

refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and complete geometry have been deposited with the IUCr (Reference: KH1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Hughes, K. H., Meetsma, A. & Teuben, J. H. (1993). *Organometallics*, **12**, 1936.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Rieger, B., Steimann, M. & Fawzi, R. (1992). *Chem. Ber.* **125**, 2373–2377.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1990). *XPREP*. Version 4.1 for MS-DOS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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## Dupeyredioxyl (1,3,5,7-Tetramethyl-2,6-diaadamantane-*N,N'*-dioxyl)

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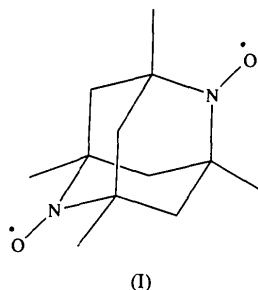
## Abstract

The title compound, C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>, exhibits two crystalline forms ( $\alpha$  monoclinic and  $\beta$  orthorhombic) in which the diaadamantane skeleton has the same structure but the packing is different. Both are obtained by crystallization in diethyl ether. The monoclinic form has been reported to possess a ferromagnetic transition.

## Comment

The title compound, (I), has been synthesized (Chiarelli & Rassat, 1993) and it has been shown that the monoclinic form undergoes a ferromagnetic transition at 1.48 K (Chiarelli & Rassat, 1991; Chiarelli, Rassat

& Rey, 1992; Fluekiger, Weber, Chiarelli, Rassat & Ellinger, 1993; Chiarelli, Novak, Rassat & Tholence, 1993; Chiarelli, Rassat, Dromzee, Jeannin, Novak & Tholence, 1993). It is one of the purely organic materials which exhibits a well characterized ferromagnetic transition (see Miller & Epstein, 1994). Above the transition temperature, crystals of the  $\alpha$  form show a spontaneous magnetization and absence of hysteresis. A simplified (partial) crystal structure of the  $\alpha$  form has been published (Chiarelli, Novak, Rassat & Tholence, 1993). Complementary information about the  $\alpha$  form and a full report of the structure of the  $\beta$  form are presented here.



By evaporation of a diethyl ether solution of (I) at room temperature, it is possible to obtain two different crystalline forms in the same crop, *i.e.* short parallelepipeds ( $\alpha$  form) and needle-like crystals ( $\beta$  form). The  $\alpha$  form is monoclinic and the  $\beta$  form is orthorhombic. We have not been able to induce a selectivity towards one type of crystallization.

Atomic coordinates are given in Tables 1 and 4 for the monoclinic and orthorhombic forms, respectively. Selected bond distances and bond angles are given in

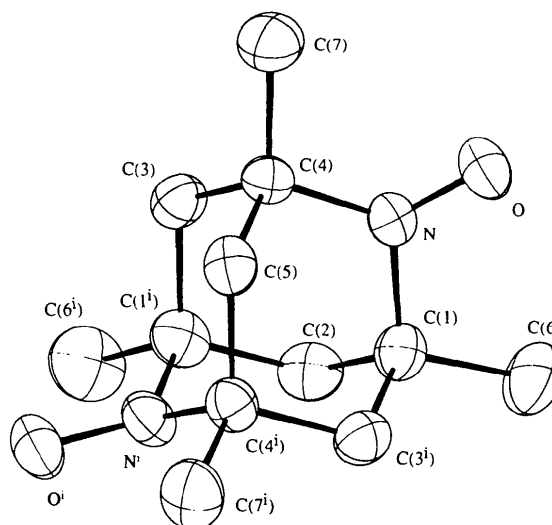


Fig. 1. The molecular structure of C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> ( $\alpha$  form; monoclinic) showing the numbering scheme employed and 50% probability displacement ellipsoids. H atoms are omitted for clarity. [Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .]

Tables 2, 3, 5 and 6. The molecular structure and atom-numbering scheme of the  $\alpha$  form are shown in Fig. 1, produced using the program CAMERON (Pearce & Watkin, 1992) included in the CRYSTALS crystallographic program system (Watkin, Carruthers & Betteridge, 1988).

