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Synthesis and structural characterization of non-planar perfluoro phthalonitriles

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Abstract

Perfluoropropene reacts with 1,2-dicyano-3,4,5,6-tetrafluorobenzene to give the first perfluoroalkyl substituted phthalonitriles. The X-ray structures of the bis- and tris-substituted products reveal planar, undistorted rings and head-to-head and head-to-tail preferred conformations for the isopropyl substituents, respectively. As a result, the CF_3 groups impart global non-planar character to the new molecules.

Keywords: Perfluoro phthalonitriles; Dinitriles

1. Introduction

Phthalonitriles are known precursors to phthalocyanines, an important class of molecules with wide applications [1] ranging from catalysis to solid state materials. While many phthalonitriles are known, among the perfluorinated ones only the parent, 1,2-dicyano-3,4,5,6-tetrafluorobenzene (**1**, TFP) is known [2] despite the fact that 'isogeometric' [3,4] replacement of C–H by strong, 107 kcal/mol, C–F bonds is expected to impart enhanced thermal stability, lipophilicity and chemical inertness.

Among perfluorinated phthalonitriles, those bearing branched substituents are expected to yield non-planar phthalonitriles and phthalocyanines exhibiting useful physical properties such as enhanced solubility and steric hindrance. The preparation and molecular level characterization of the first examples of substituted perfluorinated phthalonitriles is the subject of this paper.

2. Discussion

Techniques for efficient and facile synthesis of perfluoroalkylated aromatic molecules, including aromatic heterocycles, are rapidly evolving. Current methods for the introduction of perfluoroalkyl groups onto aromatic molecules include: addition of perfluoroalkyl radicals [5], aromatization of a perfluoroalkylated molecule [6], displacement of fluoride at highly electron deficient carbon atoms by nucleophilic perfluorocarbanions [7–9], electrophilic perfluoroalkylation by FITS (perfluoroalkylphenyliodonium trifluoromethanesulfonates) reagent [10] and reactions of perfluoroalkyl metallic reagents [11]. Conventional nucleophilic substitution of halides by nucleophiles on perfluoroalkyliodides does not take place. Perfluoroalkyliodides are generally attacked by nucleophiles at the iodine atom instead of the carbon atom because of reverse polarization caused by the inductive effect of the highly electronegative perfluoroalkyl group [12].

Chambers et al. [7,8,13] and Haszeldine et al. [9] have investigated the production of substituted fluorinated aromatics by using perfluoroalkyl anions obtained by the reaction of perfluoroalkenes with fluoride anion. For example, the reaction of fluorinated aromatic rings bearing a single CN substituent (perfluorobenzonitrile) with perfluoropropene (PFP) at 125°C gave a 30% yield of perfluoro-(4-isopropylbenzene) but loss of CN was also noted [14]. Using the CsF generated perfluoroisopropyl carbanion [13] results in the formation of 2,4 and 2,4,6 substituted nitriles without loss of CN groups [15]. Interestingly, the trisubstituted derivative

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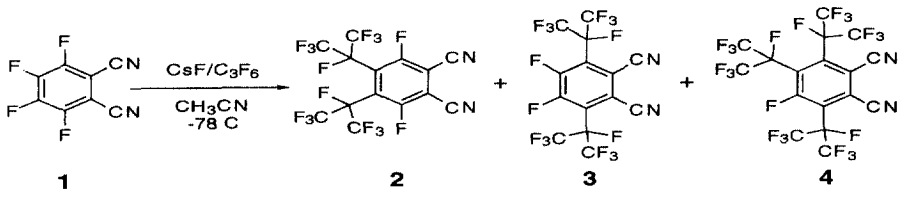
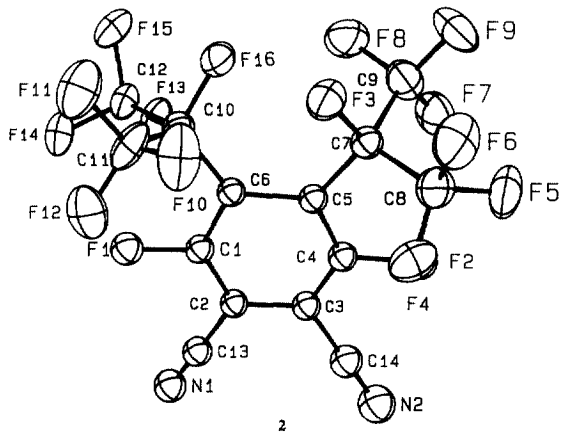


