

the molecule in the crystalline phase in Fig. 2. General comparison shows that almost all bonds (with the exception of some single bonds in which O or N atoms participate) are lengthened in the free molecule. The largest difference was found for the C(2)—N(2) bond. The calculated conformation of the amine group in the isolated molecule is nearly planar. This could be the result of the conjugation of the lone electron pair at N(1) with the two carbonyl bonds. Similarly to the crystal structure, the amide group shows deviations from planarity (see  $\chi_c$ ,  $\chi_N$  and  $\tau$  in Table 2), the C(2)—O(1) and N(2)—O(4) bonds remaining in a transoidal conformation, however.

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## Structure of Ethyl 2-(2-Amino-3-ethoxycarbonyl-4H-chromen-4-yl)-2-cyanoacetate

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**Abstract.**  $C_{17}H_{18}N_2O_5$ ,  $M_r = 330.35$ , monoclinic,  $P2_1/n$ ,  $a = 21.335$  (2),  $b = 8.516$  (1),  $c = 9.273$  (1) Å,  $\beta = 93.645$  (1)°,  $V = 1681.44$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.330$ ,  $D_x = 1.305$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.77$  mm<sup>-1</sup>,  $F(000) = 696.00$ ,  $T = 300$  K, final  $R = 0.059$  for 3184 observed reflections [ $I > 3\sigma(I)$ ]. The dihydropyran ring makes a dihedral angle of 14.6 (3)° with the benzene ring and is puckered. The ethoxycarbonyl group attached to C(3) makes a dihedral angle of 13.9 (3)° with the chromene ring but the 4-(1-ethoxycarbonyl) group is rotated about C(4) by 81.1 (4)°. The C—C≡N chain is almost

linear and makes a dihedral angle of 48.4 (3)° with the C(4) ethoxycarbonyl group. The molecule exhibits intramolecular hydrogen bonding between the amino group at C(2) and the carbonyl O atom of the C(3) ethoxycarbonyl group. Intermolecular N—H···O bonds link the molecules across the centre of symmetry.

**Introduction.** 4H-Chromene derivatives have been of synthetic (Clarke-Lewis, Ilseley & McGarry, 1976) and structural (Jurd & Waiss, 1968; Bouvier, Andrieux, Cunha & Molho, 1977) interest. They are

less common in nature compared to 4*H*-chromones. A 6,7-dimethoxy-4*H*-chromene derivative has been found to be a precursor in the transformation to rotenone (Harrison, 1979). The title compound (Fujimoto & Sakurai, 1977) was synthesised by the reaction of salicylaldehyde with 2 mol of ethyl cyanoacetate at ice-bath temperature in the presence of piperidine. Crystals suitable for X-ray analysis were obtained from carbon tetrachloride.

**Experimental.** A colourless transparent needle-shaped crystal of size 0.3 × 0.2 × 0.2 mm was mounted on an Enraf–Nonius CAD-4 diffractometer in ω/2θ scan mode. Cell dimensions were determined from least-squares refinement of 25 centred reflections in the 2θ range θ–75°. Density measurement was by flotation using potassium iodide solution. Intensity data were collected using Cu Kα radiation to a maximum of θ = 70°. Three standard reflections (412, 422, 443) monitored after every 100 reflections showed no significant variation in intensity. With *h* – 25 to 25, *k* 0 to 10, *l* – 11 to 11, a total of 3905 reflections were collected of which 3420 were unique (*R*<sub>int</sub> = 0.0000) and 3184 with *I* ≥ 3σ(*I*) were considered observed. Data were corrected for Lorentz–polarization effects. No absorption correction was applied. The structure was solved using *SHELXS86* (Sheldrick, 1986); all the H atoms except those attached to methyl and methylene groups were located from the difference Fourier maps; the methyl and methylene H atoms were fixed from geometrical considerations and assigned the isotropic temperature factors of the non-H atoms to which they are attached. Full-matrix least-squares refinement (on *F*) was performed with anisotropic thermal parameters for non-H atoms and isotropic for H atoms using *SHELXL76* (Sheldrick, 1976); 289 parameters refined; final *R* = 0.059 and *wR* = 0.071, *w* = 1/[σ<sup>2</sup>(*F*)], σ values based on counting statistics. The refinement terminated when the shift/e.s.d. ratio for non-H atoms was less than 0.3. The minimum and maximum residual electron densities in the final difference Fourier map were –0.63 and 0.31 e Å<sup>–3</sup> respectively. The final positional parameters of non-H atoms with *U*<sub>eq</sub> values are given in Table 1.\* The scattering factors for C, N, O and H are those incorporated in the *SHELXL76* program.

