

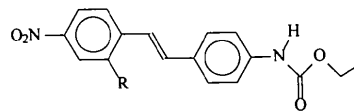
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

with a view to improving the nonlinear optical properties. The two different carbamate dyes prepared, (1) and (2), possess an enhanced  $\pi$  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 = NO<sub>2</sub>

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## 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<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>, (1), and 4-[2-(2,4-dinitrophenyl)ethenyl]phenylcarbamic acid ethyl ester, C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>, (2), are described. The crystallization from tetrahydrofuran solutions occurs in the monoclinic system with space group *P*2<sub>1</sub>/*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 be 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)°]

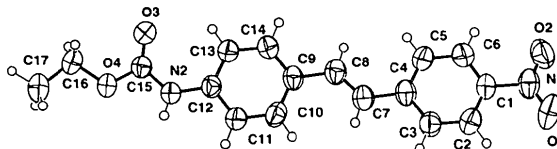


Fig. 1. Displacement ellipsoid plot of (1) at the 50% probability level.

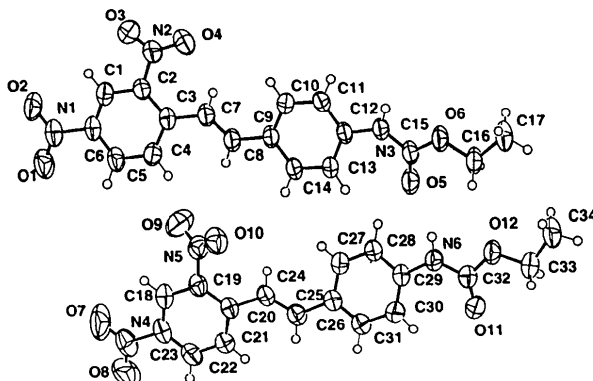


Fig. 2. Displacement ellipsoid plot of (2) at the 50% probability level.

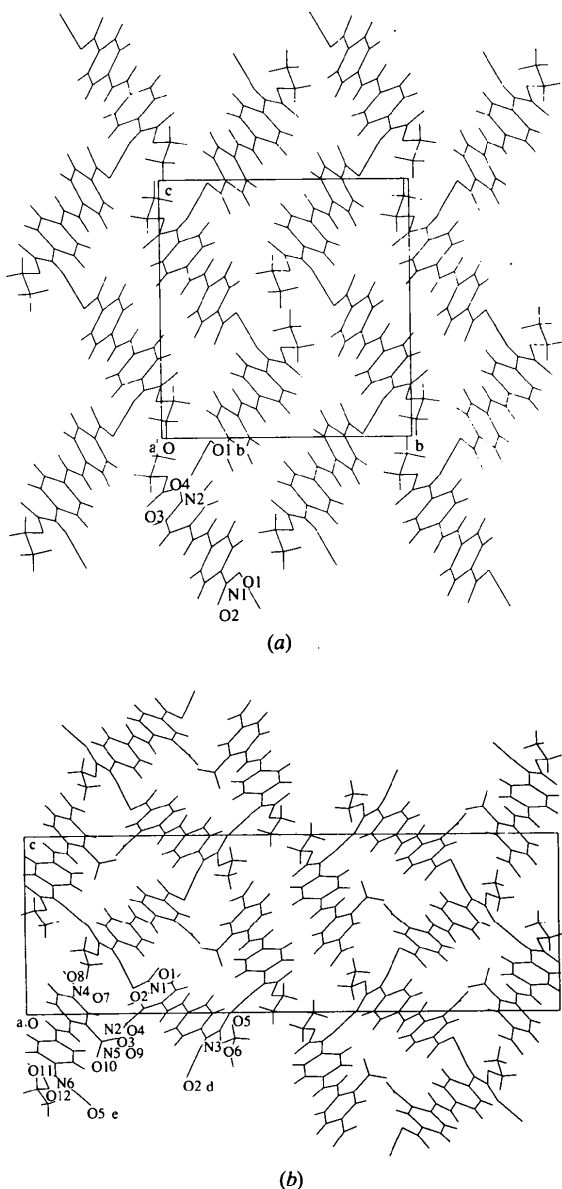


Fig. 3. Projection on the *bc* plane showing the hydrogen-bonding scheme for (a) compound (1) and (b) compound (2).

