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Three-Dimensional Refinement of Urea

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The visual data of Vaughan & Donohue (1952) for urea have been used in a three-dimensional least-squares refinement of the positional and thermal parameters. The results are in excellent agreement with the partial refinement of Sklar, Senko & Post (1961) of their zonal spectrometer data.

The results include the following bond lengths, corrected for libration: C–O = 1·276 ± 8 and C–N = 1·356 ± 7 Å; thermal vibration ellipsoids and the components of the **T** and **ω** tensors in a rigid-body analysis are also presented: the r.m.s. libration of the molecule about its twofold axis is 13°.

Introduction

The structure of urea has been investigated by a number of authors: Mez (1902), Mark & Weissenberg (1923), Hendricks (1928), Wyckoff (1930), Wyckoff & Corey (1934), Vaughan & Donohue (1952), Lobachev & Vainshtein (1961), Grenville-Wells (1956), Worsham, Levy & Peterson (1957), and Sklar, Senko & Post (1961).* The first study which included a refinement of the thermal as well as the positional parameters is that of Vaughan & Donohue, but unfortunately their treatment of the thermal parameters was not entirely correct (private communication). The primary objective of the three investigations cited last above was the determination of the thermal parameters, and in all of them only zonal data were used (*hk*0 and/or *h*0*l*). Some of the B_{ij} therefore could not be determined, and an analysis of the thermal motions of the molecule based on complete three-dimensional data is still lacking. The urea molecule, being small, planar, and fairly rigid because of multiple bond character in the C–N and C–O bonds, is well suited to a rigid-body analysis. Indeed, indications are that the molecule is librating appreciably about the C–O bond direction (Vaughan & Donohue, 1952), a condition which is expected to shorten the apparent C–N bond length (Grenville-Wells, 1956).

Refinement of the structure

In the present reinvestigation, the (*hk*0) and (*h*0*l*) parts of the three-dimensional visual data of Vaughan & Donohue† were first compared with the zonal diffractometer data of Sklar, Senko & Post, and judged to be of a quality which justified further refinement, as may be seen from Fig. 1. The complete set of visual data was then used in a complete least-squares refinement with the Palenik (1962) program. The scattering factors were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for the heavy atoms and those of McWeeny (1951) for the hydrogen atoms. The weights were assigned according to Hughes (1941), with $4F_{\text{min}} = 2{\cdot}2$. The unobserved reflections were excluded from the computations. The initial parameter values were those of Vaughan & Donohue. In addition to the coordinates and anisotropic temperature factors for C, N, and O, the coordinates and isotropic temperature factors for the hydrogen atoms were also treated as variables. After a more than sufficient number of cyles of least squares, an overall *R* value of 5·4% was attained. In the last cycle, the average ratio of shift to standard deviation was 0·044; the largest such ratio [for *x* of H(2)] was only 0·14. The values of F_o and F_c are presented in Table 1. The *R* values for the (*h*0*l*) and (*hk*0) zones separately are 5·4 and 4·2% respectively; these compare with the corresponding values of 5·5 and 12·0% calculated from Tables 1 and 2 published by Sklar *et al.* for their room temperature data.

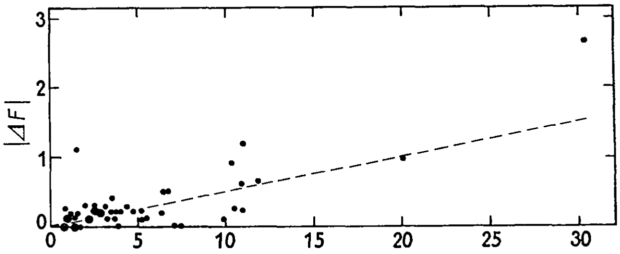

Fig. 1. The agreement between the visually estimated *F*'s of Vaughan & Donohue and the spectrometer data of Sklar, Senko & Post, *hk*0 and *h*0*l* only. Observations below the dashed line differ by less than 5%, those above the dashed line differed by more than 5%.

Discussion

In Tables 2 and 3 are listed our final positional parameters and temperature factors, together with

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* This paper includes data obtained at room temperature and at −140 °C; only the former are used in making the comparisons found below.

† Upon checking the original notebooks, a transcribing error was discovered: the entries under F_o published by Vaughan & Donohue of $F_{502} = 0{\cdot}68$ and $F_{602} = < 0{\cdot}69$ should read $F_{502} = < 0{\cdot}68$ and $F_{602} = 0{\cdot}69$.