**Discussion.** The chromene derivative has a planar benzene ring which makes a dihedral angle of 14.6 (3)° with the dihydropyran ring. Atoms O(1)

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55013 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0357]

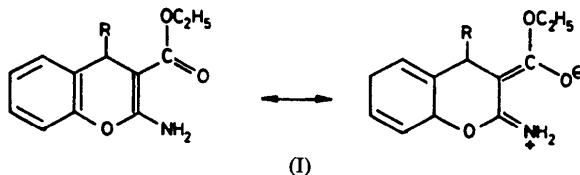
Table 1. Fractional coordinates (× 10<sup>4</sup>) and equivalent isotropic temperature factors (Å<sup>2</sup> × 10<sup>4</sup>) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	9789 (1)	1775 (2)	9498 (2)	496 (5)
C(2)	9682 (1)	1482 (2)	8054 (2)	444 (6)
C(3)	9157 (1)	2038 (2)	7292 (2)	420 (6)
C(4)	8656 (1)	2892 (2)	8062 (2)	410 (6)
C(5)	8705 (1)	5040 (3)	10003 (3)	534 (8)
C(6)	8982 (1)	5684 (3)	11244 (3)	621 (9)
C(7)	9503 (1)	4977 (3)	11932 (3)	621 (9)
C(8)	9760 (1)	3654 (3)	11342 (2)	539 (8)
C(9)	9486 (1)	3051 (2)	10085 (2)	439 (6)
C(10)	8946 (1)	3676 (2)	9403 (2)	425 (6)
N(11)	10145 (1)	628 (3)	7577 (3)	576 (7)
C(12)	9074 (1)	1723 (3)	5772 (2)	476 (7)
O(13)	9441 (1)	1039 (2)	5035 (2)	707 (7)
O(14)	8520 (1)	2271 (2)	5195 (2)	552 (6)
C(15)	8392 (1)	2027 (4)	3657 (3)	659 (10)
C(16)	7779 (2)	2718 (10)	3257 (5)	1217 (25)
C(17)	8112 (1)	1750 (2)	8415 (2)	432 (6)
C(18)	7512 (1)	2592 (3)	8760 (3)	537 (8)
O(19)	7397 (1)	3906 (3)	8417 (3)	1054 (10)
O(20)	7145 (1)	1724 (2)	9503 (3)	927 (9)
C(21)	6560 (2)	2426 (7)	10000 (6)	1136 (21)
C(22)	6050 (2)	1774 (11)	9208 (9)	1762 (40)
C(23)	8322 (1)	627 (2)	9540 (3)	487 (7)
N(24)	8521 (1)	–196 (3)	10423 (3)	723 (8)

and C(4) are below the mean plane whereas C(2) and C(3) are above the mean plane of the dihydropyran ring; the ring is puckered. The stereochemical disposition of the groups at C(4) and C(17) indicates a *gauche* relation between C(4)—H and C(17)—H; the torsion angle H(4)—C(4)—C(17)—H(17) is 73.7 (2)°. Furthermore, the carbonyl atom O(19) and cyano group are *anti* to each other; the torsion angle C(23)—C(17)—C(18)—O(19) is 146.99 (1)°. The arrangement about O(20)—C(18)—C(17)—C(23) is synperiplanar with a distance of 2.677 (3) Å between C(23) and O(20). The *peri* H atoms C(4)—H and C(5)—H are separated by 2.477 (4) Å.

