

Fig. 1. Configuration de la molécule.

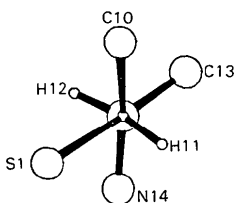


Fig. 2. Une projection de Newman suivant la direction C(11)-C(12).

Les distances C—C [moyenne = 1,515 (10) Å] et C—N, à l'intérieur du cycle pipéridine, sont en bon accord avec celles reportées pour d'autres composés (Jaskolski, Gdaniec & Kosturkiewicz, 1977). Le cycle adopte une conformation chaise.

La Fig. 2 montre une projection de Newman suivant la direction C(11)—C(12); elle met en évidence la présence du diastéréoisomère *thréo*. L'angle H(11)—C(11), C(12)—H(12) vaut 168,5 (10)°, cette valeur est en bon accord avec la constante de couplage  $^3J = 10,5$  Hz calculée à partir du spectre RMN (Grandclaoudon & Lablache-Combiér, 1982).

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## *N*-Methylacetamide Hemihydrochloride, $C_3H_7NO \cdot \frac{1}{2}HCl$

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**Abstract.**  $M_r = 91.33$ ,  $C2$ ,  $a = 8.454$  (4),  $b = 10.597$  (5),  $c = 11.754$  (5) Å,  $\beta = 111.09$  (8)°,  $V = 982$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.23$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.35$  mm<sup>-1</sup>,  $F(000) = 392$ ,  $R = 0.044$  for 1034 observed reflections. The five main atoms

within each of the two independent *N*-methylacetamide molecules are planar. HCl molecules appear to be entirely dissociated. O...H<sup>+</sup>...O and N—H...Cl<sup>-</sup> hydrogen bonds produce a structure constituted of infinite chains.

**Introduction.** In the outline of our research about the spectral properties of some proteins, we are interested at the present time in the interactions of the surrounding medium with amide groups. The X-ray structure determination of the title compound was performed in order to try to rationalize its IR and Raman spectra in the crystalline state.

**Experimental.** Precipitated by direct action of dry gaseous HCl on a 20:40 ml solution of *N*-methylacetamide in ethyl ether, single crystals by slow evaporation in dry air from CHCl<sub>3</sub> solution to which was added CCl<sub>4</sub> to give a two-layer system which apparently makes the crystallization easier; before use the two solvents were kept for a day on a mixture of 4 and 5 Å molecular sieves; octahedral, 0.4 mm edge, sealed Lindemann-glass capillary, Mo K $\alpha$ , Philips PW1100 four-circle diffractometer,  $\omega$ - $2\theta$  scan,  $4 \leq 2\theta \leq 54^\circ$ ,  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 13$ ,  $0 \leq l \leq 14$ , 1142 independent reflections, 1034 observed,  $I > 3\sigma(I)$ ; Patterson function and heavy-atom method, anisotropic full-matrix refinement, involving  $F$ , for non-hydrogen atoms, with Cl atomic scattering factor ( $R = 0.055$ ), hydrogen atoms located from difference synthesis except those of HCl molecules, which were assumed to be dissociated into H<sup>+</sup> and Cl<sup>-</sup> ions, Cl<sup>-</sup> ionic scattering factor then used, anisotropic full-matrix involving  $x, y, z, \beta_{ij}$  for non-hydrogen atoms and  $x, y, z, B$  parameters for hydrogens,  $R = 0.044$  ( $wR = 0.038$ ),  $w = (a + b |F_o|)^{-2}$ , scattering factors from *International Tables for X-ray Crystallography* (1974).\*

**Discussion.** Table 1 gives the coordinates of the non-hydrogen atoms of the structure.

The asymmetric unit contains two identical parts (I) and (II), each constituted of one Cl<sup>-</sup> ion and one *N*-methylacetamide molecule. The two *N*-methylacetamide molecules are geometrically very similar. In each case the five C,N,O atoms are very close to their least-squares mean plane, so the addition of  $\frac{1}{2}$  HCl does not alter the planarity of these atoms which was observed in crystalline *N*-methylacetamide at 238 K (Katz & Post, 1960). The angle between the two mean planes is about 179°; hence they may be considered parallel.

