Acta Cryst. (1996). C52, 458–460

trans-(3a*R*)-1,2,3,3a-Tetrahydro-3a-(methoxymethyl)-5-methyl-7-nitropyrrolo-[1,2-*a*]quinoline-4,4(5*H*)-dicarbonitrile: Four Independent Molecules in the Unit Cell

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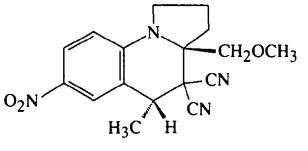
(*Received 5 September 1994; accepted 25 August 1995*)

Abstract

The structure of the title compound, $C_{17}H_{18}N_4O_3$, has been determined. The crystal structure contains four independent molecules which differ in the conformation of the methoxymethyl side chains.

Comment

Chiral pyrrolo[1,2-*a*]quinolines can be used as second-order non-linear optical materials. Non-linear optical properties of crystals of a number of these compounds have been reported (Kelderman, Verboom, Engbersen, Harkema, Heesink, Lehmusvaara, van Hulst, Reinhoudt, Derhaeg & Persoons, 1992; Kelderman, 1993). The title compound, (I), which was prepared from enantiomerically pure starting compounds, shows second-order non-linear optical properties.



(I)

Four independent molecules are found in the crystal structure of the title compound (Fig. 2). They have the same overall conformation for the molecular framework, but differ in the orientation of the methoxymethyl side chain. Satisfactory agreement is found in corresponding bond lengths and angles in the different molecules. The differences in conformation of the methoxymethyl side chains can be seen in the list of selected torsion angles given in Table 2. The compound studied is chiral. No attempts have been made to determine the absolute configuration, which was assumed to be the same as that of one of the starting materials (Nijhuis, Verboom, Reinhoudt & Harkema, 1987). Molecule 4 shows rather large displacement parameters for the nitro group and the connected phenyl ring. The shape of the ellipsoids suggests librational motion or statistical disorder in the plane of the phenyl ring. No obvious reason for this could be found from a packing diagram (Fig. 3), which shows that all nitro groups are more or less in the same plane and that the orientation of the mean planes through the molecular skeleton of the different molecules is approximately parallel.

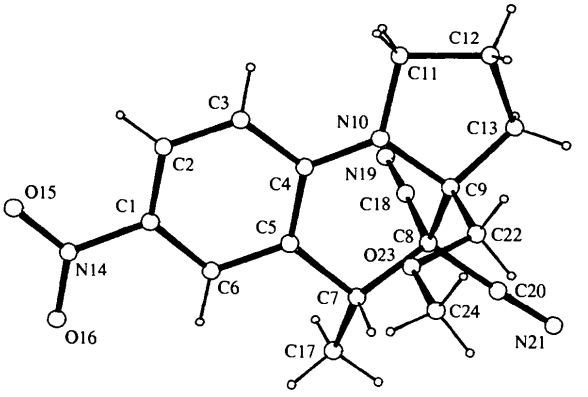


Fig. 1. *PLUTO* drawing (Motherwell & Clegg, 1978) showing the atomic numbering. Corresponding atoms of molecules 1, 2, 3 and 4 are indicated by suffixes *A*, *B*, *C* and *D*, respectively.

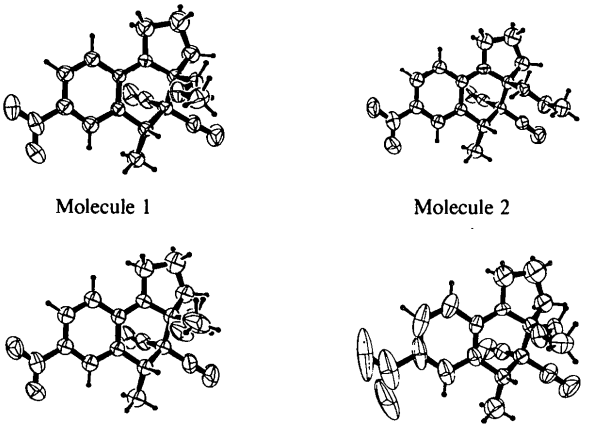


Fig. 2. *ORTEP*II view (Johnson, 1976) showing the conformations of the different molecules. Displacement ellipsoids are scaled to include 50% probability.

