

Tetramethyl 7-[(E)-1,2-Dimethoxycarbonylvinyl]-1,3-dimethyl-7a,8,9,9a-tetrahydro-cyclobuta[4,5]pyrrolo[1,2-a]quinoline-7a,8,9,9a-tetracarboxylate

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Abstract. $C_{30}H_{28}NO_{12}$, $M_r = 594$, orthorhombic, $Pbca$, $a = 25.61$ (2), $b = 24.74$ (2), $c = 9.44$ (1) Å, $U = 5981$ Å³; $D_x = 1.30$, $D_c = 1.32$ g cm⁻³, $Z = 8$; $Mo K\alpha = 0.7107$ Å, $\mu = 1.1$ cm⁻¹, $R = 0.077$. An alternative structure for the title compound was originally postulated from the limited chemical and spectral data, which are also consistent with our new formulation.

Table 1. Fractional coordinates ($\times 10^4$)

Introduction. The red material (m.p. 224 °C) crystallized from methanol as rectangular plates. The crystal (0.4 × 0.2 × 0.4 mm) was mounted along **c**, perpendicular to a small face. The setting angles of 43 reflexions, measured on each side of the incident beam, were used in a least-squares calculation to give the cell parameters and orientation matrix. An azimuthal scan about the 004 scattering vector verified that an absorption correction was not necessary. Graphite-monochromated $Mo K\alpha$ radiation was used to observe 8694 reflexions, measured with an $\omega/2\theta$ scan and a modified ordinate-analysis method (Watson, Shotton, Cox & Muirhead, 1970) yielding 5265 reflexions. The merging $R [= \Sigma(I - \hat{I})/\Sigma \hat{I}]$ was 0.014 for the 3936 reflexions with $\hat{I} \geq 3\sigma(\hat{I})$. The structure was solved by direct methods (Sheldrick, 1973) and refined by least squares (block 1, all x, y, z ; block 2, all U_{ij} 's; block 3, all U_{ij} 's; block 4, scale factor and dummy overall temperature factor) (Carruthers, 1975). H atoms were ignored. The final R was 0.077 and the Hamilton weighted R 0.111.* Unit weights were used for reflexions with $|F_o| < 25$, otherwise weight = $25/|F_o|$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic positional parameters are listed in Table 1, and the bond lengths

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	993 (1)	1329 (1)	774 (3)
C(1)	655 (1)	1573 (1)	-200 (4)
C(2)	197 (1)	1326 (1)	-772 (4)
C(3)	-122 (1)	1641 (2)	-1633 (4)
C(4)	-21 (1)	2173 (2)	-2013 (4)
C(5)	452 (2)	2393 (2)	-1554 (4)
C(6)	787 (1)	2094 (1)	-682 (4)
C(7)	1294 (2)	2312 (2)	-330 (4)
C(8)	1624 (1)	2054 (1)	530 (4)
C(9)	1469 (1)	1560 (1)	1214 (4)
C(10)	1703 (1)	1273 (1)	2283 (4)
C(11)	1349 (1)	820 (1)	2760 (4)
C(12)	1501 (1)	242 (1)	2220 (4)
C(13)	1075 (1)	279 (1)	1054 (4)
C(14)	893 (1)	842 (1)	1618 (4)
C(15)	35 (2)	737 (2)	-621 (5)
C(16)	-393 (2)	2486 (2)	-2950 (6)
C(17)	2201 (1)	1350 (1)	2968 (4)
C(18)	2374 (1)	1009 (2)	4000 (4)
C(19)	2858 (2)	1035 (2)	4777 (5)
C(20)	3675 (2)	1477 (3)	5114 (8)
C(21)	2529 (1)	1816 (1)	2506 (4)
C(22)	2754 (3)	2729 (2)	2934 (7)
C(23)	1165 (1)	864 (1)	4290 (4)
C(24)	855 (4)	1459 (3)	6045 (6)
C(25)	1429 (2)	-242 (1)	3201 (4)
C(26)	1811 (3)	-710 (2)	5129 (7)
C(27)	1293 (2)	236 (2)	-441 (4)
C(28)	1951 (2)	497 (3)	-2039 (5)
C(29)	358 (1)	881 (1)	2344 (4)
C(30)	-291 (2)	420 (2)	3603 (6)
O(1)	2976 (1)	722 (2)	5707 (4)
O(2)	3173 (1)	1438 (1)	4398 (4)
O(3)	2820 (1)	1804 (1)	1504 (3)
O(4)	2446 (1)	2252 (1)	3290 (3)
O(5)	1063 (1)	495 (1)	5036 (3)
O(6)	1103 (2)	1370 (1)	4658 (3)
O(7)	1076 (1)	-558 (1)	3159 (3)
O(8)	1833 (1)	-275 (1)	4083 (3)
O(9)	1122 (2)	-84 (2)	-1286 (4)
O(10)	1695 (1)	551 (1)	-671 (3)
O(11)	150 (1)	1303 (1)	2577 (4)
O(12)	188 (1)	407 (1)	2771 (3)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32267 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and angles, with estimated standard deviations computed from the full variance-covariance matrix, in Tables 2 and 3. Fig. 1 shows the molecular geometry and the atom designations. Structure II indicates the conventional numbering.

