C17′—C18′—O19′—C20′	165.7 (5)
C18′—O19′—C20′—C21′	172.6 (5)
O19′—C20′—C21′—S1′	−175.8 (4)
C2′—S1′—C21′—C20′	−77.9 (5)

All non-H atoms in the two crystallographically independent macrocycles were located by direct methods (*SHELXS*86; Sheldrick, 1990). A difference synthesis calculated on the basis of this phasing model exhibited three peaks of *ca* 7 e Å^{-3}, which were assigned to O atoms of water of crystallization, the H atoms of which were located in a difference synthesis performed after several cycles of least-squares refinement weighted towards the high-angle data. They were refined with O—H and H···H restrained to chemically reasonable values of 1.000 (5) and 1.59 (1) Å, respectively. Other H atoms were placed in calculated positions (C—H = 0.99 Å) and allowed to ride on their neighbouring C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Full-matrix isotropic refinement caused atom C2 to develop a displacement parameter approximately twice as large as those of the other C atoms in the macrocycle. On anisotropic refinement, C2 developed an elongated displacement ellipsoid which was interpreted as the result of C2 being disordered over two positions, C2*a* and C2*b*, with equal occupancies. Chemically reasonable restraints were placed on the geometry of the S1—C2*a*,*b*—C3—S4 units [C—C = 1.48 (1), C—S = 1.80 (1) Å]. However, even under these conditions the disordered C atoms were still highly anisotropic; it seems reasonable to conclude that the disorder is more extensive than modelled here, and C2*a* and C2*b* were therefore refined with isotropic displacement parameters.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992), *CAMERON* (Pearce & Watkin, 1993). Software used to prepare material for publication: *CALC* (Gould & Taylor, 1985).

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2-(10-Diethylaminomethyl-2,3,6,7-tetra-methoxy-9-phenanthrylmethyl)-1-pyrrolidinecarbonitrile

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Abstract

The title molecule, $C_{29}H_{37}N_3O_4$, consists of a pyrrolidine and a phenanthrene ring. The mean plane through the pyrrolidine ring atoms is almost perpendicular to that through the phenanthrene ring atoms. The pyrrolidine ring adopts a half-chair conformation, while the fused rings of the phenanthrene system are almost coplanar. In the crystal, molecules are stabilized by van der Waals interactions.

Comment

The alkaloid tylophorine, isolated from *tylophora asthmatica*, contains the interesting phenanthraindolizidine system. There are conflicting reports in the literature on the absolute configuration of tylophorine (Ferguson & Robertson, 1963; Barth & Lawton, 1971), which has a chiral centre, as derived from degradation studies and synthesis. Unfortunately, tylophorine crystals were not suitable for X-ray investigation. However, a degradation product obtained from tylophorine by treatment with cyanogen bromide followed by diethylamine yielded good single crystals. It was our aim to determine the absolute configuration of the title compound, (I), which

exhibits a small positive optical rotation in solution, but to our surprise the compound crystallized as a racemic mixture in space group $P2_1/c$. While reaction of tylophorine with cyanogen bromide is unlikely to racemize the compound, that possibility cannot be ruled out completely for the subsequent reaction, namely of the bromocyanamide with diethylamine.
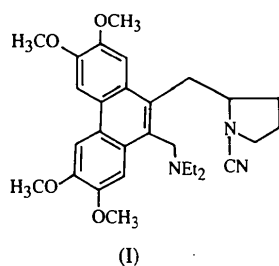

(I)