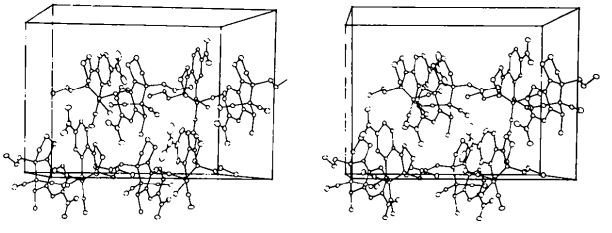


Fig. 3. *ORTEP*II stereoview (Johnson, 1976) showing the packing of the different molecules in the unit cell. Displacement ellipsoids are scaled to include 25% probability.

Experimental

The title compound was prepared by reaction of 1,2,3,3a-tetrahydro-3a-(methoxymethyl)-5-methylpyrrolo[1,2-*a*]quinoline-4,4(5*H*)-dicarbonitrile with concentrated HNO_3 in CH_2Cl_2 for 0.5 h (Nijhuis, Verboom, Abu El-Fadl, Harkema & Reinhoudt, 1989; Nijhuis, Verboom, Abu El-Fadl, van Hummel & Reinhoudt, 1989; Kelderman, Noorlander-Bunt, van Eerden, Verboom & Reinhoudt, 1991). Light-yellow crystals were obtained by recrystallization from methanol.

Crystal data

$C_{17}H_{18}N_4O_3$
$M_r = 326.4$
Monoclinic
$P2_1$
$a = 14.452\ (3)$ Å
$b = 13.089\ (3)$ Å
$c = 17.558\ (3)$ Å
$\beta = 96.01\ (3)°$
$V = 3303\ (2)$ Å^3
$Z = 8$
$D_x = 1.312$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.0$–$14.1°$
$\mu = 0.087$ mm^{-1}
$T = 293$ K
Parallelepiped
0.60 × 0.60 × 0.50 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6084 measured reflections
6084 independent reflections
4307 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 25°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.061$
$S = 2.14$
4307 reflections
635 parameters
H atoms treated as riding atoms
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $1.8\ (4) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

