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The Structure of Hydroxyurea at Liquid-Nitrogen Temperature

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(*Received* 7 *July* 1975; *accepted* 1 *August* 1975)

The crystal structure of *N*-hydroxyurea, $H_2NCONHOH$, first determined by Larsen & Jerslev [*Acta Chem. Scand.* (1966), **20**, 983] and independently by Berman & Kim [*Acta Cryst.* (1967), **23**, 180–181], has been reinvestigated at liquid-nitrogen temperature (−140°C) from densitometer-measured photographic data. The structural details reported in the above papers are confirmed, but the reduction in temperature has reduced the mean-square translational amplitudes of individual atoms by about 40% and has led to more precise values for bonds and angles. If the hydroxyl O is excluded, the remainder of the molecule vibrates as a rigid body.

Introduction

The crystal structure of *N*-hydroxyurea (Fig. 1) a substance used in cancer chemotherapy, was first determined by Larsen & Jerslev (1966) and later, independently, by Berman & Kim (1967). These were both X-ray investigations at room temperature, and the reported bonds and angles agree within the experimental errors. The present authors had also been working upon the structure of hydroxyurea when the above reports appeared. Our original data, collected at room temperature on Weissenberg films and measured by microdensitometer, refined to produce atomic positions which agreed well with both earlier studies. But an analysis of the thermal motions of the individual atoms showed that the molecule executes substantial librational motion with resulting errors in atomic coordinates. The substantial independent motion found for the hydroxyl oxygen [O(1), Fig. 1] means that the molecule as a whole does not vibrate as a rigid body and consequently the usual corrections (Cruickshank, 1956*a*) could not be applied, but the remaining four heavier atoms were found to vibrate as a rigid unit. It is not therefore possible to determine the bond lengths involving O(1) [particularly N(1)–O(1)] to the same precision as for the other bonds in the molecule, and a thermal analysis at best leads to an 'upper and lower bound' as described by Busing & Levy (1964). One way of reducing this kind of uncertainty is to reduce the vibrational amplitudes by taking data at a lower temperature; this is in addition to the other benefits which result from lowering the temperature such as improved resolution and reduction in the effects of thermal diffuse scattering. Further, hydroxyurea was found to decompose slowly at room temperature, but not at all at nitrogen temperature. For these reasons it was decided to investigate hydroxyurea at liquid-nitrogen temperature.

Experimental

Both room-temperature data and low-temperature data were taken from a pair of ground spherical crystals with Cu $K\alpha$ radiation. The first crystal of diameter 0·30 mm provided data about [010] and the second crystal of diameter 0·39 mm provided data about [100]. Both crystals were spherical to within ±1% as determined by a series of microscope photographs, and both specimens were sealed into Lindemann glass tubes after first being dipped several times into liquid nitrogen to reduce extinction. The lattice parameters were estimated from the separation of α_1 and α_2 spots of high-order reflexions on films. These are given in Table 1 for both temperatures, together with the previously reported values.

A comparison of the room and low temperature parameters reveals that the change in strain over the temperature range covered is markedly anisotropic. At both temperatures, four layers of data about [100] and five layers about [010] were recorded with a Nonius

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camera equipped with an integrating device. Low temperature was achieved by using a Dewar of the kind described by Kreuger (1955) in conjunction with the Nonius camera. Dry, cold nitrogen gas surrounded by an annular stream of dry nitrogen was directed onto the crystal. Icing of moving parts was avoided by directing a stream of warm air from a hair dryer at the appropriate points. The temperature was monitored by a low heat capacity copper-eureka thermojunction placed in the cold stream at the mouth of the Dewar. Temperature was adjusted by varying the rate of flow of cooling gas.

Difficulty was experienced in that for upper layers the distance from outlet orifice to specimen increased with layer. This was overcome as follows: the variation of temperature with distance along the gas stream was carefully measured for different flow rates, and the flow rate was thus adjusted for each layer to provide the required (constant) temperature of −140°C. It was estimated that the greatest possible variation in temperature due to this cause was ±4°C. In the case of the [010] data, the crystal was deliberately mis-set to avoid simultaneous reflexion.