Like the Cl<sup>-</sup> anions, the protons of the dissociated HCl must lie on the binary axes. It is very likely they are exactly located between the binary-axis-related O(1)

atoms and identically between the O(2) atoms, because the distances between these oxygens are extremely short (Table 2); such a short distance has already been found between I-related oxygen atoms [2.438 (5) Å], within acetamide hemihydrobromide at 113 K (Groth, 1977). By means of these protonic O...H<sup>+</sup>...O bonds and the N-H...Cl<sup>-</sup> hydrogen bonds, the structure would appear to be formed of chains generated by the binary axes passing through the Cl<sup>-</sup> anions and between the oxygen atoms. In Fig. 1, drawn with *ORTEP* (Johnson, 1965), only a link built from molecule (I) is shown. Such chains are also made in the same way by molecule (II), which are 'parallel' to the first ones. The presence of the two observed hydrogen-bond types would seem to be very helpful for our interpretation of the IR and Raman spectra of this compound.

Table 1. Refined coordinates ( $\times 10^4$ ) and  $B_{eq}$  parameters for Cl<sup>-</sup>, C, N, O

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \beta_{ij} a_i \cdot a_j$$

	Wyckoff position	$x$	$y$	$z$	$B_{eq}(\text{Å}^2)$
(I) First part of the asymmetric unit					
Cl <sup>-</sup> (1)	2(a)	0	5012 (1)	0	4.0 (1)
C(1)	4(c)	4524 (3)	3146 (3)	1579 (2)	4.3 (2)
N(1)	4(c)	3330 (2)	3838 (2)	1976 (1)	3.1 (1)
C(2)	4(c)	3552 (2)	4029 (2)	3122 (2)	2.8 (1)
O(1)	4(c)	4888 (2)	3615 (2)	3938 (1)	4.1 (1)
C(3)	4(c)	2247 (3)	4745 (2)	3429 (2)	3.7 (2)
(II) Second part (in the same order as the first)					
Cl <sup>-</sup> (2)	2(b)	0	2512	5000	3.9 (1)
C(4)	4(c)	2939 (3)	640 (3)	3426 (2)	4.4 (2)
N(2)	4(c)	1355 (2)	1334 (2)	3025 (1)	3.0 (1)
C(5)	4(c)	440 (2)	1529 (2)	1882 (2)	2.8 (1)
O(2)	4(c)	942 (2)	1112 (2)	1058 (1)	4.1 (1)
C(6)	4(c)	-1181 (3)	2245 (2)	1570 (2)	3.7 (2)

Table 2. Bond lengths (Å) and main bond angles (°) within the two parts of the asymmetric unit and hydrogen bonding

(I)		(II)	
C(1)-N(1)	1.454 (3)	C(4)-N(2)	1.450 (3)
C(2)-C(3)	1.486 (3)	C(5)-C(6)	1.492 (3)
C(1)-H(4)	1.02 (5)	C(4)-H(11)	1.04 (9)
C(3)-H(7)	0.94 (4)	C(6)-H(14)	0.97 (4)
C(2)-N(1)	1.306 (2)	C(5)-N(2)	1.303 (2)
C(1)-H(2)	0.78 (7)	C(4)-H(9)	1.03 (7)
C(3)-H(5)	0.93 (4)	C(6)-H(12)	1.02 (4)
C(2)-O(1)	1.268 (3)	C(5)-O(2)	1.269 (3)
C(1)-H(3)	0.94 (7)	C(4)-H(10)	0.97 (9)
C(3)-H(6)	1.07 (4)	C(6)-H(13)	1.06 (4)
C(1)-N(1)-C(2)	123.4 (2)	C(4)-N(2)-C(5)	123.4 (2)
N(1)-C(2)-O(1)	119.0 (2)	N(2)-C(5)-O(2)	119.6 (2)
C(3)-C(2)-O(1)	121.9 (2)	C(6)-C(5)-O(2)	121.3 (2)
N(1)-C(2)-C(3)	119.0 (2)	N(2)-C(5)-C(6)	119.0 (2)
N(1)-H(1)	1.03 (4)	N(2)-H(8)	0.85 (4)
H(1)...Cl <sup>-</sup> (1)	2.18 (4)	H(8)...Cl <sup>-</sup> (2)	2.35 (4)
N(1)...Cl <sup>-</sup> (1)	3.188 (2)	N(2)...Cl <sup>-</sup> (2)	3.189 (2)
N(1)-H(1)-Cl <sup>-</sup> (1)	165 (3)	N(2)-H(8)-Cl <sup>-</sup> (2)	171 (3)
O(1)...O(1)(1-x, y, 1-z)	2.434 (3)	O(2)...O(2)(x, y, z)	2.423 (3)

