All calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University, using programs *UNICS* (Sakurai, 1967) and *SHILCS* (Hirotsu, Yoshioka, Takusagawa & Nakatsu, 1974).

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Pentamethyl 11,11a-Dihydro-9-oxo-9*H*,10*H*-cyclobuta[4,5]cyclopenta[3,4]pyrrolo[1,2-*a*]quinoline-7,8,10,11,11a-pentacarboxylate

BY PATRICK J. ABBOTT AND R. MORRIN ACHESON

*Department of Biochemistry, South Parks Road, Oxford OX*1 3*QU, England*

R. A. FORDER AND D. J. WATKIN*

Chemical Crystallography Laboratory, 9 *Parks Road, Oxford OX*1 3*PD, England*

AND J. R. CARRUTHERS

Oxford University Computing Laboratory, 19 *Banbury Road, Oxford, England*

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Abstract. The title compound was obtained as an uncharacterized reaction product. Its structure has provided a key to the interpretation of the NMR spectra of related products. $C_{27}H_{23}NO_{11}$, $M=537$; monoclinic, $P2_1/b$ (C^5_{2h}, No. 14); $a=10{\cdot}41$ (1), $b=14{\cdot}31$ (1), $c=16{\cdot}89$ (2) Å, $\gamma=91{\cdot}91$ (5)°, $U=2514{\cdot}7$ Å^3; $D_x=1{\cdot}40$, $D_c=1{\cdot}36$ g cm^{-3}, $Z=4$; Cu$K\alpha=1{\cdot}5418$ Å, $\mu=9{\cdot}6$ cm^{-1}; $R=0{\cdot}065$.

Introduction The purple material (m.p. 227–230 °C) crystallized from methanol as thick six-sided plates. A crystal ($0{\cdot}3\times0{\cdot}3\times0{\cdot}15$ mm) was mounted perpendicular to the smallest face. The setting angles of 25 reflexions measured each side of the incident beam were used in a least-squares calculation to give the cell parameters and orientation matrix. An absorption profile (North, Phillips & Mathews, 1968) was measured for the 600 reflexion ($I_{\max}:I_{\min}=1{\cdot}4:1$) and used to correct the intensities which were measured with an $\omega/2\theta$ scan and a modified ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970). Cu $K\alpha$ radiation was used with Zr/Y balanced filters for $\theta<30°$ and a Zr β-filter for $30°<\theta<60°$. 3813 reflexions were observed yielding 2207 with $I\geq3\sigma(I)$. The structure was solved by direct methods (Sheldrick, 1973) and refined by least squares (block 1: all x,y,z; 2: all U_{ii}'s; 3: all U_{ij}'s; 4: scale factor and dummy overall temperature factor) (Carruthers, 1975). H atoms were ignored. The final R was 0·065 and the Hamilton weighted R 0·087. Weights were calculated from $w=1/\{4{\cdot}8\times T[0]'(x)+7{\cdot}4\times T[1]'(x)+3{\cdot}4\times T[2]'(x)+0{\cdot}7\times T[3]'(x)\}$ where $T[i]'$ are modified Chebychev coefficients and $x=F_o/F_o(\max)$ (Rollett, 1965). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are listed in Tables 1 and 2 and the bond lengths and angles (with estimated standard deviations computed from the full variance–covariance matrix) in Tables 3 and 4. Fig. 1 shows the molecular geometry.†

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* To whom correspondence should be addressed.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31718 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates*

