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X-Ray Crystallographic Study of α-Brominated Diketo Tetraquinanes. Conformational Effects of the Number of Halogens and their Position on Bond Length and Solid-State Conformation

Leo A. Paquette,* Bruce M. Branan, and Robin D. Rogers*[1]

Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210 and Northern Illinois University, DeKalb, Illinois 60115

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Abstract: Halogenative substitution of tetracyclo[$7.2.1.0^{4,11}.0^{6,10}$]dodecane-5,12-dione with copper(II) bromide or molecular bromine has provided synthetic entry to the monobromo, 1,4- and 1,6-dibromo, 1,4,6-tribromo, and 1,4,6,9-tetrabromo derivatives. X-ray structural analysis of the latter four compounds has shown bond lengths and bond angles not to be greatly affected by the number of bromine atoms or their relative position. On the other hand, conformational preferences are seen to vary appreciably with substitution pattern across the series.

The detailed structural features of various classes of polyquinanes have held fascination since the explosive growth of this area of chemistry began approximately two decades ago.[2] Some of the landmark molecules examined crystallographically include triquinacene,[3] *dl*- and *meso*-bivalvane,[4] elassovalene,[5] C_{16}-hexaquinacene,[6] [4]peristylanes,[7] dodecahedrane,[8] and derivatives of this completely spherical C_{20} molecule.[9]

Recently, controversy has arisen over the ground-state electronic structure of triquinacene (1). Heats of hydrogenation studies performed on 1 and its partially saturated congeners have given evidence of a 4.5 kcal/mol irregularity during the conversion of 1 to 2, not seen in the further reduction of 2 or of the tetrahydro derivative to 3.[10] Computational evaluation of these findings[11,12] has more recently suggested that the root cause of this energy difference resides not in the existence of neutral homoaromatic stabilization within 1 as originally assumed, but to the fact that the planar cyclopentene rings in 1 become twisted upon saturation.[13]

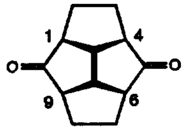

1


2


3

The question of structural distortion in molecules constructed uniquely of five-membered rings is one in which we have had an abiding interest.[9,14] Notwithstanding, information concerning the manner and direction in which polar groups attached to a central polyquinane core might modify bond lengths, bond angles, and/or the general topography of the ring system remains obscure. As already noted, progressive saturation of the olefinic linkages in 1 induces fundamental conformational changes of considerable importance. However, triene 1 is the only member of this series so far subjected to crystallographic scrutiny.

In this connection, the bromination of diketone 4 has now been studied in an effort to obtain several halogenated derivatives, which we surmised would be adequately crystalline for X-ray structural analysis. Placement on the tetracyclo[$7.2.1.0^{4,11}.0^{6,10}$]dodecane-5,12-dione framework of an increasing number of α-bromine substituents was intended to alter electron density most notably in the vicinity of the carbonyl groups and



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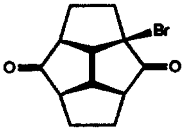

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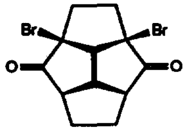

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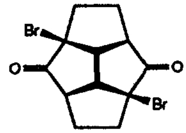

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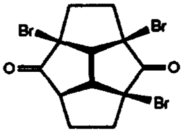

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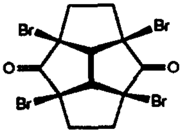

9

to introduce steric factors at positions 1, 4, 6, and 9 that could have conformational consequences. The synthesis of 5-9 and single crystal X-ray data for four of these brominated diketones form the subject of this paper.

Results and Discussion

Diketone 4, readily available by hydrogenation of the previously characterized doubly unsaturated precursor,[15] was the starting material of choice. Heating 4 with 2 equiv of copper(II) bromide in an ethyl acetate-chloroform solvent system[16] resulted in conversion to a mixture of monobromide 5 and dibromides 6 and 7. Chromatographic separation on silica gel provided pure samples in isolated yields of 42, 7, and 10%, respectively. Suitable distinction between the latter two isomers was achieved by ^{13}C NMR analysis, the C_s-symmetric 6 giving rise to seven distinct signals and the C_2-symmetric 7 to only six.

