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Neutron Diffraction Study of the 1:1 Urea:Hydrogen Peroxide Complex at 81 K*

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Abstract

The crystal structure of urea:hydrogen peroxide, $(H_2N)_2CO.H_2O_2$, has been measured at 81 ± 0·5 K. The structure is orthorhombic, *Pnca*, with a = 6·7317 (15), b = 4·8207 (8), c = 12·873 (3) Å, and $Z = 4$. Final $R_w(|F|^2)$ and S values are 0·0347 and 1·25 for 2932 observations representing roughly three sets of equivalent reflections measured on two crystals. The OO bond length in hydrogen peroxide is 1·4573 (8) Å, the OH distance is 1·0005 (7) Å, the OOH angle is 102·53 (5)°, and the HOOH dihedral angle is 98·98 (8)°. Combining the OO bond length with published moments of inertia leads to gas-phase equilibrium parameters of OH = 0·958 ± 0·004 Å, OOH = 98·7 ± 0·8°, and HOOH = 118·9 ± 0·1°, where the error limits correspond to a range of approximately ±0·003 Å in the OO distance. The urea parameters agree well with literature values.

Introduction

The importance of various oxidation states of dioxygen to both normal and aberrant life processes makes this molecule a logical subject for accurate bonding studies. A simple form of dioxygen to manipulate in the condensed phase is hydrogen peroxide, and we have chosen this molecule to begin our study. Hydrogen peroxide forms solid complexes with urea and a variety of simple salts (Adams & Pritchard, 1976; Sarin, Dudarev, Dobrynina, Fykin & Zavodnik, 1976); many of these and especially the sodium carbonate salt (Adams & Pritchard, 1977) are used as bleaches. The urea complex, $(H_2N)_2CO.H_2O_2$, has several advantages for an accurate structural study (Lu, Hughes & Giguère, 1941). It has a small unit cell, it is relatively stable and, most importantly from the point of view of relating its electron distribution to that of free hydrogen peroxide, the hydrogen peroxide conformation is skew and not too far from the minimum-energy conformation of the free molecule.

The neutron diffraction study which is necessary to establish accurate nuclear positions and patterns of thermal vibration is reported here. The refined molecular parameters are combined with results of prior spectroscopic measurements to define more precisely the gas-phase conformation of hydrogen peroxide.

Experimental

Crystals were grown by the method of Lu, Hughes & Giguère (1941). Preliminary investigation showed that the surface decomposition, which becomes perceptible after about 0·5 h in the room-temperature atmosphere, could be prevented or interrupted by storing the crystals in a cold room at 265 K. Further operations were therefore designed to isolate and cool the crystals as rapidly as feasible.

Diffraction data were collected on a computer-controlled four-circle diffractometer at the Brookhaven High Flux Beam Reactor. Collection of the full set of independent data required two crystals because of orientational constraints imposed by the cryostat or diffractometer at high scattering angle. Each of the crystals was selected from a freshly grown batch, weighed, mounted, and sealed under a quartz dome within an hour after removal from solution. The epoxy used in sealing the dome was cured for 3 h at room temperature and then overnight in the cold room. The crystals were mounted in the cryostat (Kvick, Al-Karaghouli & Koetzle, 1977) and slowly cooled to the operating temperature of 81 ± 0·5 K. Descriptions of the two crystals and summaries of the data collected with each are given in Table 1.

Lu, Hughes & Giguère (1941) report the space group to be *Pnca*, a nonstandard orientation of *Pbcn* (D_{2h}^{14}) (*International Tables for X-ray Crystallography*, 1952), with cell constants a = 6·86 (3), b = 4·83 (5), and c = 12·92 (2) Å at room temperature.

