Chlorine *versus* bromine: facial selectivity in the Diels–Alder reactions of 5-bromo-1,2,3,4,5-pentachlorocyclopenta-1,3-diene

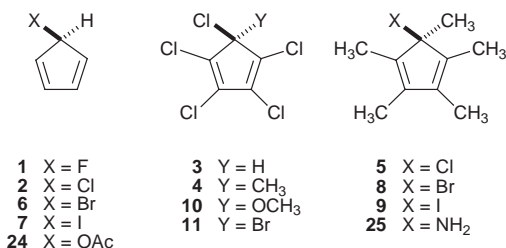Lori C. Burry, David O. Miller † and D. Jean Burnell *

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Diels–Alder reactions of diene **11** with both electron-poor and electron-rich dienophiles led to approximately 90% addition to the face of **11** *syn* to the C-5 chlorine. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione was slightly less facially selective. Adduct ratios were obtained by NMR methods; stereochemistry was determined by X-ray crystallography. The results support the view that facial selectivity in Diels–Alder reactions with heteroatom-substituted dienes is mainly controlled by steric, not stereoelectronic, interactions.

Introduction

Facial selectivity in the Diels–Alder reactions with plane-nonsymmetric cyclopentadienes substituted at C-5 by a halogen has been examined a number of times. Additions to **1** occurred overwhelmingly *syn*‡ to fluorine.[1] Dienes **2–5**, with a C-5

1 X = F	**3** Y = H	**5** X = Cl
2 X = Cl	**4** Y = CH₃	**8** X = Br
6 X = Br	**10** Y = OCH₃	**9** X = I
7 X = I	**11** Y = Br	**25** X = NH₂
24 X = OAc		

chlorine, all favoured *syn*‡ addition.[2–5] Bromine and, especially, iodine at C-5, as in **6**–**9**, directed an incoming dienophile *anti*.[4,5] Facial selectivity data had also been reported for two dienes in which chlorine was pitted against a different heteroatom. Reactions of diene **10** were examined rigorously with a variety of dienophiles, and addition was shown to be *anti* to the C-5 chlorine with every dienophile.[6] Diene **11** presented a facial choice between chlorine and bromine. Williamson and Hsu[3] stated that **11** was too thermally labile to allow a reasonable assessment of its facial selectivity. On the other hand, Shestakova *et al.*[7] did report Diels–Alder reactions with **11**, but their assignment of the stereochemistry for the adducts was based on an interpretation of the ¹H NMR chemical shift (60 MHz) data that was found to be untenable in the study of **10**.[6] We chose to re-examine the reactions of **11** with a variety of dienophiles not only because of uncertainty with regard to the published structures of the adducts but more importantly because the results might shed light on how facial selectivity is governed.

Results and discussion

Diene **11** was prepared in good yield by treatment with *N*-bromosuccinimide of the cyclopentadienyl anion derived from

3. Conditions for the Diels–Alder reactions of **11** and the facial selectivities are summarized in Table 1. Electron-deficient dienophiles such as *N*-phenylmaleimide and 1,4-naphthoquinone were very slow to react, whereas vinylene carbonate, which is electron-rich, reacted more quickly, although its adducts decomposed at elevated temperatures. Every Diels–Alder reaction provided only two adducts, and the NMR data indicated that both adducts were symmetrical. Hence, adducts were not derived from thermally isomerized dienes, and the similarity of chemical shifts suggested that adducts were epimeric at the methano bridge, *i.e.*, not mixtures of *endo-* and *exo-*addition products. Integration of the NMR spectra of every product mixture revealed that the ratio of the adducts was very similar (Table 1). The exception was a somewhat lower ratio with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). We had found, both experimentally[5] and computationally,[8] that this dienophile can impart a destabilizing interaction with a *syn* halogen, similar to the closed-shell repulsion noted by Coxon *et al.*[9] with another diene system.

