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Centrohexaindane: Six Benzene Rings Mutually Fixed in Three Dimensions – Solid-State Structure and Six-fold Nitration

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Abstract. The solid-state molecular structure of centrohexaindane (**1**), a unique hydrocarbon comprising six benzene rings clamped to each other in three dimensions around a neopentane core, and the molecular packing in crystals of **1** · CHCl$_3$ are reported. The molecular T_d-symmetry and the Cartesian orientation of the six indane wings of **1** in the solid state have been confirmed. The course and limitation of electrophilic aromatic substitution of **1** is demonstrated for the case of nitration. Based on nitration experiments of a lower congener of **1**, tribenzotriquinacene **5**, the six-fold nitrofunctionalisation of **1** has been achieved in excellent yield, giving four constitutional isomers, two nonsymmetrical (**14** and **17**) and two C_3-symmetrical ones (**15** and **16**), all of which contain one single nitro group in each of the six benzene rings. The relative yields of the four isomers (~ 3 : 1 : 1 : 3) point to a random electrophilic attack of the electrophiles at the twelve formally equivalent outer positions of the aromatic pheriphery of **1**, suggesting electronic independence of its six aromatic π-electron systems. In turn, the pronounced conformational rigidity of the centrohexacyclic framework of **1** enables the unequivocal structural identification of the isomeric hexanitrocentrohexaindanes **14**–**17** by ^{1}H NMR spectroscopy.

Keywords: Polycyclic aromatic compounds • tribenzotriquinacenes • electrophilic aromatic substitution • nitration • crystal engineering • symmetry • graph theory

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Introduction

Centrohexaindane (**1**)[1] is a unique aromatic hydrocarbon that bears six covalently bound benzene rings fixed along the three Cartesian axes of space with highest possible symmetry, T_d (Figure 1).[2,3] The electronic interaction between the six formally isolated π-electron systems appears to be negligible,[1,4] a fact which offers the possibility to subject six equivalent benzene units to identical reaction conditions within the same molecule. Centrohexaindane has been the first topologically nonplanar hydrocarbon the structure of which corresponds to the complete graph K_5[5–7] and it represents the largest member of the family of centropolyindanes.[8,9] Triptindane (**2**),[10] tribenzotriquinacene (TBTQ, **3**)[11–13] and all-*cis*-fenestrindane (**4**)[14] are the most prominent lower congeners of **1**, and their chemistry has been developed since to quite some extent.[8a,12,13,15–32] Since **2**, **3** and **4** represent structural cuttings of **1** (in fourfold and, respectively, threefold manner), centrohexaindane can also be regarded as an expanded, multiple [3.3.3]propellane, triquinacene, and fenestrane derivative of **2**, **3** and **4**, respectively. However, due to the relatively large molecular size of **1**, which may decrease the solubility of its derivatives, and to the multistep syntheses of this $C_{41}H_{24}$ hydrocarbon, the chemistry of centrohexaindane derivatives has remained limited. Thus, all derivatives of **1** known so far were synthesised from building blocks that provide the final substituents from the very beginning.[33] Functionalisation of the six benzene units of **1** by, for example, electrophilic aromatic substitution at one (or more) of the twelve equivalent peripheral aromatic CH groups has never been reported in an original paper before.[34] In the present contribution, we also disclose the results of our attempts

1 ($C_{41}H_{24}$, T_d)

K_5 **2**   **3**   **4**
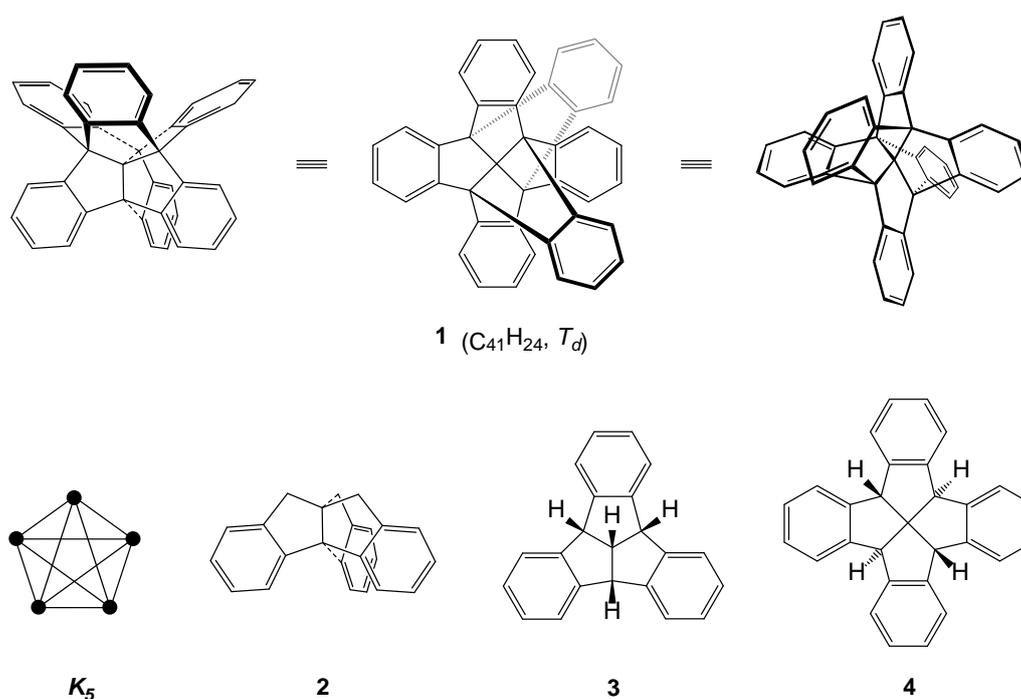
Figure 1. Centrohexaindane (**1**) shown in two perspectives (top left and right) and as a distorted 3D-structure (top centre); the complete graph K_5 and three lower centropolyindanes comprised in **1**: triptindane (**2**), tribenzotriquinacene (**3**), and fenestrindane (**4**).

along these lines. It will be shown that centrohexaindane undergoes well controllable electrophilic nitration that generates four isomeric hexanitro derivatives, **14**–**17**, which, owing to the rigidity of the centrohexacyclic structure of **1**, can be structurally identified by ^{1}H NMR spectroscopy. Before doing so, and because of the particular occasion of this issue, we take the opportunity to also report the solid-state structure of centrohexaindane – a molecule in which six benzene rings are interconnected within a unique and truly three-dimensional, centrohexacyclic arrangement, awaiting a joint future in aromatic chemistry and potentially in material science.

Results and Discussion

Solid-state structure of centrohexaindane. The unique T_d-symmetrical molecular structure of centrohexaindane (**1**) follows unequivocally from its particularly simple (AA'BB') ^{1}H NMR spectrum and its ^{13}C NMR spectrum exhibiting only five lines.[1] Therefore, in spite of the relatively large size of this $C_{41}H_{24}$ hydrocarbon, an "ultimate" structural confirmation by X-ray diffraction was never mandatory. However, X-ray structural analyses of single crystals of **1** were carried out several times and some particularly noteworthy insights had been communicated previously, such as the fact that all of the six C-C-C bond angles at the central carbon atom, C-16d, agree exactly with the theoretical value of 109.47 °, as expected for such a T_d-symmetrical centrohexaquinacene core. The crystals used for these determinations contained either *para*-xylene or triethylamine incorporated but the molecular T_d-symmetry of **1**, or at least of the centrohexacyclic core of its framework, proved to be almost undisturbed within experimental error. Here, we wish to present the original data of an X-ray structural analysis of a third co-crystal, $C_{41}H_{24} \cdot CHCl_3$, obtained by crystallization of **1** from chloroform (Figure 2).[35]

As expected, the molecular structure of **1** was found to be nearly T_d-symmetrical. The most characteristic C-C bond lengths, C-C-C bond angles, and C-C-C-C torsional angles are collected in Table 1. The dihedral angles between pairs of the benzene rings (or indane wings) and angles between the six axes of the indane wings are collected in Table 2. The molecule of chloroform occupies one of the concave faces of **1**, such that each of the three chlorine atoms forms H···Cl contacts to three adjacent molecules of **1**. In addition, two π-π-interactions shorter than 4 Å are found (Table 3).

All individual structural features analysed from the solid-state molecule structure of **1** not only confirm the high (T_d) symmetry but also the lack of any distortion of the remarkably low-strain structural subunits (Table 1). (i) The lengths of the four central C-C bonds are equal within the limits of experimental error (154.6 pm); (ii) likewise, the angles between the six pairs of bonds at the central carbon atom are the same within the limits of experimental error (109.47 °) and thus identical to the value expected for ideal sp^3-hybridisation (109.47 °); (iii) finally, the torsional angles within the carbon framework of the six cyclopentene rings within the centrohexaquinacene core are all close to zero, with maximum deviations ranging from − 0.83 ° to + 0.60 °

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and an average value of − 0.11 °. This means that all of the cyclopentene rings incorporated in hydrocarbon **1** are perfectly planar within experimental error. Hence, the six indane wings can be assumed to be planar as well, a fact that follows also from further consideration of the geometric peculiarities of **1**.
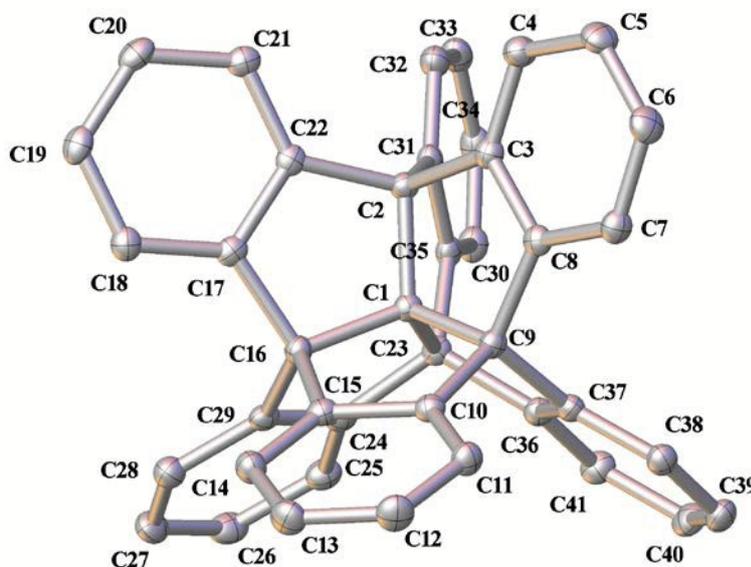
Figure 2. Molecular structure of centrohexaindane, **1** · CHCl$_3$, as obtained by X-ray diffraction at a single crystal obtained from chloroform. The molecule of CHCl$_3$ and the H atoms have been omitted for clarity (50% thermal ellipsoids).

Since centrohexaindane (**1**) may represent the hydrocarbon core of potentially even larger three-dimensional molecular building blocks once the outer arene periphery of it may be functionalised in all of the six Cartesian directions of the 3-space,[3b,8a] the mutual orientation of the six benzene rings (and the six indane wings) is of particular importance. In fact, the dihedral angles between the benzene rings again reflect the nearly perfect tetrahedral arrangement of the benzoannulation (Table 2). (i) All of the dihedral angles for the pairs of the adjacent benzene rings are very close to 120 ° and (ii) all of the dihedral angles for the pairs of opposite benzene rings are very close to 90 °. In other words, centrohexaindane (**1**) consists of (formally) twelve *fuso*-diindane (tetrahydroindeno[1,2-*a*]indene) units that adopt an otherwise avoided C_s-symmetrical conformation, and of three *spiro*-diindane (2,2'-spirobiindane) units that adopt a nearly perfect linear conformation, which is not observed in any other known 2,2'-spirobiindane derivatives either. (For the relation of *spiro*- and *fuso*-nomenclature, see ref.[36]) Furthermore, considering larger than simple diindane subunits, such as the four triptindane (**2**, or tribenzo[3.3.3]propellane) subunits, it is obvious that, within the structure of **1**, these *monofuso*-centrotriindanes are fixed in the otherwise again avoided perfect C_{3v}-symmetrical conformation. The same is true for the three D_{2d}-symmetrical but otherwise flexible fenestrindane (**4**, or *tetrafuso*-

centrotetraindane) subunits comprised in **1**.[8a,14] In view of the fact that the four tribenzotriquinacene (**3**, or *trifuso*-centrotriindane) units within **1** are conformationally rigid substructures on their own, being fixed in a C_{3v}-symmetrical ground-state conformation, the overall constraint of the structure of **1** into a single T_d-symmetrical ground-state structure has to be assigned to the stiffening effect of the four TBTQ units incorporated in the centrohexaindane framework.