## Experimental

Compound (1): 10.0 g (42 mmol) of 4'-amino-4-nitrostilbene and 8.0 g (58.6 mmol) of ethyl chloroformate were dissolved in 120 ml of dry toluene and refluxed for 24 h. After cooling to room temperature, the solvent was evaporated *in vacuo* and the residue recrystallized twice from acetone; yield 75%, m.p. 483.9 K. The compound shows solid polymorphism as well as a monotropic liquid crystalline phase: C1 440.0, C2 483.9 K I; cooling: C 461.0 N 467.0 K I. <sup>1</sup>H NMR ( $\delta$  p.p.m., CDCl<sub>3</sub>): 8.21 (*d*, 2H, nitroaromatic CH), 7.61 (*d*, 2H, nitroaromatic CH), 7.51 (*d*, 2H, aminoaromatic CH), 7.43 (*d*, 2H, aminoaromatic CH), 7.22 (*d*, 1H, CH=CH), 7.05 (*d*, 1H, CH=CH), 6.69 (*s*, 1H, NH), 4.24 (*c*, 2H, CH<sub>2</sub>), 1.33 (*t*, 3H, CH<sub>3</sub>). MS (70 eV) *m/z*: 312 (*M*<sup>+</sup>, 100%), 313 (*M*+1), 314

(*M*+2). Elemental analysis: calculated C 65.26, H 5.13, N 9.00%; found C 65.38, H 5.13, N 8.97%.

Compound (2): 11.2 g (39.3 mmol) of 4'-amino-2,4-dinitrostilbene and 6.5 g of ethyl chloroformate (60 mmol) were refluxed in 300 ml of dry toluene for 24 h under an argon atmosphere. After cooling to room temperature, the solvent was evaporated *in vacuo* and the residue recrystallized twice from acetone; yield 63%. <sup>1</sup>H NMR ( $\delta$  p.p.m., CDCl<sub>3</sub>): 8.74 (*d*, 1H, dinitroaromatic CH), 8.34 (*q*, 1H, dinitroaromatic CH), 7.90 (*d*, 1H, dinitroaromatic CH), 7.48 (*d*, 1H, CH=CH), 7.46 (*d*, 2H, aminoaromatic CH), 7.39 (*d*, 2H, aminoaromatic CH), 7.18 (*d*, 1H, CH=CH), 6.66 (*s*, 1H, NH), 4.18 (*q*, 2H, CO<sub>2</sub>—CH<sub>2</sub>), 1.29 (*t*, 3H, CO<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>); *J*<sub>*o*-dinitro</sub> 8.78, *J*<sub>*m*-dinitro</sub> 2.28, *J*<sub>*o*-amino</sub> 8.6, *J*<sub>CH=CH</sub> 16.2 Hz. MS (70 eV) *m/z*: 357 (*M*<sup>+</sup>, 100%), 358 (*M*+1), 359 (*M*+2). Elemental analysis: calculated C 57.14, H 4.20, N 11.77%; found C 56.89, H 4.18, N 11.92%.

DSC measurements (Dupont Thermal Analyzer 990) and polarizing microscopy (Leitz Orthoplan Pol), supported with a Hotstation (Mettler FP 800), were used to characterize the thermodynamic properties.

Good quality crystals of both compounds were obtained after a week, by slow evaporation from concentrated solutions (~1 g per 20 ml) in tetrahydrofuran at 308 K.

## Compound (1)

### Crystal data

C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 312.35  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 8.544 (3) Å  
*b* = 13.193 (1) Å  
*c* = 13.616 (1) Å  
 $\beta$  = 90.23 (2)°  
*V* = 1534.8 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.352 Mg m<sup>-3</sup>

### Mo K $\alpha$ radiation

$\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 3.08–17.08°  
 $\mu$  = 0.059 mm<sup>-1</sup>  
*T* = 297 (2) K  
 Needle  
 1.25 × 0.23 × 0.18 mm  
 Orange

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 5411 measured reflections  
 2123 independent reflections  
 1784 observed reflections  
 $[I > 2\sigma(I)]$