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38280 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

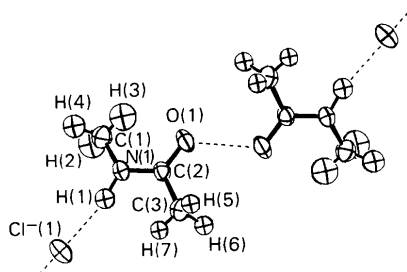


Fig. 1. 50% probability thermal ellipsoids of molecule (I) and the linkage resulting from the action of the binary axis and hydrogen bonds.

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### 3,3-Dichloro-7-(2,2-dichlorovinyl)tricyclo[4.1.0.0<sup>2,4</sup>]heptane, C<sub>9</sub>H<sub>8</sub>Cl<sub>4</sub>

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**Abstract.**  $M_r = 258.0$ , monoclinic,  $P2_1/c$ ,  $a = 9.418$  (2),  $b = 10.935$  (4),  $c = 11.272$  (2) Å,  $\beta = 116.31$  (1)°,  $U = 1040.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (at 273 K) = 1.609 (1),  $D_x$  (at 193 K) = 1.647 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.05$  mm<sup>-1</sup>,  $F(000) = 520$ . Final  $R = 0.031$  for 1611 observed reflections. The five-membered ring of the tricyclo[4.1.0.0<sup>2,4</sup>]heptane moiety is planar with the two cyclopropane rings fused in an *anti* configuration relative to each other. The geometry of the three-membered rings is consistent with the electronic effects induced by their respective substituents.

**Introduction.** The unknown adduct (3) (Fig. 1) has been isolated (Jefford, Bernardinelli, Rossier & Zuber, 1982) from the reaction mixture between dichlorocarbene and bicyclo[2.2.1]hepta-2,5-diene (2). It was shown that the formation of (3) does not result from a rearrangement of standard adducts. Mechanistic significance of adduct (3) required definite proof of its structure with special emphasis on the configuration at C(7). Therefore (3) was converted stereospecifically into (1) by dichlorocarbene addition and the resulting adduct subjected to X-ray analysis. It is worth mentioning that the double adduct (1) was also isolated from the original carbene reaction mixture.

**Experimental.** Colorless crystals of (1) grown by slow evaporation of a hexane solution at room temperature,

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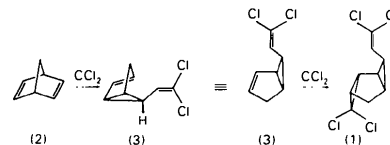


Fig. 1. Synthetic pathway for dichlorocarbene addition to 8,9,10-trinorbornadiene (2) giving the title compound (1).

m.p. = 322.7 K,  $D_m$  measured by flotation, elongated prism in a direction perpendicular to the unique axis, 0.30 × 0.20 × 0.22 mm; automatic four-circle Philips PW1100 diffractometer, graphite-monochromated Mo  $K\alpha$ ; 32 reflections within range  $25 \leq 2\theta \leq 33^\circ$  used for measuring lattice parameters; no absorption corrections applied;  $2\theta_{\text{max}} = 24^\circ$ ; range of  $hkl$ :  $0 \leq h \leq 11$ ,  $0 \leq k \leq 13$ ,  $-13 \leq l \leq 12$ ; three standard reflections varied in intensity by <3% throughout data collection; 2029 reflections measured at 193 K, 1829 independent,  $R_{\text{int}} = 0.012$ , 1611 structure amplitudes with  $|F_o| > 3\sigma(F_o)$  considered observed and used in structure analysis; structure solved by direct methods using *SINGEN* and *TANGEN* programs of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); full-matrix least-squares refinement on  $F$ ; all H atoms located from a  $\Delta F$  synthesis calculated at an intermediate stage of the resolution; calculations carried out with anisotropic temperature factors for non-H atoms and isotropic factors for H; final  $R = 0.031$ ,  $wR = 0.037$ ,  $S = 0.7173$ ;  $w = 1$  for