Of particular notice is the last feature of the solid-state structure of **1**, namely the perfectly orthogonal ("Cartesian") orientation of the three axes that dissect the whole three-dimensional structure along the three 2,2'-spirobiindane subunits. As reflected from Table 2, the angles between the pairs of axes of the individual indane wings of **1** are either very close to 90 ° for the pairs of adjacent indane wings or very close to 180 ° for the pairs of opposite indane wings. Hence the well-noticed orthogonality of the indane wings in tribenzotriquinacene (**3**)[2,13,23,37] and its derivatives is brought to perfection in its most elaborated congener, centrohexaindane (**1**).

Finally, the crystal structure of **1** deserves some comments, in particular because tribenzotriquinacene (**3**) and its derivatives were found to form unidirectional molecular stacks.[2,13,37] In contrast to the lower congener, the structure of **1** contains exclusively concave surfaces, notably just four mutually fused TBTQ units. Therefore, the molecular packing in the crystals should be more complex, which turned out to hold true. We restrict ourselves to the discussion of the packing of the crystals obtained from chloroform. **1** · CHCl$_3$ considered above. Other solvents incorporated give rise to different packing (Electronic Supplementary Information.)[35]

Table 1. Selected bond lengths, bond angles and torsional angles of the centrohexaquinacene core within the solid-state molecular structure of centrohexaindane (**1**), as determined by X-ray diffraction analysis of a single crystal obtained from chloroform.

Central C-C bonds	[Å]	Central C-C-C bond angles	[°]	Central C-C-C-C torsional angles	[°]
C1-C2	1.5454(18)	C2-C1-C9	109.64(11)	C1-C2-C3-C8	− 0.63(15)
C1-C9	1.5476(18)	C2-C1-C16	109.44(11)	C1-C2-C22-C17	+ 0.12(14)
C1-C16	1.5427(18)	C2-C1-C23	109.31(11)	C1-C2-C31-C30	− 0.83(15)
C1-C23	1.5478(18)	C9-C1-C16	109.49(11)	C1-C9-C8-C3	− 0.65(14)
		C9-C1-C23	109.44(11)	C1-C9-C10-C15	+ 0.06(15)
		C16-C1-C23	109.52(11)	C1-C9-C37-C36	− 0.22(15)
				C1-C16-C15-C10	+ 0.60(14)
				C1-C16-C17-C22	− 0.02(14)
				C1-C16-C29-C24	+ 0.65(14)
				C1-C23-C24-C29	+ 0.13(14)
				C1-C23-C30-C31	− 0.22(15)
				C1-C23-C36-C37	− 0.26(15)
Average	1.5459(18)	Average	109.47(11)	Average	− 0.11(15)

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Table 2. Selected dihedral angles between benzene rings and angles between the indane axes in the solid-state molecular structure of centrohexaindane (**1**), as determined by X-ray diffraction analysis of a single crystal obtained from chloroform.

Dihedral angles between the six benzene rings	[°]	Angles between the six indane axes (from C1 to centre of peripheral C-C bonds)	[°]
C3...C8 – C10...C15	120.62(5)	C1...(C5/C6) – C1…(C12/C13)	90.19(2)
C3...C8 – C17...C22	120.03(5)	C1...(C5/C6) – C1…(C19/C20)	90.86(2)
C3...C8 – C24...C29	90.31(5)	C1...(C5/C6) – C1…(C26/C27)	178.77(3)
C3...C8 – C30...C35	121.51(5)	C1...(C5/C6) – C1…(C33/C34)	90.76(2)
C3...C8 – C36...C41	120.02(5)	C1...(C5/C6) – C1…(C39/C40)	90.32(2)
C10...C15 – C17...C22	120.39(5)	C1...(C12/C13) – C1…(C19/C20)	90.68(2)
C10...C15 – C24...C29	121.76(5)	C1...(C12/C13) – C1…(C26/C27)	90.75(2)
C10...C15 – C30...C35	90.36(5)	C1...(C12/C13) – C1…(C33/C34)	178.71(3)
C10...C15 – C36...C41	119.36(5)	C1...(C12/C13) – C1…(C39/C40)	89.97(2)
C17...C22 – C24...C29	116.84(5)	C1…(C19/C20) – C1…(C26/C27)	88.44(2)
C17...C22 – C30...C35	117.45(5)	C1…(C19/C20) – C1…(C33/C34)	88.42(2)
C17...C22 – C36...C41	90.17(5)	C1…(C19/C20) – C1…(C39/C40)	178.65(3)
C24...C29 – C31...C35	116.00(5)	C1…(C26/C27) – C1…(C33/C34)	88.29(2)
C24...C29 – C36...C41	121.53(5)	C1…(C26/C27) – C1…(C39/C40)	90.48(2)
C31...C35 – C36...C41	122.47(5)	C1…(C33/C34) – C1…(C39/C40)	90.91(2)

Table 3. Selected intermolecular interactions in the solid-state molecular structure of centrohexaindane (**1**), as determined by X-ray diffraction analysis of a single crystal obtained from chloroform.

Cl ⋯ H contacts < 3.2 Å			π-π Interactions < 4 Å		
Atom to atom	Distance [Å]	Symmetry code of H'	Plane to plane	Centroid distance [Å]	Symmetry code
Cl1 ⋯ H41'	3.18(1)	–x, 1–y, –z	C17-C22 ⋯ C17'-C22'	3.67(1)	–x, 2–y, 1–z
Cl2 ⋯ H5'	3.09(1)	x, –1+y, z	C30-C35 ⋯ C30'-C35'	3.98(1)	–x, 2–y, –z
Cl2 ⋯ H14'	2.93(1)	–x, 1–y, 1–z			
Cl2 ⋯ H18'	3.07(1)	–x, 1–y, 1–z			
Cl2 ⋯ H27'	2.97(1)	1+x, y, z			
Cl3 ⋯ H4'	3.04(1)	x, –1+y, z			
Cl3 ⋯ H13'	3.07(1)	–x, 1–y, 1–z			
Cl3 ⋯ H21'	3.12(1)	x, –1+y, z			
Cl3 ⋯ H40'	3.07(1)	–x, 1–y, –z			

Several remarkable packing motifs can be recognised in the crystal structure of **1** (Figure 3). One of them is that one of the C_{3v}-molecular (propellane) axes, C1-C9, of each molecule nearly coincides with crystallographic *a* axis, both vectors including an angle of 2.6 ° (Figure 3a). The hydrogen atom of the $CHCl_3$ molecule points into one of the concave surfaces of **1,** whereas one chlorine atom (Cl2) makes a short contact to H27' of an adjacent molecule of **1** (Figure 3b), such that the indane wing bearing that hydrogen atom also docks to the bowl containing the molecule of chlorofom. Another bowl of each molecule of **1** is filled by the propellane-like triptindane moiety

of an adjacent hydrocarbon molecule (Figure 3c). In total, the chlorine atoms of one chloroform take part in additional Cl···H interactions of three neighbouring molecules of **1**. The two closer ones having Cl···H distances < 3 Å are also linked to each other by short π-π contacts of 3.67(1) Å, whereas the third molecule of **1** is subject to longer Cl···H contacts of 3.07(1) and 3.18(1) Å and a longer π-π contact of 3.98(1) Å (Figure 3d).
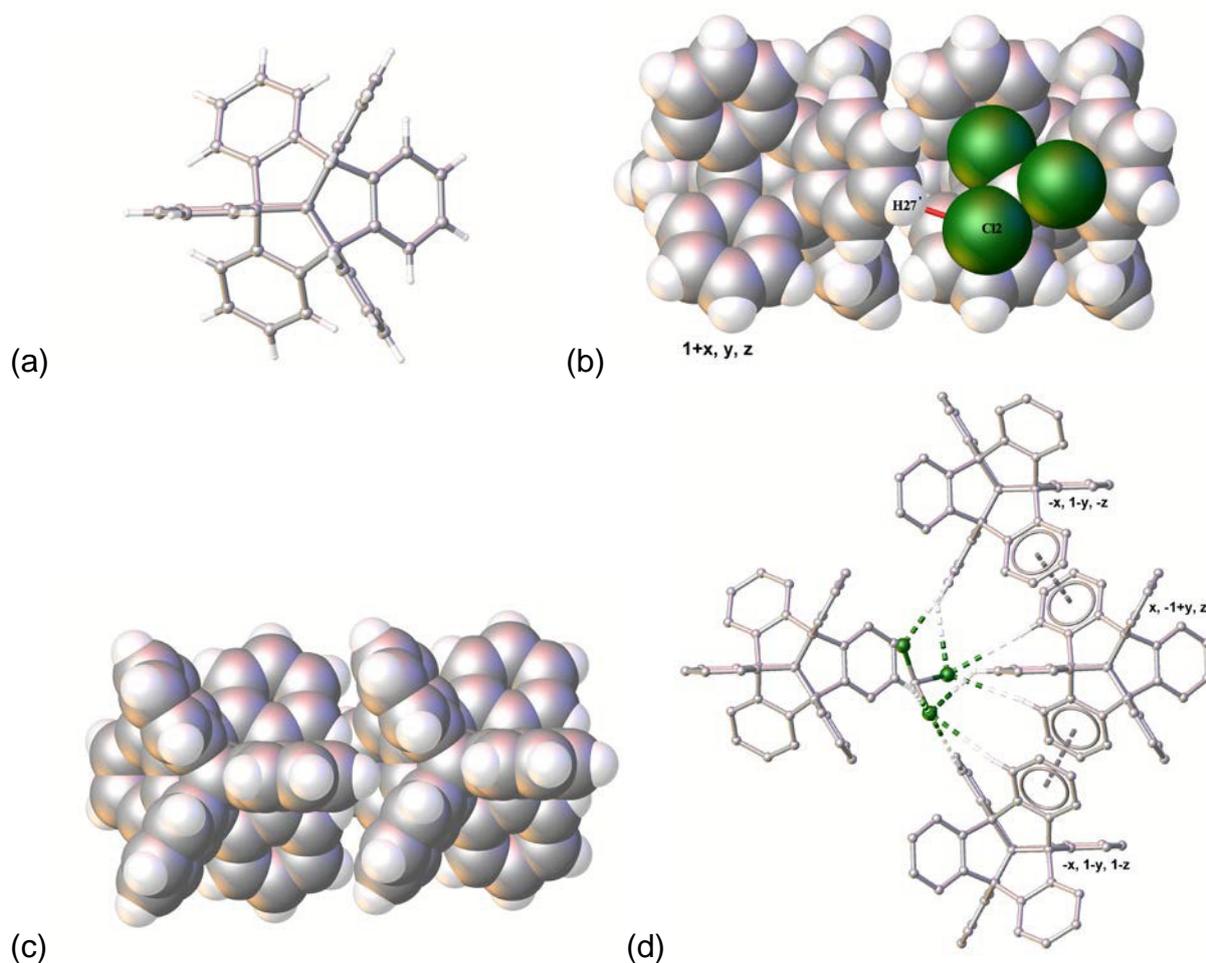
Figure 3. Crystal structure of **1** · CHCl₃; (a) view along 100, (b) view along 0ī0, showing the embedded molecule of CHCl₃ and H27'··· Cl2 contact, (c) opposite view along 010, and (d) view along 100 showing additional intermolecular H ··· Cl contacts and π-π interactions.

Nitration of tetramethyltribenzotriquinacene 5. The multiple functionalisation of lower centropolyindanes, such as certain bridgehead-methyl derivatives of **3**, in particular, by electrophilic aromatic substitution has been investigated in great detail.[8a,37] Six-fold bromination, iodination, and nitration at the six peripheral positions of **3** were found to be particular high yielding,[38] as were three-fold single nitration[39] and formylation[28a,40] at each of its three benzene rings. Since the bridgehead-tetramethyl derivative **5** is a closely related but simpler and more readily accessible analogue of centrohexaindane (**1**),[37] nitration experiments were

performed first with the former hydrocarbon and the experiences obtained were then transferred to the nitration of **1**.