Scheme 1.

accounts for the majority of the PFP even at low 1:1 propene/nitrile ratios. Higher ratios lead to increased yields of both trisubstituted derivatives and PFP oligomers, thus suggesting activation of aromatic F by PFP substituents, presumably via stabilization of aromatic carbanions intermediates [15]. Aromatic rings bearing two CN groups, viz. TFP, have also been found to react with nucleophiles [16].

We have investigated the reaction of PFP with TFP and found that a series of products with varying degrees of substitution are readily obtained (Scheme 1, above).

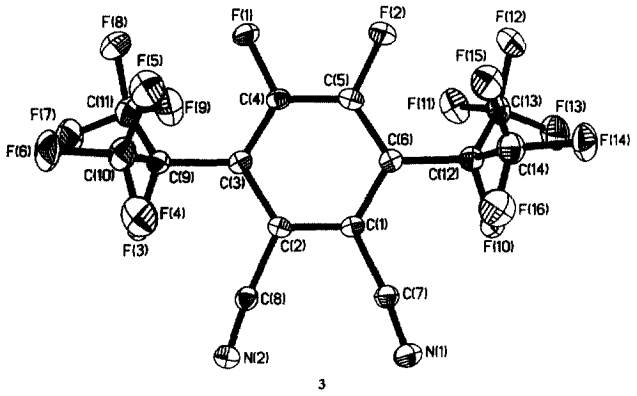
Of the four possible disubstituted isomers only perfluoro-(4,5-di-isopropyl phthalonitrile), **2**, (43% yield) and perfluoro-(3,6-di-isopropyl phthalonitrile), **3**, (6% yield) have been observed. Only one tris-substituted isomer, **4**, has been isolated (20% yield). Unlike the benzonitrile case [15], trisubstituted derivatives are not the major product. Attempts to increase their yield by using excess PFP and extended reaction times leads to several adducts with the same molecular weight as the tetra-perfluoroisopropyl phthalonitrile but possessing at least one aromatic fluorine. These products are the result of nucleophilic aromatic substitutions by dimer and trimer anions resulting from the reaction of the perfluoroisopropyl anion with PFP or, alternatively, attack by PFP on substituted nitriles. Oligomeric anions as well as PFP polymers have been observed previously [15]. No mono- or tetra-substituted derivatives have been isolated. The former observation confirms that partial aromatic substitution by a perfluoroalkyl group enhances the susceptibility of the remaining fluorines to nucleophilic attack while the latter suggests that steric crowding might be an efficient counterbalancing factor which lowers the yield of trisubstituted products and prevents the introduction of a fourth substituent. Furthermore, the 3,4- and 3,5-disubstituted products are not observed either, consistent with *ortho* and *para* aromatic F activation in the 3- and 4-monosubstituted intermediates. Specifically, a second *i*-C_3F_7 group, *ortho* with respect to the first one, results in the formation of either the 3,4-product or **2**. The formation of the latter suggests a preference for substitution adjacent to an aromatic fluorine over a nitrile, perhaps for steric reasons. Indeed, the presence of two *i*-C_3F_7 groups *ortho* to a CN is believed to force the latter out of the aromatic plane [14]. Even one *i*-C_3F_7 next to a CN is expected either to have a similar (but smaller) effect or, at least, tilt the CN group. The presence of adjacent CN and *i*-C_3F_7 substituents in **3** and **4** prompted us to seek X-ray structural information for the elucidation of the relationship between steric crowding and conformational isomers. The structures[1,2,3] of **2**, **3** and **4** are shown in the figure, below:



[1] **2**: a 0.66×0.53×0.33 mm colorless crystal obtained by vacuum sublimation was examined using MoK_α radiation ($\theta<22°$) on a CAD-4 diffractometer. Relevant data: monoclinic, $P2_1/c$, $a=15.555(2)$, $b=12.361(1)$, $c=9.167(2)$ Å, $\beta=96.64(1)°$; $V=1750.9(8)$ Å^3, $R_1=0.08$, $R_w=0.11$ for 2136 unique reflections of which 1339 had $I>2\sigma(I)$; 229 variable parameters were used for the anisotropic refinement. All calculations were performed using the MolEN (Enraf–Nonius) package. Additional information can be found in Section 4.

[2] **3**: a 0.5×0.5×0.4 mm colorless crystal obtained by evaporation from diethyl ether was examined using MoK_α radiation ($\theta<24.71°$) on a Siemens P4 diffractometer. Relevant data: monoclinic, $P2_1/n$, $a=13.16(1)$, $b=21.892(1)$, $c=18.254(1)$ Å, $\beta=103.061(1)°$; $V=5125.1(3)$ Å^3, $R_1=0.076$, $R_w=0.20$ for 8626 unique reflections of which 8621 had $I>2\sigma(I)$; 865 variable parameters were used for the anisotropic refinement. All calculations were performed using the SHELXTL (Siemens) package. Additional information can be found in Section 4.

[3] **4**: a 0.5×0.5×0.4 mm colorless crystal obtained by evaporation from diethyl ether was examined using MoK_α radiation ($\theta<23.4°$) on a Siemens P4 diffractometer. Relevant data: preliminary structure at −60°C, tetragonal, $I4_1/a$, $a=28.6953(3)$, $c=10.5091(2)$ Å; $V=8653.4(2)$ Å^3. $R_1=0.22$, due to disordered isopropyl fluorines, for 3089 unique reflections with $I>2\sigma(I)$. While the bond distances and angles are reasonable, only the molecular connectivity and general conformations are reported at this stage. All calculations were performed using the SHELXTL (Siemens) package. Additional information can be found in Section 4.



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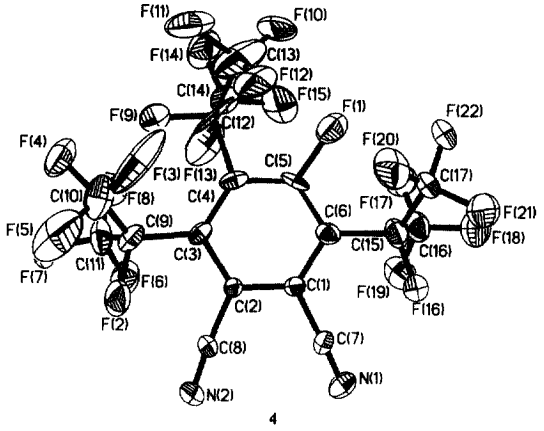

4

A comparison of **2** and **3** reveals that i-C_3F_7 groups adopt the minimum energy conformation, with the tertiary fluorines in **2** located approximately in the plane of the aromatic rings. This 'head-to-head' conformation (F and CF_3 viewed as 'head' and 'tails', respectively) forces both CF_3 groups above and below the aromatic ring thus maximizing the distance of the bulky CF_3 groups from the phthalonitrile plane. For both **2** and **3**, modeling studies suggest that this conformation is favored by a minimum in the CF_3–CF_3 and CN–CF_3 repulsions, respectively.

The CN groups in **2** and **3** could exhibit both out-of-plane and in-plane distortions. As far as the out-of-plane distortions are concerned, the two hindered N's in **3** are less than 0.2 Å away from the aromatic plane, i.e., they are virtually coplanar with the aromatic ring. In order to estimate the in-plane distortions we define 'intra-CN' distortion angles: C(8)–C(2)–C(1) and C(2)–C(1)–C(7) angles in **3**, and C(13)–C(12)–C(3) and C(2)–C(3)–C(14) angles in **2**. Their variation should reflect the steric influences of i-C_3F_7 groups. Such influences, while more significant then their out-of-plane counterparts, are still small, viz. the average 'intra-CN' angle decreases from 121.5° in **2** to 115.9° in **3**. For comparison, the 'intra' angle in **1** is 120 ± 1° [2].

