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The Crystal and Molecular Structure of Biurea

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The structure of biurea, $(NH_2CONH)_2$, has been determined by Patterson methods and refined by full-matrix least-squares calculations to a final conventional R of 0·058 for the 528 observed reflexions. The data were collected on a Hilger and Watts four-circle diffractometer. The unit cell is monoclinic, $C2/c$, with $a = 15{\cdot}780$ (2), $b = 4{\cdot}637$ (1), $c = 9{\cdot}331$ (1) Å, $\beta = 133{\cdot}84$ (1)° and $Z = 4$. The molecules are held together by extensive hydrogen bonding, so that every H atom is bonded to an O atom in a neighbouring molecule. The N–N bond, 1·391 (4) Å, is one of the shortest reported for a N–N single bond.

Introduction

Biurea is used industrially as a high-temperature blowing agent for expanding plastics such as polypropylene. The thermal decomposition of biurea is currently being studied and the crystal structure has been determined in order to provide evidence to explain the mechanism of the solid-state decomposition.

Experimental

Crystals were grown from aqueous solution in the form of hexagonal platelets. Many of the crystals were twinned but after considerable searching a crystal suitable for X-ray examination was found.

Table 1. *Distribution statistics of normalized structure factors*

	Centric	Acentric	Experimental
$\langle\vert E\vert\rangle$	0·798	0·886	0·809
$\langle\vert E^2\vert\rangle$	1·000	1·000	1·000
$\langle\vert E^2-1\vert\rangle$	0·968	0·736	0·975
$\vert E\vert > 3{\cdot}0$	0·27 %	0·01 %	0·37 %
$\vert E\vert > 2{\cdot}0$	4·55	1·83	4·82
$\vert E\vert > 1{\cdot}0$	31·73	36·79	30·75

Crystal data

$C_2H_6N_4O_2$; M.W. 118·1, $a=15·780$ (2), $b=4·637$ (1), $c=9·331$ (1), $\beta=133·84$ (1)°, $U=492·5$ Å^3, $Z=4$, $D_m=1·583$ (by flotation), $D_x=1·593$ g cm^{-3}, $F(000)=256$. Absent reflexions: hkl when $h+k$ odd, $h0l$ when l odd, monoclinic space group $C2/c$ (No. 15) or Cc (No. 9) [E statistics (Table 1) and successful refinement indicate $C2/c$]. λ(Mo $K\bar{\alpha}$)$=0·7107$, μ(Mo)$=1·47$ cm^{-1}. Crystal size 0·57 × 0·43 × 0·02 mm.

Intensities

The intensities and refined cell dimensions were obtained from a Hilger and Watts Y290 four-circle diffractometer using an $\omega/2\theta$ scan with Mo $K\alpha$ radiation and a graphite monochromator. Out of 728 reflexions measured, 200 had intensities less than 3σ of the background and were classed as unobserved. Reflexions were measured out to a maximum θ of 30°. Lorentz and polarization corrections were applied to the net intensity counts but no corrections were made for absorption or extinction.

Structure determination

Since there are four molecules of $C_2H_6N_4O_2$ in the unit cell, they must occupy special positions in the space group $C2/c$. Positions (e) were chosen, which require the presence of twofold point-group symmetry in the molecule.

The positions of all atoms except H were found from Patterson and sharpened Patterson maps. Full-matrix least-squares refinement using unit weights converged to an R of 0·174. The refinement was continued with anisotropic temperature factors which further reduced R to 0·115. Inspection of the bond lengths from the C atom to the terminal N and O atoms revealed that these two atoms should be interchanged. With this exchange, R fell to 0·085. At this stage a difference synthesis was performed which revealed all the H atoms. Inclusion of these permitted refinement to a final R of 0·058 for the observed reflexions. Out of the 200 unobserved reflexions only 26 calculated greater than the observed values and of these only one calculated greater than 1·5 times its observed value. In the final cycles of refinement the following weighting scheme was used: $w=xy$; if $AF_o>|F_c|$, $w=10^{-10}$; if $\sin\theta>B$, $x=1$; otherwise $x=\sin\theta/B$; if $C>F_o$, $y=1$; otherwise $y=C/F_o$. Values of the constants chosen were $A=0·0$, $B=0·5$, $C=24·0$.

