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The Crystal Structure of Ammonium 1, 1, 2, 6, 7, 7-Hexacyanoheptatrienide

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The crystal structure of ammonium 1,1,2,6,7,7-hexacyanoheptatrienide, ($NH_4C_{13}H_3N_6$), has been determined by single-crystal X-ray diffraction techniques. The compound forms monoclinic crystals with $a=7\cdot11$ (1), $b=13\cdot405$ (1), $c=14\cdot199$ (3) Å and $\beta=101°41'$ (10). There are four formula units in the cell. A total of 865 observed independent reflections were measured with a PAILRED diffractometer. Working in the space group $P2_1/c$, the trial structure was solved by symbolic addition procedures. Least-squares refinement resulted in a conventional R value of 0·069 and a weighted R of 0·031. The anion is only slightly distorted from a planar configuration. Observed molecular dimensions are consistent with those obtained from extended Hückel calculations.

Introduction

Previous crystal structure determinations of ammonium tricyanomethide (Desiderato & Sass, 1965), pyridinium dicyanomethide (Bugg & Sass, 1965), potassium *p*-nitrophenyldicyanomethide (Sass & Bugg, 1967), and dipotassium tetranitroethide (Dyke & Sass, 1968) indicate a certain degree of non-planarity is associated with the trigonally-bonded carbon atom of the carbanion. Ammonium 1,1,2,6,7,7-hexacyanoheptatrienide is a logical extension of these studies because of its conjugated poly-cyano-substituted character.

Experimental

A sample of the ammonium salt of 1,1,2,6,7,7-hexacyanoheptatrienide, $NH_4C_{13}H_3N_6$, was kindly supplied by Dr R. E. Benson of E. I. du Pont de Nemours and Company (Williams, Wiley & McKusick, 1962). The ammonium salt as received consisted of deep green prismatic crystals suitable for study without further recrystallization. Study crystals were usually $0\cdot2 \times 0\cdot1$ mm in cross section, and 2 to 3 mm in length. These were mounted on glass fibers with the crystal needle axis, *a*, parallel to the fiber axis.

Weissenberg and rotation photographs were collected with Cu $K\alpha$ radiation ($\lambda_{K\alpha_1} = 1\cdot54051$ Å). Systematic absences

$$
\begin{array}{ll}
0k0 & k=2n+1 \\
h0l & l=2n+1 \\
hkl & \text{no conditions}
\end{array}
$$

are consistent with the space group $P2_1/c(C_{2h}^5)$. The *a* axis and β angle cell parameters were determined from sodium chloride [a_0 (NaCl) $= 5\cdot637$ Å] calibrated rotation and Weissenberg photographs, and the *b* and *c* axis parameters determined with the PAILRED diffractometer using Mo $K\alpha$ radiation ($\lambda_{K\alpha_1} = 0\cdot70926$; $\lambda_{K\alpha_2} = 0\cdot71354$):

$$
\begin{aligned}
a &= 7\cdot11 \ (1) \ \text{Å} \\
b &= 13\cdot405 \ (1) \\
c &= 14\cdot199 \ (3) \\
\beta &= 101°41' \ (10) \ .
\end{aligned}
$$

The density calculated on the basis of four $NH_4C_{13}H_3N_6$ molecules per unit cell is $1\cdot306$ g. cm^{-3}; the density measured by flotation in a mixture of chlorobenzene and bromobenzene is $1\cdot28$ g. cm^{-3}.

Two sets of data were collected. The first set was collected on film using two crystals, one $0\cdot2 \times 0\cdot1 \times 0\cdot2$ mm mounted along the *a* axis and one $0\cdot2 \times 0\cdot4 \times 0\cdot2$ mm mounted along the *b* axis. Multiple-film equi-inclination Weissenberg photographs of the $h=0,1,2,$ 3,4 and 5 layers, and $k=0,1,2,3$ layers were taken

Table 1. *Observed and calculated structure factors* × 10 *with those rejected by statistical criteria indicated by an asterisk*

with nickel-filtered copper $K\alpha$ radiation. Intensities were estimated with a standard intensity strip and corrected for Lorentz–polarization factors. The different layers were correlated by the method of Dickerson (1959). 1168 visually estimated intensities were used in the determination and initial refinement of the trial structure.

