peaks on the final Fourier synthesis were 1·175 and −0·75 e Å^{-3}, respectively. The large maximum peak was found to be 0·8 Å from I. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).*

Fig. 1 shows the thermal ellipsoids with the atomic numbering scheme for (I). The atomic coordinates and isotropic temperature factors for all non-H atoms are shown in Table 1. Bond lengths and angles are listed in Table 2.

Related literature. The relationship between the isoxazole and phenyl rings for (I) compares favorably to the 3-phenylisoxazole dihedral angles found when the C(4) isoxazole substituent was an secondary carboxamide (31·2°; Verner, Oliver Schlicksupp & Natale, 1990) or a 4-substituted 1,4-dihydropyridine in an O-*endo* conformation (33·0°; Schauer, Anderson, Natale & Quincy, 1986), but is much smaller than that found when the C(4) group was a 4-substituted 1,4-dihydropyridine in an O-*exo* conformation (83·5°; McKenna, Schlicksupp, Natale, Willett, Maryanoff & Flaim, 1988). The dihedral angle between the ester moiety [defined by the mean plane containing C(4), C(14), O(2) and O(3)] and the isoxazole mean plane is 47·2 (7)° for the title compound [(I)], and again is fairly close to that of the previously cited secondary carboxamide (53·7°).

The Syntex $P2_1$ X-ray diffractometer and crystallographic computing system was purchased with funds provided by the National Science Foundation (Grant CHE-8408407) and The Boeing Company. NRN thanks the National Institutes of General Medical Sciences for Grant Number 1-R15-GM4209-01.

References

Campana, C. F., Shepard, D. F. & Litchman, W. M. (1980). *Inorg. Chem.* **20**, 4039–4043.

McKenna, J. I., Schlicksupp, L., Natale, N. R., Willett, R. D., Maryanoff, B. E. & Flaim, S. F. (1988). *J. Med. Chem.* **31**, 473–476.

Natale, N. R., McKenna, J. I., Niou, C.-S., Borth, M. L. & Hope, H. (1985). *J. Org. Chem.* **51**, 5660–5666.

Schauer, C. K., Anderson, O. P., Natale, N. R. & Quincy, D. A. (1986). *Acta Cryst.* C**42**, 884–887.

Sheldrick, G. M. (1985). *SHELXTL Users Manual*, revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Verner, E. J., Oliver, B. J., Schlicksupp, L. & Natale, N. R. (1990). *Heterocycles*, **31**, 327–339.

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* 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 53767 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1991). C**47**, 1330–1332

Structure of Ethyl 3′-Ethyl-6-methoxy-5′-oxo-1,2-cyclopent-1′,3′-dienonaphthalene-4′-acetate

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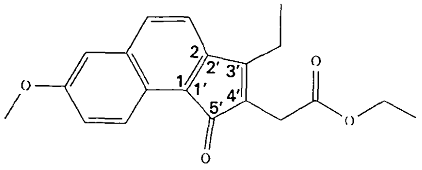
Abstract. $\mathrm{C_{20}H_{20}O_4}$, $M_r = 324·38$, monoclinic, $P2_1/c$, $a = 12·514$ (1), $b = 15·067$ (1), $c = 9·588$ (1) Å, $\beta = 107·47$ (1)°, $V = 1724·4$ (3) Å^3, $Z = 4$, $D_x = 1·249$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1·54178$ Å, $\mu = 0·665$ mm^{-1}, $F(000) = 688$, $T = 294$ K, final $R = 0·057$ for 1972 unique observed reflections with $I > 3\sigma(I)$. The cyclopentenonaphthalene ring system is planar (mean deviation, 0·014 Å). The crystal contains molecules held together by van der Waals forces (m.p. 390–391 K). Bond lengths and angles are internally consistent and the van der Waals interactions are normal. Averaged C—O bond lengths are: C(sp^2)—O = 1·338 (20); C(sp^3)—O = 1·428 (14) and C═O = 1·210 (1) Å.

Experimental. Clear bright-red needle-shaped crystals of the title compound were sequentially synthesized by a Friedel–Crafts reaction, a Stobbe condensation and cyclization (Hwang, 1962).