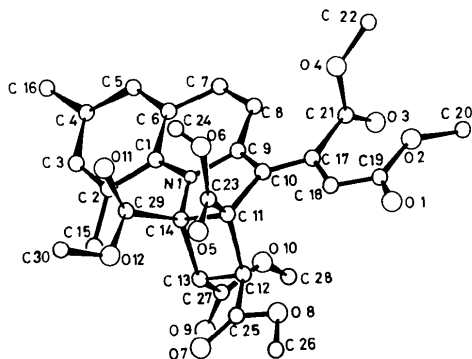


Fig. 1. The structure of the title compound showing the atom designations used in this paper.

Table 2. *Interatomic distances and e.s.d.'s (Å)*

N(1)—C(1)	1.399 (4)	C(6)—C(7)	1.446 (5)
N(1)—C(9)	1.407 (4)	C(7)—C(8)	1.335 (5)
N(1)—C(14)	1.467 (4)	C(8)—C(9)	1.438 (5)
C(1)—C(2)	1.428 (5)	C(9)—C(10)	1.373 (5)
C(1)—C(6)	1.409 (5)	C(10)—C(11)	1.510 (5)
C(2)—C(3)	1.391 (5)	C(10)—C(17)	1.442 (5)
C(2)—C(15)	1.520 (5)	C(11)—C(12)	1.566 (5)
C(3)—C(4)	1.390 (6)	C(11)—C(14)	1.592 (5)
C(4)—C(5)	1.397 (6)	C(12)—C(13)	1.554 (5)
C(4)—C(16)	1.513 (6)	C(13)—C(14)	1.564 (5)
C(5)—C(6)	1.400 (5)	C(17)—C(18)	1.362 (5)

Carboxylate group interatomic distances (Å) (all e.s.d.'s 0.005 Å)

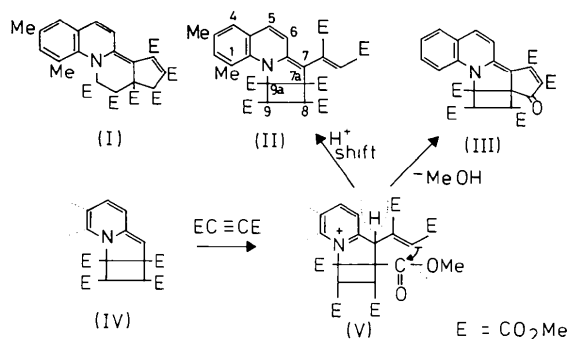
Ketonic oxygen	C=O	C—O	C—C	O—Me
O(1)	1.210	1.332	1.441	1.455
O(3)	1.205	1.324	1.493	1.459
O(5)	1.184	1.308	1.523	1.472
O(7)	1.197	1.331	1.525	1.462
O(9)	1.207	1.309	1.521	1.455
O(11)	1.192	1.314	1.533	1.458