Since each cell of the  $\alpha$  and  $\beta$  forms contains four molecules of (I), while the space groups have eight positions, some symmetry element must be common to the molecule and the crystal; the twofold axis ( $\frac{1}{2}, y, \frac{1}{4}$ ) passing through the C(2) and C(5) atoms is such a symmetry element. In both the  $\alpha$  and  $\beta$  forms, molecules related by ( $\frac{1}{2}, \frac{1}{2}, \frac{a}{c}$ ) inversion centres form chains parallel to the  $c$  axis (Fig. 2). In the monoclinic crystal, these chains are related by the translation  $\frac{1}{2}, \frac{1}{2}, 0$ , while

in the orthorhombic crystal the chains are related by the glide plane  $b; \frac{3}{2} - x, \frac{1}{2} + y, z$ .

In both forms, the structure of the molecular frame is the same; the diazaadamantane skeleton is rigid and not modified by packing. The only possible modification is the conformation of the NO group (out-of-plane bending), well known to be very sensitive to the environment (Rassat & Rey, 1973; Ricca, Hanus & Ellinger, 1995). In the  $\beta$  form, there is a disordered position of the O atom and the intermolecular distance in the  $ac$  plane is greater than in the monoclinic form. The situation is inverted in the third dimension, however, where the  $b$  parameter is 11.574 Å in the  $\beta$  form and 14.495 Å in the  $\alpha$  form. Mesh volumes are only slightly different, 1212 Å<sup>3</sup> for  $\alpha$  and 1250 Å<sup>3</sup> for  $\beta$ , and the calculated densities are quite similar, 1.23 Mg m<sup>-3</sup> for the  $\alpha$  form and 1.19 Mg m<sup>-3</sup> for the  $\beta$  form.

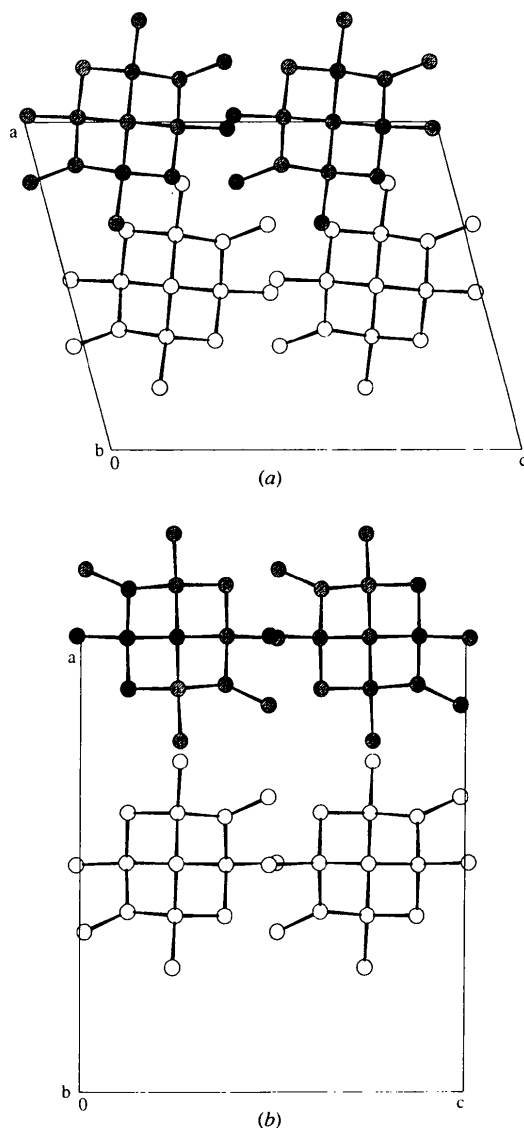


Fig. 2. Packing diagrams projected down the  $b$  axis of (a) the monoclinic  $\alpha$  form and (b) the orthorhombic  $\beta$  form.

