reaction was determined by quantitative vapor phase chromatography. The conversions in the azetidines series were run to 15% or less. The mass balance in these runs was generally better than 90%.

**Phosphorescence Emission Studies.** The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on a $x$-$y$ plotter. Samples having short radiative lifetimes (<100 sec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime ($\tau_0$).

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# Crystal and Molecular Structure of 4-Azoniaspiro[3.5]nonane Perchlorate

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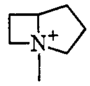
**Abstract:** The crystal and molecular structure of the title compound was determined by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $P2_1/c$, with four molecules in a unit cell of dimensions $a$ = 6.6998 ± 0.0007 Å, $b$ = 13.244 ± 0.001 Å, $c$ = 12.743 ± 0.001 Å, $\beta$ = 97.75 ± 0.01°. The structure was solved by the heavy-atom method and refined by block-diagonal matrix least squares to a final value of $R$ = 0.066 for 683 observed reflections. The azetidinium ring is very nearly planar with a dihedral angle of 176.5°, and average C–C and C–N distances of 1.50 ± 0.01 Å and 1.52 ± 0.02 Å, respectively. The piperidinium moiety is in the chair conformation with all ring distances being equivalent; the average of the C–C distances is 1.491 ± 0.02 Å and the average of the C–N distances is 1.498 ± 0.01 Å.

The study of 4-azoniaspiro[3.5]nonane perchlorate, $(C_9H_{16}N)^+ ClO_4^-$ (I), was undertaken as part of a more general study of simply substituted azetidine derivatives in various bonding situations. The interest in these compounds is due to their structural similarity to the biologically active $\beta$-lactam moiety found in the penicillins and cephalosporins, and the unusual molecular parameters generally found in the small strained rings. Several X-ray studies of simply substituted azetidine derivatives have been made since 1968.[1–5] Until the recent X-ray study of II,[6] no structural studies had been made of bicyclic derivatives of azetidine except as penicillins or cephalosporins. The present study is the first investigation of a spiro-fused azetidine derivative.

I



II

**Crystal Data.** A crystalline sample of the title compound was kindly furnished to us[7] by Professor Nelson J. Leonard of the University of Illinois. Single crystals suitable for X-ray study were obtained by recrystallization from a saturated solution of ethyl acetate and melted sharply at 169°. The crystal chosen for this study had approximate dimensions of 0.1 mm × 0.1 mm × 0.1 mm.

Systematic absences for the ($h0l$) reflections when $l$ is odd, and for the ($0k0$) reflections when $k$ is odd, led unambiguously to the assignment of the space group as $P2_1/c$. Lattice constants were determined by least-squares refinement[8] of 29 reflections whose $2\theta$ values in the range from 55 to 59° were measured under fine conditions (1° take-off angle and 0.05° receiving slit) on a G.E. XRD-5 diffractometer using Cu K$\alpha$ radiation. The constants obtained from the refinement, with their estimated standard deviations (ESD's), were: $a$ = 6.6998 ± 0.0007 Å, $b$ = 13.244 ± 0.001 Å, $c$ = 12.743 ± 0.001 Å, $\beta$ = 97.75 ± 0.01°. The calculated density of 1.338 g/cc for four molecules per unit cell was in agreement with the experimentally measured density of 1.35 g/cc using flotation techniques.

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(8) Program LSLAT, K. N. Trueblood.

Table I. Fractional Coordinates and Anisotropic Thermal Parameters[a]

