The Alleged Isolable 1,4,5,6-Tetrachloro-7,7-dimethoxynorbornadiene-2,3-dicarboxylic Anhydride

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Addition of dibromomaleic anhydride to tetrachlorocyclopentadienone dimethyl acetal gives the pseudo-lactone **11** (X-ray crystal structure analysis) and not the mixture of endo- and exo-adducts **2** previously claimed; reduction of this product with Zn/HOAc gives **13** and **14** rather than the putative isolable norbornadienone acetal **3**.

Addition of dibromomaleic anhydride to the dimethyl acetal of tetrachlorocyclopentadienone **1** and debromination of the supposed mixture of endo- and exo-adducts **2** with Zn/HOAc apparently gave the isolable norbornadienone acetal **3**[1] (Scheme 1).

Scheme 1
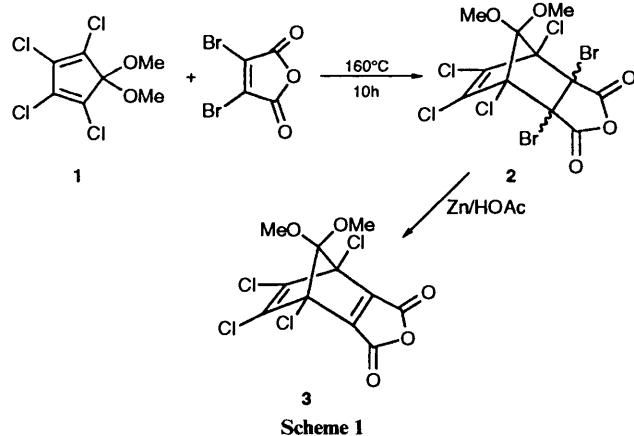
The thermal stability of the anhydride **3** up to 200 °C is in striking contrast to the instability of related diesters. Thus, addition of dimethyl acetylenedicarboxylate to **1** at 110 °C gives the hemimellitate **4**. The norbornadiene **5**, a presumed intermediate in this reaction,[2] is thought to undergo heterolysis to the stabilised zwitterion **6** which expels chloride ion **6** (arrows) to give the ion pair **7**. This then collapses to the observed products as indicated in **7** (arrows).[2] Tetrachloronorbornadi-enone acetals with carbonyl substituents at C-2 and C-3, e.g. **5**, cannot be isolated. However, in the absence of carbonyl groups such compounds are isolable.[2a] In the presence of carbonyl groups but in the absence of chlorine substituents the acetals are also isolable, but rearrange to tropone acetals at > 40 °C.[2d]

To explain the relative stability of **3** it was suggested that a concerted-forbidden 1,3-shift of C-7 gave the norcaradiene **8** which only subsequently opened to the zwitterion **6**. The greater strain in the anhydride **8** compared to the diester intermediate **9** from the diester **5** might account for the apparent failure of **3** to rearrange below 200 °C. In apparent agreement with this explanation it was observed that the product believed to be **3** gave **4** upon cleavage of the anhydride with acidic methanol.[1] However, the implied very strong preference for concerted-forbidden 1,3-shift to C-2 rather than C-6 of **3** remained puzzling. Shift of C-7 to C-6 would give the less strained **10** which would give the same highly stabilised zwitterion **6** upon heterolysis. For this reason and in connection with work on donor-accepter accelerated rearrangement of norbornadienes