Tribromo derivative 8 was produced at reasonable levels when the proportion of $CuBr_2$ was increased to 3 equiv under otherwise identical conditions. To arrive at exhaustively brominated diketone 9, it proved most expedient to heat 4 with excess bromine in acetic acid.[17] All of the bromine-containing products were colorless solids.

The crystals of dibromo diketone 6, obtained from ether, were assigned to the $P2_1/c$ space group from the systematic absences. In this instance, X-ray analysis[18] confirmed the basic skeletal features and, in addition, revealed the ethano bridges in the non-oxygenated five-membered rings to be staggered (Figure 1). As a result, these cyclopentane subunits are twisted.

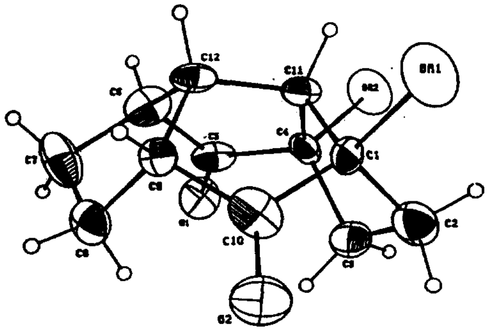

Figure 1. ORTEP drawing of 6.

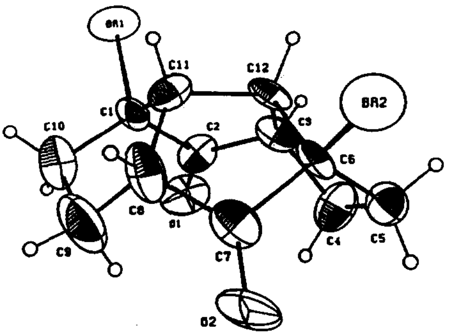

Figure 2. ORTEP drawing of 7.

The isomeric dibromide 7 was also recrystallized from ether. The crystals belonged to the Pbca space group, as confirmed by successful solution and refinement of the structure. The arrangement in the crystal is shown in Figure 2. The similarities in the conformations of 6 and 7 are rather striking. The torsion angles involving the two non-bromide substituted bridgehead carbons reflect most sensitively the extent of twisting in the two cyclopentane rings. Thus, the H-C-C-H angle is -15.1° for 6 and -18.1° for 7. For comparison, the average C-C-C-C torsion angles are -15.9° (6) and -14.3° (7).

The structures for 8 and 9 were successfully refined in the $P2_1/n$ and Pnma space groups, respectively (Figures 3 and 4). The details of X-ray collection for all four compounds are collected in Table I. In contrast to 6 and 7, the more highly brominated diketones reside in an eclipsed conformation, with 9 actually having crystallographic mirror symmetry. (The $C\text{-}CH_2CH_2\text{-}C$ torsion angles remain, however, in the narrow range of 31.3-38.6° for all four compounds). This mirror plane bisects the C(7)-C(7)' bond. Tribromide 8 has pseudomirror symmetry broken only by the one unsubstituted position. This is reflected again in the H-C-C-H and C-C-C-C torsion angles involving the bridgehead positions, which are either 0.0° by symmetry in 9 or very nearly so in 8 (-1.5° and 0.95°, respectively).

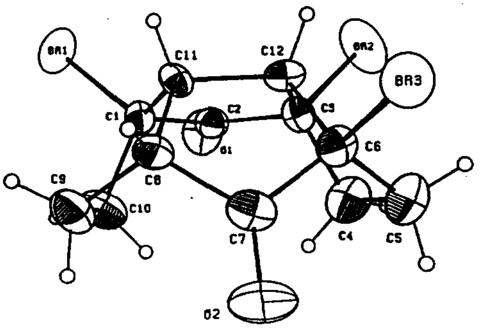

Figure 3. ORTEP drawing of 8.

