Acta Cryst. (1974). B**30**, 1167

A Study of One-Dimensional Hindered Rotation in NH_3OHClO_4

By E. Prince, B. Dickens and J. J. Rush

Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234, *U.S.A.*

(*Received* 10 *October* 1973; *accepted* 10 *January* 1974)

The structure of the phase of hydroxylammonium perchlorate, NH_3OHClO_4, which is stable at 25°C has been refined from 3-dimensional neutron diffractometer data. The structure has space group $P2_1cn$, cell dimensions $a=7{\cdot}52$ (2), $b=7{\cdot}14$ (1), $c=15{\cdot}99$ (2) Å, and 8 formula units per unit cell. There are very large thermal motions of the hydrogen atoms, and the environment of the two crystallographically different NH_3OH^+ ions suggests hindered rotation of each NH_3 group around the axis defined by the N–O bond. Therefore the structure was refined using a model in which the perchlorate groups and the hydroxyl hydrogens were given conventional anisotropic temperature factors, but the ONH_3 groups were treated as rigid bodies, each with an isotropic translation, an isotropic libration of the group as a whole, and a torsional oscillation of the NH_3 group. The final weighted R for 684 observed reflections was 0·051. There are 12 hydrogen bonds between the NH_3OH^+ ions and the ClO_4^- ions, and one hydrogen bond between NH_3OH^+ ions. The apparent r.m.s. amplitude of torsional oscillation of the NH_3–O groups about the N–O vector, as derived from the structural refinement, is $\sim 25°$, and is therefore consistent with frequent reorientation of the NH_3 parts of the NH_3OH^+ ions. Other apparent r.m.s. amplitudes in the structure are only slightly higher than normal values. The NH_3OH^+ ions are in staggered conformations and the ClO_4^- ions are essentially regular tetrahedra.

Introduction

Three crystalline phases of hydroxylammonium perchlorate, NH_3OHClO_4, have been studied by X-ray diffraction by Dickens (1969), who determined the locations of the non-hydrogen atoms in the orthorhombic phase, designated phase A, at −150°C. Preliminary neutron cross-section measurements indicated large thermal motions of the hydrogen atoms. In this paper we give a description of the neutron cross-section results and of a refinement of the structure, based on three-dimensional neutron-diffraction data, utilizing a system of constraints on thermal motion previously described by Prince & Finger (1973).

Neutron cross-section measurements

Dry polycrystalline NH_3OHClO_4 was packed between two 0·15 cm thick 2S aluminum windows in an aluminum sample holder. The samples were loaded in a dry-box and the holder was sealed with epoxy cement before removal from the dry atmosphere. Neutron transmissions were measured for NH_3OHClO_4 as a function of neutron wavelength using a crystal spectrometer, as described in detail previously (Leung, Rush & Taylor, 1972). Total neutron cross sections (σ_t) were calculated from the measured transmissions (Tr) using the relationship $\sigma_t=(1/n)\ln(1/Tr)$, where n is the number of NH_3OHClO_4 molecular units per cm² 'seen' by the neutron beam. The value of n was obtained by two independent methods (see Leung *et al.*, 1972): (1) from the measured sample weight and surface area and (2) by a transmission measurement at a neutron wavelength (0·2 Å) at which the values of σ_t for all atoms are at their known 'free-atom' values. The two values so derived agreed within 3% and their average value was used in our calculation of σ values from the measured transmissions. Finally, the known absorption cross sections for Cl, N and H (Hughes & Schwartz, 1958) were subtracted from the derived σ_t values and the resulting total scattering cross sections were divided by 4 to obtain the scattering cross section per hydrogen atom σ_s/H.