E = CO₂Me throughout
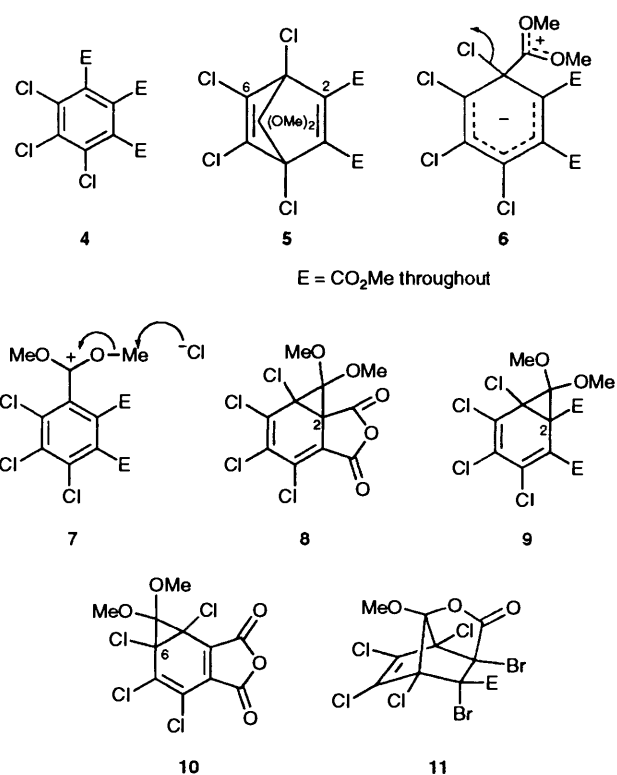
to cycloheptatrienes, which may involve either initial concerted-forbidden 1,3-shift or heterolysis to zwitterions like **6**,[2d] we have re-examined the putative reactions of Scheme 1.

After being heated in a sealed tube for 10 h at 160 °C the acetal **1** and dibromomaleic anhydride provided a compound, m.p. 154–156 °C, showing carbonyl absorption at 1833 and 1747 cm⁻¹ in agreement with reported values[1] [m.p. 151–151.5 °C, ν_{max}(Nujol)/cm⁻¹ 1830 and 1740]. The lower frequency band is less intense than the higher frequency carbonyl absorption in contrast to the intensity relationship expected for a five-membered ring anhydride. Similarly, the ¹³C NMR spectrum showed eleven rather than the seven lines expected for structure **2**. Although the spectroscopic data suggested that this compound was not completely pure the major component appeared to be the pseudo-lactone **11**. Since repeated crystallisation of this product neither raised its m.p. nor removed the extra peaks in the proton and carbon spectra an equilibrium between **11** and another compound in CDCl₃ and C₆D₆ cannot be ruled out at present.

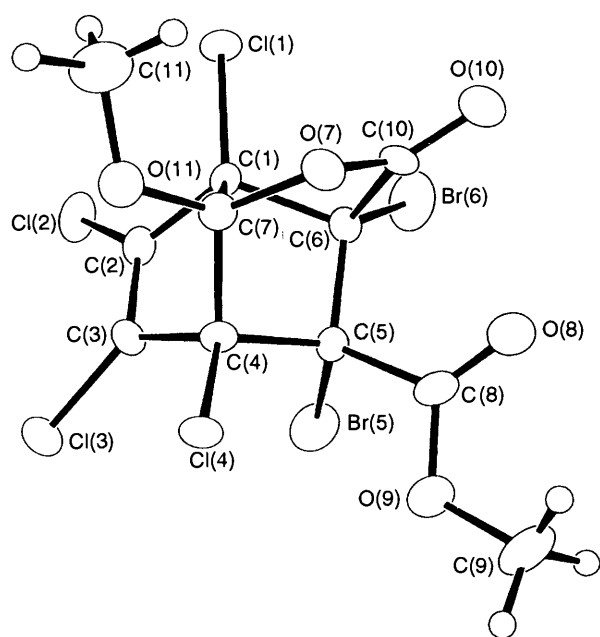High quality crystals of **11** were readily obtained from a light

Fig. 1 ORTEP[9] representation of the crystal structure of compound 11. Ellipses are shown at the 30% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for compound 11 with esds in parentheses