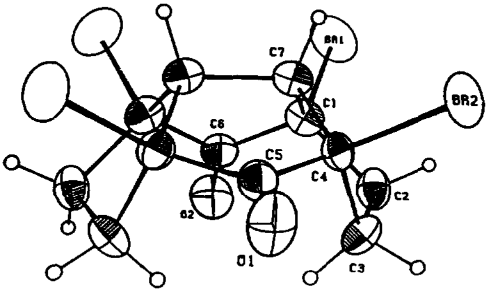

Figure 4. ORTEP drawing of 9.

The actual bond lengths and angles are not significantly different in the four compounds, nor do the average bonding parameters exhibit any obvious trends. The data presented in Table II have a narrow range within each category, at a less than 3σ confidence level of being different.

On the other hand, major conformational differences separate the two dibromo compounds from the tri- and tetra-brominated derivatives. Side views of 6-9 modeled with SYBYL software (Figure 5) clearly reveal the conformational differences. An analysis of the planes defined in Table III is presented in Table IV. These angles between planes reflect those portions of molecules 6-9 sensitive to the substitution pattern. First, the twisting of the skeletal framework is reflected in the rms deviations from the defined planes. The planes defined by the bridgehead carbons and the two carbons bonded to each carbonyl group (planes 3 and 4), those defined by two carbons bonded to one carbonyl group and the two ethano carbon atoms bonded to them (planes 5,6), and the planes defined by the four carbon atoms bonded to carbonyl groups are all significantly less planar in 6 *and* 7 than in 8 *and* 9. The ethano carbon atoms form planes in 8 *and* 9 consistent with their eclipsed confirmation.

The major conformational differences are reflected in the relative bending of the planes defined by the C-C(O)-C group (planes 1 and 2). The most prominent difference between 6/7 and 8/9 occurs in the angle between

Table I. Summary of Data Collection and Structure Refinement Parameters.

	6	**7**	**8**	**9**
molecular formula	$C_{12}H_{12}Br_2O_2$	$C_{12}H_{12}Br_2O_2$	$C_{12}H_{11}Br_3O_2$	$C_{12}H_{10}Br_4O_2$
for. wt.	348.03	348.03	426.93	505.83
space group	$P2_1/c$	Pbca	$P2_1/n$	Pnma
cell constants[a]				
a, Å	11.243(4)	12.116(3)	6.479(5)	7.909(3)
b, Å	6.5991(7)	13.423(7)	23.029(9)	15.214(5)
c, Å	16.135(4)	14.925(7)	8.722(4)	11.499(7)
β, deg	99.86(3)		90.37(5)	
cell vol, $Å^3$	1179.4	2427.3	1301	1384
formula units/unit cell	4	8	4	4
D_{calc}, g cm^{-3}	1.96	1.90	2.18	2.43
μ_{calc}, cm^{-1}	72.59	70.37	98.37	123.18
max crystal dimensions, mm	0.13 x 0.25 x 0.35	0.28 x 0.35 x 0.50	0.38 x 0.38 x 0.53	0.08 x 0.16 x 0.28
scan width	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ	0.80 + 0.35 tanθ
standard reflections	700; 020; 008	800; 080; 008	400; 0, 18, 0; 006	600; 080; 0, 0, 12
decay of standards	±1%	±2%	±2%	-2.5%
reflections measured	2380	2432	2354	1441
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of h, k, l	+13, +7, ±19	+14, +15, +17	+7, +27, ±10	+9, -18, +13
reflections observed $[F_o \geq 5\sigma(F_o)]$[b]	989	980	1638	789
computer programs[c]	SHELX[20]	SHELX[20]	SHELX[20]	SHELX[20]
structure solution	SHELXS[22]	SHELXS[22]	SHELXS[22]	SHELXS[22]
no. of parameters varied	145	145	154	88
weights	$[\sigma(F_o)^2 + 0.00068\ F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0034\ F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00071\ F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0027\ F_o^2]^{-1}$
GOF	0.70	0.88	1.34	0.42
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.048	0.066	0.048	0.035
R_w	0.052	0.083	0.062	0.050
largest feature final diff. map	0.7e⁻ $Å^{-3}$	0.9e⁻ $Å^{-3}$	0.8e⁻ $Å^{-3}$	0.5⁻ $Å^{-3}$