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Table 1. *Crystal descriptions*

	Crystal 1	Crystal 2
Weight	3·9 mg	8·6 mg
Volume	2·69 mm³	6·00 mm³
Faces	{001}, {102}, {100}, $(\bar{1}\bar{1}1)$, $(1\bar{1}1)$, (111) $(\bar{1}\bar{1}\bar{1})$, $(0\bar{1}1)$, $(0\bar{1}\bar{1})$	{001}, {102}, {100}, $(0\bar{1}0)$, $(11\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, (111), $(01\bar{1})$, $(01\bar{1})$
Approximate maximum dimesions	1·8 mm ∥ **a**, 2·4 mm ∥ **b**, 1·0 mm ∥ **c**	2·3 mm ∥ **a**, 2·2 ∥ **b**, 1·8 ∥ **c**
Orientation	{010} at $\chi = 70°$	{100} at $\chi = 86°$
Absorption* corrections	1·212 to 1·408: average 1·282	1·402 to 1·504: average 1·435
Number of reflections	1594	1338
Number of Laue-independent reflections	681	618
$R_o(\|F\|^2)$†	0·027	0·017
$R_{ow}(\|F\|^2)$†	0·004	0·004

* $\mu = 0·236$ mm^{-1}.

† $R_o(|F|^2) = \sum |\,|F_o|^2 - \overline{|F_o|^2}\,| / \sum n\overline{|F_o|^2}$; $R_{ow}(|F|^2) = \sum w|\,|F_o|^2 - \overline{|F_o|^2}\,| / \sum n\bar{w}\overline{|F_o|^2}$, where $\overline{|F_o|^2}$ and $\bar{w}$ are the mean values of $|F_o|^2$ and w for a given Laue-independent reflection, and n is the number of measurements in the corresponding average. The summations extend over all reflections having more than one contributor.

Table 2. *Crystal data*

Urea: hydrogen peroxide, $CH_4N_2O.H_2O_2$
Space group:* *Pnca* (D_{2h}^{14})

	a (Å)	b (Å)	c (Å)	U (Å³)
81 K (this work)†	6·7317 (15)‡	4·8207 (8)	12·873 (3)	417·8 (1)
263 K (Johnson, 1968)	6·84	4·83	12·91	427
Room temperature (Lu, Hughes & Giguère, 1941)	6·86 (3)	4·83 (5)	12·92 (2)	428 (2)

* Equivalent positions $+(x,y,z)$, $\pm(x, \frac{1}{2} - y, \frac{1}{2} + z)$, $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z)$, $\pm(\frac{1}{2} + x, y, -z)$. The standard setting is *Pbcn*.

† Neutron wavelength = 1·0444 (1) Å by least-squares fitting to 30 2θ measurements on a standard KBr crystal [a = 6·6000 (2) Å].

‡ Throughout this report, figures in parentheses are standard deviations in the least significant digits given.

The cell constants at 81 K, which are reported in Table 2, were determined by a least-squares fit to 64 2θ measurements representing the same 32 reflections measured on both carefully centered crystals. The systematic absences characteristic of *Pnca* were verified by measuring the intensities of all *hkl* and $hk\bar{l}$ reflections of crystal 1 to a 2θ limit of 58°.

Three sets of independent data, *hkl*, $hk\bar{l}$, and $\bar{h}k\bar{l}$, were measured on crystal 1 using a neutron beam of wavelength 1·0444 (1) Å obtained by reflection from the (002) plane of beryllium. In this 2θ range, a fixed-width θ–2θ step scan was employed, with a 2θ width of 3·2° and step size of 0·04°. At each step, counts were accumulated until a monitor count of the direct beam reached a fixed value requiring about 2 s.

In the 2θ range from 58 to 111°, corresponding to a maximum $\sin\theta/\lambda$ of 0·79 Å^{-1}, mechanical limits of the cryostat or diffractometer forced χ to remain in the range from −36 to 36°. Reflections of the same three octants available within these limits, excluding the space-group systematic absences, were collected with a similar θ–2θ step-scan technique, but with a 2θ range given by the formula $\Delta(2\theta) = 1·95(1 + 1·47 \tan\theta)$ and a varying step size. In collecting data in the first two octants, the computer was permitted to search for other Laue-equivalent reflections if the desired reflection fell outside the χ limits. Thus, reflections outside the specified octants were also occasionally measured.

Two reflections ($5\bar{2}\bar{2}$ and $\bar{3},0,\overline{10}$) were monitored about every 3·5 h as checks on the experimental stability. No trends appeared, within a limit of about 1%.