Treatment of **5** with the conventional mixture of nitric acid (65%) and sulfuric acid (98%) at ambient temperature for 6 h converted 83% of the starting material and produced a mixture of multiply nitro-substituted derivatives of **5**, which were partially separated by gravity chromatography (Scheme 1). Two trinitro derivatives were obtained in very low yield (2%) as an inseparable mixture and identified by electron ionization (EI) mass spectrometry and ^{1}H NMR analysis as the C_3- and C_1-symmetrical products, **6** and **7**, respectively (ESI). The isomer ratio was determined to be 1:3, notably in favour of the nonsymmetrical product, by analyzing the incremental chemical shifts caused by the presence of the nitro groups at spatially fixed and well defined sites. Independent studies afforded a directed synthesis of **6** and **7** (see below) and confirmed the structural assignment by reduction to the corresponding *separable* triamino derivatives.[39]
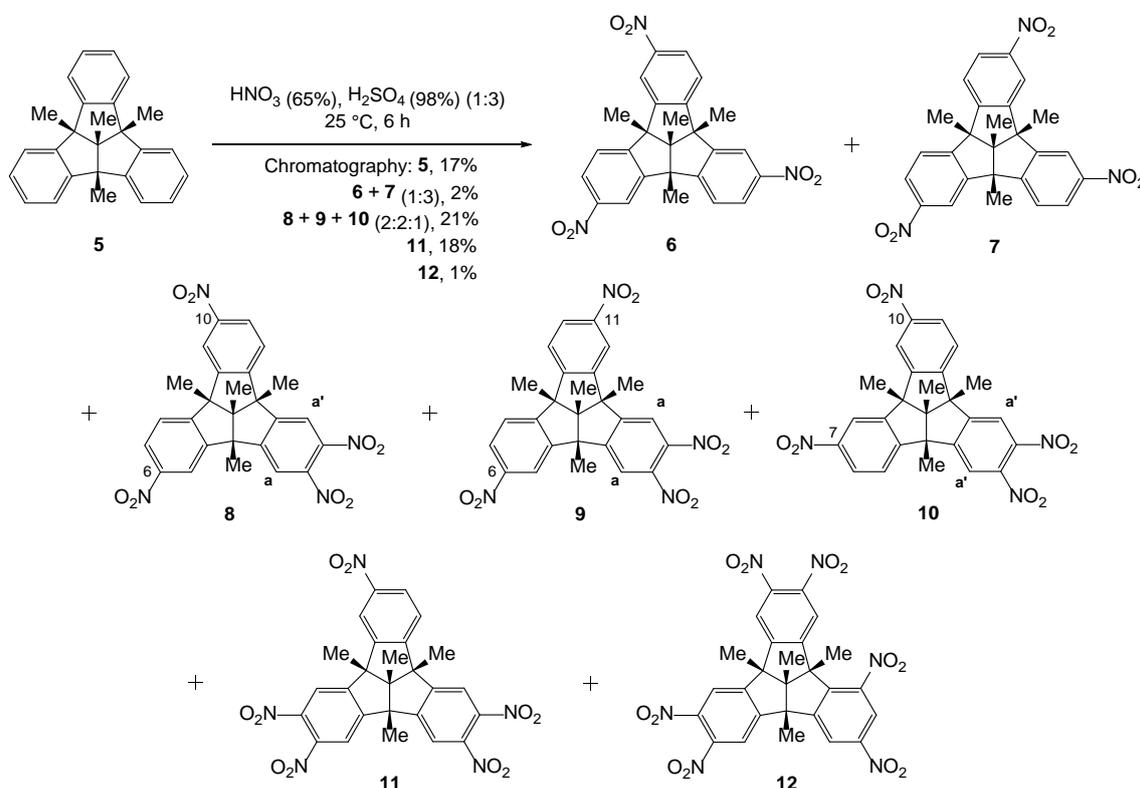
Scheme 1. Nitration of tetramethyltribenzotriquinacene **5** with standard nitration acid. The trinitro derivatives **6** and **7** and the tetranitro derivatives **8**–**7** were obtained as inseparable mixtures (see text).

The next-eluting fraction consisted of an inseparable mixture of three tetranitro derivatives, **8**–**10**, in 21% combined yield. Again, EI mass spectrometry and ^{1}H NMR spectroscopy allowed us to unequivocally identify the three isomers as those products in which all of the four nitro substituents were introduced at the aromatic periphery of the TBTQ framework (see ESI). In fact, only three isomers are possible

under these restrictions, namely, a nonsymmetrical one, **8** (C_1), and two C_s-symmetrical ones, **9** and **10**. Applying again a systematic analysis of the incremental chemical shifts caused by the four nitro groups in these isomeric structures allowed us to assign their structures and to estimate the isomer ratio [**8**] : [**9**] : [**10**] ~ 2 : 2 : 1. As an example, the isolated *ortho*-hydrogen atoms H^a and H$^{a'}$ at the doubly nitrated benzene ring of **8**–**10** can be used as an anchor point for unequivocally assigning the three isomeric structures. The proton resonances of H^a in isomers **8** and **9** are subject to the strongest downfield shift at δ 8.80 (in DMSO-d$_6$) due to the joint deshielding effects of the two adjacent nitro groups (2-NO$_2$ and 3-NO$_2$) and, in addition, that of the relatively close nitro group at the neighbouring singly nitrated benzene rings (6-NO$_2$ in **8** and 6-NO$_2$ and 11-NO$_2$ in **9**). In contrast, the proton resonances of H$^{a'}$ in isomers **8** and **10** suffer a less pronounced downfield shift to only δ 8.63. In these cases, the more remote nitro group at the neighbouring singly nitrated benzene rings (10-NO$_2$ in **8** and 7-NO$_2$ and 10-NO$_2$ in **10**) exert significantly less deshielding. The downfield-shift effects of such "proximal" and "distal" nitro substitutents at the neighbouring benzene rings can be used as a reliable feature, as shown previously for the trinitro-TBTQ derivates **6** and **7**[39] and as it will be demonstrated for the hexanitro-substituted centrohexaindanes **14**–**17** (see below). In the case of the tetranitro-TBTQ isomers **8**–**10**, the chemical shift differences of protons H^a and H$^{a'}$ is $\Delta\delta$ = 0.17 ppm. Following the same concept, all of the other resonances of the arene hydrogens of **8**–**10** can be assigned to give a consistent interpretation of the ^{1}H NMR spectra (see ESI).

Along similar lines, the structural identification of the pentanitro-TBTQ derivate **11** by EI mass spectrometry and by ^{1}H and ^{13}C NMR spectroscopy is again unequivocal. In particular, an ABC partial spectrum at δ 8.09, 8.17 and 8.70 (^3J = 8.5 Hz and ^4J = 2.0 Hz) indicates the presence of a singly nitrated benzene ring, and four singlet resonances, two of which being isochronous, reflect the four remaining isolated *ortho*-H atoms of **11**. The ^{13}C NMR spectrum of **11** exhibits eleven lines for quaternary arene carbons and seven lines for tertiary arene carbons, again in agreement with the C_1-symmetry of this structure. The lack of symmetry is also reflected by minute chemical shift differences of the outer bridgehead and methyl carbon resonances at δ 64.6 and δ 25.0.

Finally, the hexanitro-substituted TBTQ derivative **12** was isolated in minute yield (1%) but again clearly identified by EI mass spectrometry and ^{1}H NMR spectroscopy. The *meta*-dinitro substitution pattern present in one of the three benzene rings is indicated by a characteristic AB spectrum at δ 8.99 and δ 8.64 (^4J = 2.0 Hz), whereas four singlet resonances reflect the common twofold *ortho*-dinitration at the outer periphery of **12**. One of these singlets appears at unusually high field (δ 8.06, as compared to δ 8.74, 8.78 and 8.89 for the other three). Clearly, this resonance has to be attributed to the hydrogen atom at H-12, which suffers a strong shielding effect due to the orthogonally oriented nitro group at C-1 of the adjacent benzene ring (Figure 4). Introduction of a nitro group into the sterically strongly hindered *ortho*-position of the TBTQ skeleton has never been observed before and is considered an

exception of the otherwise peripheral functionalisation of centropolyindanes under conditions of electrophilic aromatic substitution.[41]
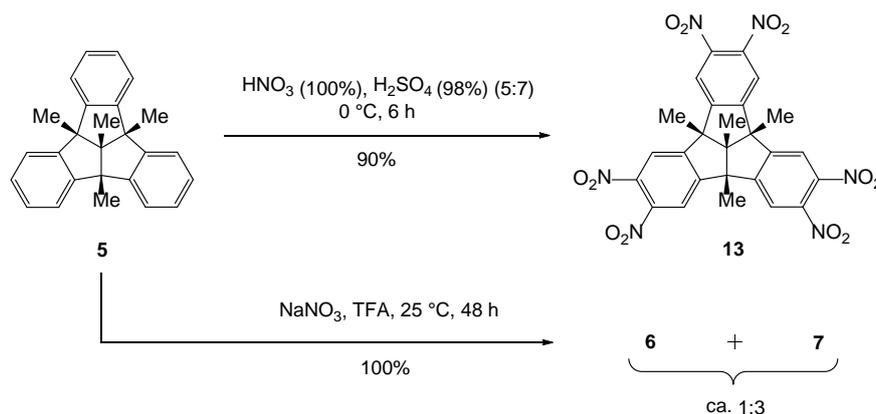
Scheme 2. Nitration of tetramethyltribenzotriquinacene **5** with fuming HNO$_3$/H$_2$SO$_4$. The trinitro derivatives **6** and **7** were obtained as inseparable mixtures (see text).[38,39]

(top view) **12** (side view)   (side view) **13** (top view)
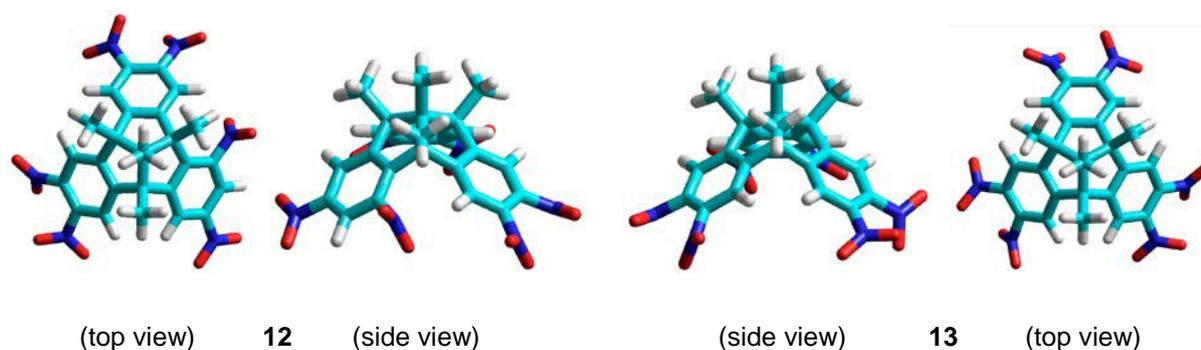
Figure 4. Molecular structures of the two isomeric hexanitrotribenzotriquinacenes **12** (left) and **13** (right) as obtained by molecular modeling (HyperChem®, AM1).

