N_2O_4: Change of Dimensions with Temperature

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LATELY, the structure of N_2O_4 has been much investigated, both physically and theoretically. It was thought that a re-determination of the cubic form of the solid (space group *Im*3) would be useful, since one result of previous work by Broadley and Robertson[1] (*viz.*, the N–N bond length) was inconsistent with results obtained by later workers.[2–4] Furthermore, it was felt that the N–N bond, being unusually long, should be more thoroughly investigated. Consequently, *X*-ray crystal structure determinations were carried out at various temperatures, and molecular vibration analyses were performed in each case.

The present work confirms the unusual length of the N–N bond, but indicates also that both the N–N and N–O bonds are sensitive to temperature; the increase in length is about 0·01 Å per 100° of temperature rise. No significant change in the ONO angle is found.

The data were obtained from Weissenberg photographs at three temperatures, using Cu-$K\alpha$ radiation. The analysis was performed by least squares, using the Leeds "Pegasus" computer.

The results show that the N–N and N–O bond lengths increase with rising temperature, and are summarised in the Table.

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From these results, regression lines have been calculated, showing the relation between the dimensions and temperature. Owing to the somewhat large standard deviations in the determinations at liquid-hydrogen temperature, and near the melting point of N_2O_4, the equations for these lines are not precise. What is important, however, is that in the case of the two bond lengths, the trend is significant. The results also illustrate the advantage of using low temperatures in that the precision increases with falling temperature. The hydrogen-temperature results are encouraging, because they gave reasonably good figures with a little over half the data. Had the full data been obtained, the results at 25° K would have been particularly useful.

The regression lines are:

$$\text{N–N bond length, } d, = 1{\cdot}339.10^{-4}T + 1{\cdot}7083 \text{ (Å)}$$

$$\text{N–O bond length, } d' = 1{\cdot}099.10^{-4}T + 1{\cdot}1883 \text{ (Å)}$$

$$\text{ONO Angle, } \Theta = 134{\cdot}55 - 4{\cdot}75.10^{-3}T,$$

where T is the absolute temperature.

To check that this temperature variation of the bond lengths is significant, in terms of the data, the bond length changes from the regression equations above must be compared with the standard deviations. For the N–N bond length, whose mean standard deviation is 0·013 Å, we obtain, for the range 25—260° K, a bond length increase of 0·031 Å; for the N–O bond, whose mean standard deviation is 0·010 Å, the increase, over the same range, is 0·026 Å. In each case, the bond length increase is more than two standard deviations, in fact, the significance levels of the two results are 98% and 99% respectively. There seems to be little doubt, therefore, of the reality of this effect in the bond lengths. For the ONO angle, on the other hand, where the mean standard deviation is 1·1°, the regression equation gives an increase of only 1·12°, *i.e.*, no significant change.

As further confirmation of the temperature effect, the dimensions calculated from the regression lines are compared with the observed results. The deviation from the line is compared with the actual standard deviation. In all cases, the predicted values are within about one standard deviation of the observed ones:

TABLE

	25° K	145° K	260° K*
N–N bond (Å)	1·712 ± 0·017	1·726 ± 0·009	1·745 ± 0·014
N–O bond (Å)	1·189 ± 0·012	1·209 ± 0·007	1·214 ± 0·010
ONO angle	134·8° ± 1·5°	133·1° ± 0·7°	133·7° ± 1·2°
Cell constant *a*, (Å)	7·655 ± 0·01†	7·725 ± 0·001	7·828 ± 0·001
3-D Data obtained	60%	100%	100%
R-Value	11·1%	11·7%	14·4%

* *cf.* Melting point 262° K.
† Extrapolated. (The correct value is within the limits of error shown).
Standard deviations are given; all figures are corrected for liberation. (These corrections, though of comparable magnitude to the standard deviations, are felt to be of good accuracy).

			Calculated	Observed	Difference Calc. —Obs.	Observed Std. Dev.
N–N	25° K	.. .. ..	1·712	1·712	0·000	0·017
(Å)	145° K	.. .. ..	1·728	1·726	0·002	0·009
	260° K	.. .. ..	1·743	1·745	—0·002	0·014
N–O	25° K	.. .. ..	1·191	1·189	0·002	0·012
(Å)	145° K	.. .. ..	1·204	1·209	—0·005	0·007
	260° K	.. .. ..	1·217	1·214	0·003	0·010
$\widehat{ONO}$	25° K	.. .. ..	134·4	134·8	—0·4	1·5
(°)	145° K	.. .. ..	133·9	133·1	0·8	0·7
	260° K	.. .. ..	133·3	133·7	—0·4	1·2

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