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***trans*-(3*aR*)-1,2,3,3*a*-Tetrahydro-3*a*-(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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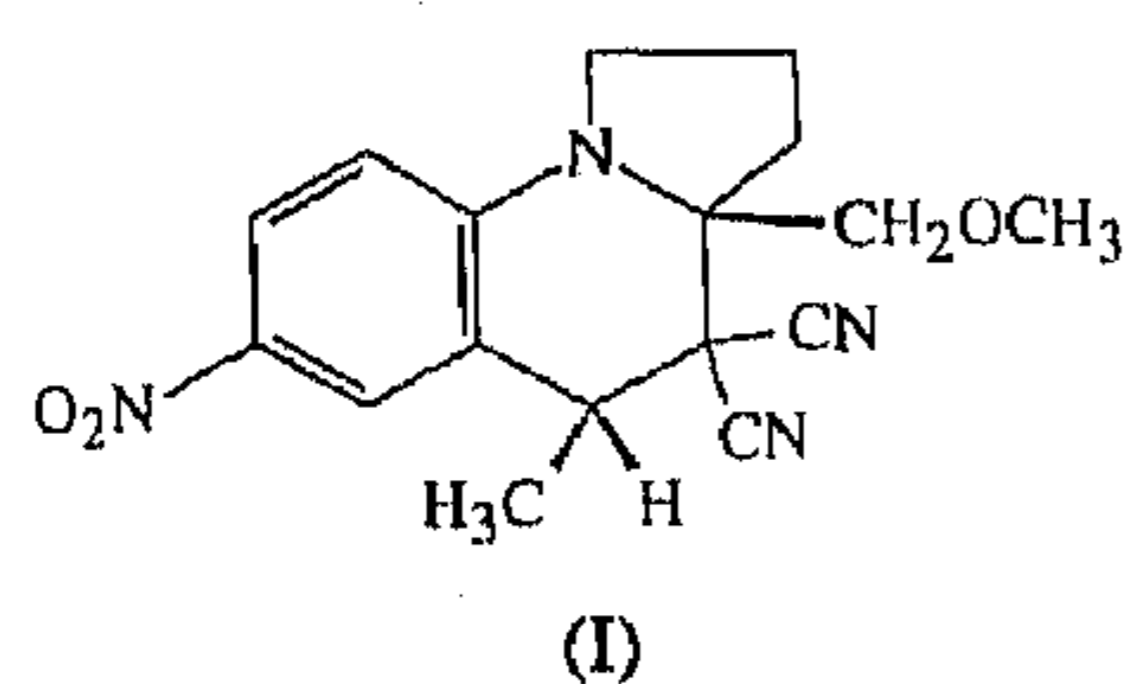
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Abstract

The structure of the title compound, C₁₇H₁₈N₄O₃, 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.



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.