The intensities were measured from films by a Joyce–Loebl densitometer for all save the very weakest reflexions which were estimated visually. All available symmetry-related reflexions were measured on each film; these were averaged, and the standard errors of the means were used to provide weights in the subsequent least-squares refinement. Agreement between equivalents was 1% for strong intensities, 2% for medium intensities and, in the worst case, 15% for the weakest (visually estimated) intensity. Of the 650 data available with Cu $K\alpha$ radiation, 465 were measured at low temperature and 376 at room temperature. Corrections were made for Lorentz and polarization effects but not for extinction or t.d.s. Absorption corrections were not necessary as the difference between the greatest and least correction factors was only 0·8%. The data about each axis were put on a common scale by a least-squares process.

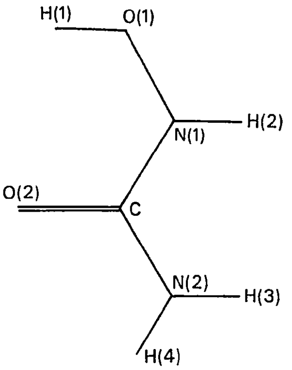

Fig. 1. Molecule showing numbering of atoms.

Refinement

Starting with the parameters determined by Berman & Kim (1967), which had by this time become available, the low-temperature data were refined with the *ORFLS* program of Busing, Martin & Levy using the spherical form factors listed in *International Tables for X-ray Crystallography* (1962). As a check, the H atom positions were first re-determined by a three-dimensional difference map in which H atom contributions were excluded from F_c. The H positions were allowed to vary in the subsequent least-squares refinement but their temperature parameters were kept fixed at $B = 2{\cdot}0$ Å^2. The weights w employed were S^{-2} where S is the standard error of the mean of equivalent observed structure factors for a given order. At an early stage in the refinement the 65 visually measured reflexions were excluded together with five reflexions which were clearly affected by extinction (*i.e.* 102, $\bar{2}11$, 011, $\bar{2}12$ and $\bar{1}21$). The data were refined to a stage at which no parameter shift was significant. The final R value was 0·048 and the weighted value R_w was 0·038, where $R = \sum||F_o|-|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o|-|F_c|)^2/\sum F_o^2]^{1/2}$. An analysis of the distribution of $\langle w\Delta^2\rangle$ with both $\sin\theta$ and $\langle F\rangle$ confirmed that the weighting scheme used was reasonable. Observed and calculated structure factors are given in Table 2,* the final positional parameters in Table 3 and the final thermal parameters in Table 4.

The refinement of room-temperature data proceeded

Table 1. *Lattice parameters and space group* (*estimated errors in parentheses*)

Lattice parameters	Present study −140°C	+20°C	Berman & Kim (room temp.)	Larsen & Jerslev (room temp.)
a (Å)	8·305 (3)	8·381 (7)	8·393 (8)	8·46
b (Å)	4·886 (2)	4·918 (3)	4·907 (5)	4·89
c(Å)	8·797 (2)	8·822 (4)	8·798 (8)	8·86
β (°)	121·41 (2)	121·24 (4)	121·2	121·9
V (Å^3)	304·66	310·90	—	—
D_x (g cm^{-3})	1·658	1·624	1·630	1·625

Space group $P2_1/c$

$D_m = 1{\cdot}63$ g cm^{-3} $\mu = 13{\cdot}5$ cm^{-1} for Cu $K\alpha$

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31317 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Low- and room-temperature fractional atomic coordinates and their standard deviations shown in parentheses*

First and second rows correspond to low and room temperature values respectively.

	x	y	z
H(1)	0·188 (7)	−0·158 (10)	−0·316 (6)
	0·187 (8)	−0·180 (10)	−0·306 (7)
H(2)	0·070 (7)	−0·237 (8)	−0·122 (7)
	0·090 (8)	−0·249 (9)	−0·110 (8)
H(3)	0·320 (7)	0·305 (8)	−0·097 (7)
	0·325 (8)	0·295 (9)	−0·107 (8)
H(4)	0·432 (7)	0·335 (9)	0·091 (6)
	0·462 (8)	0·327 (10)	0·109 (7)
C	0·2743 (4)	0·0261 (5)	0·0264 (3)
	0·2735 (4)	0·0253 (6)	0·0266 (3)
N(1)	0·1597 (3)	−0·1254 (4)	−0·1174 (3)
	0·1596 (4)	−0·1226 (5)	−0·1166 (3)
N(2)	0·3559 (4)	0·2459 (4)	0·0044 (3)
	0·3557 (4)	0·2425 (5)	0·0070 (3)
O(1)	0·1250 (3)	−0·0390 (4)	−0·2848 (2)
	0·1252 (3)	−0·0392 (4)	−0·2828 (2)
O(2)	0·3025 (2)	−0·0472 (4)	0·1761 (2)
	0·3020 (4)	−0·0498 (4)	0·1745 (3)

