THE CRYSTAL STRUCTURE OF THIOUREA.

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Introduction. Now that the crystal structure of urea CON_2H_4 has been determined by Mark and Weissenberg,[1] it may be of interest to see if there is any structural relationship between the crystals of this compound and those of an analogous one, thiourea CSN_2H_4. The present investigation was made on the thiourea crystals by the Laue photographic and the X-ray spectrometric methods, of which the procedure are almost the same as already described in detail in a paper by one of the present authors.[2] Groth[3] gives the following data concerning the crystals of this compound:

Orthorhombic bipyramidal, $a : b : c = 0.7163 : 1 : 1.1155$.
Specific gravity, 1.406.
Cleavage, $b\{010\}$ and $r\{101\}$ perfect.

As to the specific gravity, a value 1.450 considerably deviating from the above is also quoted as obtained in some occasion.[3] Hence another determination was made by means of a Westphal balance, which gave 1.407 in good agreement with the first-mentioned value.

The Unit of Structure. Thiourea from C.A.F. Kahlbaum was recrystallized from aqueous solution. In a case of rapid crystallization from somewhat supercooled solution, transparent six-sided plates of a few square millimetres were obtained. A Laue photograph taken with the X-rays[4] incident normally to the plate showed that this plate was parallel to the crystallographic $c(001)$ plane. In most cases of slow crystallization there grew thick prisms with rhombic bases. Several Laue photographs were obtained with a cleaved slip from the crystal, and it was found that the cleavage plane was $b(010)$. In Table 1 are given the Laue photographic data.

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(1) H. Mark and K. Weissenberg, *Z. Physik*, **16** (1923), 1.
(2) I. Nitta, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **4** (1926), No. 47, 49.
(3) P. v. Groth, "Chemische Krystallographie," 3. Teil, (1910), 555.
(4) X-rays from a Coolidge tube with tungsten anticathode.

TABLE 1. Laue Photographic Data.

hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
(201)	8.61	0.31	0.1055	mw	(015)	21.0	0.235	0.0515	f
(211)	9.61	0.295	0.0955	w	$(01\bar{5})$	„	0.20	0.044	f
(031)	9.80	0.295	0.094	f	(214)	21.6	0.25	0.0535	mw
(221)	12.61	0.26	0.072	w	$(\bar{2}1\bar{4})$	„	0.185	0.0395	m
(231)	17.61	0.225	0.054	s	(312)	21.8	0.25	0.0535	ms
(301)	18.35	0.215	0.0505	vs	$(\bar{3}1\bar{2})$	„	0.18	0.0385	s
(141)	18.75	0.220	0.0505	s	(115)	23.0	0.235	0.0495	f
(321)	22.4	0.20	0.0425	m	$(\bar{1}1\bar{5})$	„	0.185	0.0385	f
(251)	33.6	0.17	0.029	w	(313)	25.8	0.23	0.0455	f
(341)	34.4	0.165	0.0285	w	$(\bar{3}1\bar{3})$	„	0.165	0.0325	w
(061)	36.8	0.16	0.0265	f	(215)	28.8	0.215	0.0405	m
(161)	38.8	0.16	0.0255	f	$(\bar{2}1\bar{5})$	„	0.155	0.029	ms
(512)	53.2	0.25	0.0345	f	$(\bar{3}2\bar{3})$	„	0.34	0.0635	w
(532)	61.2	0.24	0.0305	f	(314)	31.4	0.215	0.038	ms
(013)	8.20	0.365	0.1275	f	$(\bar{3}1\bar{4})$	„	0.145	0.0255	ms
$(01\bar{3})$	„	0.33	0.116	mw	(116)	31.8	0.205	0.0365	ms
(210)	8.81	0.37	0.124	w	$(\bar{1}1\bar{6})$	„	0.155	0.0275	ms
$(\bar{2}10)$	„	0.305	0.103	m	(411)	33.0	0.205	0.036	f
(211)	9.61	0.355	0.115	mw	$(\bar{4}1\bar{1})$	„	0.14	0.0245	f
$(\bar{2}1\bar{1})$	„	0.29	0.0935	m	$(\bar{3}2\bar{4})$	34.4	0.305	0.0525	w
(212)	12.01	0.325	0.0935	w	(126)	34.8	0.355	0.060	f
$(\bar{2}1\bar{2})$	„	0.255	0.0735	mw	$(\bar{1}2\bar{6})$	„	0.315	0.0535	f
(014)	13.80	0.285	0.077	w	$(\bar{4}2\bar{1})$	36.0	0.30	0.050	f
$(01\bar{4})$	„	0.25	0.0675	w	(217)	37.6	0.175	0.029	mw
(114)	15.75	0.28	0.070	mw	(315)	38.6	0.20	0.032	f
$(\bar{1}1\bar{4})$	„	0.225	0.0565	vs	(413)	39.4	0.195	0.0315	mw
(213)	16.01	0.285	0.071	mw	$(\bar{4}1\bar{3})$	„	0.125	0.020	f
$(\bar{2}1\bar{3})$	„	0.215	0.0535	s	(325)	41.6	0.345	0.0535	w
(310)	18.55	0.26	0.0605	mw	$(\bar{3}2\bar{5})$	„	0.275	0.043	mw
$(\bar{3}10)$	„	0.205	0.0475	ms					

