PERKIN 2

Synthesis, structure and properties of various molecules based on the 4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene system with an evaluation of the effect differing molecular substitution patterns has on the space group symmetry

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4,8,12-Trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (3), 2,6,10-tri-*tert*-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (11) and 2,6,10-tri-*tert*-butyl-4,8,12-trioxa-12c-methyl-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (12) have been synthesised and their crystal structures determined. The crystal structure of 4,8,12-trioxa-12c-oxophospha-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (13) has also been determined for comparison. Compounds 3 and 11 crystallise in non-centrosymmetric space groups. Compound 12 also crystallises in a non-centrosymmetric space group but molecules of opposite chirality are present within the unit cell. Finally compound 13 crystallises in a centrosymmetric space group. The room temperature pyroelectric coefficient of 3 has been determined. The spatial extent of the trioxatriangulene ground system has been perturbed by chemical substitution and the effect of the substitutions upon the space group symmetry of the chemical derivative has been uncovered by X-ray structural resolution. The non-centrosymmetric point group symmetry of the molecules is reflected in a non-centrosymmetric space group symmetry whenever the spatial perturbations do not prohibit the stacking of the molecules.

Introduction

In applications where molecular dielectric materials are used as the active components, the molecular dielectric material always crystallises in a non-centrosymmetric manner.[1,2] The construction of particular materials with dielectric properties such as optical frequency doubling,[3] pyroelectric detectors[4–7] and piezoelectric transducer elements,[8] thus relies heavily upon the ability to make non-centrosymmetric materials.[9] The unpredictability of the way in which molecules crystallise[10] has prevented the development of a rational approach to the construction of molecular dielectric materials with desired properties. Consequently the approach has only been empirical in nature with the synthesis of molecules with the required molecular functional properties *i.e.* dipole moment, polarisability and derivatives where the spatial extent of the basic molecule is perturbed by altering the substitution pattern while retaining the molecular functional properties. Structural resolution following the synthesis and investigation of the properties, if permitted by symmetry, yielded new materials with properties of the kind mentioned above in cases where non-centrosymmetry was observed, but mostly this was by chance only. A few examples do exist where a particular tendency to crystallise in a non-centrosymmetric manner for a given class of compounds has been discovered. As an example, *meta*-substituted benzene derivatives exhibit this property.[11–13] Such a rationale is very useful when considering the design of new molecular dielectric materials with properties depending upon the absence of a centre of symmetry.

A recent investigation[14] of the properties of a particular molecular material based on a symmetric phosphine 4,8,12-trioxa-12c-phospha-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (**14**) shaped like a Chinese hat with C_{3v} point symmetry showed that the material is non-centrosymmetric and belongs to one of the 10 polar crystallographic point groups and further shown to exhibit pyroelectric properties. Pyroelectricity is of great interest when considering high performance IR detectors.[15]

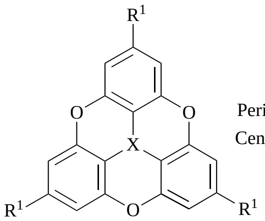


Fig. 1 4,8,12-Trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene system. The R^1 substituents at the 2,6,10-positions and the substituent X at the 12c position.

In this paper we have investigated how an alteration of the spatial extent by molecular substitution of the trioxatriangulene skeleton correlates with the space group symmetry observed in the crystalline phase and the subsequent dielectric properties (Fig. 1). The presence of a centre of symmetry was found to be linked mostly to the molecular substitution at the central position. The positions at the periphery showed a lower degree of sensitivity. All three compounds with only hydrogen or a lone pair at the central position showed non-centrosymmetry with or without *tert*-butyl substituents at the periphery. Substitution at the central position with oxygen, as in compound **13**, or methyl, as shown earlier in 4,8,12-trioxa-12c-methyl-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (**15**),[16] led to centrosymmetric space groups. Substitution with both methyl at the central position and *tert*-butyl at the periphery as in compound **12** gave rise to a non-centrosymmetric space group with molecules of opposite chirality within the unit cell. Compounds **14**[14] and **15**[16] are known and their synthesis and crystal structures have been published. The earlier findings are however included here for comparison.

Results and discussion

The trioxatriangulene system was first reported by Martin and Smith[17] through 4,8,12-trioxa-12c-hydroxy-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (**1**). The synthesis of **3** has been

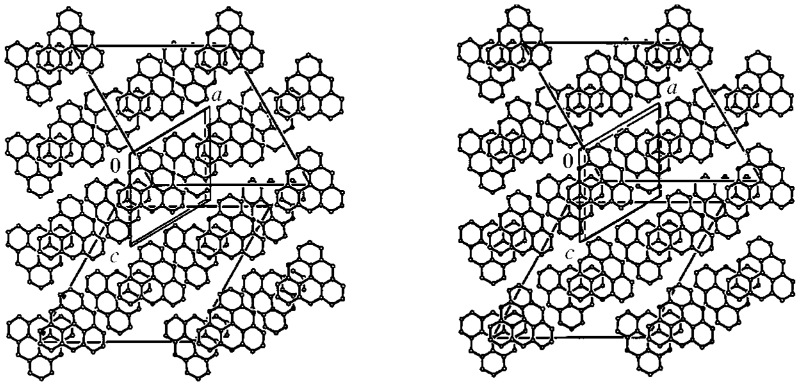
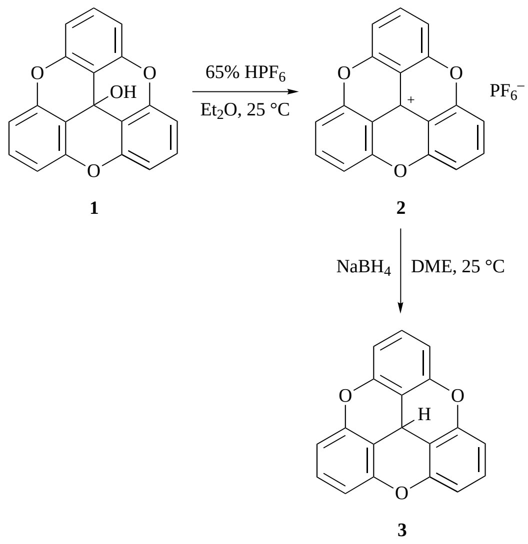