The second set of data was collected with a Norelco Philips PAILRED diffractometer, using a single crystal $3 \times 0.2 \times 0.1$ mm mounted parallel to the a axis. All data were collected with quartz-monochromatized Mo $K\alpha$ radiation and a scintillation counter. The fixed-counter moving-crystal method was used, employing a $2°$ scan range and $0.5°$ per minute scan rate for layers $h = 0$, 1 and 2. The higher layers $h = 3, 4, 5$ and 6 were measured using a $3°$ scan range and $1°$ per minute scan rate. For all reflections background was measured for a fixed time of 0.4 minute at the beginning and end of each scan. The counting statistical error was calculated for each reflection (Ladell, 1965).

$$\Delta I/I = (T + t^2 B)^{1/2}/(T - tB)$$

where

T = total counts for ω scan
t = ratio of scan time to background time
B = background count.

All reflections for which $\Delta I/I$ exceeded 0.40 were rejected. A total of 865 acceptable intensities were measured and corrected for Lorentz–polarization and Tunell factors (Bond, 1959). The maximum value of μR was 0.02; no absorption corrections were made.

The trial structure

The photographic intensity data were used for the determination and initial refinement of the trial structure.

Employing a computer version (Dewar & Stone, 1965) of the Karle & Hauptman symbolic addition procedure (Hauptman & Karle, 1953; Karle & Karle, 1966) the structure amplitudes for the ammonium salt were converted to normalized $|E_{hkl}|$ values. Nine symbolic phases were assigned to the largest E values having the greatest number of $\sum_2$ interactions. These included members of each of the eight parity groups. Three of these phases are arbitrarily assigned to place the origin. The actual assignment of the origin was not done initially, but occurred later in the procedure to avoid the use of origin phases on non-interacting symbols.

Phases of two hundred reflections were requested and, after four iterations of the program, a total of two hundred and twenty-four phases were returned as functions of the nine input symbols. The origin determining symbols were then assigned as positive, and the remaining six symbols were examined in every combination of plus and minus. For each sign combination the number of inconsistencies in the symbol equivalences list was found and a weighted index based

on these inconsistencies was determined. (Dewar & Stone, 1965).

Two sets of signs gave equally low and favorable weighted indices. Three-dimensional E maps were calculated with these sets. The correct E map was readily apparent from a consideration of the expected anion geometry. The ammonium ion peak was selected because of its placement in a hole surrounded by six cyano groups from six different anions.

The x, y and z coordinates and isotropic temperature factors of all non-hydrogen atoms were refined by the method of full-matrix least squares to an R index of 0.15. Unobserved reflections were omitted from the refinement.

Refinement

Using the diffractometer data, the positional and thermal parameters of the compound were further refined. All calculations were made on an IBM 7094 computer using a modified version of $ORFLS$ (Busing, Martin & Levy, 1962) for least-squares refinements, and portions of the X-ray 63 package (Stewart, 1964) for final refinement and calculations of bond distances and angles.

The refinement was accomplished by minimizing the quantity

$$\sum w(F_o - \frac{1}{k} F_c)^2.$$

Atomic scattering factors for non-hydrogen atoms were obtained from Cromer & Waber (1965), while those for bonded hydrogen atoms were obtained from Stewart, Davidson & Simpson (1965). The weighting scheme used for the diffractometer data was that described by Evans (1961);

$$(\sqrt{w})^{-1} = \sigma = \tfrac{1}{2}[A(1 + tb)/(1 - b)]^{1/2}$$

where
A = geometric factor applied to measured intensities,
and
b = total background divided by total number of counts.

