intermolecular contact of 2·550 (4) Å between O(4) and O(2) (−0·5 + x, 1·5 − y, 1 − z), the latter atom having a deviation of 0·03 (1) Å from the mean plane of the pyridine ring to which O(4) is attached, the C(4)—O(4)···O(2) angle being 113·2 (3)°, strongly suggests the presence of an H atom associated with O(4). All attempts to locate this H atom were unsuccessful. The short intermolecular contact, 2·807 (4) Å, between N(1) and O(2) (1 − x, −0·5 + y, 1·5 − z) is a hydrogen bond, the H(1)···O(2) distance being 2·05 Å, and the N(1)—H(1)···O(2) angle 156°. The pyridine ring in the structure is essentially planar [maximum deviation of an atom from the plane is 0·008 (2) Å for N(1)], another factor in favour of the 4-enol designation (Schwalbe & Saenger, 1973). The contents of the unit cell are shown in Fig. 2.

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Structure of 8-Methoxy-5-oxo-6,8-diazatetracyclo$[7.4.0.0^{2,4}.0^{3,7}]$trideca-1(9),10,12-triene-4-carboxylic Acid, $C_{13}H_{12}N_2O_4$

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Abstract. $M_r = 260{\cdot}2$, triclinic, $P\bar{1}$, $a = 9{\cdot}891$ (3), $b = 13{\cdot}653$ (4), $c = 9{\cdot}725$ (3) Å, $\alpha = 105{\cdot}13$ (3), $\beta = 110{\cdot}23$ (2), $\gamma = 75{\cdot}95$ (2)°, $V = 1172{\cdot}6$ (6) Å^3, $Z = 4$, $D_m = 1{\cdot}470$, $D_x = 1{\cdot}422$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}12$ mm^{-1}, $F(000) = 544$, $T =$ 293 K. Final $R = 0{\cdot}048$ for 4686 observed reflexions. The condensed quinolinium and lactam rings form a hinge in which the three-membered ring is inserted. The carbonyl and carboxy moieties form one plane with the lactam ring *via* the intramolecular O···HO hydrogen bond. A tetramer is formed by the two paired intermolecular O···HN hydrogen bonds in the crystal.

Introduction. In the course of studies on the reactions of quinolinium salts with active methylene compounds, reaction of N-methoxyquinolinium perchlorate with methyl bromocyanoacetate was found to afford the title compound (E) in the yield 25·5% as shown in Fig. 1. The formation of E may be rationalized by the course shown also in Fig. 1. Initially, the nucleophilic attack of a carbanion of B on A gives a 1,4-dihydroquinoline (C). The next step is the transformation of C to a cyclopropane ring compound (D) by nucleophilic attack of the 3-position at the side-chain C with the concerted elimination of the Br$^-$ ion. Further, a C—N bond is formed between the quinolinium C and the N atom of the cyano group in D to produce the title product E after several steps. By an X-ray diffraction method the structure of E was determined as given in the title. The molecular structure resembles that of benzomorphans which have analgetic and antagonistic activities; however, derivatives of the title compound have little activity.

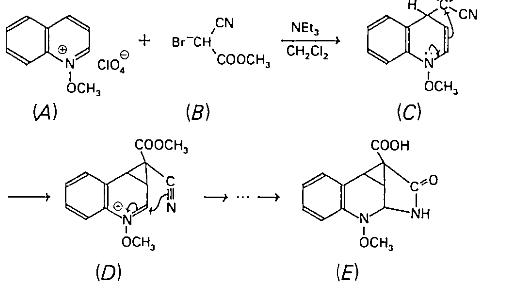

Fig. 1. Reaction scheme.