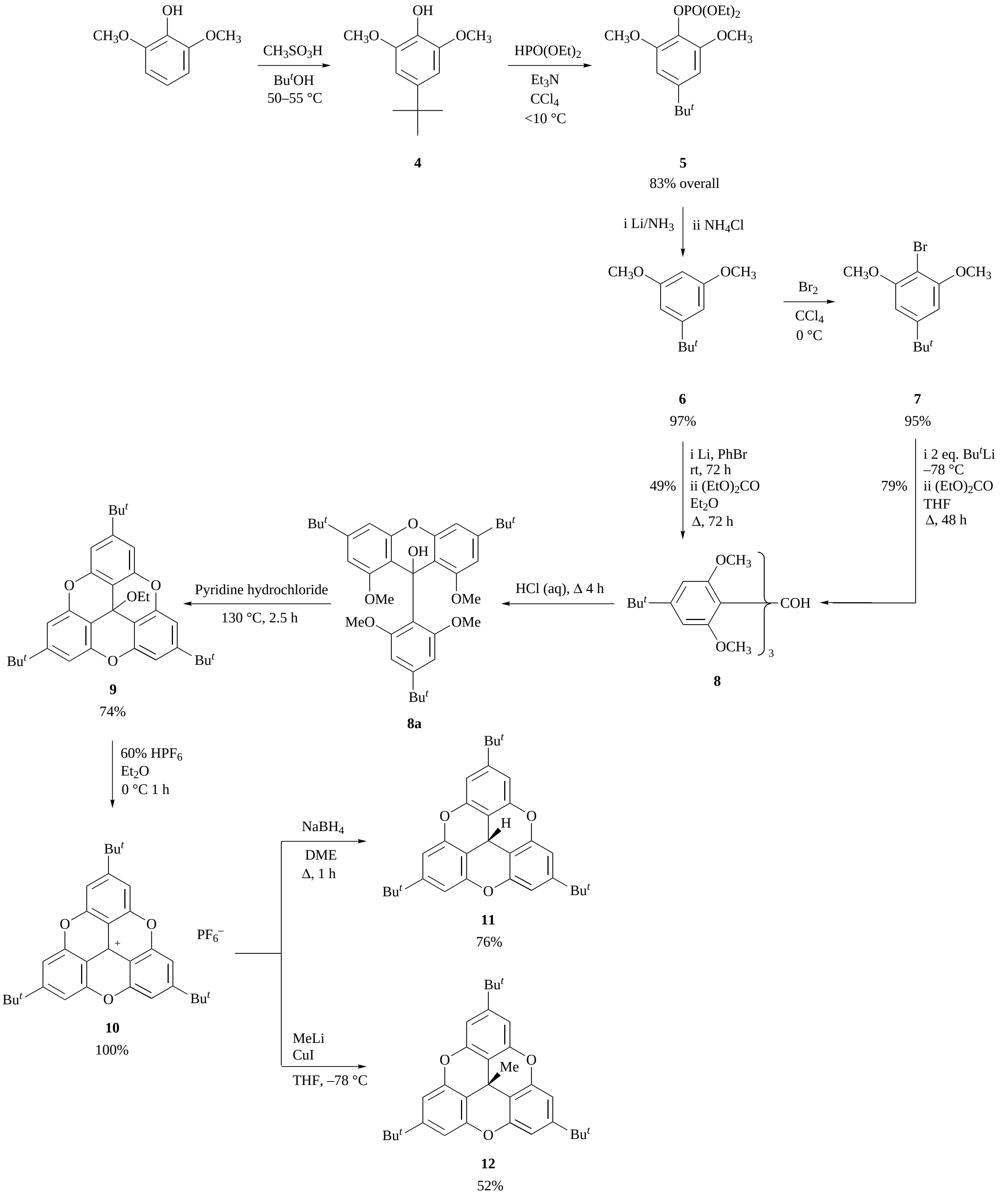
Fig. 2 Projection along the *b*-axis for compound **3** (stereoview). The unit cell is shown as the small labelled cell in the middle. The two larger trigonal cells illustrate the relationship with the structure of compound **14** (see text for details).

accomplished with $LiAlH_4$[17] or with triethylsilane.[18] Both methods are tedious and time consuming. We report the synthesis of **3** through reaction of compound **1** with aqueous hexafluorophosphoric acid which gave compound **2**. Compound **2** could be reduced with sodium borohydride in dimethoxyethane (DME) to give compound **3**. The synthesis is outlined in Scheme 1. The synthesis of 2,6,10-tri-*tert*-butyl-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene has been described previously[19] but the method presented here gives a much higher overall yield combined with a considerable reduction in time used for the total synthesis. The synthesis of the central cationic compound **10** outlined in Scheme 2 starts from the commercially available 2,6-dimethoxyphenol which was *tert*-butylated under Friedel–Crafts conditions. No attempt was made to isolate compound **4** as it was found that direct reaction with diethyl phosphite gave compound **5** in an overall yield of 83%. Reduction of compound **5** by metallic lithium in liquid ammonia gave compound **6** in an almost quantitative yield. The transformation of compound **6** to compound **8** was accomplished in two different ways. Either by direct lithiation with phenyllithium for 72 h and nucleophilic substitution on diethyl carbonate in refluxing diethyl ether for another 72 h giving compound **8** in 49% yield. It was found to be important to prepare the phenyllithium immediately before use and for some unknown reason the lithiation could not be completed faster than the indicated 72 h of reaction time at room temperature. Lithiation using commercial phenyllitium in diethyl ether under conditions identical to the above, followed by quenching with deuterated water, resulted in 61% lithiation, as determined by NMR spectroscopy, whereas lithiation with freshly prepared phenyllithium followed by quenching with deuterated water resulted in 77% lithiation, as determined by NMR spectroscopy. If the same conditions were used as in the quantitative lithiation of dimethylresorcinol following the method of Brandsma and Verkruijsee[20] only 12% of compound **6** was lithiated. This indicates that the metallation of compound **6** is not trivial and is probably governed by both base-strength and steric demands of the organometallic compound used. Bromination of compound **6** resulted in an almost quantitative yield of compound **7** which was lithiated 100% by Bu^tLi at −78 °C in THF for 1 h. The subsequent reaction with diethyl carbonate was finished after only 48 h giving compound **8** in 79% yield. The cation derived from compound **8** by dehydration upon treatment with acid has a very intense blue colour as would be expected for a large planar conjugated aromatic system. Treatment of **8** in refluxing dilute hydrochloric acid results in the isolation of the crude xanthol **8a** in a quantitative yield. The crude xanthol was reacted with neat pyridine hydrochloride at 130 °C giving compound **9** in a moderate overall yield. When reacted with HPF_6 in diethyl ether, compound **9** was converted to compound **10** which was found to be an intensely yellow coloured compound that was easily reduced by sodium borohydride to give the colourless compound **11**. Reaction of compound **10** with MeLi in THF produced **12** in only 7% yield whereas the addition of a catalytic amount of copper(I) iodide increased the yield to 36%. An even better yield was obtained when the dimethylcopperlithium reagent was produced *in situ* and reacted with compound **10** giving compound **12** in 52% yield.