Isotropic least-squares refinement resulted in a conventional R of 0.101 and a weighted R

$$[(\sum w(F_o - F_c)^2)^{1/2}/(\sum w F_o^2)^{1/2}]$$

of 0.096. Anisotropic refinement lowered the values to 0.088 and 0.081 respectively. A three-dimensional difference Fourier synthesis at this level of refinement indicated coordinates for the three hydrocarbon hydrogen atoms and two of the four ammonium hydrogen atoms. The remaining six ammonium hydrogen atom coordinates were proposed, assuming a tetrahedral configuration about the ammonium nitrogen atom and using a nitrogen–hydrogen bond distance of 1.0 Å. Additional least-square refinement was performed, varying alternate 'blocks' of parameters because of limited computer storage capacity. Refinement in 'block' form

Table 2. *Final atomic parameters*

(a) Final heavy atom parameters and their estimated standard deviations

The values have been multiplied by 10^4.

The temperature factors are in the form $T = \exp[-(\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	7 (4)	1341 (2)	5693 (2)	189 (10)	53 (2)	56 (2)	−21 (4)	3 (4)	−18 (2)
N(2)	847 (5)	1728 (2)	8823 (2)	372 (12)	73 (2)	58 (2)	−12 (5)	62 (5)	29 (2)
N(3)	2534 (5)	4452 (2)	8657 (2)	262 (11)	55 (2)	38 (2)	−7 (4)	3 (4)	−10 (2)
N(4)	4186 (5)	7397 (2)	6614 (2)	300 (11)	61 (2)	60 (2)	−40 (5)	20 (5)	−24 (2)
N(5)	5048 (5)	8353 (2)	4229 (2)	217 (10)	40 (2)	86 (3)	−45 (4)	59 (4)	3 (2)
N(6)	2779 (5)	5544 (2)	2746 (2)	236 (11)	83 (3)	33 (2)	−8 (4)	24 (4)	−10 (2)
N(7)	3012 (4)	5311 (2)	736 (2)	192 (9)	36 (2)	41 (2)	3 (4)	11 (3)	−3 (2)
C(1)	450 (5)	1844 (3)	6354 (2)	71 (11)	37 (2)	42 (2)	−3 (5)	9 (4)	8 (2)
C(2)	894 (5)	2047 (2)	8095 (2)	93 (11)	38 (2)	53 (2)	−19 (4)	24 (5)	8 (2)
C(3)	2114 (5)	4015 (2)	7972 (2)	128 (11)	37 (2)	36 (2)	−1 (5)	5 (5)	3 (2)
C(4)	3816 (5)	6865 (2)	5996 (2)	143 (11)	34 (2)	40 (2)	−8 (5)	28 (5)	(2)
C(5)	4409 (5)	7577 (3)	4240 (2)	128 (12)	41 (2)	42 (2)	14 (6)	18 (4)	3 (2)
C(6)	3154 (5)	6015 (2)	3432 (2)	97 (11)	39 (3)	37 (2)	9 (5)	22 (5)	19 (2)
C(7)	3618 (5)	6595 (2)	4293 (2)	133 (11)	26 (2)	35 (2)	2 (5)	23 (4)	−4 (2)
C(8)	3338 (5)	6207 (2)	5158 (2)	56 (10)	38 (2)	32 (2)	7 (4)	11 (4)	−2 (2)
C(9)	2648 (4)	5248 (2)	5274 (2)	46 (10)	35 (2)	25 (2)	−8 (4)	4 (4)	−7 (2)
C(10)	2408 (5)	4853 (2)	6138 (2)	64 (10)	32 (2)	30 (2)	13 (4)	8 (4)	−7 (2)
C(11)	1747 (5)	3892 (2)	6224 (2)	123 (11)	24 (2)	29 (2)	4 (4)	6 (4)	−8 (2)
C(12)	1578 (5)	3437 (2)	7078 (2)	107 (11)	32 (2)	26 (2)	8 (4)	4 (4)	4 (2)
C(13)	961 (5)	2466 (2)	7178 (2)	102 (12)	34 (2)	30 (2)	−9 (4)	18 (4)	7 (2)

continued until the R value was reduced to 0·069 and the weighted R to 0·031. No parameter shift exceeded one-tenth the value of its estimated standard deviation.