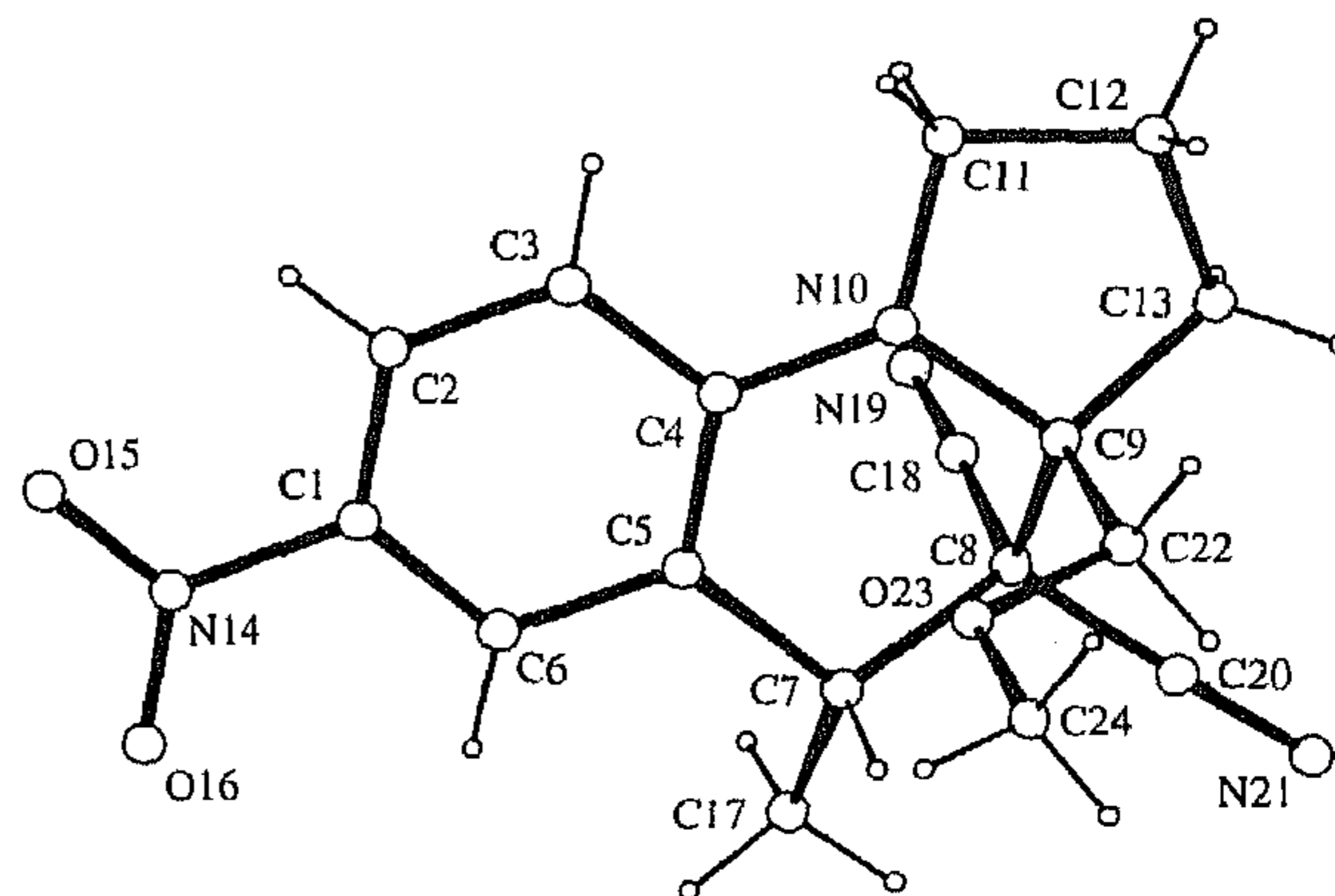


Fig. 1. PLUTO drawing (Motherwell & Clegg, 1978) showing the atomic numbering. Corresponding atoms of molecules 1, 2, 3 and 4 are indicated by suffixes A, B, C and D, respectively.

