# Selective Alkali-metal Cation Complexation by Chemically Modified Calixarenes. Part 4. Effect of Substituent Variation on the $Na^+/K^+$ Selectivity in the Ester Series and X-Ray Crystal Structure of the Trifluoroethyl Ester

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The cation complexing abilities of a series of *p-tert*-butylcalix[4]arenes bearing ligating ester groups in the cone conformation have been assessed by stability constant measurements in methanol and extraction studies from water into dichloromethane. The cations studied were $Na^+$ and $K^+$ and variations in the ester function ($CO_2R$) included R = methyl, ethyl, *n*-butyl, *tert*-butyl, benzyl, phenyl, phenacyl, methoxyethyl, trifluoroethyl, methylthioethyl and prop-2-ynyl. The effect of replacing one or two ester functions in the tetraethyl ester by methyl ester, carboxylic acid, ketone and amide functions was also studied. Selectivities for $Na^+$ relative to $K^+$ in stability constants range from 2 to 2500, the phenacyl derivative having the highest selectivity. X-Ray diffraction analysis was used to probe the conformation of the trifluoroethyl ester **11**. Crystals of **11** are monoclinic, space group $P2_1/n$, in a cell of dimensions $a = 13.987(2)$, $b = 16.194(3)$, $c = 27.630(5)$ Å; $\beta = 98.70(1)°$; $R = 0.077$ for 3172 observed data. The compound possesses a distorted cone conformation.

The ability of calix[4]arene esters of general formula **1** to bind selectively alkali-metal cations in supramolecular arrays is now well established.[1] The preference of a receptor for one cation ($M^+$) relative to another ($M'^+$) is conveniently expressed by the selectivity ratio $S_{M^+} = \beta_{M^+}/\beta_{M'^+}$ where $\beta$ is the stability constant for complexation of each cation by the receptor in a suitable solvent, *e.g.* water or methanol. The preference can also be reflected by the extent of extraction (%E), the latter referring to the ability of the receptor to transfer the cation from one phase to another, *e.g.* from water into dichloromethane. For the ethyl ester **2** we found concurring trends in $\beta$ and %E values for the alkali-metal cations, both showing a distinct preference for $Na^+$ over $K^+$ with $S_{Na^+} = 400$.[2] In the same study, however, we found that changing the alkoxy moiety of the ester group, or replacing the ester group by a ketonic or amide group, could cause significant changes in $\beta$ values for complexation and %E for extraction.[2,3] Since one of our objectives in this area is to maximise $S_{M^+}$ values for selected cations for possible applications in sensors,[4] we have now studied in greater detail substituent effects in the alkoxy group in the ester series. The compounds studied are summarised in formulae **2**–**12** and **15**–**19**, and the values for log $\beta$ and %E for $Na^+$ and $K^+$, together with the $S_{Na^+}$ values, are collected in Table 1, the data for the ethyl ester having been taken from our earlier study.[2]

**Table 1** Values of log $\beta$, %E and $S_{Na^+}$ for calix[4]arene esters **2**–**20**

| | | Complexation: log $\beta$[a] | | | Extraction %[d] | |
|---|---|---|---|---|---|---|
| Compound | R | $Na^+$ | $K^+$ | $S_{Na^+}$ | $Na^+$ | $K^+$ |
| **2**[b] | OEt | 5.0 | 2.4 | 400 | 29 | 5 |
| **3** | OMe | 4.5 | 2.3 | 160 | 15 | 3 |
| **4** | $OBu^n$ | 5.6 | 2.7 | 800 | 25 | 2 |
| **5** | $OBu^t$ | 4.7 | 4.0 | 5 | 56 | 9[e] |
| **6** | $OCH_2Ph$ | 4.6 | 2.4 | 160 | 18 | 2 |
| **7** | OPh | 5.3 | 2.4 | 800 | 11 | 4 |
| **8** | $OCH_2COPh$ | 5.1 | 1.7 | 2500 | 11 | 2 |
| **9** | $O(CH_2)_2OMe$ | 4.7 | 2.3 | 250 | 14 | 1 |
| **10** | $O(CH_2)_2SMe$ | 3.8 | <1[f] | 630 | 11 | 1 |
| **11** | $OCH_2CF_3$ | 3.4 | 2.0 | 25 | 2 | 2 |
| **12** | $OCH_2C{\equiv}CH$ | 4.4 | 2.4 | 100 | 5 | 2 |
| **15**[c] | Me | 5.2 | 2.8 | 250 | 31 | 9 |
| **16**[c] | OMe | 5.0 | 2.5 | 320 | 22 | 2 |
| **17** | OH | 5.7 | 4.9 | 6 | 0 | 0 |
| **18**[c] | $NEt_2$ | 4.3 | 4.0 | 2 | 51 | 6 |
| **19**[c] | $NC_4H_8$ | 4.4 | 3.5 | 8 | 51 | 6 |
| **20** | Cl | | | | | |

[a] Arithmetic mean of at least two experiments — standard deviation on the mean: $\sigma_{n-1} = 0.2 - 0.3$ log units. [b] Ref. 2. [c] Ref. 1. [d] Arithmetic mean of several experiments — standard deviation on the mean: $\sigma_{n-1} = 1 - 2$. [e] Corresponding value for a calix[4]arene *tert*-butyl ketone[2] with $Na^+$: 28 and with $K^+$: 19. [f] Too low to be measured by the technique employed.