The observed and final calculated structure factors are shown in Table 1. The final coordinates and temperature factors, along with estimated standard deviations, are given in Table 2.

Table 2 *(cont.)*

(b) Final hydrogen parameters and their estimated standard deviations

The positional parameters have been multiplied by 10^3.

	x	y	z	B
H(1)	394 (9)	577 (4)	063 (4)	6·8 (2·1) Å^{-1}
H(2)	197 (18)	555 (7)	023 (6)	18·2 (4·3)
H(3)	336 (12)	472 (5)	067 (4)	10·0 (2·7)
H(4)	283 (12)	544 (5)	131 (5)	11·0 (2·9)
H(9)	231 (6)	483 (2)	469 (2)	1·5 (1·1)
H(10)	275 (6)	526 (3)	680 (2)	2·3 (1·1)
H(11)	154 (6)	353 (2)	565 (2)	1·3 (1·1)

Structure of the carbanion

The observed molecular dimensions, calculated using the computer program *X-ray* 63 (Stewart, 1964) are indicated in Fig. 1. The observed bond lengths in the heptatriene chain are very similar, ranging from 1·378 to 1·394 Å with an average value of 1·387 Å. Valence bond considerations would predict four important resonance structures for the unsubstituted ion, namely:

a b c

I   II

III   IV
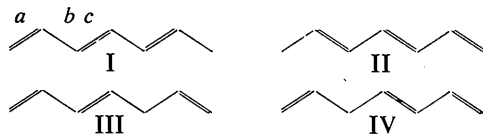
The resulting ion should be symmetrical about the central atom. If all four resonance forms are equally important, the bond numbers should be 1·75, 1·25 and 1·50 for bonds a, b and c respectively. The introduction of cyano-groups on the terminal carbon atoms of this ion should stabilize resonance structures I and II through additional resonance of the form

$$\begin{array}{c} R \\ \diagdown \\ C = C = \overline{N} . \\ \diagup \\ R \end{array}$$
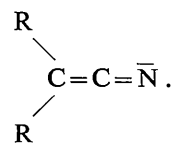
No such resonance structures can be constructed for cyano-groups substituted at position two in the chain. For the hexacyanoheptatrienide ion, valence bond theory would therefore predict that the chain carbon–carbon bond lengths should be nearly equal and similar to the value observed in benzene. Such is, in fact, what is observed. Molecular orbital calculations for the substituted carbanion were carried out using the 'ω' technique'. In this calculation α_0 for nitrogen was taken as α_0 for carbon plus $0·5\beta$. The value of ω was set equal to 1·4. All β_0 integrals were assumed to be equal and

$$\alpha_r = \alpha_0 + (1 - q_r)\, \omega\beta_0$$

where

α_r = Coulomb integral at atom r,
α_0 = uncorrected Hückel Coulomb integral, at atom r,
q_r = charge density at atom r.

The procedure was to calculate q values from simple Hückel wave functions and use these to obtain new α values. Convergence was considered complete after

three iterations. Results of these calculations are summarized in Table 3. The calculated bond orders shown in this Table correlate quite well with the observed bond lengths. Of particular interest is the difference between the bond lengths of the terminal cyano groups and those which are internal. The average observed terminal C–C bond length of 1·430 Å and C–N bond length of 1·139 Å agree well with values found in a variety of similar compounds (Goldstein, Seff & Trueblood, 1968; Sass & Bugg, 1967). The average C–C bond length of 1·468 Å found in the internal cyano-group linkages would correspond to a pure sp^2–sp single bond according to valence bond theory. The short observed average C–N bond length of 1·121 Å supports this hypothesis. Thus, the usually quoted value of 1·42 Å (Bent, 1961) for a normal single bond of this hybridization is most probably too short.