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections θ > 19° (for **6**), 23 reflections θ > 20° (for **7**, **8**, and **9**).

[b] Corrections: Lorentz-polarization and absorption (empirical, psi scan).

[c] Neutral scattering factors and anomalous dispersion corrections from ref. 21.

Table II. Comparison of Average Distances (Å) and Angles (°) for 6-9.

Parameter	6	7	8	9	Range
C-O	1.20(1)	1.20(1)	1.21(1)	1.18(1)	0.03
C-C(bridgehead)	1.55(2)	1.58(2)	1.58(1)	1.58(1)	0.03
C-C(ethano)	1.53(1)	1.54(2)	1.54(1)	1.51(1)	0.03
C-C(to ethano)	1.55(1)	1.50(2)	1.52(2)	1.545(5)	0.05
C-C(to bridgehead)	1.53(2)	1.50(2)	1.54(2)	1.532(8)	0.04
C-C(to C=O)	1.52(1)	1.51(2)	1.528(4)	1.533(7)	0.03
C-Br	1.955(5)	1.98(1)	1.94(1)	1.957(6)	0.04
C-C(bridgehead)-C(bridgehead)	107.3(5)	106(1)	107.2(6)	106.8(4)	1.3
C-C(bridgehead)-C	104.9(2)	103.5(5)	105.0(7)	105.9(6)	2.4
C-C(CO)-C	110.2(6)	110(1)	109.6(6)	107(2)	3.2
C-C(ethano)-C(ethano)	103(1)	103(2)	103(1)	104(1)	1
C-C-O	125(1)	125(3)	125(1)	126.4(8)	1.4
Br-C-C(bridgehead)	113.3(9)	113.0(8)	112.1(2)	112.5(9)	1.2
Br-C-C(CO)	106(1)	104(2)	107(2)	107(2)	3
Br-C-C(ethano)	111(1)	113(1)	111(2)	110.6(8)	2.4

plane 2 and the plane defined by the four carbons bonded to CO fragments (plane 9). The 2/9 angle varies from 46° in 6 and 58° in 7 to 18° in 8 and 11° in 9. A modest difference is also observed in the angle between plane 9

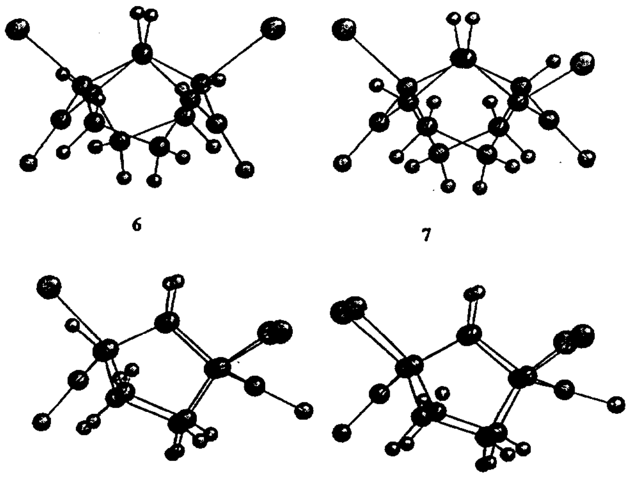
6
7
8
9

Figure 5. The conformational differences that distinguish 6-9 (obtained with the SYBYL software package).

