

- MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1972). *LSAM: A System of Computer Programs for the Automatic Solution of Centrosymmetric Crystal Structures*. Department of Physics, Univ. of York, York, England.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 93. Ithaca: Cornell Univ. Press.
- SHEEHAN, W. F. JR & SCHOMAKER, V. (1952). *J. Amer. Chem. Soc.* **74**, 3956.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. London: Macmillan.
- YANG, M. H. & LIU, S. L. (1975). *J. Chin. Chem. Soc.* **22**, 41–47.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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## Tetramethyl 3-Bromo-7a,8,9,9a-tetrahydrocyclobuta[4,5]pyrrolo[1,2-a]quinoline-7,r-7a,t-9,c-9a-tetracarboxylate

BY R. MORRIN ACHESON AND GARRY PROCTER

*Department of Biochemistry, South Parks Road, Oxford, OX1 3QU, England*

AND STEPHEN R. CRITCHLEY

*Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, England*

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**Abstract.**  $C_{22}H_{20}NO_8Br$ , monoclinic,  $P2_1/c$ ,  $a = 10.088$  (5),  $b = 12.307$  (5),  $c = 17.482$  (8) Å,  $\beta = 83.27$  (2)°,  $Z = 4$ ,  $D_m = 1.56$ ,  $D_c = 1.556$  g cm<sup>-3</sup>,  $\mu = 20.46$  cm<sup>-1</sup> (Mo  $K\alpha$  radiation). The X-ray crystal structure of one adduct from 6-bromo-2-methylquinoline and dimethyl acetylenedicarboxylate shows that it possesses a fused 5:4 ring system in place of the seven-membered ring postulated previously, and consequently the published structures of many similar adducts must be revised.

**Introduction.** The title compound was prepared by R. F. Flowerday by the published method (Acheson, Gagan & Harrison, 1968), and crystallized from methanol.

Weissenberg photographs gave the systematic absences  $h0l$  for  $l$  odd,  $0k0$  for  $k$  odd, which uniquely determined the space group. A crystal ( $1.5 \times 0.2 \times 0.4$  mm) was mounted on a Hilger & Watts Y290 four-circle diffractometer fitted with a monochromator. Accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 16 reflexions (Dobler & Duerr, 1969) and a complete data set was collected with Mo  $K\alpha$  radiation to  $2\theta \leq 60^\circ$  by an  $\omega/2\theta$  scan, ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 50 steps of  $0.02^\circ$ . 3561 independent reflexions were measured of which 2154 were considered observed [ $I > 3\sigma(I)$ ]. Lorentz and polarization corrections were applied, as was an empirical absorption correction (North, Phillips & Mathews, 1968).

The structure was solved by the heavy-atom method, and refined by full-matrix least squares to  $R = 0.134$  with isotropic temperature factors. Further refinement with anisotropic thermal motion led to the location of all the H atoms except H(163) (placed by calculation), from a difference synthesis. Further blocked-matrix refinement with H atoms included with isotropic temperature factors fixed at  $0.05$  Å<sup>2</sup>, and weights  $w = \{[(F_o - 0.30)/0.35]^2\}^{-1}$ , gave a final  $R = 0.051$ . The H atoms were constrained so that all C–H lengths were  $1.00 \pm 0.02$  Å, and all individual  $X_n$ –C–H angles ( $X = O, C, H$ ) were equal ( $\pm 2^\circ$ ) to the mean of each group (Carruthers, 1975). Anomalous scattering factors were included for Br during the final refinements.

Final atomic coordinates are listed in Table 1. Fig. 1 shows the molecular geometry, omitting the H atoms.\* Tables 2, 3 and 4 give bond distances, bond angles and deviations from the best plane.

**Discussion.** The reaction of 2-methylquinoline with dimethyl acetylenedicarboxylate was investigated by Diels & Alder (1934) who tentatively proposed a structure with which they were not satisfied. Acheson *et al.* (1968) suggested azepine structures such as (1) for this and related compounds, on the basis of UV, NMR and mass spectra. A scheme for the formation of most of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32309 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

these compounds (Acheson & Flowerday, 1975) was suggested, but the route to the title compound involved a non-stabilized carbanion, which would be energetically unfavourable.