A least-square plane was calculated through the entire carbanion using the method of Schomaker, Waser, March & Bergman (1959) incorporated in the *X-ray* 63 package (Stewart, 1964). The equation of this plane is:

$$6·648x - 4·616y - 0·573z = -0·899$$

where x, y, and z refer to the fractional coordinates of the unit cell. The root-mean-square deviation of the atoms from this plane was found to be 0·079 Å. Two other least-square planes were also calculated, one for the three carbon atoms bonded to C(13), and one for the carbon atoms bonded to C(7). The distances of all atoms from planes 1,2 and 3 respectively, are listed in Table 4. The equations for planes 2 and 3 are:

plane 2: $6·754x - 4·223y - 1·228z = -1·255$
plane 3: $6·511x - 5·169y - 0·1173z = -1·096$.

Table 3. *Results of molecular orbital calculations*

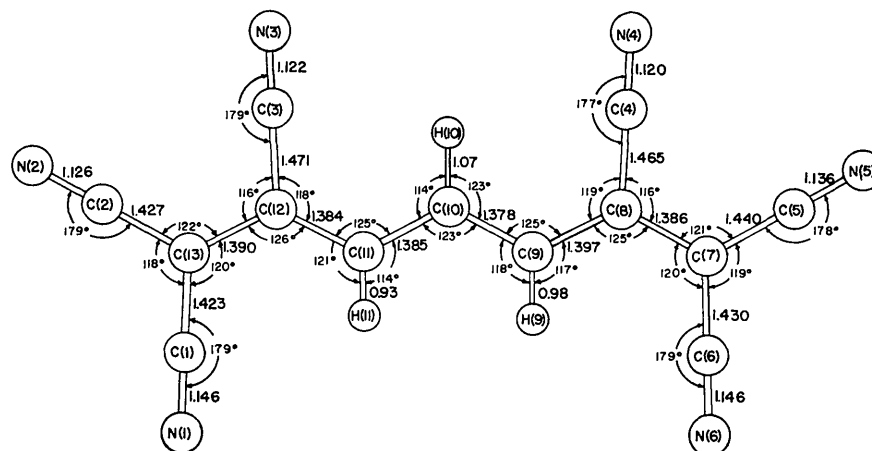| Bond	Observed bond length (Å)		π-bond order	Atom	Effective calculated π-system charge (e^-)
C(7)—C(8)	1·386			C(7), C(13)	−0·07
C(12)–C(13)	1·390	1·388	0·53	C(8), C(12)	+0·06
C(8)—C(9)	1·397			C(9), C(11)	−0·04
C(11)–C(12)	1·384	1·390₅	0·59	C(10)	+0·08
C(9)—C(10)	1·378			C(1), C(2), C(5), C(6)	+0·10
C(10)–C(11)	1·385	1·381	0·64	C(3), C(4)	+0·11
C(7)—C(5)	1·440				
C(7)—C(6)	1·430			N(1), N(2), N(5), N(6)	−0·32
C(13)–C(1)	1·423	1·430	0·51	N(3), N(4)	−0·17
C(13)–C(2)	1·427				
C(12)–C(3)	1·471				
C(8)—C(4)	1·465	1·468	0·44		
C(1)—N(1)	1·146				
C(2)—N(2)	1·126				
C(5)—N(5)	1·136	1·138₅	0·81		
C(6)—N(6)	1·146				
C(3)—N(3)	1·122				
C(4)—N(4)	1·120	1·121	0·88		

Fig. 1. Observed anion dimensions.

Table 4. *Deviations from the least-squares planes through the anion*

	Plane 1 deviation	Plane 2 deviation	Plane 3 deviation
N(1)	0·041 Å	0·005* Å	−0·341* Å
N(2)	−0·159	−0·013*	−0·650*
N(3)	−0·033	−0·023*	−0·343*
N(4)	0·111	−0·146*	0·080*
N(5)	−0·158	−0·618*	−0·015*
N(6)	−0·031	−0·454*	−0·007*
C(1)	0·016	0·000	−0·361*
C(2)	−0·085	0·000	−0·525*
C(3)	0·005	−0·008*	−0·303*
C(4)	0·076	−0·197*	0·038*
C(5)	−0·090	−0·512*	0·000
C(6)	−0·023	−0·424*	0·000
C(7)	−0·014	−0·386*	0·008*
C(8)	0·042	−0·255*	0·000
C(9)	0·065	−0·179*	−0·045*
C(10)	·0·091	−0·078*	−0·083*
C(11)	0·092	−0·027*	−0·148*
C(12)	0·043	0·000	−0·264*
C(13)	0·011	0·019*	−0·363*

* Atoms excluded from the calculation of the plane.