These rather complex results demonstrate that use of the conventional mixture of nitric acid (65%) and sulfuric acid (98%) for the multiple peripheral nitration of the bridgehead-tetramethyl-substituted TBTQ derivate **5** does not lead to efficient nitrofunctionalisation. In contrast, use of fuming nitration acid (100% HNO$_3$ and 98% H$_2$SO$_4$) gives rise to the complete nitration of **5** at all of its six outer peripheral arene positions, affording the C_{3v}-symmetrical product **13** in excellent yield (90%, Scheme 2).[38] No other products were observed under these conditions. Compound **13** proved to be a highly valuable synthesis intermediate for the construction of extended polycylic condensation products.[8a,20b–e,38] Molecular modeling of **13** and comparison to the hexanitro isomer **12** reveals that the symmetrical derivative is more stable, as expected. The molecular structures of **12** and **13** are depicted in Figure 4. Still in contrast to these findings, use of sodium nitrate in trifluoroacetic acid[42] for the nitration of **5** furnishes a mixture of trinitro derivatives **6** and **7** in apparently quantitative yield (Scheme 2).[39] The isomer ratio was found to very similar, [**6**] : [**7**] = 1 : 3, to that of observed when **6** and **7** were isolated as a binary

mixture from the complex product mixture obtained under conventional nitration conditions (Scheme 1). The $NaNO_3$/TFA method has also been successfully applied to the three-fold nitration of the corresponding *centro*-methyl derivative of **4** bearing otherwise easily oxidisable bridgehed C-H bonds.[23,27a]

Nitration of centrohexaindane. Several insights have been obtained from our nitration experiments with tribenzotriquinacenes, such as the tetramethyl derivative **5**. (i) Use of conventional nitration acid does not give rise to complete substitution of the six outer peripheral positions, whereas (2) use of fuming nitration acid does give the most interesting and useful C_{3v}-symmetrical 2,3,5,6,10,11-hexanitro derivative **13** in excellent yield. (3) The inner (*ortho*) positions of the arene periphery do not react under such harsh conditions, although one such process has been observed by isolation of the 1,3,5,6,10,11-hexanitro isomer **12** in minute amounts as a unique exception. (4) Use of sodium nitrate in trifluoroacetic acid offers a likewise highly efficient access to the 2,5,10- and 2,5,11-trinitro congeners **6** and **7**, respectively, bearing one nitro substituent at each of the three indane wings. However, separation of these isomers is extremely difficult. (5) The more interesting C_3-symmetrical isomer **6** is notoriously obtained as the minor component, pointing to a "statistical" course of the electrophilic attack during the nitration process.[38] (6) Finally, the individual location of the nitro groups at the highly rigid, bowl-shaped TBTQ framework gives rise to characteristic chemical shifts of the arene proton resonances that, in turn, can be used as increments to assign the constitution of the multiply nitro-substituted TBTQ derivatives. As will be shown below, parts of these insights and experiences can be transferred to the highest congener of the centropolyindane family, centrohexaindane (**1**), while others cannot.

In our early attempts along these lines, centrohexaindane (**1**) was reacted with an excess of nitration acid (65% HNO_3 and 98% H_2SO_4, 1 : 3) at ambient temperature for 20 h. To our delight, we found that each of the six benzene rings underwent single nitration, and chromatography of the crude product mixture furnished a mixture of hexanitrocentrohexaindanes in 67% yield. The EI mass spectrum of this mixture showed the molecular radical cation peak at *m*/*z* 786 as the base peak and only minor peaks indicating successive losses of NO and NO_2. Neither was the formation of penta- or other less highly nitrated products observed, nor was that of more highly nitrated analogues. The ^{1}H NMR spectrum of the mixture, dissolved in DMSO-d_6, confirmed the absence of non-nitrated benzene rings and suggested the presence of six singly functionalized indane wings. Repetitive chromatography afforded two isomeric hexanitro derivatives of **1**, which could be identified by ^{1}H NMR spectroscopy as the two non-symmetrical constitutional isomers, **14** and **17**. The structural assignment of these C_1-isomers will be discussed in detail together with that of two further, C_3-symmetrical hexanitro derivatives, **15** and **16** (see below).

In view of the results obtained on the nitration of the lower congener of **1**, tetramethyltribenzotriquinacene **5**, the six-fold single-wing nitration of **1** using nitration acid suggested the need of more drastic reaction conditions. Several attempts to run

the reaction at higher temperatures and for prolonged reaction time (up to 90 °C, 90 h) gave rise to complex mixtures of nitration products, as revealed by ^{1}H NMR spectroscopy. Whereas the formation of peripheral *ortho*-dinitro functionalities was indicated, in parallel to the findings with the TBTQ derivatives **5**, the desired dodecanitrocentrohexaindane **18** (Scheme 3), bearing twelve nitro groups at the twelve outer peripheral positions, was not observed – it should have been recognised easily because of the required degeneracy of the twelve remaining proton resonances due to the T_d-symmetrical structure. Therefore, in analogy to the experience made with the lower congener **5**, centrohexaindane (**1**) was reacted with an excess of fuming (100%) nitric acid and concentrated sulfuric acid, both at ambient temperature and even at 100 °C. Comparison of the ^{1}H NMR spectra of the various product mixtures obtained under these different reaction conditions indicated that the degree of nitration had increased slightly but that it was far from "exhaustive" nitration of the twelve outer peripheral positions of **1**. Hence, the unique target compound, 2,3,5,6,10,11,21,22,26,27-dodecanitrocentrohexaindane (**18**), has remained elusive.
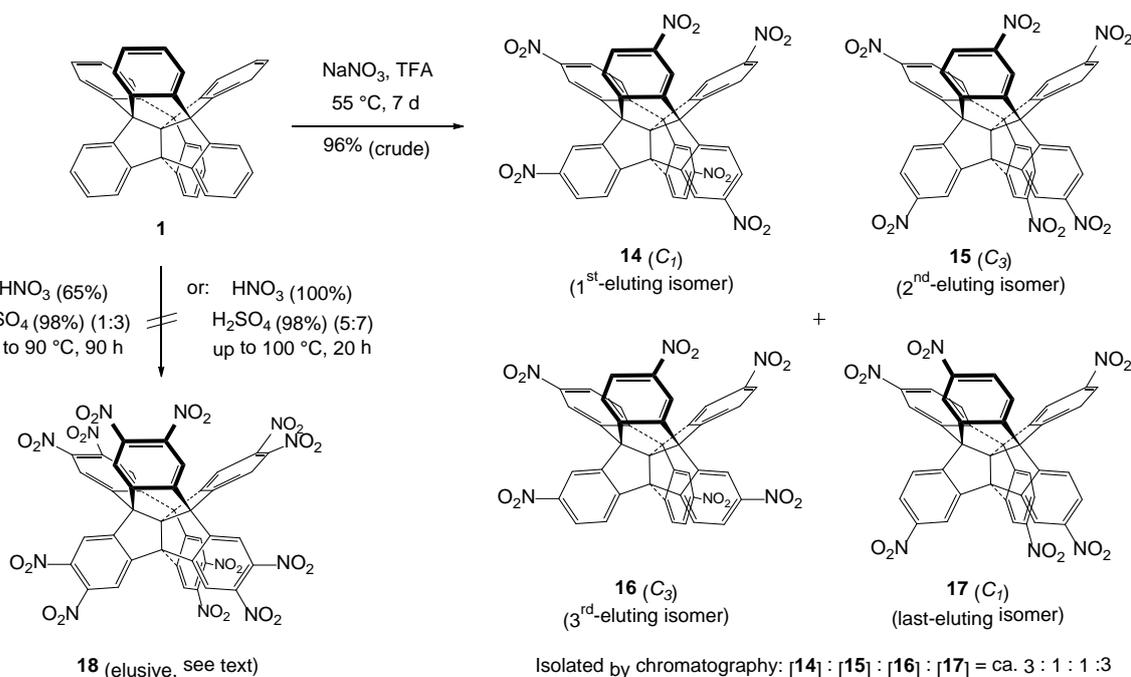
Scheme 3. Nitration of centrohexaindane (**1**) under various reaction conditions. Isomers **14**–**17** were separated by chromatography and isolated in about the statistical ratio. Use of nitration acid gave mixtures from which **14** and **17** were isolated, whereas working at enforced conditions using fuming nitration acid at higher temperatures gave mixtures of oligonitro derivatives of **1** that contain more than six nitro groups. Dodecanitrocentrohexaindane **18** was not formed under either of these conditions.

In contrast, nitration of centrohexaindane (**1**) by use of sodium nitrate in trifluoroacetic acid[42] proceeds in a well controllable manner. Similar to the TBTQ congeners, each of the benzene rings undergoes one single nitration, which results in a mixture of four constitutional isomers, the hexanitrocentrohexaindanes **14**–**17** (Scheme 3). The reaction was found to be significantly slower than for the lower congeners, reflecting the relatively low solubility of the substrate and partially nitrated

intermediates. Nevertheless, if a large excess of the reagent was used and the reaction carried out at elevated temperature (55 °C) and prolonged reaction time (7 d), a mixture of the hexanitro derivates **14**–**17** was obtained in 96% crude yield. Interestingly, the ^{1}H NMR spectra of this mixture, recorded with either DMSO-d$_6$ or THF-d$_8$, were very similar to those of the product mixture obtained with nitration acid (see above). Mass spectrometry employing the negative-ion ESI technique with use of lithium chloride as an additive generated an [M + Cl]$^−$ molecular adduct ion at m/z 821 and indicated the absence of products of lower (and higher) nitration (ESI). The crude mixture of **14**–**17** was subjected to preparative high-pressure liquid chromatography using silica gel and cyclohexane/ethyl acetate (3 : 1), which furnished the four isomers in strongly enriched form and in a ratio of [**14**] : [**15**] : [**16**] : [**17**] ≈ 3 : 1 : 1 : 3 (see below). Recrystallisation of the individual isomers from tetrahydrofuran afforded further purification.
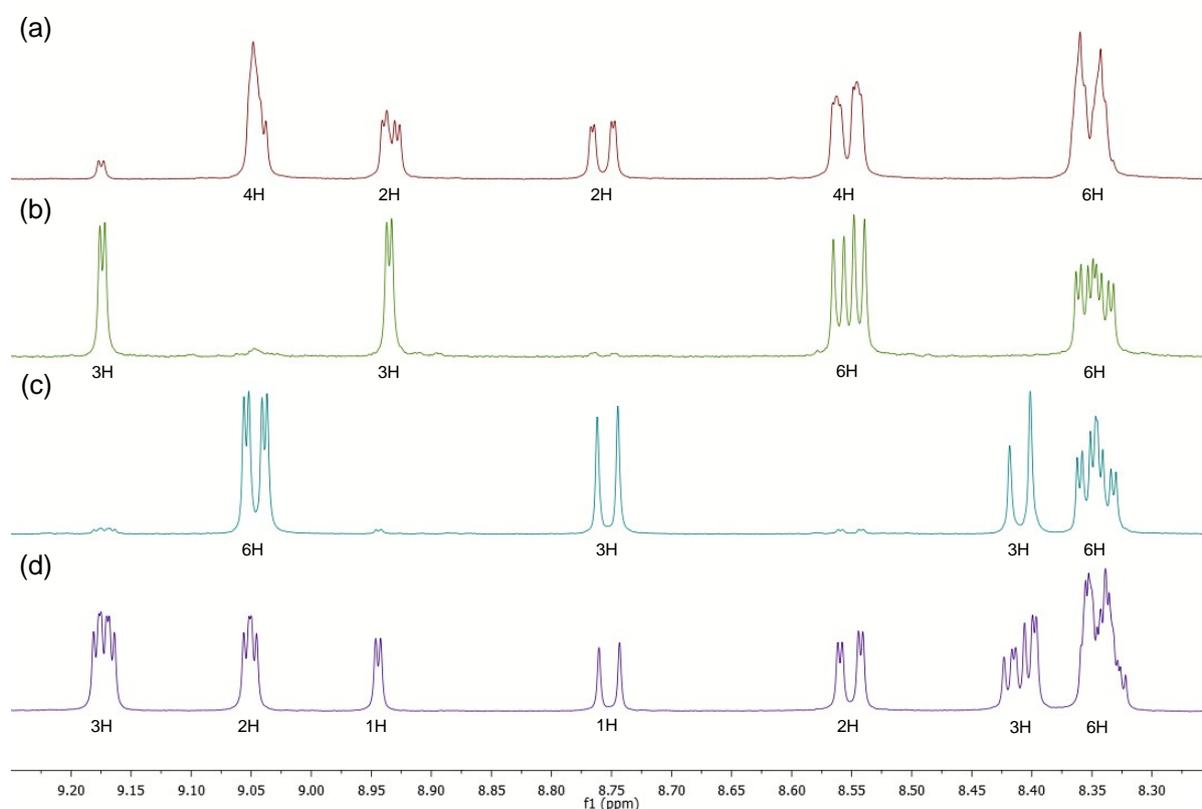
Figure 5. ^{1}H NMR spectra (500 MHz, THF-d$_8$) of the four isomeric hexanitrocentrohexaindanes **14**–**17** in order of chromatographic elution: **14** (a), **15** (b), **16** (c) and **17** (d). The resonance at δ 9.17 in the spectrum of isomer **14** reflects the presence of **15** as a minor impurity.