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c
200	11·96	12·34
400	2·42	2·27
600	3·76	3·60
110	33·16	31·27
210	12·97	13·03
310	4·88	4·76
410	1·26	1·18
510	4·23	4·17
610	0·97	1·08
710	2·17	2·24
220	11·37	12·35
320	3·44	3·29
420	6·75	6·75
520	2·40	2·42
620	2·75	2·88
330	9·73	10·20
430	1·78	1·69
530	3·92	4·11
630	<0·53	0·11
440	5·11	5·35
540	<0·65	0·36
550	0·88	1·06
001	4·42	4·31
101	11·72	13·02
201	11·96	11·84
301	7·80	7·60
401	6·86	6·89
501	<0·66	0·18
601	1·42	1·42
701	1·07	1·06
111	12·91	15·59
211	6·41	5·64
311	9·64	9·40
411	2·21	2·06
511	3·19	3·23
611	1·35	1·24
711	0·82	0·88
221	11·96	12·18
321	1·52	1·54
421	3·52	3·52
521	1·87	1·71
621	1·54	1·71
331	2·68	2·49
431	3·17	3·06
531	1·87	1·94
631	<0·47	0·19
441	1·65	1·52
541	0·70	0·50
551	1·77	1·57
002	10·66	11·49
102	10·87	11·09
202	2·50	2·22
302	3·18	2·88
402	1·98	1·70
502	<0·75	0·13
602	0·76	0·74
112	6·33	6·44
212	5·20	4·94
312	3·42	3·22
412	1·13	0·95
512	1·20	1·33
612	0·76	0·72
222	5·83	5·74
322	2·11	2·01
422	1·33	1·39
522	1·38	1·51
622	0·70	0·83
332	1·80	2·07
432	2·37	2·43
532	1·00	1·04
632	<0·47	0·36
442	1·13	1·36
542	<0·53	0·16
003	2·69	2·71
103	8·19	7·92
203	5·77	6·11
303	2·37	2·34
403	5·41	5·53
503	1·43	1·50
603	0·87	0·79
113	3·51	3·26
213	6·40	6·38
313	6·14	6·27
413	2·12	2·03
513	1·92	1·92
613	1·28	1·34
223	5·08	4·98
323	3·41	3·28
423	1·59	1·53
523	2·23	2·21
333	0·70	0·55
433	2·46	2·55
533	0·88	1·01
443	<0·60	0·68
004	4·58	4·69
104	1·43	1·16
204	3·98	3·85
304	6·97	6·60
404	2·00	2·25
504	2·42	2·25
114	5·47	5·25
214	5·16	4·97
314	3·24	3·26
414	3·56	3·70
514	2·02	2·00
224	4·88	4·79
324	2·89	2·71
424	2·24	2·37
524	1·15	1·05
334	2·37	2·33
005	5·65	5·91
105	1·60	2·58
205	1·00	0·93
305	<0·51	0·19
115	3·24	3·22
215	2·57	2·63
315	0·75	0·55
225	1·60	1·32
325	1·85	1·61
006	2·50	2·09

some of the previous results. Exhaustive comparison among the five sets of results is unneccesary — the data of Tables 2 and 3 speak for themselves. It should be noted, though, that the present results, which are based on visual data, are in excellent agreement with the results of Sklar *et al.* from their diffractometer data, especially with regard to the positional parameters. The largest difference occurs in the case of B_{11} for nitrogen, and this is the only difference in the 'possibly significant' range ($\Delta/\sigma=2·9$). On the other hand, the agreement between the neutron results of Worsham *et al.* and our results is uniformly not quite as good.

Table 2. *Positional parameters and their standard errors*

All values have been multiplied by 10^4

		VD (σ)	WLP (σ)	LV	SSP (σ)	This work (σ)
O	*z*	5987 (19)	5968 (11)	6010	5980 (8)	5998 (8)
C	*z*	3308 (32)	3330 (10)	3290	3300 (11)	3308 (12)
N	*x*	1429 (21)	1439 (9)	1450	1433 (9)	1419 (7)
	z	1848 (17)	1832 (5)	1820	1847 (7)	1857 (10)
H(1)	*x*		2522 (26)	2650	2430 (230)	2390 (100)
	z		2839 (21)	2830	2810 (110)	2770 (120)
H(2)	*x*		1365 (19)	1420	1420 (160)	1240 (70)
	z		9724 (14)	9580	280 (190)	460 (150)

VD	Vaughan & Donohue (1952).
WLP	Worsham, Levy & Peterson (1957).
LV	Lobachev & Vainshtein (1961).
SSP	Sklar, Senko & Post (1961).

Table 3. *Thermal parameters and their standard errors*

The standard errors have been multiplied by 10

		WLP (σ) (Å^2)	G-W (Å^2)	SSP (σ) (Å^2)	This work (σ) (Å^2)
N	B_{11}	4·86 (20)	5·2	5·20 (16)	5·86 (17)
	B_{33}	1·39 (9)	1·5	1·80 (9)	1·74 (17)
	B_{12}				−5·54 (57)
	B_{13}	−0·14 (24)		0·08 (9)	−0·43 (21)
C	B_{11}	2·35 (24)	3·3	2·75 (14)	2·85 (14)
	B_{33}	0·85 (14)	1·5	1·56 (16)	1·87 (21)
	B_{12}				−0·22 (107)
O	B_{11}	3·74 (34)	3·5	3·65 (16)	4·15 (16)
	B_{33}	0·80 (12)	0·6	1·68 (8)	1·38 (15)
	B_{12}				0·44 (91)
H(1)	B_{11}	6·33 (64)	6·8		
	B_{33}	3·54 (43)	1·9		2·60 (140)
	B_{13}	−0·68 (92)			
H(2)	B_{11}	6·72 (53)	6·8		
	B_{33}	1·82 (18)	1·9		1·00 (110)
	B_{13}	−0·45 (69)			

WLP	Worsham, Levy & Peterson (1957).
G-W	Grenville-Wells (1956).
SSP	Sklar, Senko & Post (1961).

