$+5°$; O(3)—C(2) $-42°$. Les trois liaisons partant de C(4) sont coplanaires. L'angle dièdre entre le plan du thiényle et le plan de symétrie de l'autre cycle est de $15°$. Les dièdres formés par les plans respectifs O(1)C(2)O(3), α, et C(4)C(5)C(6), β, avec le plan commun O(1)O(3)C(4)C(6) valent: $\alpha = 214°$ et $\beta = 150°$. La conformation observée n'est pas la conformation la plus stable prédite pour l'acide de Meldrum, sur la base de calculs d'énergie par la méthode CNDO (Köberl & Schuster, 1972). Selon ces calculs, le forme chaise, avec $\alpha = 105°$ et $\beta = 156°$, possèderait une énergie inférieure de 12 kcal mol^{-1} à celle d'une forme bateau caractérisée par $\alpha = 230°$ et $\beta = 156°$.

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1-Methoxy-3-methyl-6-chloro-6-cyanobicyclo[2.2.2]octene

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Abstract. $C_{11}H_{14}NOCl$, monoclinic, $P2_1/c$, $Z = 4$. At ca $-40°C$, $a = 10.203$ (2), $b = 8.559$ (2), $c = 12.380$ (2) Å, $\beta = 93.47$ (2)°, $D_c = 1.248$ g cm^{-3}, D_m (25°C) $= 1.236$ g cm^{-3}. Full-matrix least-squares refinement of 1814 reflections resulted in a final R of 0.038. The bicyclo[2.2.2]octene skeleton adopts a slightly staggered conformation, evidenced by torsion angles at C(2)—C(3), C(5)—C(6) and C(7)—C(8) of 2.0, 5.0 and 7.3° respectively.

Introduction. Crystals of $C_{11}H_{14}NOCl$ formed as clear tablets from an ether solution at room temperature. With an air tumbler, several large single crystals were ground to a size suitable for the single-crystal X-ray diffraction study. Details of the intensity data collection are given in Table 1. Standard deviations were assigned to the data and corrections for Lorentz and polarization factors were applied as detailed elsewhere (Riley & Davis, 1975). Based on the criteria $I_{net} \geq 2.0\sigma(I_{net})$ and $I_{peak} \geq 1.6(I_{end})$, where I_{net} is the integrated peak intensity corrected for background, I_{peak} is the highest observed count in the nineteen-step profile, and I_{end} is the average of the counts measured at the ends of the profile, 1814 reflections were accepted for use in structure determination and refinement.

The coordinates of the Cl atom were determined with the aid of a Patterson synthesis. An electron density map calculated with heavy-atom phases revealed the positions of ten non-hydrogen atoms, and a difference density map then revealed the other three. Several cycles of full-matrix least-squares refinement of these

Table 1. *Experimental summary*

Syntex $P2_1$ autodiffractometer, equipped with graphite monochromator and Syntex LT-1 low-temperature flow system (N_2, $-40°C$)

Radiation: Mo $K\alpha$, $\lambda = 0.71069$ Å

Intensity collection: ω-scan technique, with recentering after every 500 reflections

Scan range: symmetrical over $1.0°$ about the $K\alpha_{1,2}$ maximum

Scan rate: variable, 2.0 to $5.0°$ min^{-1}

Background: offset $1.0°$ and $-1.0°$ in ω from $K\alpha_{1,2}$ maximum

Check reflections: four, remeasured after every 96 reflections; analysis* of 27 sets of check reflections indicated only random fluctuation not exceeding 0.8% of the initial intensity; no decay correction applied

2470 reflections measured in octants h,k,l and $\bar{h},k,l$; $4° \leq 2\theta \leq 55°$

Data-crystal dimensions: $0.53 \times 0.44 \times 0.29$ mm

Absorption coefficient: μ(Mo $K\alpha$) $= 3.09$ cm^{-1}; no absorption correction applied