*R*<sub>int</sub> = 0.0209  
 $\theta_{\max}$  = 22.97°  
*h* = -9 → 9  
*k* = -14 → 14  
*l* = -14 → 14  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 0.8%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0470  
*wR*(*F*<sup>2</sup>) = 0.1369  
*S* = 1.116  
 2123 reflections  
 218 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.2339P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.024  
 $\Delta\rho_{\max}$  = 0.208 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.192 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N1	-1.4242 (2)	0.74871 (15)	0.5524 (2)	0.0740 (5)
N2	-0.1460 (2)	0.93050 (14)	0.19141 (14)	0.0647 (5)
O1	-1.5207 (2)	0.6959 (2)	0.51022 (14)	0.1007 (6)
O2	-1.4452 (2)	0.78436 (15)	0.6341 (2)	0.1017 (6)
O3	-0.0337 (2)	1.06853 (12)	0.26350 (12)	0.0780 (5)
O4	0.0890 (2)	0.97819 (11)	0.14675 (10)	0.0692 (4)
C1	-1.2746 (2)	0.7688 (2)	0.50406 (15)	0.0588 (5)
C2	-1.2433 (2)	0.7222 (2)	0.4167 (2)	0.0687 (6)
C3	-1.1021 (2)	0.7405 (2)	0.3720 (2)	0.0687 (6)
C4	-0.9918 (2)	0.8047 (2)	0.41323 (15)	0.0618 (5)
C5	-1.0279 (2)	0.8509 (2)	0.5023 (2)	0.0682 (6)
C6	-1.1690 (3)	0.8334 (2)	0.5484 (2)	0.0676 (6)
C7	-0.8437 (2)	0.8201 (2)	0.3612 (2)	0.0688 (6)
C8	-0.7280 (2)	0.8797 (2)	0.3865 (2)	0.0699 (6)
C9	-0.5788 (2)	0.8923 (2)	0.3340 (2)	0.0627 (5)
C10	-0.5291 (2)	0.8281 (2)	0.2595 (2)	0.0695 (6)
C11	-0.3873 (2)	0.8426 (2)	0.2130 (2)	0.0675 (6)
C12	-0.2901 (2)	0.92217 (14)	0.24007 (14)	0.0566 (5)
C13	-0.3386 (2)	0.9873 (2)	0.3132 (2)	0.0655 (6)
C14	-0.4800 (2)	0.9712 (2)	0.3590 (2)	0.0676 (6)
C15	-0.0307 (2)	0.9992 (2)	0.20683 (14)	0.0578 (5)
C16	0.2173 (2)	1.0495 (2)	0.1483 (2)	0.0714 (6)
C17	0.3262 (3)	1.0187 (2)	0.0679 (2)	0.0882 (7)

Table 2. Selected geometric parameters (Å, °) for (1)

