

only 11.26°. The C-CH<sub>3</sub> bond lengths have a mean value of 1.49 (1) Å.

There is no evidence of free rotation of any methyl group. The abnormally short C(4)-H(42) bond distance of 0.73 Å arises as a result of the disorder of C(4). The remaining C-H bond distances vary between 0.89 and 1.07 Å.

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## The Crystal Structure of the 1:1 Complex between Quinol and Urea

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(Received 31 July 1974; accepted 12 September 1974)

The complex is monoclinic, space group  $P2_1/c$ , with  $a=17.180$  (2),  $b=6.601$  (1),  $c=7.341$  (1) Å,  $\beta=94.4$  (1)°,  $Z=4$ . The structure was solved by direct methods and refined by full-matrix least-squares calculations to a final  $R$  of 0.059 for 1615 reflexions. The structure consists of alternate sheets parallel to (100) of quinol and urea molecules hydrogen-bonded together. Each oxygen atom of urea receives hydrogen bonds of lengths 2.683 (2) and 2.702 (2) Å from the OH groups of quinol molecules on either side of it in the  $x$  direction thus forming infinite chains. In addition, two of the N-H bonds of urea link to the oxygen atoms of two quinol molecules in the adjacent chain along the  $y$  direction at distances 2.980 (2) and 3.049 (3) Å and a third N-H hydrogen bonds to a quinol oxygen atom in an adjacent chain along the  $z$  direction at a distance of 3.048 (3) Å. The fourth N-H does not form a hydrogen bond.

#### Introduction

The crystal structure of the 1:1 complex between quinol, HO.C<sub>6</sub>H<sub>4</sub>.OH, and urea, CO(NH<sub>2</sub>)<sub>2</sub>, was determined as part of a series of studies of complexes formed by phenols. Each of the components is capable of forming a hydrogen-bonded framework structure which can accommodate other molecules, in cages in the case of quinol, or in channels in the case of urea. It is therefore of interest to determine the type of association which occurs when these molecules complex together.

#### Experimental

##### Crystal data

C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>.CON<sub>2</sub>H<sub>4</sub>,  $M_r=170.16$ . Monoclinic,  $a=17.180$  (2),  $b=6.601$  (1),  $c=7.341$  (1) Å,  $\beta=94.4$  (1)°;  $U=830.09$  Å<sup>3</sup>,  $D_m=1.355$  (9) g cm<sup>-3</sup>,  $Z=4$ ,  $D_c=1.360$  g cm<sup>-3</sup>;  $F(000)=360$ , Mo  $K\alpha$  ( $\lambda=0.71069$  Å),  $\mu=1.16$  cm<sup>-1</sup>. Space group  $P2_1/c$  from systematic absences.

Colourless crystals of the complex were deposited when warm solutions of 1 g of quinol in 2.5 cm<sup>3</sup> of

water (to which 0.2 g of sodium sulphite were added to prevent oxidation) and 0.555 g of urea in 0.5 cm<sup>3</sup> of water were mixed and allowed to cool. Crystals more suitable for X-ray work were obtained by recrystallization from propanol. Oscillation and Weissenberg photographs established the space group and gave approximate cell dimensions. The density was determined by flotation in mixtures of chloroform and i-hibisol. A crystal of maximum dimension 0.6 mm was mounted on a Hilger and Watts, computer-controlled, four-circle diffractometer and intensities for all reflexions having  $\theta \leq 30^\circ$  were determined with Mo  $K\alpha$  radiation, a  $\theta/2\theta$  scan and a scintillation counter. Of the 2490 reflexions so measured, 1615 had net counts greater than three standard deviations of the total count and were therefore regarded as 'observed'. The intensities were corrected for Lorentz and polarization factors but not for absorption.