The scattering factors used for C, N and O were those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965).

All calculations were carried out with the X-RAY (1972) system of programs as implemented at the University of Manchester Regional Computer Centre.

Results

The final atomic coordinates and thermal parameters are given in Table 2.* A view of the molecule looking along **a** is shown in Fig. 1 together with the numbering system. Interatomic bond lengths are listed in Table 3.

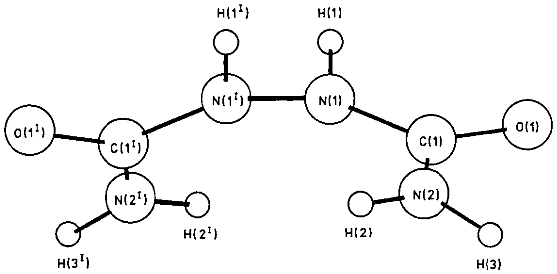

Fig. 1. View of the molecule (with numbering system) along **a**.

Table 3. *Bond lengths* (Å) *and angles* (°) *and their e.s.d.'s*

N(1)–N(1^I)	1·391 (4)	C(1)–N(1)–H(1)	121·9
N(1)–H(1)	0·982	C(1)–N(1)–N(1^I)	120·6 (3)
N(1)–C(1)	1·361 (2)	H(1)–N(1)–N(1^I)	112·5
C(1)–N(2)	1·324 (4)	C(1)–N(2)–H(2)	112·6
C(1)–O(1)	1·249 (4)	C(1)–N(2)–H(3)	122·1
N(2)–H(2)	0·867	H(2)–N(2)–H(3)	115·3
N(2)–H(3)	0·929	N(1)–C(1)–N(2)	118·1 (2)
		N(1)–C(1)–O(1)	118·7 (3)
		N(2)–C(1)–O(1)	123·2 (2)

Symmetry code

(I)	$\bar{x}$, y, $\frac{1}{2}-z$;	(IV)	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$
(II)	$\bar{x}$, $1-y$, $1-z$;	(V)	$\bar{x}$, $\bar{y}$, $1-z$
(III)	x, $\bar{y}$, $\frac{1}{2}+z$;		

Table 2. *Fractional coordinates, thermal parameters* (Å^2) *for the expressions exp* $[-2\pi^2(U_{11}a^{*2}h^2+\dots+2U_{23}b^*c^*kl+\dots)]$, *exp* $[-8\pi^2U\sin\theta^2/\lambda^2]$, *and their e.s.d.'s* (*all quantities* × 10^4)

	x	y	z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	76 (2)	3346 (5)	3328 (2)	323 (9)	415 (11)	162 (2)	46 (8)	165 (7)	15 (7)
N(2)	1601 (2)	109 (5)	4914 (3)	370 (10)	580 (15)	212 (8)	159 (10)	196 (8)	70 (9)
C(1)	995 (2)	1922 (5)	5013 (3)	247 (9)	377 (12)	179 (8)	−51 (9)	140 (8)	−19 (8)
O(1)	1206 (1)	2325 (4)	6558 (2)	329 (8)	478 (11)	167 (6)	−14 (7)	169 (6)	−23 (7)
H(1)	−294	5017	3358	380					
H(2)	1471	−94	3852	380					
H(3)	2176	−1090	5967	380					

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31360 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen-bond lengths and angles*

See Table 3 for symmetry code.

Type	N–H···O	N–O (Å)	∠N–H···O (°)	∠H–N···O (°)
A	$N(1^{II})-H(1^{II})\cdots O(1)$	2·903 (3)	167·4	8·4
B	$N(2^{III})-H(2^{III})\cdots O(1)$	2·961 (3)	161·0	13·1
C	$N(2^{IV})-H(3^{IV})\cdots O(1)$	2·949 (2)	157·3	16·2

Discussion

Knipe & Menary (1958) have reported powder data for biurea consistent with a triclinic cell ($a=4{\cdot}74$, $b=7{\cdot}22$, $c=10{\cdot}70$ Å, $\alpha=108{\cdot}90°$, $\beta=119{\cdot}03°$, $\gamma=107{\cdot}63°$). The present monoclinic cell can be transformed to a triclinic cell of dimensions $a=4{\cdot}637$, $b=8{\cdot}224$, $c=10{\cdot}42$ Å, $\alpha=118{\cdot}01°$, $\beta=116{\cdot}43°$ and $\gamma=106{\cdot}37°$. This cell gives better agreement with Knipe & Menary's published data and also predicts a density closer to the experimental one.