The structural assignment of the isomers **14**–**17** is based on the insights gained with the various nitro-substituted TBTQ derivatives and, in particular, with the trinitro congeners **6** and **7**.[38] Similar to the latter compounds, we can safely assume that the six nitro functionalities in **14**–**17** were introduced at the outer peripheral positions of **1**, generating six individual 4-nitro-*ortho*-xylene units that can stick together in only

four possible combinations. Further analysis reveals that two of the four constitutional isomers have molecular C_3-symmetry, whereas the other two are C_1-symmetrical. A random distribution of the six substituents among the six peripheral pairs of outer carbon atoms of **1** should lead to two C_3-symmetrical and two C_1-symmetrical arrangements in the "statistical" ratio of $[C_3] : [C_1] = 8 : 24 = 1 : 3$, as depicted schematically in Figure 6.


(a) C_3 (4 × 2 = 8)

(b) C_3 (4 × 2 = 8)

(c) C_1 (3 × 4 × 2 = 24)

(d) C_1 (3 × 4 × 2 = 24)
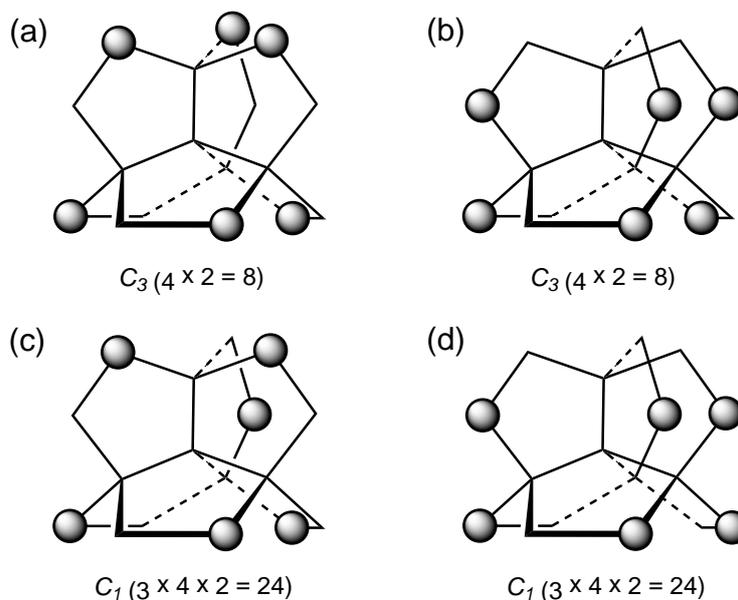
Figure 6. Schematic distribution of six substituents among the six peripheral pairs of positions of a centrohexaquinane framework. The probability factors result from the degeneracy of the tetrahedral framework (4), the chirality of the distributions (2), and the equivalent arrangements within the propellane and triquinane subunits, respectively (3).

In fact, the ^{1}H NMR spectra of **14**–**17** (Figure 5) confirm this and the absence of any products that would have resulted from nitration of inner peripheral positions of **1**. Closer inspection of the spectra reveals that the chemical shifts of the twelve inner protons in the ^{1}H NMR spectra of **14**–**17** depend distinctly on the positions of the nitro groups within the four tribenzo[3.3.3]propellane (triptindane, cf. **2**) subunits. In the TBTQ congeners **6** and **7**, a given inner proton is subject of the diamagnetic and anisotropic effects of the directly adjacent nitro substituent and of the nitro group of the adjacent indane wing, as discussed above. The centrohexaindane analogues **14**–**17** contain two such downfield-shifting nitroindane wings adjacent to a given one within a common trinitrotriptindane subunit. This leads to characteristic shift increments for the inner protons and enables the unequivocally assignment of the four constitutional isomers. The best approach to this analysis is to start with the spectra of the two C_3-symmetrical isomers, **15** and **16** (Figures 7 and 8).

The ^{1}H NMR spectra of the second-eluting isomer, **15**, and of the third-eluting one, **16**, exhibit only four distinct ranges of resonances, whereas those of the first- and last-eluting isomers, **14** and **17**, display five and even seven distinct ranges,

respectively. This suggests that **15** and **16** represent the C_3-symmetrical isomers, whereas **14** and **17** are the C_1-symmetrical ones. The spectrum of **15** shows two narrow doublets at δ 9.17 and δ 8.93 (^4J = 2.0 Hz), clearly reflecting the two sets of three equivalent inner protons having neighbouring *ortho*-nitro groups. Among these resonances, the lowest-field one indicates the presence of a triptindane subunit that bears three highly deshielded protons in a C_{3v}-symmetrical orientation and in the closest possible neighbourhood ("proximal") to the two other nitro groups at the adjacent nitroindane wings, as depicted in Figure 7a. In such an environment, the latter two nitro groups should contribute to the overall deshielding of each of the three protons by their anisotropic effects. In contrast, the other three inner protons
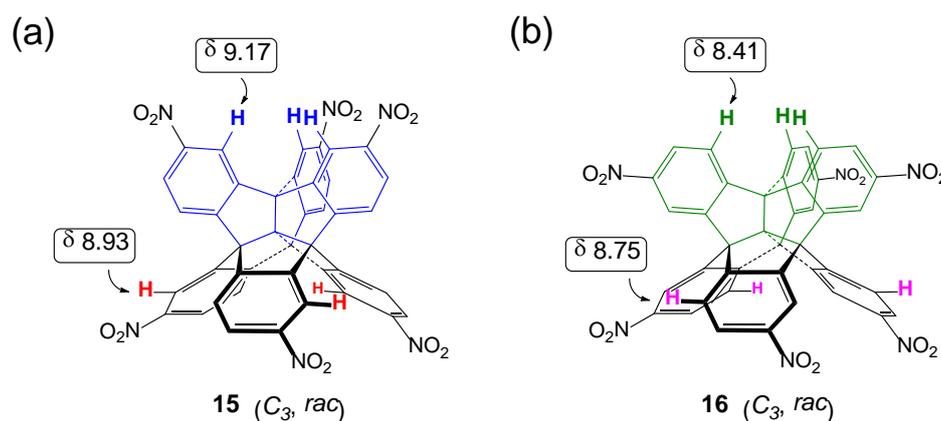
Figure 7. Four distinct magnetic situations for the four sets of three equivalent inner protons of the C_3-symmetrical hexanitrocentrohexaindanes **15** (a) and **16** (b). In isomer **15**, one triptindane subunit (marked in blue) contains three equivalent inner protons directly adjacent to a nitro group and in proximal relation to two nitro groups at the other indane wings, giving rise to the strongest downfield shift (δ 9.17). The three comparable, equivalent inner protons (marked in red) of the other three triptindane subunits have both of the nitro groups of the other two indane wings at distal positions. These protons resonate at δ 8.93 (Δδ = – 0.24 ppm). – In turn, one triptindane subunit of **16**, marked in green, contains three equivalent inner protons with a *meta*-nitro group and with the two nitro groups at the other indane wings placed in distant position, giving rise to the weakest downfield shift (δ 8.41). The three comparable, equivalent inner protons (marked in violet) of the other three triptindane subunits have both of the nitro groups of the other two indane wings at proximal positions. These protons resonate at δ 8.75 (Δδ = + 0.34 ppm).

resonating at δ 8.93 are placed at C_s-symmetrically substituted triptindane wings in which the two adjacent nitroindane wings have their nitro substituents at more remote positions. The anisotropic effect of these "distal" nitro groups should be significantly weaker. It is striking to note that the ^{1}H NMR spectrum of the other C_3-symmetrical isomer, **16**, exhibits two narrow doublets that are almost isochronous (δ 9.052 and δ 9.037, ^4J = 2.0 Hz) and virtually just at the mean value of the corresponding chemical shifts of isomer **15** (δ 9.05). Clearly, in isomer **16** each of the four triptindane subunits contains exclusively inner protons (not shown in Figure 7) that have an *ortho*-nitro substituent at the very same ring and both one proximal and one distal nitro group at the adjacent nitroindane wings (Figure 8). This shows already that the model used for the assignment of the resonances is consistent and that the effect of the three (really

remote) nitro groups at the TBTQ moieties, that is, of those opposite to the triptindane units within the centrohexaindane structure, is almost negligible.
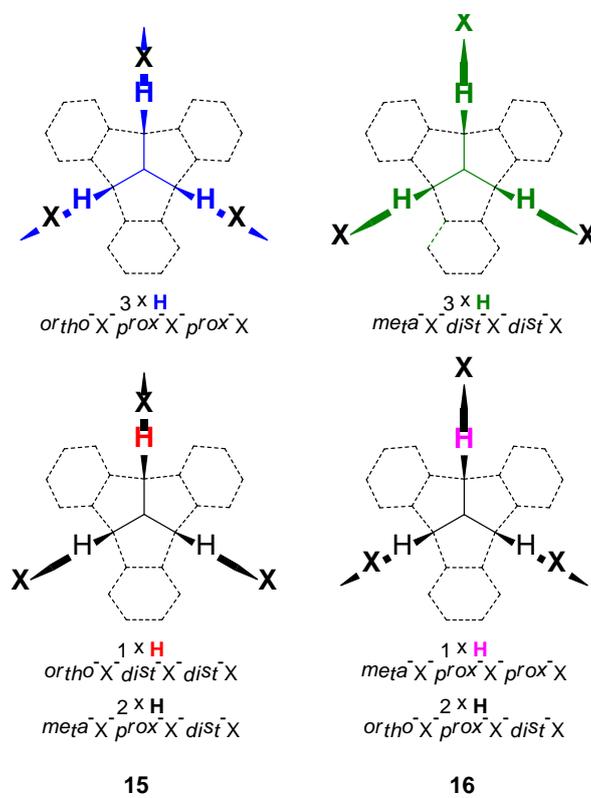

Figure 8. Schematic view on the C_3-symmetrical isomers **15** (left) and **16** (right) along the propellane axes of their C_{3v}- (top) and C_s-symmetrical (bottom) triptindane subunits. The colouring corresponds to that used in Figure 7. The residual pairs of inner H atoms of the C_s-triptindanes are also shown (black).

The chemical shifts of the other two sets of three inner protons of isomers **15** and **16** confirm the assignment of the two C_3-symmetrical isomers in a complementary way. As shown in Figure 7b, isomer **16** also contains one C_{3v}-symmetrical triptindane subunit in which, in contrast to isomer **15**, all of the three nitro groups are in a distal position to the propellane axis. Therefore, the three inner protons which stand *meta* to the nitro groups should suffer only relatively little deshielding effcts. In fact, the ^{1}H NMR spectrum of **16** exhibits a broad doublet (^3J = 8.6 Hz) at relatively high field (δ 8.41) due to these three equivalent protons. The three comparable inner protons of the other three, again, C_s-symmetrically functionalized triptindane subunits, each having a *meta*-nitro substituent at the same benzene ring, should suffer a much stronger deshielding due to the two proximal nitro groups at the adjacent indane wings. In fact, these three equivalent protons resonate at δ 8.75 (^3J = 8.6 Hz). Again in turn, the corresponding two sets of three equivalent *ortho*-protons of **15** having also *meta*-nitro groups at the respective benzene rings but both one proximal and one distal nitro group at the adjacent indane wings are almost isochronous and resonate as broad doublets at δ 8.555 and δ 8.546 (^3J = 8.6 Hz). Again, this closely corresponds to the mean value of the chemical shifts found for the respective protons

of isomer **16** (δ 8.58). The remaining two sets of equivalent inner protons of isomer **16** that are bound *ortho* to the nitro groups of the same benzene ring (δ 9.052 and δ 9.037, ^4J = 2.0 Hz) have already been mentioned above.