The carbanion as a whole is significantly distorted from planarity. The major feature of this distortion is a bend in the molecule about the central atom C(10). The ion thus consists of two essentially planar halves with approximately C_s-m symmetry. Carbon atoms C(7) and C(13) have a planar bonding arrangement indicating that the excess negative charge resides on the various nitrogen atoms. This result is in agreement with the results of the structure determination of potassium p-nitrophenyldicyanomethide (Sass & Bugg, 1967), ammonium tricyanomethide and pyridinium dicyanomethide (Bugg, Desiderato & Sass, 1964), which show that the degree of carbanion planarity increases with the extent of available resonance stabilization. This conclusion is born out by the structure of potassium 4,4-dinitro-2-butenamide (Holden & Dickerson, 1968), which is not significantly non-planar with respect to the carbon atom bonded to the two nitro-groups. As with the carbanion described in this paper, 4,4-dinitro-2-butenamide has a large π system with which to delocalize the excess charge, and consequently would not be expected to exhibit as great a degree of non-planarity as the carbon atom in question.
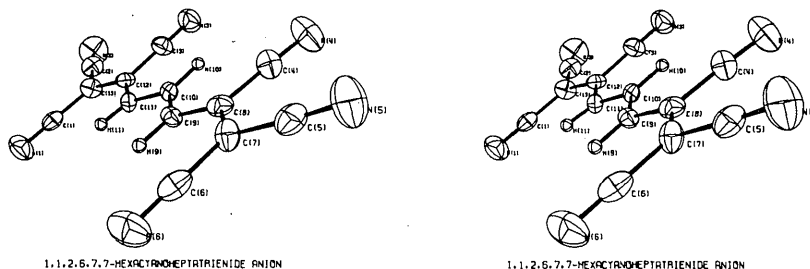
The cyano groups bonded to C(7) and C(13) are rotated slightly out of the plane of the anion. This phenomenon has also been observed in potassium p-nitrophenyldicyanomethide (Sass & Bugg, 1967) and pyridinium dicyanomethide (Bugg, Desiderato & Sass, 1964) and, though no explanation is apparent, the rotation does appear to be significant.

The ellipsoids of thermal vibration are illustrated in Fig. 2. The thermal vibrations, as expected, are large for the cyano nitrogen atoms, and correspondingly smaller for the carbon atoms in the polyene chain.

Crystal packing

Fig. 3 shows the (100) projection of the crystal structure. The packing permits close contact between the ammonium ions and cyano-nitrogen atoms of the cations. The ammonium ions occur in staggered columns parallel to the a axis with adjacent ammonium N–N distances of 3·929 and 4·447 Å. Each ammonium ion is surrounded by eight cyano-nitrogen atoms. The hydrogen bonding geometry as defined by the hydrogen coordinates listed in Table 2(b) is quite satisfactory. Atoms H(2), H(3) and H(4) are directed towards the three closest acceptor nitrogen atoms N(1) (g), N(5) (e) and N(6) (a) respectively, while H(1) is essentially midway between N(3) (c) and N(5) (d). N(1) (f) and N(3) (b) lie opposite H(1) and H(4) respectively and are involved in hydrogen bonds associated with N(7) (h). Atom N(4) (d) does not participate in hydrogen bonding. Fig. 4 shows a sketch of the ammonium nitrogen atom environment. Distances and angles pertinent to this Figure are presented in Table 5. All contacts between anions are compatible with accepted van der Waals radii.