The scattering cross sections thus derived are plotted in Fig. 1 as a function of neutron wavelength; the plot is almost linear. Linear variation of cross section with wavelength permits an estimation of the total incoherent inelastic scattering, which in turn is a measure of the freedom of motion of the NH_3OH^+ groups (Leung *et al.*, 1972). A fit of the measured hydrogen cross section *vs.* wavelength to a straight line provides a slope of 7·8(5) b/Å ($1\text{b}=10^{-24}$ cm²). This rather large value clearly suggests a low barrier to NH_3OH^+ rotation which is shown from the structural work described later in this paper to consist primarily of one-dimensional hindered rotation of the $-NH_3$ group about the N–O axis of the hydroxylammonium ion. Comparison of our results here with previous calculations and calibration curves of slope *vs.* rotational barrier for ammonium ions and methyl groups in crystals (Leung *et al.*, 1972) indicates that the average barrier height in NH_3OHClO_4 is ~6kJ/mol. Such a low barrier suggests a large amplitude of torsional vibration of the $-NH_3$ groups. Although no measurement of torsional mode frequencies has been made here, such a large amplitude of torsional motion for the $-NH_3$ group should be reflected in the hydrogen thermal parameters derived in a structure determination. For this reason, and because of the possibility that this might be an example of one-dimensional rotation in an ionic crystal, we proceeded to determine the structure by neutron diffraction in order to provide further information about the details of the hindered rotation.

Neutron diffraction measurements

Neutron diffraction data were collected from a single crystal of NH_3OHClO_4 kindly provided by G. B. Wilmot, of the Naval Ordnance Station, Indian Head, Maryland. A prismatic needle approximately 1 mm across and 5 mm long, with the needle axis parallel to the crystallographic *a* axis, was mounted on a computer-controlled 4-circle diffractometer at the National Bureau of Standards Reactor with the needle axis approximately parallel to the ϕ axis of the diffractometer. Because NH_3OHClO_4 is extremely hydroscopic, the crystal was sealed in a silica-glass capillary. It was later discovered that the crystal was not adhering firmly to the inside of the capillary and would rotate around the needle axis by one or two tenths of a degree in 24 h. In order to correct for this slow creep, a subroutine was added to the data collection program to carry out a reorientation procedure if the intensity at the predicted peak position of a sharp, low-angle standard reflection fell below a predeter-

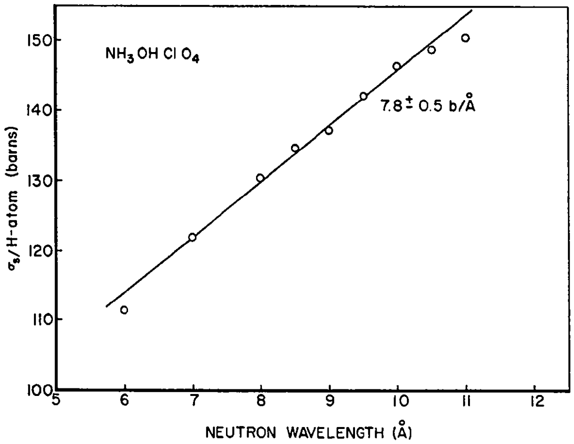


Fig. 1. Neutron-scattering cross section per hydrogen for NH_3OHClO_4. The cross-section slope is also indicated.

Table 1. *Final atom parameters for the neutron refinement of* NH_3OHClO_4

Estimated standard deviations of the least significant figures are given in parentheses. Those for the thermal parameters of the ONH_3 groups have been approximated from the diagonal elements only of the variance–covariance matrix using the formula $\sigma_p=[\sum(\partial p/\partial x_i\sigma_i)^2]^{1/2}$. Anisotropic temperature factors are the coefficients u_{ij} in the expression $\exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}lha^*c^*+2u_{23}klb^*c^*)]$. Third-cumulant parameters are coefficients of the expression $\exp[-i(C_{111}h^3+C_{222}k^3C_{333}l^3+3C_{112}h^2k+3C_{113}h^2l+3C_{122}hk^2+3C_{133}hl^2hl^2+3C_{223}k^2l+3C_{233}kl^2+6C_{123}hkl)]$. The values of u_{ij} have been multiplied by 10^3. The third cumulant parameters have been multiplied by 10^6 for O and N, 10^5 for H. Positional parameters are × 10^4.

