

The Crystal Structure of Ammonium Carbamate

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The structure of the title compound, $\text{CH}_6\text{N}_2\text{O}_2$, with $a = 17.121(6)$, $b = 6.531(2)$ and $c = 6.842(3)$ Å, space group $Pbca$, $Z = 8$, has been determined from 782 counter-measured intensities. The carbamate ion is planar with the following distances (corrected for thermal libration): C—O 1.279 (5), 1.289 (5); C—N 1.361 (5) Å.

Introduction

This compound is of interest because of the similarity of the carbamate ion and the primary amide group which has been quite extensively studied. The compound is unstable, the solid volatilizing, unless enclosed, to form ammonia and carbon dioxide. At 24.9°C according to Briggs & Migrdichian (1924) the total equilibrium pressure of these gaseous products is 88.3 mm Hg. In aqueous solution conversion to ammonium carbonate occurs, and at higher temperatures (130°C) the solid decomposes to urea with loss of water.

Crystal data

After several unsuccessful attempts to grow suitably sized crystals by sublimation, a single crystal was found in a bottle of commercial material. It had dimensions $0.6 \times 0.15 \times 0.1$ mm and was sealed in a Lindemann glass tube. By means of Weissenberg photographs the space group was established and the cell dimensions were obtained by a least-squares treatment of high-order θ values measured on a diffractometer (Small & Travers, 1961). The results are recorded in Table 1. The measured density established the asymmetric unit as one formula unit.

Table 1. *Crystal data*

Space group $Pbca$; $a = 17.121(6)$, $b = 6.531(2)$, $c = 6.742(3)$ Å (Cu $K\alpha$, $\lambda = 1.5418$ Å) $Z = 8$; $d_{\text{meas}} = 1.36$, $d_{\text{calc}} = 1.38$ g cm $^{-3}$.

Determination of the structure

Intensities were collected on a diffractometer at room temperature with Cu $K\alpha$ radiation. 836 unique reflexions with $\theta < 82^\circ$ were measured and of these 54 had intensities below the level considered significant. The statistical method of Wilson was used to derive an approximate scale and temperature factor ($B = 3.5$ Å 2). E values and structure factors for all reflexions were produced.

The structure was solved by the symbolic addition method with the programs of Germain, Main & Woolfson (1970). 157 reflexions with $E > 1.3$ were used and four possible sets of signs produced. On an E map based on the set of signs with the highest figure of merit, the five non-hydrogen atoms of the structural unit were easily recognized.

Refinement

An initial structure-factor calculation gave an R of 0.35. Refinement of atomic positions and anisotropic temperature factors was carried out with the full-matrix least-squares program ($FMLS$) of Bracher & Taylor (1967). At an intermediate stage, hydrogen atoms were introduced at positions indicated by an ($F_o - F_c$) synthesis; position parameters only of these atoms were refined by separate cycles of $FMLS$, the

Table 2. *Observed and calculated structure factors* ($\times 10^2$)