Tetraesters **2**, **3** and **5** are known compounds. Tetrabenzyl ester **6** and tetra(2-methylthioethyl) ester **10** were prepared by transesterification of **2** with benzyl alcohol and 2-methylthioethanol, respectively. Compounds **4**, **7**, **9**, **11** and **12** were prepared in a two-step sequence from the known tetraacid **13**[5] which could be readily converted into tetraacid chloride **14** using thionyl chloride. Exposure of the tetraacid chloride to the appropriate alcohol gave the ester. The phenacyl ester **8** was obtained by exposing tetraacid **13** to phenacyl bromide in the presence of potassium fluoride. All members of the series were obtained as microanalytically pure solids. That each possessed the cone conformation in solution was quickly established by $^1H$ NMR measurements which revealed the characteristic pattern of singlets for the *tert*-butyl, aromatic and $OCH_2CO$ protons and an AB system for the $ArCH_2Ar$ protons. Although

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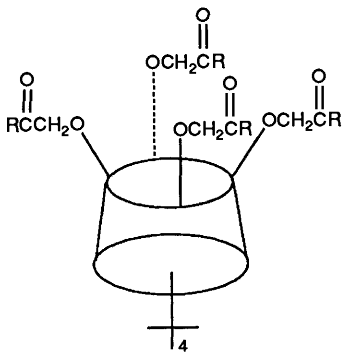
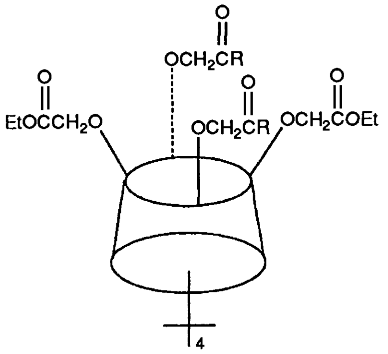
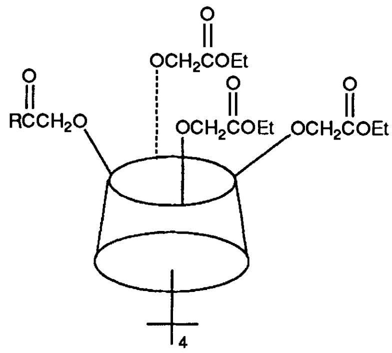


| | R |
|---|---|
| **1** | OAlkyl |
| **2** | OEt |
| **3** | OMe |
| **4** | $OBu^n$ |
| **5** | $OBu^t$ |
| **6** | $OCH_2Ph$ |
| **7** | OPh |
| **8** | $OCH_2COPh$ |
| **9** | $OCH_2CH_2OMe$ |
| **10** | $OCH_2CH_2SMe$ |
| **11** | $OCH_2CF_3$ |
| **12** | $OCH_2C{\equiv}CH$ |
| **13** | OH |
| **14** | Cl |



**15** R = Me



| | R |
|---|---|
| **16** | OMe |
| **17** | OH |
| **18** | $NEZ_2$ |
| **19** | pyrrolidin-1-yl |
| **20** | Cl |

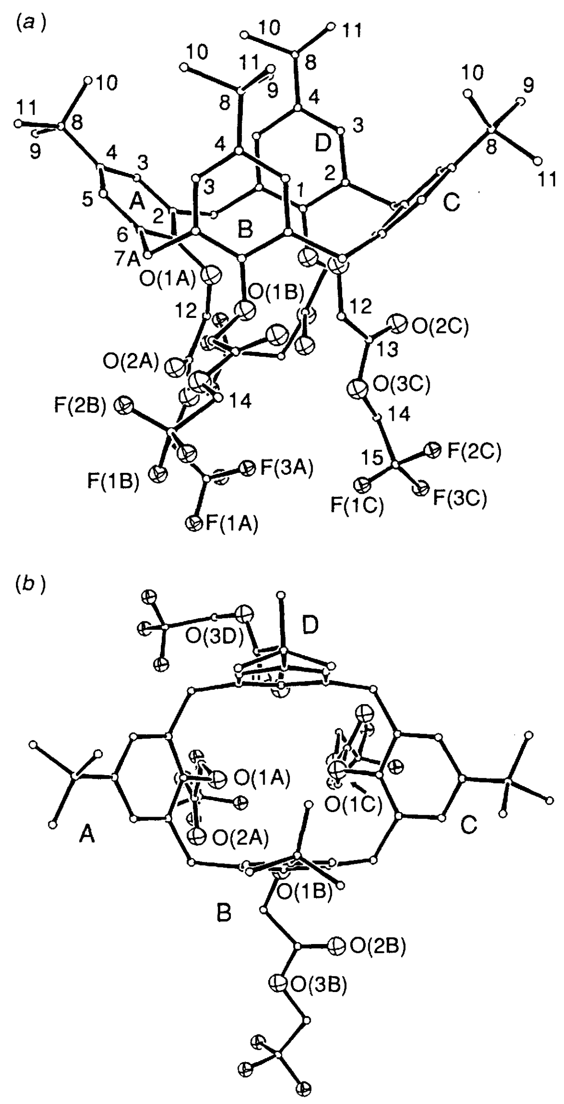


Fig. 1 (*a*) A general view of **11** showing the crystallographic numbering system. (*b*) A view of **11** looking onto the plane of the four $CH_2$ groups which link the four aromatic rings. For clarity in both diagrams, the hydrogen atoms are omitted and carbon, oxygen and fluorine atoms are shown as small spheres of arbitrary size.

the NMR data indicate four fold symmetry for these esters, X-ray analysis of the methyl and ethyl derivatives reveals that in the solid state the cone conformations are in fact highly distorted with two distal aromatic rings essentially parallel and the remaining two aromatic rings almost normal to one another. In the light of the complexation characteristics of the trifluoroethyl ester **11** (*vide infra*) we decided to probe the solid state conformation of this derivative also.

X-Ray diffraction analysis confirmed that this ester does adopt the cone conformation in the solid state [Fig. 1(*a*) and [(b)].

The conformation is defined by the angles which the aromatic rings make with the plane of the four $CH_2$ moieties which link them, *viz.* 133.3(2) (A), 82.0(2) (B), 139.0(2) (C) and 100.7(2)° (D) [interplanar angles $>90°$ indicate that the ring system is tilted so that its *tert*-butyl group is directed *away from* the ring cavity and angles of $<90°$ show that the ring is tilted so that its *tert*-butyl group is directed *towards* the ring cavity]. Two aromatic rings (A and C) are almost normal to one another [interplanar angle 92.5(2)°] while rings B and D are almost parallel [interplanar angle 2.7(2)°] with ring B being tilted so that its *tert*-butyl group is pitched slightly towards the calix cavity and ring D tilted so that its *tert*-butyl group is away from the ring cavity. The conformation leads to oxygens O(1A) and O(1C) being separated by 3.434(8) Å; the O(1B)···O(1D) separation is 5.453(8) Å. The O–O distances between adjacent ethereal O atoms are in the range 2.931(8)–3.448(8) Å. The conformations adopted by the trifluoro ester groups are