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cl(1)	1485 (6)	1516 (4)	1827 (2)	24 (1)	29 (1)	25 (1)	2 (1)	−5 (2)	0 (1)
Cl(2)	0	2453 (3)	4352 (2)	28 (1)	28 (1)	21 (1)	−1 (2)	−5 (2)	−2 (1)
O(1)	51 (10)	153 (7)	1839 (4)	40 (3)	36 (3)	43 (3)	−8 (3)	−7 (3)	−3 (2)
O(2)	2658 (10)	1105 (10)	2519 (4)	32 (3)	65 (4)	36 (3)	−8 (3)	−7 (2)	15 (3)
O(3)	716 (13)	3335 (8)	1905 (4)	79 (5)	30 (3)	51 (4)	9 (4)	−3 (4)	1 (3)
O(4)	2419 (11)	1305 (11)	1063 (4)	44 (4)	82 (5)	30 (3)	9 (4)	8 (3)	6 (3)
O(5)	1061 (10)	917 (8)	4642 (4)	52 (4)	28 (3)	44 (4)	3 (2)	10 (3)	6 (2)
O(6)	1158(11)	3995 (7)	4160 (4)	52 (4)	29 (2)	36 (3)	−5 (2)	5 (3)	8 (2)
O(7)	−950 (11)	1888 (12)	3628 (4)	44 (4)	92 (5)	39 (3)	−8 (4)	−4 (3)	−26 (3)
O(8)	−1205 (10)	3009 (9)	5013 (4)	38 (3)	55 (3)	30 (3)	8 (3)	7 (3)	−2 (2)
O(9)	5015 (11)	3486 (8)	9091 (4)	43 (1)	34 (1)	35 (1)	1 (3)	1 (0)	8 (1)
O(10)	6340 (9)	2067 (8)	6555 (3)	40 (1)	35 (1)	34 (1)	−1 (0)	−1 (0)	−6 (1)
N(1)	4916 (9)	2154 (5)	9720 (2)	43 (1)	34 (1)	35 (1)	−1 (0)	1 (0)	8 (1)
N(2)	6472 (8)	3308 (5)	7223 (2)	40 (1)	35 (1)	34 (1)	−1 (0)	−1 (0)	−6 (1)
H(1)	4300 (32)	2428 (24)	134 (10)	139 (7)	98 (4)	63 (3)	29 (2)	57 (2)	27 (1)
H(2)	4679 (37)	1067 (16)	9468 (10)	211 (7)	35 (1)	87 (4)	−31 (1)	−12 (1)	2 (1)
H(3)	6093 (25)	1962 (31)	9939 (14)	66 (3)	156 (5)	141 (4)	0 (1)	−41 (2)	88 (3)
H(4)	376 (18)	5376 (16)	631 (8)	75 (9)	52 (6)	67 (8)	4 (7)	−24 (7)	−5 (5)
H(5)	5817 (27)	2985 (25)	7656 (8)	130 (5)	99 (4)	53 (1)	45 (2)	47 (2)	−27 (1)
H(6)	7628 (22)	3451 (28)	7387 (11)	49 (3)	138 (5)	114 (4)	−1 (1)	−26 (1)	−72 (3)
H(7)	6142 (35)	4453 (16)	7028 (9)	189 (7)	35 (1)	78 (4)	31 (2)	−32 (2)	−9 (1)
H(8)	1682 (25)	9093 (16)	3233 (8)	110 (11)	48 (6)	69 (5)	−14 (8)	−21 (9)	−3 (6)

	C_{111}	C_{222}	C_{333}	C_{112}	C_{122}	C_{113}	C_{133}	C_{223}	C_{233}	C_{123}
O(9)	−6 (0)	−50 (0)	4 (0)	−29 (0)	1 (0)	14 (0)	0 (0)	−7 (0)	4 (0)	−2 (0)
O(10)	4 (0)	26 (0)	2 (0)	13 (0)	0 (0)	7 (0)	0 (0)	−2 (0)	−2 (0)	−1 (0)
N(1)	6 (0)	50 (0)	−4 (0)	29 (0)	−1 (0)	−14 (0)	0 (0)	7 (0)	−4 (0)	2 (0)
N(2)	−4 (0)	−26 (0)	−2 (0)	−13 (0)	0 (0)	−7 (0)	0 (0)	2 (0)	0 (0)	1 (0)
H(1)	377 (39)	−45 (8)	−16 (1)	57 (4)	−31 (7)	−11 (0)	−31 (3)	−53 (5)	−27 (3)	−35 (4)
H(2)	271 (28)	42 (4)	0 (0)	395 (4)	−152 (14)	94 (12)	−8 (1)	10 (1)	9 (0)	−35 (4)
H(3)	−76 (4)	137 (3)	−31 (2)	121(14)	−323 (34)	54 (6)	−47 (5)	−26 (3)	−36 (3)	−133 (14)
H(5)	342 (39)	110 (16)	−10 (1)	−87 (9)	−43 (8)	−12 (0)	−23 (2)	−63 (7)	25 (3)	40 (5)
H(6)	−29 (1)	−29 (4)	−11 (1)	−58 (7)	−236 (26)	26 (3)	−32 (4)	−20 (2)	15 (1)	91 (10)
H(7)	305 (36)	−43 (5)	3 (0)	−289 (30)	−132 (14)	46 (7)	−16 (2)	1 (2)	−12 (1)	51 (6)

mined value. The collimation on the detector side was coarse enough to ensure that slight misorientations would not affect the measurement of integrated intensities.