Scheme 1

The structure of compound **3** can be represented as a distorted trigonal structure similar to the structure of compound **14**.[14] Fig. 2 shows a stereoview of the crystalline structure of compound **13** as a projection along the *b*-axis. The unit cell is shown in the middle. The trigonal lattice found in the structure of compound **14** can be recognised here for each of two layers as shown by the large trigonal parent unit cell depictions one for each layer. The structure of compound **3** can thus be developed from the structure of compound **14** by placing a trigonal layer of molecules followed by a reduction of the symmetry in the layer from 3*m* to *m* by tilting the molecules in the same direction so that the molecular C_3 axis forms an angle with the crystallographic stacking axis (*c*-axis in compound **14** and *b*-axis in compound **3**). A second layer identical to the one described above is placed on top and rotated through 60° with respect to the first layer and translated by 6.47 Å along the mirror plane and then tilted in a direction opposing the tilt in the first layer. Fig. 3 shows a projection along the *c*-axis where the polar axis is shown along with the individual molecular dipoles each forming an angle with the polar axis of 15.8°. The polarisation in the material is not as large as the sum of molecular dipoles per unit volume would indicate following the relationship described earlier.[14] This is due to a partial cancellation of the dipoles in the solid which can be described by eqn.



Scheme 2

(2), where P is the polarisation in C m^{-2}, V is the volume of

$$P = \frac{1}{V}\sum_{i}^{z}\mu_i \cdot \cos\varphi_i \qquad (2)$$

the unit cell in m^3, μ_i is the molecular dipole moment of molecule i in the unit cell in C m, φ_i is the angle between the molecular dipole and the polar axis in the solid and Z are the number of formula units in the unit cell. In space group $P1$ there is no constraint on the direction of the polar axis with respect to crystallographic axes. The polar axis was found to be forming an angle of 0.2° with the b-axis, an angle of 90.2° with the a-axis and to be coincident with the ab-plane. Differential scanning calorimetry on compound **3** showed no phase transitions before melting, thus excluding the possibility of any abnormal dielectric properties due to a structural rearrangement. Fig. 4 shows an ORTEP drawing of the asymmetric unit.

It is noticeable that the substitution of the phosphorous in compound **14** with C–H, as in compound **3**, reduces the very high crystal symmetry of compound **14** ($R3m$) to the lowest possible ($P1$) but still maintains the polar point group symmetry. Both compounds **3** and **14** are thus pyroelectric.

Substitution at the periphery with bulky groups on compound **3** gave **11** which crystallises in an exceptionally high symmetry space group *I*-43*d*. It is however noticeable that in spite of the rare cubic crystal symmetry for organic molecules,[21,22] an absence of a centre of symmetry is still observed. Even though the molecules stack along the crystallographic three-fold symmetry axes the resulting packing does not yield a polar material as this is not possible in a cubic system.[2] Pyroelectric properties are thus not possible.[2] However, the absence of a centre of symmetry does allow for piezoelectric properties.[8,23] An attempt to establish the piezoelectric properties of **11** was made following the method of Giebe and Shiebe.[24] This was however not possible for us to achieve. Fig. 5 shows how compound **11** crystallises and Fig. 6 shows an ORTEP drawing of the molecule with a labelling of the asymmetric unit.

Fig. 7 shows the structure of compound **12**. Fig. 8 shows an ORTEP drawing of the molecule with a labelling of the atoms. Note that the structure of compound **12** belongs to the point group *mm*2. It is thus polar and should in principle also be pyroelectric like compounds **3** and **14**. Inspection of Fig. 7 clearly shows that the molecules are all opposing each other with respect to the direction of their individual molecular dipole moments (along the molecular C_3 axis) thus excluding the possibility of a large permanent dielectric polarisation. On closer inspection the molecular dipole moments however all form an angle of 0.2° with the *ab*-plane in the negative *c*-direction. There is thus a small amount of dielectric polarisation in the solid along the *c*-axis. The material should in principle exhibit pyroelectric properties, but the magnitude of the pyroelectric coefficient would be very small when considering typical values of thermal expansion and dipole moments for organic compounds.

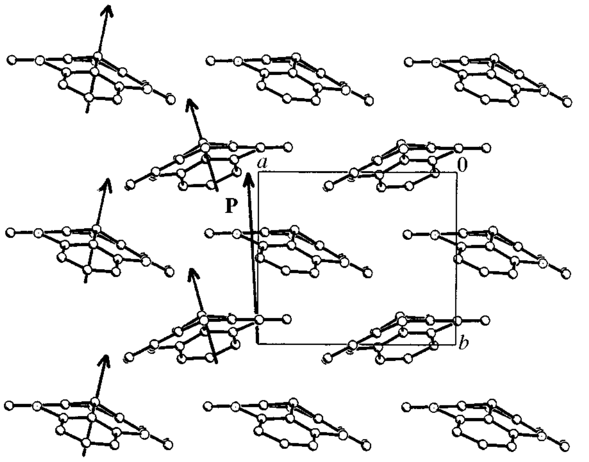


Fig. 3 Projection along the *c*-axis for compound **3** showing how the molecules stack. Some of the molecules have been drawn with their molecular dipole moment (arbitrary direction) to illustrate the origin of the permanent polarisation observed in the material. The resulting polarisation vector, **P**, has been illustrated. Notice the angle it forms with the *a*- and *b*-axes.

Fig. 9 shows the structure of compound **13** and Fig. 10 shows an ORTEP drawing of the asymmetric unit with labelling of the atoms. Compound **13** crystallises in a centrosymmetric space group and does not possess any interesting dielectric properties. It has however one important structural feature in common with compound **12**, namely, that in both cases the molecules do not stack due to the substituent at the central position.

The *tert*-butyl groups of compounds **11** and **12** were found to be subject to some degree of disorder. However, it was not possible to obtain data for which subsequent structure solution and refinement would yield an *R*(*F*) value below 0.05. One likely explanation for the problems associated with obtaining good data is that neither molecule gives rise to a dense packing in the crystalline state as evidenced by their low densities in the order of 1.1 g cm^{-3}, as compared to compounds **3**, **13**–**15** with densities in the order of 1.5 g cm^{-3}.

The molecules can be grouped as shown in Fig. 11 according to their substitution pattern at the central position. Compounds with a hydrogen or lone pair at the central position form a group exhibiting an absence of a centre of symmetry in the crystalline phase. Compounds with larger substituents like oxygen or methyl at the central position form another distinct group exhibiting centrosymmetric crystalline structures. Substitution at the periphery with substituents as bulky as *tert*-butyl has little effect on the nature of packing when the central substituent is hydrogen or lone pair. When however substitution at both the central position and the periphery is made, a non-centrosymmetric structure is also observed but molecules of opposite chirality are present within the unit cell.