## Experimental

Crystals of both the  $\alpha$  and  $\beta$  forms of (I) were obtained by evaporation of a diethyl ether solution at room temperature.

### The $\alpha$ form

#### Crystal data

$C_{12}H_{20}N_2O_2$   
 $M_r = 224.3$   
 Monoclinic  
 $C2/c$   
 $a = 8.381(3)$  Å  
 $b = 14.495(3)$  Å  
 $c = 10.351(3)$  Å  
 $\beta = 105.35(2)^\circ$   
 $V = 1212$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.23$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069$  Å  
 Cell parameters from 25 reflections  
 $\theta = 14\text{--}15^\circ$   
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 293$  K  
 Parallelepiped  
 $0.76 \times 0.38 \times 0.26$  mm  
 Yellow–orange

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1627 measured reflections  
 1461 independent reflections  
 886 observed reflections  
 $[I > 3\sigma(I)]$

$R_{int} = 0.06$   
 $\theta_{max} = 28^\circ$   
 $h = -11 \rightarrow 10$   
 $k = 0 \rightarrow 19$   
 $l = 0 \rightarrow 13$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: not significant

#### Refinement

Refinement on  $F$   
 $R = 0.035$   
 $wR = 0.031$   
 $S = 3.2$   
 549 reflections  
 74 parameters  
 Unit weights applied  
 $(\Delta/\sigma)_{max} < 0.1$

$\Delta\rho_{max} = 0.15$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.12$  e Å<sup>-3</sup>  
 Extinction correction: Larson (1970)  
 Extinction coefficient:  $55 \times 10^{-6}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for the α form
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U <sub>eq</sub>
N	0.6321 (2)	0.37648 (9)	0.4037 (1)	0.0422
O	0.6843 (2)	0.40392 (9)	0.5241 (1)	0.0599
C(1)	0.4853 (2)	0.3140 (1)	0.3680 (2)	0.0422
C(2)	1/2	0.2548 (2)	1/4	0.0454
C(3)	0.6677 (2)	0.3752 (1)	0.1776 (2)	0.0426
C(4)	0.6554 (2)	0.4372 (1)	0.2940 (2)	0.0405
C(5)	1/2	0.4973 (2)	1/4	0.0432
C(6)	0.4799 (2)	0.2552 (1)	0.4879 (2)	0.0579
C(7)	0.8109 (2)	0.4946 (1)	0.3428 (2)	0.0557

Table 2. Selected geometric parameters (Å, °) for the α form

N—O	1.270 (2)	C(1)—C(6)	1.516 (2)
N—C(1)	1.494 (2)	C(3)—C(4)	1.528 (2)
N—C(4)	1.490 (2)	C(4)—C(5)	1.532 (2)
C(1)—C(2)	1.524 (2)	C(4)—C(7)	1.516 (2)
C(1)—C(3 <sup>1</sup> )	1.528 (2)		
C(1)—N—O	118.6 (1)	C(1)—C(2)—C(1 <sup>1</sup> )	111.5 (2)
C(4)—N—O	118.8 (1)	C(4)—C(3)—C(1 <sup>1</sup> )	111.0 (1)
C(1)—N—C(4)	115.8 (1)	N—C(4)—C(3)	107.6 (1)
N—C(1)—C(2)	107.7 (1)	N—C(4)—C(5)	106.8 (1)
N—C(1)—C(6)	109.9 (1)	N—C(4)—C(7)	110.2 (1)
N—C(1)—C(3 <sup>1</sup> )	107.1 (1)	C(3)—C(4)—C(5)	109.3 (1)
C(2)—C(1)—C(6)	111.4 (1)	C(3)—C(4)—C(7)	110.7 (1)
C(2)—C(1)—C(3 <sup>1</sup> )	108.6 (1)	C(5)—C(4)—C(7)	112.1 (1)
C(6)—C(1)—C(3 <sup>1</sup> )	112.0 (1)	C(4)—C(5)—C(4 <sup>1</sup> )	110.7 (2)

Symmetry code: (i) 1 - x, y, 1/2 - z.