The unit cell at 25°C, $a=7{\cdot}52$ (2), $b=7{\cdot}14$ (1), $c=15{\cdot}99$ Å, and the space group, $P2_1cn$ (No. 33), are as given by Dickens (1969). The neutron wavelength used was 1·232 Å. All possible reflections with a 2θ less than 100° in two octants of reciprocal space were measured by a procedure described previously (Prince, 1972). 684 of 933 independent reflections had observable intensity. The agreement index for equivalent reflections, defined by $R=\sum||F_{hkl}|-|F_{hk\bar{l}}||/\sum|F_{hkl}|$, was 0·028. Because the size and shape of the crystal were not precisely known no absorption corrections were made. The maximum variation in transmission factor was estimated to be less than 3%.

Refinement of the structure

Refinement started from a trial structure consisting of the parameters for the non-hydrogen atoms determined by Dickens (1969) together with hydrogen atom positions inferred from a Fourier synthesis using phases calculated from the non-hydrogen atom parameters and the observed structure factors in a preliminary, less extensive data set. All least-squares refinement was performed using the program *RFINE* (Finger, 1972), and sought to minimize the function $\sum w(|F_o|-|F_c|)^2$. Weights were assigned according to the formulae $w=1/\sigma^2$ and $\sigma=[\sigma_s^2+(0{\cdot}015F_o)^2]^{1/2}$, where σ_s is an estimated standard deviation computed from counting statistics.

After one cycle in which only the scale factor was refined and one additional cycle in which all atoms were assigned isotropic temperature factors the value of the weighted residual, R_w $(R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2})$ was 0·123. Anisotropic temperature factors were then assigned to the atoms in the perchlorate groups and the hydroxyl hydrogen atoms, the temperature factors for the remaining atoms were kept isotropic, and a correction for isotropic secondary extinction along the lines suggested by Zachariasen (1968) was included. Five cycles reduced the value of R_w to 0·081.

A scattering density synthesis based on F_o showed that the amine hydrogen atoms of both NH_3OH^+ ions were undergoing appreciable libration about the N–O vector. These librations were so large that there was a 'doughnut' of continuous scattering density, although the main positions of the hydrogens could be discerned. The amount of libration obviously required a more sophisticated model for hydrogen motion than can be obtained by representing their motions as thermal ellipses. Therefore we constructed a model for the thermal motion of the ONH_3 groups which treated them as rigid bodies. Each group was allowed an isotropic translation and an isotropic libration, while hydrogen atoms were allowed an additional torsional oscillation around the axis defined by the N–O bond. This model was incorporated into the least-squares program using the relations derived by Prince & Finger (1973). The atoms of the perchlorate groups and the hydroxyl hydrogen atoms were treated with conventional anisotropic temperature factors, as before. After two cycles in which the extinction parameter was held fixed and three more in which all parameters were allowed to vary, the value of R_w was 0·051. The largest ratio of a parameter shift to its standard deviation in the last cycle was 0·06. The largest correlation coefficient was 0·78 between the extinction and scale parameters. There were three other coefficients greater than

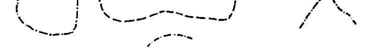


Fig. 3. A section of a Fourier map passing through the three hydrogen atoms bonded to nitrogen atom N(1). Negative contours are indicated by dashed lines and the 0 contour by a dot-dash line. The ×'s indicate the corrected positions of the hydrogen atoms.