| Atom | $X$ | $Y$ | $Z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cl | 0.3210 (4) | 0.2238 (2) | 0.0727 (2) | 0.0396 (7) | 0.0072 (2) | 0.0078 (2) | −0.0070 (3) | 0.0019 (3) | −0.0016 (2) |
| O$_1$ (0.8)[b] | 0.2600 (19) | 0.1792 (14) | 0.9811 (14) | 0.063 (5) | 0.041 (3) | 0.037 (2) | −0.011 (3) | −0.005 (3) | −0.029 (2) |
| O$_2$ (0.8)[b] | 0.1157 (20) | 0.2237 (14) | 0.0763 (15) | 0.077 (5) | 0.027 (2) | 0.041 (3) | 0.002 (3) | 0.025 (3) | 0.000 (2) |
| O$_3$ (0.6)[b] | 0.2990 (22) | 0.2385 (11) | 0.1817 (11) | 0.080 (5) | 0.014 (1) | 0.013 (1) | −0.003 (2) | 0.016 (2) | −0.001 (1) |
| O$_4$ (0.6)[b] | 0.3972 (22) | 0.3064 (9) | 0.0314 (11) | 0.093 (6) | 0.007 (1) | 0.015 (1) | −0.005 (2) | 0.017 (3) | 0.004 (1) |
| O$_5$ (0.4)[b] | 0.4092 (37) | 0.1315 (10) | 0.0708 (18) | 0.133 (2) | 0.000 (1) | 0.024 (3) | 0.005 (3) | 0.045 (5) | 0.000 (1) |
| O$_6$ (0.4)[b] | 0.4847 (35) | 0.1746 (17) | 0.1267 (19) | 0.084 (2) | 0.015 (2) | 0.017 (2) | 0.016 (4) | −0.025 (4) | −0.002 (2) |
| O$_7$ (0.4)[b] | 0.4131 (53) | 0.3002 (29) | 0.0791 (32) | 0.144 (8) | 0.036 (5) | 0.038 (6) | −0.51 (8) | −0.025 (8) | −0.008 (4) |
| N | 0.8010 (10) | 0.4156 (5) | 0.2967 (6) | 0.025 (2) | 0.006 (1) | 0.008 (7) | 0.003 (1) | 0.005 (1) | −0.000 (1) |
| C$_1$ | 0.8388 (15) | 0.3059 (6) | 0.2785 (9) | 0.048 (3) | 0.003 (1) | 0.012 (1) | 0.001 (1) | 0.004 (1) | 0.000 (1) |
| C$_2$ | 0.7159 (16) | 0.2782 (9) | 0.3634 (9) | 0.051 (4) | 0.013 (1) | 0.011 (1) | −0.000 (2) | 0.011 (2) | 0.002 (1) |
| C$_3$ | 0.6821 (20) | 0.3882 (9) | 0.3881 (10) | 0.069 (4) | 0.008 (1) | 0.015 (1) | 0.002 (2) | 0.016 (2) | 0.000 (1) |
| C$_4$ | 0.9828 (15) | 0.4799 (8) | 0.3349 (9) | 0.030 (3) | 0.008 (1) | 0.014 (1) | 0.000 (1) | −0.006 (1) | −0.002 (1) |
| C$_5$ | 0.0978 (15) | 0.5007 (10) | 0.2408 (13) | 0.028 (3) | 0.013 (1) | 0.029 (2) | −0.009 (2) | 0.011 (2) | −0.007 (1) |
| C$_6$ | 0.9681 (23) | 0.5452 (10) | 0.1498 (11) | 0.089 (6) | 0.011 (1) | 0.017 (1) | −0.012 (2) | 0.020 (3) | −0.000 (1) |
| C$_7$ | 0.7883 (24) | 0.4819 (10) | 0.1188 (10) | 0.108 (7) | 0.011 (1) | 0.009 (1) | −0.009 (2) | −0.006 (2) | 0.003 (1) |
| C$_8$ | 0.6732 (15) | 0.4672 (7) | 0.2084 (9) | 0.036 (3) | 0.008 (1) | 0.011 (1) | 0.000 (1) | −0.005 (1) | 0.000 (1) |

[a] Anisotropic temperature factors of the form $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$. Standard deviation × $10^4$ in parentheses. [b] Final fractional weights used for the oxygen atoms. All other atoms are at unit weight.

Intensity data were taken on a G.E. XRD-490 automated diffractometer using Cu K$\alpha$ radiation and Ross balanced filters (Fe and Ni) by the stationary crystal–stationary counter method. A counting time of 10 sec through each filter and a take-off angle of 5° were used. A set of three standards was monitored every 25 reflections, with the crystal being manually realigned whenever any of the standards deviated from its original value by more than twice its standard deviation (based on counting statistics). Within a $2\theta$ limit of 100°, 1286 reflections were measured of which 683 were observed. The criterion for an unobserved reflection was taken as: $(I_{\mathrm{Zr}} - 2\sigma(I_{\mathrm{Zr}})) - (I_{\mathrm{Y}} + 2\sigma(I_{\mathrm{Y}})) > 30$ counts. Intensities were converted to structure factors using a program modified for the P.D.P.-10.[9] Lorentz–polarization corrections were applied as a function of $2\theta$, and absorption (6% maximum) was corrected as a function of $\varphi$ only. The linear absorption coefficient for the compound is 29.82 cm$^{-1}$. Finally, an $\alpha_1 - \alpha_2$ splitting correction was applied as a function of $2\theta$.