TABLE 1 *Continued*

$h\,k\,l$	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	$h\,k\,l$	$\frac{b^2}{d_2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
(423)	42.4	0.345	0.053	f	($\bar{5}30$)	57.8	0.365	0.048	w
($\bar{4}2\bar{3}$)	„	0.275	0.042	f	(523)	60.0	0.29	0.0375	f
(027)	43.2	0.32	0.049	w	($\bar{5}2\bar{3}$)	„	0.225	0.029	f
(02$\bar{7}$)	„	0.285	0.0435	mw	(327)	60.8	0.29	0.037	f
(414)	45.0	0.185	0.028	f	($\bar{3}2\bar{7}$)	„	0.225	0.029	w
(127)	45.2	0.32	0.0475	w	($\bar{5}3\bar{2}$)	61.0	0.355	0.0455	w
($\bar{1}2\bar{7}$)	„	0.275	0.0405	w	(524)	65.6	0.28	0.0345	f
(316)	47.4	0.18	0.025	w	($\bar{5}2\bar{4}$)	„	0.215	0.0265	f
(510)	49.8	0.175	0.0245	mw	(534)	70.6	0.39	0.0465	f
(227)	51.0	0.305	0.043	f	($\bar{5}3\bar{4}$)	„	0.325	0.0385	w
($\bar{2}2\bar{7}$)	„	0.25	0.035	f	(129)	70.8	0.26	0.031	f
(415)	52.2	0.175	0.0245	w	($\bar{1}2\bar{9}$)	„	0.215	0.0255	f
(512)	53.0	0.17	0.0235	w	(525)	72.8	0.265	0.031	f
(521)	53.6	0.30	0.041	f	($\bar{5}2\bar{5}$)	„	0.20	0.023	f
($\bar{5}2\bar{1}$)	„	0.24	0.033	f	(631)	80.1	0.365	0.041	w
(118)	54.2	0.16	0.022	f	($\bar{6}3\bar{1}$)	„	0.305	0.034	w
(522)	56.0	0.30	0.040	f	(536)	86.6	0.36	0.0385	f
($\bar{5}2\bar{2}$)	„	0.235	0.0315	f	($\bar{5}3\bar{6}$)	„	0.29	0.031	f
(128)	57.2	0.285	0.038	w	(721)	100.4	0.23	0.023	f
($\bar{1}2\bar{8}$)	„	0.24	0.032	w					

Note: In this Table vs, s, ms, m, mw, w and f represent very strong, strong, medium strong, medium, medium weak, weak and faint.

The dimensions of the unit cell found from the spectrometric measurements are:

$$a = 5.47,\ b = 7.64,\ \text{and}\ c = 8.54\ \text{Å.},$$

the axial ratio being thus $a:b:c = 0.716:1:1.118$. The number of chemical molecules CSN_2H_4 in the unit cell is four, and followingly the calculated density is 1.408. These values of the axial ratio and the density are in good agreement with the above-mentioned values obtained by other means than X-rays. In Table 2 are shown the results of the measurements with the ionization spectrometer.