#### Structure determination and refinement

The solution of the structure was by direct methods. The observed and unobserved reflexions were used to obtain a scaling curve in a manner based on Wilson's

Table 1. Final fractional atomic coordinates and thermal parameters (all  $\times 10^4$  for C, O and N and  $\times 10^3$  for H)

$U$  is the mean square amplitude of vibration in  $\text{\AA}^2$  and the temperature factor is given by

$$\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + hkU_{12}a^*b^* + hlU_{13}a^*c^* + klU_{23}b^*c^*)].$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	4780 (1)	1358 (3)	1301 (3)	339 (9)	344 (9)	427 (10)	-55 (8)	77 (8)	-120 (8)
C(2)	4248 (1)	-24 (3)	552 (3)	243 (7)	277 (8)	350 (9)	-2 (6)	52 (6)	18 (7)
C(3)	4462 (1)	-1381 (3)	-756 (3)	298 (8)	366 (9)	444 (10)	-84 (7)	56 (8)	-109 (8)
C(4)	245 (1)	1523 (3)	1215 (3)	316 (9)	346 (9)	420 (10)	21 (8)	64 (8)	-83 (8)
C(5)	763 (1)	9 (3)	787 (3)	273 (8)	309 (9)	354 (9)	67 (7)	50 (7)	16 (7)
C(6)	516 (1)	-1514 (3)	-417 (3)	310 (8)	313 (9)	438 (10)	52 (7)	87 (7)	-55 (8)
C(7)	2473 (1)	5318 (3)	750 (3)	294 (8)	276 (8)	427 (10)	2 (7)	14 (7)	-5 (7)
O(1)	3504 (1)	8 (2)	1149 (2)	273 (6)	342 (7)	543 (8)	-28 (5)	125 (6)	-41 (6)
O(2)	1509 (1)	85 (2)	1622 (2)	278 (6)	410 (8)	578 (9)	47 (6)	-26 (6)	-82 (7)
O(3)	2447 (1)	7177 (2)	405 (2)	331 (7)	246 (6)	666 (10)	-1 (4)	88 (7)	15 (6)
N(1)	2032 (1)	4490 (3)	1972 (3)	708 (14)	378 (10)	695 (14)	-7 (10)	357 (12)	31 (10)
N(2)	2945 (1)	4090 (3)	-94 (3)	524 (11)	338 (9)	677 (13)	106 (8)	237 (10)	35 (9)

(1942) method. This curve was used to convert the  $F$  values into  $E$  values and 148 reflexions with  $E > 1.9$  were used as input to *MULTAN* (Germain, Main & Woolfson, 1971). Sixteen sets of signs were deduced for the 148 reflexions and  $E$  maps were calculated for the two sets of signs having the highest figures of merit. The set with the second highest figure of merit (1.0613) gave a map having a chemically reasonable set of peaks corresponding to all the non-hydrogen atoms in the structure. The quinol molecules occur in two independent twofold special positions lying across centres of symmetry at 000 and  $\frac{1}{2}00$  and have different orientations.

Four cycles of full-matrix, least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms reduced  $R$  from 0.455 to 0.147. The resulting structure factors were used to compute a difference map and this showed peaks at all the positions where hydrogen atoms were expected. Hydrogen atoms were introduced into the refinement at these peak positions. Thermal parameters for the heavier atoms were allowed to become anisotropic and a weighting scheme was introduced:  $w = 1/\{1 + [(F_o -$

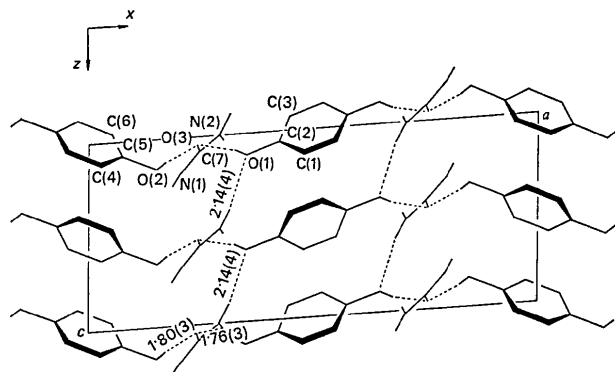


Fig. 1. The structure projected along the  $y$  axis showing the O-H...O hydrogen bonds within sheets of molecules parallel to (001) at  $z=0$  and  $z=\frac{1}{2}$  and the one N-H...O hydrogen bond per asymmetric unit which connects these sheets (H...O distances in  $\text{\AA}$ ).

Table 1 (cont.)