Column chromatography failed to separate the adducts. Enrichment of any adduct by crystallization was unsuccessful.§ Therefore, the stereochemistry of the adducts from five of the six Diels–Alder reactions was determined by X-ray crystallography with the crystalline mixtures of the *syn–anti* adduct pairs. In order to effect a structural analysis, each mixture was modelled with both halogens on the methano bridge as bromine, and the proportions of the bromines were varied to obtain the best refinement values. Thus, the bromine occupancy on the methano bridge reflected the proportion of chlorine and bromine on the methano bridge, and the molecular diagrams, *e.g.* Fig. 1, showed no obvious distortions. Structures **12**, **14**, **16**, **20** and **22** were assigned from the crystallographic work, and spectroscopic parallels allowed a confident assignment of **18** as the major isomer with 3-nitrostyrene. The preferred mode of attack by the dienophile was *syn* to the chlorine of **11** in every instance. Furthermore, from the optimized partial occupancy data, the proportions of the minor adducts **13**, **15**, **17** and **23** in the recrystallized samples could be estimated. The adduct mixture derived from vinylene carbonate contained a significant proportion of a third hexachloro component, making estimation of the amount of **21** difficult. Adduct ratios determined in this crystallographic manner should be considered
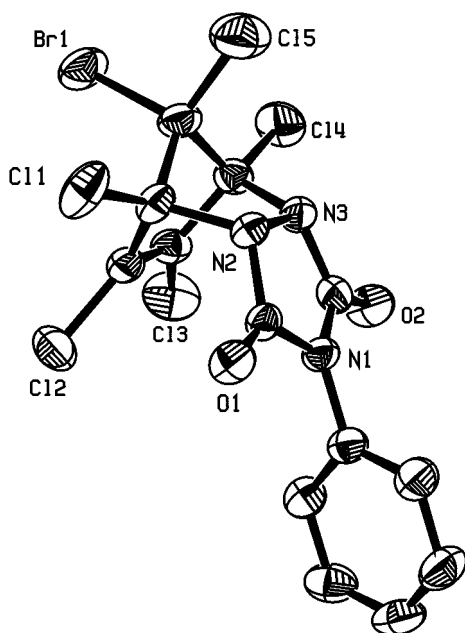
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† Author to whom correspondence regarding X-ray crystal structures should be addressed.

‡ In this paper "*syn*" and "*anti*" are relative to the chlorine at C-5 of the diene, or, for dienes without chlorine at C-5, "*syn*" and "*anti*" are with respect to the heteroatom at C-5.

§ The adduct mixture derived from vinylene carbonate also co-crystallized with some adduct derived from hexachlorocyclopentadiene.

Table 1 Reaction conditions, yields and facial selectivities of the Diels–Alder reactions of diene **11**

Dienophile and reaction conditions	Yield (%)	Adduct ratio by NMR	Adduct ratio by X-ray
N-Phenylmaleimide (2 equiv.); toluene reflux, 21 days	44	**12**:**13** 92:8	**12**:**13** 90:10
1,4-Naphthoquinone (2 equiv.); toluene reflux, 28 days	45	**14**:**15** 89:11	**14**:**15** 95:5
Styrene (1.5 equiv.); benzene reflux, 6 days	63	**16**:**17** 94:6	**16**:**17** 95:5
3-Nitrostyrene (1.5 equiv.); toluene reflux, 3 days	36	**18**:**19** 94:6	—
Vinylene carbonate (1.2 equiv.); neat, 150 °C, 3 h	9	**20**:**21** 88:12	**20**:**21** 93:7
4-Phenyl-1,2,4-triazoline-3,5-dione (1 equiv.); benzene reflux, 2 days	83	**22**:**23** 82:18	**22**:**23** 85:15

Fig. 1 ORTEP diagram for **22/23**.

12 X = Br, Y = Cl
13 X = Cl, Y = Br

14 X = Br, Y = Cl
15 X = Cl, Y = Br

16 X = Br, Y = Cl, Z = H
17 X = Cl, Y = Br, Z = H
18 X = Br, Y = Cl, Z = NO₂
19 X = Cl, Y = Br, Z = NO₂

20 X = Br, Y = Cl
21 X = Cl, Y = Br

22 X = Br, Y = Cl
23 X = Cl, Y = Br

approximate, but, as shown in Table 1, these ratios were similar to those obtained by NMR techniques.