**Structure Determination.** The chlorine coordinates were obtained from a three-dimensional Patterson synthesis and allowed the data to refine to $R = 0.44$. A three-dimensional Fourier synthesis was calculated based on the magnitudes of the observed reflections and the phases obtained from the refined chlorine coordinates. Although every atom in the bicyclic cation was resolved at a height of from 2 to 6 e/Å$^3$, the region of the perchlorate group showed diffuse peaks of lower than normal height for oxygen atoms (2–4 e/Å$^3$).

Since it was apparent from the Fourier map that the oxygen atoms about the chlorine were badly disordered, an initial series of least-squares refinements were carried out excluding the oxygens. This isotropic refinement led to a value of $R = 0.24$ and was the basis of a new difference Fourier map.

Initial attempts at further refinement assumed two disordered sets of tetrahedrally arranged oxygens about the perchlorate group. Refinement, after appropriately weighting the oxygens and assigning anistropic temperature factors, led only to a value of $R = 0.11$. Further attempts, assuming a spherical distribution of charge about the chlorine at a reasonable Cl–O distance, led to even poorer results.

Finally, an empirical technique based on the difference Fourier map and subsequent least-squares results led to the most satisfactory solution. The four largest "peaks" about the chlorine at distances from 1.3 to 1.4 Å were included in an isotropic least-squares refinement with the atoms weighted proportionately to their map heights. Then a new difference Fourier map was calculated based on this result. Regions of very high electron density were assigned as fractional oxygens; the weights of the previously included oxygens were readjusted so that the total of all fractional oxygens would equal the four oxygens expected about the chlorine; and the iterative process involving least squares and difference Fourier maps was repeated. This procedure was repeated until the difference Fourier map had no region greater than 0.5 e/Å$^3$ in the vicinity of the perchlorate oxygen atoms. At this stage the model refined isotropically to a value of $R = 0.15$ and contained seven fractional oxygen positions. This was followed by anisotropic refinement of the oxygen atoms which reduced the value of the reliability index to $R = 0.089$.

The difference Fourier maps at this stage showed residual peaks around the organic moiety at heights of 0.5–1.0 e/Å$^3$. Based on chemical considerations, hydrogen coordinates were calculated and compared to these residual peaks. Since the calculated hydrogen positions lay on, or very near, these peak centers, the hydrogens were included in the next series of refinements. Further refinements of only the coordinates led to a value of $R = 0.064$. Finally, the hydrogen coordinates and temperature factors were fixed and five additional cycles varying all other atom coordinates and temperature factors were carried out. The $R$ increased slightly to 0.066, but the molecular parameters of the nonhydrogen atoms did not shift significantly, and since the largest shift in either coordinate or temperature factor was less than one-tenth of the corresponding standard deviation, the structure determination was considered completed.

Throughout the refinement, the block-diagonal approximation of the variable matrix was used.[10] Since

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(9) Program INCON, R. E. Davis, University of Texas at Austin, 1966.

(10) Program BDLS, R. Sparks and K. N. Trueblood. A block-diagonal least-squares program modified for the P.D.P.-10.

the space group of the compound was centrosymmetric, only the real part of the anomalous dispersion correction ($\Delta f'$) was applied to the chlorine scattering factor table during refinement.

A final difference map showed no peaks of height greater than 0.25 e/Å$^3$ except in the region of the perchlorate ion (which showed a maximum electron density of 0.4 e/Å$^3$ or less).

## Results and Discussion

The estimated standard deviation (ESD's) for the various atoms (based upon the last cycle of least-squares refinement) were estimated at less than 0.004 Å for the chlorine atom, and less than 0.02 Å for all of the lighter atoms except the disordered oxygen atoms of the perchlorate group. The errors in the oxygen positions are undoubtedly larger than their ESD's based on statistics. Table I lists the final coordinates and anisotropic temperature factors of the nonhydrogen atoms. Figure 1 is a perspective drawing of the bicyclic cation with the individual bond angles and bond distances indicated; the ESD's calculated from the final cycle of least squares are in parentheses. In Table II the bond distances and angles are arranged according to type, with the average deviations given where equivalent bonds are present.

Table II

| Atoms involved | Average bond distances, Å | Atoms involved | Angles, deg |
|---|---|---|---|
| | Azetidinium | | |
| $\overline{\text{C–N}}$ | 1.520 ± 0.021[a] | $\overline{\text{CCC}}$ | 91.6 |
| $\overline{\text{C–C}}$ | 1.502 ± 0.011 | $\overline{\text{CNC}}$ | 90.2 |
| | | $\overline{\text{NCC}}$ | 89.0 ± 1.2 |
| | | All azet. | 89.9 ± 1.0 |
| | Piperidinium | | |
| $\overline{\text{C–N}}$ | 1.498 ± 0.013 | $\overline{\text{CCC}}$ | 111.4 ± 0.6 |
| $\overline{\text{C–C}}$ | 1.491 ± 0.022 | $\overline{\text{CNC}}$ | 110.0 |
| | | $\overline{\text{NCC}}$ | 109.1 ± 0.6 |
| | | All piperid. | 110.5 ± 1.0 |

[a] Average deviations.