**Table 2** Summary of bond lengths/Å for **11**

| Bond | Range | Mean |
|---|---|---|
| $C_{ar}$–O | 1.380(9)–1.390(9) | 1.384 |
| $C_{sp^3}$–O | 1.392(10)–1.416(10) | 1.403 |
| $CH_2$–$C_{sp^2}$ | 1.468(12)–1.501(15) | 1.485 |
| $C_{sp^2}$=O | 1.149(13)–1.183(10) | 1.169 |
| $C_{sp^2}$–O | 1.264(13)–1.368(10) | 1.335 |
| $C_{sp^3}$–O | 1.398(12)–1.496(16) | 1.431 |
| $CH_2$–$CF_3$ | 1.411(17)–1.531(24) | 1.481 |
| $C_{sp^3}$–F | 1.131(19)–1.393(14) | 1.291 |
| $C_{ar}$–$CH_2$ | 1.490(11)–1.531(12) | 1.513 |
| $C_{ar}$–$C_{Bu^t}$ | 1.492(12)–1.548(12) | 1.520 |
| $C_{sp^3}$–$C_{Me}$ | 1.440(17)–1.535(20) | 1.494 |

presumably the consequences of crystal packing effects; the ester group on ring B is oriented *exo* (Fig. 1) and the other three are oriented below the calix cone. Molecular dimensions (bond lengths are summarised in Table 2) are unexceptional. The trifluoro ester groups are markedly anisotropic, but there was no clear indication from difference maps of more than one conformation being adopted.

In view of the fact that ketonic and amide carbonyl groups are also efficient binders when attached to the lower rim of calix[4]arenes, we decided to include in the study the influence of various functional group combinations on the complexation preference. Two modifications were examined. In one, two distal ester functions were replaced by methyl ketones as in **15** and in the second modification one ethyl ester group of **2** was replaced successively by a methyl ester **16**, a carboxylic acid **17**, a diethylamide **18**, and a pyrrolidine amide **19**. Compounds **15**[6] and **17**[7] were already in hand and the latter of the two provided easy access to **16** (*via* treatment with diazomethane) and **18** and **19** *via* monoacid chloride (**20**) formation followed by exposure to the appropriate secondary amine.[8] Although the $^1H$ NMR data for these mixed functionality derivatives were more complex than those of their homo-substituted counterparts, there was little doubt that they are all members of the cone conformation family.

Physicochemical studies on receptors **2**–**12** and **15**–**19** were carried out with respect to $Na^+$ and $K^+$ complexation using the techniques of stability constant ($\beta$) determination in methanol and picrate extraction from water into dichloromethane according to the procedure of Pedersen. Details are given in the Experimental section.

## Results and Discussion

In the main, the results in Table 1 demonstrate a broad measure of agreement between log $\beta$ and %E. With the exception of the monocarboxylic acid **17**, for which there was no response to either $Na^+$ or $K^+$ in extraction, with the procedure used here there is a preference for $Na^+$ over $K^+$ in both sets of measurements. More interesting, however, is the sensitivity of both $\beta$ and %E values to seemingly small changes in the ester podands. Thus, simple alkyl group variation in the ester has a significant effect on $S_{Na^+}$. Whereas a methyl group decreases $S_{Na^+}$ relative to the value for the ethyl group, the reverse is the case for the *n*-butyl group (compound **4**). A *tert*-butyl residue, on the other hand, has the effect of diminishing selectivity, an effect similar to that observed earlier with the tetra-*tert*-butyl ketone.[2] The influence of a benzyl group (compound **6**) is rather similar to that of a methyl group. The preference for $Na^+$ shown in stability constants is also found in extraction but here, with the exception of the *tert*-butyl ester **5**, the effect is less pronounced with the ethyl and *n*-butyl esters showing identical %E values for both $Na^+$ and $K^+$ relative to the other alkyl esters. The sodium selectivity of the phenyl ester **7** is very similar to that of the *n*-butyl ester, though the latter is about twice as efficient in extraction.

Ester groups containing heteroatoms or multiple bonds are capable of producing very large changes in $S_{Na^+}$ with values ranging from *ca.* 2500 for the phenacyl group to 25 for the trifluoroethyl group. The phenacyl ester offers two potential binding sites since the $-OCH_2CO-$ moiety in the side chain is known to have good ligating properties, *cf.* the ketone series referred to earlier. It is also possible that the high discrimination of the phenacyl ester is the result of a better preorganisation of the receptor and better match with $Na^+$ resulting from the more rigid phenacyl moiety. Compounds **9** and **10** are ethyl esters with β-methoxy and thiomethyl, respectively, in the side chain, all capable of participating in binding. Of the two, the thiomethyl derivative shows the higher $Na^+$ selectivity.

The $S_{Na^+}$ values for the trifluoroethyl ester **11** and the prop-2-ynyl ester **12** are among the lowest measured. They are also among the lowest in extraction; within the limits of accuracy the trifluoroethyl ester does not extract either sodium or potassium ion. The trifluoroethyl ester, like the other esters in the series, does occupy the cone conformation. Indeed, the similarities between the X-ray crystal structure of **12** and those of the methyl and ethyl esters are striking, suggesting that poor preorganisation of the binding groups in the fluorinated compound is not a significant feature of its inability to extract the alkali-metal cations from aqueous solution.

In the mixed functional group series introduction of one methyl ester among three ethyl esters, as in **16**, has predictably little effect on $S_{Na^+}$. Similarly, introduction of two methyl ketone residues in place of two ethyl esters has little effect on $S_{Na^+}$ (compound **15**). However, here both log $\beta$ and %E values point to stronger binding of both $Na^+$ and $K^+$ relative to the tetraethyl ester, an effect consistent with the stronger binding power of the tetramethyl ketone. The behaviour of the monoacid triester **17** was significantly different from the other members of the series. Whereas the log $\beta$ values for both sodium and potassium ion were the highest measured, though $S_{Na^+}$ was very low, there was no evidence of picrate ion extraction for either cation under the conditions used here. However, this evidence does not exclude the extraction of $Na^+$ or $K^+$ as a *neutral* complex of the calixarene in its monocarboxylate anionic form. The titration technique used to measure log $\beta$ for $Na^+$ and $K^+$ in methanol clearly demonstrated the formation of the carboxylate ion from **17**. The log $\beta$ values for **17** reflect stronger binding as one would expect for a carboxylate ion as compared with a neutral ester group.