Steric hindrance and torsional effects have been used to explain the facial selectivity in the Diels–Alder reactions of some cyclic, plane-nonsymmetric dienes,[4,8,10] but additions to dienes **1**,[1] **2**,[5] **24** and analogues[11] and **25**[4] all took place preferentially *syn* to the C-5 heteroatom. These reactions, and the reactions of some dienes fused to bicyclic systems,[12] led to the formulation of a number of hypotheses concerning factors that govern stereoelectronic control of this facial selectivity. The data in Table 1 indicate that none of these phenomena control facial selectivity with **11**. That the adduct ratios (Table 1) were the same with *N*-phenylmaleimide and 1,4-naphthoquinone ("normal" Diels–Alder reactions) as with vinylene carbonate ("inverse-electron-demand") ruled out control of facial selectivity by a facial bias in the π_{HOMO}[13] or the nucleophilicity[14] of the diene, or of orbital mixing between the heteroatom lone pairs and the incoming dienophile.[15] Control of facial selectivity in Diels–Alder reactions by a process similar to that originally hypothesized by Cieplak[16] for carbonyl additions would involve at the transition state σ-donation from the *anti* substituent at C-5 of the diene.[4,17] σ-Donation by a C–Cl bond should be similar to that of a C–Br bond,[18] so this hypothesis would predict little facial preference with **11**. Williamson and Hsu[3] have proposed that van der Waals/London type forces control facial selectivity with **3**, and he predicted that, since the polarizability of bromine is greater than that of chlorine, Diels–Alder additions to **11** should be mainly *syn* to bromine. Photoelectron spectra and calculations by Werstiuk and co-workers[19] have ruled out some of these hypotheses, and a recent *ab initio* computational study pointed out that steric control of facial selectivity with 5-substituted cyclopentadienes correlated very well with a computed steric factor.[8] That the facial selectivity with diene **11** is little affected by the electronic nature of its Diels–Alder
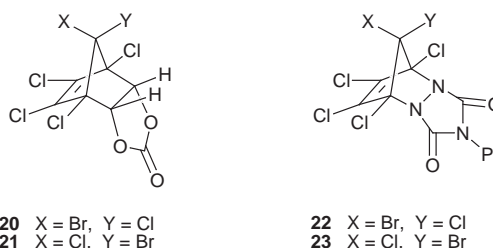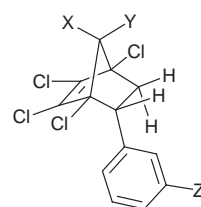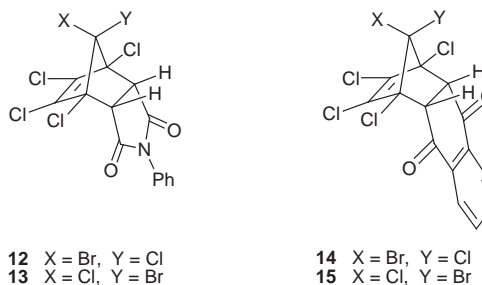
reactions is strong experimental corroboration for the proposal for control of facial selectivity by steric effects.

Experimental

General

Uncorrected mps were determined on a Fisher-Johns apparatus. IR spectra were measured as thin films on a Mattson Polaris FT instrument. A General Electric GE 300-NB spectrometer provided the ^{1}H and ^{13}C NMR spectra. Mass spectra (EI) were obtained on a V. G. Micromass 7070HS instrument or a Hewlett-Packard 5970 mass selective detector (GC–MS). The X-ray diffractometer was a Rigaku AFC6S instrument.

5-Bromo-1,2,3,4,5-pentachlorocyclopenta-1,3-diene 11

A 2.5 M solution of *n*-butyllithium (1.72 ml, 4.31 mmol) in hexane was added dropwise to a solution of 1,2,3,4,5-pentachlorocyclopenta-1,3-diene[5] (0.790 g, 3.32 mmol) in dry tetrahydrofuran (THF) (30 ml) at −78 °C. A solution of *N*-bromosuccinimide (0.804 g, 4.51 mmol) in THF (15 ml) was added, and the mixture was allowed to warm slowly to room temperature. The solution was concentrated under vacuum, and the orange–brown residue was redissolved in diethyl ether. The solution was washed with H₂O and brine, and dried over anhydrous MgSO₄. Flash chromatography with hexane as the

eluent gave *diene* **11** (0.834 g, 79%) as an orange–brown oil: ν_{max}(film)/cm^{-1} 1599, 1567, 1231, 1188 and 1136; δ_C 133.8, 127.3 and 67.7; *m/z* 322 (1%), 320 (5), 318 (9), 316 (10) and 314 (4) all M$^+$, 285 (3), 283 (8), 281 (10), 279 (4), 243 (3), 241 (21), 239 (68), 237 (100), 235 (61), 171 (0.2), 169 (5), 167 (15), 165 (16), 134 (3), 132 (14), 130 (23), 97 (10), 95 (31) and 60 (20).