	x	y	z
O(1)	1·2753 (4)	0·2813 (3)	−0·1850 (2)
O(2)	1·3002 (5)	0·3988 (3)	0·1247 (3)
O(3)	1·3647 (4)	0·2541 (3)	0·1498 (2)
O(4)	1·5128 (4)	0·3791 (3)	−0·1241 (2)
O(5)	1·5287 (4)	0·3730 (3)	0·0079 (2)
O(6)	1·3722 (4)	0·0826 (4)	−0·1417 (3)
O(7)	1·2160 (4)	0·0372 (3)	−0·2251 (2)
O(8)	0·9165 (4)	−0·0116 (3)	−0·0827 (3)
O(9)	0·8392 (4)	0·0450 (3)	−0·1964 (2)
O(10)	0·9156 (4)	0·3012 (3)	−0·1940 (2)
O(11)	0·9892 (4)	0·3744 (3)	−0·0853 (2)
N(1)	0·9623 (4)	0·2011 (3)	−0·0088 (2)
C(1)	0·8324 (5)	0·1852 (4)	0·0090 (3)
C(2)	0·7407 (6)	0·1722 (4)	−0·0507 (4)
C(3)	0·6125 (6)	0·1513 (4)	−0·0298 (4)
C(4)	0·5780 (6)	0·1467 (5)	0·0513 (4)
C(5)	0·6680 (6)	0·1651 (5)	0·1099 (4)
C(6)	0·7975 (6)	0·1844 (4)	0·0892 (3)
C(7)	0·8921 (6)	0·2051 (5)	0·1482 (3)
C(8)	1·0201 (6)	0·2223 (4)	0·1283 (3)
C(9)	1·0556 (5)	0·2164 (4)	0·0471 (3)
C(10)	1·1751 (5)	0·2273 (4)	0·0115 (3)
C(11)	1·2856 (5)	0·2819 (4)	0·0242 (3)
C(12)	1·3454 (5)	0·3065 (4)	−0·0492 (3)
C(13)	1·2650 (5)	0·2706 (4)	−0·1131 (3)
C(14)	1·1610 (5)	0·2085 (4)	−0·0747 (3)
C(15)	1·1531 (5)	0·1049 (4)	−0·1046 (3)
C(16)	1·0210 (5)	0·1229 (4)	−0·1431 (3)
C(17)	1·0137 (5)	0·2116 (4)	−0·0910 (3)
C(18)	1·3196 (5)	0·3206 (4)	0·1043 (3)
C(19)	1·3990 (8)	0·2835 (6)	0·2320 (3)
C(20)	1·4684 (6)	0·3561 (4)	−0·0617 (3)
C(21)	1·6569 (6)	0·4168 (5)	0·0025 (4)
C(22)	1·2611 (6)	0·0753 (4)	−0·1584 (3)
C(23)	1·3155 (8)	0·0069 (6)	−0·2810 (5)
C(24)	0·9220 (6)	0·0446 (4)	−0·1359 (3)
C(25)	0·7333 (7)	−0·0267 (5)	−0·1950 (5)
C(26)	0·9643 (5)	0·2998 (4)	−0·1307 (3)
C(27)	0·9559 (9)	0·4652 (5)	−0·1195 (5)

Discussion. 2-Methylquinoline and dimethyl acetylenedicarboxylate in methanol yield a mixture of compounds (Acheson & Nisbet, 1973). Among these, a purple and a blue adduct (Acheson, Gagan & Harrison, 1968) are successively eluted on column chromatography over alumina.

The structure of the purple compound (I) has been determined by X-ray methods. The bond lengths along the conjugated chain N(1), C(9), C(10), C(11), C(12), C(13), O(11) give evidence for the type of interaction found in 1,10-dihydro-10-methyl-1-acridone (II), which has almost the same chromophore and for which the colour is associated with resonance involving the charged structure (III) (Nitzsche, 1939). The deep purple colour [$\lambda_{\max}$ for MeOH 207 nm (2·86), 232 (1·84), 252 (1·69), 275 infl. (1·02), 307 infl. (1·07), 328 (1·38), 554 (2·97) and 583 ($3\cdot22\times10^{-4}\varepsilon$)] vanishes on acidification [$\lambda_{\max}$ 207 (3·12), 243 (4·25) and 325 (1·18)] when protonation occurs mainly at position 6b to give a quinolinium type of chromophore.

The formation of a cyclobutane ring in additions of dimethyl acetylenedicarboxylate has not been reported before, but the purple adduct could be built up with known types of processes (Acheson, 1963; Acheson & Woollard, 1975).