A possible reason for this structural sensitivity towards substitution at the central position, as opposed to the structural insensitivity at the periphery is that small substituents at the central position do not prevent the stacking of the molecules. The molecules outlined in Fig. 2 ideally belong to the molecular point group C_{3v} and are all polar in nature with no molecular centre of symmetry. Stacking of polar molecules gives rise to a polar stack. Subsequent non-centrosymmetric crystallographic packing depends upon the manner in which the stacks arrange

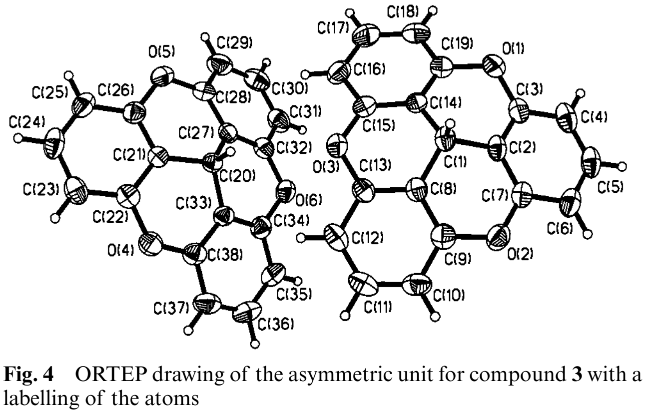


Fig. 4 ORTEP drawing of the asymmetric unit for compound **3** with a labelling of the atoms

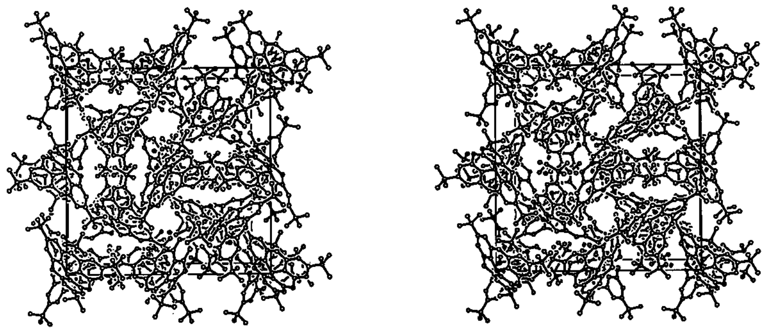


Fig. 5 Illustration of the packing for compound **11** (stereoview) as a projection along one of the crystallographic axes. Notice how the molecules stack in a staggered manner along the three-fold crystallographic symmetry axes.

themselves with respect to each other. If the stacking is prevented it is more difficult to maintain an absence of a centre of symmetry.

The immediate consequence of the results presented in this paper is that given a molecule with a polar point group symmetry (in this case idealised C_{3v}) one can with provision of the proper spatial extent of the molecule anticipate that the space group of the material will be non-centrosymmetric if the molecules are capable of some degree of stacking. This is a very powerful rationale as many properties of advanced materials are only observed when the crystalline material does not possess a centre of symmetry. An example of such a property is the pyroelectricity found for compound **3**.

Experimental

Synthetic methods and materials

All reagents used were standard grade unless otherwise mentioned. THF and diethyl ether were dried by distillation from Na–benzophenone under argon. 1,2-Dimethoxyethane (DME) was treated with and stored over CaH_2 before use. All operations using lithium were conducted under an atmosphere of argon. The concentration of Bu^{n}Li in hexane and Bu^{t}Li in pentane was determined by titration of *N*-(2-methylphenyl)-2,2-dimethylpropanamide[25] in the appropriate dry solvent (*e.g.* THF or diethyl ether) before usage in reactions where the stoichiometry was critical. The crystals used for X-ray crystallography were obtained from a saturated solution of the compound (**3**, **11**, **12** or **13**) in HPLC grade ethyl acetate.

Spectroscopy and analysis

NMR spectra were recorded on a Bruker Advance DPX 250 MHz spectrometer using tetramethylsilane (TMS) as internal standard. $CDCl_3$ was dried over basic Al_2O_3 (70–230 mesh). Melting points were determined using a Büchi 510 melting point apparatus. Mass spectra were determined using a Hewlett Packard 6890 Series GC–MS system with a 5% phenyl methyl siloxane column and Hewlett Packard G2025A MALDI-TOF mass spectrometer. Elemental analyses were performed at DB Lab, Stenhuggervej 9, DK-5230 Odense M, Denmark and Mikro Kemi AB, Seminariegatan 29, 75228 Uppsala, Sweden.

Preparation of 4,8,12-trioxa-4,8,12-trihydrodibenzo[*cd,mn*]-pyrenium hexafluorophosphate (2)

4,8,12-Trioxa-12c-hydroxy-4,8,12,12c-tetrahydrodibenzo-[*cd,mn*]pyrene[17] (**1**) (2 g, 6.6 mmol) was suspended in diethyl ether (150 cm^3) in a 500 cm^3 conical flask. The solution was stirred vigorously while adding HPF_6 (aq.) (65% w/w) (1.5 cm^3,

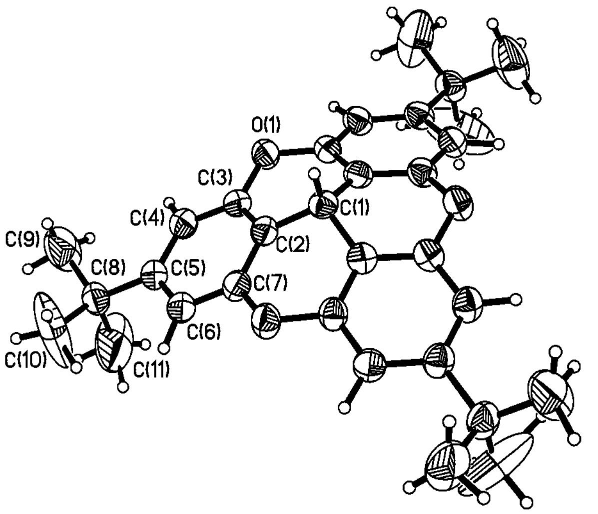


Fig. 6 ORTEP drawing of the molecule for compound **11**. Only the asymmetric unit has been labelled.