The bond lengths and angles for the molecule are given in Table 2. The C(2)—C(3) bond length [1.369 (3) Å] is longer than the normal C≡C (1.35 Å) bond because of the contribution from charged resonance (I), which is also apparent in the shortening of bond lengths C(2)—N(11) [1.327 (3) Å] and C(3)—CO [1.435 (3) Å]. The bond lengths and angles in the benzene ring are normal. The C—C≡N chain is almost linear with the angle C(17)—C(23)—N(24) being 175.6 (2)°.



It is interesting to compare the bond angles at the carbonyl C atom of the two ester groups at C(3) and C(17), which are given in Table 3. There is no

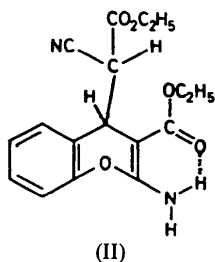
Table 2. Bond lengths (Å), angles (°) and hydrogen-bond geometry (Å, °) with e.s.d.'s in parentheses

O(1)—C(2)	1.367 (3)	C(12)—O(13)	1.220 (3)	
C(2)—C(3)	1.369 (3)	C(12)—O(14)	1.350 (3)	
C(3)—C(4)	1.510 (3)	O(14)—C(15)	1.449 (3)	
C(5)—C(6)	1.374 (4)	C(15)—C(16)	1.459 (6)	
C(6)—C(7)	1.384 (3)	C(4)—C(17)	1.565 (3)	
C(7)—C(8)	1.181 (4)	C(17)—C(18)	1.518 (3)	
C(8)—C(9)	1.371 (3)	C(18)—O(19)	1.184 (3)	
C(9)—C(10)	1.385 (3)	C(18)—O(20)	1.305 (3)	
C(9)—O(1)	1.392 (3)	O(20)—C(21)	1.484 (5)	
C(4)—C(10)	1.509 (3)	C(21)—C(22)	1.389 (8)	
C(5)—C(10)	1.400 (3)	C(17)—C(23)	1.465 (3)	
C(2)—N(11)	1.327 (3)	C(23)—N(24)	1.139 (3)	
C(3)—C(12)	1.435 (3)			
C(9)—O(1)—C(2)	118.2 (2)	C(10)—C(5)—C(6)	121.0 (2)	
C(3)—C(2)—O(1)	121.5 (2)	C(7)—C(6)—C(5)	120.2 (2)	
N(11)—C(2)—O(1)	110.2 (2)	C(8)—C(7)—C(6)	120.0 (2)	
N(11)—C(2)—C(3)	128.3 (2)	C(9)—C(8)—C(7)	118.9 (2)	
C(4)—C(3)—C(2)	120.2 (2)	C(8)—C(9)—O(1)	116.2 (2)	
C(12)—C(3)—C(2)	119.2 (2)	C(10)—C(9)—O(1)	121.0 (2)	
C(12)—C(3)—C(4)	120.5 (2)	C(10)—C(9)—C(8)	122.9 (2)	
C(10)—C(4)—C(3)	109.7 (2)	C(5)—C(10)—C(4)	123.6 (2)	
C(17)—C(4)—C(10)	110.9 (2)	C(9)—C(10)—C(4)	119.5 (2)	
C(17)—C(4)—C(10)	111.9 (2)	C(9)—C(10)—C(5)	116.9 (2)	
O(13)—C(12)—C(3)	126.6 (2)	C(23)—C(17)—C(18)	112.5 (2)	
O(14)—C(12)—C(3)	112.0 (2)	O(19)—C(18)—C(17)	123.5 (2)	
O(14)—C(12)—O(13)	121.4 (2)	O(20)—C(18)—C(17)	112.7 (2)	
C(15)—O(14)—C(12)	116.5 (2)	O(20)—C(18)—O(19)	123.8 (2)	
C(16)—C(15)—O(14)	107.7 (3)	C(21)—O(20)—C(18)	118.8 (3)	
C(18)—C(17)—C(4)	113.4 (2)	C(22)—C(21)—O(20)	108.8 (5)	
C(23)—C(17)—C(4)	110.9 (2)	N(24)—C(23)—C(17)	175.6 (2)	
X—H...Y	X—H	H...Y	X...Y	X—H...Y
N(11)—H(11A)...O(1 <sup>i</sup> )	0.870 (24)	2.233 (25)	2.209 (3)	77 (2)
N(11)—H(11B)...O(13 <sup>i</sup> )	0.937 (38)	2.094 (35)	2.736 (3)	125 (3)
N(11)—H(11B)...O(13 <sup>ii</sup> )	0.937 (21)	2.178 (38)	2.988 (3)	144 (3)