Intensity data were collected in an exactly parallel manner for crystal 2, except that the reflections collected were *hkl*, $hk\bar{l}$, and $\bar{h}kl$, and that the 2θ scan width for $2\theta > 58°$ was calculated from the relationship $\Delta(2\theta) = 1·73(1 + 1·92 \tan\theta)$. In all cases, the scan widths were chosen so that at least 10% of the scan range at either end represented background.

Calculations and results

Squared structure magnitudes, $|F_o|^2$, were extracted from the intensities by application of the Lorentz factor and an analytically calculated absorption correction (de Meulenaer & Tompa, 1965). The range of the latter, for which an empirical mass-absorption coefficient of 2430 mm² g^{-1} was used for H (McMullan & Koetzle, 1979), is given in Table 1. The variance was calculated for each reflection by the relation $\sigma^2(|F_o|^2) = L^{-2}[C + (t_C/t_B)^2 B + p^2 I^2]$, where L is the Lorentz factor, C is the number of counts in the central 80% of the scan (the 'peak'), B is the number of counts in the two outer 10% portions of the scan (the 'background'), t_C/t_B (=4) is the ratio of peak time to background time, I is the net intensity, and p is an estimate of non-Poisson errors in the data. A value of p in the range from 0·004 to 0·007 was derived by analyzing the variance of the monitor reflections for both crystals, but the slightly larger value of 0·01 was used.

An internal 'R factor' on $|F_o^2|$, as defined in Table 1, was used to estimate the quality of the data. $R_o(|F|^2)$ was 0·027 for crystal 1 and 0·017 for crystal 2, with all multiply measured reflections except standards included.

Throughout the least-squares refinement described below, all 2932 unaveraged $|F_o|^2$ values were used as data, each with its corresponding absorption-weighted path length [approximated by $-\ln(A)/\mu$] and associated **D** and **N** vectors (Thornley & Nelmes, 1974), so that anisotropic extinction factors could be refined. The starting parameters were those of Lu, Hughes & Giguère (1941) with the peroxide H assumed to lie along the O···N direction and urea H atoms in the expected locations. These starting parameters, with isotropic B values of 1·0 Å² for H and 0·75 Å² for the remaining atoms, gave $R(|F|) = 0·19$.

The parameters were refined by differential synthesis, followed by full-matrix minimization of the quantity $\sum w|\|F_o|^2 - |F_c|^2|^2$, with $w = \sigma^{-2}(|F_o|^2)$. Neutron scattering lengths of 5·803, 9·36, 6·6484, and −3·7409 fm (Koester, 1977) were used for O, N, C, and H, respectively. Refinement converged with $R_w(|F|^2) = 0{\cdot}038$, $R(|F|^2) = 0{\cdot}035$, $R(|F|) = 0{\cdot}041$ and the goodness of fit $S = 1{\cdot}25$. The final model included an isotropic extinction parameter for crystal 1 (in which the minimum effective transmission due to extinction was 0·94) and an anisotropic quadratic form for crystal 2, using the model of Thornley & Nelmes (1974) for a type 1 crystal with a Lorentzian distribution of mosaicity (Becker & Coppens, 1974). The smallest effective transmission factor for crystal 2 is 0·80. Tensor components, Z_{ij}, of the two mosaicity ellipsoids and their standard deviations are given in Table 3.

Because of Pedersen's (1972) warning about substitutional disorder in perhydrates, a difference map calculated at this time was examined with particular care. No feature on this map exceeded about 1% the largest peak on the F_o map in magnitude.

The use of two crystals permitted testing the degree to which the positional and thermal parameters are independent of the particular specimen studied. Two additional least-squares calculations were performed, in each of which data from only one of the crystals were employed. In each calculation, only one of the positional parameters shifted by more than twice its new standard deviation. No thermal parameters shifted by more than 2σ except for the U_{22} parameters of N(1), H(2), and H(3). These, and all other U_{22} values became larger for crystal 1 and smaller for crystal 2. The median magnitude of the U_{22} shifts was $1{\cdot}7\sigma$ in each crystal.

