It is believed that this is the first case in which an accurate comparison of molecular dimensions can be made for each component in a complex with the same molecule in an uncomplexed state. This comparison shows that, even in this case where there is some specific interaction between the components, there is very little change in molecular dimensions on forming the complex. It is fairly certain, therefore, that interactions of a more general nature, which bind the components in weaker π–π complexes, will have negligible effects on the dimensions of the molecules involved.

We are indebted to the Director of the Manchester University Department of Computer Science for allowing computing facilities on the ATLAS computer, to the Director of the Oxford University Computing Laboratory for allowing computing facilities on the MERCURY computer, and to Dr M. M. Harding, Dr R. D. Diamand and Dr J. S. Rollett for the use of their computer programs. We are also grateful to Dr J. S. Rollett for assistance with the MERCURY computing, and to the Science Research Council for a maintenance grant (to R.M.W.).

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Position and Thermal Parameters of Oxygen Atoms in Sodium Nitrate*

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(*Received* 4 *November* 1966)

The thermal and position parameters of the oxygen atoms in sodium nitrate, at room temperature and at intervals up to 200°C, have been determined. Intensities of reflections to which only the oxygen atoms contribute were measured carefully by film and counter techniques. The N–O bond length, uncorrected for thermal effects, is 1·241 (σ=0·002) Å at 25°C and appears to decrease progressively as the temperature is raised. This effect is attributed to increasing libration of the nitrate groups about threefold axes in the crystal.

Introduction

Sodium nitrate crystallizes in the rhombohedral subgroup of the trigonal system in space group $R\bar{3}c$, with two formula units of $NaNO_3$ per unit cell. The nitrogen and sodium atoms lie on threefold axes, the former at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, and the latter at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$. The three oxygen atoms of each nitrate group are arranged symmetrically about the nitrogen atoms in planes normal to the threefold axes; each oxygen atom lies on a twofold axis. Successive nitrate groups are rotated 60° relative to one another as shown in Fig. 1.

The atomic arrangement in crystalline $NaNO_3$ differs from a completely body centered one only by virtue of rotations of successive nitrate groups by 60° about the body diagonal of the unit cell. Only the oxygen atoms therefore contribute to reflections of the type $h+k+l=2n+1$.

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* This work was supported by the Office of Aerospace Research of the U.S. Air Force and, in part, by the U.S. Atomic Energy Commission.

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We will discuss the structure in terms of a triply primitive unit cell referred to hexagonal axes; in this cell the oxygen atoms are at $x,0,\frac{1}{4}$; $0,x,\frac{1}{4}$; $\bar{x},\bar{x},\frac{1}{4}$; $\bar{x},0,\frac{3}{4}$; $0,\bar{x},\frac{3}{4}$; $x,x,\frac{3}{4}$ (*International Tables for X-ray Crystallography*, 1952).

Sodium nitrate is isostructural with calcium carbonate (calcite). The x coordinate of an oxygen atom (*i.e.* at $x,0,\frac{1}{4}$) is the only variable position parameter. That coordinate determines the length of the C–O bond in calcite and the N–O bond in sodium nitrate.

The crystal structure of sodium nitrate, like that of calcite, has been studied repeatedly over the past forty years but, as is clear from Table 1, serious discrepancies still exist among the N–O bond lengths reported by different investigators.

We have tried to determine this bond length with high precision and have investigated the variation of the position and thermal parameters of the oxygen atoms with increasing temperature. The treatment of the temperature factors is simplified somewhat by the fact that the oxygen atoms lie on twofold axes. This fixes the orientation of one of the principal axes of the thermal vibration ellipsoid of the oxygen atoms and there remain only four independent thermal parameters, since $b_{12}=\frac{1}{2}b_{22}$ and $b_{13}=\frac{1}{2}b_{23}$ for the oxygen atom at $x,0,\frac{1}{4}$, where $b_{ij}=\sum_k q_k g_{ki} g_{kj} p_i^* p_j^*$; q_k is the thermal vibration parameter in direction k; g_{ki},g_{kj} are the directional cosines, and p_i^*,p_j^* are the reciprocal lattice parameters.