N1—O1	1.221 (3)	C4—C5	1.392 (3)
N1—O2	1.221 (3)	C4—C7	1.466 (3)
N1—C1	1.465 (3)	C5—C6	1.382 (3)
N2—C15	1.354 (3)	C7—C8	1.309 (3)
N2—C12	1.405 (3)	C8—C9	1.473 (3)
O3—C15	1.197 (2)	C9—C14	1.383 (3)
O4—C15	1.341 (2)	C9—C10	1.388 (3)
O4—C16	1.445 (3)	C10—C11	1.383 (3)
C1—C2	1.367 (3)	C11—C12	1.388 (3)
C1—C6	1.378 (3)	C12—C13	1.380 (3)
C2—C3	1.375 (3)	C13—C14	1.378 (3)
C3—C4	1.385 (3)	C16—C17	1.496 (3)
O1—N1—O2	123.2 (2)	C7—C8—C9	126.5 (2)
O1—N1—C1	118.7 (2)	C14—C9—C10	116.8 (2)
O2—N1—C1	118.1 (2)	C14—C9—C8	119.6 (2)
C15—N2—C12	128.1 (2)	C10—C9—C8	123.6 (2)
C15—O4—C16	115.9 (2)	C11—C10—C9	121.5 (2)
C2—C1—C6	122.0 (2)	C10—C11—C12	120.4 (2)
C2—C1—N1	119.0 (2)	C13—C12—C11	118.8 (2)
C6—C1—N1	119.1 (2)	C13—C12—N2	123.9 (2)
C1—C2—C3	118.8 (2)	C11—C12—N2	117.3 (2)
C2—C3—C4	121.7 (2)	C14—C13—C12	119.8 (2)
C3—C4—C5	117.9 (2)	C13—C14—C9	122.7 (2)
C3—C4—C7	118.4 (2)	O3—C15—O4	124.7 (2)
C5—C4—C7	123.7 (2)	O3—C15—N2	126.5 (2)
C6—C5—C4	121.3 (2)	O4—C15—N2	108.9 (2)
C1—C6—C5	118.4 (2)	O4—C16—C17	106.7 (2)
C8—C7—C4	127.4 (2)		
O1—N1—C1—C2	-4.6 (3)	C10—C11—C12—N2	178.3 (2)
O2—N1—C1—C2	174.2 (2)	C15—N2—C12—C13	1.3 (3)
O1—N1—C1—C6	176.0 (2)	C15—N2—C12—C11	-177.9 (2)
O2—N1—C1—C6	-5.2 (3)	N2—C12—C13—C14	-177.9 (2)
N1—C1—C2—C3	-179.3 (2)	C16—O4—C15—O3	-3.9 (3)
C3—C4—C7—C8	177.7 (2)	C16—O4—C15—N2	175.2 (2)
C5—C4—C7—C8	-2.5 (3)	C12—N2—C15—O3	-2.9 (3)
C4—C7—C8—C9	178.7 (2)	C12—N2—C15—O4	178.0 (2)
C7—C8—C9—C14	168.1 (2)	C15—O4—C16—C17	-173.1 (2)
C7—C8—C9—C10	-12.4 (3)		
D—H...A		D...A	
N2—HN2...O1 <sup>i</sup>	0.82 (2)	2.38 (2)	3.168 (3)
			162 (2)

Symmetry code: (i)  $\frac{3}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$ .

## Compound (2)

## Crystal data

C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>  
*M<sub>r</sub>* = 714.64  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 8.607 (2) Å  
*b* = 33.918 (8) Å  
*c* = 11.430 (2) Å  
 $\beta$  = 90.54 (2)°  
*V* = 3337 (1) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.423 Mg m<sup>-3</sup>

## Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 4872 measured reflections  
 4608 independent reflections  
 3260 observed reflections  
 $[I > 2\sigma(I)]$

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0435  
*wR* (*F*<sup>2</sup>) = 0.2022  
*S* = 1.044  
 4566 reflections  
 478 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0680P)^2 + 1.5520P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.077$   
 $\Delta\rho_{max} = 0.255 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.212 \text{ e } \text{Å}^{-3}$

## Mo Kα radiation

$\lambda = 0.71069 \text{ Å}$   
 Cell parameters from 25  
 reflections  
 $\theta = 2.99\text{--}16.53^\circ$   
 $\mu = 0.110 \text{ mm}^{-1}$   
*T* = 301 (2) K  
 Needle  
 1.25 × 0.15 × 0.15 mm  
 Orange

*R*<sub>int</sub> = 0.060 $\theta_{max} = 22.98^\circ$ *h* = -9 → 9*k* = 0 → 37*l* = 0 → 12

3 standard reflections

frequency: 120 min

intensity decay: 0.2%

## Extinction correction:

*SHELXL93* (Sheldrick, 1993)

## Extinction coefficient:

0.0039 (6)

## Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C1	0.3817 (3)	0.28776 (9)	0.5676 (3)	0.0603 (8)
C2	0.2328 (3)	0.27978 (9)	0.5274 (3)	0.0559 (7)
C3	0.1523 (3)	0.24543 (9)	0.5571 (2)	0.0525 (7)
C4	0.2334 (3)	0.21920 (9)	0.6300 (2)	0.0602 (8)
C5	0.3802 (3)	0.22704 (10)	0.6731 (2)	0.0607 (8)
C6	0.4518 (3)	0.26141 (9)	0.6404 (2)	0.0546 (7)
C7	-0.0019 (3)	0.23541 (9)	0.5121 (3)	0.0594 (8)
C8	-0.0930 (3)	0.20771 (9)	0.5521 (3)	0.0595 (8)
C9	-0.2457 (3)	0.19707 (9)	0.5045 (2)	0.0542 (7)
C10	-0.3224 (3)	0.21935 (9)	0.4197 (2)	0.0584 (8)
C11	-0.4635 (3)	0.20780 (9)	0.3746 (2)	0.0570 (7)
C12	-0.5336 (3)	0.17350 (9)	0.4132 (2)	0.0519 (7)
C13	-0.4601 (3)	0.15088 (9)	0.4973 (3)	0.0596 (8)
C14	-0.3191 (3)	0.16316 (9)	0.5432 (3)	0.0609 (8)
C15	-0.7840 (3)	0.13769 (9)	0.4041 (3)	0.0570 (7)
C16	-1.0305 (3)	0.10992 (11)	0.3596 (3)	0.0711 (9)
C17	-1.1600 (3)	0.11836 (12)	0.2745 (3)	0.0820 (11)
O1	0.6647 (3)	0.24904 (8)	0.7587 (2)	0.0854 (7)
O2	0.6769 (3)	0.29864 (8)	0.6426 (2)	0.0827 (7)
O3	0.2536 (3)	0.32827 (9)	0.3872 (3)	0.1207 (12)
O4	0.0256 (3)	0.31420 (8)	0.4461 (3)	0.1055 (9)