* Henslee & Davis (1975).

atoms, treated eventually as anisotropic thermal ellipsoids, yielded a preliminary agreement index $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.08$ and weighted agreement index $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.11$. At this stage, a difference density map was generated to locate the H atoms. Inclusion of the H positional-thermal parameters in the refinement resulted in full convergence, with a final R value of 0.038 and a final R_w value of 0.041.* The function minimized in refinement was $\Sigma w(|F_o| - |F_c|)^2$, where the weights are $1/\sigma^2(|F_o|)$. In the final cycle of least-squares refinement

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* A list of structure factor amplitudes and complete tables of thermal parameters, hydrogen positional parameters, bond distances, bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32780 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional parameters of the non-hydrogen atoms, with estimated standard deviations in parentheses*

	x	y	z
Cl	0.11417 (5)	0.39065 (6)	0.44578 (4)
O	0.4049 (1)	0.3384 (2)	0.4452 (1)
N	0.2638 (2)	0.5583 (3)	0.2259 (2)
C(1)	0.3301 (2)	0.2254 (2)	0.3855 (1)
C(2)	0.2816 (2)	0.0923 (2)	0.4510 (2)
C(3)	0.2026 (2)	−0.0074 (2)	0.3978 (2)
C(4)	0.1808 (2)	0.0309 (3)	0.2792 (2)
C(5)	0.1204 (2)	0.1954 (3)	0.2685 (2)
C(6)	0.2058 (2)	0.3120 (2)	0.3374 (1)
C(7)	0.3996 (2)	0.1606 (3)	0.2877 (2)
C(8)	0.3147 (2)	0.0351 (3)	0.2295 (2)
C(9)	0.5267 (2)	0.2841 (3)	0.4946 (2)
C(10)	0.1370 (3)	−0.1450 (3)	0.4454 (3)
C(11)	0.2403 (2)	0.4508 (3)	0.2752 (2)

the largest non-hydrogen parameter shift was less than 0.01 of its e.s.d. and the largest H parameter shift was less than 0.03 of its e.s.d. A difference density map calculated from the final atomic parameters gave no peak greater than 0.3 e Å^{-3}. For all 2470 reflections measured, R and R_w were 0.052 and 0.043 respectively. Neutral-atom scattering factors for Cl, O, N, C (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965) were used. Corrections for the real $(\Delta f')$ and imaginary $(\Delta f'')$ parts of the anomalous scattering of Mo $K\alpha$ radiation were applied to the Cl scattering factor (Cromer, 1965).

The final non-hydrogen atomic coordinates and thermal parameters, with standard deviations as estimated from the final least-squares refinement cycle, are presented in Table 2.

Discussion. A method of synthesizing naturally occurring bicyclo[3.2.1]octane compounds *via* rearrangement of a bicyclo[2.2.2]octene system differentially substituted at the bridgehead position has recently been studied by Dr S. A. Monti and co-workers at the University of Texas at Austin (Monti, Yuan, Schmidt & Chen, 1975). Structural determination of 1-methoxy-3-methyl-6-chloro-6-cyanobicyclo[2.2.2]octene was undertaken to unequivocally determine the stereochemistry of the bridgehead substitution site. The molecule, including atom labels, is shown in Fig. 1.