Table 3. *Mosaicity ellipsoids*

	Z_{11}‡	Z_{22}	Z_{33}	Z_{12}	Z_{13}	Z_{23}
Crystal 1†	1640 (540)	1640	1640	0	0	0
Crystal 2	76 (6)	52 (12)	60 (11)	17 (7)	−1 (5)	−28 (9)

† Constrained to be isotropic.
‡ The quadratic form is defined as $(g^*)^{-2} = \sum_{i=1}^{3}\sum_{j=1}^{3} d_i d_j Z_{ij}$, with $Z_{ij} = Z_{ji}$.

An attempt was also made to determine possible nonquadratic components of thermal motion by the use of Johnson's (1970*a*,*b*) cumulant procedure. Introduction of third-order (γ) tensors for all atoms gave no significant improvement in the goodness of fit.

The final positional and thermal parameters, with their standard deviations, were taken from the last cycle of standard least-squares refinement employing all observations, and are listed in Table 4.* Distances and angles derived from these data, as well as the atomic numbering scheme, are illustrated in Fig. 1. Additional details of the hydrogen-bonding environment of the peroxide are illustrated in Fig. 2, and a stereographic view of the unit cell is given in Fig. 3.

* Lists of structure amplitudes for both crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35886 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

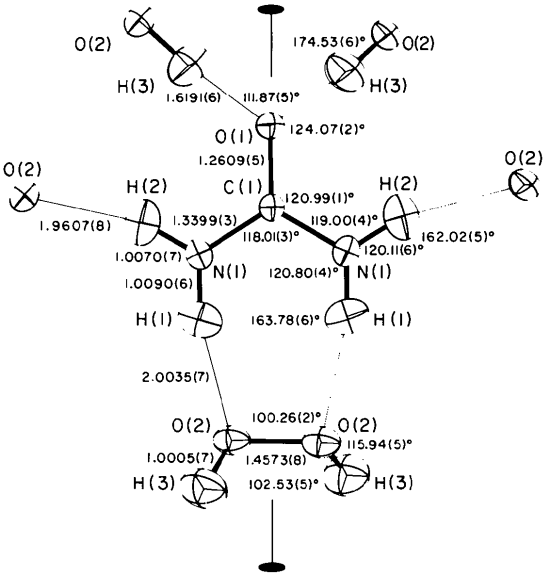

Fig. 1. Atomic numbering, interatomic distances (Å) and angles (°). The N(1)H(1)···O(2) distance is 2·9857 (7) Å, N(1)H(2)···O(2) is 2·9350 (5) Å, and O(1)···H(3)O(2) is 2·6168 (5) Å.

Table 4. *Positional and thermal parameters*

All parameters have been multiplied by 10^5. The temperature factor has the form
$\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	25000	0	2108 (3)	1944 (24)	1276 (19)	913 (15)	459 (20)	0	0
C(1)	25000	0	11904 (2)	1175 (19)	941 (15)	914 (12)	177 (16)	0	0
N(1)	13712 (4)	17867 (4)	17263 (1)	1910 (10)	1608 (9)	1184 (6)	796 (9)	47 (7)	−120 (7)
O(2)	15836 (6)	8042 (7)	40135 (2)	1741 (17)	1361 (13)	1197 (10)	−361 (13)	−148 (12)	−167 (10)
H(1)	14266 (10)	18471 (15)	25092 (4)	3404 (35)	3281 (34)	1692 (18)	800 (32)	108 (24)	−318 (23)
H(2)	5222 (11)	31529 (15)	13351 (5)	3362 (36)	2939 (34)	2630 (25)	1501 (31)	−121 (26)	239 (25)
H(3)	18975 (10)	23480 (13)	45063 (4)	2999 (34)	2252 (28)	2130 (22)	−317 (24)	−198 (21)	−544 (20)