along similar lines. Here the 011 reflexion was omitted on account of severe extinction and the H atoms were given a fixed temperature factor of 4·0 Å^2. The data refined to an R value of 0·056 and a weighted R_w value of 0·051. The observed and calculated structure factors are given in Table 2, and the positional and thermal parameters in Tables 3 and 4 respectively. The thermal ellipsoid parameters are given in Table 5 for both temperatures; the direction cosines of the axes of the ellipsoids are specified with respect to an orthogonal frame having axes parallel to **a**, **b** and **c***.

Vibration analysis

The extent to which the molecule as a whole vibrates as a rigid body at room temperature was investigated by first deducing the elements of the **T** and **ω** tensors (Cruickshank, 1956*b*) which describe respectively the rectilinear and rotational oscillations of a rigid body. The **T** and **ω** tensors, referred to inertial frame of the molecule, are given in Table 6. Values of $U_{ij}^{\rm calc}$ were determined for each atom from **T**, **ω** and the atomic positions, and these are compared in Table 7 with the $U_{ij}^{\rm obs}$ which are obtained by transforming the β_{ij} of Table 4 to the inertial frame and using the relationship $U_{ij}=\beta_{ij}/2\pi^2a_i^*a_j^*$. If the molecule vibrates substantially as a rigid body, a good measure of agreement would be expected between corresponding $U_{ij}^{\rm obs}$ and $U_{ij}^{\rm calc}$ values. The agreement is not good; this is perhaps only to be expected as there is considerable internal flexibility of the molecule, such as to prevent the

Table 5. *Thermal ellipsoids at low and room temperature*

	Mean-square vibration amplitude (Å^2 × 10^3)	Direction cosines of ellipsoid axes (× 10^3)*		
(1) Low temperature				
C	24	678	648	350
	11	−713	693	98
	15	−177	−314	934
N(1)	33	734	−545	345
	18	404	821	404
	14	−505	−169	847
N(2)	34	897	−440	33
	19	442	894	−73
	14	2	80	997
O(1)	27	801	571	186
	24	−555	821	−129
	14	−227	0	974
O(2)	28	934	−332	131
	21	242	857	454
	15	−262	−392	881
(2) Room temperature				
C	35	837	546	37
	22	−505	744	437
	29	211	−384	899
N(1)	55	819	−517	249
	32	399	824	402
	23	−413	−232	881
N(2)	51	885	−465	17
	28	358	706	610
	31	−296	−534	791
O(1)	52	906	402	136
	37	−402	916	−26
	20	−134	−31	991
O(2)	54	894	−443	66
	36	386	838	388
	22	−228	−321	919

* The ellipsoids are specified with respect to an orthogonal frame with axes parallel to **a**, **b** and **c***.

Table 4. *Low- and room-temperature thermal vibration parameters with standard deviations* (× 10^5) *in the form* $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

First and second rows correspond to low and room temperature values respectively.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	721 (45)	1211 (97)	597 (35)	304 (50)	382 (32)	105 (38)
	1227 (57)	2186 (119)	960 (54)	199 (54)	583 (43)	−122 (45)
N(1)	1105 (46)	1810 (90)	606 (36)	−398 (51)	527 (31)	−90 (38)
	1832 (59)	3066 (116)	919 (41)	−542 (65)	748 (37)	−62 (48)
N(2)	1029 (51)	1837 (112)	433 (31)	−307 (48)	269 (30)	−15 (40)
	1604 (54)	2761 (107)	1032 (42)	−475 (51)	555 (37)	−71 (38)
O(1)	960 (44)	1956 (90)	491 (30)	128 (43)	362 (27)	−19 (33)
	1742 (53)	3229 (94)	737 (30)	293 (50)	529 (31)	70 (35)
O(2)	990 (46)	1702 (87)	535 (30)	−103 (37)	359 (27)	46 (25)
	1776 (53)	3092 (91)	840 (32)	−290 (51)	582 (30)	184 (35)