Experimental

The lattice constants of sodium nitrate were computed from measurements made on powdered specimens, using a counter diffractometer. Our values of $a=5{\cdot}071 \pm 0{\cdot}002$ and $c=16{\cdot}825 \pm 0{\cdot}003$ Å at 25°C agree well with those reported by Swanson & Fuyat (1953) ($a=5{\cdot}070$, $c=16{\cdot}829$), and others.

Rhombohedral indices of the type $h+k+l=2n+1$ transform in the hexagonal system to h',k',l', with $l'=2n+1$. Since only the oxygen atoms contribute to these reflections, they are particularly sensitive to variations of the thermal and position parameters of these atoms. Our analysis has been based entirely on measurements of reflections of this type.

Six crystals were ground to spherical shape and used for X-ray diffraction measurements. Their diameters ranged from 0·1 to 0·4 mm. Room temperature intensity data were obtained using Cu $K\alpha$ and Mo $K\alpha$ radiations with a Weissenberg film camera, a Weissenberg camera base adapted for counter measurements, and a General Electric Crystal Orienter.

Only data obtained with Cu $K\alpha$ radiation were corrected for absorption effects; all measurements were corrected for Lorentz and polarization effects, placed on a common scale, and compared. The average deviation of structure factors derived from film measurements (after correction for $K\alpha_1,K\alpha_2$ separation) from the mean of counter and film results was 2·5%; the corresponding deviation of counter data was 1·5%.

Altogether, 86 independent 'oxygen' reflections were used in the room temperature analysis (Table 3). Intensity measurements were also made at 100, 150 and 200°C, using Mo $K\alpha$ radiation and a counter detector (Table 4). The lattice parameters were redetermined at each temperature (Table 2). For measurements above room temperature the spherical crystals were encased in thin-walled glass capillary tubes to prevent evaporation. Temperatures were varied by blowing heated air across the crystals. Temperature measurements were made with thermocouples placed in the air stream ad-

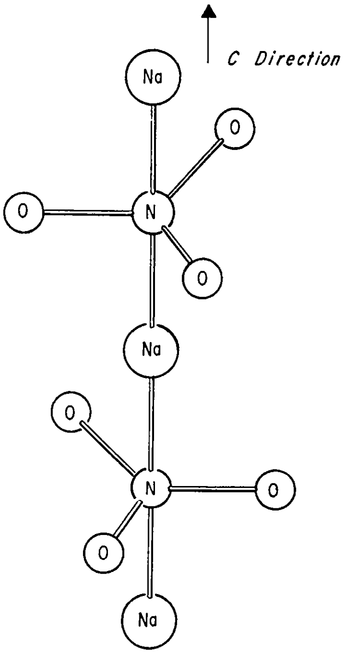

Fig. 1. Arrangement of atoms in $NaNO_3$ along a threefold axis.

Table 1. *Oxygen coordinates and* N–O *bond lengths reported for* $NaNO_3$

	x/a	N–O bond
Wyckoff (1920)	0·24 to 0·26	1·2 to 1·3 Å
Elliott (1937)	0·2394 ± 0·006	1·214 ± 0·03
Tahvonen (1947)	0·242 ± 0·003	1·23 ± 0·02
Sass, Vidale & Donohue (1957)	0·2402 ($\sigma=0{\cdot}0008$)	1·218 ($\sigma=0{\cdot}004$)
Inkinen (1960)	0·2411 ± 0·002	1·222 ± 0·01
Kurki-Suonio (1962)	0·2433 ($\sigma=0{\cdot}0006$)	1·234 ($\sigma=0{\cdot}003$)
This work (1966)	0·2448 ($\sigma=0{\cdot}0003$)	1·241 ($\sigma=0{\cdot}002$)

Table 2. *Lattice constants* (Å) *of* $NaNO_3$ *at various temperatures*

T	Saini & Mercier* a	Saini & Mercier* c	Kantola & Vilhonen† a	Kantola & Vilhonen† c	This work a	This work c
25 °C	5·070	16·818	5·071	16·878	5·071 ± 0·002	16·825 ± 0·003
100	5·075	16·965	5·076	16·97	5·074 ± 0·002	16·976 ± 0·004
150	5·079	17·084	5·079	17·09	5·075 ± 0·003	17·070 ± 0·004
200	5·084	17·221	5·082	17·24	5·079 ± 0·003	17·164 ± 0·005

* Saini & Mercier (1934).
† Kantola & Vilhonen (1960).