The final entries demonstrate the effect of introducing one tertiary amide function among three ethyl ester groups. We have earlier demonstrated that calix[4]arene tertiary amides are much stronger binders than esters for $Na^+$ and $K^+$ but much less discriminating in terms of selectivity. The results obtained with **18** and **19** suggest that one amide group among three ester groups is sufficient to reduce the $Na^+$ selectivity by increasing log $\beta$ for potassium for which the value of log $\beta$ for the corresponding tetraamide is 5.8. The stronger binding power of monoamides **18** and **19** is also seen in extraction where the selectivity still favours the $Na^+$ ion.

## Conclusions

In conclusion, it is clear that substituent variation in the ester podands of these chemically modified calixarenes can have significant effects on cation binding selectivity for alkali metals. Although all the derivatives studies here have the cone conformation in solution, it is very likely that the substituents do influence the disposition of the ligating atoms around the hydrophilic cavity and therefore their binding power. Where substituent effects have been observed with crowns and cryptands they are believed to be the result of substituent-induced conformation changes in the vicinity of the ligating oxygen or nitrogen atoms.[9] In benzo crown ethers, substituents on the benzene nucleus can cause changes in stability constants for complexation of sodium and potassium ions, an effect probably of electronic rather than steric origin.[10]

## Experimental

*Materials.*—The solvent methanol (Carlo Erba, max. 0.01% water) was used without further purification. The metallic salts were either perchlorates or chlorides according to the method: NaCl (Merck, *pa*), KCl (Merck, *pa*), $NaClO_4$ (Merck, *pa*), $KClO_4$ (Prolabo, Normapur) and $AgClO_4$ (Fluka). They were dried under vacuum for 24 h before use. The supporting electrolyte, either tetraethylammonium perchlorate $Et_4NClO_4$ (Fluka, *purum*) or chloride, $Et_4NCl$ (Fluka, *purum*), were first recrystallised from methanol and acetone, respectively, and dried under vacuum for 24 h.

*Physical Measurements.*—For all compounds except the monoacid derivative **17** the stability constant measurements were determined by UV absorption spectrophotometry at 25 °C. The highest values for compounds **4** and **7** were checked by potentiometry using the competition with $Ag^+$ as the auxiliary cation and knowing the corresponding stability constants for the corresponding $Ag^+$ complexes ($\log \beta = 4.1$ in both cases). The potentiometric results are given in Table 1. The procedure and the experimental details were as previously described.[3] For the acid derivative **17** the stability constants were measured by potentiometry using the competition with the proton. Solutions of ligand in methanol ($c_L \simeq 10^{-3}$ mol dm$^{-3}$), in the presence of different amounts of the metallic salt, were titrated with a solution of $Et_4NOH$ in the same solvent. $Et_4NClO_4$ was used to maintain the ionic strength to $10^{-2}$ mol dm$^{-3}$. The drop in the pH values with the respect to the same titration without the metallic salt is directly related to the extent of complexation. The stability constants were determined from the treatment of the experimental curves by the program MINIQUAD.[11] The following protonation constant of the ligand, obtained from titrations in the same conditions but in the absence of the metallic salt, was used in the calculations: $\log K = 10.24$.[12]

The titrations were performed with an automatic titrator (Titroprocessor Metrohm 636) at 25 °C. The standard filling solution (saturated aqueous KCl) of the external reference of the combined glass electrode (Ingold) was replaced by a 0.01 mol dm$^{-3}$ $Et_4NCl$ methanolic solution saturated with AgCl. The electrode was calibrated at pH = 2 (pH being the cologarithm of the concentration of $H^+$) with a solution of $10^{-2}$ mol dm$^{-3}$ $HClO_4$ in methanol. As the junction potential varies exponentially with pH,[12] eqn. (1) was used to correct the

$$\mathrm{pH_{real}} = \mathrm{pH_{read}} + a + b10^{-\mathrm{pH}} \qquad (1)$$

pH reading. Constants $a = 0.2$ and $b = 20.0$ were determined by measuring the pH for $10^{-3}$ mol dm$^{-3}$ $HClO_4$ in methanol ($9.10^{-3}$ mol dm$^{-3}$ in $Et_4NClO_4$).

The extraction measurements from water to dichloromethane were performed as already published.[3] The results are expressed as the percentage of cation extracted.

*Preparation of Compounds* **1–12**.—The ethyl, methyl and *tert*-butyl esters, **2**,[2] **3**[2] and **5**,[2] diester–diketone **15**,[6] triester monoacid **17**[7] and triester monoacid chloride **20** were already available from our earlier studies. Coupling constant values *J* are given in Hz throughout.

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetracarboxymethoxycalix*[4]*arene* (**13**).—A suspension of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(ethoxycarbonylmethoxy)calix[4]arene (**2**) (20 g, 0.02 mol) in ethanol (300 cm$^3$) and water (200 cm$^3$) containing sodium hydroxide (20 g, 0.5 mol) was heated under reflux for 21 h. The cooled solution was acidified with 50% sulfuric acid to pH 1 and the resulting precipitate was isolated, washed with water and dried at 40 °C. Recrystallization from ethanol–water gave the tetraacid **13** as needles (17.8 g, 89%), m.p. 278–281 °C (Found: C, 70.6; H, 7.40. $C_{52}H_{64}O_{16}$ requires C, 70.9; H, 7.3%); $\nu_{max}$(KBr/cm$^{-1}$) 3600–2500 and 1750; $\delta_H(C_5D_5N)$ 270 MHz 1.25 (36 H, s, $\mathrm{Bu}^t$), 3.58 (4 H, d, $H_B$, $J = 15.1$, $ArCH_2Ar$), 5.27 (8 H, $OCH_2$), 5.52 (4 H, d, $H_A$, $J = 15.1$ Hz, $ArCH_2Ar$) and 7.25 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*(*chloroformylmethoxy*)*calix*[4]*arene* (**14**).—Tetraacid **13** (1.0 g, 1.13 mmol) was dissolved in thionyl chloride (5 cm$^3$, 68 mmol) and the solution was heated under reflux for 2 h. The cooled solution was evaporated to dryness to afford acid chloride **14** (1.07 g) which was used without purification; $\nu_{max}$(KBr)/cm$^{-1}$ 1800; $\delta_H(CDCl_3)$ 1.08 (36 H, s, $\mathrm{Bu}^t$), 3.21 (4 H, d, $H_B$, $J = 13.0$, $ArCH_2Ar$), 4.56 (4 H, d, $H_A$, $J = 13.0$, $ArCH_2Ar$), 5.05 (8 H, s, $OCH_2$) and 6.78 (8 H, s, ArH).