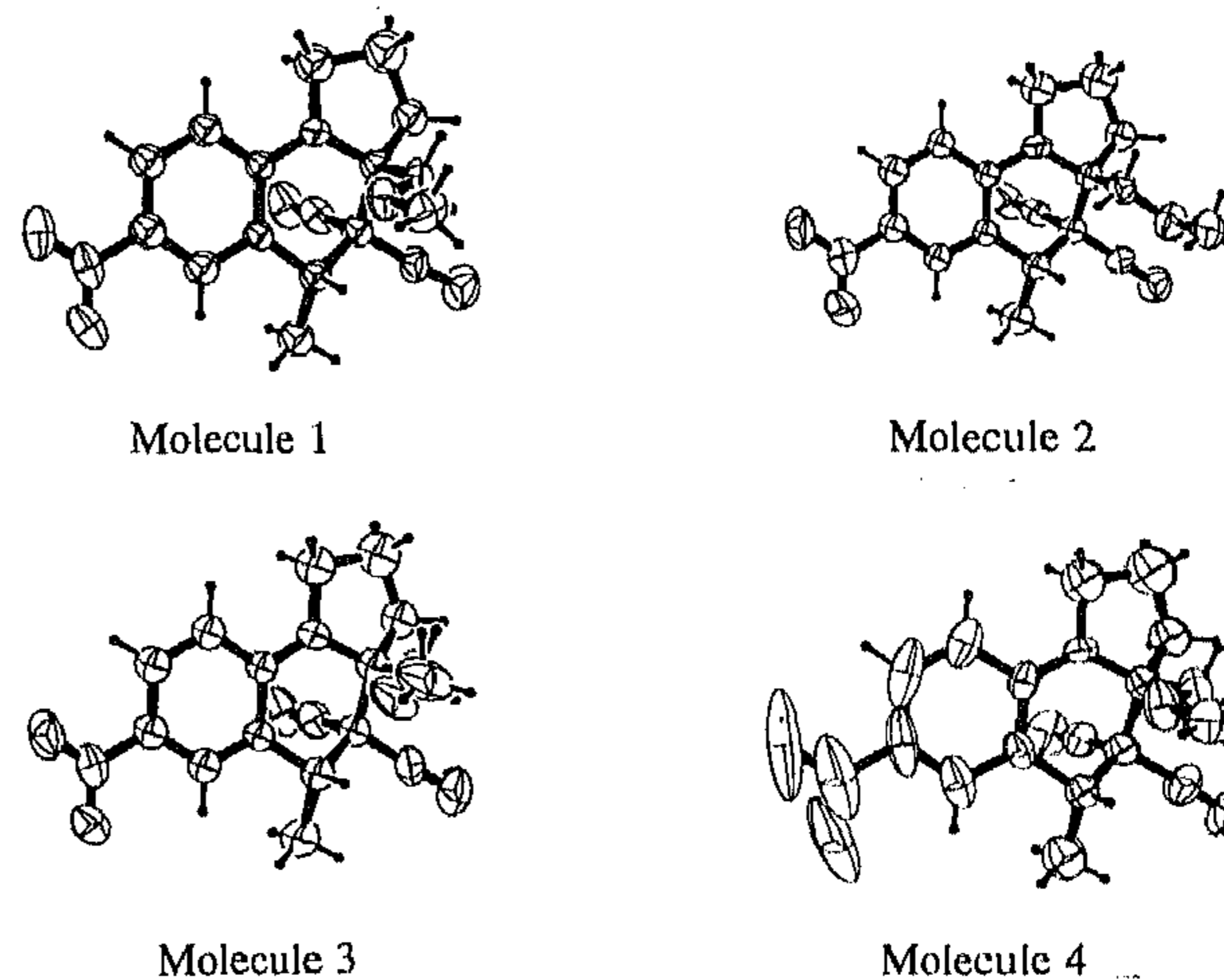


Fig. 2. ORTEPII view (Johnson, 1976) showing the conformations of the different molecules. Displacement ellipsoids are scaled to include 50% probability.