Symmetry code: (i)  $x, y, z$ ; (ii)  $2 + x, y, 1 + z$ .

difference in O—C—O angles. However, the variations in  $\theta_i$  and  $\theta_j$  would result in minimum strain owing to non-bonded interactions.

An ORTEP (Johnson, 1965) plot of the molecule with 50% probability thermal ellipsoids is shown in Fig. 1. The molecule exhibits intramolecular hydrogen bonding between the amino group at C(2) and the carbonyl O atom of the ester group at C(3) [O(13)...H(11B) = 2.094 (4) Å]; such bonding is a geometrical necessity for the formation of a stable six-membered ring. It is clear from the resonance structures that O(13), H(11B) and N(11) are coplanar and form a stable six-membered ring (II).



The C≡O distances are normal; the small change in the bond length of the methyl and methylene group may result from the thermal vibrations of the terminal C atoms.

Table 3. Bond angles (°) in the two ester groups

	$\theta_i$	$\theta_j$	$\theta_k$
C(3)	121.4	126.6	112.0
C(17)	123.8	123.5	112.7

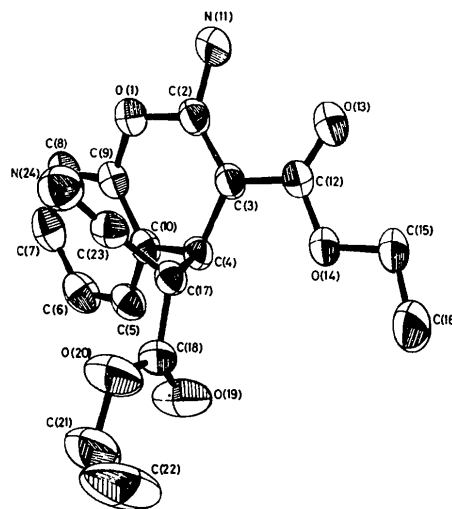
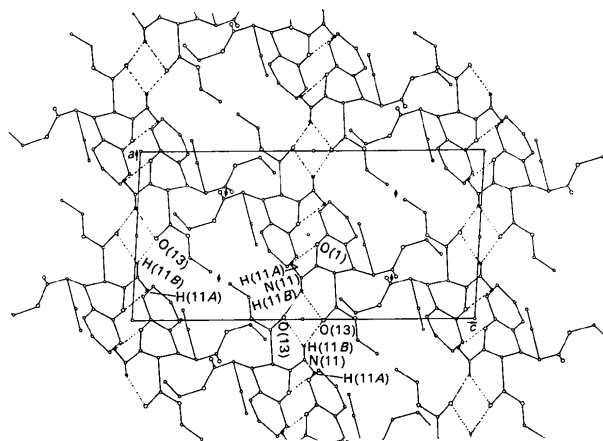


Fig. 1. Thermal ellipsoids with 50% probability.

Fig. 2. The molecular packing viewed down the  $b$  axis.