O5	-0.7760 (2)	0.11973 (7)	0.4940 (2)	0.0772 (7)	C11—C10—C9	121.3 (3)	C28—C27—C26	121.5 (3)
O6	-0.9043 (2)	0.13617 (7)	0.3290 (2)	0.0682 (6)	C10—C11—C12	120.4 (3)	C27—C28—C29	120.7 (3)
N1	0.6092 (3)	0.27033 (9)	0.6835 (2)	0.0652 (7)	C13—C12—C11	119.4 (2)	C30—C29—C28	118.9 (3)
N2	0.1652 (3)	0.30978 (9)	0.4492 (3)	0.0805 (8)	C13—C12—N3	123.2 (3)	C30—C29—N6	124.1 (3)
N3	-0.6775 (3)	0.16310 (8)	0.3616 (2)	0.0600 (7)	C11—C12—N3	117.4 (2)	C28—C29—N6	117.0 (3)
C18	1.2437 (3)	0.11524 (10)	1.0073 (3)	0.0629 (8)	C12—C13—C14	119.5 (3)	C31—C30—C29	119.4 (3)
C19	1.1078 (3)	0.11178 (9)	0.9427 (2)	0.0555 (7)	C13—C14—C9	122.0 (3)	C30—C31—C26	122.8 (3)
C20	0.9964 (3)	0.08247 (9)	0.9636 (2)	0.0541 (7)	O5—C15—O6	124.7 (3)	O11—C32—O12	124.7 (3)
C21	1.0334 (3)	0.05609 (10)	1.0533 (3)	0.0649 (8)	O5—C15—N3	126.9 (3)	O11—C32—N6	126.6 (3)
C22	1.1681 (4)	0.05857 (10)	1.1174 (3)	0.0680 (9)	O6—C15—N3	108.4 (3)	O12—C32—N6	108.7 (3)
C23	1.2708 (3)	0.08806 (10)	1.0930 (3)	0.0639 (8)	O6—C16—C17	106.3 (3)	O12—C33—C34	106.5 (3)
C24	0.8469 (3)	0.08094 (9)	0.9027 (3)	0.0584 (8)	C15—O6—C16	116.4 (2)	C32—O12—C33	116.2 (2)
C25	0.7361 (3)	0.05468 (9)	0.9168 (3)	0.0607 (8)	O1—N1—O2	123.5 (3)	O8—N4—O7	124.6 (3)
C26	0.5857 (3)	0.05498 (9)	0.8563 (2)	0.0536 (7)	O1—N1—C6	118.0 (3)	O8—N4—C23	117.8 (4)
C27	0.5301 (3)	0.08781 (9)	0.7964 (2)	0.0580 (7)	O2—N1—C6	118.4 (3)	O7—N4—C23	117.6 (4)
C28	0.3919 (3)	0.08672 (9)	0.7351 (2)	0.0561 (7)	O4—N2—O3	123.0 (3)	O10—N5—O9	123.4 (3)
C29	0.3037 (3)	0.05245 (9)	0.7307 (2)	0.0525 (7)	O4—N2—C2	119.3 (3)	O10—N5—C19	119.4 (3)
C30	0.3552 (3)	0.01969 (9)	0.7917 (3)	0.0632 (8)	O3—N2—C2	117.6 (3)	O9—N5—C19	117.1 (3)
C31	0.4939 (3)	0.02154 (10)	0.8531 (3)	0.0643 (8)	C15—N3—C12	127.2 (3)	C32—N6—C29	126.8 (3)
C32	0.0444 (3)	0.02876 (10)	0.6695 (3)	0.0578 (7)				
C33	-0.2074 (3)	0.01802 (10)	0.5912 (3)	0.0720 (9)	C6—C1—C2—N2	179.9 (3)	C23—C18—C19—N5	-177.7 (3)
C34	-0.3134 (4)	0.03785 (13)	0.5061 (4)	0.0953 (12)	N2—C2—C3—C4	178.4 (3)	N5—C19—C20—C21	178.0 (3)
O7	1.5082 (4)	0.11666 (13)	1.1329 (3)	0.1402 (14)	N2—C2—C3—C7	1.8 (4)	N5—C19—C20—C24	-6.3 (4)
O8	1.4312 (4)	0.07047 (10)	1.2466 (3)	0.1245 (12)	C2—C1—C6—N1	-179.4 (3)	C19—C18—C23—N4	-179.7 (3)
O9	1.1396 (3)	0.17381 (8)	0.8670 (2)	0.1027 (9)	C4—C5—C6—N1	-179.1 (3)	C21—C22—C23—N4	178.8 (3)
O10	1.0270 (3)	0.13119 (8)	0.7573 (2)	0.0786 (7)	C2—C3—C7—C8	-167.0 (3)	C21—C20—C24—C25	-4.5 (5)
O11	0.0329 (2)	0.00104 (7)	0.7326 (2)	0.0795 (7)	C3—C7—C8—C9	-178.2 (3)	C20—C24—C25—C26	178.0 (3)
O12	-0.0656 (2)	0.04068 (7)	0.5932 (2)	0.0681 (6)	C7—C8—C9—C14	169.7 (3)	C24—C25—C26—C31	163.1 (3)
N4	1.4153 (4)	0.09172 (12)	1.1625 (3)	0.0887 (9)	C7—C8—C9—C10	-9.6 (5)	C24—C25—C26—C27	-14.6 (5)
N5	1.0884 (3)	0.14094 (9)	0.8489 (2)	0.0653 (7)	C10—C11—C12—N3	-179.0 (3)	C27—C28—C29—N6	-177.0 (3)
N6	0.1680 (3)	0.05332 (8)	0.6615 (2)	0.0615 (7)	N3—C12—C13—C14	179.8 (3)	N6—C29—C30—C31	177.2 (3)
					O5—C15—O6—C16	-1.5 (5)	O11—C32—O12—C33	1.1 (4)
					N3—C15—O6—C16	179.4 (3)	N6—C32—O12—C33	-179.2 (2)
					C17—C16—O6—C15	170.8 (3)	C34—C33—O12—C32	176.9 (3)
					C1—C6—N1—O1	171.8 (3)	C18—C23—N4—O8	171.9 (3)
					C5—C6—N1—O1	-8.7 (4)	C22—C23—N4—O8	-6.8 (5)
					C1—C6—N1—O2	-7.9 (4)	C18—C23—N4—O7	-6.2 (5)
					C5—C6—N1—O2	171.6 (3)	C22—C23—N4—O7	175.2 (4)
					C1—C2—N2—O4	-151.3 (3)	C18—C19—N5—O10	143.6 (3)
					C3—C2—N2—O4	29.6 (5)	C20—C19—N5—O10	-35.9 (4)
					C1—C2—N2—O3	31.1 (4)	C18—C19—N5—O9	-34.5 (4)
					C3—C2—N2—O3	-148.0 (3)	C20—C19—N5—O9	146.0 (3)
					O5—C15—N3—C12	0.8 (5)	O11—C32—N6—C29	-4.1 (5)
					O6—C15—N3—C12	179.8 (3)	O12—C32—N6—C29	176.2 (3)
					C13—C12—N3—C15	19.7 (5)	C30—C29—N6—C32	21.6 (5)
					C11—C12—N3—C15	-161.6 (3)	C28—C29—N6—C32	-159.7 (3)