25,26,27,28-*Tetrakis*(*butoxycarbonylmethoxy*)-5,11,17,23-*tetra*-tert-*butylcalix*[4]*arene* (**4**).—To acid chloride **14** (3.08 g, 0.0032 mol) in dry THF (20 cm$^3$) at 0 °C was added, dropwise with stirring, a solution of *n*-butanol (2.34 cm$^3$, 0.026 mol) in pyridine (2.04 g, 0.026 mol) over 15 min. The solution was then allowed to warm to room temperature and stirring was continued for 72 h. Water (100 cm$^3$) was added and the solution was extracted with dichloromethane (3 x 50 cm$^3$). The combined extracts were washed with water, dried and concentrated to leave a solid (3.1 g) which on recrystallisation from ethanol furnished ester **4** (2.7 g, 76%) as colourless crystals m.p. 95–97 °C (Found: C, 73.5; H, 8.7. $C_{68}H_{96}O_{12}$ requires C, 73.9; H, 8.8%); $\delta_H(CDCl_3)$ 0.91 (12 H, s, $CH_3$), 1.07 (36 H, s, $\mathrm{Bu}^t$), 1.35 (8 H, m, $CH_2$), 1.63 (8 H, m, $CH_2$), 3.19 (4 H, d, $H_B$, $ArCH_2Ar$), 4.13 (8 H, t, $OCH_2$), 4.80 (8 H, s, $OCH_2CO$), 4.87 (8 H, d, $H_A$, $ArCH_2Ar$) and 6.77 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27-*tris*(*ethoxycarbonylmethoxy*)-28-*methoxycarbonylmethoxycalix*[4]*arene* (**16**).—To an ethereal solution of diazomethane (34 cm$^3$, 0.05 mol) at 0 °C was added dropwise an ethereal solution (30 cm$^3$) of 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(ethoxycarbonylmethoxy)-28-carboxymethoxycalix[4]arene (**17**) (2.45 g, 0.0025 mol). The solution was then allowed to warm to room temperature. Removal of the solvent, followed by recrystallisation from methanol, gave compound **16** as colourless needles (2.22 g, 89%), m.p. 134–135 °C (Found: C, 72.5; H, 8.0. $C_{59}H_{78}O_{12}$ requires C, 72.4; H, 7.9%); $\nu_{max}$(cm$^{-1}$/KBr) 1755 and 1735; $\delta_H(CDCl_3)$ 1.06 (36 H, s, $\mathrm{Bu}^t$), 1.25 (9 H, t, Me of Et), 3.14 (4 H, d, $H_B$, $J = 13.0$, $ArCH_2Ar$), 3.68 (3 H, s, $CO_2Me$), 4.17 (6 H, q, $CH_2$ of Et), 4.61–5.00 (12 H, m, $H_A$ of $ArCH_2Ar$ and $OCH_2CO$ superimposed) and 6.73 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27-*tris*(*ethoxycarbonylmethoxy*)-28-*diethylcarbamoylmethoxy*[4]*arene* (**18**).—5,11,17,23-Tetra-*tert*-butyl-25-chloroformylmethoxy-26,27,28-tris(ethoxycarbonylmethoxy)calix[4]arene (**20**) (2.61 g, 0.0026 mmol) in benzene (50 cm$^3$) was added, dropwise with stirring, to a solution of diethylamine (0.82 cm$^3$, 7.34 mmol) in benzene (10 cm$^3$) at room temperature. The reaction mixture was stirred at room temperature after which it was washed with water, dried and concentrated to a residue which on crystallisation from acetonitrile furnished amide **18** (1.84 g, 70%) as white cubic crystals, m.p. 71–74 °C (Found: C, 73.4; H, 8.3; N, 1.2. $C_{62}H_{88}NO_{11}$ requires C, 73.0; H, 8.3; N, 1.4%); $\nu_{max}$(KBr/cm$^{-1}$) 1750 and 1660; $\delta_H$($CDCl_3$) 0.66–1.48 (51 H, m, Bu$^t$ and Me of $Et_2N$ and EtO), 2.96–3.57 (8 H, m, $H_b$ and $CH_2$ of $Et_2N$), 3.89–4.34 (6 H, m, $CH_2$ of EtO), 4.59–5.07 (12 H, m, $H_A$ and $OCH_2CO$) and 6.52–6.94 (8 H, 3 s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27-*tris*(*ethoxycarbonylmethoxy*)-28-(*pyrrolidin*-1-*yl*)*carbonylmethoxycalix*[4]*arene* (**19**). The monochloride **20** was treated with pyrrolidine in benzene exactly as described above for amide **18** to yield **19** (58%) as a crystalline solid, m.p. 78–82 °C, after recrystallisation from acetonitrile (Found: C, 73.6; H, 8.2; N, 1.6. $C_{62}H_{83}NO_{11}$ requires C, 73.2; H, 8.2; N, 1.4%); $\nu_{max}$(KBr/cm$^{-1}$) 1750 and 1660; $\delta_H$($CDCl_3$) 0.60–1.41 (45 H, m, Bu$^t$ and Me of OEt), 1.68–2.00 (4 H, m, $CH_2$), 2.93–3.66 (8 H, m, $H_B$ and $NCH_2$), 3.88–4.33 (6 H, m, $CH_2$ of OEt), 4.45–5.05 (12 H, m, $H_A$ and $OCH_2CO$) and 6.56–6.83 (8 H, 3 s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27-*tris*(*ethoxycarbonylmethoxy*)-28-*phenacylmethoxycarbonylmethoxycalix*[4]*arene* (**8**).—A mixture of tetraacid **13** (11.0 g, 0.0125 mol), potassium fluoride (9.4 g, 0.16 mol) and phenacyl bromide (10.0 g, 0.05 mol) in dry HMPA (100 cm$^3$) was stirred and heated at 100 °C for 17 h. The cooled reaction mixture was poured onto ice and the precipitate was collected by filtration and crystallised from acetonitrile to afford the ester (11.84 g, 70%), m.p. 97–99 °C (Found: 74.3; H, 6.6. $C_{84}H_{88}O_{16}$ requires C, 74.6; H, 6.5%); $\nu_{max}$(KBr/cm$^{-1}$) 1703 and 1770; $\delta_H$ 1.092 (36 H, s, Bu$^t$), 3.251 (4 H, d, $H_B$, $J$ = 13.0, $ArCH_2Ar$), 4.920 (4 H, d, $H_A$ $J$ = 13.0, $ArCH_2Ar$), 5.028 (8 H, s, $OCH_2$), 5.465 (8 H, s, $OCH_2$), 6.811 (8 H, s, ArH), 7.325 (4 H, t, ArH), 7.479 (8 H, t, ArH) and 7.776 (8 H, d, ArH).