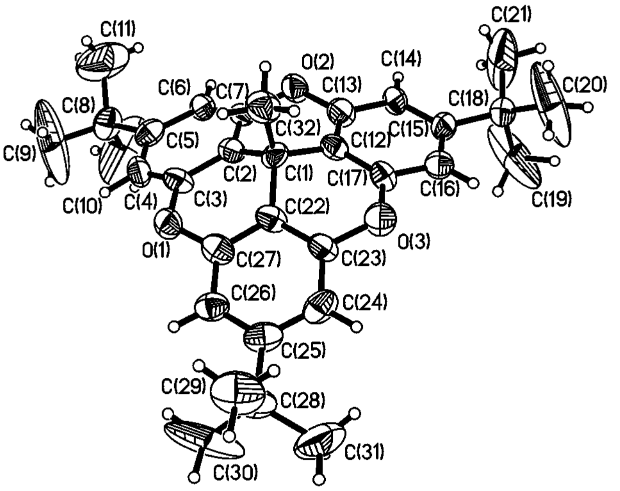


Fig. 8 ORTEP drawing of the asymmetric unit for compound **12** with the labelling of the atoms

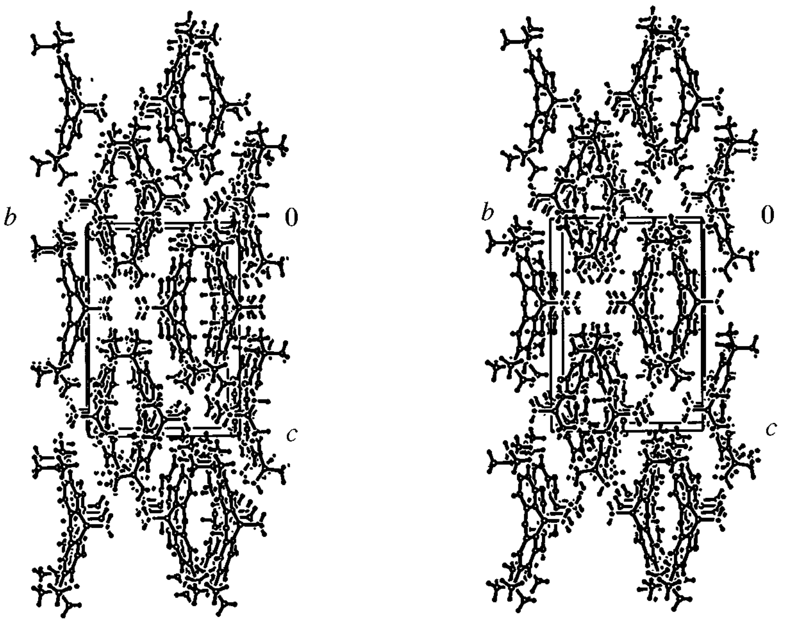


Fig. 7 Illustration of the packing for compound **12** (stereoview) along the *a*-axis. The molecules do not form stacks; they are arranged in layers.

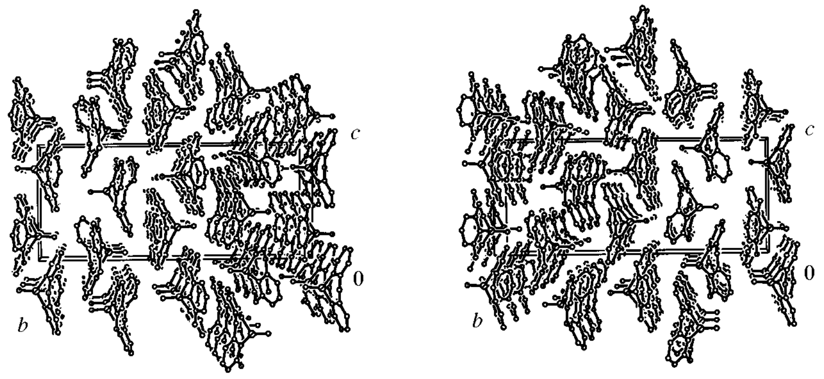


Fig. 9 Stereoview illustrating the packing of compound **13** in the crystalline phase

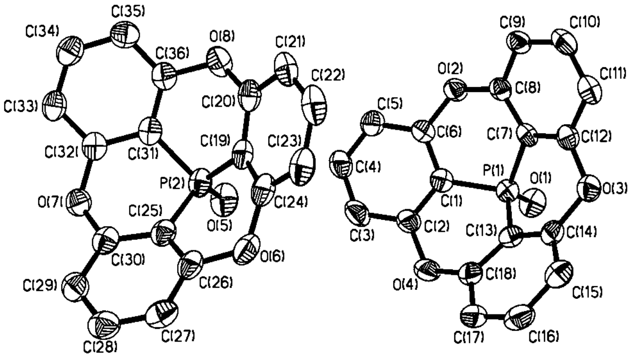


Fig. 10 ORTEP drawing of the asymmetric unit for compound **13** with the labelling of the atoms

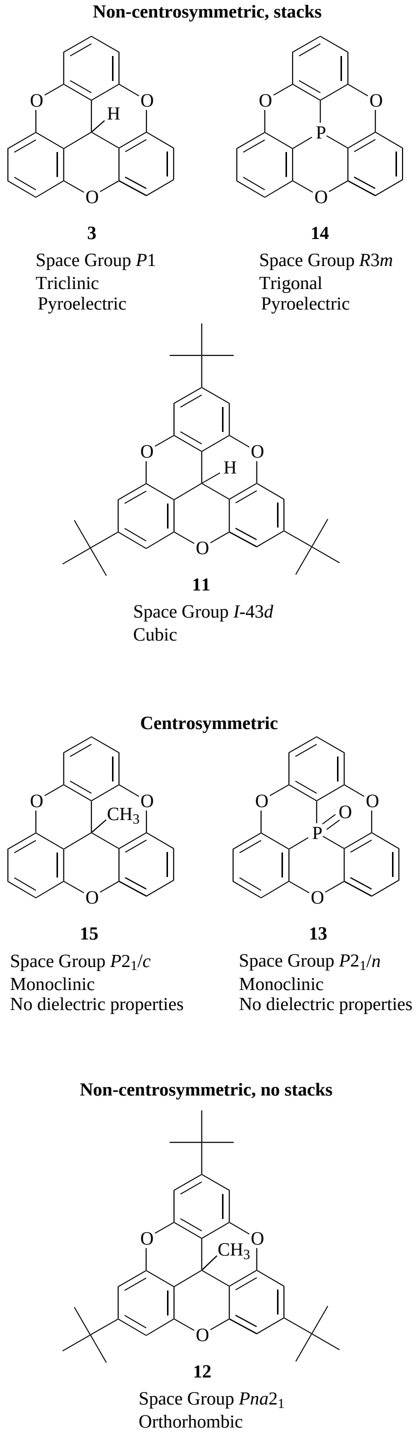
17 mmol). After stirring for 0.5 h light petroleum (bp 30–40 °C) (150 cm^3) was added and a thick bright yellow precipitate was isolated by suction filtration on a sintered funnel, washed with light petroleum (bp 30–40 °C) (50 cm^3) and dried in a vacuum oven at 40 °C for 1 h. This gave **2** (2.75 g, 96%) as a bright yellow material which was used in the subsequent step without further purification, mp >275 °C (dec.); δ_H(250 MHz, [$^2H_6$]DMSO, TMS) 8.56 (1H, t, *J* 8.5), 7.98 (2H, d, *J* 8.5); δ_C(62.9 MHz, $CDCl_3$, TMS) 153.8, 146.3, 144.3, 113.3, 107.1.