Table 3. $|F_{obs}|$ (Mo $K\alpha$ *and* Cu $K\alpha$) *and* F_c *at* 25 °C

HKL	F_o	F_c	$\Delta F/\sigma$	HKL	F_o	F_c	$\Delta F/\sigma$	HKL	F_o	F_c	$\Delta F/\sigma$
113	9.87	9.80	0.36	$15\bar{7}$	1.08	-1.08	0.02	253	1.422	1.34	0.32
119	5.75	-5.54	0.96	1,5,11	1.04	0.93	0.49	$25\bar{9}$	1.37	1.31	0.24
1,1,15	2.41	2.45	0.14	$1,5,\bar{13}$	0.80	0.74	0.34	259	1.00	0.95	0.28
1,1,21	1.09	-1.05	0.17	1,5,17	0.66	-0.62	0.28	$2,5,\bar{15}$	0.70	0.95	1.58
1,1,27	0.63	0.40	1.86	$1,5,\bar{19}$	0.48	-0.44	0.24	2,5,15	0.57	0.55	0.12
$12\bar{1}$	7.76	7.76	0.01	$1,5,\bar{25}$	0.33	0.23	0.82	$2,5,\bar{21}$	0.47	0.57	0.75
125	6.59	-6.69	0.46	161	1.16	-1.13	0.14	2,5,21	0.36	-0.27	0.73
$12\bar{7}$	5.32	-5.30	0.08	$16\bar{5}$	1.07	1.05	0.09	271	0.59	0.58	0.06
1,2,11	3.77	3.82	0.19	167	1.01	0.99	0.09	$27\bar{5}$	0.64	-0.64	0.01
$1,2,\bar{13}$	2.61	2.59	0.07	$1,6,\bar{11}$	0.77	-0.82	0.23	$2,7,\bar{11}$	0.54	0.57	0.15
1,2,17	1.75	-1.84	0.33	1,6,13	0.65	-0.73	0.40	333	1.81	-1.96	0.79
$1,2,\bar{19}$	1.10	-1.16	0.26	$1,6,\bar{17}$	0.49	0.52	0.20	339	1.35	1.51	0.85
1,2,23	0.87	0.87	0.48	1,6,19	0.45	0.45	0.05	3,3,15	0.87	-0.98	0.65
$1,2,\bar{25}$	0.54	0.49	0.69	223	0.69	0.64	0.37	3,3,21	0.45	0.55	0.74
131	0.17	-0.16	0.17	229	0.58	-0.42	1.52	3,3,27	0.34	-0.27	0.74
$13\bar{5}$	0.35	-0.33	0.26	2,2,15	0.11	0.22	3.84	$34\bar{1}$	0.47	0.38	0.52
137	0.50	0.55	0.51	$23\bar{1}$	3.13	-3.33	0.96	345	0.47	-0.22	1.31
$1,3,\bar{11}$	0.49	0.47	0.12	235	2.54	2.69	0.66	$34\bar{7}$	0.47	-0.40	0.38
1,3,13	0.49	-0.55	0.75	$23\bar{7}$	2.73	2.86	0.58	$3,4,\bar{13}$	0.41	0.32	0.75
$1,3,\bar{17}$	0.41	-0.38	0.28	2,3,11	1.55	-1.59	0.21	351	0.37	-0.22	1.26
1,3,19	0.56	0.41	1.27	$2,3,\bar{13}$	1.80	-1.87	0.32	$35\bar{5}$	0.43	0.37	0.54
$14\bar{3}$	0.78	0.83	0.56	2,3,17	0.84	0.80	0.21	$3,5,\bar{11}$	0.37	-0.40	0.27
143	0.54	-0.49	0.44	$2,3,\bar{19}$	1.00	1.08	0.39	$3,5,\bar{17}$	0.30	0.32	0.27
$14\bar{9}$	0.79	-0.82	0.36	2,3,23	0.46	-0.36	0.79	363	0.56	0.52	0.21
149	0.06	0.09	0.90	$2,3,\bar{25}$	0.43	-0.54	0.91	363	0.60	-0.55	0.17
$1,4,\bar{15}$	0.55	0.60	0.28	241	0.40	0.31	1.30	$36\bar{9}$	0.43	-0.41	0.13
$1,4,\bar{21}$	0.47	-0.36	1.04	$24\bar{5}$	0.45	-0.32	2.00	369	0.53	0.49	0.30
151	1.33	1.27	0.28	247	0.50	-0.22	4.54	3,6,15	0.39	-0.36	0.28
155	1.27	-1.21	0.27	$25\bar{3}$	1.68	1.50	0.71				