The molecular packing viewed down  $b$  is shown in Fig. 2. The intermolecular N—H...O bonds link the molecules across the centre of symmetry. The hydrogen-bond parameters are given in Table 2.

The present crystal structure analysis shows that the absolute configuration at C(4) is *R* and at C(17), *S*.

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## A Chiral *N*-Crotonyloxazolidinone Diels–Alder Adduct

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**Abstract.** (4*S*)-4-Benzyl-3-[(4*S*,5*S*)-(1-methoxy-5-methylcyclohexen-4-yl)carbonyl]-2-oxazolidinone, C<sub>19</sub>H<sub>23</sub>NO<sub>4</sub>, *M<sub>r</sub>* = 329.40, monoclinic, *P*2<sub>1</sub>, *a* = 11.453 (3), *b* = 7.163 (4), *c* = 11.929 (2) Å, β = 111.86 (2)°, *V* = 908.3 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.20 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 0.79 cm<sup>-1</sup>, *F*(000) = 352, *T* = 297 K, *R* = 0.034 for 885 reflections with *F<sub>o</sub>*<sup>2</sup> > 0. The molecule is extended in the crystal; there is a small twist, -13.1 (2)°, about the amide-like C—N bond joining the oxazolidinone ring to the carbonyl group. The configurations at the two optical centers in the cyclohexene ring confirm the anticipated stereospecificity of the Diels–Alder cycloaddition synthesis.

**Introduction.** In a study of the Diels–Alder reaction of 2-methoxy-1,3-butadiene with 4-benzyl-3-crotonyl-2-oxazolidinone of known absolute stereochemistry [4*S* (Myers & Kukkola, 1991)], the conditions that we developed for optimum diastereoselectivity and yield deviated substantially from reported literature procedures for analogous substrates (Evans, Chapman & Bisaha, 1988). Accordingly, the relative stereochemistry of the cycloadduct (1) which we synthesized could not be confidently assigned by analogy with earlier examples. As reported herein, the structure of (1) is established by X-ray crystallography as (4*S*)-4-benzyl-3-[(4*S*,5*S*)-(1-methoxy-5-methylcyclohexen-4-yl)carbonyl]-2-oxazolidinone. Cycloaddition under the modified

conditions thus proceeds with the same stereochemical sense as related substrates under the original protocol of Evans *et al.* (1988).

**Experimental.** A diamond-shaped plate crystal, 0.16 × 0.23 × 0.09 mm, was used for data collection on a CAD-4 diffractometer with ω scans. Cell dimensions were determined from 25 reflections with 28 < 2θ < 35°. No absorption correction was applied (μ<sub>r,max</sub> = 0.01). (sinθ/λ)<sub>max</sub> = 0.48 Å<sup>-1</sup>; *h* from -10 to 10, *k* from -6 to 6, *l* from 0 to 10; two check reflections (212̄ and 302̄) decayed 14% and 15%, respectively, during the 52 h of data collection and a quadratic correction was applied. 3500 reflections were measured, those to θ = 17.5° four times, and those from 17.5 to 20° twice. 925 independent reflections were measured; goodness of fit for merging was 0.985 (*R*<sub>merge</sub> = 0.038 for 266 reflections with exactly two observations). All reflections were used in solution and refinement of the structure. The structure was solved by Patterson methods plus structure factor–Fourier calculations [*MULTAN*88 (Debaerdmacker, Germain, Main, Refaat, Tate & Woolfson, 1988) did not readily give a solution], *F*<sup>2</sup> values, positive and negative, were used in the refinement with weights = 1/σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>). H atoms were positioned by calculation (C—H = 0.95 Å), assuming a staggered conformation for C12; H-atom parameters were not refined but adjusted once, near the end of the refinement. Coordinates (except *y* of N) and anisotropic displacement parameters of all non-H atoms, a scale factor and a secondary-extinction

\* Contribution No. 8475.