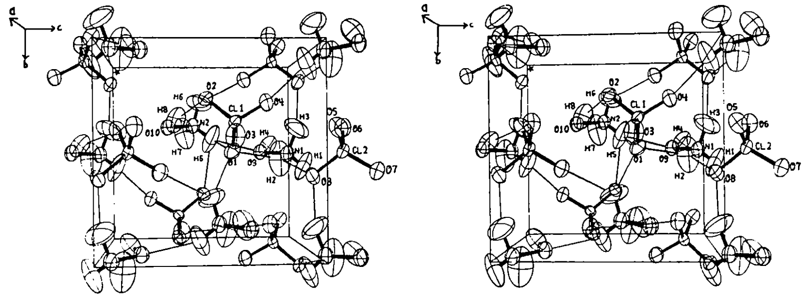


Fig. 2. The crystal structure of NH_3OHClO_4. Half the unit cell is shown viewed along **a**. The origin of the crystallographic coordinate system is marked by a star. A unique set of atoms is labelled. The thin lines denote hydrogen bonds.

0·60. All correlation coefficients involving the $-NH_3$ groups were less than 0·40. The improved fit is highly significant in view of the fact that the rigid-body model actually has fewer parameters than the one in which each atom in the ONH_3 groups has an isotropic temperature factor and is treated independently. Table 1 gives the final atomic parameters and Table 2 gives observed and calculated structure factors.† The extinction parameter, which represents the product $\bar{T}r^*$, refined to

Table 3. *Interatomic distances and angles in* NH_3OHClO_4

Because of the large effects of thermal motion on the interatomic distances, the standard deviations (in parentheses) should not be taken as implying that the mean bond distances are known to that accuracy. Interatomic distances marked with an asterisk involve hydrogen bonds.

R: With riding model correction (Busing & Levy, 1964).

RB: Derived from first moments resulting from the rigid-body parameters (Prince & Finger, 1973).

i	*j*	*k*	D_{ij}		D_{jk}		D_{ik}	∠*ijk*
O(9)	N(1)	H(1)	1·419 (6)		0·92 (2)^{RB}	0·96^{R}		113·8 (10)
O(9)	N(1)	H(2)	1·419 (6)		1·00 (1)^{RB}	1·00^{R}		105·5 (9)
O(9)	N(1)	H(3)	1·419 (6)		1·07 (2)^{RB}	1·07^{R}		106·4 (10)
N(1)	O(9)	H(4)			0·95 (2)	0·97^{R}		104·4 (9)
N(1)	H(1)	O(4)	0·96		2·10 (2)		2·861 (8)*	140 (2)
N(1)	H(2)	O(1)	1·00		2·16 (2)		2·955 (6)*	135 (1)
N(1)	H(2)	O(8)	1·00		2·34 (1)		2·930 (8)*	130 (1)
N(1)	H(3)	O(8)	1·07		1·90 (2)		2·930 (8)*	160 (2)
O(9)	H(4)	O(5)	0·97		1·88 (1)		2·752 (8)*	152 (1)
O(10)	N(2)	H(5)	1·408 (6)		0·96 (2)^{RB}	0·97^{R}		111 (1)
O(10)	N(2)	H(6)	1·408 (6)		1·01 (2)^{RB}	0·96^{R}		109 (1)
O(10)	N(2)	H(7)	1·408 (6)		1·01 (1)^{RB}	1·00^{R}		106 (1)
N(2)	O(10)	H(8)			0·92 (2)	0·98^{R}		105 (1)
N(2)	H(5)	O(9)	0·97		2·27 (1)		3·155 (8)*	145 (1)
N(2)	H(5)	O(1)	0·97		2·37 (2)		3·085 (7)*	129 (1)
N(2)	H(5)	O(2)	0·97		2·41 (2)		2·911 (8)*	112 (2)
N(2)	H(6)	O(1)	0·96		2·16 (2)		2·946 (8)*	134 (2)
N(2)	H(6)	O(7)	0·96		2·17 (2)		2·920 (8)*	130 (2)
N(2)	H(7)	O(6)	1·00		2·08 (2)		2·911 (6)*	138 (1)
N(2)	H(7)	O(3)	1·00		2·29 (1)		2·796 (7)*	110 (1)
O(10)	H(8)	O(2)	0·98		1·96 (1)		2·859 (9)*	165 (1)
O(1)	Cl(1)	O(2)	1·444 (7)	1·458^{R}	1·425 (6)	1·440^{R}	2·320 (9)	107·9 (4)
O(1)	Cl(1)	O(3)	1·444 (7)	1·458^{R}	1·422 (7)	1·449^{R}	2·322 (7)	108·2 (5)
O(1)	Cl(1)	O(4)	1·444 (7)	1·458^{R}	1·395 (7)	1·421^{R}	2·297 (9)	107·9 (4)
O(2)	Cl(1)	O(3)	1·425 (6)	1·440^{R}	1·422 (7)	1·449^{R}	2·356 (10)	111·7 (5)
O(2)	Cl(1)	O(4)	1·425 (6)	1·440^{R}	1·395 (7)	1·421^{R}	2·296 (8)	109·0 (4)
O(3)	Cl(1)	O(4)	1·422 (7)	1·449^{R}	1·395 (7)	1·421^{R}	2·335 (10)	111·9 (5)
O(5)	Cl(2)	O(6)	1·425 (7)	1·439^{R}	1·429 (7)	1·441^{R}	2·319 (7)	108·7 (4)
O(5)	Cl(2)	O(7)	1·425 (7)	1·439^{R}	1·399 (7)	1·430^{R}	2·294 (10)	108·7 (5)
O(5)	Cl(2)	O(8)	1·425 (7)	1·439^{R}	1·429 (6)	1·446^{R}	2·327 (8)	109·3 (4)
O(6)	Cl(2)	O(7)	1·429 (7)	1·441^{R}	1·399 (7)	1·430^{R}	2·329 (9)	110·9 (4)
O(6)	Cl(2)	O(8)	1·429 (7)	1·441^{R}	1·429 (6)	1·446^{R}	2·323 (9)	108·7 (4)
O(7)	Cl(2)	O(8)	1·399 (7)	1·430^{R}	1·429 (6)	1·446^{R}	2·324 (8)	110·6 (5)