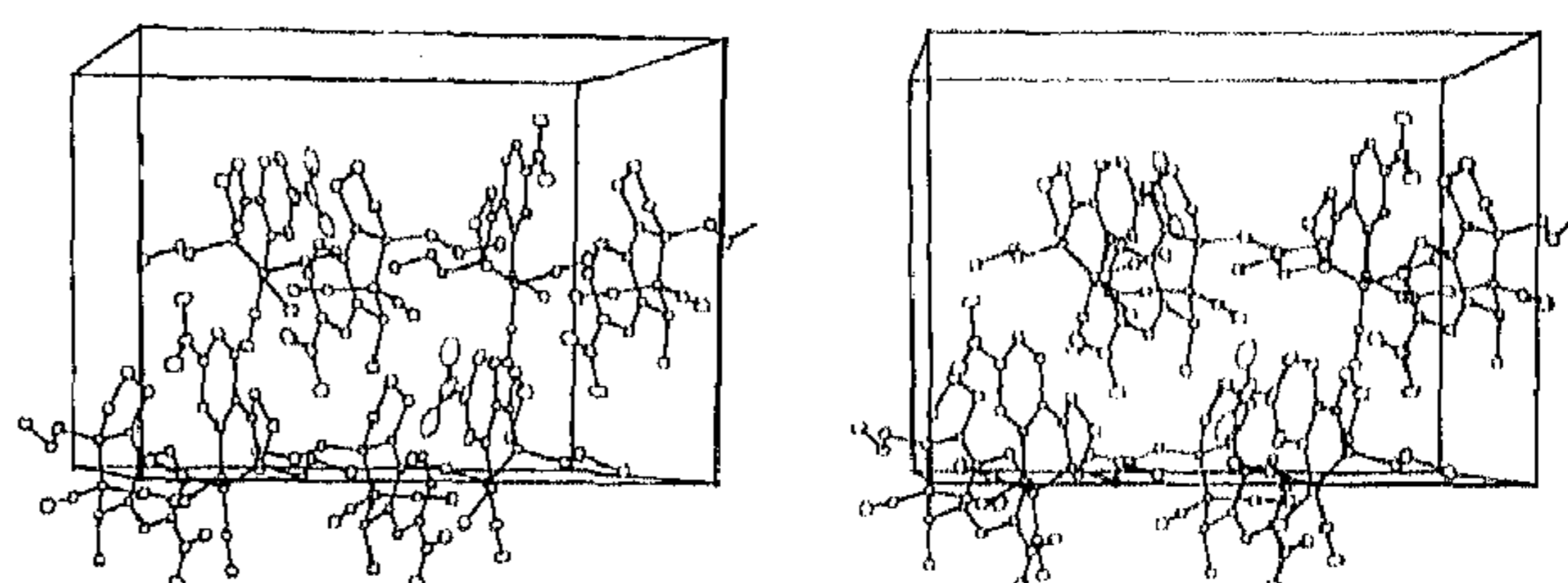


Fig. 3. ORTEPII stereoview (Johnson, 1976) showing the packing of the different molecules in the unit cell. Displacement ellipsoids are scaled to include 25% probability.

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 HNO₃ in CH₂Cl₂ 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*C₁₇H₁₈N₄O₃*M_r* = 326.4

Monoclinic

*P*2₁*a* = 14.452 (3) Å*b* = 13.089 (3) Å*c* = 17.558 (3) Å

β = 96.01 (3)°

V = 3303 (2) Å³*Z* = 8*D_x* = 1.312 Mg m⁻³Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.0–14.1°

μ = 0.087 mm⁻¹*T* = 293 K

Parallelepiped

0.60 × 0.60 × 0.50 mm

Light yellow

Data collection

Enraf-Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

none

6084 measured reflections

6084 independent reflections

4307 observed reflections

[*I* > 3σ(*I*)]θ_{max} = 25°*h* = -17 → 17*k* = 0 → 15*l* = 0 → 20

3 standard reflections

frequency: 60 min

intensity decay: <1%

*Refinement*Refinement on *F*²*R* = 0.052*wR* = 0.061*S* = 2.14

4307 reflections

635 parameters

H atoms treated as riding

atoms

w = 1/σ²(*F*)(Δ/σ)_{max} = 0.02Δρ_{max} = 0.28 e Å⁻³Δρ_{min} = -0.24 e Å⁻³

Extinction correction:

Zachariasen (1963)

Extinction coefficient:

1.8 (4) × 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 (Å²)

*B*_{iso} for starred atoms; *B*_{eq} = (8π²/3)Σ_{*i*}Σ_{*j*}*U*_{*ij*}*a*_{*i*}^{*}*a*_{*j*}^{*}*a*_{*i*}*a*_{*j*} for others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
O15A	-0.0004 (3)	0.4058 (3)	0.0707 (3)	8.2 (1)
O16A	-0.0571 (3)	0.2583	0.0455 (3)	8.4 (1)
O23A	0.1887 (2)	0.0448 (3)	0.3273 (2)	4.64 (7)
O15B	0.9149 (3)	-0.6810 (3)	0.2368 (2)	6.8 (1)
O16B	0.9836 (3)	-0.7966 (3)	0.3085 (3)	7.7 (1)
O23B	1.3115 (2)	-0.4696 (3)	0.6141 (2)	5.73 (9)
O15C	1.0515 (3)	-0.1762 (3)	0.2714 (2)	6.8 (1)
O16C	0.9777 (3)	-0.2920 (3)	0.2022 (2)	6.9 (1)
O23C	0.8145 (3)	0.0571 (3)	-0.0612 (2)	7.1 (1)
O15D	1.0542 (4)	-0.2083 (6)	0.4811 (3)	17.9 (2)
O16D	1.0470 (3)	-0.3683 (7)	0.5098 (3)	15.3 (2)
O23D	0.7728 (2)	-0.4416 (3)	0.1804 (2)	5.50 (9)