	$x$	$y$	$z$	$U$
H(1)	458 (2)	232 (5)	216 (5)	43 (9)
H(2)	320 (2)	-103 (5)	84 (4)	29 (8)
H(3)	406 (2)	-237 (5)	-121 (4)	35 (8)
H(4)	44 (2)	263 (5)	211 (4)	38 (9)
H(5)	177 (2)	-100 (4)	120 (4)	28 (7)
H(6)	89 (2)	-253 (4)	-71 (4)	27 (8)
H(7)	196 (2)	318 (5)	203 (5)	43 (9)
H(8)	184 (2)	542 (6)	271 (6)	57 (11)
H(9)	300 (2)	273 (5)	24 (4)	33 (8)
H(10)	319 (2)	459 (5)	-112 (5)	47 (10)

$B)/A]^2\}$  where  $A$  and  $B$  were given the values 9.0 and 3.0, respectively, and  $F_o$  was on the absolute scale. After six further cycles of refinement under these conditions  $R$  converged to 0.059, the largest shifts being about half the corresponding standard deviations. One fairly weak reflexion (14,1,3) was omitted from the least-squares sums in the last two cycles because it had a weighted  $\Delta F$  much larger than average.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and thermal parameters are listed in Table 1. Least-squares planes were calculated for each of the three independent molecules and the results are given in Table 2.\*

Apart from the *MULTAN* program referred to above, the computer programs used were *SAP 1* and *SAP 2* from the NRC crystallographic programs written by F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Saunderson, the X-RAY system of programs edited by J. M. Stewart, F. A. Kundell and J. C. Baldwin, and the *MANTAP*, *DRAWCELL* and *MOLPLOT* programs written by T. J. King of Nottingham University.

\* A comparison of observed and final calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30661 (8 pp.). Copies of this table may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Details of molecular planes (distances in Å)

	Atoms defining plane	Distance out of plane	Atoms not defining plane	Distance out of plane
Plane 1*	C(1)	0.0038 (20)	H(1)	0.055 (35)
	C(2)	0.0004 (18)	H(2)	-0.172 (30)
	C(3)	0.0037 (20)	H(3)	-0.031 (31)
	O(1)	-0.0021 (14)		
Plane 2*	C(4)	-0.0013 (20)	H(4)	0.004 (32)
	C(5)	0.0056 (18)	H(5)	0.004 (29)
	C(6)	-0.0014 (20)	H(6)	0.018 (29)
	O(2)	-0.0021 (15)		
Plane 3	C(7)	0.0000 (19)	H(7)	-0.188 (33)
	N(1)	0.0000 (24)	H(8)	0.233 (39)
	N(2)	0.0000 (21)	H(9)	0.083 (30)
	O(3)	0.0000 (15)	H(10)	-0.169 (35)

## Equations of the planes

Plane 1  $-3.917x + 4.321y - 5.147z + 1.958 = 0$

Plane 2  $5.972x + 3.628y - 5.756z = 0$

Plane 3  $11.565x + 1.071y + 4.902z - 3.797 = 0$

\* Each quinol plane was calculated with the atoms shown and the atoms related to these by a centre of symmetry at the centre of the molecule.

## Description and discussion of the structure

Fig. 1 shows the structure projected along  $y$ . It consists of alternate layers of quinol and urea molecules parallel to (100) but the molecules are so arranged that they are hydrogen-bonded mainly into sheets parallel to (001). The strongest hydrogen bonds are those formed between the OH groups at each end of the two independent quinol molecules and O(3) of the urea molecules. These are of length 2.633 (2) Å between O(1) and O(3) and 2.702 (2) Å between O(2) and O(3) and they may be compared with the average length of 2.72 Å reported by Wallwork (1962) for OH...O hydrogen bonds. They link alternate quinol and urea molecules into infinite chains parallel to  $x$ . These chains are further hydrogen-bonded together to form the sheets parallel to (001) by two N-H...O hydrogen bonds of length 2.980 (2) and 3.049 (3) from each urea molecule to two quinol molecules in an adjacent chain in the  $y$  direction. These are somewhat longer than the average N-H...OH hydrogen-bond distance of 2.94 Å found by Wallwork (1962). The molecular arrangement in such a sheet at  $z=0$  is illustrated in Fig. 2; the sheet at  $z=\frac{1}{2}$  is related to this by the operation of the  $c$ -glide plane. Finally these sheets are weakly linked together side-