Table III. Definition of Planes.

Plane	Atoms (6)	rms deviation	Atoms (7)	rms deviation	Atoms (8)	rms deviation	Atoms (9)	rms deviation
1	C(1),C(9),C(10),O(2)	0.016	C(1),C(2),C(3),O(1)	0.018	C(6),C(7),C(8),O(2)	0.0010	C(1),C(6),O(2),C(1)'[a]	0.015
2	C(4),C(5),C(6),O(1)	0.013	C(6),C(7),C(8),O(2)	0.0093	C(1),C(2),C(3),O(1)	0.0042	C(4),C(5),O(1),C(4)'	0.00041
3	C(1),C(9),C(11),C(12)	0.078	C(1),C(3),C(11),C(12)	0.065	C(6),C(8),C(11),C(12)	0.00071	C(1),C(1)',C(7),C(7)'	0.0
4	C(4),C(6),C(11),C(12)	0.076	C(6),C(8),C(11),C(12)	0.072	C(1),C(3),C(11),C(12)	0.0090	C(4),C(4)',C(7),C(7)'	0.0
5	C(1),C(2),C(8),C(9)	0.032	C(1),C(3),C(4),C(10)	0.019	C(5),C(6),C(8),C(9)	0.0026	C(1),C(1)',C(2),C(2)'	0.0
6	C(3),C(4),C(6),C(7)	0.021	C(5),C(6),C(8),C(9)	0.016	C(1),C(3),C(4),C(10)	0.0010	C(4),C(4)',C(3),C(3)'	0.0
7	C(6),C(9),C(12)	0.0	C(3),C(6),C(12)	0.0	C(1),C(8),C(11)	0.0	C(1)',C(4)',C(7)'	0.0
8	C(1),C(4),C(11)	0.0	C(1),C(8),C(11)	0.0	C(3),C(6),C(12)	0.0	C(1),C(4),C(7)	0.0
9	C(1),C(4),C(6),C(9)	0.17	C(1),C(3),C(6),C(8)	0.13	C(1),C(3),C(6),C(8)	0.0046	C(1),C(1)',C(4),C(4)'	0.0
10					C(4),C(5),C(9),C(10)	0.0015	C(2),C(3),C(2)',C(3)'	0.0

[a] Primed atoms are related by the crystallographic mirror plane which bisects the C(7),C(7)' bond.

and plane 6 (defined by the two carbon atoms bonded to the CO group and the two ethano carbon atoms bonded to plane 2 and the plane defined by the four carbons bonded to CO fragments (plane 9). The 2/9 angle varies from 46° in **6** and 58° in **7** to 18° in **8** and 11° in **9**. A modest difference is also observed in the angle between plane 9 and plane 6 (defined by the two carbon atoms bonded to the CO group and the two ethano carbon atoms bonded to them). The 6/9 angle averages 62° in **6**/**7** and 68° in **8**/**9**. The angle between plane 6 and plane 5 (the similar plane involving the CO group on the left side of the molecules depicted in Figure 5) contracts from an average 56° in **6**/**7** to 49.5° in **8**/**9**. Similarly, the plane 4/6 angle contracts from 84° in **6**/**7** to 79° in **8**/**9**.

The remaining angles involving the planes defined by the C-C(O)-C moieties (1 and 2) do not exhibit general trends but rather have deviations among themselves which apparently are related to the different substitution patterns. For example, the 1/2 angles vary from 86° in **6**, 67° in **7**, 77° in **8**, to 62° in **9**. Other variations in the 1/3, 1/5, 1/9, 2/4, and 2/6 angles probably have similar origins. The remaining planes (involving carbon atoms only) show remarkable consistency throughout the **6**-**9** series.

Table IV. Comparison of Plane Angles.