Fig. 1 presents an *ORTEP* diagram (Johnson, 1965) of the title molecule, together with the atomic labelling scheme. The pyrrolidine ring adopts a half-chair conformation (Duax, Weeks & Rohrer, 1976). The phenanthrene ring system is nearly planar and is perpendicular to the *b* axis. The dihedral angles between the mean planes of rings *A*, *B* and *C* are: $A^\wedge B$ 1.7 (2), $B^\wedge C$ 177.5 (2) and $C^\wedge A$ 176.7 (2)°. The slight noncoplanarity of the fused-ring system arises from steric hindrance. All the exocyclic O atoms lie in the mean aromatic plane of their respective rings, while the methyl atoms C17, C18, C19 and C20 deviate from their respective planes by 0.023 (6), 0.102 (7), −0.046 (7) and −0.161 (6) Å, respectively. To minimize the steric hindrance, angles C1—C2—O1 [122.7 (4)°], C4—C3—O2 [123.9 (4)°], C5—C6—O3 [125.4 (5)°] and C8—C7—O4 [124.3 (4)°] are widened, while angles C3—C2—
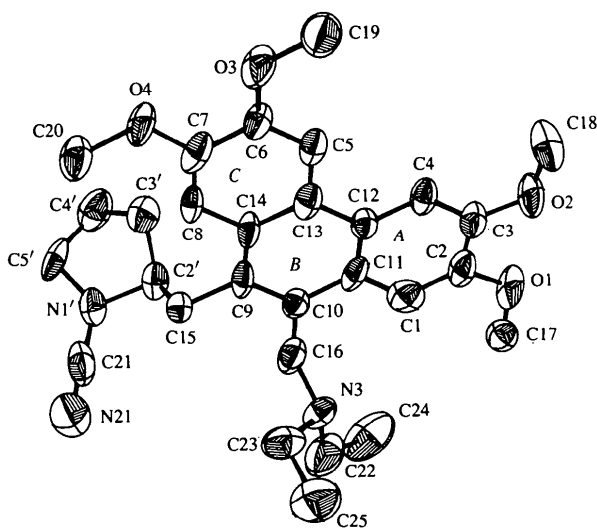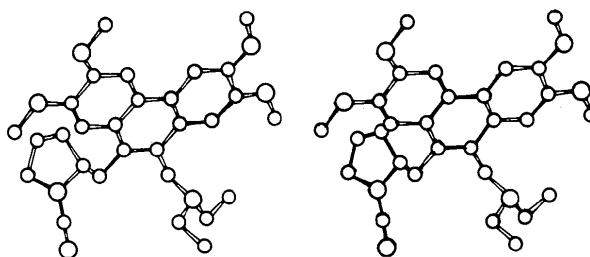

Fig. 2. Stereoview of the title molecule.

O1 [115.4 (4)°] C2—C3—O2 [116.6 (4)°], C7—C6—O3 [116.7 (4)°] and C6—C7—O4 [113.4 (4)°] are narrowed. The molecules are stabilized by van der Waals interactions.

Experimental

The title compound was synthesized by Professor Nagarajan at the Bangalore Pharmaceutical and Research Laboratory, Bangalore, and recrystallized from methanol. The density D_m was measured by flotation in bromoform and benzene.

Crystal data

C₂₉H₃₇N₃O₄	Cu $K\alpha$ radiation
$M_r = 491.6$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 12.563 (3)$ Å	$\theta = 10-17.5°$
$b = 14.083 (4)$ Å	$\mu = 0.625$ mm⁻¹
$c = 15.308 (3)$ Å	$T = 295$ K
$\beta = 102.17 (2)°$	Needle
$V = 2648 (1)$ Å³	0.3 × 0.15 × 0.1 mm
$Z = 4$	Colourless
$D_x = 1.24 (2)$ Mg m⁻³	
$D_m = 1.233$ Mg m⁻³	

Data collection

Enraf–Nonius diffractometer	$\theta_{max} = 60°$
$\omega/2\theta$ scans	$h = -14 \rightarrow 13$
Absorption correction:	$k = 0 \rightarrow 15$
none	$l = 0 \rightarrow 17$
3232 measured reflections	3 standard reflections
3232 independent reflections	frequency: 200 min
1896 observed reflections	intensity decay: 4%
[$F > 6\sigma(F)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.149$
$R = 0.067$	$\Delta\rho_{max} = 0.20$ e Å⁻³
$wR = 0.072$	$\Delta\rho_{min} = -0.24$ e Å⁻³
$S = 1.8$	Atomic scattering factors
1896 reflections	from *International Tables*
325 parameters	*for X-ray Crystallography*
H-atom parameters not	(1974, Vol. IV, Table
refined	2.3.1)
$w = 1/[\sigma^2(F) + 0.001F^2]$	