The chemical shift difference of the low-field and high-field inner protons bound *meta* to a nitro group ($\Delta\delta$ = 0.34 ppm) in **16** is even larger than the corresponding difference between the low-field and high-field inner protons of **15** ($\Delta\delta$ = 0.24 ppm) but the "symmetrical" splitting due to the two-fold proximal or two-fold distal orientation of the adjacent nitro groups is found in both cases. Finally, it is almost needless mentioning that the six outer peripheral arene protons that are bound *ortho* to the nitro groups in both isomers **15** and **16** appear in both of their ^{1}H NMR spectra at the same chemical shift (δ 8.35) as two mutually overlapping double-doublets.
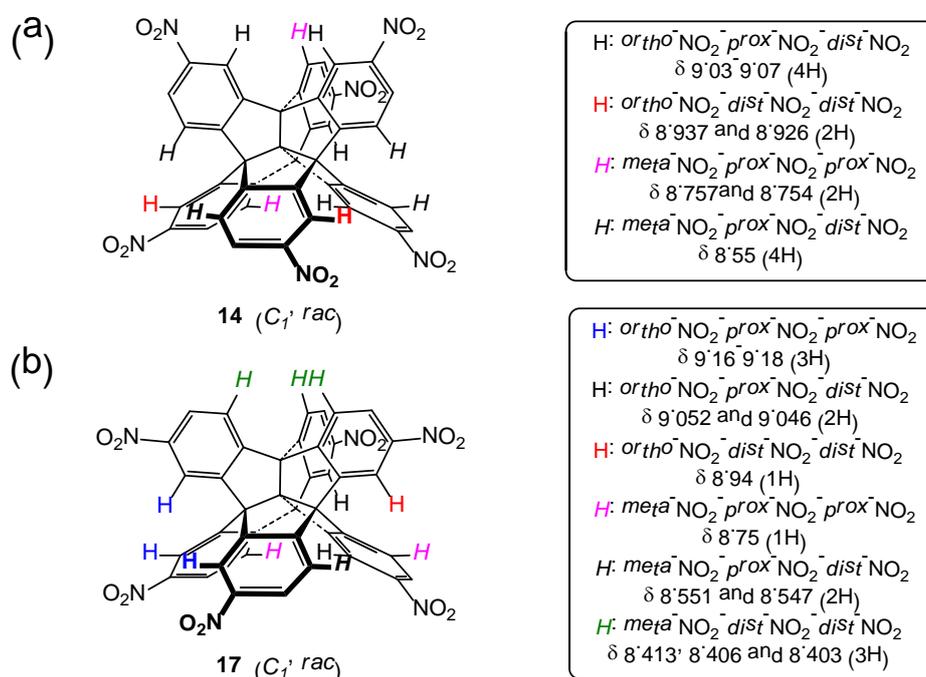
Figure 9. Chemical shifts of the twelve inner protons of the C_1-symmetrical hexanitrocentrohexaindanes **14** (a) and **17** (b), arranged in groups of similar magnetic environment (see Figures 7 and 8, and discussion). The hydrogen atoms bound *meta* to a nitro group are marked in italics; the colouring of a set of H atoms in similar magnetic environment corresponds to that used in Figure 7.

The highly systematic through-space deshielding effects of the nitro substitutents at the adjacent indane wings operate with the two C_1-symmetrical isomers **14** and **17** as well and can be used consistently for the assignment of their constitution (Figure 9). For example, the ^{1}H NMR spectrum of the first-eluting isomer **14** does not exhibit the lowest-field resonance in the range of δ 9.15–9.20, which was found to be characteristic for isomer **15**, whereas the spectrum of isomer **17** does show such a multiplet for three hydrogens at δ 9.16–9.18. In fact, among the C_1-symmetrical isomers, **17** contains three inner protons that are bound *ortho* to a nitro group at the same benzene ring and stand proximal to the two nitro groups at the adjacent indane

wings. Instead, the spectrum of isomer **14** shows a multiplet at δ 9.03–9.07 for four inner protons bound *ortho* to a nitro group and having both a proximal and a distal nitro group in the neighbourhood. Two other such protons of **14**, appearing at δ 8.937 and δ 8.926 ($^4J \approx$ 2.0 Hz each), see both nitro groups at the adjacent indane wings in distal positions. The reverse order of resonances is found with **14** for its inner protons having a *meta*-nitro group at the same ring (δ 8.757 and δ 8.754, 2 H, ^3J = 8.6 Hz, and δ 8.55, 4 H, $^3J \approx$ 8.4 Hz). In turn, the spectrum of isomer **17** exhibits two almost isochronous narrow doublets at δ 9.052 and δ 9.046 ($^4J \approx$ 2.2 Hz) for two inner "*ortho*-nitro" protons with one adjacent proximal and one adjacent distal nitro group and another narrow doublet at δ 8.94 (^4J = 2.0 Hz) for a single proton that has two distal nitro groups. Again, the six "*meta*-nitro" protons of **17** appear in the reverse order as broad doublets (^3J = 8.6 Hz) at δ 8.75 (1 H), almost isochronous at δ 8.551 and δ 8.547 (2 H) and nearly isochronous at δ 8.413, δ 8.406 and δ 8.403 (3 H). Taken altogether, the incremental chemical shifts caused by the three nitro groups within each of the triptindane units of the hexanitrocentorhexaindanes **14**–**17** were found to be fully consistent throughout the whole series and allowed us to unequivocally assign the structures of these four constitutional isomers. Finally, it should be mentioned that ^{1}H,^{1}H-COSY measurements of **14**–**17** were also in agreement with all these assignments (see ESI).

The ^{13}C NMR spectra of **14**–**17** exhibit the expected diversity of aromatic and aliphatic resonances (see ESI). The molecular C_3-symmetry of **15** and **16** is confirmed by the required restriction to only six quaternary as well as six tertiary arene carbon resonances in both cases. Notably, the central (aliphatic) carbon atoms of all isomers **14**–**17** resonate at virtually the same chemical shift (δ 98.74–98.76). In agreement with symmetry, the four partially equivalent outer bridgehead carbon atoms (C^α) of **15** give rise to two lines at δ 74.15 and δ 73.67 in the intensity ratio of $\sim$ 1 : 3, whereas those of isomer **16** are reflected by two lines at δ 73.81 and δ 73.67 in the (reverse) intensity ratio of $\sim$ 3 : 1. Thus, it appears that the different relative positioning of the six nitro groups at the periphery of the rigid skeleton of centrohexaindane generates slight differences in the effective chemical shifts of the outer carbon nuclei of the neopentane core, which level off for the central carbon. As expected, the ^{13}C NMR spectra of the nonsymmetrical isomers **14** and **17** exhibit definitively more than six lines for the quaternary and tertiary arene carbons. In accordance with the lack of symmetry in these cases, the four nonequivalent outer bridgehead carbon atoms (C^α) of **14** and **17** are clearly distinguishable by four distinct lines in a narrow range of δ 73.68–73.85 and δ 73.63–74.14, respectively. The minute differences of the chemical shifts appear to be due, in a systematic way, to the different combinations of the nitro substituents oriented *meta* and *para* with respect to the benzylic α-carbon atoms of the neopentane core of the four isomers **14**–**17**. However, a more detailed analysis of this puzzling set of data is clearly beyond the scope of this report.[43] The major message concerns the magnetic effect at the central carbon atom of the four constitutional isomers: The relative orientation of the six 5-nitroindane units comprised in **14**–**17** has no effect on the efficient magnetic

field at the central carbon atom and but gives rise to a combined downfield shift of about $\Delta\delta \approx 3.5$ ppm as compared to the parent hydrocarbon **1**.[1]

On the whole, the finding that the four constitutional isomers **14**–**17** are formed in the "statistical" ratio is reminiscent of the corresponding observation made with the simpler trinitrotribenzotriquinacenes **6** and **7**.[38] As discussed previously,[1] it appears that the π-electron systems of centrohexaindane (**1**) do not interact with each other. In fact, the UV/vis spectra of **14**–**17** do not show any difference in their λ_{max} absorption (274 nm) which, however, was found to be slightly higher in energy as compared to that of 4-nitro-*ortho*-xylene (282 nm).

Conclusion

With its unique Cartesian geometry, the polycyclic framework of centrohexaindane (**1**) should become a valuable core for various kinds of structural, covalent and supramolecular, extensions three-dimensions. As stated earlier, this hydrocarbon is synthetically accessible in only six steps starting from 1,3-indanedione.[1b,8] Besides the directed introduction of functional groups at the molecular periphery by use of suitably pre-functionalised building blocks, functionalisation of the six electronically isolated benzene rings of **1** by electrophilic aromatic substitution is also possible, as demonstrated in this report for the case of *six-fold single nitration* of each of the benzene rings. Whereas such a process gives rise to mixtures of four constitutional isomers, the structure of which can be assigned owing to consistent chemical shift effects in their ^{1}H NMR spectra, further, and possibly twelve-fold ("exhaustive") functionalisation of all twelve outer peripheral positions of centrohexaindane should be achievable in spite of potential solubility problems with such large and massive three-dimensional molecules.

Experimental

General. The syntheses of 4b,8b,12b,12d-tetramethyltribenzotriquinacene (**5**) and centrohexaindane (**1**) have been reported elsewhere. Reagents and solvents were used as purchased without further purification. Gravity chromatography was performed by use of silica gel 0.063–0.2 mm (Macherey & Nagel) and chloroform or a mixture of chloroform and ethyl acetate (1:1 v/v). Thin layer chromatography was carried out with silica gel 60 F254 on alumina foil (Merck). A mixture of chloroform and ethyl acetate was used in varying ratios. The fractions were identified by UV absorption at $\lambda = 254$ nm (minUVIS, Desaga). Preparative HPLC was performed by use of a Merck-Hitachi L-6250 Intelligent pump, a Merck-Hitachi L 7420 UV/vis detector, VP 50/21 pre-column and column containing nucleosil 100-7 (Macherey & Nagel) and cyclohexane/ethyl acetate 3:1 (v/v). ^{1}H NMR and ^{13}C NMR spectra of compounds **6**–**12** were recorded on a Bruker AM 250 spectrometer ([1]H: 250 MHz, [13]C: 62.9 MHz) with DMSO-d$_6$ as the solvent and tetramethylsilane as an internal

standard. The NMR spectra of compounds **14–17** were recorded on a Bruker DRX 500 or a Bruker Avance III 500 spectrometer (^{1}H; 500 MHz, ^{13}C: 125.7 MHz) using the (residual) solvent resonances as references: THF-d$_8$, 3.580 ppm (^{1}H), THF-d$_8$ 67.570 ppm (^{13}C). Electron ionization (EI) mass spectra were recorded with an Autospec X sector-field instrument with EBE geometry (Vacuum Generators, Manchester, UK) at 70 eV electron energy and 8 kV acceleration voltage. Infrared spectra were measured with a Nicolet 380 FT-IR instrument. UV/vis spectra were recorded with a Jasco V-630 spectrophotometer.

Nitration of tetramethyltribenzotriquinacene 5 with nitration acid. Nitration acid (10.4 mL) prepared from concentrated sulfuric acid (98%) and concentrated nitric acid (65%) in a ratio of 3:1 (v/v) was cooled to 0 °C and stirred while tetramethyltribenzotriquinacene **5** (750 mg, 2.2 mmol) was added in small portions. After the addition was completed, the light-yellow suspension was allowed to warm to ambient temperature and stirring was continued for a further 6 h. Then the mixture was cooled to 0 °C and diluted with ice/water; the solid was collected by suction filtration and washed thoroughly with aqueous sodium bicarbonate and then with water. The crude product obtained was subjected to gravity chromatography with silica gel and chloroform/ethyl acetate (25:1 v/v), giving five fractions in total, the first of which consisted of the starting material **5** (126 mg, 17%).

The second fraction (24 mg, 2%) consisted of a mixture of **2,6,10-trinitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene** (**6**, C_3-isomer) and **2,6,11-trinitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene** (**7**, C_1-isomer) and was obtained as a light-yellow solid, mp. > 360 °C.
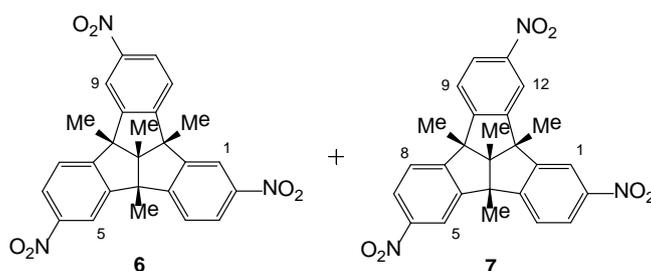
^{1}H NMR (250 MHz, DMSO-d$_6$): δ 8.66 (d, ^4J = 1.8 Hz, 6H, 1-H and 12-H of **7**), 8.50 (d, ^4J = 1.8 Hz, 6H, 1-H, 5-H, 9-H of **6** and 5-H of **7**), 8.07–8.11 (m, 18H, Ar-H), 7.96 (d, ^3J = 8.5 Hz, 6H, 8-H and 9-H of **7**), 1.81, 1.78 and 1.74 (all s, 36H, 4b-, 8b- and 12d-CH$_3$), 1.40 (s, 12H, 12d-CH$_3$); the integral values refer to the actual ratio [**6**] : [**7**] = 1 : 3. MS (EI, 70 eV): m/z (%) 471 (9, M$^{•+}$), 456 (100, [M – CH$_3$]$^+$), 410 (9), 395 (7).