Table 4. Selected geometric parameters (Å, °) for (2)

C1—C6	1.359 (4)	C18—C23	1.363 (4)
C1—C2	1.384 (4)	C18—C19	1.383 (4)
C2—C3	1.399 (4)	C19—C20	1.404 (4)
C2—N2	1.471 (4)	C19—N5	1.466 (4)
C3—C4	1.400 (4)	C20—C21	1.395 (4)
C3—C7	1.459 (4)	C20—C24	1.458 (4)
C4—C5	1.378 (4)	C21—C22	1.368 (4)
C5—C6	1.372 (4)	C22—C23	1.365 (4)
C6—N1	1.468 (4)	C23—N4	1.475 (4)
C7—C8	1.309 (4)	C24—C25	1.316 (4)
C8—C9	1.463 (4)	C25—C26	1.462 (4)
C9—C14	1.387 (4)	C26—C31	1.383 (4)
C9—C10	1.391 (4)	C26—C27	1.390 (4)
C10—C11	1.372 (4)	C27—C28	1.375 (4)
C11—C12	1.385 (4)	C28—C29	1.389 (4)
C12—C13	1.379 (4)	C29—C30	1.382 (4)
C12—N3	1.412 (3)	C29—N6	1.405 (4)
C13—C14	1.382 (4)	C30—C31	1.381 (4)
C15—O5	1.195 (3)	C32—O11	1.190 (4)
C15—O6	1.340 (3)	C32—O12	1.343 (3)
C15—N3	1.352 (4)	C32—N6	1.355 (4)
C16—O6	1.450 (3)	C33—O12	1.442 (3)
C16—C17	1.500 (4)	C33—C34	1.488 (5)
O1—N1	1.217 (3)	O7—N4	1.214 (4)
O2—N1	1.219 (3)	O8—N4	1.208 (4)
O3—N2	1.219 (4)	O9—N5	1.216 (3)
O4—N2	1.210 (3)	O10—N5	1.215 (3)
C6—C1—C2	118.6 (3)	C23—C18—C19	117.7 (3)
C1—C2—C3	122.8 (3)	C18—C19—C20	123.0 (3)
C1—C2—N2	115.2 (3)	C18—C19—N5	115.0 (3)
C3—C2—N2	122.0 (2)	C20—C19—N5	122.0 (2)
C2—C3—C4	115.4 (2)	C21—C20—C19	115.3 (3)
C2—C3—C7	124.0 (3)	C21—C20—C24	121.5 (3)
C4—C3—C7	120.5 (3)	C19—C20—C24	123.0 (3)
C5—C4—C3	122.7 (3)	C22—C21—C20	122.7 (3)
C6—C5—C4	118.6 (3)	C23—C22—C21	118.8 (3)
C1—C6—C5	121.8 (2)	C18—C23—C22	122.4 (3)
C1—C6—N1	118.3 (3)	C18—C23—N4	117.9 (3)
C5—C6—N1	119.9 (3)	C22—C23—N4	119.7 (3)
C8—C7—C3	126.2 (3)	C25—C24—C20	127.0 (3)
C7—C8—C9	125.9 (3)	C24—C25—C26	125.2 (3)
C14—C9—C10	117.2 (2)	C31—C26—C27	116.7 (3)
C14—C9—C8	119.8 (3)	C31—C26—C25	120.7 (3)
C10—C9—C8	123.0 (3)	C27—C26—C25	122.6 (3)

D—H...A	D—H	H...A	D...A	D—H...A
N3—H3N...O2 <sup>i</sup>	0.88 (3)	2.22 (3)	3.076 (3)	166 (3)
N6—H6N...O5 <sup>ii</sup>	0.86 (3)	2.17 (3)	2.999 (4)	162 (3)

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (ii)  $1 + x, y, z$ .