Table 5. *Ammonium ion environment*

	Distances		
N(7)–N(6a)	2·909 Å	H(1)–N(3c)	2·522 Å
N(7)–N(5e)	2·960	H(1)–N(5d)	2·571
N(7)–N(1g)	2·978	H(2)–N(1g)	2·016
N(7)–N(1f)	3·068	H(3)–N(5e)	2·145
N(7)–N(3b)	3·122	H(4)–N(6a)	2·048
N(7)–N(3c)	3·125	N(7)–H(1)	0·937
N(7)–N(5d)	3·337	N(7)–H(2)	0·977
N(7)–N(4d)	3·357	N(7)–H(3)	0·839
N(7)–N(7h)	4·448	N(7)–H(4)	0·871
N(7)–N(7i)	3·929		

1,1,2,6,7,7-HEXACYANOHEPTATRIENIDE ANION   1,1,2,6,7,7-HEXACYANOHEPTATRIENIDE ANION

Fig. 2. Steroscopic representation of the anion thermal ellipsoids.

Table 5 (*cont.*)

Angles

N(7)–H(1)–N(3c)	122·32°
N(7)–H(1)–N(5d)	139·20
N(7)–H(2)–N(1g)	167·74
N(7)–H(3)–N(5e)	163·82
N(7)–H(4)–N(6a)	169·85

(a)	x	,	y	,	z
(b)	x	,	y	,	$z-1$
(c)	$-x+1,$	$-y+1,$	$-z+1$
(d)	x	,	$-y+\frac{3}{2},$	$z-\frac{1}{2}$
(e)	$-x+1,$	$y-\frac{1}{2},$	$-z+\frac{1}{2}$
(f)	x	,	$-y+\frac{1}{2},$	$z-\frac{1}{2}$
(g)	$-x$	,	$y+\frac{1}{2},$	$-z+\frac{1}{2}$
(h)	$-x$	,	$-y+1,$	$-z$
(i)	$-x+1,$	$-y+1,$	$-z$

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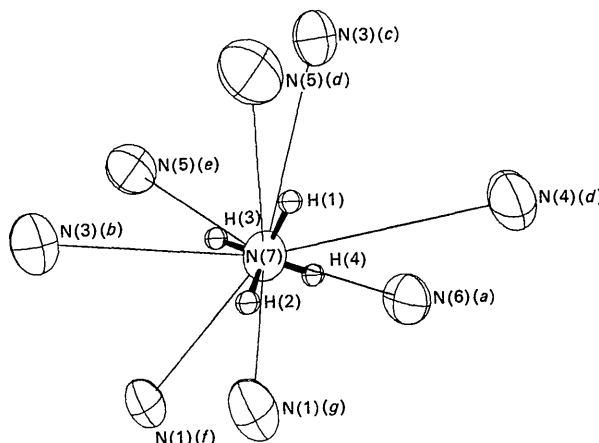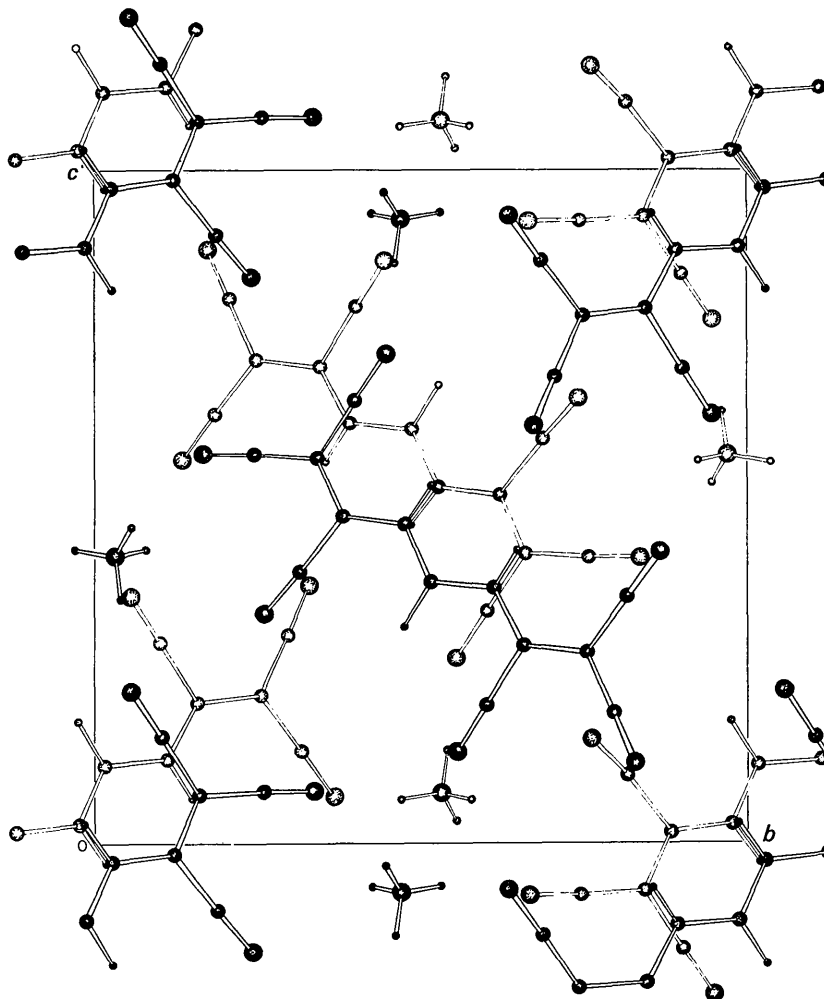
Fig. 4. Ammonium ion environment.

