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## Structure of a Triazoxatricyclodecadiene Derivative. Partial Disorder and a Packing Energy Study

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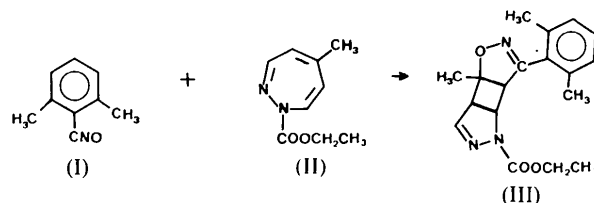
### Abstract

The crystal structure of ethyl 5-(2,6-dimethylphenyl)-2-methyl-3-oxa-4,8,9-triazatricyclo[5.3.0.0<sup>2,6</sup>]deca-4,9-diene-8-carboxylate, C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> (III), has been determined. The reaction between 2,6-dimethylbenzotrile oxide (I) and ethyl 5-methyl-1,2-diazepine-1-carboxylate (II) gives rise to an *anti* tricyclo derivative with a rigid skeleton formed by 2-pyrazoline, cyclobutane and 2-isoxazoline planar rings. With respect to the central cyclobutane system, the bond lengths of which range

from 1.539 (5) to 1.558 (5) Å and the bond angles of which range from 89.7 (2) to 90.7 (2)°, the 2-pyrazoline and the 2-isoxazoline planes form dihedral angles of 116 and 112°, respectively. The methyl group at the end of the ethyl carboxylate chain is disordered. Both of the corresponding orientations of the final part of the chain are consistent with the results of packing energy and semi-empirical molecular-orbital calculations.

### Comment

1,3-Cycloadditions of aryl nitrile oxides to ethyl 5-methyl-1,2-diazepine-1-carboxylate (II) give rise to three different types of products, one of which is definitely predominant (Beltrame, Cadoni, Carnasciali, Gelli, Lai, Mugnoli & Pani, 1992). The crystal structure of the main adduct from this type of reaction has been reported (Beltrame, Gelli, Cadoni, Carnasciali, Pani & Mugnoli, 1993). The present work deals with the determination of the structure of compound (III), one of the two minor products obtained by the 1,3-cycloaddition of the aryl nitrile oxide (I) to the 1,2-diazepine (II) with concomitant [2+2] internal cycloaddition (Beltrame *et al.*, 1992).



Three condensed cycles are present in compound (III), as shown in Fig. 1, where atoms have been numbered in agreement with our previous work (Beltrame *et al.*, 1992). To the best of our knowledge no previous crystal structure determination has been performed on similar triazoxatricyclodecadiene derivatives. In the rigid part of the molecule each of the three condensed rings is planar within 0.012 (3) Å (for the 2-isoxazoline ring), 0.019 (4) Å (for the 2-pyrazoline ring) and 0.002 (3) Å (for the cyclobutane ring); the dihedral angles between the cyclobutane ring mean plane and those of the two adjacent rings are 112.3 (1) and 116.0 (1)°, respectively. The phenyl ring, which is planar to within 0.014 (6) Å, is rotated with respect to the 2-isoxazoline ring, the torsion angle C13—C12—C4—N3 being 73.3 (4)°. The geometric parameters of the four-membered ring are in good agreement with the corresponding values found in seven similar three-ring derivatives in which planar five-membered rings are fused to a central cyclobutane ring, as retrieved from the Cambridge Structural Database Version 5.05 (Allen, Kennard & Taylor, 1983).

In view of the unexpected structure of compound (III), some further particular geometry checks seemed appropriate. The distances N3=C4 [1.276 (4) Å] and

N8=C9 [1.278(5) Å] compare fairly well with the corresponding values found for 2-isoxazoline and 2-pyrazoline derivatives having similarly substituted planar structures in which all the H-atom positions have been determined [the corresponding data from the Cambridge Structural Database are 1.280(12) Å (12 hits) and 1.286(8) Å (8 hits), with the sample e.s.d.'s given in parentheses]. A better agreement is obtained with the average value reported by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) for the C<sub>sp<sup>2</sup></sub>=N bond distance [1.279(8) Å; sample e.s.d. given in parentheses]. Even the geometry of the side chain is normal, with the exception of one short bond length involving the terminal methyl group, which is split over two different positions [C23—C24 1.51(1) and C23—C24' 1.45(2) Å]. The corresponding torsion angles are C20—O22—C23—C24 ( $\tau_1$ ) -173.2(6)° and C20—O22—C23—C24' ( $\tau_2$ ) 155.4(8)°, respectively.