TABLE 2.

X-ray Spectrometric Data.

hkl	Spacing		Comparative Intensities of Reflection							
	Calc.	Obs.	I	II	III	IV	V	VI	VII	VIII
(100)	5.48	5.48	0 (0)	60 (55)	0 (0)	7 (8.6)	0 (0)	0 (2.1)	0 (0)	0 (2.9)
(010)	7.65	7.64	0 (0)	200 (274)	0 (0)	0 (2.3)	0 (0)	5.2 (5.4)	0 (0)	2 (3.2)
(001)	8.54	8.54	0 (0)	220 (280)	0 (0)	22 (29)	0 (0)	31 (36)	0 (0)	13 (18)
(021)	3.49	3.48	80 (90)	16 (22)						
(011)	5.70	5.70	0 (0)	80 (89)	0 (0)	16 (18)				
(012)	3.73	3.73	0 (0)	40 (24)						
(201)	2.61	2.61	0 (0)	16 (13)						
(101)	4.61	4.60	45 (83)	9 (14)	13 (14)	20 (11)				
(102)	3.37	3.37	0 (0)	18 (19)						
(210)	2.58	2.58	0 (0.9)	10 (9)	1 (4)					
(110)	4.45	4.46	170 (183)	0 (3.3)	0 (2.7)	10 (8.5)				
(120)	3.14	3.13	210 (141)	15 (21)	3 (7)					

The Space Group. On inspecting the data in Tables 1 and 2, various reflecting planes were found to show the following characteristics:

(1) In the first order reflection from pyramidal planes, there are all kinds of combinations of even and odd integers for their indices h, k and l.

(2) No odd order reflection is observed from any of the planes (100), (010) and (001).

(3) All prismatic planes are divided into two groups, (A) and (B):

(A) The prismatic planes, having the indices of (zero, even, odd), (odd, zero, odd), (odd, odd, zero), (odd, even, zero) or (even, odd, zero), show odd order reflections; e. g. (021), (061), (027), (101), (301), (110), (310), (510), (120), (210).

(B) Those, having the indices of (zero, odd, odd), (zero, odd, even), (even, zero, odd) or (odd, zero, even), show no odd order reflection; e. g. (011), (012), (201), (102).

From (1) it is obvious that the corresponding space group should be one of those that are based upon the simple orthorhombic translation group

Γ_0; viz. one of the space groups C_{2v}^1 to C_{2v}^{10}, V^1 to V^4, and V_h^1 to V_h^{16}.[1] While, in the general criteria of the space groups, the conditions for the presence of certain reflection may not fully correspond to the experimental data, all the requirements for the absence should be necessarily satisfied, or, in the present case, any space group that is in conflict with the evidence (3A) can never be chosen as the corresponding one. Accordingly (3A) was first used to sort out the possible space groups, and these were found to be C_{2v}^1, C_{2v}^2, C_{2v}^4, C_{2v}^7, C_{2v}^9, V^1, V^2, V^3, V^4, V_h^1, V_h^5, V_h^{13} and V_h^{16}. Of these space groups C_{2v}^9 and V_h^{16} are fitted exactly to all the conditions (1) to (3), whereas the rest may show odd order reflections from more sorts of planes than those in (3A). As already noticed, it may also be possible for any of the above space groups other than C_{2v}^9 and V_h^{16} to account for the observed nonpresence of the predicted reflections, but, to do this, atoms should be arranged at some special positions. In the present case, however, this is very improbable, if not impossible, and it seems unnecessary to treat such space groups further. As to C_{2v}^9 and V_h^{16}, it is impossible so far to distinguish one from the other, the general criteria coming to the same.[2]

The Atomic Arrangement. In case that the corresponding space group is C_{2v}^9,[3] the crystals of thiourea must have hemimorphic polarity along the c-axis, whose existence, however, has never been proved. On the other hand, since the space group V_h^{16} is in accord with the observed symmetry, it may be regarded as the correct one, if there is found an arrangement of atoms which accounts for the observed data respecting the comparative intensities of reflection. The space group V_h^{16} has the following equivalent positions[4] in all:

Four-fold positions

(a) $0\,\frac{1}{4}\,\frac{1}{4}$; $0\,\frac{1}{4}\,\frac{3}{4}$; $\frac{1}{4}\,\frac{3}{4}\,\frac{3}{4}$; $\frac{1}{2}\,\frac{3}{4}\,\frac{1}{4}$.