The third fraction (245 mg, 21%) consisted of a mixture of **2,3,6,10-tetranitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene** (**8**, C_1-isomer), **2,3,6,11-trinitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-**

tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**9**, *C$_s$*-isomer), and **2,3,7,10-trinitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene** (**10**, *C$_s$*-isomer), and was obtained as a light-yellow solid, mp. > 360 °C.
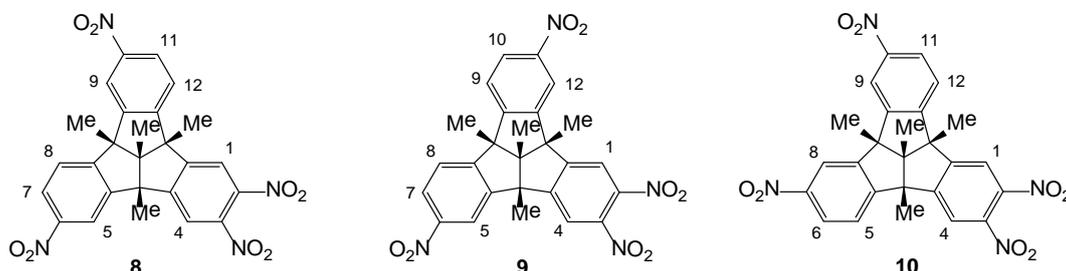
^{1}H NMR (250 MHz, DMSO-d$_6$): δ 8.80 (s, 6H, 4-H of **8** and **9**), 8.70 (d, ^4J = 2.0 Hz, 2H, 5-H of **8**), 8.68 (d, ^4J = 2.1 Hz, 6H, 5-H and 12-H of **9**, 8-H and 9-H of **10**), 8.63 (s, 4H, 1-H of **8**, 1-H and 4-H of **10**), 8.53 (d, ^4J = 2.0 Hz, 2H, 8-H of **8**), 8.07–8.16 (m, 16H, 12-H of **8** and **10**, 7-H and 11-H of **8**, 7-H and 10-H of **9**, 6-H and 11-H of **10**), 7.98 (d, ^3J = 8.6 Hz, 4H, 8-H and 9-H of **19**), 1.82, 1.79 and 1.75 (all s, 45H, 4b-, 8b- and 12d-CH$_3$), 1.40 (s, 15H, 12d-CH$_3$); the integral values refer to the actual ratio [**8**] : [**9**] : [**10**] = 2 : 2 : 1. MS (EI, 70 eV): *m/z* (%) 516 (10, M$^{•+}$), 501 (100, [M – CH$_3$]$^+$), 455 (5), 409 (12).

The fourth fraction (220 mg, 18%) consisted of pure **2,3,6,7,10-pentanitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene** (**11**) and was obtained as light-yellow crystals, mp. > 360 °C.
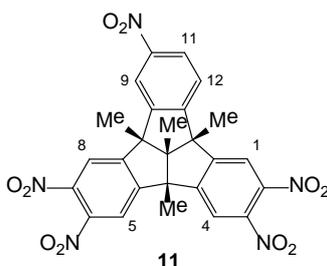
^{1}H NMR (250 MHz, DMSO-d$_6$): δ 8.84 (s, 1H, 8-H), 8.75 (s, 2H, 4- and 5-H), 8.70 (d, ^4J = 2.0 Hz, 1H, 9-H), 8.65 (s, 1H, 1-H), 8.17 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 1H, 11-H), 8.09 (d, ^3J = 8.6 Hz, 1H, 12-H), 1.82 (s, 6H, 4b- and 8b-CH$_3$), 1.79 (s, 3H, 12b-CH$_3$), 1.41 (s, 3H, 12d-CH$_3$). ^{13}C NMR (62 MHz, acetone-d$_6$): δ 155.1 (C), 154.8 (C), 154.7 (C), 153.6 (C), 153.4 (C), 150.2 (C), 149.6 (C), 144.8 (C), 144.7 (C), 144.5 (C), 144.4 (C), 125.8 (CH), 125.3 (CH), 122.16 (CH), 122.10 (CH), 121.92 (CH), 121.81 (CH), 120.0 (CH), 72.8 (C, C^{centro}), 64.73 (C), 64.55 (C), 64.50 (C), 25.14 (CH$_3$), 25.07 (CH$_3$), 24.88 (CH$_3$), 16.0 (12d-CH$_3$). MS (EI, 70 eV): *m/z* (%) 561 (11, M$^{•+}$), 546 (100, [M – CH$_3$]$^+$), 454 (12), 362 (7).

The fifth fraction (13 mg, 1%) consisted of **1,3,6,7,10,11-hexanitro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene** (**12**) and was obtained as light-yellow crystals, mp. > 360 °C.

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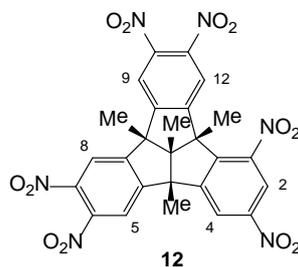
^{1}H NMR (250 MHz, DMSO-d$_6$): δ 8.99 (d, ^4J = 2.1 Hz, 1H, 2-H), 8.89 (s, 1H, Ar-H), 8.78 (s, 1H, Ar-H), 8.74 (s, 1H, Ar-H), 8.64 (d, ^4J = 1.9 Hz, 1H, 4-H), 8.06 (s, 1H, 12-H), 1.88 (s, 3H, CH$_3$), 1.80 (s, 3H, CH$_3$), 1.77 (s, 3H, CH$_3$), 1.41 (s, 3H, 12d-CH$_3$). MS (EI, 70 eV): m/z (%) 606 (5, M$^{•+}$), 591 (100, [M − CH$_3$]$^+$).

Nitration of centrohexaindane with sodium nitrate/trifluoroacetic acid. A solution of centrohexaindane (**1**, 220 mg, 426 μmol) in trifluoroacetic acid (30 mL) was stirred while sodium nitrate (680 mg, 8.00 mmol) was added. The mixture was stirred and heated to 55 °C for 24 h. Progress of the reaction was monitored by TLC (silica gel, CHCl$_3$). Further trifluoroacetic acid (10 mL) and sodium nitrate (400 mg, 6.00 mmol) was added and the mixture was stirred at 55 °C Stirring was continued for a further 6 d. The mixture was allowed to cool to ambient temperature and then poured into water (100 mL) and solid sodium hydroxide was added until the pH 13 was reached. The mixture obtained was extracted with chloroform (4 × 30 mL), the combined extracts were dried with sodium sulfate and the solvent was removed under reduced pressure. The crude mixture of hexanitrocentrohexaindanes **13**−**16** (320 mg, ~ 96%) was obtained as a light-yellow solid. This mixture was subjected to chromatography (HPLC, Nucleosil 100-7, *c*-C$_6$H$_{12}$/EtOAc 3:1) and yielded four fractions (**I**–**IV**), each of which contained one of the four constitutional isomers **13**–**16**, eluting in this order. The isomers were obtained as solids that were recrystallised from tetrahydrofuran.

2,6,10,14,21,26-Hexanitro-4b,12b[1',2']:8b,16b[1'',2'']dibenzenodibenzeno[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (2,6,10,14,21,26-Hexanitrocentrohexaindane 14).

14 (C_1, *rac*)
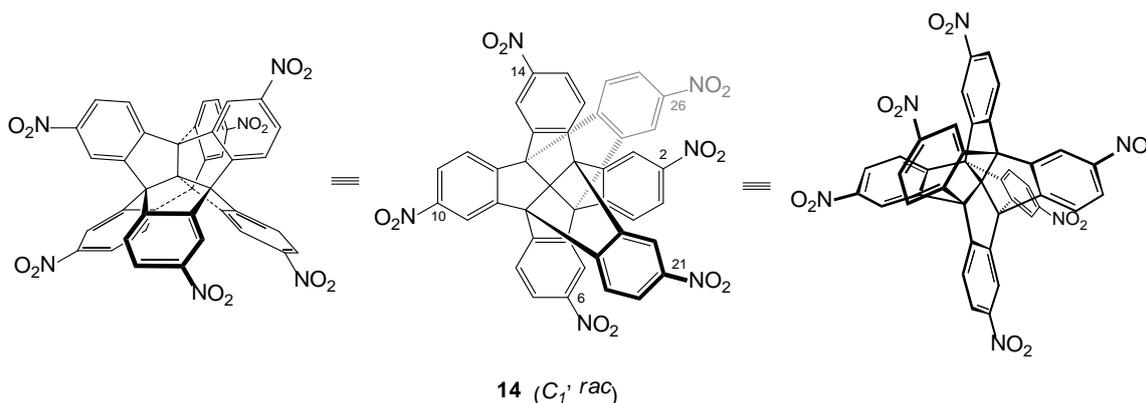
This compound was obtained as the first-eluting isomer as a light-yellow solid (98.6 mg, 29.4%). After recrystallisation from THF, a crystalline solid was formed, m.p. > 410 °C. ^{1}H NMR (500 MHz, THF-d$_8$): δ 9.03–9.07 (m, 4H, Ar-H), 8.937 (d, 1H, ^4J = 2.0 Hz, Ar-H), 8.926 (d, 1H, ^4J = 2.1 Hz, Ar-H), 8.757 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.754 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.55 (d of m, $^3J \approx$ 8.5 Hz, 4H, Ar-H), 8.35 (overlapping d, $^3J \approx$ 8.6 Hz, 6H, Ar-H). ^{13}C NMR (125.7 MHz, THF-d$_8$): δ 153.34 (C), 153.22 (C), 153.16 (C), 153.06 (C), 153.03 (C), 151.29 (C), 151.27 (C), 151.15 (C), 151.13 (C), 148.44 (C), 148.42 (C), 148.32 (C), 148.27 (C), 148.17 (C), 127.36 (CH), 127.29 (CH), 127.08 (CH), 127.01 (CH), 126.66 (CH), 121.17 (CH), 121.09 (CH), 121.01 (CH), 120.92 (CH), 98.74 (C^{centro}), 73.85 (C), 73.80 (C), 73.73 (C), 73.68 (C). MS [(−)-ESI, MeCN, LiCl]: m/z (%) 821 (100, [M + ^{35}Cl]$^−$), 822 (38, [^{13}C$_1$-M + ^{35}Cl]$^−$), 823 (37, [M + ^{37}Cl]$^−$), 824 (16, [^{13}C$_1$-M + ^{37}Cl]$^−$). IR IR (neat): $\tilde{\nu}$ = 3066, 2954, 2916, 2870, 1766, 1708, 1587, 1522, 1468, 1430, 1344, 1281, 1259, 1230, 1215, 1154, 1119, 1084, 1064, 1033, 900, 887, 860, 833, 804, 775, 766, 744, 680, 640, 620, 576, 530 cm^{-1}. UV/vis (MeCN, c = 1 · 10^{-5} M): λ$_{max}$ = 274 nm (ε ≈ 32000). – The ^{1}H NMR spectrum of **14** indicated the presence of isomer **15** in minor amounts (~ 10%), which could no be removed even by repeated recrystallisation.

2,6,10,15,21,27-Hexanitro-4b,12b[1',2']:8b,16b[1'',2'']dibenzenodibenzeno[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (2,6,10,15,21,27-Hexanitrocentrohexaindane 15).

