, W. R. (2000). *J. Chem. Soc. Perkin Trans.* pp. 471–476.

Nonius (1997). *KappaCCD Server Software*, Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pedersen, B. F. (1969). *Acta Chem. Scand.* **23**, 1871–1877.

Pedersen, B. F. & Kvick, A. (1989). *Acta Cryst.* C**45**, 1724–1727.

Pedersen, B. F. & Kvick, A. (1990). *Acta Cryst.* C**46**, 21–23.

Pedersen, B. F. & Pedersen, B. (1964). *Acta Chem. Scand.* **18**, 1454–1468.

Pritchard, R. G. (1978). PhD thesis, University of Wales.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.