Table 4. $|F_{obs}|$ (Mo $K\alpha$) *and* F_c *at various temperatures*

HKL	25°C		100°C		150°C		200°C	
	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c
113	9.72	9.87	9.06	9.28	7.68	7.74	5.77	5.86
119	5.85	-5.59	5.27	-4.95	4.20	-4.30	2.87	-2.86
1,1,15	2.57	2.49	1.99	1.94	1.42	1.42	0.91	0.90
1,1,21	1.06	-1.08	0.69	-0.69	0.44	-0.39		
$12\bar{1}$	7.75	7.77	7.30	7.18	6.36	6.64	4.63	4.66
125	6.80	-6.69	6.15	-6.14	5.39	-5.67	3.80	-3.79
$12\bar{7}$	5.45	-5.33	4.69	-4.68	3.87	-3.99	2.70	-2.81
1,2,11	3.86	3.83	3.19	3.28	2.57	2.78	1.64	1.74
$1,2,\bar{13}$	2.74	2.62	2.09	2.05	1.53	1.48	1.00	0.97
1,2,17	1.90	-1.85	1.34	-1.38	0.87	-0.98	0.48	-0.56
$1,2,\bar{19}$	1.17	-1.19	0.71	-0.78	0.42	-0.43	0.23	-0.24
1,2,23	0.77	0.88	0.44	0.54				
143	0.48	-0.47	0.44	-0.48	0.37	-0.43		
$15\bar{1}$	1.48	1.34	0.80	0.81	0.46	0.50		
155	1.33	-1.28	0.80	-0.76	0.48	-0.48		
$15\bar{7}$	1.13	-1.14	0.61	-0.68	0.43	-0.43		
1,5,11	1.03	0.97	0.56	0.56	0.40	0.36		
$1,5,\bar{13}$	0.80	0.78	0.44	0.44	0.33	0.28		
1,5,17	0.75	-0.64	0.48	-0.34	0.38	-0.22		
161	1.12	-1.15	0.59	-0.70	0.40	-0.49		
$16\bar{5}$	1.05	1.07	0.60	0.66	0.53	0.49		
167	1.02	1.02	0.58	0.58	0.42	0.34		
$1,6,\bar{11}$	0.79	-0.82	0.47	-0.47	0.36	-0.33		
1,6,13	0.70	-0.75	0.38	-0.39	0.28	-0.22		
$1,6,\bar{17}$	0.51	0.52	0.31	0.29	0.23	0.17		
223	0.65	0.57	0.74	0.67	0.72	0.67	0.50	0.65
$23\bar{1}$	3.18	-3.37	2.63	-2.72	2.27	-2.28	1.39	-1.43
235	2.69	2.74	2.08	2.09	1.59	1.59	0.83	0.95
$23\bar{7}$	2.84	2.88	2.33	2.31	1.89	1.95	1.11	1.18
2,3,11	1.59	-1.64	1.11	-1.11	0.75	-0.69	0.42	-0.35
$2,3,\bar{13}$	1.91	-1.88	1.45	-1.40	1.11	-1.09	0.66	-0.60
2,3,17	0.89	0.85	0.55	0.47	0.33	0.21	0.15	0.08
$2,3,\bar{19}$	1.10	1.09	0.72	0.70	0.48	0.46	0.25	0.22
253	1.44	1.38	0.96	0.87	0.69	0.57		
259	1.00	-0.98	0.62	-0.56	0.42	-0.31		
2,5,15	0.60	0.58	0.38	0.28				
333	1.88	-1.99	1.35	-1.42	0.96	-1.02	0.57	-0.34
339	1.46	1.53	1.02	1.05	0.70	0.75	0.37	0.22
3,3,15	1.02	-0.99	0.62	-0.62	0.40	-0.42	0.20	-0.11
363	0.67	-0.58	0.34	-0.28				
369	0.59	0.51	0.28	0.23				

jacent to the crystals and are estimated to be accurate to better than ±4°C.