25,26,27,28-*Tetrakis*(*benzyloxycarbonylmethoxy*)-5,11,17,23-*tetra*-tert-*butylcalix*[4]*arene* (**6**).—Tetraester **2** was heated in an excess of benzyl alcohol containing a catalytic amount of toluene-*p*-sulfonic acid at 140 °C for 48 h. Distillation at 100 °C and 10 mmHg removed excess benzyl alcohol and the residue was taken up in dichloromethane and washed several times with water. The organic solution was dried and concentrated to afford the crude benzyl ester. Several recrystallisations from acetone yielded **6** as a white amorphous powder (60% yield), m.p. 105–106 °C [Found: C, 77.0; H, 6.8. $C_{76}H_{80}O_{12}$ requires C, 77.0; H, 6.8%); $\nu_{max}$(KBr/cm$^{-1}$) 1760 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 60 MHz), 1.09 (36 H, s, Bu$^t$), 3.03 (4 H, d, $H_B$, $J$ = 13.0, $ArCH_2Ar$), 4.89 (4 H, d, $H_A$, $J$ = 13.0, $ArCH_2Ar$), 5.17 (8 H, s, $ArCH_2$), 6.88 (8 H, br, ArH) and 7.431 (20 H, br s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*[(2-*methoxyethyl*)*oxycarbonylmethoxy*]*calix*[4]*arene* (**9**).—To tetraacid chloride **14** (2.38 g, 0.0025 mol) was added methoxyethanol (1.52 g, 0.02 mol) followed by pyridine (1.6 g, 0.02 mol) and the mixture was stirred at room temperature for 24 h. The mixture was then concentrated under reduced pressure and the residue taken up in dichloromethane (25 cm$^3$). The organic solution was washed with water, dried, and concentrated to a colourless oil (2.5 g, 90%) which crystallized on standing at room temperature overnight. Recrystallization from methoxyethanol gave the ester, m.p. 109–110 °C (Found: C, 69.0; H, 7.9. $C_{64}H_{88}O_{16}$ requires C, 69.1; H, 7.9%); $\nu_{max}$(KBr/cm$^{-1}$) 1743 cm$^{-1}$; $\delta_H$($CDCl_3$) 1.08 (36 H, s, Bu$^t$), 3.20 (4 H, d, $H_B$, $J$ = 13.0, $ArCH_2Ar$), 3.35 (12 H, s, $OCH_3$), 4.90 (4 H, d, $H_A$, $J$ = 13.0, $ArCH_2Ar$), 3.60 and 4.90 (16 H, t, $OCH_2CH_2O$), 4.85 (8 H, s, $OCH_2$) and 6.75 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*[(2-*methylthioethyl*)*oxycarbonylmethoxy*]*calix*[4]*arene* (**10**). A mixture of tetraester **2** (2.5 g, 0.0025 mol) and methylthioethanol (19.0 g, 0.25 mol) containing a catalytic amount of toluene-*p*-sulfonic acid was heated with stirring at 160 °C for 48 h. The product precipitated on cooling. The cooled mixture was heated with stirring at 160 °C for 48 h. The product precipitated on cooling. The cooled mixture was filtered and the precipitate washed with cold ethanol to afford ester **10** (2.35 g, 90%), m.p. 67–69 °C [Found: C, 65.2; H, 7.4; S, 10.9. $C_{64}H_{88}O_8S_4$ requires C, 65.3; H, 7.5; S, 10.9%]; $\nu_{max}$(KBr/cm$^{-1}$) 1749; $\delta_H$($CDCl_3$) 1.07 (36 H, s, Bu$^t$), 2.16 (12 H, s, $SCH_3$), 2.75 (8 H, t, $OCH_2CH_2S$), 3.20 (4 H, d, $J$ = 20.0, $H_B$, $ArCH_2Ar$), 4.34 (8 H, t, $OCH_2CH_2S$), 4.37 (4 H, d, $J$ = 20.0, $H_A$, $ArCH_2Ar$), 4.82 (8 H, s, $OCH_2CO$) and 6.78 (8 H, m, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*[(*prop*-2-*ynyl*)*oxycarbonylmethoxy*]*calix*[4]*arene* (**12**).—Acid chloride **14** (7.1, 0.0074 mol) was treated with prop-2-yn-1-ol (3.11 cm$^3$, 0.055 mol) in the presence of pyridine (4.9 cm$^3$, 0.06 mol) in tetrahydrofuran as described above for tetraester **9** to yield the acetylenic ester **12** (4.3 g, 56%), m.p. 142–145 °C (from methanol) [Found: C, 74.6; H, 6.9. $C_{64}H_{72}O_{12}$ requires C, 74.4; H, 7.0%]; $\nu_{max}$(KBr/cm$^{-1}$) 2130 and 1755; $\delta_H$($CDCl_3$) 1.03 (36 H, s, Bu$^t$), 2.50 (4 H, t, C=CH), 3.10 (4 H, d, $J$ = 17.0, $H_B$, $ArCH_2Ar$), 4.80 (8 H, d, $OCH_2C$=CH), 4.83 (4 H, d, $J$ = 17.0, $H_A$, $ArCH_2Ar$), 4.87 (8 H, s, $OCH_2CO$) and 8.60 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*[(1,1,1-*trifluoroethyl*)*oxycarbonylmethoxy*]*calix*[4]*arene* (**11**).—Acid chloride **14** (2.5 g, 0.0026 mol) was treated with trifluoroethanol (1.5 g, 0.02 mol) in tetrahydrofuran (20 cm$^3$) containing pyridine (1.7 cm$^3$) as described above for tetraester **9** to yield the trifluoro ester **11** (1.8 g, 57%), m.p. 172–176 °C (from ethanol–dichloromethane) [Found: C, 60.0; H, 5.7; F, 18.5. $C_{60}H_{68}O_{12}F_{12}$ requires C, 59.6; H, 5.6; F, 18.9%]; $\nu_{max}$(KBr/cm$^{-1}$) 1785; $\delta_H$($CDCl_3$) 1.01 (36 H, s, Bu$^t$), 3.16 (4 H, d, $J$ = 12.0, $H_B$, $ArCH_2Ar$), 4.50 (8 H, q, $OCH_2CF_3$), 4.70 (4 H, d, $J$ = 12.0, $H_A$, $ArCH_2Ar$), 4.81 (8 H, s, $OCH_2$) and 6.76 (8 H, s, ArH).