N10A	0.3132 (2)	0.1369 (3)	0.2402 (2)	3.35 (8)
N14A	0.0044 (3)	0.3125 (4)	0.0746 (2)	5.7 (1)
N19A	0.3662 (3)	0.0295 (4)	0.0654 (2)	6.2 (1)
N21A	0.3017 (3)	-0.2233 (4)	0.2019 (3)	6.2 (1)
N10B	1.2329 (3)	-0.4231 (3)	0.4131 (2)	3.79 (8)
N14B	0.9763 (3)	-0.7085 (4)	0.2862 (2)	5.3 (1)
N19B	1.3973 (3)	-0.5620 (4)	0.3315 (2)	5.9 (1)
N21B	1.4723 (3)	-0.6150 (4)	0.5664 (3)	6.4 (1)
N10C	0.7514 (3)	0.0914 (3)	0.0816 (2)	4.00 (9)
N14C	0.9906 (3)	-0.2030 (4)	0.2215 (2)	5.2 (1)
N19C	0.5744 (3)	-0.0682 (4)	0.1407 (3)	7.1 (1)
N21C	0.5356 (4)	-0.0816 (5)	-0.1020 (3)	8.8 (2)
N10D	0.6879 (2)	-0.3350 (3)	0.2854 (2)	3.77 (8)
N14D	1.0172 (3)	-0.2906 (7)	0.4738 (3)	11.7 (2)
N19D	0.6088 (3)	-0.4596 (4)	0.4500 (2)	6.4 (1)
N21D	0.6103 (4)	-0.6910 (4)	0.2772 (3)	8.3 (2)
C1A	0.0851 (3)	0.2668 (4)	0.1175 (3)	4.16 (9)*
C2A	0.1534 (3)	0.3286 (4)	0.1530 (2)	4.06 (9)*
C3A	0.2299 (3)	0.2840 (4)	0.1922 (2)	3.56 (8)*
C4A	0.2377 (3)	0.1781 (3)	0.1988 (2)	2.88 (7)*
C5A	0.1683 (3)	0.1156 (3)	0.1605 (2)	3.00 (8)*
C6A	0.0917 (3)	0.1611 (4)	0.1197 (2)	3.87 (9)*
C7A	0.1754 (3)	-0.0001 (3)	0.1626 (2)	3.20 (8)*
C8A	0.2791 (3)	-0.0283 (4)	0.1813 (2)	3.45 (8)*
C9A	0.3219 (3)	0.0274 (3)	0.2551 (2)	3.34 (8)*
C11A	0.3998 (3)	0.1905 (4)	0.2603 (3)	5.0 (1)*
C12A	0.4600 (4)	0.1128 (5)	0.3062 (3)	6.4 (1)*
C13A	0.4266 (3)	0.0113 (4)	0.2723 (3)	4.8 (1)*
C17A	0.1325 (3)	-0.0519 (4)	0.0911 (3)	4.6 (1)*
C18A	0.3299 (3)	0.0034 (4)	0.1163 (2)	4.2 (1)
C20A	0.2909 (3)	-0.1387 (4)	0.1912 (3)	4.3 (1)
C22A	0.2750 (3)	-0.0033 (4)	0.3258 (2)	4.4 (1)
C24A	0.1448 (4)	0.0153 (5)	0.3918 (2)	6.2 (1)
C1B	1.0431 (3)	-0.6341 (4)	0.3182 (3)	4.13 (9)*
C2B	1.0380 (3)	-0.5358 (4)	0.2931 (3)	4.3 (1)*
C3B	1.1018 (3)	-0.4655 (4)	0.3240 (2)	4.03 (9)*
C4B	1.1712 (3)	-0.4930 (3)	0.3824 (2)	3.28 (8)*
C5B	1.1770 (3)	-0.5964 (4)	0.4070 (2)	3.32 (8)*
C6B	1.1117 (3)	-0.6648 (4)	0.3738 (2)	3.91 (9)*