C(1)–C(2)	1.488(9)	C(1)–C(6)	1.593(8)
C(1)–C(7)	1.600(7)	C(1)–Cl(1)	1.779(6)
C(2)–C(3)	1.378(9)	C(2)–Cl(2)	1.702(6)
C(3)–C(4)	1.505(8)	C(3)–Cl(3)	1.700(6)
C(4)–C(7)	1.556(8)	C(4)–C(5)	1.602(8)
C(4)–Cl(4)	1.772(5)	C(5)–C(8)	1.537(8)
C(5)–C(6)	1.579(8)	C(5)–Br(5)	1.938(6)
C(6)–C(10)	1.548(8)	C(6)–Br(6)	1.871(6)
C(7)–O(11)	1.360(7)	C(7)–O(7)	1.429(7)
O(7)–C(10)	1.375(8)	C(8)–O(8)	1.160(9)
C(8)–O(9)	1.327(8)	O(9)–C(9)	1.431(9)
C(10)–O(10)	1.181(8)	O(11)–C(11)	1.407(8)
C(2)–C(1)–C(6)	116.8(5)	C(2)–C(1)–C(7)	101.4(4)
C(6)–C(1)–C(7)	89.9(4)	C(2)–C(1)–Cl(1)	116.4(4)
C(6)–C(1)–Cl(1)	112.2(4)	C(7)–C(1)–Cl(1)	116.8(4)
C(3)–C(2)–C(1)	107.6(5)	C(3)–C(2)–Cl(2)	127.5(5)
C(1)–C(2)–Cl(2)	124.8(5)	C(2)–C(3)–C(4)	107.4(5)
C(2)–C(3)–Cl(3)	127.0(5)	C(4)–C(3)–Cl(3)	125.5(5)
C(3)–C(4)–C(7)	100.3(4)	C(3)–C(4)–C(5)	106.6(5)
C(7)–C(4)–C(5)	101.2(4)	C(3)–C(4)–Cl(4)	116.4(4)
C(7)–C(4)–Cl(4)	114.2(4)	C(5)–C(4)–Cl(4)	116.0(4)
C(8)–C(5)–C(6)	112.7(5)	C(8)–C(5)–C(4)	115.3(5)
C(6)–C(5)–C(4)	99.8(4)	C(8)–C(5)–Br(5)	106.6(4)
C(6)–C(5)–Br(5)	110.8(4)	C(4)–C(5)–Br(5)	111.7(4)
C(10)–C(6)–C(5)	106.7(4)	C(10)–C(6)–C(1)	97.5(5)
C(5)–C(6)–C(1)	102.8(4)	C(10)–C(6)–Br(6)	112.7(4)
C(5)–C(6)–Br(6)	118.3(4)	C(1)–C(6)–Br(6)	116.5(4)
O(11)–C(7)–O(7)	111.2(5)	O(11)–C(7)–C(4)	110.6(5)
O(7)–C(7)–C(4)	114.7(5)	O(11)–C(7)–C(1)	121.6(5)
O(7)–C(7)–C(1)	105.2(4)	C(4)–C(7)–C(1)	92.5(4)
C(10)–O(7)–C(7)	108.3(4)	O(8)–C(8)–O(9)	124.9(6)
O(8)–C(8)–C(5)	123.5(6)	O(9)–C(8)–C(5)	111.6(6)
C(8)–O(9)–C(9)	115.0(6)	O(10)–C(10)–O(7)	125.1(6)
O(10)–C(10)–C(6)	129.8(6)	O(7)–C(10)–C(6)	105.0(5)
C(7)–O(11)–C(11)	118.4(5)		

petroleum solution which enabled a single crystal X-ray analysis to be undertaken. An ORTEP[3] diagram of 11 is shown in Fig. 1 and selected bond lengths and angles are given in Table

1. The structure is confirmed as being that of a pseudo-lactone. Bond lengths are all within expected limits but, not surprisingly, the structure shows evidence of considerable strain. At the carbon–carbon double bond the ring angles are considerably reduced to 107.4(5) and 107.6(5) which compare well with the value of ca. 105° seen in norbornadiene itself.[4] Strain in the lactone ring is particularly notable about the carbonyl group where angle O(7)–C(10)–C(6) is 105.0(5)°. This angle compares well with the value of 106° which is observed in the previously reported[5] lactone 12 which has a similar overall ring structure to 11.