General procedure for the Diels–Alder reactions: (3aα,4β,7β,7aα,8s)- 12 and (3aα,4β,7β,7aα,8r)-8-bromo-4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1H-isoindole-1,3-(2H)-dione 13

A solution of diene **11** (122 mg, 0.385 mmol) and *N*-phenylmaleimide (125 mg, 0.724 mmol) in toluene (8.0 ml) was heated under reflux for 21 days. The solution was concentrated under vacuum. TLC (EtOAc–hexanes) showed a single spot, but ^{1}H NMR analysis indicated this was a mixture of **12** and **13**, in a ratio of 11:1, respectively, and unreacted dienophile. The mixture was redissolved in CH$_2$Cl$_2$ (20 ml) and heated under reflux. 1,2,3,4-Tetramethyl-5,5-dimethoxycyclopenta-1,3-diene was added to consume the unreacted dienophile. Flash chromatography (5% EtOAc–hexanes) provided 83 mg (44%) of colourless crystals composed of both **12** and **13**, in the same ratio (by ^{1}H NMR) as before chromatography. Recrystallization (acetone–hexane) gave colourless needles with no change in the **12**:**13** ratio. For these crystals (Found C, 36.75; H, 1.52; N, 2.83. C$_{15}$H$_7$BrCl$_5$NO$_2$ requires C, 36.74; H, 1.44; N, 2.86%); mp 235–236 °C; ν_{max}(film)/cm^{-1} 1723; δ_H (for **12** from mixture) 7.50–7.38 (3 H, m), 7.16–7.09 (2 H, m) and 4.02 (2 H, s); δ_H (for **13** from mixture) 4.08 (s); δ_C (for **12** from mixture) 169.1, 132.1, 130.6, 129.5, 126.4, 95.2, 79.9 and 51.4; δ_C (for **13** from mixture) 94.6; *m/z* 497 (1%), 495 (6), 493 (21), 489 (38) and 487 (15) all M$^+$, 458 (2), 456 (4), 454 (4), 452 (2), 313 (2), 311 (11), 309 (29), 307 (35), 305 (15), 267 (4), 265 (12), 263 (18), 261 (12), 241 (2), 239 (7), 237 (11), 235 (7), 173 (100), 119 (19), 91 (15) and 54 (17).

(1α,4α,4aβ,9aβ,11r)- 14 and (1α,4α,4aβ,9aβ,11s)-11-bromo-1,2,3,4,11-pentachloro-1,4,4a,9a-tetrahydro-1,4-methano-anthracene-9,10-dione 15

Colourless crystals (mixture of **14** and **15**) were obtained from ether–petroleum ether: mp 139–140 °C; δ_H (for **14** from mixture) 8.02 (2 H, symmetrical m), 7.80 (2 H, symmetrical m) and 4.09 (2 H, s); δ_H (for **15** from mixture) 4.16 (s); δ_C (for **14** from mixture) 189.1, 135.2, 134.7, 132.3, 93.6, 82.3 and 54.2; *m/z* 480 (1%), 479 (0.8), 478 (4), 477 (2), 476 (8), 475 (2), 474 (8), 473 (0.7) and 472 (3) all M$^+$, 445 (0.2), 444 (0.1), 443 (2), 442 (1), 441 (4), 440 (1), 439 (5), 438 (0.7), 437 (3), 435 (0.2), 402 (0.5), 401 (1), 400 (0.5), 399 (3), 398 (2), 397 (8), 396 (2), 395 (12), 394 (2), 393 (7), 366 (0.4), 355 (1), 364 (2), 363 (2), 362 (6), 361 (4), 360 (14), 359 (6), 358 (13), 357 (4), 356 (3), 326 (3), 325 (9), 324 (6), 323 (10), 322 (12), 321 (3), 320 (43), 319 (5), 318 (83), 317 (5), 316 (81), 315 (2), 314 (33), 245 (0.7), 238 (9), 237 (100), 236 (6), 235 (61), 169 (22), 167 (64), 158 (12), 104 (66), 76 (98) and 50 (41).