h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	1000	1000	1	1	1	100	100
0	0	1	1000	1000	1	2	1	100	100
0	0	2	1000	1000	1	3	1	100	100
0	0	3	1000	1000	1	4	1	100	100
0	0	4	1000	1000	1	5	1	100	100
0	0	5	1000	1000	1	6	1	100	100
0	0	6	1000	1000	1	7	1	100	100
0	0	7	1000	1000	1	8	1	100	100
0	0	8	1000	1000	1	9	1	100	100
0	0	9	1000	1000	1	10	1	100	100
0	0	10	1000	1000	1	11	1	100	100
0	0	11	1000	1000	1	12	1	100	100
0	0	12	1000	1000	1	13	1	100	100
0	0	13	1000	1000	1	14	1	100	100
0	0	14	1000	1000	1	15	1	100	100
0	0	15	1000	1000	1	16	1	100	100
0	0	16	1000	1000	1	17	1	100	100
0	0	17	1000	1000	1	18	1	100	100
0	0	18	1000	1000	1	19	1	100	100
0	0	19	1000	1000	1	20	1	100	100
0	0	20	1000	1000	1	21	1	100	100
0	0	21	1000	1000	1	22	1	100	100
0	0	22	1000	1000	1	23	1	100	100
0	0	23	1000	1000	1	24	1	100	100
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0	0	25	1000	1000	1	26	1	100	100
0	0	26	1000	1000	1	27	1	100	100
0	0	27	1000	1000	1	28	1	100	100
0	0	28	1000	1000	1	29	1	100	100
0	0	29	1000	1000	1	30	1	100	100
0	0	30	1000	1000	1	31	1	100	100
0	0	31	1000	1000	1	32	1	100	100
0	0	32	1000	1000	1	33	1	100	100
0	0	33	1000	1000	1	34	1	100	100
0	0	34	1000	1000	1	35	1	100	100
0	0	35	1000	1000	1	36	1	100	100
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0	0	37	1000	1000	1	38	1	100	100
0	0	38	1000	1000	1	39	1	100	100
0	0	39	1000	1000	1	40	1	100	100
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0	0	41	1000	1000	1	42	1	100	100
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0	0	45	1000	1000	1	46	1	100	100
0	0	46	1000	1000	1	47	1	100	100
0	0	47	1000	1000	1	48	1	100	100
0	0	48	1000	1000	1	49	1	100	100
0	0	49	1000	1000	1	50	1	100	100
0	0	50	1000	1000	1	51	1	100	100
0	0	51	1000	1000	1	52	1	100	100
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0	0	78	1000	1000	1	79	1	100	100
0	0	79	1000	1000	1	80	1	100	100
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0	0	82	1000	1000	1	83	1	100	100
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0	0	88	1000	1000	1	89	1	100	100
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0	0	91	1000	1000	1	92	1	100	100
0	0	92	1000	1000	1	93	1	100	100
0	0	93	1000	1000	1	94	1	100	100
0	0	94	1000	1000	1	95	1	100	100
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0	0	96	1000	1000	1	97	1	100	100
0	0	97	1000	1000	1	98	1	100	100
0	0	98	1000	1000	1	99	1	100	100
0	0	99	1000	1000	1	100	1	100	100
0	0	100	1000	1000	1	101	1	100	100
0	0	101	1000	1000	1	102	1	100	100
0	0	102	1000	1000	1	103	1	100	100
0	0	103	1000	1000	1	104	1	100	100
0	0	104	1000	1000	1	105	1	100	100
0	0	105	1000	1000	1	106	1	100	100
0	0	106	1000	1000	1	107	1	100	100
0	0	107	1000	1000	1	108	1	100	100
0	0	108	1000	1000	1	109	1	100	100
0	0	109	1000	1000	1	110	1	100	100
0	0	110	1000	1000	1	111	1	100	100
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0	0	115	1000	1000	1	116	1	100	100
0	0	116	1000	1000	1	117	1	100	100
0	0	117	1000	1000	1	118	1	100	100
0	0	118	1000	1000	1	119	1	100	100
0	0	119	1000	1000	1	120	1	100	100
0	0	120	1000	1000	1	121	1	100	100
0	0	121	1000	1000	1	122	1	100	100
0	0	122	1000	1000	1	123	1	100	100
0	0	123	1000	1000	1	124	1	100	100
0	0	124	1000	1000	1	125	1	100	100
0	0	125	1000	1000	1	126	1	100	100
0	0	126	1000	1000	1	127	1	100	100
0	0	127	1000	1000	1	128	1	100	100
0	0	128	1000	1000	1	129	1	100	100
0	0	129	1000	1000	1	130	1	100	100
0	0	130	1000	1000	1	131	1	100	100
0	0	131	1000	1000	1	132	1	100	100
0	0	132	1000	1000	1	133	1	100	100
0	0	133	1000	1000	1	134	1	100	100
0	0	134	1000	1000	1	135	1	100	100
0	0	135	1000	1000	1	136	1	100	100
0									

temperature factors being constrained to those values of the atoms of attachment. A later modification of the refinement was the substitution of observed structure factors corrected for absorption of X-rays by the method of De Meulenaer & Tompa (1965) and in the final cycles, a weighting scheme ($w = 1$ for $F_o > 4.0$ and $w = F_o/4.0$ for $F_o < 4.0$) was used. Refinement was terminated when parameter shifts were less than one fifth of the corresponding standard deviations. The final value of R was 0.082. The plane (021), which was considered to show pronounced secondary extinction, was omitted. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). A final ($F_o - F_c$) synthesis showed no features of significance. The observed and calculated structure factors are listed in Table 2 and the positional and thermal parameters in Tables 3 and 4 respectively.