5,11,17,23-*Tetra*-tert-*butyl*-25,26,27,28-*tetrakis*(*phenoxycarbonylmethoxy*)*calix*[4]*arene* (**7**).—To acid chloride **14** (3.08 g, 0.0032 mol) in dry tetrahydrofuran (20 cm$^3$) at 0 °C was added, dropwise with stirring, a solution of phenol (2.45 g, 0.026 mol) in pyridine (2.04 g, 0.026 mol) over 15 min. The solution was then allowed to warm to room temperature and stirring was continued for 72 h. Water (100 cm$^3$) was added and the solution was extracted with dichloromethane (3 × 50 cm$^3$). The combined extracts were washed with water, dried and concentrated to leave a solid (3.0 g) which on recrystallisation from ethanol furnished ester **7** (2.6 g, 69%) as colourless crystals, m.p. 154–155 °C [Found: C, 76.4; H, 7.0. $C_{76}H_{80}O_{12}$ requires C, 77.0; H, 6.8%]; $\nu_{max}$(KBr/cm$^{-1}$) 1765; $\delta_H$($CDCl_3$), 1.11 (36 H, s, Bu$^t$), 3.28 (4 H, d, $H_B$, $J$ = 13.0, $ArCH_2Ar$), 4.98 (4 H, d, $H_A$, $J$ = 13.0, $ArCH_2Ar$), 5.13 (8 H, s, $OCH_2$), 6.84 (8 H, s, ArH), 6.99 (4 H, d, ArH), 7.21 (4 H, d, ArH) and 7.23 (12 H, m, ArH).

*Crystal Data for* **11**.—Formula $C_{60}H_{68}F_{12}O_{12}$, $M$ = 1209.2, monoclinic, $a$ = 13.987(2), $b$ = 16.194(3), $c$ = 27.630(5) Å, $\beta$ = 98.70(1)°, $U$ = 6186(2) Å$^3$, $Z$ = 4, $D_x$ = 1.30 g cm$^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.710 73 Å, $\mu$ = 1.1 cm$^{-1}$, $F$(000) = 2528, $T$ = 294 K. Space group $P2_1/n$, uniquely from the systematic absences ($h0l$ absent if $h + l = 2n + 1$; $0k0$ absent if $k = 2n + 1$).

A colourless crystal of **11** (0.13 × 0.38 × 0.45 mm) was used for the crystal structure analysis. The setting angles of 25 reflections with $12 < 2\theta < 28°$ were measured on a CAD4 diffractometer and used to determine cell constants and crystal