Planes	Angle (deg, **6**)	Angle (deg, **7**)	Angle (deg, **8**)	Angle (deg, **9**)
1/3	14	19	24	17
1/5	70	63	59	66
1/9	48	55	59	51
1/10			73	64
2/4	11	23	16	22
2/6	73	60	85	79
2/9	46	58	18	11
2/10			3	2
1/2	86	67	77	62
3/4	69	70	68	67
3/5	84	82	83	83
3/9	35	35	34	34
4/6	84	83	79	79
4/9	34	35	34	33
5/9	62	63	63	63
5/10			48	50
5/6	56	55	50	49
6/9	62	62	67	68
6/10			82	82
7/9	61	63	61	61
8/9	61	62	61	61
7/8	58	55	58	57
9/10			15	13

Thus, the crystallographic data presented herein confirm that the tetracyclo[$7.2.1.0^{4,11}.0^{6,10}$]dodecane 5,12-dione framework is subject to varied conformational distortion as a function of bromine substitution. However, bond distances are little affected as the halogen content is progressively increased.

Experimental Section[19]

Tetracyclo[$7.2.1.0^{4,11}.0^{6,10}$]dodecane-5,12-dione (4). A solution of the 2,7-diene precursor[15] (3.78 g, 20.3 mmol) in ethyl acetate (300 mL) was hydrogenated over 5% Pd-C (55 mg) at 50 psi in a Parr apparatus. Filtration through Celite to remove the catalyst and solvent evaporation gave 3.67 g (95%) of 4 as a colorless solid, mp 129-131 °C; IR (KBr, cm^{-1}) 1715; ^1H NMR (300 MHz, $CDCl_3$) δ 3.56-3.45 (m, 2 H), 3.00-2.96 (m, 4 H), 1.99-1.79 (m, 8 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 223.91, 55.54, 44.01, 30.72; MS *m/z* (M^+) calcd 190.0994, obsd 190.0982.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.56; H, 7.43.

Bromination of 4 with Copper(II) Bromide. A nitrogen-blanketed refluxing solution of 4 (504 mg, 2.65 mmol) in 1:1 ethyl acetate-chloroform (10 mL) was treated portionwise (*ca* 200 mg) with $CuBr_2$ (1.19 g, 2 equiv), with care to add the subsequent amount only after the initial green color had disappeared. Solid CuBr was observed to precipitate and the solution turned yellow. The cooled mixture was filtered through Celite and the pad was washed well with ethyl acetate. The evaporated filtrate gave a residue that was separated into its components by chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether). The first product to elute was 7 (R_f = 0.88, 93 mg, 10%); colorless crystals, mp 117-118 °C (from ether); IR (CCl_4, cm^{-1}) 1748; ^1H NMR (300 MHz, $CDCl_3$) δ 3.76-3.68 (m, 2, H), 3.59-3.46 (m, 2 H), 2.60-2.51 (m, 2 H), 2.27-2.11 (m, 4 H), 1.65-1.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 212.50, 65.68, 51.83, 49.79, 39.41, 27.21; MS *m/z* (M^+) calcd 345.9204, obsd 345.9206.

Anal. Calcd for $C_{12}H_{12}Br_2O_2$: C, 41.63; H, 3.50. Found: C, 41.84; H, 3.49.

The second compound to elute was 6 (R_f = 0.73, 62 mg, 7%); colorless solid, mp 127-128 °C (from ether); IR (CCl_4, cm^{-1}) 1730; ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (d, *J* = 10.1 Hz, 1 H), 3.64 (q, *J* = 10.3 Hz, 1 H), 3.42-3.35 (m, 2 H), 2.50-2.40 (m, 2 H), 2.36-2.25 (m, 2 H), 2.08-1.97 (m, 2 H), 1.94-1.85 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 213.47, 64.80, 64.00, 51.90, 40.58, 38.83, 30.06; MS *m/z* (M^+) calcd 345.9203, obsd 345.9201.

Anal. Calcd for $C_{12}H_{12}Br_2O_2$: C, 41.63; H, 3.50. Found: C, 41.85; H, 3.62.