(1R*,4S*,5R*,7R*)- 16 and (1R*,4S*,5R*,7S*)-7-bromo-1,2,3,4,7-pentachloro-5-phenylbicyclo[2.2.1]hept-2-ene 17

Colourless crystals (mixture of **16** and **17**) were obtained from ether–petroleum ether (Found C, 37.08; H, 1.73. C$_{13}$H$_8$BrCl$_5$ requires C, 37.06; H, 1.91%); mp 67–68 °C; ν_{max}(film)/cm^{-1} 1603; δ_H (for **16** from mixture) 7.33 (3 H, narrow m), 7.10 (2 H, narrow m), 4.01 (1 H, dd, *J* 4.3 and 9.1), 2.96 (1H, dd, *J* 9.1 and 12.9) and 2.51 (1H, dd, *J* 4.3 and 12.9); δ_H (for **17** from mixture) 4.07 (1 H, dd, *J* 4.1 and 9.1); δ_C (for **16** from mixture) 134.3, 132.3, 132.2, 128.9, 128.5, 94.6, 84.5, 79.4, 51.1 and 39.9; δ_C (for **17** from mixture) 52.1 and 41.1; *m/z* 424 (0.5%), 420 (0.5) and 418 (0.1) all M$^+$, 243 (0.2), 241 (1), 239 (3), 238 (0.7), 237 (5), 236 (0.5), 235 (4), 234 (0.8), 233 (3), 127 (16), 125 (55), 104 (100), 103 (10), 78 (11), 77 (7) and 51 (6).

(1R*,4S*,5R*,7R*)- 18 and (1R*,4S*,5R*,7S*)-7-bromo-1,2,3,4,7-pentachloro-5-(3-nitrophenyl)bicyclo[2.2.1]hept-2-ene 19

Colourless crystals (mixture of **18** and **19**) were obtained from ether–ethyl acetate–petroleum ether: mp 116–117 °C; ν_{max}(film)/cm^{-1} 1601, 1530 and 1349; δ_H (for **18** from mixture) 8.22 (1 H, d, *J* 8.1), 8.02 (1 H, narrow m), 7.58–7.43 (2 H, m), 4.14 (1 H, dd, *J* 4.3 and 9.2), 3.05 (1 H, dd, *J* 9.2 and 12.8) and 2.54 (1 H, dd, *J* 4.3 and 12.8); δ_H (for **19** from mixture) 4.20 (1 H, dd, *J* 4.8 and 9.8); δ_C (for **18** from mixture) 148.2, 136.7, 134.7, 133.2, 131.6, 129.6, 123.9, 123.5, 93.9, 84.3, 79.2, 50.8 and 39.9; δ_C (for **19** from mixture) 51.8 and 41.1; *m/z* 471 (0.6%), 470 (0.2), 469 (2), 468 (0.5), 467 (3), 466 (0.6), 465 (3), 464 (0.1) and 463 (1) all M$^+$, 324 (2), 323 (1), 322 (14), 321 (3), 320 (50), 319 (6), 318 (99), 317 (6), 316 (100), 315 (2), 314 (38), 310 (2), 300 (0.8), 299 (10), 298 (2), 297 (25), 296 (2), 295 (31), 294 (1), 293 (14), 243 (3), 242 (1), 241 (19), 240 (3), 239 (57), 238 (5), 237 (88), 236 (3), 235 (55), 220 (2), 219 (0.7), 218 (5), 217 (1), 216 (11), 215 (1), 214 (9), 172 (9), 170 (28), 149 (15), 133 (14), 103 (33) and 77 (34).

(3aα,4β,7β,7aα,8s)- 20 and (3aα,4β,7β,7aα,8r)-8-bromo-4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one 21

Sublimation then recrystallization from ether–petroleum ether gave colourless crystals (mixture of **20**, **21** and the adduct derived from hexachlorocyclopentadiene): mp 145–155 °C (subl.); ν_{max}(film)/cm^{-1} 1822; δ_H (for **20** from mixture) 5.40 (s); δ_H (for **21** from mixture) 5.44 (s); δ_H (for hexachloro adduct from mixture) 5.37 (s); δ_C (for **20** from mixture) 151.3, 132.7, 88.8, 82.0 and 81.1; *m/z* (GC–MS) 406 (3%), 404 (14) and 402 (11) all M$^+$, 322 (18), 320 (59), 319 (17), 318 (98), 317 (2), 316 (100), 314 (38), 296 (15), 294 (18), 292 (9), 254 (2), 252 (16), 251 (7), 250 (23), 249 (2), 248 (16), 241 (17), 239 (59), 238 (3), 237 (86), 236 (2), 235 (55), 218 (17), 217 (10), 216 (40), 215 (21), 214 (34), 213 (16), 145 (17), 144 (10), 143 (33), 142 (4), 141 (15), 108 (40) and 73 (19).