Table 3. Contact distances (Å) for the α form

N...N <sup>i</sup>	3.361 (3)	N...O <sup>iii</sup>	4.340 (2)
N...O <sup>i</sup>	4.536 (2)	O...O <sup>iii</sup>	4.654 (3)
O...O <sup>i</sup>	5.697 (2)	N...N <sup>iv</sup>	6.294 (2)
N...N <sup>ii</sup>	4.903 (3)	N...O <sup>iv</sup>	5.165 (2)
N...O <sup>ii</sup>	4.333 (2)	O...O <sup>iv</sup>	5.877 (1)
O...O <sup>ii</sup>	4.091 (3)	N...N <sup>v</sup>	6.294 (2)
N...N <sup>iii</sup>	4.386 (3)	O...O <sup>v</sup>	5.877 (1)

Symmetry codes: (i) 1 - x, y, 1/2 - z; (ii) 1 - x, 1 - y, 1 - z; (iii) 3/2 - x, 1/2 - y, 1 - z; (iv) x, 1 - y, z - 1/2; (v) x, 1 - y, 1/2 + z.

**The β form****Crystal data**C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>M<sub>r</sub> = 224.3

Orthorhombic

Pbcn

a = 11.1558 (8) Å

b = 11.574 (1) Å

c = 9.680 (2) Å

V = 1250 Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.19 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 14–15°

μ = 0.08 mm<sup>-1</sup>

T = 293 K

Needle

0.70 × 0.12 × 0.10 mm

Yellow–orange

**Data collection**

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

none

1099 measured reflections

1099 independent reflections

443 observed reflections

[I &gt; 2σ(I)]

θ<sub>max</sub> = 25°

h = 0 → 10

k = 0 → 13

l = 0 → 11

2 standard reflections

frequency: 60 min

intensity decay: not

significant

**Refinement**

Refinement on F

R = 0.040

wR = 0.034

S = 2.6

443 reflections

86 parameters

Unit weights applied

(Δ/σ)<sub>max</sub> < 0.1Δρ<sub>max</sub> = 0.12 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.12 e Å<sup>-3</sup>

Extinction correction:

Larson (1970)

Extinction coefficient:

91 × 10<sup>-6</sup>

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>) for the β form
$$U_{iso} \text{ for O(2), } U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ for all others.}$$

	x	y	z	U <sub>iso</sub> /U <sub>eq</sub>
N	0.6036 (3)	0.3273 (3)	0.3751 (4)	0.0567
O(1)	0.6510 (4)	0.3603 (4)	0.4881 (4)	0.0679
O(2)	0.6946 (8)	0.307 (1)	0.442 (1)	0.090 (5)
C(1)	0.4974 (5)	0.2511 (3)	0.3792 (4)	0.0587
C(2)	1/2	0.1762 (4)	1/4	0.0655
C(3)	0.6139 (3)	0.3257 (4)	0.1238 (4)	0.0569
C(4)	0.6127 (3)	0.4040 (3)	0.2530 (5)	0.0516
C(5)	1/2	0.4785 (4)	1/4	0.0567
C(6)	0.5028 (5)	0.1770 (4)	0.5103 (5)	0.0891
C(7)	0.7264 (3)	0.4753 (4)	0.2589 (5)	0.0778