Bond distances for all non-hydrogen atoms are shown in Fig. 2. No abnormalities were observed in C—H bonds (see footnote regarding supplementary information). The slightly shortened value for the C≡N distance, 1.138 (3) Å, is probably attributable to the thermal motion of this group (Little, Pautler & Coppens, 1971). The C—C≡N angle of 178.3 (3)° agrees well with normal values for carbon—cyanogen angles. Comparison of C—C and C=C distances and
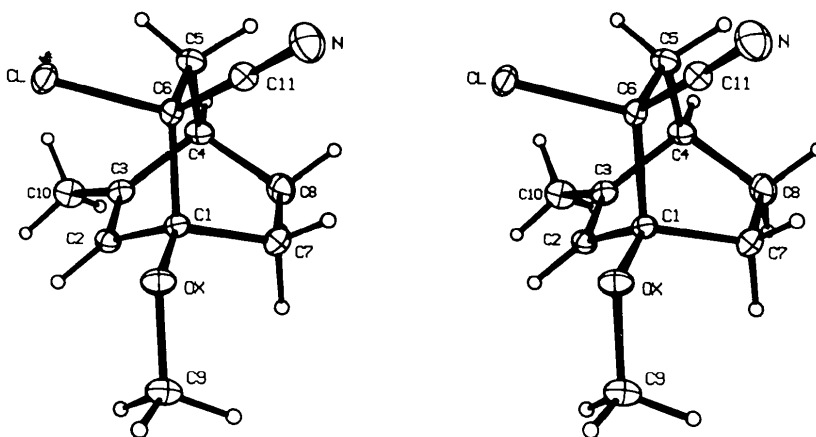

Fig. 1. Stereoscopic view of the molecule, with numbering scheme. Atoms are shown as 15% equiprobability ellipsoids.
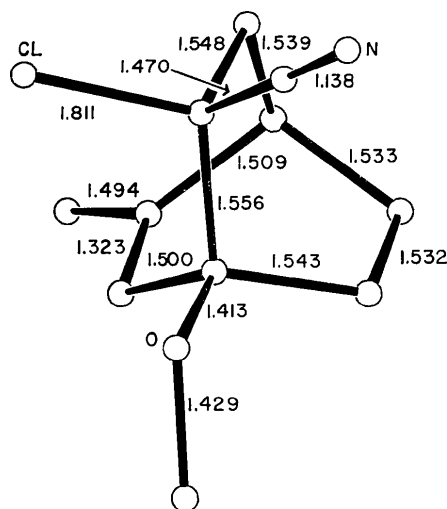
Fig. 2. Bond lengths. Estimated standard deviations are calculated to be in the range 0·002–0·003 Å. For ease of identification, the molecule is shown in the same orientation as in Fig. 1, and atoms other than C are identified.

angles in the bicyclo[2.2.2]octene skeleton with similar fused-ring compounds (Cameron, Ferguson & Morris, 1968; Ermer & Dunitz, 1969; Destro, Filippini, Gramaccioli & Simonetta, 1971; Liu & Davis, 1977) reveals no significant differences. Angles at the sp^3 C atoms in the ring skeleton range from 105·9 (2) to 110·4 (2)°.

Slight twisting of the bicyclic system results in non-zero torsion angles and slight deviations from planarity in the three wings of this ring system (Table 3). The smaller values of the torsion angles and mean displacements involving the group of four atoms C(1), C(2), C(3) and C(4) result from the constraint of the sp^2 atoms.

Table 3. *Conformation of the* [2.2.2]*octene skeleton*

(a) Selected torsion angles*

Bond torsion angles (°)

C(1)–C(2)–C(3)–C(4)	2·0
C(1)–C(5)–C(6)–C(4)	5·0
C(1)–C(7)–C(8)–C(4)	7·3

Cross-ring torsion angles (°)

C(2)–C(1)···C(4)–C(3)	1·0
C(5)–C(1)···C(4)–C(6)	3·0
C(7)–C(1)···C(4)–C(8)	4·4

(b) Least-squares planes

Plane	Atoms in plane	Root-mean-square displacement (Å)
I	C(1),C(2),C(3),C(4)	±0·008
II	C(1),C(5),C(6),C(4)	±0·023
III	C(1),C(7),C(8),C(4)	±0·034

Planes	Dihedral angle (°)
I–II	120·4
I–III	122·7
II–III	116·8

* The convention followed in defining torsion angles is that used in *Molecular Structures and Dimensions* (1972) [suggested by Klyne & Prelog (1960)].

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