(b) $\frac{1}{2}\,\frac{1}{4}\,\frac{1}{4}$; $\frac{1}{2}\,\frac{1}{4}\,\frac{3}{4}$; $0\,\frac{3}{4}\,\frac{3}{4}$; $0\,\frac{3}{4}\,\frac{1}{4}$.

(c) $u\,v\,0$; $-u, \frac{1}{2}-v, \frac{1}{2}$; $\frac{1}{2}-u, \frac{1}{2}+v, 0$; $\frac{1}{2}+u, -v, \frac{1}{2}$.

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(1) See for instance R.W.G. Wyckoff, *Am. J. Sci.* 9 (1925), 145, or H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," (1926), 387.

(2) Very recently Professor S. Nishikawa and Mr. K. Matukawa (*Proc. Imp. Acad. (Japan)*, 4 (1928), March) have found an effect of hemihedry of zincblende upon X-ray reflection, but it it not yet applicable to the present case.

(3) As the general equivalent positions are four-fold here and the unit cell contains four chemical molecules CSN_2H_4, it can be inferred that the shape of the molecule is not restricted by any condition of symmetry, the parameters to be determined being more than ten.

(4) See for instance R.W.G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," (1922), or H. Mark, loc. cit., Table 52.

Eight-fold positions

(d) $x\,y\,z$; $-x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$; $\frac{1}{2}+x, -y, \frac{1}{2}-z$;

$-x, \frac{1}{2}-y, \frac{1}{2}-z$; $x, y, -z$; $\frac{1}{2}+x, -y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$.

The positions (a) and (b) coincide with the centres of symmetry, and (c) are in the planes of symmetry. There are four molecules in the unit cell, so that four atoms of carbon, four atoms of sulphur, eight atoms of nitrogen and sixteen atoms of hydrogen should be arranged in it. As is generally the case for organic crystals, it is highly probable that the crystals of thiourea will form a molecular lattice. If so, the 4C atoms or the 4S atoms cannot be placed in the positions (a) or (b); for no atomic arrangement can give a centre of symmetry to a single molecule CSN_2H_4. The observed comparative intensities of reflection from principal planes also favour to exclude such possibilities. Accordingly the atoms of carbon and sulphur should be arranged in the planes of symmetry, their positions being (c) with respective set of parameter values. That the nitrogen atoms should be arranged in the general equivalent positions (d) comes out directly from the inspection of the distribution of intensities of reflection among various orders from (001) plane. Sixteen hydrogen atoms will be divided into two groups, each being situated at (d).

In determining the arrangement, the atoms of hydrogen may be neglected as usually done, then there is only one parameter z_N for the nitrogen atoms in the direction of the c-axis. A value about 0.144 for z_N was found to account well for the observed distribution of the intensities of reflection among various orders from (001). With this value the distance between the two nitrogen atoms in a molecule becomes about 2.46 Å. As this seemed not in the least inadequate, it was further attempted to determine the values of the remaining parameters, which, being as many as six, will hardly be evaluated without some assumption. Therefore, it was assumed that one carbon atom and two nitrogen atoms form an isosceles triangle NCN (Fig. 1), the distance between the two N atoms being the above value 2.46Å., and that between the carbon atom and one of the nitrogen atoms being very nearly 1.44—1.48 Å. as found in the case of hexamethylene tetramine.[1] Upon this a trial survey was made, and it was

(1) R.G. Dickinsonand A.L. Ra ymond, *J. Am. Chem. Soc.*, **45** (1923), 22; H.W. Gonell and H. Mark, *Z. physik. Chem.*, **107** (1923), 181.