B_{iso} for starred atoms; $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	B_{eq}/B_{iso}
O15*A*	−0.0004 (3)	0.4058 (3)	0.0707 (3)	8.2 (1)
O16*A*	−0.0571 (3)	0.2583	0.0455 (3)	8.4 (1)
O23*A*	0.1887 (2)	0.0448 (3)	0.3273 (2)	4.64 (7)
O15*B*	0.9149 (3)	−0.6810 (3)	0.2368 (2)	6.8 (1)
O16*B*	0.9836 (3)	−0.7966 (3)	0.3085 (3)	7.7 (1)
O23*B*	1.3115 (2)	−0.4696 (3)	0.6141 (2)	5.73 (9)
O15*C*	1.0515 (3)	−0.1762 (3)	0.2714 (2)	6.8 (1)
O16*C*	0.9777 (3)	−0.2920 (3)	0.2022 (2)	6.9 (1)
O23*C*	0.8145 (3)	0.0571 (3)	−0.0612 (2)	7.1 (1)
O15*D*	1.0542 (4)	−0.2083 (6)	0.4811 (3)	17.9 (2)
O16*D*	1.0470 (3)	−0.3683 (7)	0.5098 (3)	15.3 (2)
O23*D*	0.7728 (2)	−0.4416 (3)	0.1804 (2)	5.50 (9)
N10*A*	0.3132 (2)	0.1369 (3)	0.2402 (2)	3.35 (8)
N14*A*	0.0044 (3)	0.3125 (4)	0.0746 (2)	5.7 (1)
N19*A*	0.3662 (3)	0.0295 (4)	0.0654 (2)	6.2 (1)
N21*A*	0.3017 (3)	−0.2233 (4)	0.2019 (3)	6.2 (1)
N10*B*	1.2329 (3)	−0.4231 (3)	0.4131 (2)	3.79 (8)
N14*B*	0.9763 (3)	−0.7085 (4)	0.2862 (2)	5.3 (1)
N19*B*	1.3973 (3)	−0.5620 (4)	0.3315 (2)	5.9 (1)
N21*B*	1.4723 (3)	−0.6150 (4)	0.5664 (3)	6.4 (1)
N10*C*	0.7514 (3)	0.0914 (3)	0.0816 (2)	4.00 (9)
N14*C*	0.9906 (3)	−0.2030 (4)	0.2215 (2)	5.2 (1)
N19*C*	0.5744 (3)	−0.0682 (4)	0.1407 (3)	7.1 (1)
N21*C*	0.5356 (4)	−0.0816 (5)	−0.1020 (3)	8.8 (2)
N10*D*	0.6879 (2)	−0.3350 (3)	0.2854 (2)	3.77 (8)
N14*D*	1.0172 (3)	−0.2906 (7)	0.4738 (3)	11.7 (2)
N19*D*	0.6088 (3)	−0.4596 (4)	0.4500 (2)	6.4 (1)
N21*D*	0.6103 (4)	−0.6910 (4)	0.2772 (3)	8.3 (2)
C1*A*	0.0851 (3)	0.2668 (4)	0.1175 (3)	4.16 (9)*
C2*A*	0.1534 (3)	0.3286 (4)	0.1530 (2)	4.06 (9)*
C3*A*	0.2299 (3)	0.2840 (4)	0.1922 (2)	3.56 (8)*
C4*A*	0.2377 (3)	0.1781 (3)	0.1988 (2)	2.88 (7)*
C5*A*	0.1683 (3)	0.1156 (3)	0.1605 (2)	3.00 (8)*
C6*A*	0.0917 (3)	0.1611 (4)	0.1197 (2)	3.87 (9)*
C7*A*	0.1754 (3)	−0.0001 (3)	0.1626 (2)	3.20 (8)*
C8*A*	0.2791 (3)	−0.0283 (4)	0.1813 (2)	3.45 (8)*
C9*A*	0.3219 (3)	0.0274 (3)	0.2551 (2)	3.34 (8)*
C11*A*	0.3998 (3)	0.1905 (4)	0.2603 (3)	5.0 (1)*
C12*A*	0.4600 (4)	0.1128 (5)	0.3062 (3)	6.4 (1)*
C13*A*	0.4266 (3)	0.0113 (4)	0.2723 (3)	4.8 (1)*
C17*A*	0.1325 (3)	−0.0519 (4)	0.0911 (3)	4.6 (1)*
C18*A*	0.3299 (3)	0.0034 (4)	0.1163 (2)	4.2 (1)
C20*A*	0.2909 (3)	−0.1387 (4)	0.1912 (3)	4.3 (1)
C22*A*	0.2750 (3)	−0.0033 (4)	0.3258 (2)	4.4 (1)