(1)

Crystal size 0·53 × 0·16 × 0·06 mm, glass-fiber mount, Enraf–Nonius CAD-4F four-circle diffrac-

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

Equivalent isotropic thermal parameter (U_{eq}) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(3)	3883 (2)	1850 (2)	− 908 (3)	92 (1)
O(11)	− 256 (2)	913 (1)	2033 (2)	89 (1)
O(15a)	− 3026 (2)	1489 (2)	873 (2)	116 (1)
O(15)	− 3405 (2)	900 (1)	2793 (2)	78 (1)
C(1)	1661 (3)	1366 (2)	608 (3)	70 (1)
C(2)	2493 (3)	1287 (2)	6 (3)	79 (1)
C(3)	3044 (3)	2043 (2)	− 331 (3)	74 (1)
C(4)	2714 (3)	2872 (2)	− 55 (3)	71 (1)
C(5)	1840 (3)	2983 (2)	580 (3)	64 (1)
C(6)	1283 (3)	2218 (2)	928 (3)	62 (1)
C(7)	1476 (3)	3835 (2)	900 (3)	71 (1)
C(8)	643 (3)	3945 (2)	1528 (3)	72 (1)
C(9)	110 (3)	3197 (2)	1862 (3)	63 (1)
C(10)	439 (3)	2357 (2)	1564 (3)	62 (1)
C(11)	− 269 (3)	1722 (2)	2079 (3)	67 (1)
C(12)	− 1032 (3)	2263 (2)	2677 (3)	69 (1)
C(13)	− 791 (3)	3127 (2)	2577 (3)	67 (1)
C(14)	− 1859 (3)	1832 (2)	3297 (3)	79 (1)
C(15)	− 2817 (3)	1405 (2)	2172 (3)	73 (1)
C(16)	− 4348 (3)	433 (3)	1838 (4)	90 (2)
C(17)	− 4870 (4)	− 105 (3)	2718 (4)	113 (2)
C(18)	− 1337 (3)	3906 (2)	3031 (3)	80 (1)
C(19)	− 2240 (4)	4309 (3)	1801 (4)	111 (2)
C(20)	4496 (3)	2572 (3)	− 1218 (4)	103 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(3)—C(3)	1·357 (5)	C(7)—C(8)	1·361 (5)
O(3)—C(20)	1·414 (5)	C(8)—C(9)	1·395 (4)
O(11)—C(11)	1·220 (3)	C(9)—C(10)	1·387 (4)
O(15a)—C(15)	1·200 (4)	C(9)—C(13)	1·489 (5)
O(15)—C(15)	1·318 (4)	C(10)—C(6)	1·385 (5)
O(15)—C(16)	1·441 (4)	C(10)—C(11)	1·485 (4)
C(1)—C(2)	1·339 (6)	C(11)—C(12)	1·495 (5)
C(1)—C(6)	1·434 (4)	C(12)—C(13)	1·345 (4)
C(2)—C(3)	1·418 (5)	C(12)—C(14)	1·489 (5)
C(3)—C(4)	1·366 (4)	C(13)—C(18)	1·487 (5)
C(4)—C(5)	1·412 (5)	C(18)—C(19)	1·496 (5)
C(5)—C(7)	1·426 (4)	C(14)—C(15)	1·497 (4)
C(5)—C(6)	1·437 (4)	C(16)—C(17)	1·458 (6)

C(9)—C(13)—C(12)	108·5 (3)	C(8)—C(9)—C(13)	130·1 (3)
C(12)—C(13)—C(18)	127·6 (3)	C(10)—C(9)—C(13)	110·0 (3)
C(12)—C(14)—C(15)	113·7 (3)	C(9)—C(10)—C(6)	122·8 (3)
O(15a)—C(15)—C(14)	125·5 (3)	C(9)—C(10)—C(11)	106·0 (3)
O(15)—C(16)—C(17)	109·1 (3)	C(6)—C(10)—C(11)	131·2 (2)
C(3)—O(3)—C(20)	117·2 (3)	C(1)—C(6)—C(5)	117·0 (3)
C(15)—O(15)—C(16)	117·1 (2)	C(1)—C(6)—C(10)	125·0 (3)
C(2)—C(1)—C(6)	121·4 (3)	C(5)—C(6)—C(10)	117·9 (3)
C(1)—C(2)—C(3)	121·4 (3)	O(11)—C(11)—C(10)	128·0 (3)
O(3)—C(3)—C(2)	114·2 (3)	O(11)—C(11)—C(12)	125·2 (3)
O(3)—C(3)—C(4)	126·2 (3)	C(10)—C(11)—C(12)	106·8 (2)
C(2)—C(3)—C(4)	119·7 (3)	C(11)—C(12)—C(13)	108·6 (3)
C(3)—C(4)—C(5)	120·7 (3)	C(11)—C(12)—C(14)	121·0 (3)
C(4)—C(5)—C(7)	122·5 (3)	C(13)—C(12)—C(14)	130·4 (3)
C(4)—C(5)—C(6)	119·8 (3)	C(9)—C(13)—C(18)	123·8 (3)
C(7)—C(5)—C(6)	117·6 (3)	C(13)—C(18)—C(19)	113·3 (3)
C(5)—C(7)—C(8)	122·7 (3)	O(15a)—C(15)—O(15)	123·5 (3)
C(7)—C(8)—C(9)	119·1 (3)	O(15)—C(15)—C(14)	111·0 (2)
C(8)—C(9)—C(10)	119·8 (3)		