Table 3. Fractional atomic coordinates and their standard deviations ($\times 10^5$)

	x	y	z
C(1)	10633 (19)	7650 (50)	84631 (46)
O(1)	10459 (14)	- 5433 (38)	98553 (36)
O(2)	16688 (13)	11313 (43)	74099 (37)
N(1)	31895 (18)	7953 (52)	86836 (46)
N(2)	4115 (20)	18512 (58)	80749 (51)
H(1)	- 53 (312)	35988 (818)	36150 (758)
H(2)	4264 (285)	21800 (981)	22858 (866)
H(3)	26450 (284)	43124 (742)	31779 (654)
H(4)	32807 (288)	52726 (843)	43621 (728)
H(5)	33935 (266)	29786 (812)	40598 (719)
H(6)	34111 (293)	45721 (823)	27902 (772)

Interpretation of the thermal vibration parameters

According to the treatment of Schomaker & Trueblood (1968) the thermal vibration of a rigid body is most effectively described by three tensors, T , ω , and S . In the case of the carbamate ion in this compound the number of b_{ij} values is insufficient to define these three rigid-body tensors. A simpler but less adequate model ignoring the screw tensor S was used. Values

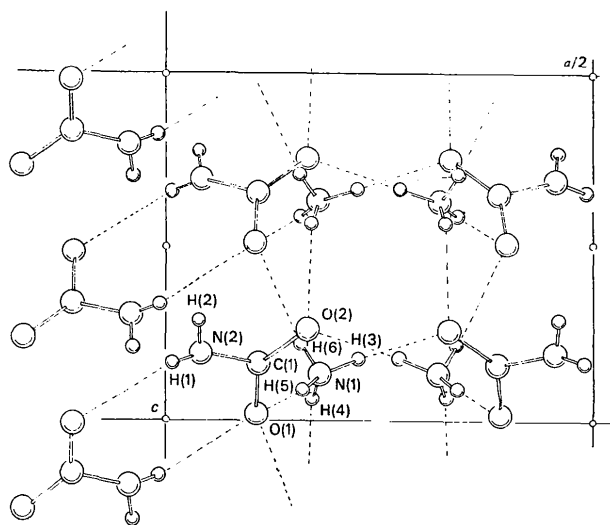


Fig. 1. Arrangement of ions. Projection down b .

Table 4. Temperature factors, b_{ij} , with standard deviations for C, N and O atoms

$$T.F. = \exp\{-10^{-5}(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})\}.$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	181 (11)	1304 (74)	830 (61)	26 (48)	- 91 (43)	- 196 (117)
O(1)	229 (9)	1584 (61)	1160 (51)	173 (39)	- 37 (35)	667 (100)
O(2)	161 (8)	2679 (77)	1070 (52)	- 93 (42)	190 (34)	101 (114)
N(1)	193 (10)	1614 (76)	1064 (61)	- 81 (46)	- 9 (42)	- 107 (117)
N(2)	195 (10)	2315 (94)	1638 (94)	347 (54)	72 (48)	1622 (145)

Table 5. Rigid-body vibrational mean square tensors, referred to crystal axes

Translation tensor ($T_{ij} \times 10^4$), \AA^2

T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
246 (28)	288 (35)	183 (33)	12 (26)	0 (26)	- 37 (33)

Libration tensor ($\omega_{ij} \times 10^4$), rad^2

ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{13}	ω_{23}
125 (64)	62 (30)	159 (30)	31 (23)	- 12 (23)	- 65 (27)

Table 6. Values of $U_{ij} \times 10^4$ (\AA^2) (a) from b_{ij} values, (b) from rigid-body model

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
C(1)	269	248	282	291	191	185	15	19	- 27	- 1	- 22	- 35
O(1)	334	286	342	363	267	246	98	47	- 11	- 12	74	102
O(2)	239	272	579	533	246	243	- 53	68	56	22	11	64
N(2)	290	325	500	516	377	406	197	229	21	30	181	112

of \mathbf{T} and ω for the molecular vibration about a fixed centre were obtained, the most satisfactory fit for this model being for a centre of libration displaced 0.25 Å from the carbon atom along the C–O(1) bond. Values of the tensors \mathbf{T} and ω are given in Table 5. A comparison of U_{ij} values calculated from the rigid-body model involving the tensors \mathbf{T} and ω with those derived from B_{ij} values is made in Table 6. Bond distances and angles within the carbamate ion were corrected for the effects of librational motion and are given in Table 7.