C24*A*	0.1448 (4)	0.0153 (5)	0.3918 (2)	6.2 (1)
C1*B*	1.0431 (3)	−0.6341 (4)	0.3182 (3)	4.13 (9)*
C2*B*	1.0380 (3)	−0.5358 (4)	0.2931 (3)	4.3 (1)*
C3*B*	1.1018 (3)	−0.4655 (4)	0.3240 (2)	4.03 (9)*
C4*B*	1.1712 (3)	−0.4930 (3)	0.3824 (2)	3.28 (8)*
C5*B*	1.1770 (3)	−0.5964 (4)	0.4070 (2)	3.32 (8)*
C6*B*	1.1117 (3)	−0.6648 (4)	0.3738 (2)	3.91 (9)*
C7*B*	1.2550 (3)	−0.6323 (4)	0.4662 (3)	3.58 (9)*
C8*B*	1.3370 (3)	−0.5552 (4)	0.4665 (2)	3.55 (8)*
C9*B*	1.3005 (3)	−0.4449 (4)	0.4786 (2)	3.50 (8)*
C11*B*	1.2465 (4)	−0.3226 (4)	0.3812 (3)	5.4 (1)*
C12*B*	1.3219 (4)	−0.2741 (5)	0.4344 (3)	6.5 (1)*
C13*B*	1.3751 (3)	−0.3624 (4)	0.4739 (3)	4.6 (1)*
C17*B*	1.2835 (3)	−0.7417 (4)	0.4543 (3)	5.1 (1)*
C18*B*	1.3732 (3)	−0.5592 (4)	0.3907 (3)	3.9 (1)
C20*B*	1.4124 (3)	−0.5861 (4)	0.5247 (3)	4.4 (1)
C22*B*	1.2527 (3)	−0.4355 (4)	0.5510 (2)	4.6 (1)
C24*B*	1.2738 (4)	−0.4496 (5)	0.6836 (3)	6.9 (2)
C1*C*	0.9294 (3)	−0.1263 (4)	0.1847 (3)	4.11 (9)*
C2*C*	0.9353 (3)	−0.0268 (4)	0.2102 (3)	4.6 (1)*
C3*C*	0.8771 (3)	0.0461 (4)	0.1753 (2)	4.27 (9)*
C4*C*	0.8114 (3)	0.0201 (4)	0.1135 (2)	3.57 (8)*
C5*C*	0.8072 (3)	−0.0830 (4)	0.0868 (2)	3.44 (8)*
C6*C*	0.8654 (3)	−0.1533 (4)	0.1246 (2)	4.09 (9)*
C7*C*	0.7379 (3)	−0.1131 (4)	0.0189 (3)	3.88 (9)*
C8*C*	0.6532 (3)	−0.0386 (4)	0.0164 (3)	3.89 (9)*
C9*C*	0.6859 (3)	0.0743 (4)	0.0148 (3)	4.15 (9)*
C11*C*	0.7382 (4)	0.1925 (4)	0.1152 (3)	5.4 (1)*
C12*C*	0.6587 (4)	0.2402 (5)	0.0652 (4)	7.2 (1)*
C13*C*	0.6081 (4)	0.1518 (4)	0.0243 (3)	5.4 (1)*
C17*C*	0.7085 (4)	−0.2236 (4)	0.0190 (3)	5.3 (1)*
C18*C*	0.6068 (3)	−0.0553 (4)	0.0859 (3)	4.5 (1)
C20*C*	0.5860 (4)	−0.0632 (5)	−0.0501 (3)	6.0 (1)
C22*C*	0.7296 (4)	0.1005 (5)	−0.0591 (3)	6.6 (1)
C24*C*	0.8734 (5)	0.1108 (5)	−0.1060 (4)	8.8 (2)
C1*D*	0.9319 (3)	−0.3025 (6)	0.4231 (3)	7.4 (2)
C2*D*	0.8889 (4)	−0.2173 (5)	0.3911 (3)	7.7 (1)
C3*D*	0.8089 (4)	−0.2290 (4)	0.3447 (3)	5.6 (1)
C4*D*	0.7704 (3)	−0.3271 (4)	0.3284 (2)	3.68 (9)
C5*D*	0.8176 (3)	−0.4126 (4)	0.3596 (2)	3.8 (1)
C6*D*	0.8972 (3)	−0.4001 (5)	0.4086 (3)	6.0 (1)
C7*D*	0.7808 (3)	−0.5197 (4)	0.3396 (3)	3.91 (9)*
C8*D*	0.6734 (3)	−0.5121 (4)	0.3222 (3)	3.89 (9)*
C9*D*	0.6471 (3)	−0.4316 (4)	0.2592 (2)	3.87 (9)*
C11*D*	0.6279 (4)	−0.2497 (5)	0.2630 (3)	6.5 (1)*
C12*D*	0.5412 (5)	−0.2959 (6)	0.2215 (4)	8.2 (2)*