Table 5. Selected geometric parameters (Å, °) for the β form

O(1)—O(2)	0.90 (1)	C(1)—C(3 <sup>1</sup> )	1.513 (6)
N—O(1)	1.274 (4)	C(1)—C(6)	1.533 (5)
N—O(2)	1.227 (7)	C(3)—C(4)	1.545 (5)
N—C(1)	1.478 (5)	C(4)—C(5)	1.524 (4)
N—C(4)	1.481 (5)	C(4)—C(7)	1.514 (5)
C(1)—C(2)	1.522 (4)		
O(1)—N—O(2)	42.1 (6)	C(6)—C(1)—C(3 <sup>1</sup> )	111.6 (4)
C(1)—N—O(1)	119.2 (4)	C(1)—C(2)—C(1 <sup>1</sup> )	110.6 (4)
C(1)—N—O(2)	122.4 (7)	C(4)—C(3)—C(1 <sup>1</sup> )	110.1 (3)
C(4)—N—O(1)	118.5 (4)	N—C(4)—C(3)	107.2 (3)
C(4)—N—O(2)	118.6 (7)	N—C(4)—C(5)	107.3 (3)
C(1)—N—C(4)	115.8 (3)	N—C(4)—C(7)	110.7 (4)
N—C(1)—C(2)	107.6 (3)	C(3)—C(4)—C(5)	108.9 (3)
N—C(1)—C(6)	108.9 (4)	C(3)—C(4)—C(7)	110.1 (4)
N—C(1)—C(3 <sup>1</sup> )	108.4 (3)	C(5)—C(4)—C(7)	112.6 (3)
C(2)—C(1)—C(6)	111.2 (3)	C(4)—C(5)—C(4 <sup>1</sup> )	111.2 (4)
C(2)—C(1)—C(3 <sup>1</sup> )	109.0 (3)		

Symmetry code: (i) 1 - x, y, 1/2 - z.

Table 6. Contact distances (Å) for the β form

N...N <sup>i</sup>	3.347 (7)	N...O(1 <sup>iii</sup> )	4.784 (5)
N...O(1 <sup>i</sup> )	4.536 (6)	N...O(2 <sup>iii</sup> )	5.66 (1)
N...O(2 <sup>i</sup> )	4.533 (9)	O(1)...O(1 <sup>iii</sup> )	4.68 (1)
O(1)...O(1 <sup>i</sup> )	5.710 (7)	O(1)...O(2 <sup>iii</sup> )	5.49 (1)
O(1)...O(2 <sup>i</sup> )	5.709 (9)	N...O(1 <sup>iv</sup> )	5.123 (5)
O(2)...O(2 <sup>i</sup> )	5.72 (2)	N...O(2 <sup>iv</sup> )	5.01 (1)
O(1)...O(1 <sup>ii</sup> )	5.901 (5)	O(1)...O(1 <sup>iv</sup> )	5.901 (5)
O(1)...O(2 <sup>ii</sup> )	5.10 (1)	O(1)...O(2 <sup>iv</sup> )	5.89 (1)
O(2)...O(2 <sup>ii</sup> )	5.169 (7)	O(2)...O(2 <sup>iv</sup> )	5.169 (7)
N...N <sup>iii</sup>	5.211 (8)		

Symmetry codes: (i) 1 - x, y, 1/2 - z; (ii) 3/2 - x, 1/2 - y, 1/2 + z; (iii) 1 - x, 1 - y, 1 - z; (iv) 3/2 - x, 1/2 - y, z - 1/2.

Corrections were made for Lorentz and polarization effects. In the α form, observed systematic absences for *hkl*, *h + k = 2n + 1*, and for *h0l*, *l = 2n + 1*, were compatible with space groups *Cc* or *C2/c*. The centrosymmetric space group