The scale, position and temperature parameters were refined by least-squares methods, using the Brookhaven National Laboratory version of the Busing & Levy (1959) least-squares program. Weights applied to the structure factors for use in the refinement procedure were based on standard deviations estimated by a procedure similar to that described by Evans (1961), *i.e.*

$$\sigma=\tfrac{1}{2}\left[C\frac{A+B}{A-B}\right]^{\frac{1}{2}}$$

where

A is the total number of counts recorded for a reflection,

B is the corresponding number of background counts and

C represents geometrical factors applied to the measured intensities, such that $F^2=C(A-B)$.

The weighting scheme appeared to be reasonable, since $\{\Sigma_{hkl}w(\Delta F)^2/m-n\}^{\frac{1}{2}}$ equalled 0·947 at the conclusion of the refinement of the room temperature data; where $\Delta F=|F_{obs}|-|F_{cal}|$, m is the number of independent reflections and n is the number of variable parameters. For an ideal weighting scheme this sum should equal unity (see *e.g.* Hamilton, 1964).

Discussion

The results of the least-squares refinement of the 25 °C data (averaged film and counter measurements taken with Cu $K\alpha$ and Mo $K\alpha$ radiation) are shown in Table 5. The N–O bond length is substantially greater than those previously reported for sodium nitrate (Table 1). The mean-square-amplitude tensor U_{ij} is defined as $U_{ij}=b_{ij}/2\pi^2p_j^*p_i^*$. The root mean square amplitude of thermal motion for the oxygen atom is smallest (0·135 Å) along the N–O bond, and reaches a maximum (0·226 Å) in the plane normal to the bond direction at an angle of 48° to the c axis (measured from the positive **c** direction towards the negative **b** direction). The amplitude along the third principal axis is 0·156 Å.

Table 5. *Position and thermal parameters of oxygen atoms in sodium nitrate* (25 °C)

x	0·2488	(σ = 0·0003)
N–O	1·241 Å	(σ = 0·002)
U_{11}	0·2301 Å²	(σ = 0·0009)
U_{22}	0·3833	(σ = 0·0015)
U_{33}	0·0359	(σ = 0·0010)
U_{23}	−0·0134	(σ = 0·0067)

A comparison of Table 3 and the first column of Table 4 reveals that many weak room temperature reflections which could not be detected when Mo $K\alpha$ was used were detected with Cu $K\alpha$ radiation. At elevated temperatures, however, these weak reflections were not observed with either radiation and measurements at these temperatures were therefore made with Mo *Kα* only. The results of the least-squares analyses of these measurements are shown in Table 6. A comparison of the room temperature results listed in Tables 5 and 6 reveals a difference of 0·0008 in the *x* parameter. Although a difference of this magnitude is barely significant, it may indicate a small systematic error in the Mo *Kα* data. Consequently, it was felt that absolute values of 25 °C parameters were established most precisely with the combined Mo *Kα*–Cu *Kα* room temperature data, but that changes in these values could be reliably computed from the Mo *Kα* measurements at different temperatures.

The angle between the long axis of the thermal ellipsoid and the *c* axis of the unit cell does not appear to change significantly with increasing temperature, nor does the r.m.s. amplitude of thermal motion along the bond. Along the other two principal directions the amplitudes of thermal motion increase by a factor of about two between 25 °C and 200 °C, and this increase appears to be accelerating as 200 °C is approached. This is also clearly indicated by the variation of the r.m.s. radial amplitude $(r^2)^{\frac{1}{2}}$ with temperature (Table 6). The change in parameters and orientation of the thermal ellipsoid is shown in Fig. 3. The third axis of the ellipsoid, which is not shown, is parallel to **a**.

This increase in thermal motion is accompanied by increasing attenuation of the intensities of the 'oxygen' reflections. Forty-one such reflections could be detected and measured with Mo *Kα* radiation at 25° and 100 °C; the number dropped to 21 at 200 °C, of which all but six or seven were barely detectable. In view of this, efforts to make similar measurements above 200 °C were abandoned.