Data characterizing the vibrational ellipsoids for the heavy atoms calculated by the method of Rollett & Davies (1955) with the program of Coulter, Gantzel & Trueblood (1962) are listed in Table 4. The results of a rigid-body analysis (Cruickshank, 1956) giving the translational and librational r.m.s. amplitudes are presented in Table 5. The symmetry requirements are such that the principal axes of $\mathbf{T}$ and $\boldsymbol{\omega}$ are fixed to the directions $a+b$, $a-b$, and c. The calculations were further simplified by assuming that the center of gravity is at the carbon position. The errors introduced by this simplification are negligible, and involve a translation of the center of gravity of only 0·027 Å. Ideally, the translational amplitudes should be those of the carbon ellipsoid; in reality, they deviate by less than 10%.

Table 4. *Ellipsoids of vibration*

	i	$\lvert\overline{r^2}_i\rvert^{1/2}$	q_{ia}	q_{ib}	q_{ic}
O	1	0·235 Å	−0·7071	−0·7071	0
	2	0·223	−0·7071	0·7071	0
	3	0·132	0	0	1
C	1	0·186	−0·7071	−0·7071	0
	2	0·194	−0·7071	0·7071	0
	3	0·154	0	0	1
N	1	0·200	−0·6918	−0·6918	0·2066
	2	0·331	−0·7071	0·7071	0
	3	0·146	0·1461	0·1461	0·9784

Table 5. *Translational and librational root-mean-square amplitudes*

$\mathbf{T}^{1/2}$	$\boldsymbol{\omega}^{1/2}$	Direction
0·202 ± 0·011 Å	6·08 ± 0·96°	$a+b$
0·188 ± 0·011	2·70 ± 1·77	$a-b$
0·141 ± 0·008	13·13 ± 0·47	c

The librational amplitudes are quite large. The relative order of those amplitudes may be rationalized to the extent that it corresponds to the inverse order of the moments of inertia; moreover, the largest libration amplitude, around c, involves the least disruption of the hydrogen bonds.

The atomic coordinates, after transformation to the system of the principal axes, were then corrected for libration as follows: $x_{\text{corr}} = x_{\text{uncorr}}\,(\sec\omega_y + \sec\omega_z - 1)$, where ω_y and ω_z are the librational r.m.s. amplitudes around the y and z librational axes. The corrected coordinates referred to the crystal axes are $z_O = 0{\cdot}6016$, $x_N = 0{\cdot}1459$, and $z_N = 0{\cdot}1847$.

The corrected and uncorrected values of the bond lengths and angles are presented in Table 6, together with those of the previous studies. The standard errors in the corrections are incorporated into the standard errors of the corrected values. The corrected C–N and C–O bond lengths are approximately those expected on the basis of current bond length — bond order considerations. Nevertheless, revision of the values assigned to 'pure' single and double C–N and C–O bonds, and to the form of the curve giving bond lengths of intermediate type, is probably much to be desired, but such a treatment must be deferred until strictly comparable data are available. Any discussion which lumps uncorrected interatomic distances with those corrected for libration is, perforce, inadequate.

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Table 6. *Interatomic distances*

					This work	
	VD	WLP	LV	SSP	Uncorrected	Corrected
C–O	1·262 ± 0·016 Å	1·243 ± 0·006 Å	1·28 Å	1·264 ± 0·006 Å	1·268 ± 0·007 Å	1·276 ± 0·008 Å
C–N	1·335 ± 0·013	1·351 ± 0·007	1·35	1·336 ± 0·007	1·326 ± 0·006	1·356 ± 0·007
N–H ··· O	2·989	2·994 ± 0·006	2·97	2·998 ± 0·005	2·985 ± 0·006	2·985 ± 0·007
N–H ··· O′	3·035	3·034 ± 0·005	3·02	3·036 ± 0·007	3·040 ± 0·007	3·009 ± 0·008
N–C–N	118·0 ± 1·3°	117·0 ± 0·3°	118·2°	118·2 ± 0·3°	117·9 ± 0·6°	119·0 ± 0·6°
N–C–O	121·0 ± 0·65	121·5 ± 0·25	120·9	120·9 ± 0·3	121·0 ± 0·3	120·5 ± 0·3

VD Vaughan & Donohue (1952) WLP Worsham, Levy & Peterson (1957)
LV Lobachev & Vainshtein (1961) SSP Sklar, Senko & Post (1961)