Fig. 1. Perspective view (*ORTEP*; Johnson, 1965) of the title molecule with displacement ellipsoids plotted at the 50% probability level.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.5514 (4)	0.3747 (4)	0.5225 (3)	0.043 (3)
C2	0.4574 (4)	0.3751 (4)	0.5544 (3)	0.049 (3)
C3	0.3562 (4)	0.3754 (4)	0.4982 (3)	0.050 (3)
C4	0.3481 (4)	0.3760 (4)	0.4057 (3)	0.047 (3)
C5	0.3357 (4)	0.3718 (4)	0.2130 (3)	0.049 (3)
C6	0.3293 (4)	0.3712 (4)	0.1214 (3)	0.047 (3)
C7	0.4271 (4)	0.3762 (4)	0.0908 (3)	0.047 (3)
C8	0.5240 (4)	0.3809 (4)	0.1466 (3)	0.044 (3)
C9	0.6371 (4)	0.3844 (4)	0.3019 (3)	0.041 (3)
C10	0.6449 (4)	0.3780 (4)	0.3944 (3)	0.041 (3)
C11	0.5446 (4)	0.3769 (3)	0.4275 (3)	0.039 (3)
C12	0.4433 (4)	0.3765 (4)	0.3712 (3)	0.039 (3)
C13	0.4373 (4)	0.3767 (4)	0.2743 (3)	0.040 (3)
C14	0.5338 (4)	0.3817 (3)	0.2427 (3)	0.038 (3)
C15	0.7423 (4)	0.3923 (4)	0.2666 (3)	0.046 (3)
C16	0.7525 (4)	0.3767 (4)	0.4613 (3)	0.050 (3)
C17	0.5585 (5)	0.3718 (4)	0.7064 (4)	0.067 (4)
C18	0.1646 (5)	0.3676 (5)	0.4827 (4)	0.084 (5)
C19	0.1373 (5)	0.3584 (5)	0.0867 (4)	0.084 (5)
C20	0.5084 (5)	0.3686 (4)	−0.0382 (3)	0.065 (4)
C21	0.9636 (5)	0.4381 (6)	0.2486 (4)	0.072 (5)
C22	0.8739 (5)	0.2933 (6)	0.5796 (5)	0.093 (6)
C23	0.7997 (5)	0.2159 (5)	0.4417 (5)	0.082 (5)
C24	0.8490 (7)	0.3458 (6)	0.6604 (5)	0.110 (6)
C25	0.8065 (7)	0.1148 (6)	0.4785 (7)	0.127 (7)
N21	1.0336 (5)	0.3867 (6)	0.2664 (4)	0.116 (5)
N3	0.7777 (3)	0.2858 (4)	0.5056 (3)	0.056 (3)
O1	0.4572 (3)	0.3749 (3)	0.6451 (2)	0.064 (2)
O2	0.2685 (3)	0.3765 (3)	0.5379 (2)	0.066 (2)
O3	0.2363 (3)	0.3672 (3)	0.0584 (2)	0.061 (2)
O4	0.4119 (3)	0.3748 (3)	−0.0021 (2)	0.058 (2)
N1′	0.8847 (4)	0.4962 (4)	0.2283 (3)	0.082 (5)
C2′	0.7862 (4)	0.4928 (5)	0.2702 (4)	0.064 (4)
C3′	0.7142 (5)	0.5681 (5)	0.2178 (5)	0.086 (5)
C4′	0.7926 (6)	0.6393 (5)	0.1915 (4)	0.078 (5)
C5′	0.8803 (5)	0.5790 (5)	0.1683 (4)	0.072 (4)