ways in the  $z$  direction by N-H...O hydrogen bonds of length 3.048 (3) Å from each urea molecule in one sheet to the nearest quinol OH in the next. In this way each quinol oxygen atom of type O(1) donates one hydrogen bond and receives two, giving it a roughly tetrahedral environment but each quinol oxygen atom of type O(2) donates one hydrogen bond and receives one and has one tetrahedral position unoccupied. All the quinol OH groups and three of the four hydrogen

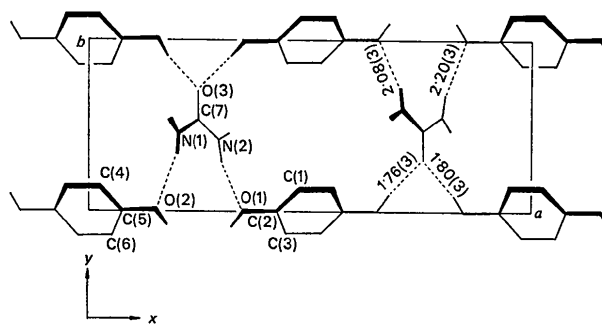
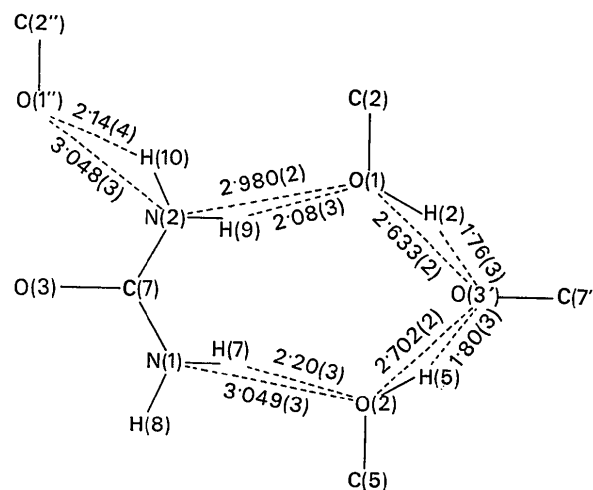
Fig. 2. One hydrogen-bonded sheet of molecules at  $z=0$  (H...O distances in Å).Fig. 3. Schematic diagram showing hydrogen-bond distances (in Å). (Primed atoms are related to unprimed atoms by the operation  $x, y-1, z$  and double-primed atoms are related by  $x, \frac{1}{2}-y, -\frac{1}{2}+z$ .)

Table 3. Angles in the hydrogen-bond system (°)

C(2)—O(1)...O(3')	124.2 (1)	C(5)—O(2)...O(3')	112.7 (1)
C(2)—O(1)...N(2)	101.6 (1)	C(5)—O(2)...N(1)	109.3 (1)
C(2)—O(1)...H(9)	106.5 (8)	C(5)—O(2)...H(7)	113.8 (8)
C(2'')—O(1'')...N(2)	130.8 (1)	C(7)—N(2)...O(1)	126.9 (2)
C(2'')—O(1'')...H(10)	127.5 (9)	C(7)—N(2)...O(1'')	123.2 (2)
C(7)—N(1)...O(2)	120.9 (2)	C(7')—O(3')...O(2)	129.9 (1)
C(7')—O(3')...O(1)	129.8 (1)	C(7')—O(3')...H(5)	127.1 (10)
C(7')—O(3')...H(2)	127.4 (10)	H(2)...O(3')...H(5)	88 (1)
O(1)...O(3')...O(2)	81.2 (1)	O(2)—H(5)...O(3')	169 (3)
O(1)—H(2)...O(3')	169 (3)	N(2)—H(9)...O(1)	161 (3)
N(1)—H(7)...O(2)	163 (3)	N(2)—H(10)...O(1'')	162 (3)

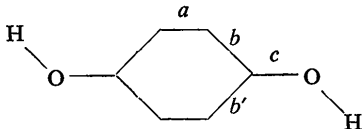
atoms on each urea molecule are thus involved in hydrogen bonding. The details of the hydrogen-bond geometries are shown in Fig. 3 and Table 3.