Table 2. *Anisotropic temperature factors* ($\times 10^3$)

$T=\exp[-\pi^2(h^2a^{2*}U_{11}\ldots+2hka^*b^*U_{12})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	60 (3)	74 (3)	28 (2)	8 (2)	1 (2)	−7 (2)
O(2)	118 (4)	49 (3)	51 (3)	−10 (2)	−5 (3)	16 (3)
O(3)	66 (3)	56 (3)	34 (2)	−2 (2)	−11 (2)	10 (2)
O(4)	62 (3)	89 (3)	42 (2)	5 (2)	11 (2)	−19 (2)
O(5)	56 (3)	64 (3)	43 (2)	1 (2)	−6 (2)	−10 (2)
O(6)	46 (3)	89 (3)	88 (3)	−29 (3)	−8 (2)	12 (2)
O(7)	65 (3)	71 (3)	52 (3)	−24 (2)	7 (2)	1 (2)
O(8)	75 (3)	59 (3)	57 (3)	17 (2)	−11 (2)	−10 (2)
O(9)	54 (3)	60 (3)	50 (2)	1 (2)	−12 (2)	−10 (2)
O(10)	85 (3)	71 (3)	34 (2)	6 (2)	−15 (2)	18 (2)
O(11)	82 (3)	47 (3)	51 (2)	−0 (2)	−15 (2)	11 (2)
N(1)	45 (3)	45 (3)	28 (2)	4 (2)	1 (2)	2 (2)
C(1)	38 (3)	45 (3)	38 (3)	4 (3)	6 (3)	3 (3)
C(2)	41 (3)	54 (4)	53 (4)	3 (3)	−2 (3)	8 (3)
C(3)	50 (4)	56 (4)	68 (4)	−2 (3)	8 (3)	5 (3)
C(4)	51 (4)	66 (5)	74 (5)	−1 (4)	12 (3)	2 (3)
C(5)	47 (4)	66 (4)	65 (4)	8 (4)	11 (3)	6 (3)
C(6)	50 (4)	53 (4)	41 (3)	6 (3)	8 (3)	12 (3)
C(7)	55 (4)	68 (4)	39 (3)	4 (3)	6 (3)	7 (3)
C(8)	58 (4)	57 (4)	30 (3)	5 (3)	7 (3)	5 (3)
C(9)	45 (3)	46 (4)	29 (3)	4 (2)	−1 (3)	2 (3)
C(10)	46 (3)	46 (3)	23 (3)	4 (2)	−1 (2)	4 (3)
C(11)	41 (3)	40 (3)	32 (3)	−4 (2)	−2 (2)	5 (3)
C(12)	41 (3)	39 (3)	35 (3)	1 (3)	2 (3)	2 (3)
C(13)	44 (3)	48 (3)	32 (3)	1 (3)	3 (3)	7 (3)
C(14)	44 (3)	47 (3)	25 (3)	2 (2)	0 (2)	2 (3)
C(15)	46 (3)	44 (3)	35 (3)	−3 (3)	−1 (3)	8 (3)
C(16)	40 (3)	44 (3)	32 (3)	−2 (2)	−2 (2)	−1 (3)
C(17)	42 (3)	50 (3)	25 (3)	2 (2)	1 (2)	1 (3)
C(18)	42 (3)	51 (4)	34 (3)	1 (3)	0 (3)	3 (3)
C(19)	93 (5)	99 (6)	27 (3)	−9 (3)	−18 (3)	3 (4)
C(20)	51 (4)	46 (4)	43 (3)	−3 (3)	−0 (3)	6 (3)
C(21)	46 (4)	81 (5)	80 (5)	4 (4)	−7 (4)	−24 (3)
C(22)	55 (4)	45 (4)	45 (3)	−5 (3)	−2 (3)	−2 (3)
C(23)	96 (6)	93 (6)	73 (5)	−33 (4)	35 (4)	4 (5)
C(24)	54 (4)	52 (4)	38 (3)	−3 (3)	−1 (3)	4 (3)
C(25)	59 (4)	70 (5)	88 (5)	−7 (4)	−9 (4)	−30 (3)
C(26)	41 (3)	54 (4)	36 (3)	4 (3)	5 (3)	9 (3)
C(27)	113 (6)	50 (4)	87 (5)	17 (4)	−8 (5)	20 (4)