**Table 3** Final fractional co-ordinates for **11** with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| F(1A) | 0.5491(6) | 0.0583(5) | 0.1326(3) | F(1C) | 0.2443(9) | 0.0898(10) | 0.1676(3) |
| F(2A) | 0.5111(12) | 0.1864(6) | 0.1319(3) | F(2C) | 0.0959(9) | 0.1116(9) | 0.1645(4) |
| F(3A) | 0.4071(8) | 0.0961(8) | 0.1066(5) | F(3C) | 0.1912(5) | 0.1692(5) | 0.2182(2) |
| O(1A) | 0.2702(4) | 0.2284(3) | −0.0682(2) | O(1C) | 0.0469(4) | 0.2071(3) | −0.0323(2) |
| O(2A) | 0.3872(5) | 0.0991(4) | −0.0220(2) | O(2C) | 0.0545(5) | 0.2666(3) | 0.0654(2) |
| O(3A) | 0.4508(5) | 0.1875(4) | 0.0357(2) | O(3C) | 0.1598(6) | 0.1672(4) | 0.0895(2) |
| C(1A) | 0.2943(6) | 0.2578(5) | −0.1121(3) | C(1C) | −0.0514(6) | 0.1986(5) | −0.0478(3) |
| C(2A) | 0.2980(6) | 0.3411(5) | −0.1210(3) | C(2C) | −0.0897(6) | 0.1261(5) | −0.0652(3) |
| C(3A) | 0.3231(6) | 0.3655(5) | −0.1649(3) | C(3C) | −0.1905(6) | 0.1236(5) | −0.0822(4) |
| C(4A) | 0.3421(6) | 0.3117(5) | −0.2011(3) | C(4C) | −0.2492(6) | 0.1931(6) | −0.0845(3) |
| C(5A) | 0.3322(6) | 0.2278(5) | −0.1912(3) | C(5C) | −0.2040(6) | 0.2661(5) | −0.0687(3) |
| C(6A) | 0.3093(6) | 0.2005(5) | −0.1465(3) | C(6C) | −0.1063(6) | 0.2716(5) | −0.0495(3) |
| C(7A) | 0.2863(6) | 0.1099(5) | −0.1402(3) | C(7C) | −0.0597(6) | 0.3516(5) | −0.0329(3) |
| C(8A) | 0.3653(8) | 0.3430(6) | −0.2510(3) | C(8C) | −0.3546(6) | 0.1898(6) | −0.1053(4) |
| C(9A) | 0.4452(13) | 0.4035(9) | −0.2435(6) | C(9C) | −0.4079(9) | 0.2676(9) | −0.1019(7) |
| C(10A) | 0.2813(13) | 0.3885(13) | −0.2750(5) | C(10C) | −0.3711(9) | 0.1570(14) | −0.1543(5) |
| C(11A) | 0.3969(13) | 0.2752(8) | −0.2831(5) | C(11C) | −0.4028(9) | 0.1325(12) | −0.0719(6) |
| C(12A) | 0.3390(7) | 0.2419(6) | −0.0259(3) | C(12C) | 0.0901(6) | 0.1612(5) | 0.0084(3) |
| C(13A) | 0.3912(6) | 0.1674(5) | −0.0066(3) | C(13C) | 0.0966(7) | 0.2077(5) | 0.0550(3) |
| C(14A) | 0.5118(8) | 0.1259(7) | 0.0584(4) | C(14C) | 0.1826(16) | 0.2045(9) | 0.1365(4) |
| C(15A) | 0.4985(11) | 0.1165(8) | 0.1078(5) | C(15C) | 0.1830(8) | 0.1334(13) | 0.1719(4) |
| F(1B) | 0.3301(6) | −0.3109(4) | −0.0383(3) | F(1D) | 0.5435(6) | 0.4643(6) | 0.1098(4) |
| F(2B) | 0.2924(7) | −0.3131(5) | −0.1136(3) | F(2D) | 0.4653(8) | 0.5408(7) | 0.0585(4) |
| F(3B) | 0.2204(6) | −0.3900(4) | −0.0696(4) | F(3D) | 0.4570(12) | 0.4121(10) | 0.0458(6) |
| O(1B) | 0.1766(4) | 0.0411(3) | −0.0659(2) | O(1D) | 0.1503(4) | 0.3641(3) | −0.0137(2) |
| O(2B) | 0.0881(4) | −0.1132(3) | −0.0700(3) | O(2D) | 0.2698(7) | 0.3511(5) | 0.0733(3) |
| O(3B) | 0.2279(4) | −0.1749(3) | −0.0710(2) | O(3D) | 0.2824(7) | 0.4805(5) | 0.0755(3) |
| C(1B) | 0.1272(6) | 0.0664(5) | −0.1105(3) | C(1D) | 0.1039(6) | 0.3879(4) | −0.0593(3) |
| C(2B) | 0.1766(6) | 0.0969(5) | −0.1467(3) | C(2D) | 0.0025(6) | 0.3880(5) | −0.0677(3) |
| C(3B) | 0.1223(6) | 0.1237(5) | −0.1900(3) | C(3D) | −0.0420(6) | 0.4238(5) | −0.1128(3) |
| C(4B) | 0.0228(6) | 0.1247(5) | −0.1986(3) | C(4D) | 0.0068(6) | 0.4540(5) | −0.1477(3) |
| C(5B) | −0.0229(6) | 0.0983(5) | −0.1608(3) | C(5D) | 0.1080(7) | 0.4472(5) | −0.1386(3) |
| C(6B) | 0.0262(6) | 0.0695(4) | −0.1162(3) | C(6D) | 0.1573(6) | 0.4132(5) | −0.0936(3) |
| C(7B) | −0.0294(6) | 0.0509(5) | −0.0750(3) | C(7D) | 0.2652(6) | 0.4058(5) | −0.0871(3) |
| C(8B) | −0.0376(8) | 0.1610(7) | −0.2449(4) | C(8D) | −0.0397(7) | 0.4999(6) | −0.1919(3) |
| C(9B) | −0.0667(20) | 0.2444(10) | −0.2316(7) | C(9D) | −0.0441(13) | 0.5910(8) | −0.1792(5) |
| C(10B) | 0.0195(9) | 0.1624(10) | −0.2879(4) | C(10D) | 0.0141(12) | 0.4946(11) | −0.2337(5) |
| C(11B) | −0.1267(9) | 0.1104(9) | −0.2626(4) | C(11D) | −0.1420(10) | 0.4700(8) | −0.2093(5) |
| C(12B) | 0.2300(6) | −0.0315(5) | −0.0678(3) | C(12D) | 0.1595(7) | 0.4284(6) | 0.0202(3) |
| C(13B) | 0.1716(6) | −0.1085(5) | −0.0687(3) | C(13D) | 0.2513(11) | 0.4140(6) | 0.0550(3) |
| C(14B) | 0.1815(7) | −0.2520(6) | −0.0713(4) | C(14D) | 0.3787(12) | 0.4711(10) | 0.1069(6) |
| C(15B) | 0.2569(9) | −0.3151(6) | −0.0731(4) | C(15D) | 0.4653(8) | 0.4723(12) | 0.0790(8) |

orientation matrix. Intensities of reflections with indices $h$ − 13 to 13, $k$ 0 to 15, $l$ 0 to 26 with $2 < 2\theta < 40°$ were measured [$\omega$–$2\theta$ scans; $\omega$ scan width (0.6 + 0.35 tan$\theta$)°] with graphite monochromatized Mo-K$\alpha$ radiation. Data collection was stopped at $2\theta$ of 40° as no 'observed' reflections were being measured. Lorentz and polarisation corrections were applied to the data; the intensities of three standard reflections measured every 120 min remained constant and no decay correction was required. 6052 Reflections were measured of which 5752 were unique ($R_{int}$ 0.012), and the 3172 with $I > 2.5\sigma(I)$ were labelled observed and used in the structure analysis. The structure was solved by direct methods.[13] Initial refinement was by full-matrix least-squares calculations with isotropic thermal parameters. Difference maps had maxima in the expected locations for the H atoms and these were positioned geometrically (C–H 0.95 Å) and allowed for as riding atoms in subsequent refinement cycles. For the final rounds of refinement, all non-hydrogen atoms were allowed anisotropic motion and block-diagonal least-squares methods were employed. At convergence, $R = 0.076$, $R_w = 0.105$, goodness-of-fit 2.67. The minimum shift/e.s.d. ratio in the final cycle was 0.005; the range of density in the final difference map was −0.33 to +0.51 e Å$^{-3}$ (adjacent to the markedly anisotropic CF groups). The weighting scheme used was of the form, $w = 1/[\sigma^2(F_o) + 0.0004(F_o^2)]$. All calculations were performed on a Silicon Graphics 4D-380 computer using the NRCVAX suite of programs.[13] Scattering factors and anomalous-dispersion corrections were obtained from the *International Tables for X-Ray Crystallography*.[14] A summary of the dimensions is given in Table 2 and atomic co-ordinates are given in Table 3. Fig. 1 presents views of molecule **11** prepared using ORTEPII[15] showing the crystallographic numbering scheme. Full lists of bond lengths and bond angles, hydrogen atom co-ordinates, thermal parameters, torsion angles and tables of least-squares planes have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

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