Effects of the thermal motion on atomic peak heights are illustrated in Fig. 2. Sass, Vidale & Donohue (1957) have shown that in calcite-type structures an electron density map computed from Fourier series, whose coefficients are structure factors of terms with odd *l* indices, is equivalent to a difference electron density map in which $\varrho(x,y,\frac{1}{4})$ is subtracted from $\varrho(x,y,\frac{3}{4})$.

The crystal symmetry fixes the orientation of one principal axis of the oxygen thermal ellipsoid. The inclination of the other principal axes relative to the crystal axes has an interesting effect on the relative magnitudes of the structure factors of selected pairs of reflections. Five such pairs are listed in Table 7. Reflections from both members of each pair could be identical because the F_c of each member of the pair have identical trigonometric terms, but as a result of the inclination of the long axis relative to **c**, the anisotropic temperature factors for members of each pair differ significantly leading to the effects displayed in Table 7.

Table 7. $|F_{\text{obs}}|$ *and* $|F_c|$: *Selected pairs of reflections*

HKL	F_o	F_c
143	0·54	0·49
$14\bar{3}$	0·78	0·83
149	0·06	0·09
$14\bar{9}$	0·79	0·82
253	1·42	1·34
$25\bar{3}$	1·68	1·50
259	1·00	0·95
$25\bar{9}$	1·37	1·31
2,5,15	0·57	0·55
$2,5,\overline{15}$	0·70	0·95
2,5,21	0·36	0·27
$2,5,\overline{21}$	0·47	0·57

Busing & Levy (1964) have described a procedure to correct bond lengths to account for the effects of thermal motion. If the oxygen atoms in $NaNO_3$ are assumed to 'ride' on the nitrogen atoms then:

$$R_{\text{corr.}} = R_o + \frac{1}{2R_o}\{(\mu'_O)^2 - (\mu'_N)^2\},$$

where $(\mu'_i)^2$ is the mean square displacement of atom *i* in the plane normal to the N–O bond. At 25 °C $(\mu'_O)^2$ is 0·0785 Å², and $(\mu'_N)^2$ (taken from Felty, 1963) is 0·0338 Å². The indicated correction is 0·017 Å; the 'corrected' bond length is 1·258 Å. Low temperature studies are needed to check the validity of the 'riding' hypothesis.

Table 6. *Position and thermal parameters of oxygen atoms in* $NaNO_3$ *as a function of temperature* (Mo *Kα data*)

	25 °C	100 °C	150 °C	200 °C
x	0·2456 ($\sigma=0·0003$)	0·2436 ($\sigma=0·0005$)	0·2426 ($\sigma=0·0008$)	0·2393 ($\sigma=0·0012$)
N–O (Å)	1·245 ($\sigma=0·002$)	1·236 ($\sigma=0·003$)	1·232 ($\sigma=0·004$)	1·215 ($\sigma=0·006$)
U_{11} (Å)	0·0220 ($\sigma=0·0005$)	0·0336 ($\sigma=0·0007$)	0·0415 ($\sigma=0·0013$)	0·0811 ($\sigma=0·0038$)
U_{22} (Å)	0·0370 ($\sigma=0·0010$)	0·0553 ($\sigma=0·0017$)	0·0710 ($\sigma=0·0033$)	0·2320 ($\sigma=0·0183$)
U_{33} (Å)	0·0394 ($\sigma=0·0007$)	0·0558 ($\sigma=0·0011$)	0·0767 ($\sigma=0·0020$)	0·105 ($\sigma=0·010$)
U_{23} (Å)	−0·0129 ($\sigma=0·0010$)	−0·0195 ($\sigma=0·0010$)	−0·0319 ($\sigma=0·0040$)	−0·0815 ($\sigma=0·016$)
R.m.s. amplitude along bond (Å)*	0·1305 ($\sigma=0·0031$)	0·1627 ($\sigma=0·0039$)	0·1774 ($\sigma=0·0062$)	0·1769 ($\sigma=0·0110$)
Next smallest (Å)*	0·1598 ($\sigma=0·0031$)	0·1898 ($\sigma=0·0040$)	0·2045 ($\sigma=0·0063$)	0·2220 ($\sigma=0·0097$)
Longest (Å)*	0·2328 ($\sigma=0·0040$)	0·2740 ($\sigma=0·0055$)	0·3256 ($\sigma=0·0094$)	0·5038 ($\sigma=0·0255$)
Angle of latter with **c**	42·9° ($\sigma=1·3°$)	44·6° ($\sigma=1·5°$)	42·4° ($\sigma=1·8°$)	45·8° ($\sigma=3·0°$)
R	0·029	0·040	0·075	0·054
$(r\ )^{\frac{1}{2}}$ (Å)†	0·3111 ($\sigma=0·0027$)	0·3708 ($\sigma=0·0025$)	0·4235 ($\sigma=0·0048$)	0·5783 ($\sigma=0·0184$)
Number of reflections	41	41	37	21

* r.m.s. amplitudes along principal axes.