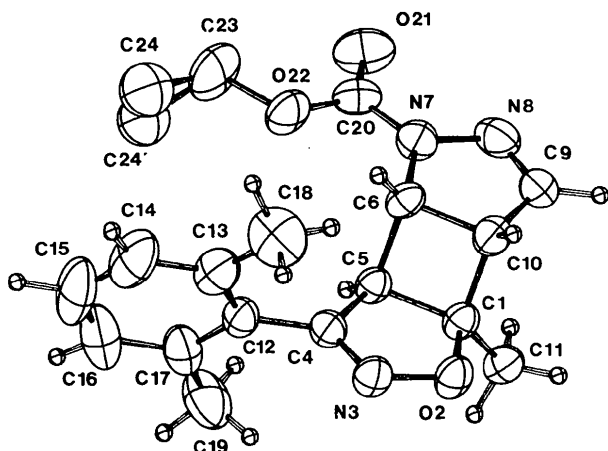


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound (III) showing the atom-numbering scheme. Heavy atoms are represented as 40% probability displacement ellipsoids and H atoms as spheres of arbitrary size.

In order to gain a better understanding of the coexistence of the two different conformations, semi-empirical calculations on the isolated molecule and packing energy calculations in the crystal state were carried out. To study the isolated molecule, the NDDO approach was applied within the AM1 approximation (Dewar, Zoebisch, Healy & Stewart, 1985; Stewart, 1983). The experimental Z-matrix was used as a starting point for a full optimization. The resulting geometry is independent of the two different orientations of the methyl group in the starting model, the final torsion angle being  $\tau = 179^\circ$  in both cases. By repeating the calculation for fixed values of the torsion angle  $\tau$  in the range 0 to 360°, with  $\Delta\tau = 10^\circ$ , an energy curve with an essentially flat minimum from 80 to 280° was obtained. Outside this range,

the interactions C24···C20 and C24···O21 play a significant role. The variation of the packing energy in the crystal as a function of the rotation angle of the terminal part of the chain was calculated for the same range and intervals of the torsion angle  $\tau$ ; for this the programs *ROTENER* (Nardelli, 1988) and *OPEC* (Gavezzotti, 1983) were used. Two kinds of calculations were performed, always including all the molecules having at least one atom within 12 Å from each atom of a reference molecule. In a first approach, using *ROTENER* and *OPEC*, the surrounding molecules were held fixed (experimental geometry, torsion  $\tau_1$ ) while the central molecule was allowed to assume a different value for  $\tau$  at every calculation. In a second approach, using the *OPEC* program, 36 model crystals were constructed with the same value of  $\tau$  for the central and all the surrounding molecules in every calculation. The resulting energy curves show the same qualitative behaviour for both of the methods considered; in the latter case, shown in Fig. 2, the packing potential energy changes by less than 4 kJ mol<sup>-1</sup> as the torsion angle  $\tau$  varies from 140 to 230°. These results are consistent with the observed values for  $\tau_1$  and  $\tau_2$ .