Table 6. **T** *and* **ω** *tensors for whole molecule at room temperature* (*standard deviations in parentheses*)

$$\mathbf{T}=\begin{pmatrix} 3{\cdot}5\ (5) & 0{\cdot}2\ (3) & 0{\cdot}1\ (3) \\ & 3{\cdot}0\ (3) & 0{\cdot}2\ (2) \\ & & 2{\cdot}4\ (2) \end{pmatrix}\times 10^{-2}\text{Å}^2$$

$$\boldsymbol{\omega}=\begin{pmatrix} 3{\cdot}7\ (1{\cdot}3) & 0{\cdot}8\ (1{\cdot}5) & 1{\cdot}0\ (2{\cdot}6) \\ & 2{\cdot}9\ (2{\cdot}1) & 1{\cdot}7\ (2{\cdot}7) \\ & & 11{\cdot}7\ (3{\cdot}9) \end{pmatrix}\times 10^{-3}\text{ radian}^2$$

T and **ω** are expressed with respect to the inertial frame of the molecule.
The matrix **U** which transforms a vector from the frame with axes parallel to **a**, **b**, **c*** to the inertial frame is:

$$\mathbf{U}=\begin{pmatrix} 0{\cdot}814 & -0{\cdot}564 & 0{\cdot}137 \\ 0{\cdot}574 & 0{\cdot}818 & -0{\cdot}046 \\ -0{\cdot}086 & 0{\cdot}116 & 0{\cdot}990 \end{pmatrix}$$

molecule as a whole vibrating as a rigid body – which it clearly does not.

When the procedure was repeated with O(1) excluded, it was found that the vibrations of the remaining four atoms correspond quite closely to that of a rigid body. The **ω** and **T** tensors for these four atoms are given in Table 8 and the corresponding U_{ij}^{obs} and U_{ij}^{calc} in Table 9. From this analysis it is concluded that O(1) has substantial individual motion.

The rigid body vibration corresponds qualitatively to the known intermolecular forces to the extent that the zero value of ω_{11} (Table 8) can be explained in terms of the four strong hydrogen bonds which operate in a plane perpendicular to the direction to which ω_{11} relates, and which might be expected considerably to suppress libration about this direction. The changes in the vibration pattern brought about by reducing the temperature are apparent from Tables 4 to 9. If the traces of the U_{ij} tensors (specified with respect to an orthogonal frame) are compared (taking the trace as an overall indication of the vibration of an atom), it is found that the trace of N(2) is reduced by 39% and those of the remaining four atoms by 41%; the difference between these values is not statistically significant.

Molecular details and discussion

Table 8. **T** *and* **ω** *tensors for urea nucleus* [*i.e. omitting* O(1)] (*standard deviations in parentheses*)

Room temperature

$$\mathbf{T}=\begin{pmatrix} 2{\cdot}5\ (3) & 0{\cdot}3\ (2) & 0{\cdot}3\ (2) \\ & 2{\cdot}8\ (2) & 0{\cdot}3\ (1) \\ & & 3{\cdot}0\ (2) \end{pmatrix}\times 10^{-2}\ \text{Å}^2$$

$$\boldsymbol{\omega}=\begin{pmatrix} 0{\cdot}0\ (1{\cdot}3) & 1{\cdot}3\ (1{\cdot}6) & 2{\cdot}3\ (1{\cdot}7) \\ & 15{\cdot}8\ (2{\cdot}2) & 2{\cdot}6\ (1{\cdot}4) \\ & & 16{\cdot}3\ (2{\cdot}4) \end{pmatrix}\times 10^{-3}\text{ radian}^2$$

Low temperature

$$\mathbf{T}=\begin{pmatrix} 1{\cdot}2\ (2) & 0{\cdot}2\ (1) & 0{\cdot}3\ (1) \\ & 1{\cdot}7\ (1) & 0{\cdot}2\ (1) \\ & & 2{\cdot}0\ (1) \end{pmatrix}\times 10^{-2}\ \text{Å}^2$$

$$\boldsymbol{\omega}=\begin{pmatrix} -0{\cdot}9\ (0{\cdot}8) & 1{\cdot}2\ (0{\cdot}9) & 2{\cdot}0\ (1{\cdot}0) \\ & 11{\cdot}4\ (1{\cdot}2) & -0{\cdot}8\ (0{\cdot}8) \\ & & 10{\cdot}6\ (1{\cdot}4) \end{pmatrix}\times 10^{-3}\text{ radian}^2$$