The comparison of similar values in the literature to those obtained here is in agreement within the calculated ESD's. The average C–C bond distance of 1.50 ± 0.01 Å found in this study is on the short side of the range for the C–C bond distances of 1.51 to 1.55 Å found in previously studied unfused azetidines,[1–5] but this difference is not statistically significant. The average C–N distance of 1.52 ± 0.02 Å found in this study is well inside the range from 1.51 to 1.53 Å found in these same earlier studies. The angles of the azetidinium ring are equivalent, and average to 90.0 ± 1.0°. The best plane through the azetidinium ring has an ESD of 0.016 Å.

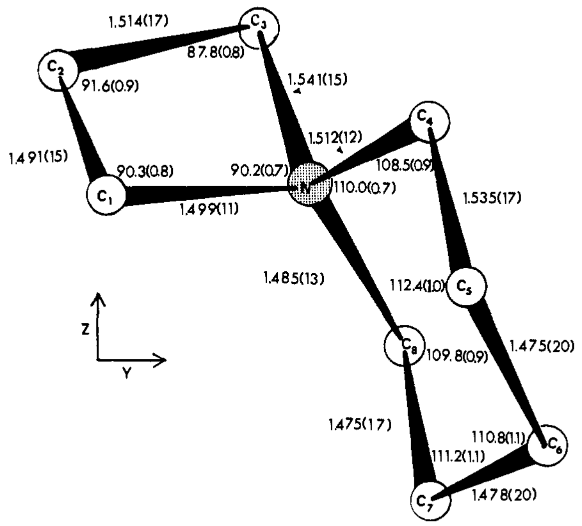
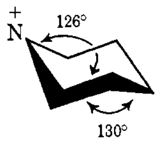


Figure 1. Perspective drawing of the spiro-fused organic moiety with distances and angles given (ESD in parentheses).

In the current study of the spiro-fused piperidinium derivative, the two C–N bond distances in the piperidinium ring average to $1.49_8$ with an average deviation of 0.013 Å, and the C–C bond distances average to $1.49_1$ ± 0.22 Å, indicating that here also, all of the distances in the six-membered ring are equivalent. The CNC angle of 110.5° is identical with the average of all the other angles in this ring of 110.5 ± 1.1°, and in good agreement with an earlier study of the unfused piperidinium ion.[11] The range of values for all angles in the six-membered ring is from 108.5 to 112.4°. The piperidinium ring in this study is also in the chair conformation, with dihedral angles of 126 and 130° as illustrated in III. The two planes containing the atoms involved in the spiro-fusion are perpendicular to each other, this angle between the CNC plane in the azetidinium ring and the CNC plane in the piperidinium ring being 90.8°.



III

The final coordinates of the hydrogen atoms and their isotropic temperature factors are given in Table III.

Table III. Refined Hydrogen Positions and Isotropic Thermal Parameters

| Atom | *X* | *Y* | *Z* | *B* |
|---|---|---|---|---|
| $H_{1,1}$ | 0.97 | 0.29 | 0.28 | 15 |
| $H_{2,1}$ | 0.77 | 0.29 | 0.18 | 6 |
| $H_{1,2}$ | 0.80 | 0.24 | 0.44 | 7 |
| $H_{2,2}$ | 0.54 | 0.27 | 0.32 | 12 |
| $H_{1,3}$ | 0.50 | 0.40 | 0.34 | 11 |
| $H_{2,3}$ | 0.80 | 0.42 | 0.46 | 16 |
| $H_{1,4}$ | 0.09 | 0.44 | 0.40 | 5 |
| $H_{2,4}$ | 0.95 | 0.55 | 0.37 | 10 |
| $H_{1,5}$ | 0.21 | 0.44 | 0.25 | 14 |
| $H_{2,5}$ | 0.18 | 0.53 | 0.29 | 9 |
| $H_{1,6}$ | 0.02 | 0.57 | 0.08 | 10 |
| $H_{2,6}$ | 0.90 | 0.62 | 0.16 | 9 |
| $H_{1,7}$ | 0.83 | 0.40 | 0.09 | 8 |
| $H_{2,7}$ | 0.72 | 0.51 | 0.09 | 6 |
| $H_{1,8}$ | 0.54 | 0.41 | 0.19 | 8 |
| $H_{2,8}$ | 0.64 | 0.53 | 0.23 | 9 |

The hydrogen atoms occupy staggered positions around the six-membered ring as shown in Figure 2, with all nonbonded distances between hydrogens on different carbon atoms being greater than 2.3 Å.