15 (*C*$_3$, *rac*)
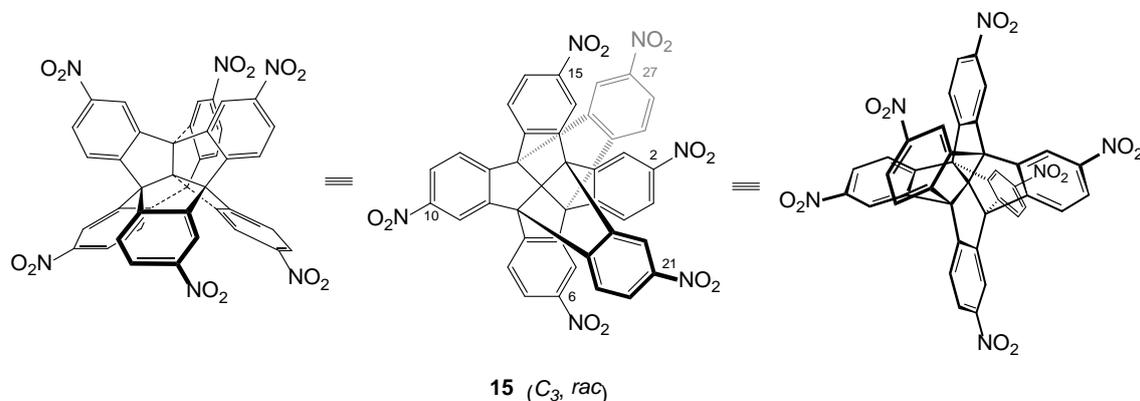
This compound was obtained as the second-eluting isomer as a light-yellow solid (28.1 mg, 8.4%). After recrystallisation from THF, isomer **15** was obtained as an off-white powder, m.p. > 410 °C. ^{1}H NMR (500 MHz, THF-d$_8$): δ 9.17 (d, ^4J = 2.1 Hz, 3H, Ar-H), 8.93 (d, ^4J = 2.0 Hz, 3H, Ar-H), 8.555 (d, ^3J = 8.6 Hz, 3H, Ar-H), 8.546 (d, ^3J = 8.6 Hz, 3H, Ar-H), 8.351 (dd, ^3J = 8.6 Hz, ^4J = 2.1 Hz, 3H, Ar-H), 8.341 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 3H, Ar-H). ^{13}C NMR (125.7 MHz, THF-d$_8$): δ 153.19 (C), 152.89 (C), 151.50 (C), 151.15 (C), 148.55 (C), 148.32 (C), 127.05 (CH), 126.89 (CH), 126.68 (CH), 126.65 (CH), 121.43 (CH), 120.97 (CH), 98.74 (C^{centro}), 74.15 (1 C), 73.67 (3 C). MS [(−)-ESI, MeCN, LiCl]: m/z (%) 821 (100, [M + ^{35}Cl]$^−$), 822 (42, [^{13}C$_1$-M + ^{35}Cl]$^−$), 823 (41, [M + ^{37}Cl]$^−$), 824 (16, [^{13}C$_1$-M + ^{37}Cl]$^−$). IR (neat): $\tilde{\nu}$ = 3077, 2951, 2915, 2867, 1771, 1716, 1586, 1521, 1468, 1430, 1340, 1280, 1260, 1230, 1192, 1153, 1110, 1080, 1064, 1033, 963, 899, 861, 830, 807, 764, 744, 732, 679, 664,

638, 576, 554, 541, 523 cm^{-1}. UV/vis (MeCN, c = 1 · 10^{-5} M): λ_{max} = 274 nm ($\varepsilon \approx$ 30000).

2,6,10,15,20,26-Hexanitro-4b,12b[1',2']:8b,16b[1'',2'']dibenzenodibenzeno[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (2,6,10,15,20,26-Hexanitrocentrohexaindane 16).

16 (C_3, *rac*)
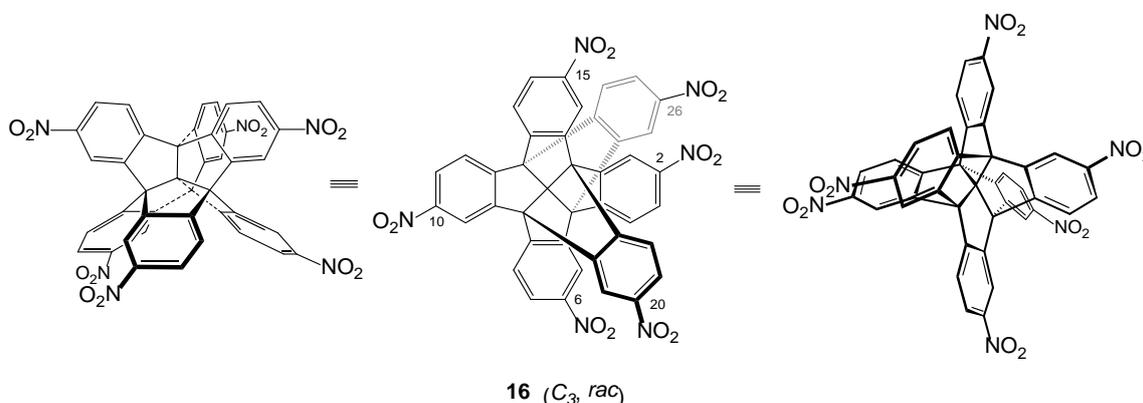
This compound was obtained as the third-eluting isomer as a light-yellow solid (34.0 mg, 10.1%). After recrystallisation from THF, isomer **16** was obtained as an off-white powder, m.p. > 410 °C. ^{1}H NMR (500 MHz, THF-d$_8$): δ 9.052 (d, ^4J = 2.0 Hz, 3H, Ar-H), 9.037 (d, ^4J = 2.0 Hz, 3H, Ar-H), 8.75 (d, ^3J = 8.6 Hz, 3H, Ar-H), 8.41 (d, ^3J = 8.6 Hz, 3H, Ar-H), 8.378 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 3H, Ar-H), 8.339 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 3H, Ar-H). ^{13}C NMR (125.7 MHz, THF-d$_8$): δ 153.22 (C), 152.91 (C), 151.30 (C), 151.27 (C), 148.53 (C), 148.30 (C), 127.28 (CH), 126.89 (CH), 126.66 (CH), 126.58 (CH), 121.22 (CH), 121.08 (CH), 98.73 (C^{centro}), 73.81 (3 C), 73.67 (1 C). MS [(−)-ESI, MeCN, LiCl]: m/z (%) 821 (100, [M + ^{35}Cl]$^-$), 822 (37, [^{13}C$_1$-M + ^{35}Cl]$^-$), 823 (41, [M + ^{37}Cl]$^-$), 824 (16, [^{13}C$_1$-M + ^{37}Cl]$^-$). IR (neat): $\tilde{v}$ = 3085, 3070, 2958, 2873, 1762, 1714, 1589, 1522, 1468, 1431, 1343, 1281, 1260, 1225, 1184, 1154, 1112, 1062, 1034, 991, 960, 923, 865, 853, 836, 804, 769, 756, 742, 733, 679, 635, 555, 541, 523 cm^{-1}. UV/vis (MeCN, c = 1 · 10^{-5} M): λ_{max} = 274 nm ($\varepsilon \approx$ 39000).

2,6,11,14,21,27-Hexanitro-4b,12b[1',2']:8b,16b[1'',2'']dibenzenodibenzeno[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (2,6,11,14,21,27-Hexanitrocentrohexaindane 17).

17 (C_1, *rac*)
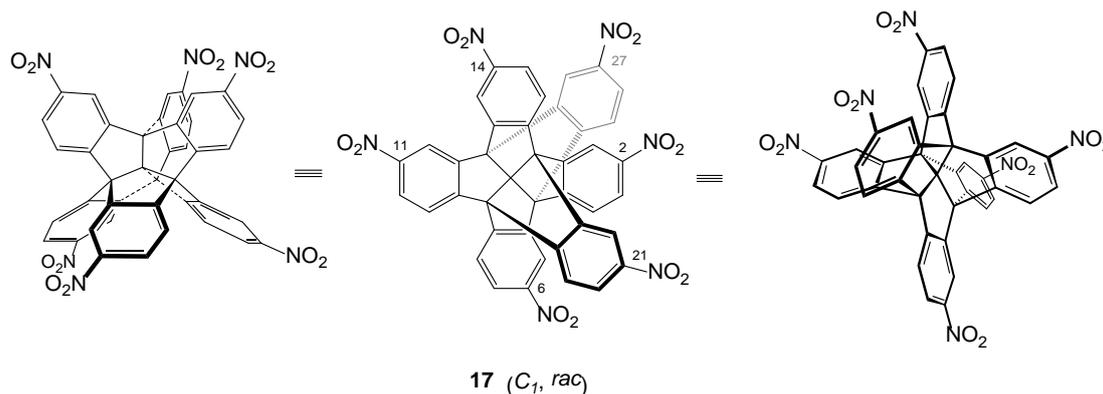
This compound was obtained as the last-eluting isomer as a light-yellow solid (99.9 mg, 29.8%). After recrystallisation from THF, isomer **17** was obtained as an off-white powder, m.p. > 410 °C. ^{1}H NMR (500 MHz, THF-d_8): δ 9.177 (d, $^4J \approx$ 2.0 Hz, 1H, Ar-H), 9.171 (d, $^4J \approx$ 2.3 Hz, 1H, Ar-H), 9.164 (d, ^4J = 2.2 Hz, 1H, Ar-H), 9.052 (d, $^4J \approx$ 2.2 Hz, 1H, Ar-H), 9.046 (d, ^4J = 2.2 Hz, 1H, Ar-H), 8.94 (d, ^4J = 2.0 Hz, 1H, Ar-H), 8.75 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.551 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.547 (d, ^3J = 8.5 Hz, 1H, Ar-H), 8.413 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.406 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.403 (d, ^3J = 8.6 Hz, 1H, Ar-H), 8.32–8.36 (m, 6H, Ar-H). ^{13}C NMR (125.7 MHz, THF-d_8): δ 153.08 (C), 153.06 (C), 153.04 (C), 152.92 (C), 151.48 (C), 151.30 (C), 151.28 (C), 151.16 (C), 148.56 (C), 148.54 (C), 148.44 (C), 148.40 (C), 127.20 (CH), 127.00 (CH), 126.95 (CH), 126.93 (CH), 126.88 (CH), 126.82 (CH), 126.67 (CH), 126.64 (CH), 125.60 (CH), 126.58 (CH), 121.46 (CH), 121.40 (CH), 121.33 (CH), 121.20 (CH), 121.15 (CH), 121.04 (CH), 98.72 (C^{centro}), 74.14 (C), 73.74 (C), 73.67 (C), 73.63 (C). MS [(−)-ESI, MeCN, LiCl]: m/z (%) 821 (100, [M + ^{35}Cl]$^-$), 822 (40, [$^{13}C_1$-M + ^{35}Cl]$^-$), 823 (42, [M + ^{37}Cl]$^-$), 824 (16, [$^{13}C_1$-M + ^{37}Cl]$^-$). IR (neat): $\tilde{\nu}$ = 3098, 3070, 2955, 2874, 1762, 1721, 1589, 1527, 1460, 1432, 1345, 1281, 1252, 1233, 1186, 1159, 1120, 1061, 1034, 992, 959, 923, 860, 835, 806, 765, 756, 743, 733, 679, 636, 560 cm^{-1}. UV/vis (MeCN, c = 1 · 10^{-5} M): λ$_{max}$ = 274 nm (ε ≈ 27000).

X-ray single crystal structure analysis of centrohexaindane (1 · CHCl$_3$). A single crystal of C$_{42}$H$_{25}$Cl$_3$ was selected and kept at 100.0(3) K during data collection with Cu-Kα radiation (λ = 1.54178 Å) on a SuperNova diffractometer. Using Olex2,[44] the structure was solved and refined by use of ShelX-97.[45] **Crystal Data:** C$_{42}$H$_{25}$Cl$_3$, M = 635.97, triclinic, a = 8.51239(19) Å, b = 12.4653(2) Å, c = 14.2625(2) Å, α = 91.3139(14) °, β = 93.6817(15) °, γ = 101.2353(17) °, V = 1480.35(5) Å^3, T = 100.0(3), space group P (no. 2), Z = 2, μ(Cu K$_α$) = 3.041, 25642 reflections measured, 5821 unique (R_{int} = 0.0222) which were used in all calculations. The final wR_2 was 0.0933 for all data and R_1 was 0.0353 for 5584 reflections with $I > 2σ (I)$. CCDC 1436522 contains supplementary crystallographic data for this paper (1 · CHCl$_3$). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. In addition, CCDC 1436523 and CCDC 1436470, respectively, contain the crystallographic data for 1 · 0.5 p-xylene and 1 · triethylamine.

Supporting Information: ^{1}H NMR spectra (250 MHz) and EI (70 eV) mass spectra of the mixtures of compounds **6** and **7** and compounds **8**–**10**, and of compounds **11** and **12**; ^{1}H NMR spectra (500 MHz), ^{13}C NMR spectra (126 MHz), ^{1}H,^{1}H-COSY spectra; (−)-ESI mass spectra of compounds **14**–**17**; and illustrations of the space-filling structures of **1** and with a co-crystallsed solvent molecule as well as of the molecular packing in the crystals of **1** · CHCl$_3$, **1** · 0.5 p-xylene and **1** · triethylamine.

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