Treatment of 11 with Zn/HOAc gave two products readily separable by silica chromatography. The higher melting product (m.p. 95 °C) is probably identical with the product, m.p. 100–102 °C, earlier assigned structure 3; it shows v_{max}(Nujol)/cm^{-1} 1831 and 1753 similar to that reported for the product thought to be 3 [v_{max}(Nujol)/cm^{-1} 1830 and 1750]. The ^{13}C NMR spectrum of the product currently prepared was consistent with structure 13, the product expected upon Zn/HOAc reduction of 11. Moreover, the second product from Zn/HOAc reduction of 11 had spectroscopic properties in agreement with structure 14 (Experimental section). Again, the spectroscopic data suggested 13 and 14 were not completely pure. Accordingly we sought independent evidence for the structure of 13 by its preparation from the acetal 1 and monobromomaleic anhydride. After being heated for 340 min at 160 °C these reactants gave mainly the

16 R = Me, R' = H or R = H, R' = Me   17
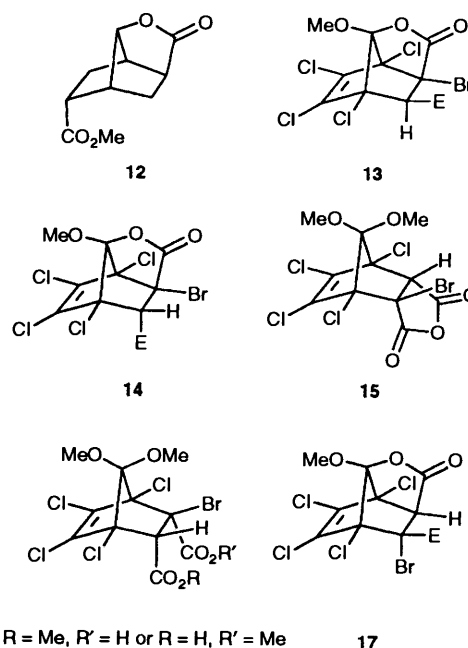
endo-adduct 15, v_{max}(Nujol)/cm^{-1} 1798vs and 1867m as expected for a 5-membered ring anhydride. When the reaction was repeated and the crude product treated with methanol the main product was the monomethyl ester 16. However, chromatography also allowed isolation of a highly crystalline mixture of 13 and an isomeric compound tentatively identified as 17. The ^{13}C NMR spectrum of this mixture clearly displayed all those peaks associated with compound 13 obtained by Zn/HOAc reduction of 11, and, in addition, showed a complementary set of peaks for the isomer 17; the IR spectrum also showed peaks due to 13 and extra absorptions for 17.

With the apparent stability of 5 explained the balance of evidence favours a zwitterionic mechanism for the reactions of the chlorinated and non-chlorinated donor-acceptor substituted norbornadienes.[2d]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Philips PU 8706 IR spectrophotometer, and referenced to a peak at 1601 cm^{-1} of polystyrene. ^{1}H NMR spectra were determined, with tetramethylsilane as internal standard at 400 MHz for protons and 100 MHz for carbon spectra on a Bruker WH-400 instrument. Coupling constants are in Hz. Mass spectra were obtained on an Autospec mass spectrometer. Chromatography on silica refers to short-column chromatography over Kieselgel G60 (Merck).[6] Ether refers to diethyl ether and light petroleum (LP) to the fraction b.p. 60–80 °C. Unfortunately, samples and spectra obtained in the original work are unavailable so that direct comparison with the samples prepared herein was not possible.