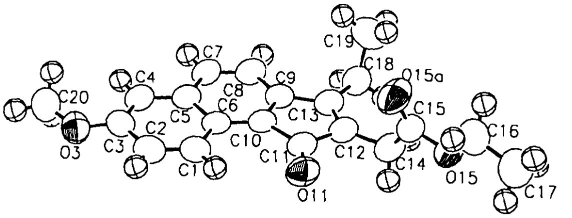

Fig. 1. The ethyl 3′-ethyl-6-methoxy-5′-oxo-1,2-cyclopent-1′,3′-dienonaphthalene-4′-acetate molecule showing the atomic numbering scheme, 50% equiprobability ellipsoids.

tometer, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, take-off angle 5·8°; cell parameters obtained from 25 reflections ($20 \le \theta \le 28°$); intensity data collected by ω–2θ scan technique ($1{\cdot}5 \le \theta \le 70°$; h 0→11, k0→18, l −15→15), varied scan rate of 0·35–2·78° min^{-1}; two standards ($2\bar{1}0$, $03\bar{1}$) measured every 2 h, no significant systematic variations; 3987 measured reflections of which 3229 were independent, 1972 with $I > 3\sigma(I)$ included in the refinement; $R_{int} = 0{\cdot}0099$; Lp corrections, no absorption correction; systematic absences $0k0$ for k odd and $h0l$ for l odd; structure solved by direct methods (*SHELXTL-PC*; Siemens, 1989) and refined by full-matrix least squares (*SHELXTL-PC*). The non-H atoms were refined with anisotropic thermal parameters. All H-atom positions were placed in geometrically calculated positions (C—H = 0·96 Å) and allowed to ride on covalently bonded neighbors. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(|F_o|) + 0{\cdot}0016(F_o)^2]$. Final convergence was reached at $R = 0{\cdot}057$ ($wR = 0{\cdot}074$, $R_{all} = 0{\cdot}096$) for 218 varying parameters, $S = 1{\cdot}80$, $g = 3{\cdot}7\ (12) \times 10^{-5}$, $(\Delta/\sigma)_{max} = 0{\cdot}001$, no residual density outside the range $-0{\cdot}18$ and $0{\cdot}19$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic fractional coordinates with equivalent isotropic thermal parameters are listed in Table 1.* Table 2 lists bond distances and valence angles. The atomic labeling scheme is shown in Fig. 1 which was generated using the *SHELXTL-PC* package.

Related literature. A method for the synthesis of cyclic compounds *via* stable ozonides has been shown to be suitable for the preparation of steroid-type structures having O atoms in the 11 and 12 positions (Belew & Layton, 1956). The ozonization of the title indenone produced a stable ozonide that was reduced by hydrogen and platinum(IV) oxide yielding ethyl 1-ethyl-7-methoxy-3,4-dioxo-2-phen-

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* Lists of anisotropic thermal parameters, H-atom coordinates and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53763 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

anthrenecarboxylate whose structure was analyzed by Mullica, Milligan, Belew, Grossie & Sappenfield (1984). Interest in stable ozonides employed in the synthesis of steroid intermediates led to the first two complete single-crystal structure analyses of such compounds (Mullica, Korp, Milligan, Belew, McAtee & Karban, 1979; Oliver, Mullica, Milligan, Karban, McAtee & Belew, 1979).