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.389 (6)	O3—C6	1.350 (5)
O1—C17	1.414 (7)	O3—C19	1.406 (8)
O2—C3	1.366 (7)	O4—C7	1.395 (5)
O2—C18	1.403 (7)	O4—C20	1.437 (7)
C2—O1—C17	118.2 (4)	N21—C21—N1′	179.8 (7)
C3—O2—C18	117.8 (4)	C24—C22—N3	112.4 (6)
C6—O3—C19	118.2 (4)	C25—C23—N3	112.8 (6)
C7—O4—C20	116.6 (4)	C22—N3—C23	108.9 (5)
O1—C2—C1	122.7 (4)	C16—N3—C23	109.6 (5)
O1—C2—C3	115.4 (4)	C16—N3—C22	111.0 (5)
O2—C3—C2	116.6 (4)	C21—N1′—C5′	125.8 (6)
O2—C3—C4	123.9 (4)	C21—N1′—C2′	122.8 (5)
O3—C6—C5	125.4 (5)	C2′—N1′—C5′	111.2 (5)
O3—C6—C7	116.7 (4)	C15—C2′—N1′	109.8 (5)
O4—C7—C6	113.4 (4)	N1′—C2′—C3′	101.8 (5)
O4—C7—C8	124.3 (4)	N1′—C5′—C4′	103.5 (5)
C10—C16—N3	113.7 (4)		
C17—O1—C2—C1	−1.6 (7)	C9—C10—C16—N3	−110.7 (6)
C17—O1—C2—C3	178.2 (5)	C11—C10—C16—N3	72.2 (6)
C18—O2—C3—C2	−174.0 (5)	C9—C15—C2′—N1′	−175.9 (4)
C18—O2—C3—C4	7.0 (7)	C10—C16—N3—C22	−170.9 (5)
C19—O3—C6—C5	−3.2 (8)	C10—C16—N3—C23	68.7 (6)
C19—O3—C6—C7	177.6 (5)	C24—C22—N3—C16	73.4 (7)
C20—O4—C7—C6	−173.0 (4)	C24—C22—N3—C23	−165.8 (6)
C20—O4—C7—C8	6.4 (7)	C25—C23—N3—C16	−169.6 (6)
C11—C1—C2—O1	−178.7 (4)	C25—C23—N3—C22	68.9 (7)
O1—C2—C3—O2	0.7 (7)	C21—N1′—C2′—C15	−49.2 (8)
C1—C2—C3—O2	−179.5 (5)	C21—N1′—C5′—C4′	−161.4 (6)
O1—C2—C3—C4	179.8 (4)	C21—N1′—C2′—C3′	−174.6 (6)
O2—C3—C4—C12	178.9 (5)	C5′—N1′—C2′—C15	135.5 (5)
C13—C5—C6—O3	−179.6 (5)	C2′—N1′—C5′—C4′	13.7 (6)
O3—C6—C7—O4	−0.9 (7)	C5′—N1′—C2′—C3′	10.1 (6)
C5—C6—C7—O4	179.8 (4)	N1′—C2′—C3′—C4′	−29.8 (6)
O3—C6—C7—C8	179.7 (5)	N1′—C5′—C4′—C3′	−32.0 (6)
O4—C7—C8—C14	−179.8 (4)		

Data were collected using standard Enraf–Nonius CAD-4 software. Cell refinement and data reduction were performed using *SDP* (Frenz, 1978). The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Attempts to solve the structure using *MULTAN*80 (Main *et al.*, 1980) and *SHELXS*86 (Sheldrick, 1985) were not successful because of the 'chickenwire' problem. The solution was obtained using *DIRDIF* (Beurskens *et al.*, 1990). A *DIRDIF* run using the *ORIENT* option with the rigid phenanthrene group taken from *DIRDIF-ORBASE* as the input model revealed 23 non-H atoms; the structure was completed by a subsequent *DIRDIF* run using the weighted-Fourier option. The non-H atoms were refined anisotropically. H atoms were fixed by geometrical considerations and were included in the final structure-factor calculations with isotropic temperature factors taken as $1.1U_{eq}$ of the C atoms to which they are bonded. The structure was refined using *SHELX*76 (Sheldrick, 1976). The geometrical calculations were carried out using *PARST* (Nardelli, 1983). Molecular graphics were prepared using *ORTEP* (Johnson, 1965). All calculations were performed on VAX730 and MicroVAX II systems.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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with a view to improving the nonlinear optical properties. The two different carbamate dyes prepared, (1) and (2), possess an enhanced π system *via* a stilbene core, which is present in many dyes that exhibit strong nonlinear optical properties. However, neither structure presented here is non-centrosymmetric.