(10s)- 22 and (10r)-10-bromo-5,6,7,8,10-pentachloro-5,8-dihydro-2-phenyl-5,8-methano-1H-[1,2,4]triazolo[1,2-a]-pyridazine-1,3(2H)-dione 23

Colourless crystals (mixture of **22** and **23**) were obtained from CH$_2$Cl$_2$–hexane (Found C, 31.69; H, 1.00; N, 8.50. C$_{13}$H$_5$BrCl$_5$-N$_3$O$_2$ requires C, 31.71; H, 1.02; N, 8.53%); mp 137–141 °C but turning pink first at 130 °C; ν_{max}(film)/cm^{-1} 3076, 3046, 3022, 1804, 1749 and 1596; δ_C (for **22** from mixture) 154.6, 129.6, 129.5, 129.4, 125.5, 92.7 and 87.0; δ_C (for **23** from mixture) 127.8 and 86.4; *m/z* 460 (0.4%), 458 (1.5), 456 (1.7) and 454 (0.7) all M$^+$ − Cl, 324 (0.6), 322 (5), 320 (18), 318 (34), 316 (34), 314 (13), 287 (0.3), 285 (3), 283 (7), 281 (8), 279 (4), 243 (3), 241 (20), 239 (64), 237 (100), 235 (62), 119 (68), 91 (31) and 64 (19).

X-Ray analysis of 12/13

Crystal data. Colourless irregular crystal 0.15 × 0.10 × 0.40 mm; C$_{15}$H$_7$BrCl$_5$NO$_2$, *M* = 490.39. Monoclinic, *a* = 7.762(2), *b* = 37.419(2), *c* = 12.518(2) *β* = 90.81(2)°, *V* = 3635.4(8) Å^3 (from a least-squares refinement using the settings of 16 carefully centred reflections in the range 58.52 < 2θ < 59.69°, λ = 1.54178 Å, *T* = 26.0 °C), space group *P*2$_1$/*c* (#14), *Z* = 8, D_{calc} = 1.79 g cm^{-3}, μ(Cu-Kα) = 99.3 cm^{-1}.

Data collection and processing. Graphite-monochromated Cu-Kα radiation, ω-2θ scans, with 2θ maximum 120.1°, ω scan width (0.94 + 0.14 tan θ)°; 5985 reflections collected (2.5 ≤ θ ≤ 60°, ±8 *h*, ±40 *k*, 14 *l*), of which 5533 (R_{int} = 0.034) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on

azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.68 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 6.41292e^{-7}).

Structure analysis and refinement. The structure was solved by and expanded using Fourier techniques.[20] Non-H atoms were refined anisotropically; H atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3340 observed reflections ($I = 2.00\sigma(I)$) and 434 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 90% bromine *anti* at C-8, the agreement factors were R ($\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) = 0.045 and R_w ($[\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o^2)]^{1/2}$) = 0.046 with GOF = 1.64 (for 85% bromine *anti* at C-8, $R = 0.047$, $R_w = 0.048$, GOF = 1.71; for 95% bromine *anti* at C-8, $R = 0.047$, $R_w = 0.049$, GOF = 1.76). The weighting scheme was based on counting statistics and included a factor ($p = 0.022$) to downweight the intense reflections. Plots of $\Sigma_w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.44 and −0.45 e Å^{-3}, respectively. Neutral atom scattering factors were from the *International Tables for X-ray Crystallography*.[21a] Anomalous dispersion effects were included in F_{calc};[22] the values for $\Delta f'$ and $\Delta f''$ and for the mass attenuation coefficients were from the *International Tables for Crystallography*.[23a,b] Calculations used the TEXSAN crystallographic software package.[24]

X-Ray analysis of 14/15

Crystal data. Colourless irregular crystal 0.20 × 0.05 × 0.40 mm mounted on a glass fibre; $C_{15}H_6BrCl_5O_2$, $M = 475.38$. Triclinic, $a = 13.562(5)$, $b = 14.154(5)$, $c = 11.188(2)$ Å, $a = 108.29(2)$, $\beta = 95.32(2)$, $\gamma = 116.92(3)°$, $V = 1746.8(13)$ Å^3 (from a least-squares refinement using the settings of 21 carefully centred reflections in the range $20.08 < 2\theta < 25.10°$, $\lambda = 0.71069$ Å, $T = 26.0 °C$), space group P-1 (#2), $Z = 4$, $D_{calc} = 1.81$ g cm^{-3}, μ(Mo-Kα) = 31.3 cm^{-1}.