The structures were solved by direct methods. The positional and anisotropic displacement parameters of all non-H atoms were refined by full-matrix least squares on  $F^2$ . All H atoms except those on the amino group were geometrically positioned using idealized C—H bond lengths.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *REDU4* (Stoe & Cie, 1991); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLUTON93* (Spek, 1993); software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Archangelin

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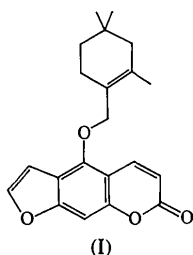
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## Abstract

In the title compound, 4-[(2,4,4-trimethyl-1-cyclohexen-1-yl)methoxy]-7*H*-furo[3,2-*g*][1]benzopyran-7-one, C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>, the furocoumarin system is planar. The cyclohexene ring adopts a half-chair conformation and makes a dihedral angle of 130.3 (1)° with the fused ring system. Molecules are held together in the crystal by C—H···O hydrogen bonds.

## Comment

This paper presents the results of a structural study of archangelin, (I), a furocoumarin isolated from the roots of *Angelica archangelica* L. (Thappa, 1989), and is part of a systematic study of coumarin derivatives isolated from plants of the *Umbelliferae* family.



An *ORTEPII* (Johnson, 1976) drawing of the title molecule with the atomic numbering scheme is shown in Fig. 1. The rings of the furocoumarin moiety are coplanar, as in other furocoumarin derivatives (Bideau, Bravic & Desvergne, 1979; Bravic & Bideau, 1978; Dall'Acqua, Benetollo & Bombieri, 1981). The deviations of atoms from the least-squares plane of the three rings range from  $-0.029$  (4) to  $0.027$  (4) Å, indicating a reasonably planar system. The cyclohexene ring shows a half-chair conformation with the twofold axis bisecting the C16—C17 and C19—C20 bonds, and an asymmetry parameter  $\Delta C_2$ (C16—C17) of  $4.0^\circ$  (Duax & Norton, 1975). The observed variations in bond lengths and angles in the phenyl ring have also been reported for various coumarin derivatives and may be attributed to the fusion of the pyrone and furan rings (Shimizu, Kashino & Haisa, 1975). The mean value of the four C—O bonds in the two heterocyclic rings is  $1.376$  (4) Å, which is in agreement with the normal  $C_{sp^2}$ —O distance (1.369 Å; Allen *et al.*, 1987). The C5—C11 and C6—C7 bond distances of  $1.424$  (4) and  $1.442$  (3) Å, respectively, are consistent with the values of  $1.427$  (3) and  $1.448$  (4) Å found in furocoumarin (Borowiak & Wolska, 1989).

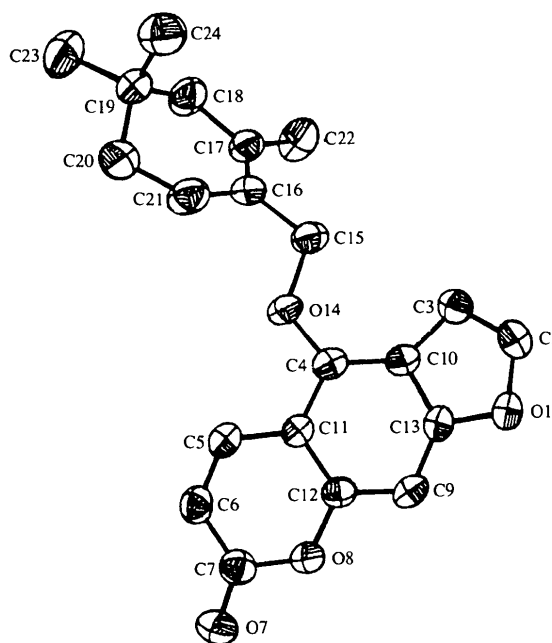


Fig. 1. *ORTEPII* (Johnson, 1976) view of the title compound with displacement ellipsoids plotted at the 50% probability level. H atoms have been omitted for clarity.

The intra- and intermolecular C—H···O hydrogen bonds which contribute to the stabilization of the molecular and crystal structure are summarized in Table 2.