The structure shows many points of similarity to that of the 1:1 complex between quinol and acetone (Lee & Wallwork, 1959). In that structure there were alternate layers of quinol and acetone molecules, each layer having a similar structure to the corresponding layer in the present structure. The molecules were hydrogen-bonded into chains by similarly arranged  $\text{OH}\cdots\text{CO}\cdots\text{HO}$  hydrogen bonds and the main point of difference from the present structure is that there was no possibility of further hydrogen bonding of these chains to form sheets. The  $\text{OH}\cdots\text{O}$  hydrogen bonds to acetone were weaker, having a length of 2.74 Å.

The dimensions of the two crystallographically independent quinol molecules are shown in Fig. 4. Table 4 shows that there is good agreement between the two molecules in the present structure and dimensions previously determined. The only consistent pattern that emerges from the table is the enlargement of the C—C—O angle ( $b'c$ ) on the side of the molecule nearest to the hydrogen atom of the OH group, owing to  $\text{H}\cdots\text{H}$  and  $\text{H}\cdots\text{C}$  repulsions, and the consequent reduction in the other C—C—O angle ( $bc$ ). This divergence from  $mmm$  symmetry does not seem to affect the rest of the dimensions and, in addition, the benzene ring seems to approximate very closely to a regular hexagon. The mean C—O distance for all the determinations in the table is 1.384 Å.

Table 4. Comparison of average dimensions of quinol molecules

Bond lengths in Å, bond angles in degrees; standard deviations refer to the separate values averaged.