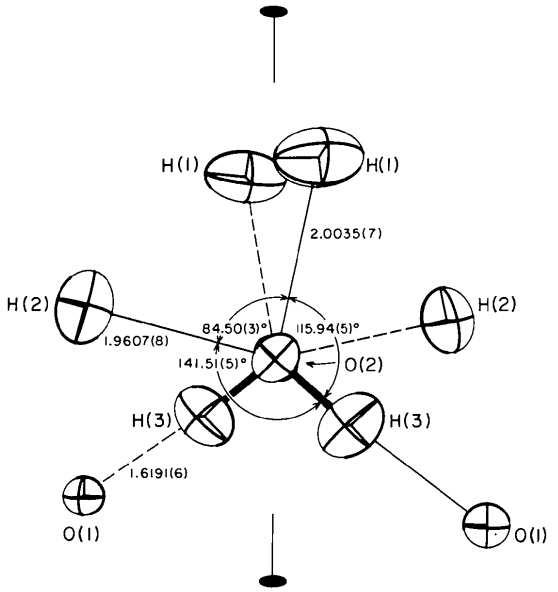

Fig. 2. Environment of the hydrogen peroxide, viewed along the OO bond. Additional angles are: O(2)O(2)···H(1) = 100·26 (2) and O(2)O(2)···H(2) = 105·38 (4)°. The dihedral angles H(3)O(2)O(2)H(3) and O(1)···O(2)O(2)···O(1) are 98·98 (8) and 105·88 (4)° respectively.

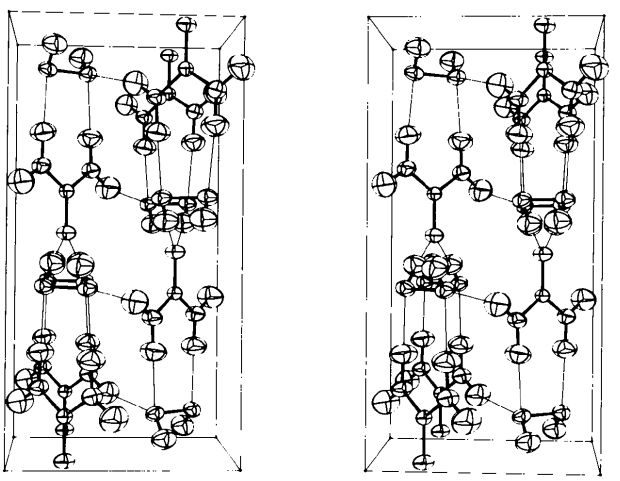

Fig. 3. A stereogram of the unit cell. The **c** direction is vertical, with **a** horizontal. The thermal ellipsoids are scaled to enclose 80% probability surfaces.

CDC 7600, CDC 6600, and DEC 11/40 computers were used in the data analysis. Major programs included Brookhaven versions of: *AGNOST* (Templeton & Templeton, 1973) for absorption correction; *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinement; *ORFFE* (Busing, Martin & Levy, 1964) for analysis of errors in distances and angles; *FORDAP* (A. Zalkin, unpublished) for Fourier summation; and *ORTEP* II (Johnson, 1972) for illustration.

Discussion

The separate least-squares calculations using data from individual crystals apparently indicate that the two specimens differ slightly with regard to high-order intensities near the b^* axis, although it must be noted that data in this region having sin θ/λ greater than 0·46 Å^{-1} were not available for crystal 1. Somewhat larger standard deviations for all U_{22} parameters than are given in Table 4 should therefore be employed in any analysis where these magnitudes are critical. The change is not significant in the discussion which follows.

Hydrogen peroxide

Although this study was conducted principally to lay the groundwork for analyzing bonding densities in the component molecules by a parallel X-ray diffraction study, the unusual precision of the results permits combining them with moments of inertia determined in infrared and microwave studies of H_2O_2 to provide an accurate description of the gas-phase molecule as well.

The geometry of hydrogen peroxide as determined in this investigation is compared with the results of earlier neutron diffraction studies on the urea complex and solid H_2O_2 or D_2O_2 in Table 5. Within a tolerance of ±0·004 Å, the more accurate conventional studies provide similar estimates of the O—O bond length. The semi-rigid-body refinement of D_2O_2 diffraction data by Prince, Trevino, Choi & Farr (1975) leads to an O—O bond length 0·034 Å longer than that determined here.