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(11) C. Rerat, *Acta Crystallogr.*, **13**, 72 (1960).

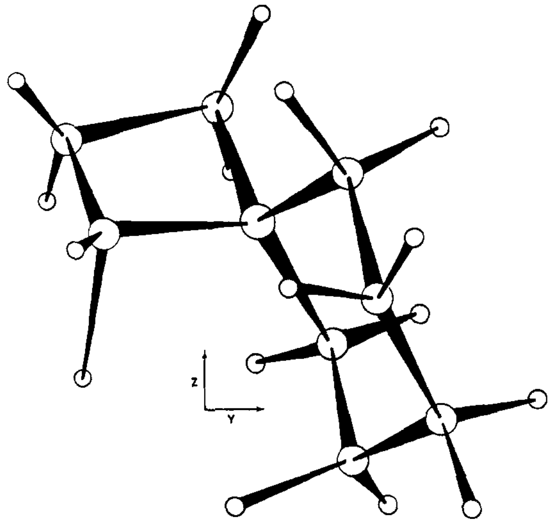

Figure 2. Bicyclic cation with hydrogens included.

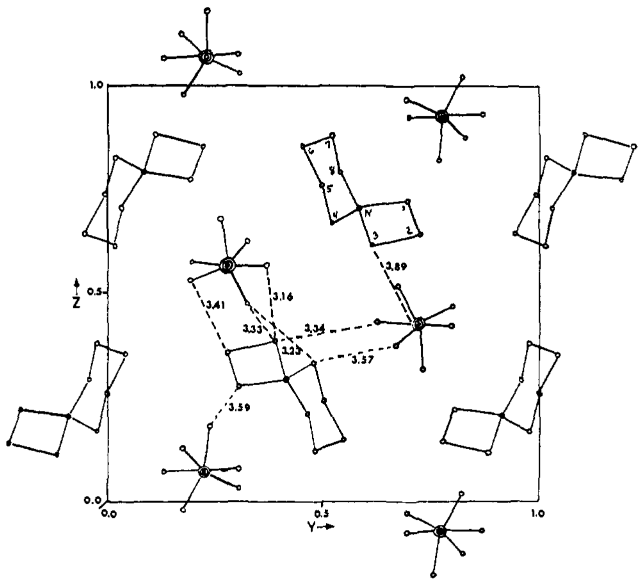

Figure 3. Contents of the unit cell projected down the *X* axis. All close contact between molecules involving chlorine which are less than 4.0 Å are shown. Close contacts shown for atoms other than chlorine are in the range 3.16–3.59 Å.

The torsion angles in the piperidinium ring are in good agreement with an idealized chair conformation for a six-membered ring, based on conformational analysis and X-ray diffraction studies of cyclohexane and its derivatives.[12–14] In good agreement with these values, the torsion angles in this investigation have magnitudes in the range from 54 to 61°, with an average value of 57 ± 2°.

The lack of abnormally close intermolecular contact distances as shown in Figure 3 indicates that crystal packing does not exhibit a significant effect on the molecular parameters or conformation of the piperidinium ring found in this study.

The most important conclusion which can be drawn from the results of this investigation is that spiro-fusion of the strained azetidinium ring to the relatively unstrained piperidinium ring shows no observable effect on either the molecular parameters or the conformations of either ring system when observed in other environments.

The electron density in the region of the perchlorate ion was accounted for by using the empirical approach described. The weights of the seven fractional oxygens are given in parentheses in Table I. The short Cl–O bond distances obtained are undoubtedly an experimental artifact of the perchlorate disordering. The range of values obtained for six of the seven Cl–O bond distances was from 1.32 to 1.43 Å. One Cl–O distance had an unusually low value of 1.18 Å. This was an oxygen whose position corresponded to a diffuse region on the difference map. Shortening of the observed Cl–O bond distances as a result of perchlorate disorder is shown in another recent X-ray study.[15] The normal Cl–O bond distance is in the range from 1.43 to 1.48 Å; the normal angle is tetrahedral.[16] The O–Cl–O angles in this study are chemically meaningless, of course.

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(16) B. Dickens, *ibid., Sect. B*, **25**, 1875 (1969).