(1) R = H
(2) R = NO₂
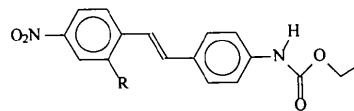
Two New Stilbene Carbamates

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Abstract

The syntheses and solid-state structures of two stilbene carbamates, 4-[2-(4-nitrophenyl)ethenyl]phenylcarbamic acid ethyl ester, $C_{17}H_{16}N_2O_4$, (1), and 4-[2-(2,4-dinitrophenyl)ethenyl]phenylcarbamic acid ethyl ester, $C_{17}H_{15}N_3O_6$, (2), are described. The crystallization from tetrahydrofuran solutions occurs in the monoclinic system with space group $P2_1/n$. Both molecules display hydrogen bonding. For compound (2), there are two different molecules in the asymmetric unit.

Comment

Nonlinear optical properties of inorganic crystals are well known and devices are commercially available. Organic crystals promise to be useful in a broader range of applications. Second harmonic efficiencies of alkyl esters of nitrophenylcarbamic acids have been investigated previously (Francis & Tiers, 1992). These compounds had been found to crystallize with non-centrosymmetric structures. The strength of the nonlinear optical properties of these systems depended on the solvent of crystallization. Therefore, our first task in the search for non-centrosymmetric structures was to synthesize molecules of the same type with large conjugated systems,

Both compounds display hydrogen bonding (Tables 2 and 4). For compound (1), hydrogen bonds are formed between the NH of the carbamate group and the nitro group in an adjacent molecule (Fig. 3a). For compound (2), a second molecule is present in the asymmetric unit with its amino group H atom bonded to the carbonyl group of the first molecule (Fig. 3b). As can been seen in Fig. 3(b), the difference between the two molecules in compound (2) is that the second molecule is 'hanging' by one hydrogen bond from a zigzag net created for the first molecule *via* two hydrogen bonds. Also, the planarity of the second molecule is slightly distorted (by *ca* 10°), probably as a result of steric hindrance between the lateral nitro groups in both molecules. This is evidenced by the torsion angles C2—C3—C7—C8 [−167.0 (3)°] and C19—C20—C24—C25 [−180.0 (3)°]
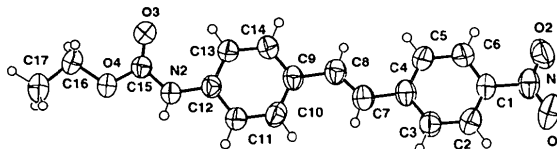

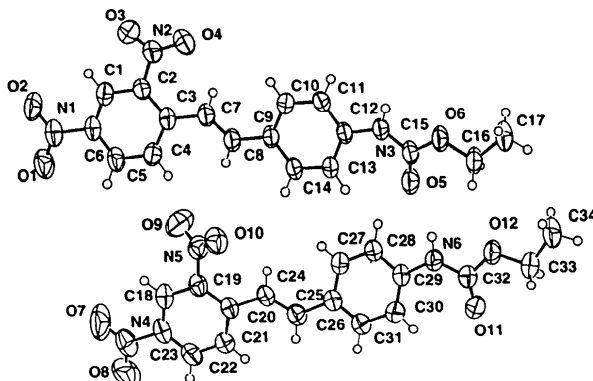Fig. 1. Displacement ellipsoid plot of (1) at the 50% probability level.

Fig. 2. Displacement ellipsoid plot of (2) at the 50% probability level.