Table 3. *Interbond angles (°) and e.s.d.'s (×10)*

C(1)—N(1)—C(9)	123.7 (3)	C(11)—C(10)—C(17)	119.7 (3)	C(18)—C(19)—O(2)	114.7 (4)
C(1)—N(1)—C(14)	127.0 (3)	C(10)—C(11)—C(12)	115.5 (3)	O(1)—C(19)—O(2)	121.5 (4)
C(9)—N(1)—C(14)	108.9 (3)	C(10)—C(11)—C(14)	102.3 (3)	C(19)—O(2)—C(20)	117.4 (4)
N(1)—C(1)—C(2)	124.9 (3)	C(10)—C(11)—C(23)	114.5 (3)	C(17)—C(21)—O(3)	124.0 (3)
N(1)—C(1)—C(6)	117.3 (3)	C(12)—C(11)—C(14)	89.7 (3)	C(17)—C(21)—O(4)	112.0 (3)
C(2)—C(1)—C(6)	117.8 (3)	C(12)—C(11)—C(23)	116.9 (3)	O(3)—C(21)—O(4)	123.9 (3)
C(1)—C(2)—C(3)	117.6 (3)	C(14)—C(11)—C(23)	114.4 (3)	C(21)—O(4)—C(22)	116.3 (4)
C(1)—C(2)—C(15)	126.8 (3)	C(11)—C(12)—C(13)	90.2 (3)	C(11)—C(23)—O(5)	125.2 (3)
C(15)—C(2)—C(3)	115.5 (3)	C(11)—C(12)—C(25)	119.3 (3)	C(11)—C(23)—O(6)	111.1 (3)
C(2)—C(3)—C(4)	125.0 (4)	C(13)—C(12)—C(25)	113.0 (3)	O(5)—C(23)—O(6)	123.6 (4)
C(3)—C(4)—C(5)	116.7 (4)	C(12)—C(13)—C(14)	91.2 (3)	C(23)—O(6)—C(24)	115.6 (4)
C(3)—C(4)—C(16)	121.3 (4)	C(12)—C(13)—C(27)	113.3 (3)	C(12)—C(25)—O(7)	125.8 (4)
C(16)—C(4)—C(5)	121.9 (4)	C(14)—C(13)—C(27)	119.1 (3)	C(12)—C(25)—O(8)	109.5 (3)
C(4)—C(5)—C(6)	120.5 (4)	C(13)—C(14)—N(1)	119.6 (3)	O(7)—C(25)—O(8)	124.6 (4)
C(5)—C(6)—C(7)	119.2 (3)	C(13)—C(14)—C(11)	88.9 (3)	C(25)—O(8)—C(26)	116.0 (4)
C(5)—C(6)—C(1)	121.8 (3)	C(13)—C(14)—C(29)	118.2 (3)	C(13)—C(27)—O(9)	121.7 (4)
C(7)—C(6)—C(1)	118.9 (3)	N(1)—C(14)—C(11)	105.6 (3)	C(13)—C(27)—O(10)	113.7 (3)
C(6)—C(7)—C(8)	121.9 (3)	N(1)—C(14)—C(29)	110.4 (3)	O(9)—C(27)—O(10)	124.8 (4)
C(7)—C(8)—C(9)	120.4 (3)	C(11)—C(14)—C(29)	110.8 (3)	C(27)—O(10)—C(28)	116.5 (4)
C(8)—C(9)—N(1)	116.9 (3)	C(10)—C(17)—C(18)	121.8 (3)	C(14)—C(29)—O(11)	122.4 (3)
C(8)—C(9)—C(10)	130.4 (3)	C(10)—C(17)—C(21)	118.0 (3)	C(14)—C(29)—O(12)	112.2 (3)
N(1)—C(9)—C(10)	112.7 (3)	C(17)—C(18)—C(19)	128.0 (4)	O(11)—C(29)—O(12)	125.2 (4)
C(9)—C(10)—C(11)	109.9 (3)	C(18)—C(19)—O(1)	123.8 (4)	C(29)—O(12)—C(30)	115.1 (4)
C(9)—C(10)—C(17)	130.4 (3)				