Table 3. *Interatomic distances and e.s.d.'s* (Å)

O(1)—C(13)	1·229 (6)	C(3)—C(4)	1·417 (9)
O(2)—C(18)	1·195 (6)	C(4)—C(5)	1·382 (9)
O(3)—C(18)	1·321 (6)	C(5)—C(6)	1·412 (8)
O(3)—C(19)	1·490 (7)	C(6)—C(7)	1·425 (8)
O(4)—C(20)	1·192 (6)	C(7)—C(8)	1·389 (8)
O(5)—C(20)	1·351 (7)	C(8)—C(9)	1·424 (7)
O(5)—C(21)	1·459 (7)	C(9)—C(10)	1·386 (7)
O(6)—C(22)	1·192 (7)	C(10)–C(11)	1·385 (7)
O(7)—C(22)	1·330 (7)	C(10)–C(14)	1·486 (7)
O(7)—C(23)	1·477 (8)	C(11)–C(12)	1·426 (7)
O(8)—C(24)	1·206 (6)	C(11)–C(18)	1·499 (7)
O(9)—C(24)	1·338 (7)	C(12)–C(13)	1·448 (8)
O(9)—C(25)	1·481 (7)	C(12)–C(20)	1·459 (8)
O(10)–C(26)	1·182 (6)	C(13)–C(14)	1·522 (7)
O(11)–C(26)	1·334 (7)	C(14)–C(15)	1·567 (8)
O(11)–C(27)	1·474 (8)	C(14)–C(17)	1·560 (7)
N(1)—C(1)	1·396 (7)	C(15)–C(16)	1·550 (7)
N(1)—C(9)	1·366 (7)	C(15)–C(22)	1·517 (8)
N(1)—C(17)	1·494 (6)	C(16)–C(17)	1·548 (7)
C(1)—C(2)	1·397 (8)	C(16)–C(24)	1·503 (8)
C(1)—C(6)	1·402 (8)	C(17)–C(26)	1·533 (8)
C(2)—C(3)	1·403 (8)		

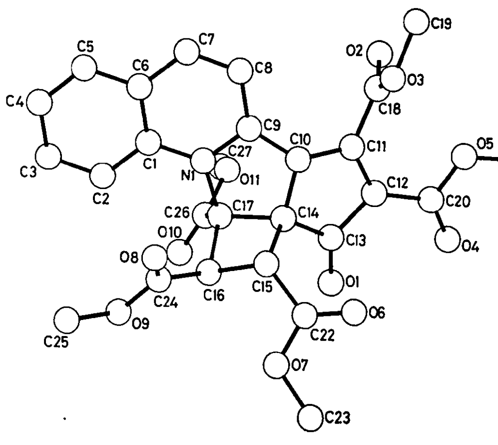
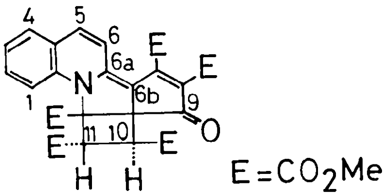
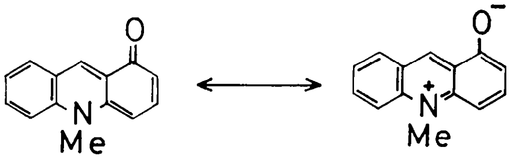


Fig. 1. Pentamethyl 11,11a-dihydro-9-oxo-9*H*,10*H*-cyclobuta[4,5]cyclopenta[3,4]pyrrolo[1,2-*a*]quinoline-7,8,10,11,11a-pentacarboxylate: atom designations.