The most polar constituent was 5 (R_f = 0.35), a colorless solid (301 mg, 42%) having mp 87-88 °C (from ether); IR (CCl_4, cm^{-1}) 1735; ^1H NMR (300 MHz, $CDCl_3$) δ 3.69-3.53 (m, 2 H), 3.45-3.38 (m, 1 H), 3.14-3.05 (m, 1 H), 3.02-2.95 (m, 1 H), 2.53-2.44 (m, 1 H), 2.24-2.07 (m, 2 H), 2.04-1.84 (m, 4 H), 1.65-1.52 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 221.91, 214.66, 66.58, 55.54, 54.21, 53.95, 51.93, 42.30, 40.16, 30.98, 29.75, 28.94; MS *m/z* (M^+) calcd 268.0098, obsd 268.0133.

Anal. Calcd for $C_{12}H_{13}BrO_2$: C, 53.73; H, 4.89. Found: C, 53.32; H, 4.90.

1,4,6-Tribromotetracyclo[$7.2.1.0^{4,11}.0^{6,10}$]dodecane-5,12-dione (8). A refluxing solution of 1 (890 mg, 4.7 mmol) in 1:1 ethyl acetate-chloroform (20 mL) was treated under nitrogen with $CuBr_2$ (3.14 g, 14.1 mmol, 3 equiv) as described above. Purification by MPLC removed all bromination products except the 1,6-dibromide which co-eluted with 8. Repeated recrystallization of this material from ethyl ether afforded pure 8 (274 mg, 14%) as colorless crystals, mp 124-126 °C; IR (CCl_4, cm^{-1}) 1755; ^1H NMR (300 MHz, $CDCl_3$) δ 3.96 (d, *J* = 10.3 Hz, 1 H), 3.82 (t, *J* = 10.8 Hz, 1 H), 3.54-3.45 (m, 1 H), 2.62-2.36 (m, 4 H), 2.33-2.15 (m, 2 H), 2.03-1.92 (m, 1 H), 1.71-1.55 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 212.50, 208.97, 63.77, 63.47, 61.52, 58.93, 51.76, 50.82, 41.50, 39.97, 38.56, 28.59; MS *m/z* (M^+) calcd 432.8310, obsd 432.8312.

Anal. Calcd for $C_{12}H_{11}Br_3O_2$: C, 33.98; H, 2.62. Found: C, 33.99; H, 2.73.

1,4,6,9-Tetrabromotetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane-5,12-dione (9). A solution of **4** (108 mg, 0.57 mmol) in glacial acetic acid (20 mL) was heated to reflux under nitrogen and treated with bromine (0.35 mL, 1.09 g, 6.9 mmol) over 5 min. Heating was continued for 2 h. The cooled reaction mixture was diluted with water (10 mL) and CH_2Cl_2 (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with water (3 x 10 mL), saturated $NaHCO_3$ solution (3 x 10 mL) and brine (10 mL) prior to drying and solvent evaporation. The residue was purified by chromatography (silica gel, elution with 20% ethyl acetate in petroleum ether) to give 229 mg (80%) of **9** as a colorless solid, mp 180-200 °C (from ether); IR ($CHCl_3$, cm^{-1}) 1750; ^1H NMR (300 MHz, $CDCl_3$) δ 4.01 (s, 2 H), 2.61-2.49 (m, 4 H), 2.26-2.13 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 208.41, 62.77, 58.78, 39.65; MS *m/z* (M^+) calcd 501.7415, obsd 501.7352.

Anal. Calcd for $C_{12}H_{10}Br_4O_2$: C, 28.70; H, 2.01. Found: C, 28.52; H, 2.06.

X-ray quality crystals of **9** were grown from CH_2Cl_2.

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Supplementary Material Available: Tables of bond distances and angles, least-squares planes, final fractional coordinates, thermal parameters, and structure factor data for **6-9** (33 pages). This information can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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