Reaction of Dibromomaleic Anhydride with Tetrachlorocyclopentadienone Dimethyl Acetal.—Dibromomaleic anhydride[7] (0.5 g) and tetrachlorocyclopentadienone dimethyl acetal (0.5 g) were heated in an evacuated (water pump) and sealed tube completely immersed in an oil bath at 160 ± 0.5 °C (10 h). The product was digested with methanol (2.5 cm^3) and stored for 16 h; no crystals had appeared at this point. The mixture was boiled (10 min), evaporated and the residue chromatographed on silica (40 g) in benzene–light petroleum (1:1) to give first an oily product (0.328 g) which afforded crystals (*ca.* 60 mg), m.p. 235–237 °C (sealed tube) from light petroleum. This material lacked the higher frequency carbonyl band reported for the desired product[1] showing ν_{max}(Nujol)/cm^{-1} 1734 and was also produced by addition of monobromomaleic anhydride and tetrachlorocyclopentadienone dimethyl acetal; it presumably arises from decomposition of the acetal and was not further examined. Continued elution of the column gave the *pseudo-lactone* 11 (153 mg), m.p. 154–156 °C (from LP) (lit.,[1] m.p. 151–151.5 °C). The m.p. of our sample remained unchanged after repeated crystallisation from light petroleum [Found: C, 25.1; H, 1.1; Br + Cl (calc. as Cl), 39.55%; M (osmometer) 470. C$_{11}$H$_6$Cl$_4$Br$_2$O$_5$ requires C, 25.4; H, 1.15; Br + Cl (calc. as Cl), 41.0%; M 520]; ν_{max}(Nujol)/cm^{-1} 1833vs, 1747s, 1600m (lit.,[1] 1830, 1740 and 1600 cm^{-1}); δ_H(400 MHz, CDCl$_3$) 3.81 (3 H, s) and 3.86 (3 H, s); additional peaks of ≈20% intensity at δ 3.84 and 3.89, may be due to impurities; δ_H(C$_6$D$_6$, 400 MHz) 3.31 (3 H, s) and 3.33 (3 H, s) and additional small peaks at 3.28 and 3.41; δ_C(100 MHz, C$_6$D$_6$) 164.15 (C=O), 162.08 (C=O), 139.22 (C=C), 126.25 (C=C), 115.45 [C(OMe)$_2$], 84.55, 80.96, 75.41, 74.26, 55.61 (OMe) and 54.84 (OMe); small 'extra' peaks observed at 162.18, 55.84, 55.50 and 55.00; δ_C(100 MHz, CDCl$_3$) 163.44, 161.54, 137.85, 125.16, 114.21, 83.35, 79.20, 74.59, 72.93, 55.33 and 54.73; small 'extra' peaks at 161.73, 136.05, ≈126, 73.91, 55.53, 55.22 and 54.92; the Cs-atom FAB mass spectrum measured for a *m*-nitrobenzyl alcohol matrix showed a strong cluster for the (M + 1) peak at 517, 519, 520, 521, 522, 523, 524, 525 (22.80, 77.93, 9.67, 100.00, 11.87, 62.96, 7.52 and 23.21%).

Reaction of the Pseudo-lactone 11 with Zinc in Acetic Acid.— The foregoing pseudo-lactone (250 mg) in acetic acid (1.5 cm^3) was cooled in an ice-bath and activated zinc dust (45 mg) and a small crystal of iodine were added to the solution. After the mixture had been stirred for 18 h, it was diluted with water (≈2.5 cm^3), extracted into dichloromethane and the extract washed with aqueous sodium hydrogen carbonate and water, dried (MgSO$_4$) and evaporated to give an oil (204 mg). Chromatography of this on silica in benzene–LP (1:1) afforded first an oil (70 mg) that gave crystalline 14 from pentane, m.p. 71–74 °C [Found: C, 29.8; H, 1.55; Br + Cl (as Cl), 38.9. C$_{11}$H$_7$Cl$_4$BrO$_5$ requires C, 29.9; H, 1.60; Br + Cl (as Cl), 40.25%]; ν_{max}(Nujol)/cm^{-1} 1833, 1751 and 1593; δ_H(CDCl$_3$; 400 MHz) 3.61 (1 H, s), 3.79 (3 H, s) and 3.83 (3 H, s); δ_C(CDCl$_3$;

100 MHz) 55.31 (CH$_3$), 53.45 (CH$_3$), 60.96 (CH), 64.41, 75.06, 82.86, 114.59 [C(OMe)$_2$], 131.96 (C=C), 125.19 (C=C), 163.68 (C=O) and 163.76 (C=O); impurity peaks (?) at 61.71 and 60.55 remained positive in an INEPT experiment.