0108-2701/83/121690-03$01.50

Experimental. Colorless prisms approx. 0·4 × 0·5 × 0·6 mm, grown from ethanol. Density measured by flotation in KI solution. Single-crystal data collected on an automated Syntex $P\overline{1}$ diffractometer, graphite-monochromatized Mo $K\alpha$. Cell parameters determined by least squares from setting angles of 15 reflexions. 5560 reflexions measured using θ–2θ variable scans (4·8–12·0° min^{-1} for 2θ) up to $2\theta = 55°$; range of *hkl*: $-12 \le h \le 12$, $0 \le k \le 17$, $-12 \le l \le 12$. Three standard reflexions measured every 100 reflexions. Data corrected for geometrical factors and for monitored intensities but not for absorption. 4686 independent reflexions $[I > 2{\cdot}33\sigma(I)]$ considered observed. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); 244 largest E values and six symbols used; an E map calculated from a phase set of highest combined figure of merit (2·60) revealed all non-H atoms. H atoms determined by a difference Fourier synthesis. All coordinates, anisotropic thermal parameters for non-H atoms and isotropic ones for H refined by block-diagonal least-squares procedure to minimize $\sum w(|F_o| - |F_c|)^2$, $w = 1{\cdot}0$; final $R = 4{\cdot}8\%$, $S = 0{\cdot}83$, $(\Delta/\sigma)_{\max} = 0{\cdot}3$ for non-H atoms. Final residual electron density of difference Fourier synthesis $<0{\cdot}27\ \text{e}\ \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on a FACOM M-200 computer at the Computer Center of Kyushu University using *UNICS*III program system (Sakurai & Kobayashi, 1979).

Table 1. *Fractional atomic coordinates with their e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

$$B_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Molecule *A*				Molecule *B*			
	x	*y*	*z*	$B_{\text{eq}}(\text{Å}^2)$	*x*	*y*	*z*	$B_{\text{eq}}(\text{Å}^2)$
C(1)	0·2551 (3)	−0·0895 (2)	0·7748 (3)	2·2	0·0025 (3)	0·3452 (2)	0·6732 (3)	2·9
C(2)	0·2470 (3)	−0·0256 (2)	0·9259 (3)	2·3	−0·0167 (3)	0·4604 (2)	0·7360 (3)	2·9
C(3)	0·2875 (3)	0·0765 (2)	0·9529 (3)	2·3	−0·1342 (3)	0·5189 (2)	0·6312 (3)	2·6
C(4)	0·3706 (3)	0·0916 (2)	0·8613 (3)	2·2	−0·1851 (3)	0·4689 (2)	0·4721 (3)	2·5
C(5)	0·4095 (3)	0·1868 (2)	0·8806 (3)	2·9	−0·2984 (3)	0·5191 (2)	0·3698 (3)	3·4
C(6)	0·4991 (3)	0·1989 (2)	0·8054 (3)	3·4	−0·3358 (3)	0·4765 (3)	0·2183 (4)	3·9
C(7)	0·5515 (3)	0·1154 (2)	0·7119 (3)	3·3	−0·2588 (3)	0·3835 (3)	0·1689 (3)	3·6
C(8)	0·5153 (3)	0·0192 (2)	0·6914 (3)	2·8	−0·1447 (3)	0·3320 (2)	0·2677 (3)	2·9
C(9)	0·4249 (3)	0·0073 (2)	0·7668 (3)	2·2	−0·1078 (3)	0·3740 (2)	0·4203 (3)	2·4
C(10)	0·1233 (3)	0·0634 (2)	0·8918 (3)	2·2	−0·1650 (3)	0·4885 (2)	0·7605 (3)	2·7
C(11)	0·0326 (3)	0·1124 (2)	0·9938 (3)	2·8	−0·2001 (4)	0·5739 (2)	0·8794 (3)	3·5
C(12)	0·0546 (3)	0·0436 (2)	0·7271 (2)	2·0	−0·2225 (3)	0·3908 (2)	0·7248 (3)	2·9
C(Me)	0·4875 (4)	−0·2524 (3)	0·6400 (4)	4·8	0·1774 (3)	0·1769 (3)	0·4706 (4)	4·0
N(1)	0·3965 (2)	−0·0916 (2)	0·7583 (2)	2·3	0·0149 (2)	0·3262 (2)	0·5225 (2)	2·6
N(2)	0·1340 (2)	−0·0377 (2)	0·6669 (2)	2·2	−0·1293 (3)	0·3150 (2)	0·6736 (3)	3·2
O(1)	0·3980 (2)	−0·1556 (1)	0·6154 (2)	3·1	0·0310 (2)	0·2165 (1)	0·4709 (2)	3·2
O(2)	−0·0994 (2)	0·1624 (2)	0·9340 (2)	3·6	−0·3130 (3)	0·5679 (2)	0·9191 (3)	5·2
O(3)	0·0748 (2)	0·1077 (2)	0·1241 (2)	4·2	−0·1341 (3)	0·6448 (2)	0·9368 (3)	5·4
O(4)	−0·0610 (2)	0·0938 (1)	0·6601 (2)	2·6	−0·3355 (3)	0·3842 (2)	0·7458 (3)	4·3