† r.m.s. radial amplitude.

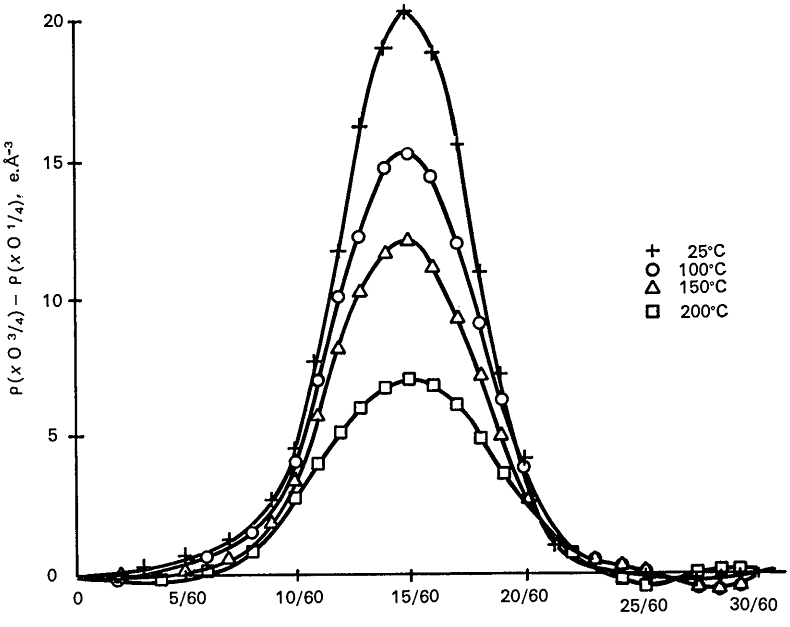

Fig. 2. Variation of electron density distribution along **a** as a function of temperature.

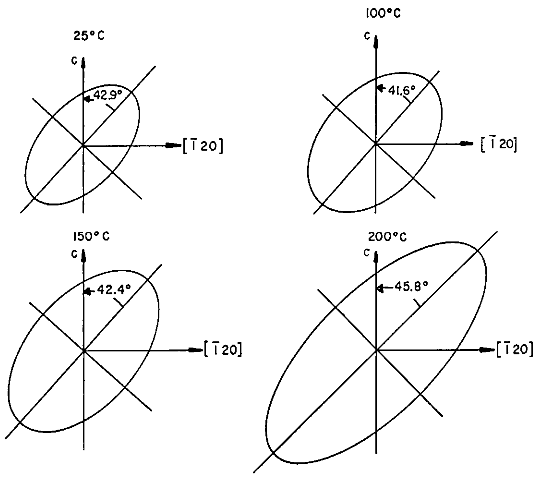

Fig. 3. Variation of the dimension and orientation of the thermal ellipsoid as a function of temperature viewed along **a**.

Values of the N–O bond length computed from data obtained at 100, 150 and 200°C are listed in Table 6. The striking decrease to 1·211 Å at 200°C is evidently caused by the increased thermal vibrations, or librations, of the oxygen atoms above room temperature. Unfortunately, the value of $(\mu'_N)^2$ at elevated temperatures is not known. It is, however, possible to estimate the approximate magnitude of the 'riding' corrections, if we assume that the motion of the nitrogen atom is isotropic and that the magnitude of this motion is the same as the motion of the oxygen atom along the N–O bond as is the case at 25°C. The indicated corrections are then 0·024, 0·032, and 0·100 Å at 100, 150, and 200°C, respectively, yielding 'corrected' bond lengths of 1·260, 1·264, and 1·315 Å. It should be noted that these bond lengths have been corrected upward, by an additional 0·004 Å, to account for the possible systematic error resulting from the use of Mo *Kα* data alone. It is interesting to note that at 200°C the thermal motion is so great that either our assumptions, Busing & Levy's riding hypothesis, the assumption of harmonic motions or all three no longer hold.