Continued elution of the column with the same solvent mixture gave highly crystalline 13 (76 mg), m.p. 95 °C (from pentane) [Found: C, 29.3; H, 1.5%; M (osmometer, CHCl$_3$) 372. C$_{11}$H$_7$Cl$_4$BrO$_5$ requires M, 441]; ν_{max}(Nujol)/cm^{-1} 1831, 1753 and 1596; δ_H(CDCl$_3$; 400 MHz) 3.34 (1 H, s), 3.81 (3 H, s) and 3.83 (3 H, s); δ_C(CDCl$_3$; 100 MHz) 164.1 (C=O, 162.6 (C=O), 136.3 (C=C), 124.0 (C=C), 113.82 [C(OMe)$_2$] 84.0, 73.6, 65.79 (CH), 63.57, 55.0 (OMe) and 53.6 (OMe); small impurity peaks at 66.13, 66.04, 65.62 and 64.85; the Cs–FAB mass spectrum measured for a *m*-nitrobenzyl alcohol matrix showed a strong (M + 1) cluster: 438.84, 439.83, 440.84, 441.84, 442.84, 443.84, 444.84 and 446.84 (40.48, 5.35, 100, 12.31, 78.06, 10.61, 30.49 and 7.59%).

Addition of Monobromomaleic Anhydride to Tetrachlorocyclopentadienone Dimethyl Acetal.—The dimethyl acetal (1.32 g) and monobromomaleic anhydride (0.96 g) were heated in an evacuated sealed tube (water pump) in an oil bath at 160 °C (340 min). The mixture was then digested with methanol (5 cm^3), stored at 20 °C (16 h) and evaporated under reduced pressure. The residue was crystallised from benzene–LP (1:1) to give the monoester 16 (1.2 g), m.p. 158–162 °C [Found: C, 30.6; H, 2.3; Br + Cl (as Cl), 37.34. C$_{12}$H$_{11}$O$_6$BrCl$_4$ requires C, 30.4; H, 2.3; Br + Cl (as Cl), 38.9%]; ν_{max}(Nujol)/cm^{-1} 3240br, 1759s and 1718s; δ_H(400 MHz, CDCl$_3$) 3.57 (3 H, s), 3.70 (3 H, s), 3.75 (3 H, s), 4.30 (1 H, s), 7.51 (1 H, br s); δ_C(100 MHz, CDCl$_3$) 168.64(C=O), 167.68(C=O), 132.98(C=C), 128.48(C=C), 112.70 [C(OMe)$_2$], 79.24, 74.06, 64.60 (C-H), 62.48, 52.85, 52.83 and 52.16. The mother liquor from crystallisation of the foregoing monoester was evaporated and chromatographed on silica in benzene–LP (1:1) to give a crystalline material (67 mg) that recrystallised from benzene–LP as a *ca.* 1:1 mixture of 17 and the isomer 13 previously prepared by zinc–acetic acid reduction of the pseudo-lactone. The mixture showed strong carbonyl absorption at 1831 and weaker bands at 1757 and 1744 cm^{-1} similar to that previously described for 13. The ^{13}C spectrum convincingly demonstrated the presence of 13 and the isomer 17; peaks due to the latter are as follows: δ_C(100 MHz, CDCl$_3$) 164.27 (C=O), 164.14 (C=O), 136.42 (C=C), 125.84 (C=C), 116.48 [C(OMe)$_2$], 78.82, 67.14, 62.86, 62.69 (CH), 55.20 and 54.47. The ^{1}H NMR spectrum of the mixture (400 MHz, CDCl$_3$) in addition to the signals previously assigned to 13 gave the following signals assigned to 17: δ_H 3.55 (1 H, s), 3.79 (3 H, s) and 3.86 (3 H, s). In a similar experiment on a reduced scale (0.66 g of acetal) work-up without the use of methanol and recrystallisation of the crude from benzene–light petroleum gave oily crystals (0.6 g). Crystallisation (2 ×) from the same solvent mixture gave the *anhydride* 15 (250 mg), m.p. 156–158 °C (Found: C, 30.15; H, 1.55. C$_{11}$H$_7$BrCl$_4$O$_5$ requires C, 29.9; H, 1.6%); ν_{max}(Nujol)/cm^{-1} 1867m, 1798vs and 1599.