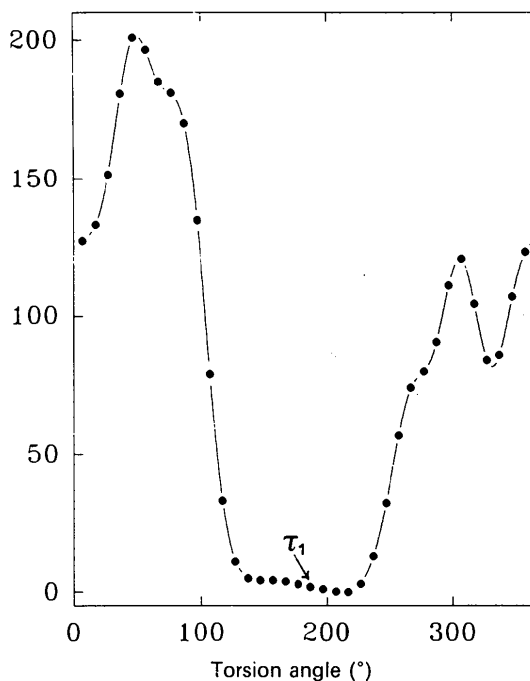


Fig. 2. Packing potential energy differences obtained by *OPEC* (Gavezzotti, 1983) as a function of  $\tau$ . First point at  $\tau = 7^\circ$ , experimental value at  $\tau_1$ ,  $\Delta\tau = 10^\circ$ .

## Experimental

### Crystal data

C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 327.38

Mo *K*α radiation  
 $\lambda = 0.71069$  Å

Monoclinic  
 $P2_1/c$   
 $a = 8.414 (4) \text{ \AA}$   
 $b = 9.253 (3) \text{ \AA}$   
 $c = 23.38 (1) \text{ \AA}$   
 $\beta = 100.72 (4)^\circ$   
 $V = 1788 (1) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.216 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections  
 $\theta = 13.2\text{--}17.2^\circ$   
 $\mu = 0.084 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prism  
 $0.48 \times 0.48 \times 0.40 \text{ mm}$   
 Colourless

Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

C1—O2	1.454 (4)	C6—C10	1.539 (5)
C1—C5	1.552 (4)	N7—N8	1.391 (4)
C1—C10	1.558 (5)	N7—C20	1.352 (5)
C1—C11	1.497 (4)	N8—C9	1.278 (5)
O2—N3	1.413 (3)	C9—C10	1.471 (5)
N3—C4	1.276 (4)	C20—O21	1.196 (4)
C4—C5	1.497 (4)	C20—O22	1.329 (5)
C4—C12	1.475 (5)	O22—C23	1.464 (6)
C5—C6	1.546 (4)	C23—C24	1.51 (1)
C6—N7	1.462 (4)	C23—C24'	1.45 (2)
C10—C1—C11	119.3 (3)	C6—N7—C20	125.3 (3)
C5—C1—C10	89.8 (2)	C6—N7—N8	112.7 (3)
O2—C1—C11	108.2 (2)	N7—N8—C9	107.3 (3)
O2—C1—C10	111.8 (3)	N8—C9—C10	115.9 (4)
O2—C1—C5	104.3 (2)	C6—C10—C9	101.9 (3)
C1—O2—N3	110.2 (2)	C1—C10—C9	116.3 (3)
O2—N3—C4	109.9 (3)	C1—C10—C6	89.8 (3)
N3—C4—C12	121.2 (3)	C4—C12—C17	118.9 (3)
N3—C4—C5	114.3 (3)	C4—C12—C13	120.2 (3)
C1—C5—C4	101.2 (2)	N7—C20—O22	107.7 (3)
C4—C5—C6	112.6 (3)	N7—C20—O21	126.6 (4)
C1—C5—C6	89.7 (2)	O21—C20—O22	125.7 (3)
C5—C6—C10	90.7 (2)	C20—O22—C23	115.9 (3)
C5—C6—N7	115.4 (3)	O22—C23—C24'	108.4 (7)
N7—C6—C10	102.1 (3)	O22—C23—C24	106.1 (6)
C5—C1—C10—C6	−0.3 (2)		
O2—C1—C10—C9	151.1 (3)		
O2—C1—C5—C6	112.8 (3)		
C10—C1—C5—C6	0.3 (2)		
C1—O2—N3—C4	1.9 (4)		
N3—C4—C12—C13	73.3 (5)		
C12—C4—C5—C6	85.2 (4)		
C4—C5—C6—N7	−154.5 (3)		
C1—C5—C6—C10	−0.3 (2)		
C5—C6—C10—C1	0.3 (2)		
C6—N7—C20—O21	−175.1 (4)		
C6—N7—C20—O22	5.7 (5)		
N8—N7—C20—O21	−1.4 (6)		
C20—N7—N8—C9	−176.5 (4)		
N7—C20—O22—C23	−178.7 (4)		
O21—C20—O22—C23	2.1 (6)		
C20—O22—C23—C24	−173.2 (6)		
C20—O22—C23—C24'	155.4 (8)		