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References

Belew, J. S. & Layton, R. (1956). 129th Meet. Am. Chem. Soc., Dallas, Texas, USA.
Hwang, T.-R. (1962). MS Thesis, Baylor Univ., Texas, USA.
Mullica, D. F., Korp, J. D., Milligan, W. O., Belew, J. S., McAtee, J. L. Jr & Karban, J. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1703–1707.
Mullica, D. F., Milligan, W. O., Belew, J. S., Grossie, D. A. & Sappenfield, E. A. (1984). *Acta Cryst.* C**40**, 1923–1925.
Oliver, J. D., Mullica, D. F., Milligan, W. O., Karban, J., McAtee, J. L. Jr & Belew, J. S. (1979). *Acta Cryst.* B**35**, 2273–2276.
Siemens (1989). *SHELXTL-PC*. Siemens Analytical X-ray Instruments, Madison, WI, USA.

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Structures of 3-Formylthiachromen-4-one and 3-(Chloromethyl)chromen-4-one

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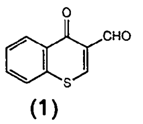
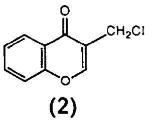
Abstract. (1) 3-Formylthiachromen-4-one, $C_{10}H_6O_2S$, $M_r = 190{\cdot}22$, monoclinic, $P2_1/c$, $a = 7{\cdot}715\,(10)$, $b = 7{\cdot}089\,(11)$, $c = 15{\cdot}64\,(4)$ Å, $\beta = 95{\cdot}43\,(16)^\circ$, $V = 852\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}484$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}21$ cm^{-1}, $F(000) = 391{\cdot}6$, room temperature, final $R = 0{\cdot}0574$ for 747 independent reflections with $|F| > 3\sigma|F|$. The two six-membered rings which comprise the structure are each planar and are mutually inclined at 1°. The aldehyde group is almost coplanar with the heterocyclic ring to which it is attached [deviation of oxygen atom 0·057 (7) Å]. Bond lengths imply aromaticity confined to the benzenoid ring. (2) 3-(Chloromethyl)chromen-4-one, $C_{10}H_7ClO_2$, $M_r = 194{\cdot}62$, triclinic, $P\bar{1}$, $a = 6{\cdot}523\,(6)$, $b = 7{\cdot}044\,(5)$, $c = 10{\cdot}389\,(12)$ Å, $\alpha = 79{\cdot}49\,(7)$, $\beta = 71{\cdot}74\,(8)$, $\gamma = 75{\cdot}42\,(7)^\circ$, $V = 435{\cdot}9\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}483$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}93$ cm^{-1}, $F(000) = 199{\cdot}98$, room temperature, final $R = 0{\cdot}0451$ for 1164 independent reflections with $|F| > \sigma|F|$. The two six-membered rings which comprise the structure are each planar and are mutually inclined at 1°. The Cl atom is not coplanar with the heterocyclic ring to which the chloromethyl substituent is attached [deviation 1·537 (2) Å]. Bond lengths imply aromaticity confined to the benzenoid ring.

Experimental. Crystals were grown from the products obtained (Giles & Marson, 1990) by the action of dimethylformamide–phosphorus oxychloride at 373 K on the heterocyclic ketones thiachromen-4-one and chroman-4-one.



(1)



(2)

3-Formylthiachromen-4-one (1) was crystallized from propan-2-ol as light-brown plates. Diffraction intensities were measured using a crystal of dimensions 0·40 × 0·20 × 0·10 mm; X-ray data in the range $3{\cdot}5 < 2\theta < 45^\circ$ on a Nicolet $R3$ four-circle diffractometer, ω-scan method. Cell parameters determined from 14 reflections in the range $0 < \theta < 25^\circ$. 747 independent reflections (of 1327 measured) were corrected for Lorentz and polarization effects, and for absorption by analysis of seven azimuthal scans (min. and max. transmission coefficients 0·766 and 0·866).

The structure was solved by multiple solution direct methods and refined by blocked-cascade least squares. H atoms were detected and most were refined in riding mode; those on C(2) and C(9) were allowed free positional refinement; their isotropic thermal parameters were related to those of the supporting atom. Refinement converged at a final $R = 0{\cdot}0574$ ($wR = 0{\cdot}0461$, 124 parameters, all final shift/e.s.d = 0·00), with allowance for the thermal anisotropy of all non-H atoms. A final difference

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