Tensors expressed with respect to the inertial frame of the nucleus. Transformation from the crystal orthogonal frame (*a*, *b*, *c**) to the inertial frame is effected by the matrix:

$$\mathbf{U}=\begin{pmatrix} 0{\cdot}814 & -0{\cdot}563 & 0{\cdot}143 \\ 0{\cdot}509 & 0{\cdot}572 & -0{\cdot}644 \\ 0{\cdot}281 & 0{\cdot}597 & 0{\cdot}752 \end{pmatrix}$$

The very large librations at room temperature (a mean square rotation amplitude of over 60 deg² about one axis) show that significant errors in atomic positions through rotational effects are to be expected. Corrections have therefore been applied by the method of Busing & Levy (1964). In the case of the part of the molecule which behaves as a rigid body this is straightforward, but in the case of O(1) the so-called riding motion of Busing & Levy was believed to be appropriate and this led to lower and upper bounds for the N(1)–O(1) bond corresponding to parallel and anti-parallel displacements of the atoms concerned.

The full internal molecular geometry, both corrected and uncorrected for libration (in the case of bonds), is given in Table 10 for both temperatures. The corrections bring the room and low temperature values of bonds into much closer agreement as expected. In particular, it will be seen that reducing the temperature has almost halved the uncertainty in the N(1)–O(1) bond length, and that the corrections to the other bonds at room temperature are highly significant in relation to the standard deviations.

The more important distances between atoms on different molecules, including hydrogen-bond distances, are given in Table 11. The structural details reported by Larsen & Jerslev (1966) are confirmed by the present

Table 7. U_{ij}^{obs} *determined from room-temperature* β_{ij} *of Table* 4 *and* U_{ij}^{calc} *determined from the* **T** *and* **ω** *tensors of Table* 6

Parameters referred to inertial frame of Table 6.

$U_{ij}\times 10^{-2}$ Å²

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs	Calc.	Obs.	Calc.	Obs.	Calc.
C	2·54	3·57	3·35	3·07	2·67	2·36	0·37	0·24	0·33	0·10	−0·10	0·20
N(1)	5·46	4·02	3·00	3·11	2·54	2·54	0·05	0·30	0·33	0·01	0·37	0·05
N(2)	5·06	5·50	2·95	3·04	2·98	3·05	0·26	0·29	−0·22	−0·14	−0·16	−0·01
O(1)	4·14	4·46	4·74	4·24	2·12	2·36	0·68	0·52	0·01	0·09	0·37	0·19
O(2)	5·32	4·97	3·36	3·94	2·49	2·49	0·34	0·34	−0·26	0·14	0·51	0·55

Table 9. U_{ij}^{obs} *determined from the room-temperature* β_{ij} (*Table* 4) *and* U_{ij}^{calc} *determined from the room-temperature* **T** *and* **ω** *values in Table* 8

$U_{ij}\times 10^{-2}$ Å^2

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Cal
C	2·54	2·54	3·20	2·82	2·82	3·00	0·09	0·26	0·49	0·33	0·31	0·28
N(1)	5·46	5·46	2·46	2·84	3·07	3·00	−0·15	−0·02	0·28	0·30	0·32	0·28
N(2)	5·06	5·06	3·13	2·83	2·82	3·01	0·35	0·37	−0·03	0·15	−0·06	0·27
O(2)	5·31	5·31	2·53	2·83	3·31	3·01	0·44	0·11	−0·01	−0·04	0·54	0·28

Table 10. *Intramolecular bond lengths* (Å) *and angles* (°)

First and second columns correspond to the room and low temperature values respectively. The values in parentheses are the corresponding e.s.d.'s. The second line values are the bond lengths corrected for thermal motion.