Recently, Inkinen (1960) published the results of careful counter measurements of reflection intensities from finely powdered $NaNO_3$ specimens. Filtered Cu *Kα* radiation was used and the data were placed on an absolute scale by direct comparison with intensities from a powdered $NaNO_3$–NaCl mixture. Many of the weak 'oxygen' reflections which were readily measured by single-crystal techniques were not observed by Inkinen. Only sixteen of the reflections measured were 'oxygen' reflections.

The agreement between Inkinen's measurements and ours is very satisfactory,

$$\frac{\sum\limits_{\substack{\text{observed}\\\text{reflections}}} \big|\,|F_o|_{\text{CHP}} - |F_o|_{\text{I}}\big|}{\sum\limits_{\substack{\text{observed}\\\text{reflections}}} |F_o|_{\text{CHP}}} = 0{\cdot}0686,$$

particularly when the differences in experimental techniques are considered. The comparison indicates that extinction did not seriously affect our measurements and lends support to our confidence in the physical validity of our calculated scale factor.

Table 8. *Comparison of the present results with those of Felty* (1963)

	Felty	This work
$d_{\mathrm{N-O}}$	1·245 (σ=0·004) Å (*l* odd reflections) 1·250 (σ=0·002) Å (all reflections)	1·241 (σ=0·002) Å (*l*-odd reflections)
R.m.s. amplitude (Å)		
1. along bond	0·156 (σ=0·008)	0·135 (σ=0·004)
2. long axis	0·221 (σ=0·006)	0·226 (σ=0·004)
3. third axis	0·153 (σ=0·006)	0·156 (σ=0·003)
Angle: long axis of thermal ellipsoid *vs* **c**	47° (σ=3°)	48° (σ=2°)

Inkinen found N–O to be 1·222 ± 0·01 Å. More recently Kurki-Suonio (1962) subjected Inkinen's data to a detailed refinement and reported N–O as 1·234 (σ=0·003 Å.)

Felty (1963) measured 266 independent $NaNO_3$ reflections, including 72 'oxygen' reflections, using Mo $K\alpha$ radiation and film methods. Our results are compared with his in Table 8. Agreement between the two sets, particularly with respect to the thermal parameters, is very good. Felty's analysis of the 'oxygen' reflections yielded an N–O bond length of 1·246 Å; our corresponding value is 1·241 Å. When all 266 reflections were included in the calculations he obtained N–O 1·250 Å.

Our results may be compared with corresponding results recently reported for calcite (Chessin, Hamilton & Post, 1965). Although the magnitudes of the thermal motions of the oxygen atoms in calcite are substantially smaller than corresponding values for sodium nitrate, the degree and the type of anisotropy is very similar in both cases. The largest amplitude of thermal motion occurs in the plane normal to the C–O bond in calcite and the N–O bond in sodium nitrate. The longest principal axis of the thermal ellipsoid is inclined 48° to the *c* axis in both calcite and sodium nitrate (full data) at 25°C.

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The Crystal Structure of Diosgenin Iodoacetate

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(*Received* 27 *July* 1966 *and in revised form* 31 *January* 1967)

The crystal structure of diosgenin iodoacetate, has been determined by the heavy-atom technique and has been refined by Fourier and least-squares analyses of the three-dimensional data. The stereochemistry of diosgenin iodoacetate has been confirmed; it may be formulated as 25ε-methyl-22β-spirost-5(6)-en-3β-yl iodoacetate, and may be classified as a sterol structure, type *ab*(21)2.

Introduction

The sapogenins are produced by hydrolysis of the plant glycosides and they may be classified as steroid sapogenins or as triterpenoid sapogenins according to the products of their dehydrogenation: the steroid sapogenins yield 3′-methyl-1,2-cyclopentenophenanthrene, and the triterpenoid sapogenins yield derivatives of naphthalene and of picene.

The use of steroid sapogenins as inexpensive precursors of hormones and of their intermediates, for example, cortisone from diosgenin, has prompted their