The structure is in fact (2), for which an attractive synthetic pathway may be written (Acheson, Procter & Critchley, 1976). The planarity of the conjugated system (Table 4) is strong evidence for extensive

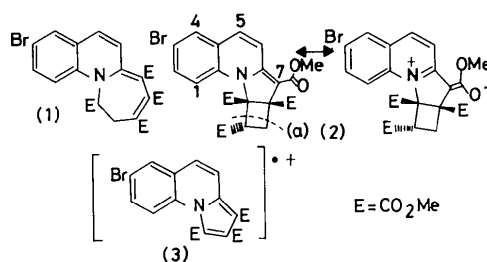


Table 1. Final atomic coordinates with estimated standard deviations in parentheses

	x	y	z
Br(3)	0.10475 (7)	0.36881 (6)	0.73930 (4)
O(1)	0.8866 (4)	0.0403 (4)	0.3578 (2)
O(2)	0.6727 (4)	0.0422 (3)	0.3344 (2)
O(3)	1.0587 (4)	0.2180 (4)	0.4683 (3)
O(4)	0.9042 (4)	0.2958 (3)	0.4049 (2)
O(5)	0.6376 (4)	0.0525 (3)	0.6827 (2)
O(6)	0.7220 (4)	0.1796 (3)	0.7543 (2)
O(7)	0.8572 (5)	0.3987 (3)	0.5826 (3)
O(8)	0.6780 (4)	0.4083 (3)	0.5184 (3)
N(10)	0.6047 (4)	0.2058 (3)	0.5478 (2)
C(1)	0.4996 (6)	0.3020 (5)	0.6603 (3)
C(2)	0.3831 (6)	0.3380 (5)	0.7037 (4)
C(3)	0.2610 (5)	0.3155 (5)	0.6799 (3)
C(4)	0.2506 (5)	0.2553 (5)	0.6138 (3)
C(4a)	0.3659 (5)	0.2185 (4)	0.5697 (3)
C(5)	0.3616 (5)	0.1570 (4)	0.5002 (3)
C(6)	0.4733 (5)	0.1221 (4)	0.4576 (3)
C(6a)	0.6016 (5)	0.1476 (4)	0.4798 (3)
C(7)	0.7287 (5)	0.1244 (4)	0.4469 (3)
C(7a)	0.8285 (5)	0.1655 (4)	0.4969 (3)
C(8)	0.8673 (6)	0.0903 (5)	0.5617 (3)
C(9)	0.8055 (5)	0.1723 (4)	0.6238 (3)
C(9a)	0.7407 (5)	0.2343 (4)	0.5599 (3)
C(10a)	0.4911 (5)	0.2420 (4)	0.5931 (3)
C(11)	0.7711 (5)	0.0655 (4)	0.3770 (3)
C(12)	0.7120 (7)	-0.0151 (6)	0.2637 (4)
C(13)	0.9459 (5)	0.2270 (5)	0.4556 (3)
C(14)	1.0032 (7)	0.3671 (6)	0.3653 (5)
C(15)	0.7132 (6)	0.1268 (5)	0.6891 (3)
C(16)	0.6318 (8)	0.1468 (6)	0.8199 (4)
C(17)	0.7658 (6)	0.3577 (5)	0.5570 (3)
C(18)	0.6999 (9)	0.5246 (5)	0.5071 (5)
H(11)	0.588 (2)	0.319 (5)	0.677 (3)
H(21)	0.388 (2)	0.375 (5)	0.754 (2)
H(41)	0.161 (2)	0.239 (5)	0.598 (3)
H(51)	0.273 (2)	0.145 (5)	0.481 (2)
H(61)	0.468 (2)	0.077 (5)	0.411 (3)
H(81)	0.966 (2)	0.085 (3)	0.564 (2)
H(82)	0.813 (3)	0.022 (2)	0.566 (2)
H(91)	0.876 (2)	0.217 (2)	0.644 (1)
H(121)	0.778 (4)	0.031 (3)	0.230 (2)
H(122)	0.755 (5)	-0.085 (2)	0.276 (2)
H(123)	0.630 (2)	-0.029 (4)	0.238 (2)
H(141)	0.979 (4)	0.390 (3)	0.314 (2)
H(142)	1.014 (4)	0.434 (2)	0.395 (2)
H(143)	1.094 (2)	0.334 (3)	0.357 (3)
H(161)	0.536 (2)	0.157 (4)	0.812 (2)
H(162)	0.642 (4)	0.068 (2)	0.833 (2)
H(163)	0.647 (4)	0.187 (3)	0.867 (1)
H(181)	0.638 (4)	0.552 (2)	0.471 (2)
H(182)	0.795 (2)	0.536 (2)	0.485 (3)
H(183)	0.683 (5)	0.562 (2)	0.558 (1)

Table 2. Interatomic distances (Å) and estimated standard deviations

For H atom constraints, see text. All C—H distances in ester methyl groups are in the range 0.992–1.006 (19) Å.