Fig. 3. Crystal packing diagram, [100] projection.

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Konformation und Kristallstruktur von 4,4-Dichlor-2a-aza-A-homo-cholestan-3-on, einem modifizierten Steroid mit ε-Lactamgruppierung

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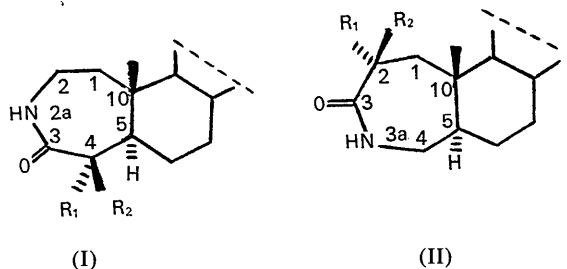
The compound 4,4-dichloro-2a-aza-A-homocholestan-3-one, $C_{27}H_{45}NOCl_2$, crystallizes in space group $P2_12_12_1$ with four molecules in the unit cell. The lattice parameters are $a=7\cdot492$, $b=9\cdot910$, and $c=35\cdot889$ Å. The crystal structure has been determined from three-dimensional X-ray diffraction data collected on an automatic diffractometer. The final R index of 1148 observed independent reflexions was $0\cdot079$. In agreement with optical rotatory dispersion and circular dichroism of this and related compounds the ε-lactam ring is in the chair form, the configuration C–NH–CO–C being planar within the limits of error. A hydrogen bond NH···O=C links molecules into unlimited chains around screw axes parallel to a.

Einleitung

Für Konfigurationsbestimmungen optisch aktiver Lactone und Lactame durch Untersuchung ihrer optischen Rotationsdispersion (Crabbé, 1965) und ihres Zirkulardichroismus (Velluz, Legrand & Grosjean, 1965) scheint die Kenntnis der Konformation des heterocyclischen Ringes notwendige Voraussetzung zu sein (Wolf, 1966; Wolf & Schulze, 1967; Klyne, Scopes, Sheppard & Turner, 1968).

Für sechs konstitutionsisomere bzw. epimere α-chlorierte ε-Lactame, nämlich die 4-Chlor-2a-aza-3-ketone (Ia, b, c) und die 2-Chlor-3a-aza-3-ketone (IIa, b, c) der 5α-Cholestanreihe (Wolf & Schulze, 1967) wurde

(I)   (II)

	a	b	c
R_1:	Cl	Cl	H
R_2:	Cl	H	Cl