Preparation of 4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene (3)

Compound **2** (0.1 g, 0.23 mmol) was suspended in 1,2-dimethoxyethane (50 cm^3) and stirred with a magnetic stirrer. $NaBH_4$ (0.2 g, 5.3 mmol) was added in two portions of 0.1 g, the second portion being added 15 min after the first. The yellow colour of the starting material disappears and the mixture becomes colourless. After 45 min diethyl ether (50 cm^3) was added and the mixture was stirred for 15 min. After addition the solution was allowed to stir for 0.5 h before being poured into water (100 cm^3). The mixture was extracted with diethyl ether (2 × 50 cm^3). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo* to yield the crude product (0.06 g, 91%). The product was dissolved in boiling ethyl acetate (15 cm^3) and left to crystallise. Well-formed needles of **1** (0.04 g, 61%) were obtained; DSC showed melting in the range 291–319 °C, onset at 309.75 °C, peak at 312.63 °C, 31.52 kJ mol^{-1} (Found: C, 79.56; H, 3.61. Calc. for $C_{19}H_{10}O_3$: C, 79.71; H, 3.52); δ_H(250 MHz; $CDCl_3$, TMS) 7.25 (1H, t, *J* 8.2), 6.93 (2H, d, *J* 8.2), 4.93 (1H, s); δ_C(62.9 MHz, $CDCl_3$, TMS) 153.3, 128.8, 111.7, 109.4, 21.1.

Preparation of 4-*tert*-butyl-2,6-dimethoxyphenol (4)[19]

A solution of 2,6-dimethoxyphenol (99.17 g, 0.64 mol) in CH_3SO_3H (150 cm^3) was warmed to 40 °C. Bu^tOH (185 cm^3, 1.985 mol) was added slowly for $3\frac{1}{2}$ h in order to keep the temperature between 50–55 °C. After addition the temperature



Non-centrosymmetric, stacks

3
Space Group *P*1
Triclinic
Pyroelectric

14
Space Group *R*3*m*
Trigonal
Pyroelectric

11
Space Group *I*-43*d*
Cubic

Centrosymmetric

15
Space Group *P*2$_1$/*c*
Monoclinic
No dielectric properties

13
Space Group *P*2$_1$/*n*
Monoclinic
No dielectric properties

Non-centrosymmetric, no stacks

12
Space Group *Pna*2$_1$
Orthorhombic

Fig. 11 Illustration of the molecules discussed in this paper along with an indication of how they can be grouped according to their substitution pattern at the central position was maintained at 50 °C for 2 h. The reaction mixture was poured onto ice (1 kg) followed by extraction with diethyl ether (3 × 100 cm^3). The combined organic phases were washed with water (3 × 100 cm^3), saturated $NaHCO_3$ (2 × 500 cm^3), water (2 × 50 cm^3), dried ($MgSO_4$) and concentrated using a rotary evaporator giving a yellow oil **4** that was used without further purification in the preparation of compound **5**.

Preparation of diethyl 4-*tert*-butyl-2,6-dimethoxyphenyl phosphate (5)

Compound **4** (obtained above, entire quantity) was dissolved in a mixture of CCl_4 (100 cm^3) and diethyl phosphite (105 cm^3, 0.765 mol) at 0 °C under argon. Triethylamine (115 cm^3, 0.825 mol) was added at such a rate that the temperature was kept below 10 °C, followed by stirring overnight at room temperature. The reaction mixture was concentrated on a rotary evaporator and the crude product was dissolved in a mixture of diethyl ether (500 cm^3) and water (500 cm^3). The organic phase was separated, washed with water (100 cm^3), 1 M HCl (aq.) (2 × 100 cm^3), water (100 cm^3), 4 M NaOH (aq.) (2 × 100 cm^3), water (100 cm^3), dried ($MgSO_4$) and evaporated to dryness. Recrystallisation from *n*-hexane yielded compound **5** (184.74 g, 83% overall yield) as white flakes, mp 74–75 °C (Found: C, 55.1; H, 7.9; P, 9.25. Calc. for $C_{16}H_{27}O_6P$: C, 55.5; H, 7.9; P, 8.9%); δ_H(250 MHz, $CDCl_3$, TMS) 6.59 (2H, s, Ar*H*), 4.30 (4H, q, J_{AB} 7.10, $^3J_{PH}$ 7.20, $POCH_2CH_3$), 3.86 (6H, s, OCH_3), 1.38 (6H, td, J_{AB} 7.10, $^4J_{PH}$ 1.15, $POCH_2CH_3$), 1.30 [9H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 151.6 (d, J_{PC} 3.5), 148.8 (d, J_{PC} 2.0), 127.9 (d, J_{PC} 7.9), 103.0 (d, J_{PC} 1.5), 64.6 (d, J_{PC} 6.0, $POCH_2CH_3$), 56.5 (OCH_3), 35.4, 31.8, 16.5 (d, J_{PC} 7.4, $POCH_2CH_3$); *m*/*z* 346 (M^+, 23%), 331 ($M^+ - Me$, 23) and 177 [$M^+ - OPO(OEt)_2$, 100].

Preparation of 1-*tert*-butyl-2,5-dimethoxybenzene (6)

Compound **5** (97.75 g, 0.282 mol) was dissolved in a mixture of dry THF (50 cm^3) and dry diethyl ether (250 cm^3). This solution was added slowly under reflux to metallic lithium (4.50 g, 0.648 mol) in liquid NH_3 (600 cm^3) for 2 h. Towards the end of the addition the blue colour disappeared. More lithium was added (1.01 g, 0.146 mol) in order to maintain the blue colour. After the addition the blue mixture was stirred for 1 h under reflux followed by quenching with NH_4Cl (sat.) (200 cm^3) and overnight stirring at room temperature. After evaporation of the ammonia, diethyl ether (500 cm^3) was added and the organic phase was separated, washed with water (100 cm^3), 2 M NaOH (aq.) (2 × 200 cm^3), water (2 × 100 cm^3), dried (K_2CO_3) and concentrated. The crude product was recrystallised from light petroleum (bp 30–50 °C) yielding compound **6** (53.40 g, 97%) as a white powder, mp 50–51 °C (Found: C, 74.4; H, 9.6. Calc. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3%); δ_H(250 MHz, $CDCl_3$, TMS) 6.54 (2H, d, J_{meta} 2.2), 6.30 (1H, t, J_{meta} 2.2), 3.80 (6H, s, OCH_3), 1.30 [9H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 160.5, 153.9, 104.1, 96.8, 55.2, 35.0, 31.3; *m*/*z* 194 (M^+, 50%), 179 ($M^+ - CH_3$, 100).