The preliminary structure of **4** reveals the same conformational trends for both i-C_3F_7 which are adjacent to CN groups, despite the presence of an additional i-C_3F_7 on C(5). The currently unresolved disorder of fluorines in **4** precludes a detailed discussion on the relative steric demands of C(2) cyano and C(3), C(4) i-C_3F_7 groups. Nevertheless, the formation of a tetrasubstituted phthalonitrile seems to be sterically impeded, in accord with the experimental observations.

Head-to-head conformations are also expected to occur in other phthalonitriles with *iso*-substituted fluoroalkanes, since carbon chain homologation results in tail expansion above and/or below the aromatic ring. Other members of the non-planar fluoronitrile class could be constructed this way.

The influence of perfluorosubstituents upon the reactivity of CN groups in non-planar phthalonitriles is currently being explored.

3. Experimental

All chemical reactions have been carried out under a nitrogen atmosphere. Solvents have been dried using conventional methods except for the solvents used for extraction and chromatography which were not purified. Anhydrous CsF, PFP and TFP (Aldrich) have been used without purification. Melting points were not corrected. NMR spectra have been recorded on Bruker 250 and 400 MHz instruments. FAB mass spectra have been obtained in *m*-nitrobenzyl alcohol (NBA)/NaI matrices using a Kratos MS80 spectrometer.

A Fischer–Porter bottle, containing 0.464 g (2.32 mmol) of TFP, 0.103 g (0.69 mmol) of anhydrous CsF and 30 ml of dry acetonitrile was cooled to −78°C. Approximately 2.5 g (16.7 mmol) of hexafluoropropene was condensed and the bottle was sealed. The cooling bath was removed and the reaction was allowed to warm to room temperature. After stirring for 45 min at room temperature the reaction was vented to release unreacted hexafluoropropene, and quenched by addition to 100 ml of brine. The mixture was extracted with ethyl acetate and flash chromatographed on 40 μm silica gel using toluene/hexanes (1:5) to give 0.50 g (43%) of **2**, 0.49 g (43%) of **4**, and finally 0.07 g (6%) of **3** (order of elution).

2: mp 101–101.5°C, ^{19}F NMR (d_6-acetone, $CFCl_3$ std, J in Hz) d: −71.1 (dt, J=32.2, 6.4), −93.7 (md, J=6.4), −165.43 (m). ^{13}C NMR (d_6-acetone) d: 158.6, 123.7, 120.5, 112.8, 109.0, 94.1. MS: 523 (**2**+Na^+), 500 (**2**), 431 (**2**-CF_3).

3: mp 122.5–123°C, ^{19}F NMR (d_6-acetone, $CFCl_3$ std, J in Hz) d −73.2 (dd, J=22.5, 6.4), −114.3 (m), −171.1 (m). ^{13}C NMR (d_6-acetone) d: 152.3, 123.5, 120.1, 118.1, 112.2, 92.0. MS: 676 (**3**+NBA+Na^+), 523 (**3**+Na^+).

4: mp 89.5–90°C, ^{19}F NMR (d_6-acetone, $CFCl_3$ std, J in Hz) d −68.0 (d, J=54.6), −71.7 (d, J=32.1), −73.2 (dd, J=25.7, 6.4), −138.6 (s), −170.3 (m), −171.6 (m, J=51.4–54.6). ^{13}C NMR (d_6-acetone) d: 158.7, 138.3, 127.5, 124.0, 123.9, 123.1, 120.8, 120.6, 120.5, 113.5, 112.6, 96.6, 95.6, 92.7. MS: 826 (**4**+NBA+Na^+), 673 (**4**+Na^+).

4. Supplementary material

Computational details and list of atomic coordinates and their estimated standard deviations for compounds **2**, **3** and **4**.

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