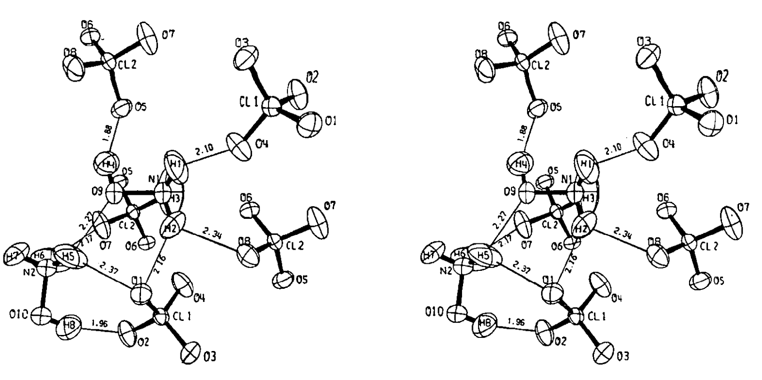


Fig. 4. The environment of the $N(1)H_3OH^+$ ion in NH_3OHClO_4.

---

† Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30338 (8pp.). Copies may be obtained through the Executive Secretary International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the satisfactory value 1·32 (11) × 10^{-4} cm. The minimum value of the extinction factor y (Zachariasen, 1968) is 0·470, for the 014 reflection. Eight other reflections have y values less than 0·70.

Discussion

The structure is shown in Fig. 2. Although the thermal ellipsoids are generally larger than normal, as might be expected for a phase within 35°K of a first-order phase transition (see Dickens, 1969), they nevertheless show that the thermal motion is especially large for the hydrogen atoms attached to nitrogen in the NH_3OH^+ ions. The rigid-body translation and libration parameters are 0·0254 (10) $Å^2$ and 0·0336 (23) $radians^2$ respectively for the $N(1)H_3OH^+$ ions and 0·0275 (10) $Å^2$ and 0·0238 (22) $radians^2$ respectively for the $N(2)H_3OH^+$ ion. The apparent r.m.s. amplitudes of torsional oscillation for the $O–NH_3$ groups about their N–O bonds are 0·44 radians for the $N(1)H_3OH^+$ ion and 0·43 radians for the $N(2)H_3OH^+$ ion, giving an r.m.s. angular displacement of 25°. If these units are considered to be simple harmonic oscillators, this average value corresponds to a peak angular displacement from the equilibrium position of about 35°. Since the potential function appropriate to this oscillation cannot be parabolic, but rather must be at least sinusoidal with a period of 120°, this represents a displacement half way to the potential maximum, which suggests that there must be a rather low barrier to reorientation of the $–NH_3$ groups, in agreement with our neutron cross-section measurements. Fig. 3 is a section of a Fourier map passing through the positions of the three hydrogen atoms bonded to nitrogen atom N(1). The 'lumpy doughnut' of negative scattering power and the skewed density distributions are clearly visible. The largest peak in a difference map had a height about 0·4 of the lowest contour.