C13*D*	0.5429 (4)	−0.4051 (4)	0.2482 (3)	5.5 (1)*
C17*D*	0.8093 (4)	−0.6002 (5)	0.3989 (3)	6.6 (1)*
C18*D*	0.6340 (3)	−0.4828 (4)	0.3938 (3)	4.5 (1)
C20*D*	0.6359 (4)	−0.6128 (4)	0.2977 (3)	5.5 (1)
C22*D*	0.6789 (3)	−0.4632 (5)	0.1822 (3)	5.0 (1)
C24*D*	0.8097 (4)	−0.4785 (5)	0.1149 (3)	6.6 (1)

Table 2. *Selected geometric parameters (Å, °) for molecule 1 and selected torsion angles (°)*

O15*A*—N14*A*	1.225 (6)	C3*A*—C4*A*	1.396 (6)
O16*A*—N14*A*	1.207 (5)	C4*A*—C5*A*	1.411 (5)
O23*A*—C22*A*	1.399 (6)	C5*A*—C6*A*	1.389 (6)
O23*A*—C24*A*	1.409 (6)	C5*A*—C7*A*	1.518 (6)
N10*A*—C4*A*	1.357 (5)	C7*A*—C8*A*	1.544 (6)
N10*A*—C9*A*	1.460 (6)	C7*A*—C17*A*	1.503 (6)
N10*A*—C11*A*	1.446 (6)	C8*A*—C9*A*	1.558 (6)
N14*A*—C1*A*	1.450 (6)	C8*A*—C18*A*	1.480 (6)
N19*A*—C18*A*	1.135 (6)	C8*A*—C20*A*	1.463 (7)
N21*A*—C20*A*	1.130 (7)	C9*A*—C13*A*	1.526 (6)
C1*A*—C2*A*	1.374 (6)	C9*A*—C22*A*	1.529 (6)
C1*A*—C6*A*	1.386 (7)	C11*A*—C12*A*	1.515 (8)
C2*A*—C3*A*	1.370 (6)	C12*A*—C13*A*	1.514 (8)
C22*A*—O23*A*—C24*A*	111.7 (4)	C5*A*—C7*A*—C17*A*	114.1 (3)
C4*A*—N10*A*—C9*A*	122.3 (3)	C8*A*—C7*A*—C17*A*	112.1 (4)
C4*A*—N10*A*—C11*A*	124.4 (4)	C7*A*—C8*A*—C9*A*	110.9 (3)
C9*A*—N10*A*—C11*A*	112.1 (3)	C7*A*—C8*A*—C18*A*	108.5 (3)
O15*A*—N14*A*—O16*A*	121.8 (4)	C7*A*—C8*A*—C20*A*	111.1 (4)
O15*A*—N14*A*—C1*A*	118.6 (5)	C9*A*—C8*A*—C18*A*	108.9 (4)
O16*A*—N14*A*—C1*A*	119.6 (4)	C9*A*—C8*A*—C20*A*	109.4 (3)
N14*A*—C1*A*—C2*A*	119.5 (4)	C18*A*—C8*A*—C20*A*	108.0 (4)
N14*A*—C1*A*—C6*A*	118.3 (5)	N10*A*—C9*A*—C8*A*	106.9 (3)
C2*A*—C1*A*—C6*A*	122.1 (4)	N10*A*—C9*A*—C13*A*	103.7 (3)
C1*A*—C2*A*—C3*A*	118.7 (5)	N10*A*—C9*A*—C22*A*	111.5 (4)
C2*A*—C3*A*—C4*A*	121.3 (4)	C8*A*—C9*A*—C13*A*	113.6 (4)
N10*A*—C4*A*—C3*A*	119.5 (4)	C8*A*—C9*A*—C22*A*	112.4 (3)
N10*A*—C4*A*—C5*A*	121.2 (4)	C13*A*—C9*A*—C22*A*	108.5 (3)
C3*A*—C4*A*—C5*A*	119.3 (3)	N10*A*—C11*A*—C12*A*	103.8 (4)
C4*A*—C5*A*—C6*A*	119.1 (4)	C11*A*—C12*A*—C13*A*	103.7 (4)
C4*A*—C5*A*—C7*A*	121.6 (3)	C9*A*—C13*A*—C12*A*	103.1 (4)
C6*A*—C5*A*—C7*A*	119.3 (4)	N19*A*—C18*A*—C8*A*	177.6 (5)
C1*A*—C6*A*—C5*A*	119.4 (4)	N21*A*—C20*A*—C8*A*	177.2 (5)
C5*A*—C7*A*—C8*A*	107.8 (3)	O23*A*—C22*A*—C9*A*	111.7 (3)

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
C24—O23—C22—C9	179.1 (4)	172.4 (5)	−153.1 (5)	173.4 (5)
N10—C9—C22—O23	42.9 (5)	171.7 (4)	48.9 (6)	40.4 (6)
C8—C9—C22—O23	−77.1 (5)	54.3 (5)	−72.0 (6)	−80.5 (5)
C13—C9—C22—O23	156.4 (4)	−74.4 (5)	161.9 (4)	152.2 (4)

The O, N and C atoms of the cyano and methoxymethyl groups were refined with anisotropic displacement parameters. The atoms of the phenyl ring in molecule 4 were also refined anisotropically in view of their rather large thermal motion. H atoms were placed at calculated positions (C—H 0.95 Å) and treated as riding atoms.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. Weights for each reflection in the refinement were $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma(F_o^2)$, $\sigma(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined to be 0.03. All calculations were performed using *SDP* (B. A. Frenz & Associates Inc., 1983). Data collection used *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AB1224). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl(2-{[2,3-di(*p*-tolyl)-5-methyl-1-indenylidene](*p*-tolyl)methyl}-5-methoxyphenylmethyl)amine†

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(*Received 25 October 1994; accepted 24 July 1995*)

Abstract

In the title compound, $C_{42}H_{41}NO$, all the phenyl rings are twisted out of the plane of the indenylidene ring. The molecules are held together in the crystal by van der Waals interactions.

Comment

It has been reported that the reaction between cyclopalladated *N*,*N*-dimethylbenzylamine bis(acetonitrile)tetrafluoroborate and diphenylacetylene gives a polycyclic compound as its main product (Tao, Sil-

† Contribution No. 1328 of the Instituto de Química, UNAM.