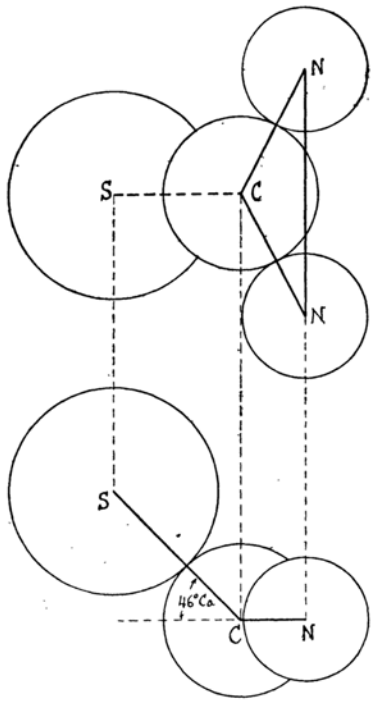

Fig. 1.

Discussion of the Structure. With the above parameter values the C, S and 2N atoms in a molecule do not lie in the same plane, but the direction from the carbon to the sulphur atom makes an angle of about 46° to the plane NCN. The interatomic distance between sulphur and carbon is 1.81Å., which is in good agreement with the sum of radii of the neutral atoms for S and C, 1.04+0.77=1.81Å. according to Wyckoff[1] or Goldschmidt.[2] Each one of the found that a set of parameter values accounted for the comparative intensities given in Table 2. These values are: $u_C = 0.186$, $v_c = 0.144$ for the carbon atoms; $u_S = -0.095$, $v_S = 0.270$ for the sulphur atoms; and $x_N = 0.300$, $y_N = 0.164$, $z_N = 0.144$ for the nitrogen atoms. In Table 2, the figures without brackets are the intensities observed and those within brackets right under them are the intensities calculated by a formula $\left(\frac{d}{n}\right)^{2.35} |S|$, where d denotes the spacing, n the order of reflection and $|S|$ the absolute value of structure amplitude, the reflecting powers of the atoms being roughly assumed to be proportional to their atomic numbers.

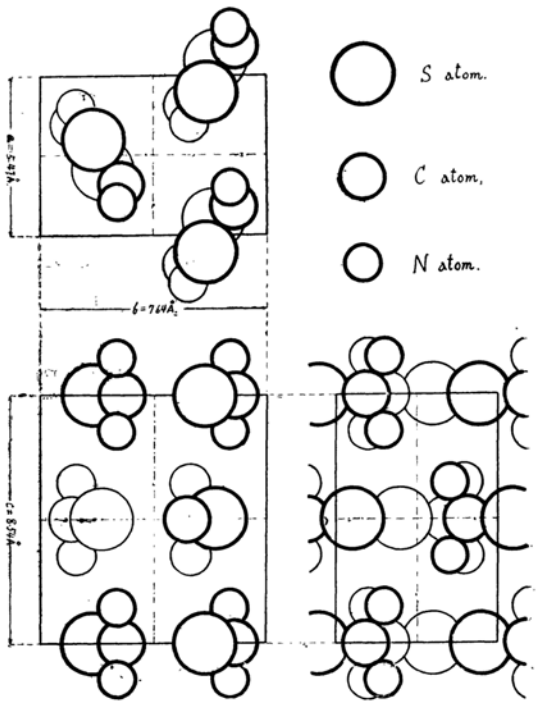

Fig. 2.

(1) R.W.G. Wyckoff, *Proc. Nat. Acad. Sci.*, 9 (1923), 33.