The crystal structure comprises biurea molecules linked together by a three-dimensional network of N–H···O hydrogen bonds. Each O atom is involved in close contacts with three separate NH groups as shown in Fig. 2. The geometry of these contacts is summarized in Table 4. The molecule is therefore involved in a total of six donating and six accepting hydrogen bonds. The only other intermolecular contacts of any significance are $O(1)\cdots N(1^{V})$ 3·363 (3) Å and $C(1)\cdots O(1^{V})$ 3·321 (3) Å, which are normal van der Waals contacts.

The N–C and C–O bond lengths compare well with those found in urea (Caron & Donohue, 1964). The N–N bond is one of the shortest reported for a N–N single bond although it agrees well with a value of 1·392 (7) found in diformylhydrazine (Tomiie, Koo & Nitta, 1958) and one of 1·39 (2) reported for β,β'-dimethylcinnamaldazine (Lepicard, Berthou, Delettré, Laurent & Mornon, 1973).

The asymmetric unit in the molecule is planar except for the H atoms (Table 5) but the molecule as a whole is non-planar since the two symmetry-related halves of the molecule are inclined at 83·6° to one another. There are two separate bond rotations which cause this non-planarity. Firstly a rotation about the N–N bond which causes the planes through N(1), $N(1^{I})$, $C(1^{I})$ and $N(1^{I})$, N(1), C(1) to be inclined at 68·7°, and secondly rotations about N(1)–C(1) and $N(1^{I})$–$C(1^{I})$ directions which cause the planes through N(1), C(1), N(2), O(2) and $N(1^{I})$, $C(1^{I})$, $N(2^{I})$, $O(1^{I})$ to be inclined at 83·6°.

Table 5. *Least-squares plane through* N(1), C(1), O(1) *and* N(2), *and atom deviations* (Å)

The equation of the plane is expressed as:

$$9{\cdot}574X+3{\cdot}458Y-2{\cdot}320Z=0{\cdot}462$$

N(1)	−0·003	H(1)	0·207
N(2)	−0·003	H(2)	0·047
C(1)	0·009	H(3)	−0·101
O(1)	0·003		

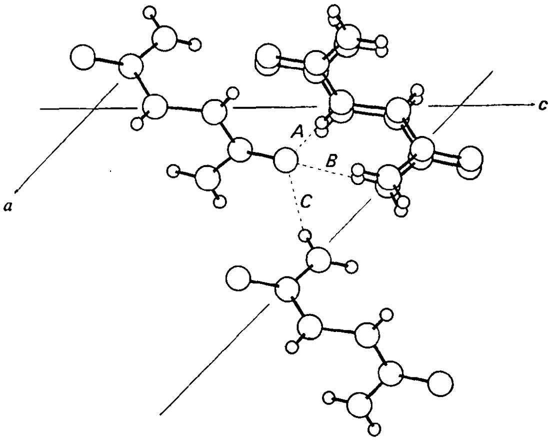

Fig. 2. View of part of the unit cell along **b** showing the three types of hydrogen bonds.

The shape of the molecule can be explained by considering the following interactions. The repulsion of the lone pairs on the adjacent N atoms will be very strong due to their *pπ* nature and a rotation about the N–N bond will reduce this interaction. However, as the N–N bond rotates the two C atoms start to approach each other. Thus the final degree of rotation (68·7°) is a compromise between lowering the repulsion of the lone pairs and not allowing the two C atoms to approach too closely. The final contact distance between these two atoms is 3·384 (3) Å. The further rotation about the N–C bonds may be imposed by the geometry of the hydrogen-bonding system.

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