The average N–O distance in the NH_3OH^+ ions is 1·41 Å. The details of the NH_3OH^+ ion configurations and environments are given in Table 3 and Figs. 4 and 5. Both NH_3OH^+ ions are in the staggered conformation. All hydrogen atoms enter into hydrogen bonds. Those on the $N(1)H_3OH^+$ ion bond solely to ClO_4^- ions, but H(5) on the $N(2)H_3OH^+$ ion hydrogen bonds to O(9) of the $N(1)H_3O(9)H^+$ ion, providing a link between NH_3OH^+ ions. Because of the unusually large amount of thermal motion in the structure and the necessary assumptions in the refinement model, it is not possible to discuss meaningful differences in N–H distances or O–N–H angles. However, comparison of the individual H···O distances with an assumed maximum hydrogen-bonding distance of 2·4 Å shows that some hydrogen bonds in NH_3OHClO_4 are fairly strong. Not surprisingly, the weaker bonds are bifurcated. The one-dimensional hindered rotation of the $O–NH_3$ groups does not arise because of extreme weakness in the hydrogen bonding, but rather because hydrogen binding opportunities are more or less continuously available as each $O–NH_3$ group rotates about its N–O axis.

The ordering of the ClO_4^- ions in NH_3OHClO_4 [in contrast to the disordered ClO_4^- ions observed in $C(C_6H_5)_3ClO$ (Gomes de Mesquita, MacGillavry & Eriks, 1965), $C_{20}H_{31}N_3(ClO_4)_2$ (Karle & Karle, 1966), and $(C_6H_5C)_3ClO_4$ (Sundaralingam & Jensen, 1966)] is probably a consequence of the relatively strong O–H···O hydrogen bonds. With corrections for riding motion (Busing & Levy, 1964) applied, the Cl–O distances (Table 3) average 1·442 Å in $Cl(1)O_4^-$, 1·439 Å in $Cl(2)O_4^-$, and 1·441 Å overall. Although each ClO_4^- ion has one Cl–O distance appreciably shorter than the other three when the 'raw' distances are used, the short distances become more comparable with the others after application of the riding correction. Further the Cl–O distances do not correlate with the number of hydrogen bonds accepted by the oxygen atoms or with the directions of the bonds in the unit cell. We therefore believe that there is no real difference between Cl–O distances in NH_3OHClO_4 at our present level of precision (the greatest discrepancy, the case of Cl(1)–O(4), is only 3σ from the mean) and that these ions are not significantly distorted from regular tetrahedra. Table 3 shows that the $Cl(1)O_4$ group accepts seven hydrogen bonds and that the $Cl(2)O_4$ group accepts five.

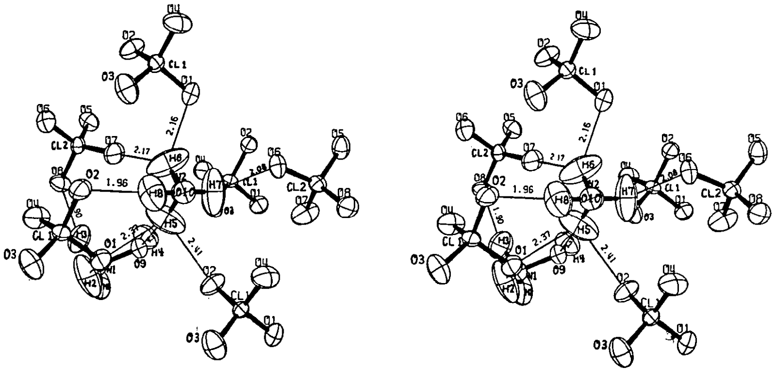


Fig. 5. The environment of the $N(2)H_3OH^+$ ion in NH_3OHClO_4.

References

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

DICKENS, B. (1969). *Acta Cryst.* B**25**, 1875–1882.