(I)



(II) (III)

The NMR spectrum, at 60 MHz for $CDCl_3$ solutions, showed Ar–H_4, τ 2·38–2·85 m; ester-methyls, 6·16, 6·32, 6·34, 6·41, 6·67; 5-H, 3·26*d*; 6-H, 2·79*d*, $J_{5,6}$ 6·5 Hz; 10-H, 11-H, 5·03*d*, 6·10*d*, $J_{10,11}$ 10Hz. The dihedral angle between the bonds to these last H atoms is 170·7°, and the coupling constant is less than that expected on the basis of Karplus's equation. In the mass spectrometer the molecular ion (*m/e* 537, 22%) is seen and the base peak (*m/e* 393, 100%) corresponds to the concerted loss of dimethyl fumarate because a metastable peak is present at *m/e* 287·5.

We thank D. F. Nisbet for providing this material.

Table 4. *Interbond angles* (°), *e.s.d.'s* 0·4–1·4°

C(18)–O(3)—C(19)	115·3	C(12)–C(13)–C(14)	106·3
C(20)–O(5)—C(21)	115·8	C(10)–C(14)–C(13)	104·4
C(22)–O(7)—C(23)	114·9	C(10)–C(14)–C(15)	119·2
C(24)–O(9)—C(25)	116·7	C(10)–C(14)–C(17)	105·0
C(26)–O(11)–C(27)	115·8	C(13)–C(14)–C(15)	115·4
C(1)—N(1)—C(9)	123·8	C(13)–C(14)–C(17)	126·1
C(1)—N(1)—C(17)	123·9	C(15)–C(14)–C(17)	87·1
C(9)—N(1)—C(17)	112·0	C(14)–C(15)–C(16)	89·8
N(1)—C(1)—C(2)	121·3	C(14)–C(15)–C(22)	116·2
N(1)—C(1)—C(6)	117·3	C(16)–C(15)–C(22)	117·7
C(2)—C(1)—C(6)	121·4	C(15)–C(16)–C(17)	88·1
C(1)—C(2)—C(3)	119·2	C(15)–C(16)–C(24)	115·6
C(2)—C(3)—C(4)	119·4	C(17)–C(16)–C(24)	121·0
C(3)—C(4)—C(5)	121·0	N(1)—C(17)–C(14)	100·5
C(4)—C(5)—C(6)	119·8	N(1)—C(17)–C(16)	118·2
C(1)—C(6)—C(5)	119·1	N(1)—C(17)–C(26)	111·2
C(1)—C(6)—C(7)	119·8	C(14)–C(17)–C(16)	90·1
C(5)—C(6)—C(7)	121·1	C(14)–C(12)–C(26)	117·3
C(6)—C(7)—C(8)	121·3	C(16)–C(12)–C(26)	116·9
C(7)—C(8)—C(9)	118·2	O(2)—C(18)–O(3)	125·5
N(1)—C(9)—C(8)	119·4	O(2)—C(18)–C(11)	124·2
N(1)—C(9)—C(10)	110·4	O(3)—C(18)–C(11)	110·2
C(8)—C(9)—C(10)	130·2	O(4)—C(20)–O(5)	123·2
C(9)—C(10)–C(11)	136·1	O(4)—C(20)–C(12)	126·0
C(9)—C(10)–C(14)	108·8	O(5)—C(20)–C(12)	110·9
C(11)–C(10)–C(14)	109·2	O(6)—C(22)–O(7)	124·4
C(10)–C(11)–C(12)	110·6	O(6)—C(22)–C(15)	124·1
C(10)–C(11)–C(18)	122·0	O(7)—C(22)–C(15)	111·5
C(12)–C(11)–C(18)	126·7	O(8)—C(24)–O(9)	123·8
C(11)–C(12)–C(13)	108·5	O(8)—C(24)–C(16)	125·0
C(11)–C(12)–C(20)	127·9	O(9)—C(24)–C(16)	111·3
C(13)–C(12)–C(20)	123·5	O(10)–C(26)–O(11)	125·3
O(1)—C(13)–C(12)	130·2	O(10)–C(26)–C(17)	124·5
O(1)—C(13)–C(14)	123·4	O(11)–C(26)–C(17)	110·2

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