Preparation of 2-bromo-5-*tert*-butyl-1,3-dimethoxybenzene (7)

A solution of Br_2 (58.86 g, 0.368 mol) in CCl_4 (110 cm^3) was added to compound **6** (71.56 g, 0.368 mol) in CCl_4 (600 cm^3) during 2 h at 0 °C. After addition the solution was stirred for 1 h at 0 °C followed by evaporation to dryness. Recrystallisation from *n*-hexane yielded compound **7** (95.88 g, 95%) as a white powder, mp 119–120 °C (Found: C, 52.7; H, 6.4. Calc. for $C_{12}H_{17}BrO_2$: C, 52.8; H, 6.3%); δ_H(250 MHz, $CDCl_3$, TMS) 6.60 (2H, s, Ar*H*), 3.89 (6H, s, OCH_3), 1.33 [9H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 154.9, 150.5, 100.7, 96.3, 54.65, 33.5, 29.6; *m*/*z* 272 (M^+, 58%, the isotopic pattern was consistent with that for mono-bromo compounds), 257 ($M^+ - CH_3$, 100), m* 178 (272→257).

Preparation of tris(4-*tert*-butyl-2,6-dimethoxyphenyl)methanol (8) by lithiation of 6

A solution of bromobenzene (33.60 g, 0.214 mol) in dry diethyl ether (100 cm^3) was added to lithium containing 0.5–1% sodium (3.07 g, 0.439 mol) in dry diethyl ether (100 cm^3) under argon. After 4 h of stirring at room temperature a solution of compound **6** (36.01 g, 0.185 mol) in benzene (270 cm^3) was added and the reaction mixture was stirred for 72 h at room temperature. During this period of time the colour changed from dark brown to yellow. Diethyl carbonate (7.22 g, 61.16 mmol) in benzene (130 cm^3) was added dropwise followed by reflux for another 72 h. The brown mixture was cooled and poured onto ice–water (1 kg) and stirred for 15 min. The organic phase was separated and the aqueous phase was washed with diethyl ether (100 cm^3). The combined organic phases were washed with water (2 × 100 cm^3), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from *n*-hexane gave compound **8** (18.49 g, 49%) as a white powder, mp 175–180 °C (dec.) (Found: C, 70.35; H, 8.5. Calc. for $C_{37}H_{52}O_7$: C, 73.0; H, 8.6%; the carbon content was very high which could arise from loss of water during heating); δ_H(250 MHz, $CDCl_3$, TMS) 6.72 (1H, s, O*H*), 6.49 (6H, s, Ar*H*), 3.39 (18H, s, OCH_3), 1.27 [27H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 158.2, 149.2, 125.9, 124.9, 104.2, 56.6, 34.6, 31.3.

Preparation of tris(4-*tert*-butyl-2,6-dimethoxyphenyl)methanol (8) by lithiation of 7

A solution of **7** (4.00 g, 14.64 mmol) in dry THF (50 cm^3) was cooled to −78 °C under argon and added dropwise 1.5 M Bu^{t}Li in *n*-pentane (19.50 cm^3, 29.29 mmol, 2 equiv.) at a rate keeping the temperature below −60 °C. The intensely yellow solution was stirred for 1 h at −78 °C followed by dropwise addition of diethyl carbonate (0.58 g, 4.88 mmol) dissolved in dry THF (10 cm^3) at −78 °C. The reaction mixture was allowed to reach room temperature followed by reflux for 48 h. The green reaction mixture was cooled to room temperature, quenched by the slow addition of 96% EtOH (15 cm^3) and washed with diethyl ether (2 × 100 cm^3). The organic phase was separated and washed with water (100 cm^3), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from *n*-hexane gave compound **8** (2.33 g, 79%) as a white powder. The compound was found to be extremely sensitive to acid. Any presence of acid resulted in a colour change from colourless to a very intense blue colour. The physical constants for the products prepared following the two above procedures were identical.

Preparation of 2,6,10-tri-*tert*-butyl-12c-ethoxy-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (9)

A mixture of compound **8** (22.70 g, 37.33 mmol) in water (2.6 l) was treated with conc. hydrochloric acid (60 cm^3) and the blue mixture was refluxed for 4 h. The reaction mixture was filtered and the filter cake was washed several times with water until the crude off-white xanthon was obtained. This crude product was dried in vacuum (60 °C, 0.8 mmHg) for 3 h. The dried material was mixed with pyridine hydrochloride (40.24 g, 0.348 mol) and heated to 130 °C for $2\frac{1}{2}$ h. During this period of time the reaction mixture changed from dark-red to orange–yellow indicating that the reaction had finished. The mixture was cooled, poured into water (500 cm^3), filtered and the filter-cake was washed several times with water, 2 M HCl (aq.) and water again. The filtrate was treated with 25% NaOH (aq.) (approx. 150 cm^3) until basic reaction to litmus and precipitation of a white compound occurred. The white material was collected by filtration and dissolved in 96% EtOH (400 cm^3) under reflux. Upon cooling the solution product precipitated. This gave compound **9** (13.81 g, 74%) as a white powder, mp >230 °C (dec.) (Found: C, 79.1; H, 7.7. Calc. for $C_{33}H_{38}O_4$: C, 79.5; H, 7.7%); δ_H(250 MHz, $CDCl_3$, TMS) 7.06 (6H, s, Ar*H*), 3.13 (2H, q, $^3J_{AB}$ 7.0,

Table 1 Crystallographic data for compounds **3**, **11**–**13**

Compound	**3**	**11**	**12**	**13**
Formula	$C_{19}H_{10}O_3$	$C_{31}H_{34}O_3$	$C_{32}H_{36}O_3$	$C_{18}H_9O_4P$
Formula wt	286.3	454.6	468.6	320.2
Crystal system	Triclinic	Cubic	Orthorhombic	Monoclinic
Space group	*P*1	*I*-43*d*	$Pna2_1$	$P2_1/n$
Z	2	16	4	8
a/Å	9.9471(2)	21.692(3)	12.578(3)	10.080(3)
b/Å	7.43240(10)	21.692(3)	12.305(3)	25.322(5)
c/Å	10.0028(2)	21.692(3)	17.314(4)	10.709(2)
α/°	89.9950(10)	90	90	90
β/°	119.8090(10)	90	90	94.41(3)
γ/°	89.9370(10)	90	90	90
V/Å^3	641.67(2)	10 206.7(20)	2679.9(9)	2725.4(9)
ρ/g cm^{-3}	1.482	1.183	1.161	1.561
Crystal dimensions/mm	0.35 × 0.23 × 0.18	0.35 × 0.30 × 0.28	0.35 × 0.10 × 0.075	0.23 × 0.13 × 0.10
Type of radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
μ/cm^{-1}	0.100	0.074	0.073	0.221
T/K	293(2)	293(2)	293(2)	293(2)
Number of reflections	4312	32 456	26 728	7389
Unique reflections (with $I > 2\sigma$)	3452	1736	2822	2974
R_{int}	0.0301	0.0509	0.0873	0.0312
$R(F)$, $R_w(F^2)$ all data	0.0496, 0.1481	0.0565, 0.1284	0.0714, 0.1635	0.0436, 0.1102

OCH_2CH_3), 1.35 [27H, s, $C(CH_3)_3$], 0.92 (3H, t, $^3J_{AB}$ 7.0, OCH_2CH_3); δ_C(62.9 MHz, $CDCl_3$, TMS) 154.0, 153.0, 125.9, 108.4, 106.9, 56.9, 35.3, 31.4, 15.3.