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(1)–C(2)	1·518 (4)	1·522 (4)	C(3)–C(10)	1·562 (4)	1·564 (5)	C(8)–C(9)	1·396 (5)	1·395 (4)	C(11)–O(3)	1·203 (4)	1·203 (4)
C(1)–N(1)	1·455 (4)	1·463 (4)	C(4)–C(5)	1·392 (4)	1·388 (4)	C(9)–N(1)	1·421 (4)	1·417 (3)	C(12)–N(2)	1·322 (3)	1·324 (4)
C(1)–N(2)	1·464 (3)	1·461 (5)	C(4)–C(9)	1·395 (4)	1·401 (4)	C(10)–C(11)	1·488 (4)	1·481 (4)	C(12)–O(4)	1·241 (3)	1·231 (5)
C(2)–C(3)	1·476 (4)	1·477 (4)	C(5)–C(6)	1·389 (5)	1·388 (4)	C(10)–C(12)	1·487 (3)	1·488 (4)	C(Me)–O(1)	1·428 (4)	1·418 (4)
C(2)–C(10)	1·514 (4)	1·509 (4)	C(6)–C(7)	1·376 (4)	1·374 (5)	C(11)–O(2)	1·326 (3)	1·327 (6)	N(1)–O(1)	1·438 (3)	1·438 (3)
C(3)–C(4)	1·482 (5)	1·480 (4)	C(7)–C(8)	1·391 (4)	1·382 (4)						

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(2)–C(1)–N(1)	109·7 (2)	109·6 (3)	C(4)–C(5)–C(6)	120·9 (3)	121·0 (3)	C(11)–C(10)–C(12)	120·6 (2)	120·4 (3)
C(2)–C(1)–N(2)	104·3 (2)	104·0 (2)	C(5)–C(6)–C(7)	119·6 (3)	119·4 (3)	C(10)–C(11)–O(2)	116·6 (2)	115·0 (3)
N(1)–C(1)–N(2)	112·5 (3)	112·2 (2)	C(6)–C(7)–C(8)	120·8 (3)	121·0 (3)	C(10)–C(11)–O(3)	122·7 (2)	123·9 (4)
C(1)–C(2)–C(3)	111·9 (3)	112·0 (2)	C(7)–C(8)–C(9)	119·6 (3)	119·8 (2)	O(2)–C(11)–O(3)	120·8 (3)	121·1 (3)
C(1)–C(2)–C(10)	105·4 (2)	105·6 (3)	C(4)–C(9)–C(8)	120·1 (3)	119·8 (2)	C(10)–C(12)–N(2)	108·6 (2)	108·3 (3)
C(3)–C(2)–C(10)	63·0 (2)	63·1 (2)	C(4)–C(9)–N(1)	118·9 (3)	119·2 (2)	C(10)–C(12)–O(4)	124·8 (2)	124·2 (3)
C(2)–C(3)–C(4)	118·4 (2)	118·8 (2)	C(8)–C(9)–N(1)	120·8 (2)	120·8 (2)	N(2)–C(12)–O(4)	126·6 (2)	127·5 (3)
C(2)–C(3)–C(10)	59·7 (2)	59·4 (2)	C(2)–C(10)–C(3)	57·3 (2)	57·5 (2)	C(1)–N(1)–C(9)	113·7 (2)	114·0 (2)
C(4)–C(3)–C(10)	124·2 (2)	124·0 (3)	C(2)–C(10)–C(11)	121·6 (3)	122·8 (3)	C(1)–N(1)–O(1)	106·6 (2)	106·1 (2)
C(3)–C(4)–C(5)	120·7 (2)	121·2 (2)	C(2)–C(10)–C(12)	106·6 (2)	106·8 (2)	C(9)–N(1)–O(1)	110·1 (2)	109·0 (2)
C(3)–C(4)–C(9)	119·8 (3)	119·5 (2)	C(3)–C(10)–C(11)	116·7 (2)	116·7 (3)	C(1)–N(2)–C(12)	114·7 (2)	115·1 (3)
C(5)–C(4)–C(9)	119·1 (3)	119·0 (2)	C(3)–C(10)–C(12)	117·8 (3)	117·0 (2)	C(Me)–O(1)–N(1)	108·2 (2)	109·3 (2)