Br(3)—C(3)	1.902 (5)	C(4a)—C(10a)	1.402 (7)
O(1)—C(11)	1.215 (6)	C(5)—H(51)	1.000 (19)
O(2)—C(11)	1.341 (6)	C(5)—C(6)	1.347 (8)
O(2)—C(12)	1.439 (7)	C(6)—H(61)	1.002 (19)
O(3)—C(13)	1.190 (6)	C(6)—C(6a)	1.429 (6)
O(4)—C(13)	1.333 (7)	C(6a)—N(10)	1.393 (7)
O(4)—C(14)	1.447 (8)	C(6a)—C(7)	1.374 (7)
O(5)—C(15)	1.209 (6)	C(7)—C(7a)	1.498 (7)
O(6)—C(15)	1.327 (7)	C(7)—C(11)	1.443 (8)
O(6)—C(16)	1.436 (8)	C(7a)—C(8)	1.552 (8)
O(7)—C(17)	1.185 (6)	C(7a)—C(9a)	1.580 (8)
O(8)—C(17)	1.331 (7)	C(7a)—C(13)	1.518 (8)
O(8)—C(18)	1.467 (8)	C(8)—H(81)	1.003 (19)
C(1)—H(11)	0.995 (19)	C(8)—H(82)	1.005 (19)
C(1)—C(2)	1.395 (8)	C(8)—C(9)	1.562 (9)
C(1)—C(10a)	1.401 (8)	C(9)—H(91)	0.999 (19)
C(2)—H(21)	0.993 (19)	C(9)—C(9a)	1.561 (7)
C(2)—C(3)	1.375 (8)	C(9)—C(15)	1.495 (9)
C(3)—C(4)	1.389 (8)	C(9a)—N(10)	1.457 (6)
C(4)—H(41)	0.997 (19)	C(9a)—C(17)	1.549 (8)
C(4)—C(4a)	1.395 (8)	N(10)—C(10a)	1.389 (7)
C(4a)—C(5)	1.440 (8)		

delocalization of charge on to the ester group in the 7-position. This can be associated with the very long wavelength absorption at 498 nm, which might be charge transfer in nature. The mass spectrum of (2) shows a base peak corresponding to concerted loss of the methyl acrylate residue, by cleavage at (a) to give the stable indolizinium system (3).

The <sup>1</sup>H NMR spectrum shows very-high-field reso-

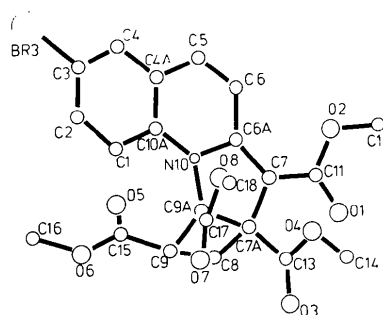


Fig. 1. Molecular geometry with H atoms omitted.

Table 3. *Interbond angles (°), with estimated standard deviations in parentheses (H atoms omitted)*