Some correction for apparent shrinkage caused by curvilinear thermal motion is certainly needed in the OO bond, but at least two arguments indicate that a properly corrected bond length is far smaller than that obtained in the semi-rigid-body refinement of Prince *et al.* (1975). First, although the small number of

Table 5. *Comparison of hydrogen peroxide geometries*

O–O (Å)	O–(H,D) (Å)	O···O (Å)	O–O–(H,D) (°)	Temperature (K)	Reference
1·4573 (8)	1·0005 (7)	2·6168 (5)	102·53 (5)	81	H_2O_2-urea; this work
1·47 (3)	0·94 (3)	2·619 (16)	103·6 (13)	263	H_2O_2-urea; Johnson (1968)
1·453 (7)	0·988 (5) 1·008 (5)[a]	2·799 (8)	102·7 (3)	223–248	H_2O_2; Busing & Levy (1965)
1·455 (2)[b]	0·978 (2) 0·993 (2)[a]	2·782 (1)	102·1 (1)	258	D_2O_2; Prince, Trevino, Choi & Farr (1975)
1·491 (2)[c]	1·011 (2)	2·760 (1)	102·9 (1)	258	D_2O_2; Prince, Trevino, Choi & Farr (1975)
1·458 (4) 1·461 (3)[d]	0·988 (3)	2·761 (5) 2·758 (6)	101·9 (1)	110	H_2O_2; Savariault & Lehmann (1980)

Notes: (*a*) Corrected by the Busing & Levy (1964) riding model. (*b*) Conventional refinement. (*c*) Semi-rigid-body refinement. (*d*) X-ray study.

independent thermal parameters in the H_2O_2 molecule prevented a rigid-body thermal analysis by the Schomaker–Trueblood–Cruickshank technique (Schomaker & Trueblood, 1968; Cruickshank, 1956), corrections in molecules of similar size and thermal parameters do not exceed 0·003 to 0·010 Å. Second, the failure of third-order cumulants to improve the goodness of fit significantly also suggests that librational components of the thermal motion (and hence bond-length corrections) are minimal. Thus, a ground-state OO bond length in the range 1·457 to 1·460 Å in the solid state is assumed in the discussion which follows. Hydrogen bonding will have stretched this value slightly from its gas-phase value, but the magnitude is difficult to estimate. A maximum stretch of 0·002 Å due to this effect is assumed.

The observed OH bond length of 1·0005 (7) Å is also certainly several thousandths of an ångström short of its crystalline ground-state value. Unlike the OO bond, however, the OH bond is stretched by several hundredths of an ångström from its gas-phase length by hydrogen bonding in the solid. Because the uncertainty in a thermal correction is of the same order of magnitude as the correction, none has been made.

Two sets of investigators (Redington, Olson & Cross, 1962; Oelfke & Gordy, 1969) have obtained estimates of the three ground-state moments of inertia for gaseous H_2O_2; in addition, Khachkurusov & Przhevalskii (1974) have estimated the equilibrium moments of inertia from the data of Redington, Olson & Cross (1962). The four independent structural parameters for H_2O_2, the OO and OH bond lengths, the OOH angle, and the HOOH torsion angle, can be obtained from these data only by imposing an additional constraint, and in the above reports this has been an assumed value for the OH bond length, chosen by analogy with similar compounds. The OO bond as measured in the present study can serve as a more direct fourth constraint.

Table 6. *Proposed gas-phase geometry for* H_2O_2

The extreme values in each parameter correspond to the estimated maximum uncertainty in the OO bond length, and are calculated from moments of inertia taken from the quoted reference.

OO (Å)	OH (Å)	OOH (°)	HOOH (°)	Reference
1·455[a]	0·980	102·5	120·5	Redington, Olson & Cross (1962)
1·457	0·976	101·8	120·4	
1·460	0·971	100·7	120·3	
1·455[a]	0·980	102·7	121·0	Oelfke & Gordy (1969)
1·457	0·977	102·0	120·9	
1·460	0·972	100·9	120·8	
1·455[b]	0·961	99·4	119·0	Khachkurusov & Przhevalskii (1974)
1·457	0·958	98·7	118·9	
1·460	0·954	97·5	118·8	

Notes: (*a*) Ground vibrational state. (*b*) Equilibrium state.