Discussion. Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* There are two pairs of racemic molecules in the unit cell as shown, together with the atom-numbering scheme, in Fig. 2. The four molecules of groups *A* and *B* are held together around the center of symmetry $(\frac{1}{2},0,\frac{1}{2})$ by two paired hydrogen bonds O(4*A*)···H(N2*A*) and O(4*A*)···H(N2*B*) with distances of 2·06 (3) and 2·09 (3) Å. Although the molecule has a flexible methoxy tail, these four molecules form a close-packed cluster *via* the four hydrogen bonds. The clusters are held together by van der Waals forces to form the crystal.

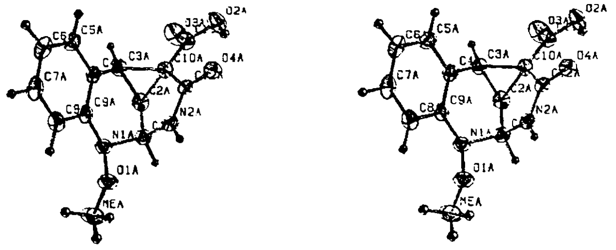

Fig. 3. Stereoview of molecule *A*.

The unique molecules *A* and *B* in the asymmetric unit have almost the same conformation, as shown in Table 2. Fig. 3 shows a stereoview of molecule *A* drawn with *ORTEP* (Johnson, 1965). The molecule consists of three condensed rings: quinolinium, three-membered and lactam. The hydroxy radical in the carboxy group at the junction between the lactam and three-membered rings is connected to the carbonyl O of the lactam ring by an O(4)···H(O2) intramolecular hydrogen bond with distances of 1·87 (4) and 1·70 (4) Å for molecule *A* and *B* respectively. For both molecules, the bond distances of C(12)—N(2) are shorter and those of C(12)—O(4) are longer than normal values as shown in Table 2. It seems likely that the lone-pair electrons of N(2) are strongly conjugated with the carbonyl group and those of O(4) cause the formation of the inter- and intramolecular hydrogen bonds.

The dihedral angle between the quinolinium and lactam rings is 102° for both molecules *A* and *B*. As shown in Table 2, the three-membered rings are considerably distorted from a regular triangle and have bond lengths and angles differing from those reported by Guggenberger & Jacobson (1969), Jones & Karle (1974), Bordner (1976) and Guth & Deppisch (1976) for other three-membered rings. These distortions are mainly caused by steric repulsions at the junction between the lactam and quinolinium rings. The bond lengths and angles in molecules *A* and *B* are mostly normal except for those of the lactam and three-membered rings.

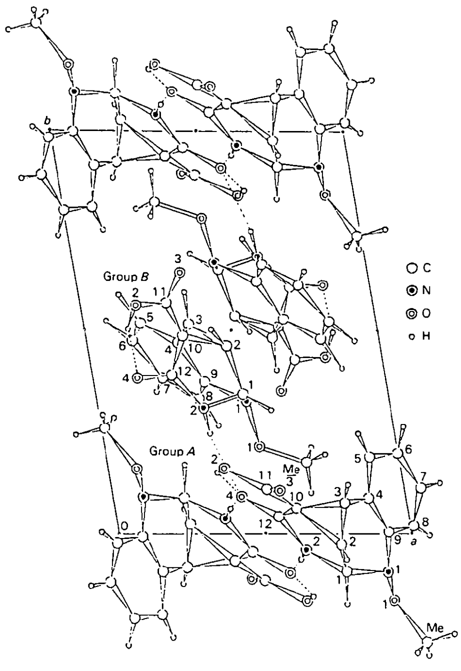

Fig. 2. Crystal structure projected along the *c* axis. Dotted lines represent hydrogen bonds.

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and bond distances and angles related to H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38785 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.