FINGER, L. W. (1972). *RFINE* 2 *a Fortran* IV *Computer Program for Structure-Factor Calculation and Least-Squares Refinement of Crystal Structures.* Geophysical Laboratory, Carnegie Institution of Washington (unpublished).

GOMES DE MESQUITA, A. H., MACGILLAVRY, C. H. & ERIKS, K. (1965). *Acta Cryst.* **18**, 437–443.

HUGHES, D. J. & SCHWARTZ, R. B. (1958). *Neutron Cross Sections.* Brookhaven National Laboratory Report BNL 325.

KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **21**, 860–868.

LEUNG, P. S., RUSH, J. J. & TAYLOR, T. I. (1972). *J. Chem. Phys.* **57**, 175–182.

PRINCE, E. (1972). *J. Chem. Phys.* **56**, 4352–4355.

PRINCE, E. & FINGER, L. W. (1973). *Acta Cryst.* B**29**, 179–183.

SUNDARALINGAM, M. & JENSEN, L. H. (1966). *J. Amer. Chem. Soc.* **88**, 198–204.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* A**24**, 421–424.

Acta Cryst. (1974). B30, 1172

The Crystal Structure of 2,3,6,7,7,8-Hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one

BY CAROL G. BIEFELD AND HARRY A. EICK

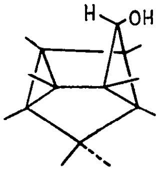
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, *U.S.A.*

(*Received* 13 *September* 1973; *accepted* 27 *November* 1973)

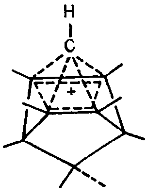
The structure of 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one ($C_{26}H_{28}O$) has been determined from room-temperature X-ray diffractometer data. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a=9{\cdot}155$ (3), $b=14{\cdot}635$ (9), $c=15{\cdot}425$ (4) Å, $\beta=100{\cdot}7$ (2)°; $Z=4$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to a final R value of 0·062. The cyclobutane ring is non-planar with a dihedral angle of 133 (1)° and contains two exceptionally long C–C bonds of 1·608 (8) and 1·602 (10) Å which reflect the internal strain of the cage system. The molecule, disregarding the phenyl rings, exhibits near mirror symmetry.

Introduction

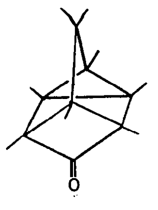
Recently Stohrer & Hoffmann (1972) predicted the existence of a novel intermediate, $(CH)_5^+$, in the carbonium ion rearrangements of the tricyclo[2,1,0,$0^{2,5}$]-pentane system. Soon thereafter many reports appeared (Masamune, Sakai, Ona & Jones, 1972; Goldstein & Kline, 1973; Hogeveen & Kwant, 1973; and Lustgarten, 1972) concerning $(CH)_5^+$-type carbonium ions as intermediates in other carbonium ion rearrangements. In one case, Hart & Kuzuya (1972) reported, on the basis of spectroscopic data and various labelling experiments, that alcohol (I) ionizes in fluorosulfonic acid to the pyramidal cation (II), a $(CH)_5^+$-type carbonium ion.



(I)



(II)



(III)

Since the geometry of the tetracyclic system was unknown, a structural analysis of (I) or the closely related compound (III) could provide additional evidence to support the existence of $(CH)_5^+$-type ions if the molecular parameters obtained were consistent with those expected for rearrangement to the ion. In addition data would be provided on how the molecular parameters are affected by the strain present in this system. For these reasons the investigation of the crystal structure of (III) – 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one – was undertaken.

Experimental

A sample of 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one (HDTO) was supplied by Professor H. Hart. Recrystallization (Hart & Love, 1971) from petroleum spirit produced clear, colorless crystals in the form of flat plates. Preliminary measurements of the lattice parameters and space-group determination were made by precession camera techniques with Zr-filtered Mo $K\alpha$ radiation. All subsequent measurements were made *via* a computer-controlled, four-circle, Picker goniometer with Mo $K\alpha$ radiation, graphite monochromator, and at a temperature of 23 (2)°. The crystal used was roughly a rectangular prism (0·144 × 0·182 × 0·328 mm) mounted with the long dimension [100] parallel to the φ axis of the goniometer. Cell constants were obtained from least-squares refinement of 12 reflections which had been hand-centered on the goniometer. The density was determined by flotation in aqueous potassium iodide.