Table 7. *Intra-ionic bond distances (Å) and angles (°) (corrected for libration)*

Carbamate ion			
C(1)–O(1)	1.279 (5)	O(1)–C(1)–O(2)	123.5 (3)
C(1)–O(2)	1.289 (5)	O(1)–C(1)–N(2)	118.7 (3)
C(1)–N(2)	1.361 (5)	O(2)–C(1)–N(2)	117.9 (3)
N(2)–H(1)	0.86 (5)	H(1)–N(2)–H(2)	115 (4)
N(2)–H(2)	0.82 (6)	H(2)–N(2)–C(1)	120 (3)
		H(1)–N(2)–C(1)	125 (5)
Ammonium ion			
N(1)–H(3)	0.99 (5)	H(3)–N(1)–H(4)	107 (4)
N(1)–H(4)	0.85 (5)	H(3)–N(1)–H(5)	121 (4)
N(1)–H(5)	0.91 (5)	H(3)–N(1)–H(6)	100 (5)
N(1)–H(6)	0.75 (5)	H(4)–N(1)–H(5)	120 (5)
		H(4)–N(1)–H(6)	94 (5)
		H(5)–N(1)–H(6)	108 (5)

Description and discussion of the structure

A view of the structure projected along \mathbf{b} is shown in Fig. 1. The carbamate ions form a double-sided layer parallel to (100). Sandwiched between these layers and interpenetrating them slightly is a double layer of ammonium ions. Each ammonium ion is bonded by its hydrogen atoms to oxygens of four separate carbamate ions; three of these carbamate ions are part of one side of a layer. Every carbamate oxygen is bonded to two different ammonium ions. The ammonium ions therefore link together the carbamate ions into continuous layers and also join pairs of layers to form the 'sandwich'. Further bonding between the 'sandwiches' occurs by hydrogen bonding between centrosymmetric pairs of carbamate ions in the manner found in typical primary amide structures. The entire structure is thus hydrogen bonded in three dimensions. A point of interest is that one of the hydrogen atoms of the carbamate ion, H(2), does not appear to be involved in a hydrogen bond.

Interionic distances and angles are listed in Table 8. The N...O hydrogen-bonded distance between the pairs of carbamate ions is close to that usually found in amide structures. The four N...O distances which occur between oppositely charged ions are all at least 0.1 Å shorter.

Table 8. *Hydrogen-bond distances and angles*

Bond ($a \cdots b-c$)	Distances ab, ac (Å)		Angles abc (°)
	O(1)···H(1)–N(2)	2.12 (5)	2.982 (5)
O(1)···H(6)–N(1)	2.19 (5)	2.899 (5)	158 (5)
O(1)···H(5)–N(1)	1.93 (5)	2.839 (5)	173 (4)
O(2)···H(3)–N(1)	1.77 (5)	2.750 (5)	166 (4)
O(2)···H(4)–N(1)	2.13 (5)	2.823 (5)	138 (5)
H(1)···O(1)–C(1)			124 (1)
H(6)···O(1)–C(1)			129 (2)
H(5)···O(1)–C(1)			110 (1)
H(4)···O(2)–C(1)			125 (2)
H(3)···O(2)–C(1)			125 (2)

Within the limits of error the carbamate ion is planar (Table 9). There are no other structures reported involving the carbamate ion, but a comparison of the bond distances with those found in the ester, ethyl carbamate, by Bracher & Small (1967) shows a similarity of the C–N distance (1.349 Å in ethyl carbamate). The two C–O distances found here do not differ significantly, and have values near to the mean of the significantly different distances found in the ester (1.223 and 1.333 Å). Similar differences between the C–O distances in the ionic and ester forms of carboxylate groups are now well established.

Table 9. *Deviations of atoms from the 'best' plane defined by C(1), O(1), O(2), N(2) (Å)*

$$0.2887x + 0.7011y + 0.6520z = 4.5995$$

C(1)	–0.0024	N(2)	0.008
O(1)	0.0008	H(1)	–0.181
O(2)	0.0008	H(2)	0.090

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