C(11)—O(2)—C(12)	115.85 (46)	C(7a)—C(8)—C(9)	90.17 (41)
C(13)—O(4)—C(14)	116.99 (50)	C(8)—C(9)—C(9a)	89.36 (40)
C(15)—O(6)—C(16)	116.53 (50)	C(8)—C(9)—C(15)	116.52 (48)
C(17)—O(8)—C(18)	115.64 (52)	C(9a)—C(9)—C(15)	117.13 (45)
C(2)—C(1)—C(10a)	119.63 (53)	C(7a)—C(9a)—C(9)	89.22 (39)
C(3)—C(2)—C(1)	119.89 (56)	C(7a)—C(9a)—N(10)	103.16 (38)
Br(3)—C(3)—C(2)	118.62 (46)	C(7a)—C(9a)—C(17)	115.67 (45)
Br(3)—C(3)—C(4)	120.14 (43)	C(9)—C(9a)—N(10)	117.74 (44)
C(2)—C(3)—C(4)	121.24 (51)	C(9)—C(9a)—C(17)	115.38 (42)
C(3)—C(4)—C(4a)	119.70 (52)	N(10)—C(9a)—C(17)	112.83 (43)
C(4)—C(4a)—C(5)	122.26 (49)	C(6a)—N(10)—C(9a)	111.45 (41)
C(4)—C(4a)—C(10a)	119.48 (51)	C(6a)—N(10)—C(10a)	123.66 (41)
C(5)—C(4a)—C(10a)	118.26 (48)	C(9a)—N(10)—C(10a)	124.51 (42)
C(4a)—C(5)—C(6)	121.99 (49)	C(1)—C(10a)—C(4a)	120.03 (48)
C(5)—C(6)—C(6a)	120.30 (51)	C(4a)—C(10a)—N(10)	118.52 (46)
C(6)—C(6a)—C(7)	132.07 (50)	O(1)—C(11)—O(2)	122.64 (52)
C(6)—C(6a)—N(10)	117.24 (46)	O(1)—C(11)—C(7)	122.85 (50)
C(7)—C(6a)—N(10)	110.68 (43)	O(2)—C(11)—C(7)	114.50 (45)
C(6a)—C(7)—C(7a)	109.99 (46)	O(3)—C(13)—O(4)	124.61 (56)
C(6a)—C(7)—C(11)	129.04 (47)	O(3)—C(13)—C(7a)	125.02 (56)
C(7a)—C(7)—C(11)	120.91 (44)	O(4)—C(13)—C(7a)	110.33 (44)
C(7)—C(7a)—C(8)	117.82 (45)	O(5)—C(15)—O(6)	124.15 (58)
C(7)—C(7a)—C(9a)	103.35 (39)	O(5)—C(15)—C(9)	124.04 (53)
C(7)—C(7a)—C(13)	115.66 (46)	O(6)—C(15)—C(9)	111.79 (49)
C(8)—C(7a)—C(9a)	89.04 (41)	O(7)—C(17)—O(8)	125.61 (58)
C(8)—C(7a)—C(13)	113.52 (43)	O(7)—C(17)—C(9a)	122.81 (54)
C(9a)—C(7a)—C(13)	113.76 (43)	O(8)—C(17)—C(9a)	111.45 (45)

Table 4. *Deviations from the best plane (Å)*

The equation of the best plane is  
 $0.162x - 10.635y + 8.930z = 2.775.$

C(1)	-0.09	C(5)	0.08	N(10)	0.03
C(2)	-0.02	C(6)	0.09	C(10a)	0.03
C(3)	-0.02	C(6a)	0.04	C(11)	0.02
Br(3)	-0.09	C(7)	0.01	C(12)	-0.15
C(4)	0.03	C(7a)	0.04	O(1)	0.14
C(4a)	0.05	C(9a)	-0.15	O(2)	0.13

nances for the proton at position 1, and the 9-ester methyl group. These features are readily accounted for by shielding of the ester methyl group by the aromatic system, and the 1-hydrogen atom by the 9-ester carbonyl group. The <sup>13</sup>C NMR spectrum shows resonances at  $\delta 57.60$  and  $78.20$  p.p.m. for the C atoms at 7a and 9a respectively. Comparison with the <sup>13</sup>C NMR spectra of many other adducts previously assigned structures similar to (1) [for references see Acheson *et*

*al.* (1976)] has shown that these adducts are actually analogous to (2) and a full discussion will be presented later.

#### References

- ACHESON, R. M. & FLOWERDAY, R. F. (1975). *J. Chem. Soc. Perkin I*, pp. 394–396.
- ACHESON, R. M., GAGAN, J. M. F. & HARRISON, D. R. (1968). *J. Chem. Soc. (C)*, pp. 362–378.
- ACHESON, R. M., PROCTER, G. & CRITCHLEY, S. R. (1976). *Chem. Commun.* pp. 692–693.
- CARRUTHERS, J. R. (1975). *CRYSTALS User Manual*, Oxford Univ. Computing Laboratory.
- DIELS, O. & ALDER, K. (1934). *Liebigs Ann.* **510**, 87–128 and earlier papers.
- DOBLER, M. & DUERR, B. (1969). Personal communication.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- WATSON, H. C., SHOTTON, D. M., COX, J. M. & MUIRHEAD, H. (1970). *Nature, Lond.* **225**, 806–811.