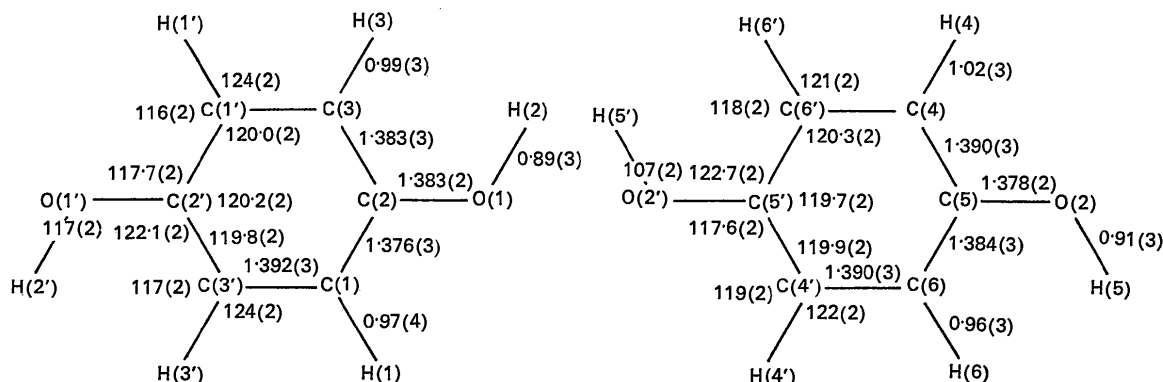


	<i>a</i>	<i>b</i>	<i>b'</i>	<i>c</i>	<i>ab</i>	<i>ab'</i>	<i>bb'</i>	<i>bc</i>	<i>b'c</i>
$\gamma$ -Quinol* (Maartmann-Moe, 1966)	1.401 (6)	1.365 (6)	1.384 (6)	1.392 (5)	118.1 (5)	121.0 (5)	120.9 (5)	118.6 (5)	120.5 (5)
<i>p</i> -Benzoquinone complex (Sakurai, 1965)	1.401 (6)	1.380 (6)	1.366 (6)	1.394 (5)	119.2 (5)	119.8 (5)	121.1 (5)	117.5 (5)	121.4 (5)
Lumiflavinium bromide complex§ (Tillberg & Norrestam, 1972)	1.387 (8)	1.365 (8)	1.396 (8)	1.385 (8)	120.2 (5)	118.9 (5)	120.8 (5)	117.9 (5)	121.3 (5)
Lumiflavinium chloride complex (Karlsson, 1972)	1.384 (10)	1.380 (10)	1.376 (9)	1.384 (8)	119.6 (6)	120.3 (6)	120.2 (6)	118.3 (6)	121.7 (6)
Urea complex (present work)	1.397 (9)	1.363 (10)	1.374 (9)	1.393 (7)	120.7 (6)	118.3 (6)	121.0 (6)	118.1 (6)	120.9 (6)
	1.382 (5)	1.372 (5)	1.392 (5)	1.369 (5)	120.5 (5)	119.2 (5)	120.2 (5)	118.4 (5)	121.4 (5)
	1.375 (5)	1.387 (5)	1.384 (5)	1.381 (5)†	120.6 (5)	120.0 (5)	119.5 (5)	118.0 (5)	122.5 (5)
	1.390 (3)	1.390 (3)	1.384 (3)	1.378 (2)	119.9 (2)	120.3 (2)	119.7 (2)	117.6 (2)	122.7 (2)
	1.392 (3)	1.376 (3)	1.383 (3)	1.383 (2)	120.0 (2)	119.8 (2)	120.2 (2)	117.7 (2)	122.1 (2)

\* Standard deviations estimated.

† One value (the second value, 1.344, seems incorrect).

§ The first molecule has a *cis* arrangement of hydrogen bonds.



Molecule at  $\frac{1}{2}00$

Molecule at 000

Fig. 4. Dimensions of the two independent quinol molecules. (Distances in Å and angles in degrees.)

The dimensions of the urea molecule are shown in Fig. 5. The C=O bond length is identical with the value reported by Pryor & Sanger (1970) from neutron data without correction for librational motion. It is slightly smaller than the values obtained from various refinements based on X-ray data (Vaughan & Donohue, 1952; Caron & Donohue, 1964; Pryor & Sanger, 1970). The C-N distances 1.335 (3) and 1.332 (3) are in good agreement with each other and with the values obtained from the X-ray and neutron data before correction for librational motion. The bond angles involving C, N and O are also in good agreement with the previous X-ray and neutron diffraction values.

The C and O skeletons of both quinol molecules and the C, N and O skeleton of the urea molecule are all planar within experimental error, but the OH hydrogen H(2) is slightly but significantly (*ca* 5 $\sigma$ ) out of the quinol plane to which it is attached. This corresponds to a dihedral angle of 12° between the plane C(2)O(1)H(2) and the quinol plane. All the hydrogen atoms of urea apart from H(9) are significantly out of the urea plane, the NH<sub>2</sub> group N(1)H(7)H(8) being twisted by 16° and N(2)H(9)H(10) by 10°. The plane of the quinol molecule centred at the origin of the cell makes a dihedral angle of 40.6° with the (001) plane and its O-O axis is inclined at 25.2° to this plane. The corresponding angles for the quinol molecule centred at  $\frac{1}{2}00$  are 43.9° and 17.6°, and the plane of the urea skeleton makes a dihedral angle of 43.8° with (001).

We thank the Ministry of Higher Education and Scientific Research of Iraq for a maintenance grant (to M.M.M.), the Science Research Council for contributing to the cost of the diffractometer, the Director of the Cripps Computing Centre of Nottingham Univer-

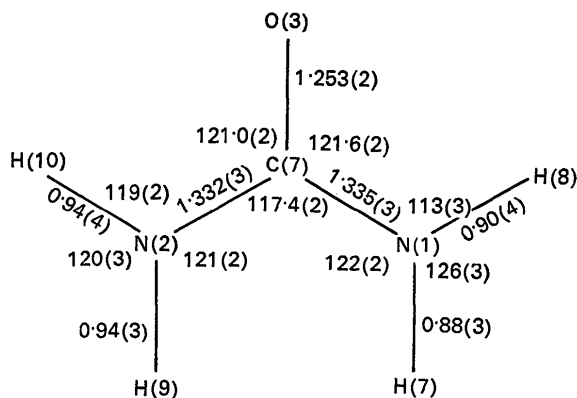


Fig. 5. Dimensions of the urea molecule (distances in Å and angles in degrees).

sity for computing facilities, and the authors of all the computer programs used.

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