C7B	1.2550 (3)	-0.6323 (4)	0.4662 (3)	3.58 (9)*
C8B	1.3370 (3)	-0.5552 (4)	0.4665 (2)	3.55 (8)*
C9B	1.3005 (3)	-0.4449 (4)	0.4786 (2)	3.50 (8)*
C11B	1.2465 (4)	-0.3226 (4)	0.3812 (3)	5.4 (1)*
C12B	1.3219 (4)	-0.2741 (5)	0.4344 (3)	6.5 (1)*
C13B	1.3751 (3)	-0.3624 (4)	0.4739 (3)	4.6 (1)*
C17B	1.2835 (3)	-0.7417 (4)	0.4543 (3)	5.1 (1)*
C18B	1.3732 (3)	-0.5592 (4)	0.3907 (3)	3.9 (1)
C20B	1.4124 (3)	-0.5861 (4)	0.5247 (3)	4.4 (1)
C22B	1.2527 (3)	-0.4355 (4)	0.5510 (2)	4.6 (1)
C24B	1.2738 (4)	-0.4496 (5)	0.6836 (3)	6.9 (2)
C1C	0.9294 (3)	-0.1263 (4)	0.1847 (3)	4.11 (9)*
C2C	0.9353 (3)	-0.0268 (4)	0.2102 (3)	4.6 (1)*
C3C	0.8771 (3)	0.0461 (4)	0.1753 (2)	4.27 (9)*
C4C	0.8114 (3)	0.0201 (4)	0.1135 (2)	3.57 (8)*
C5C	0.8072 (3)	-0.0830 (4)	0.0868 (2)	3.44 (8)*
C6C	0.8654 (3)	-0.1533 (4)	0.1246 (2)	4.09 (9)*
C7C	0.7379 (3)	-0.1131 (4)	0.0189 (3)	3.88 (9)*
C8C	0.6532 (3)	-0.0386 (4)	0.0164 (3)	3.89 (9)*
C9C	0.6859 (3)	0.0743 (4)	0.0148 (3)	4.15 (9)*
C11C	0.7382 (4)	0.1925 (4)	0.1152 (3)	5.4 (1)*
C12C	0.6587 (4)	0.2402 (5)	0.0652 (4)	7.2 (1)*
C13C	0.6081 (4)	0.1518 (4)	0.0243 (3)	5.4 (1)*
C17C	0.7085 (4)	-0.2236 (4)	0.0190 (3)	5.3 (1)*
C18C	0.6068 (3)	-0.0553 (4)	0.0859 (3)	4.5 (1)
C20C	0.5860 (4)	-0.0632 (5)	-0.0501 (3)	6.0 (1)
C22C	0.7296 (4)	0.1005 (5)	-0.0591 (3)	6.6 (1)
C24C	0.8734 (5)	0.1108 (5)	-0.1060 (4)	8.8 (2)
C1D	0.9319 (3)	-0.3025 (6)	0.4231 (3)	7.4 (2)
C2D	0.8889 (4)	-0.2173 (5)	0.3911 (3)	7.7 (1)
C3D	0.8089 (4)	-0.2290 (4)	0.3447 (3)	5.6 (1)
C4D	0.7704 (3)	-0.3271 (4)	0.3284 (2)	3.68 (9)
C5D	0.8176 (3)	-0.4126 (4)	0.3596 (2)	3.8 (1)
C6D	0.8972 (3)	-0.4001 (5)	0.4086 (3)	6.0 (1)
C7D	0.7808 (3)	-0.5197 (4)	0.3396 (3)	3.91 (9)*
C8D	0.6734 (3)	-0.5121 (4)	0.3222 (3)	3.89 (9)*
C9D	0.6471 (3)	-0.4316 (4)	0.2592 (2)	3.87 (9)*
C11D	0.6279 (4)	-0.2497 (5)	0.2630 (3)	6.5 (1)*
C12D	0.5412 (5)	-0.2959 (6)	0.2215 (4)	8.2 (2)*