was chosen on the basis of statistical tests and confirmed by subsequent results. In the  $\beta$  form, the observed systematic absences  $0kl$ ,  $k = 2n + 1$ ,  $h0l$ ,  $l = 2n + 1$ , and  $hk0$ ,  $h + k = 2n + 1$ , indicated space group *Pbcn*. Computations were performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988) adapted on a MicroVAXII. Scattering factors for all atoms were as incorporated in *CRYSTALS*. The structures were solved by direct methods. All remaining non-H atoms were found by successive electron-density map calculations. For the  $\beta$  (orthorhombic) form, the density map showed two prominent but unequal peaks, one on either side of the plane. The only satisfactory explanation of this was the assumption of a disordered model. Fractional oxygen, referred to as O(1) and O(2), was assigned to these two positions, with occupancy factors summing to unity and with the same isotropic displacement parameters. The refinement of occupancy led to 0.69 for O(1) and 0.31 for O(2). Atomic coordinates were refined together with anisotropic displacement parameters [isotropic for O(2)]. At this stage, the H atoms were located on a difference electron-density map, their coordinates refined with an overall isotropic displacement parameter and then included as fixed contributors for further structure-factor calculations. Least-squares refinements were carried out by minimizing the function  $\sum w(|F_o| - |F_c|)^2$ . The models reached convergence with *R* and *wR* having the values listed. The criteria for a satisfactory complete analysis were the ratios of the r.m.s. shift to standard deviation being less than 0.1 and there being no significant features in the final difference maps.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Chiarelli, R., Novak, M. A., Rassat, A. & Tholence, J. L. (1993). *Nature*, **363**, 147–149.
- Chiarelli, R. & Rassat, A. (1991). *Magnetic Properties of Some Biradicals of  $D_{2d}$  Symmetry. Magnetic Molecular Materials*, edited by D. Gatteschi *et al.*, pp. 191–202. Dordrecht: Kluwer Academic Publishers.
- Chiarelli, R. & Rassat, A. (1993). *Bull. Soc. Chim. Fr.* **130**, 299–303.
- Chiarelli, R., Rassat, A., Dromzee, Y., Jeannin, Y., Novak, M. A. & Tholence, J.-L. (1993). *Physica Scr.* **T49**, 706–710.
- Chiarelli, R., Rassat, A. & Rey, P. (1992). *J. Chem. Commun.* **15**, 1081–1082.
- Fluekiger, P., Weber, J., Chiarelli, R., Rassat, A. & Ellinger, Y. (1993). *Int. J. Quant. Chem.* **45**, 649–663.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Miller, J. S. & Epstein, A. S. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 385–415.
- Pearce, L. J. & Watkin, D. J. (1992). *CAMERON. Molecular Graphics Program*. Chemical Crystallography Laboratory, University of Oxford, England.
- Rassat, A. & Rey, P. (1973). *Tetrahedron*, **29**, 1599–1603.
- Ricca, A., Hanus, M. & Ellinger, Y. (1995). *Chem. Phys. Lett.* **232**, 54–60.
- Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1988). *CRYSTALS*. Chemical Crystallography Laboratory, University of Oxford, England.

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## A Second Triclinic Polymorph of Coumarin 153

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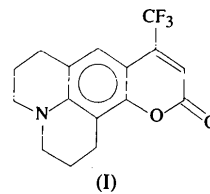
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### Abstract

Coumarin 153, 2,3,6,7-tetrahydro-9-(trifluoromethyl)-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one,  $C_{16}H_{14}F_3NO_2$ , was found to exist in a new polymorphic form in the triclinic system. There is an earlier report of a crystal structure determination of this compound, also in the triclinic system, but with a different cell volume and packing mode [Gridunova *et al.* (1992). *Kristallografiya*, **37**, 366–372]. There are three molecules in the asymmetric unit of the title polymorph compared with two in the latter case; all three molecules show disorder in the piperidine ring system. The molecules are planar and are stacked parallel to the (011) plane. The crystal structure is stabilized by C—H...O hydrogen bonds.

### Comment

The title compound, (I), a rigidized aminocoumarin, has attracted extensive study since it has been used as a laser dye (Maeda, 1984; Priyadarsini, Naik & Moorthy, 1989; Kunjappu, 1993; McCarthy & Blanchard, 1993). The crystal structure determination of this compound was undertaken as part of our structural studies on laser dyes. In the present study, we found coumarin 153 to crystallize in a new triclinic unit cell (space group  $P\bar{1}$ ), with three molecules, *A*, *B* and *C*, in the asymmetric unit (Fig. 1). This is different from the structure reported earlier by Gridunova *et al.* (1992), which has a smaller triclinic unit cell (also  $P\bar{1}$ ) and only two molecules in the asymmetric unit. This compound has also been found to crystallize in the orthorhombic system (Sivakumar & Chinnakali, 1991). Recently,



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