## Data collection

Enraf–Nonius CAD-4F diffractometer  
 $\omega$ – $\theta$  mode scans  
 Absorption correction: none  
 4066 measured reflections  
 4066 independent reflections  
 2381 observed reflections  
 $[F > 4\sigma(F)]$

$\theta_{\max} = 27.50^\circ$   
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 12$   
 $l = -30 \rightarrow 30$   
 2 standard reflections  
 frequency: 120 min  
 intensity variation: 18%

## Refinement

Refinement on  $F$   
 $R = 0.0704$   
 $wR = 0.0993$   
 $S = 2.82$   
 2381 reflections  
 217 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F) + 0.0014F^2]$   
 $(\Delta/\sigma)_{\max} = 0.02$

$\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A) 2.3.1 for C, O and N and Table 2.2C for H)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$U_{\text{iso}}$  for C24 and C24';  $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$  for other atoms.

	$x$	$y$	$z$	$U_{\text{iso}}/U_{\text{eq}}$
C1	0.3251 (4)	0.6236 (3)	0.0163 (1)	0.0477 (10)
O2	0.4190 (3)	0.5192 (2)	0.0551 (1)	0.0597 (8)
N3	0.4241 (3)	0.5594 (3)	0.1138 (1)	0.0574 (9)
C4	0.3409 (4)	0.6738 (3)	0.1161 (1)	0.0489 (10)
C5	0.2681 (4)	0.7352 (3)	0.0578 (1)	0.0466 (10)
C6	0.3769 (4)	0.8511 (3)	0.0369 (1)	0.0494 (10)
N7	0.2923 (3)	0.9576 (3)	−0.0040 (1)	0.0590 (10)
N8	0.2934 (4)	0.9222 (4)	−0.0617 (1)	0.0696 (12)
C9	0.3751 (5)	0.8058 (4)	−0.0616 (2)	0.0702 (16)
C10	0.4348 (4)	0.7412 (3)	−0.0041 (2)	0.0559 (12)
C11	0.2075 (4)	0.5425 (3)	−0.0282 (1)	0.0577 (11)
C12	0.3252 (4)	0.7390 (3)	0.1723 (1)	0.0549 (12)
C13	0.4567 (5)	0.8134 (4)	0.2058 (2)	0.0735 (14)
C14	0.4343 (7)	0.8786 (6)	0.2568 (2)	0.1013 (21)
C15	0.2915 (9)	0.8691 (7)	0.2759 (2)	0.1151 (26)
C16	0.1641 (7)	0.7932 (7)	0.2433 (2)	0.1089 (23)
C17	0.1777 (5)	0.7288 (5)	0.1909 (2)	0.0758 (15)
C18	0.6187 (6)	0.8212 (6)	0.1879 (2)	0.1067 (21)
C19	0.0366 (6)	0.6500 (7)	0.1561 (2)	0.1058 (22)
C20	0.2082 (4)	1.0722 (4)	0.0105 (2)	0.0624 (13)
O21	0.1300 (4)	1.1556 (3)	−0.0224 (1)	0.0926 (11)
O22	0.2294 (3)	1.0771 (3)	0.0682 (1)	0.0745 (11)
C23	0.1440 (7)	1.1931 (5)	0.0926 (3)	0.1156 (25)
C24	0.2025 (22)	1.1880 (14)	0.1577 (5)	0.1043 (48)
C24'	0.1205 (28)	1.1492 (18)	0.1498 (6)	0.0973 (64)