(2) V.M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo. I. Matemat.-Natur. Klasse*, (1926), No. 2.

nitrogen atoms is at a distance of 1.39 Å. from the carbon atom, which is somewhat less than the value in hexamethylene tetramine or the sum of radii of the neutral carbon and nitrogen atoms 0.77 + 0.71 = 1.48A. according to Goldschmidt, but is concordant with the sum 0.77 + 0.63 = 1.40 Å. given by Wyckoff. To complete the crystal structure of thiourea, the positions of the hydrogen atoms hitherto neglected should be considered, and, as a matter of fact, there is a vacant place left for them to be so arranged that the molecular structure may correspond to the usual chemical formula $SC(NH_2)_2$. As for the connection between neighbouring molecules, it is closer in the *zx*-plane than in the direction of the *y*-axis, which corresponds to the existence of perfect cleavage on (010) plane. Besides, it may also be noted that the largest spacing was found in the direction of the *c*-axis to be $d_{(001)} = 8.54$ Å., and, as already described, there was actually observed a case in which thiourea crystallized in plates parallel to (001)[1]. The arrangement of atoms in the crystal is shown in Fig. 2.

According to Hark and Weissenberg, urea crystallizes in the space group V_d^3 of the tetragonal scalenohedral class, the unit cell being of the dimensions $a = 5.63$ and $c = 4.70$ Å. The molecule is tied up spatially in one group, is flat on neglection of H atoms and has the proper symmetry of C_2^v. Such a structure of urea seemingly bears no close relation to that of thiourea. This may correspond to the separate crystallization from the aqueous solution containing these compounds. The unit cell of the former contains two chemical molecules CON_2H_4, and the line joining the two nitrogen atoms of a molecule stands perpendicular to that of the other, while the unit cell of the latter contains four molecules CSN_2H_4, and the corresponding lines for every pair of nitrogen atoms are all parallel to each other. The distance between the two N atoms in the molecule is about 2 Å. for urea, and 2.46 Å. for thiourea. As to the molecular symmetry, C_s of the latter is lower than C_2^v of the former. In spite of these differences, however, they are not quite unrelated to each other; for it is also possible to change the crystal structure of thiourea into that of urea by making every molecule flat in the *zx*-plane and giving it a small amount of translation and a rotation through half a right angle about the axis C–S.

In conclusion, the authors wish to express their best thanks to Professor S. Nishikawa for his kind interest and encouragement during the work.

(1) cf. H. Mark, loc. cit., 340.

Summary.

Using the Laue photographic and X-ray spectrometric methods the crystal structure of thiourea was investigated. The unit of structure built upon the simple orthorhombic translation group Γ_0, is of the dimensions $a = 5.47$, $b = 7.64$ and $c = 8.54$ A., and contains four chemical molecules of CSN_2H_4. Thus the density is 1.408. The plausible space group being V_h^{16}, a possible atomic arrangement, neglecting H atoms, was found to be as follows:

$$4C \left\{u, v, 0\,; \quad -u, \tfrac{1}{2}-v, \tfrac{1}{2}\,; \quad \tfrac{1}{2}-u, \tfrac{1}{2}+v, 0\,; \quad \tfrac{1}{2}+u, -v, \tfrac{1}{2}\right\}$$

with $u = 0.186$, $v = 0.144$;

$$4S \left\{u, v, 0\,; \quad -u, \tfrac{1}{2}-v, \tfrac{1}{2}\,; \quad \tfrac{1}{2}-u, \tfrac{1}{2}+v, 0\,; \quad \tfrac{1}{2}+u, -v, \tfrac{1}{2}\right\}$$

with $u = -0.095$, $v = 0.270$; and

$$8N \begin{Bmatrix} x, y, z\,; & -x, \tfrac{1}{2}-y, \tfrac{1}{2}+z\,; & \tfrac{1}{2}-x, \tfrac{1}{2}+y, -z\,; & \tfrac{1}{2}+x, -y, \tfrac{1}{2}-z\,; \\ -x, \tfrac{1}{2}-y, \tfrac{1}{2}-z\,; & x, y, -z\,; & \tfrac{1}{2}+x, -y, \tfrac{1}{2}+z\,; & \tfrac{1}{2}-x, \tfrac{1}{2}+y, z \end{Bmatrix},$$

with $x = 0.300$, $y = 0.164$ and $z = 0.144$. The molecule has the symmetry of C_s, i.e. it has one plane of symmetry in it. In such a model, the distance C–S is 1.81 Å., and that C–N is 1.39 Å. Discussion was also made upon its crystalline and molecular structures in comparison with those of urea.

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