Reaction of the Pseudo-Lactone 14 with Methanol–Toluene-p-sulfonic Acid.—The lactone (20 mg), methanol (10 cm^3) and toluene-p-sulfonic acid (40 mg) were boiled under reflux (3 h) after which the mixture was diluted with water and extracted into ether. The extract was washed with saturated aqueous sodium hydrogen carbonate and water, dried (MgSO$_4$) and evaporated. Chromatography of the product on silica in benzene–ether (97:3) gave trimethyl 4,5,6-trichlorophenyltricarboxylate (10 mg), m.p. 86–88 °C (from LP) identical (mixed m.p. and IR spectrum) with an authentic sample.[8]

Single Crystal X-Ray Diffraction Analysis of Compound 11.— All crystallographic measurements were carried out on a

Stoe STAD14 diffractometer operating in the ω–θ scan mode using graphite monochromated Mo-Kα X-radiation (λ = 71.069 pm). Two equivalents of data were collected and corrected for absorption semi-empirically using azimuthal Ψ-scans (max. and min. transmission factors 0.1682 and 0.2867, respectively).

Systematic absences indicated that two space groups were possible, $C2/c$ or Cc. Whilst no solution could be obtained for the former, the structure was readily determined for space group Cc by direct methods using SHELXS-86;[9] and was refined by full-matrix least-squares (based on F^2) using SHELXL-93.[10] All data were used for refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl hydrogen atoms were located on a Fourier difference synthesis, their positional co-ordinates were freely refined but each atom was assigned a fixed isotropic thermal parameter of 1.5 (U_{eq}) of the parent carbon atom. The direction of the polar axis was confirmed by refinement of a 'Flack' parameter[11] to 0.09(1). The weighting scheme $w = [\sigma^2(F_o^2) + 0.0696P)^2 + 6.9311P]^{-1}$ [where $P = (F_o^2 + 2F_c^2)/3$] was used. The final Fourier difference synthesis was flat and showed no features of chemical significance (max. and min. densities 0.776 and −0.531 e Å^{-3}, respectively).

Crystal data. $C_{11}H_6Br_2Cl_4O_5$, M = 519.784, monoclinic, space group Cc, a = 14.235(2), b = 9.595(2), c = 12.609(2) Å, β = 109.034(10)°, U = 1627.8(5) Å^3, Z = 4, D_x = 2.121 mg m^{-3}, μ = 5.653 mm^{-1}, $F(000)$ = 1000.

Data collection. $4.0 < 2\theta < 50.0°$, scan widths = 1.05 + α-doublet splitting, scan speeds 1.0–8.0° min^{-1}. Number of data collected = 6108; number of unique data, n = 2863; number with $F_o > 4.0$ $\sigma(F_o)$ = 2662; $R_{int}\{=\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]\}$ = 0.0176; $R_{sig}\{=\Sigma[\sigma F_o^2]/\Sigma[F_o^2]\}$ = 0.0221; T = 200 K.

Structure refinement. Number of parameters, p = 201; R_1-$\{=\Sigma||F_o| - |F_c||/\Sigma|F_o|\}$ = 0.0357; $wR_2\{=(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{\frac{1}{2}}\}$ = 0.1060; goodness of fit s $(=\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{\frac{1}{2}}\}$ = 1.064; max. Δ/σ = 0.002, mean Δ/σ = 0.000.

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