Discussion. Several 2-methylquinolines react with dimethyl acetylenedicarboxylate to yield a mixture of products, including dark-red 1:3 molar adducts having closely similar UV and NMR spectra. The highest yield of these adducts is obtained with methanol as the reaction medium (Acheson & Nisbet, 1973). Two dark-red adducts, obtained from 2,6,8-trimethylquinoline, have been previously assigned geometrically isomeric struc-

tures based on (I). For one of these, the 'first' red adduct (m.p. 224°C) (Acheson & Nisbet, 1973), the structure has now been determined and the new formulation (II) requires the revision, by analogy, of all the structures given for a number of compounds of this type. The 'second' red adduct (m.p. 252°C), corresponding to structure II, probably differs only in that the side chain possesses the *Z* arrangement.



The new structure is closely related to that of a purple compound (m.p. 227–230°C) obtained from quinoline and for which structure III has been determined (Abbott, Acheson, Forder, Watkin & Carruthers, 1976). The partial structure IV can be easily built up from 2-methylquinolines and the acetylenic ester by known processes (Acheson, 1976). (IV), as an enamine (Dyke, 1973; Cook, 1969), with more of the ester could yield the ylide (V). This could either cyclize as indicated and lose methanol to give the purple series of compounds [e.g. (III)] or undergo addition and loss of a proton to give dark-red compounds such as (II).

The NMR coupling constants for the 8 and 9 protons of (II) and the corresponding 10 and 11 protons of (III) have been measured. Karplus* deduced a relationship between the coupling constant and the dihedral angle subtended by vicinal H atoms, and pointed out that other factors could also affect the coupling constant. The dihedral angles for those protons in (II) and (III) are 108.0 and 123.9° (not 170.7° as previously reported), and as for some other cyclobutanes with strongly electronegative substituents (Georgian, Georgian & Robertson, 1963) the simple form of Karplus's equation does not accommodate our data.

The system containing all the quinoline and five-membered ring atoms, and the side chain including the C and O atoms of the terminal ester group (Table 2), is essentially coplanar (Table 4). The slight but observable twist is probably because of the short non-bonded contacts C(15)···C(29) (2.94 Å) and C(8)···C(21) (3.03 Å). This is consistent with the presence of a strong resonance interaction involving the N atom and the ester carbonyl O atom. For (III) this type of resonance could involve the corresponding 8-ester group, and/or the 9-carbonyl group as suggested earlier. Mean planes were computed for both cases (Table 4) with results indicating that neither conjugated system has a marked planarity advantage.

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

Table 4. Deviations (Å × 10²) of atoms from the mean planes

Atoms in (II): deviation from the plane with equation

$$-12.20x + 11.99y + 6.93z = 1.01$$

N(1)	-9	C(8)	-16	C(18)	8
C(1)	-6	C(9)	-9	C(19)	6
C(2)	-19	C(10)	2	C(20)	-18
C(3)	-2	C(11)	24	C(21)	-18
C(4)	23	C(14)	3	O(1)	18
C(5)	23	C(15)	-60	O(2)	-11
C(6)	7	C(16)	41		
C(7)	-4	C(17)	-2		

Atoms in (III): deviation from the plane with equation

$$4.29x - 13.16y - 1.51z = 1.71$$

N(1)*	-21	C(11)	6	C(21)	9
C(9)	-10	C(12)	11	O(4)	2
C(10)	33	C(20)	0	O(5)	7

Atoms in (III): deviation from the plane with equation

$$3.62x - 13.57y - 0.47z = 0.89$$

N(1)*	-13	C(11)	7	O(1)	0
C(9)	-2	C(12)	15		
C(10)	28	C(13)	8		

* See Abbott *et al.* (1976) for atom numbering.

* See Jackman & Sternhell (1969).

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