C13D	0.5429 (4)	-0.4051 (4)	0.2482 (3)	5.5 (1)*
C17D	0.8093 (4)	-0.6002 (5)	0.3989 (3)	6.6 (1)*
C18D	0.6340 (3)	-0.4828 (4)	0.3938 (3)	4.5 (1)
C20D	0.6359 (4)	-0.6128 (4)	0.2977 (3)	5.5 (1)
C22D	0.6789 (3)	-0.4632 (5)	0.1822 (3)	5.0 (1)
C24D	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 (°)

O15A—N14A	1.225 (6)	C3A—C4A	1.396 (6)
O16A—N14A	1.207 (5)	C4A—C5A	1.411 (5)
O23A—C22A	1.399 (6)	C5A—C6A	1.389 (6)
O23A—C24A	1.409 (6)	C5A—C7A	1.518 (6)
N10A—C4A	1.357 (5)	C7A—C8A	1.544 (6)
N10A—C9A	1.460 (6)	C7A—C17A	1.503 (6)
N10A—C11A	1.446 (6)	C8A—C9A	1.558 (6)
N14A—C1A	1.450 (6)	C8A—C18A	1.480 (6)
N19A—C18A	1.135 (6)	C8A—C20A	1.463 (7)
N21A—C20A	1.130 (7)	C9A—C13A	1.526 (6)
C1A—C2A	1.374 (6)	C9A—C22A	1.529 (6)
C1A—C6A	1.386 (7)	C11A—C12A	1.515 (8)
C2A—C3A	1.370 (6)	C12A—C13A	1.514 (8)
C22A—O23A—C24A	111.7 (4)	C5A—C7A—C17A	114.1 (3)
C4A—N10A—C9A	122.3 (3)	C8A—C7A—C17A	112.1 (4)
C4A—N10A—C11A	124.4 (4)	C7A—C8A—C9A	110.9 (3)
C9A—N10A—C11A	112.1 (3)	C7A—C8A—C18A	108.5 (3)
O15A—N14A—O16A	121.8 (4)	C7A—C8A—C20A	111.1 (4)
O15A—N14A—C1A	118.6 (5)	C9A—C8A—C18A	108.9 (4)
O16A—N14A—C1A	119.6 (4)	C9A—C8A—C20A	109.4 (3)
N14A—C1A—C2A	119.5 (4)	C18A—C8A—C20A	108.0 (4)
N14A—C1A—C6A	118.3 (5)	N10A—C9A—C8A	106.9 (3)
C2A—C1A—C6A	122.1 (4)	N10A—C9A—C13A	103.7 (3)
C1A—C2A—C3A	118.7 (5)	N10A—C9A—C22A	111.5 (4)
C2A—C3A—C4A	121.3 (4)	C8A—C9A—C13A	113.6 (4)
N10A—C4A—C3A	119.5 (4)	C8A—C9A—C22A	112.4 (3)
N10A—C4A—C5A	121.2 (4)	C13A—C9A—C22A	108.5 (3)
C3A—C4A—C5A	119.3 (3)	N10A—C11A—C12A	103.8 (4)
C4A—C5A—C6A	119.1 (4)	C11A—C12A—C13A	103.7 (4)
C4A—C5A—C7A	121.6 (3)	C9A—C13A—C12A	103.1 (4)
C6A—C5A—C7A	119.3 (4)	N19A—C18A—C8A	177.6 (5)
C1A—C6A—C5A	119.4 (4)	N21A—C20A—C8A	177.2 (5)
C5A—C7A—C8A	107.8 (3)	O23A—C22A—C9A	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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Abstract

In the title compound, C₄₂H₄₁NO, 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.