Preparation of 2,6,10-tri-*tert*-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrenium hexafluorophosphate (10)

HPF_6 (aq.) (60% w/w) (0.95 cm^3, 1.36 mmol) was added dropwise to a solution of compound **9** (3.00 g, 6.04 mmol) in diethyl ether (300 cm^3) at 0 °C. Preparation of the yellow product took place immediately. The reaction mixture was stirred for an additional 1 h at 0 °C, filtered, washed with cold diethyl ether and dried in vacuum giving compound **10** (3.62 g, 100%) as a fine intensely yellow powder, mp >300 °C (dec.) (Found: C, 62.15; H, 5.7; P. 5.3. Calc. for $C_{31}H_{33}F_6O_3P$: C, 62.2; H, 5.6; P, 5.2%); δ_H(250 MHz, $CDCl_3$, TMS) 7.67 (6H, s, Ar*H*), 1.50 [27H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 170.2, 153.9, 142.7, 110.5, 104.2, 38.2, 31.4; MALDI-TOF 453 (one peak, $C_{31}H_{33}O_3^+$).

Preparation of 2,6,10-tri-*tert*-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (11)

$NaBH_4$ (0.50 g, 13.20 mmol) was added in one portion to a solution of compound **10** (0.50 g, 0.84 mmol) in DME (50 cm^3). The reaction mixture changed from yellow to colourless during the additional 1 h of reflux. The reaction mixture was cooled to room temperature, poured into ice–water (200 g) and diethyl ether (100 cm^3) was added. The organic phase was extracted with water (2 × 100 cm^3), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from ethyl acetate produces very clear crystals suitable for X-ray diffraction. It was also possible to precipitate compound **11** as a white powder by addition of diethyl ether (approx. 10 cm^3) (0.29 g, 76%), mp >300 °C (dec.) (Found: C, 81.8; H, 7.8. Calc. for $C_{31}H_{34}O_3$: C, 81.9; H, 7.5%); δ_H(250 MHz, $CDCl_3$, TMS) 6.94 (6H, s, Ar*H*), 4.74 (1H, s, 12c-*H*), 1.32 [27H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 152.9, 152.8, 108.6, 106.9, 35.1, 31.4, 20.3.

Preparation of 2,6,10-tri-*tert*-butyl-12c-methyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd*,*mn*]pyrene (12)

A solution of compound **10** (0.50 g, 0.87 mmol) in dry THF (40 cm^3) was cooled to −78 °C under argon. CuI (0.33 g, 1.75 mmol) was added. After stirring for 10 min, 1.0 M MeLi (5.2 cm^3, 5.20 mmol) was added slowly. The reaction mixture changed colour from yellow to green. The mixture was stirred for 1 h at −78 °C. The reaction mixture adapted an off-white colour which indicated that the reaction had finished. The temperature was allowed to reach room temperature followed by addition of NH_4Cl (sat.) (20 cm^3) to quench excess copper/lithium reagent. The aqueous phase was extracted with $CHCl_3$ (2 × 50 cm^3) and the combined organic phases were washed with water (2 × 50 cm^3), dried (Na_2SO_4) and evaporated to give clear oil. This crude product was mixed with boiling acetone (50 cm^3) and stored in the freezer for 6 h. After this period of time filtration gave compound **12** (0.21 g, 52%) as white crystals. Recrystallisation from ethyl acetate produced clear crystals suitable for X-ray diffraction, mp >290 °C (Found: C, 82.4; H, 8.0. Calc. for $C_{32}H_{36}O_3$: C, 82.0; H, 7.7%); δ_H(250 MHz, $CDCl_3$, TMS) 6.96 (6H, s, Ar*H*), 1.57 (3H, s, CH_3), 1.32 [27H, s, $C(CH_3)_3$]; δ_C(62.9 MHz, $CDCl_3$, TMS) 152.33, 152.28, 112.5, 108.5, 35.1, 31.4, 31.2, 23.8.

Crystallographic methods

The crystals were mounted on glass capillaries using epoxy glue. Data were collected on a Siemens SMART Platform diffractometer with a CCD (charge coupled device) area sensitive detector. No absorption corrections were made for compounds **3** and **11**. Absorption corrections were made for compounds **12** and **13** using SADABS.[26] Direct methods for the structure solution and full-matrix least-squares refinements were used for all compounds. Hydrogen atoms were found close to the observed positions and included in the final refinements for compound **3**. For compounds **11**–**13** hydrogen atoms were in calculated positions. Programs used were SMART, SAINT and SHELXTL from Siemens.[27,28] All four structures were checked for overlooked symmetry using MISSYM and for voids in PLATON.[29] General crystallographic data for compounds **3**, **11**–**13** are given in Table 1. Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/101.

Pyroelectric measurements

The method employed was the temperature step method.[30] The set-up used for pyroelectric measurements has been described in an earlier paper.[14] The mean value of the pyroelectric coefficient in the temperature interval 24–35 °C for compound **3** was determined to be 0.5 ± 0.4 μC m^{-2} K^{-1}. Measurements were made on five different crystals and repeated five times for each crystal. Eqn. (1) was used for the calculations, where p^T is the

$$p^T = \frac{C_{\text{total}}\Delta V}{A\Delta T} \qquad (1)$$

stress-free pyroelectric coefficient, $\Delta T = 11$ K and $C_{\text{total}} = 100$ pF, A was found to vary between 0.091 and 0.035 mm^2 and ΔV was found to vary between 9 and 31 mV. The typical crystal dimensions were 0.7 × 0.3 × 0.3 mm. The polar axis was found to be along the longest dimension of crystals.

Statistical analysis

The pyroelectric data given with an indication of experimental error represents $\langle x\rangle \pm 2\sigma$, where $\langle x\rangle$ represents the population mean and 2σ represents two standard deviations. X-Ray data are given in the general form, x(σ), where x represents the mean and σ represents one standard deviation.

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