C–O(2)	1·254 (4)	1·263 (3)
	1·261	1·267
C–N(1)	1·336 (3)	1·347 (3)
	1·347	1·355
C–N(2)	1·330 (4)	1·334 (4)
	1·337	1·339
Lower bound	1·401 (4)	1·413 (3)
N(1)–O(1)	1·407	1·416
Upper bound	1·511	1·477
O(1)–H(1)	0·948 (65)	1·049 (58)
N(1)–H(2)	0·875 (64)	0·940 (52)
N(2)–H(3)	0·936 (70)	0·937 (63)
N(2)–H(4)	0·972 (46)	0·896 (42)
N(2)–C——O(2)	122·69 (23)	123·17 (20)
N(1)–C——N(2)	118·58 (29)	118·22 (25)
N(1)–C——O(2)	118·71 (29)	118·60 (25)
C——N(1)–O(1)	119·24 (27)	118·30 (23)
N(1)–O(1)–H(1)	100·0 (3·6)	99·3 (2·9)
O(1)–N(1)–H(2)	119·7 (3·9)	115·2 (3·3)
C——N(1)–H(2)	119·9 (4·3)	125·6 (3·6)
H(3)–N(2)–H(4)	119·1 (5·2)	119·4 (4·4)
C——N(2)–H(3)	119·3 (3·0)	123·3 (2·7)
C——N(2)–H(4)	120·7 (3·7)	116·9 (3·8)

Table 11. *Intermolecular hydrogen-bond lengths* (Å) *and angles* (°)

The angles (second lines) are those between X–H and X···Y in the hydrogen bond X–H···Y. The hydrogen bonds are formed between the molecule occupying a general position x,y,z and the ones generated with symmetry code given below.

(i)	x,	$-\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(ii)	x,	$-\frac{1}{2}-y$,	$\frac{1}{2}+z$
(iii)	$-x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}-z$
(iv)	$-x$,	$-\frac{1}{2}+y$,	$-\frac{1}{2}-z$
(v)	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
(vi)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(vii)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
(viii)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$

	Room temp.	Low temp.
O(1)——H(1)·····O(2^{i})	2·646 (4)	2·627 (3)
	4·3 (3·6)	7·2 (3·0)
O(1^{ii})—H(1^{ii})····O(2)	----	----
N(1^{iii})–H(2^{iii})···O(1)	2·913 (4)	2·878 (3)
	18·3 (3·9)	16· 8 (3·3)
N(1)——H(2)·····O(1^{iv})	----	----
N(2^{v})—H(4^{v})····O(2)	2·968 (4)	2·940 (3)
	5·4 (3·7)	17·0 (3·7)
N(2)——H(4)·····O(2^{vi})	----	----
N(2^{vii})–H(3^{vii}) ··O(2)	3·118 (4)	3·064 (3)
	14·1 (3·0)	10·2 (2·7)
N(2)——H(3)·····O(2^{viii})	----	----

study in all important respects, and these will not therefore be described again here. A low-temperature difference map (Fig. 2), in which the F_c are calculated with the final low-temperature parameters from Tables 3 and 4 and spherical form factors, exhibits non-spherical features such as concentration of charge along the C–O(2) double bond and anti-bonding density distributions in the neighbourhoods of N(1), N(2) and C. Peaks near H(3) and H(4) could indicate that the temperature factors assigned to these atoms are too high.

Finally, it is of some interest to compare the results of different studies, at different laboratories (in different parts of the world) with different specimens. Comparisons of bond lengths (room temperature, uncorrected) in this study and those of Berman & Kim (the more precise of the two previous studies) show remarkably good agreement. The worst disagreement in bond lengths is 1·5σ and that of angles 1·3σ. The standard deviations of bond lengths and angles of the present room-temperature study are about half those of Larsen & Jerslev (1966) and about the same as those of Berman & Kim (1967), but the low-temperature