Table 6 reports the values of the OH bond length and the OOH and HOOH angles determined from the two assumed limits in the OO distance, 1·455 and 1·460 Å, as well as from the observed value of 1·457 Å, which because of the balancing effects of thermal motion and hydrogen-bond stretching may be the best estimate of the gas-phase length.

The range of 0·971 to 0·980 Å derived for the ground-state OH bond length lies beyond previous estimates. It considerably exceeds the ground-state lengths for this bond in water (0·9579 Å; Laurie & Herschbach, 1962) and in methanol [0·945 (3) Å; Lees & Baker, 1968] but includes that in the hydroxyl radical (0·9800 Å; Laurie & Herschbach, 1962). The mean value of the ground-state OOH bond angle in H_2O_2 is approximately 101·8 to 102·0°, several degrees smaller than the HOH angle in water (104·93°; Laurie & Herschbach, 1962).

Previous workers have noted that the HOOH dihedral angle in the gas phase is a relatively insensitive function of the values chosen for other parameters, but that a value near 120° is required. The present study confirms this observation. It is also no surprise that the dihedral angle varies so much from solid to solid. The observed angles range from about 89° in $RbF.H_2O_2$ (Sarin, Dudarev, Dobrynina, Fykin & Zavodnik, 1977) to 180° in several structures where the peroxide is required to have $C_{\bar{1}}$ symmetry.

Urea

Distances and angles within the urea molecule are presented in Fig. 1. The CO and CN distances are compared in Table 7 with those from several other accurate structures. The agreement of the uncorrected distances with those determined in Mullen & Hellner's (1978) X-ray study of urea at 123 K is excellent. Rigid-body thermal corrections were estimated by the Schomaker–Trueblood–Cruickshank method, both with and without the H atoms. In neither case was agreement with the individual U_{ij} values excellent, but

Table 7. CO *and* CN *distances* (Å) *in urea*

CO	CN	Compound and temperature	Reference
1·2609 (5)[a]	1·3399 (3)	Urea: H_2O_2, 81 K	This work
1·262 (2)[a]	1·338 (4)	Urea, 123 K	Mullen & Hellner (1978)
1·278 (4)[a]	1·312 (4) 1·320 (4)	Urea: H_3PO_4, room temperature	Nozik, Fykin, Bukin & Muradyan (1976)
1·259 (1)[b]	1·348 (1) 1·351 (1)	Urea: parabanic acid, 116 K	Weber, Ruble, Craven & McMullan (1980)
1·260 (3)[c]	1·352 (2)	Urea, room temperature	Pryor & Sanger (1970)

Notes: (*a*) No thermal correction. (*b*) Rigid-body thermal correction. (*c*) Rigid-body correction with explicit inclusion of the curvilinear effect.

the corrections are approximately 0·005 to 0·008 Å. Corrections of this magnitude make the CO bond appear longer than that found for urea at room temperature by the sophisticated analysis of Pryor & Sanger (1970), but barely bring the CN bond within range of their determination. Inconsistencies of this sort illustrate the failings of available models for extrapolating apparent bond lengths to ground-state values.

Deviation of CN and CO bond lengths in the urea–phosphoric acid complex from the remaining ones may be associated with the very short O···O hydrogen bond of 2·40 Å from the urea O to a phosphate hydroxyl group, in which the H atom is actually closer to the urea than to the phosphate. This complex could be formulated as a uronium salt, in which a long CO and a shorter than usual CN bond would be expected.

Distances of atoms from the least-squares plane $5{\cdot}0932x + 3{\cdot}1522y - 1{\cdot}2733 = 0$ are N(1) = −0·012, H(1) = 0·036, and H(2) = −0·014 Å. The urea molecule is thus not precisely planar, but the distortions are not easily explained. Both O(2) atoms which serve as acceptors for the NH···O hydrogen bonds are approximately 0·2 Å below the plane and, although the NH_2 group is twisted slightly in the direction of the shorter of these two hydrogen bonds, the slight pyramidal distortion of the CNH_2 group is opposite to that which would occur if both H atoms were bent toward their acceptors.

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