Data collection and processing. Graphite-monochromated Mo-Kα radiation, $\omega + 2\theta$ scans, with 2θ maximum 50.1°, ω scan width (1.15 + 0.35 tan θ)°; 6459 reflections collected ($2.5 \leq \theta \leq 25°$, ±16 h, ±16 k, 13 l), of which 6174 ($R_{int} = 0.051$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.74 to 1.00. Data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The structure was solved by direct methods and expanded Fourier techniques.[20,25] Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2811 observed reflections ($I = 2.00\sigma(I)$) and 415 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 95% bromine *anti* at C-11, the agreement factors were $R = 0.049$ and $R_w = 0.047$ with GOF = 1.41 (for 90% bromine *anti* at C-11, $R = 0.050$, $R_w = 0.047$, GOF = 1.44; for 100% bromine *anti* at C-11, $R = 0.051$, $R_w = 0.050$, GOF = 1.52). The weighting scheme was based on counting statistics and included a factor ($p = 0.027$) to downweight the intense reflections. Plots of $\Sigma_w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.47 and −0.45 e Å^{-3}, respectively. Neutral atom scattering factors were from the *International Tables for X-ray Crystallography*.[21a] Anomalous dispersion effects were included in F_{calc}.[22] The values for $\Delta f'$ and $\Delta f''$ were from the *International Tables for Crystallography*.[23a]

Calculations used the TEXSAN crystallographic software package.[24]

X-Ray analysis of 16/17

Crystal data. Colourless irregular crystal 0.20 × 0.30 × 0.40 mm mounted on a glass fibre; $C_{13}H_8BrCl_5$, $M = 421.38$. Monoclinic, $a = 14.075(2)$, $b = 10.224(3)$, $c = 11.551(3)$ Å, $\beta = 70.33(2)°$, $V = 1565(1)$ Å^3 (from a least-squares refinement using the settings of 14 carefully centred reflections in the range $29.45 < 2\theta < 32.39°$, $\lambda = 0.71069$ Å, $T = 26.0 °C$), space group $P2_1/c$ (#14), $Z = 4$, $D_{calc} = 1.788$ g cm^{-3}, μ(Mo-Kα) = 34.4 cm^{-1}.

Data collection and processing. Graphite-monochromated Mo-Kα radiation, ω-2θ scans, with 2θ maximum 50.1°, ω scan width (1.37 + 0.35 tan θ)°; 3083 reflections collected ($2.5 \leq \theta \leq 25°$, ±16 h, ±12 k, 13 l), of which 2941 ($R_{int} = 0.050$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.87 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.33243e^{-7}).

Structure analysis and refinement. The structure was solved by direct methods.[20,26] Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1573 observed reflections ($I < 2.0\sigma(I)$) and 197 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 95% bromine *anti* at C-7, the factors were $R = 0.041$ and $R_w = 0.040$ with GOF = 1.40 (for 90% bromine *anti* at C-7, $R = 0.045$, $R_w = 0.043$, GOF = 1.52; for 100% bromine *anti* at C-7, $R = 0.043$, $R_w = 0.043$, GOF = 1.50). The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma_w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.33 and −0.44 e Å^{-3}, respectively. Neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were from the *International Tables for X-ray Crystallography*.[21a,b] Anomalous dispersion effects were included in F_{calc}.[22] Calculations used the TEXSAN crystallographic software package.[27]

X-Ray analysis of 20/21

Crystal data. Colourless irregular crystal 0.30 × 0.25 × 0.40 mm mounted on a glass fibre; $C_8H_2Br_{0.7}Cl_{5.3}O_3$, $M = 389.94$. Monoclinic, $a = 12.453(2)$, $b = 23.838(2)$, $c = 8.853(5)$ Å, $\beta = 84.84(3)°$, $V = 2617(2)$ Å^3 (from a least-squares refinement using the settings of 20 carefully centred reflections in the range $23.85 < 2\theta < 31.07°$, $\lambda = 0.71069$ Å, $T = 26.0 °C$), space group $P2_1/c$ (#14), $Z = 8$, $D_{calc} = 1.979$ g cm^{-3}, μ(Mo-Kα) = 32.8 cm^{-1}.