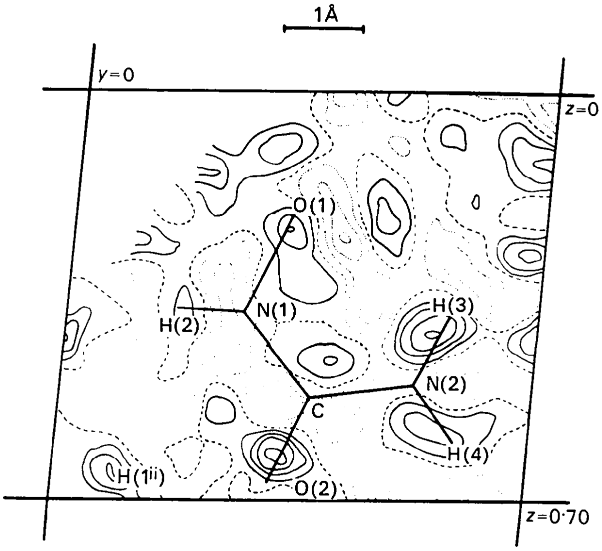

Fig. 2. Section, through the plane of the molecule, of the low-temperature difference synthesis. Positive, zero and negative contours are shown respectively by full, broken and dotted lines. The contour interval is 0·05 e Å^{-3}

values from the present study show an improvement over Berman & Kim's values. This improvement in accuracy combined with corrections for thermal motion represents a significant improvement over the earlier geometrical details and has enabled the equivalence of the C–N bonds and the non-equivalence of the two N–C–O angles to be confirmed at a higher level of precision.

A comparison of the room-temperature thermal parameters from the three studies can be made from Table 12 which shows that those from the present study lie between those of the two earlier studies, but as the early reports do not quote standard deviations for thermal parameters, no statistical comparison can be made.

Table 12. *Room-temperature* U_{ij} (*w.r.t. reciprocal axis*) ($\text{Å}^2 \times 10^2$)

First row: present work. Second row: Larsen & Jerslev (1966). Third row: Berman & Kim (1967).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	3 16	2 69	2·75	0·35	1·59	−0·23
	3·53	1·32	2·30	−0·43	1·74	−0·18
	2·75	2·09	2·53	0·43	1·37	0·22
N(1)	4·72	3·77	2·63	−0·97	2·03	−0·12
	5·20	3·09	2·67	1·18	2·25	0·27
	4·52	3·36	2·38	−1·10	1·81	−0·30
N(2)	4·14	3·40	2·95	−0·85	1·51	−0·13
	4·81	3·00	2·67	0·36	1·53	−0·09
	3·78	3·19	2·67	−0·72	1·35	0·10
O(1)	4·49	3·97	2·11	0·52	1·44	0·13
	4·97	2·99	2·01	−0·48	1·53	−0·14
	4·35	3·36	1·99	0·56	1·37	0·34
O(2)	4·58	3·80	2·40	−0·52	1·58	0·34
	4·91	2·95	2·32	0·33	1·86	−0·27
	4·07	3·47	2·21	−0·20	1·49	0·29

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The Key Shift Method. II. Application to Superstructures of Molecular Crystals

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(*Received* 28 *June* 1975; *accepted* 31 *July* 1975)

The key shift method, a kind of minimum residual method, has been successfully applied to the structure analysis of superstructures, one known and one unknown, of molecular crystals with eight and eleven non-hydrogen atoms respectively in the asymmetric units. In the latter case, symmetry considerations of the substructure–superstructure relationship were important for the solution. In another case of a known superstructure in which there were 30 independent non-hydrogen atoms at the start of the analysis, shifts of rigid-body molecules were found to be more efficient than those of individual atoms.

Introduction

The key shift method for the structure analysis of superstructures was proposed in a previous paper (Ito, 1973; hereinafter called paper I). The computational procedure is analogous to that of the minimum residual method of Bhuiya & Stanley (1963). Two superstructures of mineral crystals, freieslebenite and jordanite, were solved by this method (Ito & Nowacki, 1974*a*, *b*); a successful application to aramayoite has also been reported (Mullen & Nowacki, 1974). The present paper deals with the application of the method to superstructures of molecular crystals.

Application

The key shift method was first applied to a known structure, triclinic quinhydrone (T. Sakurai, 1965), and then to an unknown structure, 3-amino-4,5-dicyano-1-methylpyrazole (ADCMP) (Prusiner, Sundaralingam, Ito & Sakurai, 1976).

(*a*) *Triclinic quinhydrone*

The triclinic modification of quinhydrone, $C_6H_4O_2.C_6H_4(OH)_2$, is a 1:1 molecular complex of quinone and hydroquinone. The space group is $P\bar{1}$, $Z=1$. Since the hydroquinone and quinone molecules