During the measurements the crystal showed a gradual decay, for which correction was made in the data reduction process. In the refinement the atoms C24 and C24' were considered as isotropic and the sum of their site occupancy factors was constrained to unity [final values: 0.58 (3) and 0.42 (3), respectively]. No further constraints were imposed. Most of the H atoms were located by  $\Delta\rho$  syntheses; those bonded to C10, C15 and C18, and one belonging to the C19 methyl group were placed in calculated positions. For the ethyl group affected by disorder no H atoms were considered. Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989); *CADABS* (local software). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*; *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976). Geometrical parameters for (III) were calculated by means of the program *PARST* (Nardelli, 1983) and the CIF file was prepared with the program *PARSTCIF* (Nardelli, 1992).

The Cambridge Structural Database was accessed through 'Servizio Italiano Diffusione Dati Cristallografici del CNR', University of Parma. Financial support from the Italian National Research Council (CNR) is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Roburic Acid, a Triterpene 3,4-Seco Acid

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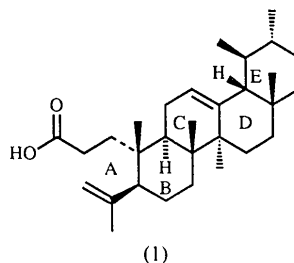
### Abstract

The structure and stereochemistry of roburic acid [3,4-secoursa-4(23),12-dien-3-oic acid,  $C_{30}H_{48}O_2$ ], isolated as the main component from the Chinese drug 'Ch'in-Chiao' (*Gentiana macrophylla pall.*) has been established.

### Comment

The title compound, (1), has been isolated and its chemical structure verified by partial synthesis from  $\alpha$ -amyrin via peracid oxidation (Mangoni & Belardini, 1963). The compound was obtained by

silica-gel chromatography of the chloroform extract of *G. macrophylla*. The mass spectrum showed the base peak at 218, indicating a 12-ursane or oleanane-type triterpenoid. The IR spectrum showed no evidence of a 3-hydroxyl group, so a 3,4-seco acid was assumed. This X-ray analysis establishes the molecular structure and conformation of the compound.



The triterpenoid ring *A* has been opened at the C(3)—C(4) bond to give a carboxylic acid group at C(3) and an olefin at C(4). Rings *B*, *D* and *E* have chair forms, the *B/C* rings are *trans* fused while the

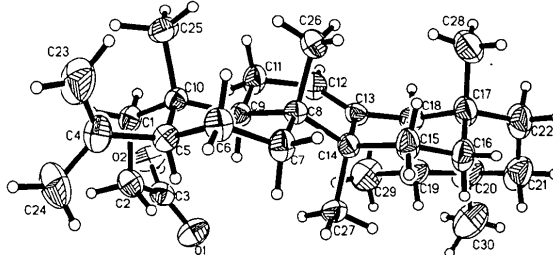


Fig. 1. An ORTEPII (Johnson, 1976) drawing of  $C_{30}H_{48}O_2$ .

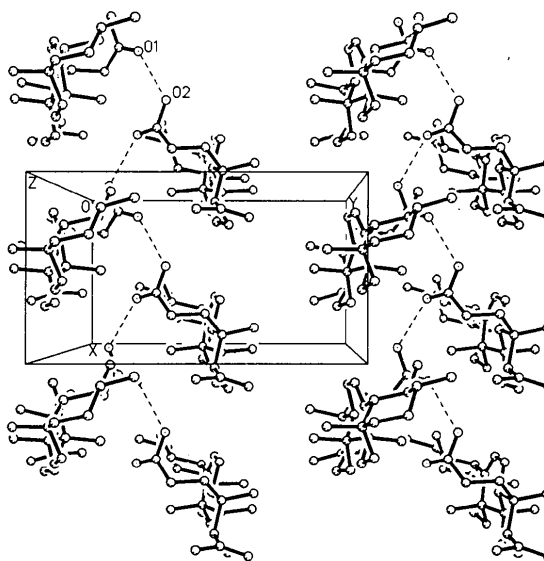


Fig. 2. A view of the unit cell along the *c* axis with O(1)—H...O(2)-type hydrogen bonding.