Data collection and processing. Graphite-monochromated Mo-Kα radiation, ω-2θ scans, with 2θ maximum 50.1°, ω scan width (1.15 + 0.35 tan θ)°; 5081 reflections collected ($2.5 \leq \theta \leq 25°$, ±14 h, ±28 k, 10 l), of which 4763 ($R_{int} = 0.044$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.89 to 1.00. Data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The structure was solved by direct methods.[20,26] Non-H atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2180 observed reflections ($I < 2.0\sigma(I)$) and 307

variable parameters and converged (largest parameter shift was 0.00 times its esd). With 65% bromine *anti* at C-8 (**20**), 5% *syn* at C-8 (**21**) and 30% of the hexachloro-adduct, the agreement factors were $R = 0.047$ and $R_w = 0.047$ with GOF = 1.46 (for 70% **20** and 30% of the hexachloro-adduct $R = 0.049$, $R_w = 0.048$, GOF = 1.51; for 65% **20**, 8% **21** and 27% hexachoro-adduct $R = 0.049$, $R_w = 0.048$, GOF = 1.51). The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma_w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to $+0.45$ and -0.40 e Å^{-3}, respectively. Neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were from the *International Tables for X-ray Crystallography*.[21a,b] Anomalous dispersion effects were included in F_{calc}.[22] Calculations used the TEXSAN crystallographic software package.[27]

X-Ray analysis of 22/23

Crystal data. Colourless irregular crystal $0.30 \times 0.30 \times 0.30$ mm mounted on a glass fibre; $C_{13}H_5BrCl_5N_3O_2$, $M = 492.37$. Monoclinic, $a = 9.019(6)$, $b = 13.339(9)$, $c = 14.876(4)$ Å, $\beta = 104.00(4)°$, $V = 1736.4(15)$ Å^3 (from a least-squares refinement using the settings of 21 carefully centred reflections in the range $36.70 < 2\theta < 44.96°$, $\lambda = 0.71069$ Å, $T = 26.0$ °C), space group $P2_1/c$ (#14), $Z = 4$, $D_{calc} = 1.88$ g cm^{-3}, μ(Mo-Kα) = 31.5 cm^{-1}.

Data collection and processing. Graphite-monochromated Mo-Kα radiation, ω-2θ scans, with 2θ maximum 50.1°, ω scan width $(0.94 + 0.35 \tan \theta)°$; 3435 reflections collected $(2.5 \leq \theta \leq 25°$, ± 10 h, ± 15 k, 17 l), of which 3222 ($R_{int} = 0.023$) were unique. Intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.92 to 1.00. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.58686e^{-7}).

Structure analysis and refinement. The structure was solved by direct methods and expanded Fourier techniques.[20,25] Non-H atoms were refined anisotropically. The H-atom coordinates were refined but their isotropic B's were held fixed. The final cycle of full-matrix least-squares refinement was based on 2285 observed reflections ($I < 2.0\sigma(I)$) and 233 variable parameters and converged (largest parameter shift was 0.00 times its esd). With 85% bromine *anti* at C-10, the agreement factors were $R = 0.038$ and $R_w = 0.038$ with GOF = 1.87 (for 75% bromine *anti* at C-10, $R = 0.048$, $R_w = 0.052$, GOF = 2.58; for 95% bromine *anti* at C-10, $R = 0.045$, $R_w = 0.050$, GOF = 2.49). The weighting scheme was based on counting statistics and included a factor ($p = 0.020$) to downweight the intense reflections. Plots of $\Sigma_w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to $+0.41$ and -0.40 e Å^{-3}, respectively. Neutral atom scattering factors were from the *International Tables for X-ray Crystallography*.[21a] Anomalous dispersion effects were included in F_{calc}.[22] The values for $\Delta f'$ and $\Delta f''$ and the values for the mass attenuation coefficients were from the *International Tables for Crystallography*.[23a,b] Calculations used the TEXSAN crystallographic software package.[24]

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/265.

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