Synthesis and Reactivity of a Novel, Dimeric Derivative of Octafluoro[2.2]paracyclophane. A New Source of Trifluoromethyl Radicals

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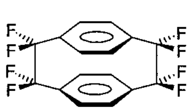
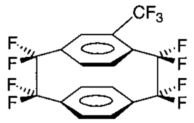
Abstract: Novel radical addition chemistry, involving addition of $CF_3^{\bullet}$ radicals to octafluoro[2.2]paracyclophane (AF4), leads to formation of an unprecedented new class of dimeric CF_3-substituted AF4 derivatives. These chemically stable, but highly sterically constrained compounds undergo a clean thermal homolytic retro process to form monomeric CF_3-substituted radicals. These radicals can be trapped by atom-transfer agents such as 1,4-cyclohexadiene or I_2, but in the absence of such agents, they undergo further homolysis to form trifluoromethyl radicals in a process that is amenable to their use as free-radical initiators, as was shown by a study of the polymerization of vinylidene fluoride.

The unique chemical characteristics of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (AF4) have been amply demonstrated by a number of recent publications related to its synthesis,[1−3] its chemical reactivity,[4,5] and its role as the CVD precursor of the highly thermally stable, low-dielectric thin-film polymer known as parylene-HT.[6−8]


AF4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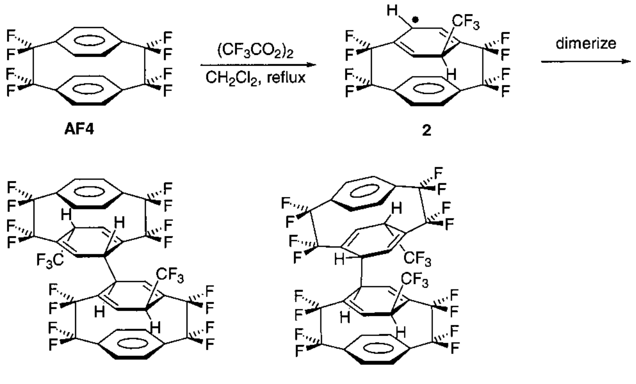
Because ring-substituted derivatives of AF4 have the potential to produce parylene films with enhanced properties, efforts have been directed at the synthesis of compounds such as trifluoromethyl derivative **1**. Although **1** has been prepared by a traditional four-step synthetic sequence beginning with nitration of AF4,[4] a more direct method based on Sawada's free-radical trifluoromethylation methodology appeared potentially attractive.[9]

However, when trifluoroacetyl peroxide was allowed to decompose in the presence of AF4 in refluxing CH_2Cl_2, although the trifluoromethyl radical indeed added to one of the aromatic rings of AF4, no rearomatization to **1** was observed. Instead, the intermediate cyclohexadienyl radical **2** proved to be uncommonly stable, so stable that it survived sufficiently long to dimerize to a 57:43 mixture of the novel and structurally unprecedented diasteromeric products, *d,l*- and *meso*-**3**, in a total yield of 60%.[10]



Not surprisingly, the new C−C bond in **3,** which was formed as a result of joining the two radical fragments, proved to be quite weak, with both isomers undergoing homolysis to regenerate radical **2** at temperatures above 150 °C. Thus, when a 4×10^{-4} M solution of pure *d,l*-**3** in acetonitrile was heated to 170 °C in the presence of 1.8 M 1,4-cyclohexadiene, radical **2** was trapped quantitatively by H-transfer to form dihydro product **4**, with no concomitant isomerization to *meso*-**3** being observed. In contrast, when *d,l*-**3** was similarly heated in the presence of 0.65 M I_2, isomerization to *meso*-**3** was observed to be competitive with trapping of **2** by I_2 to form a nondetected, but presumed intermediate product, **5**, which rapidly loses HI to

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(1) Dolbier, W. R.; Asghar, M. A.; Pan, H. Q.; Celewicz, L. *J. Org. Chem.* **1993**, *58*, 1827−1830.

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(5) Roche, A. J.; Dolbier, W. R., Jr. *J. Org. Chem.* **2000**, *65*, 5282−5290.

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(10) Although similar reactions to form analogous dimers are observed for other fluorinated diacyl peroxides, including $(C_2F_5CO_2)_2$ and $(C_7F_{15}CO_2)_2$, such dimers were not observed to be formed in the reactions of either AF4 with hydrocarbon diacyl peroxides or hydrocarbon [2.2]-paracyclophane with fluorinated diacyl peroxides.

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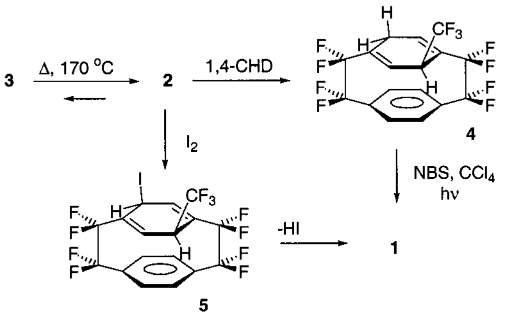


produce the rearomatized CF_3-substituted AF4 derivative, **1**. Such results indicate clearly that homolysis of **3** occurs, with recombination being competitive with atom transfer.

Since the thermolysis of **3** in the presence of 1,4-CHD appeared to involve rate-determining homolysis of **3** to form two radicals, **2**, the kinetics for this process for the two diastereomers of **3** were studied, with rates being determined at five temperatures for each, and the activation parameters for both isomers calculated and given in Table 1. The weak C−C bonds represented by these E_a's derive from a combination of delocalization and B-stain effects, and they are consistent with their long bond lengths (1.583 Å for *meso*-**3**).

Notably, both isomers of **3** were found to be highly resistant to oxidative or dehydrogenative aromatization procedures (DDQ, Pd/C, or *t*-BuOOH) to what would have been a novel bis[2.2]-paracyclophane, with neither electron transfer nor H-atom transfer from **3** proving productive, the former because of **3**'s electron deficiency, and the latter because of the steric inaccessibility of either of the two H-atoms that must be removed. Even treatment with *N*-bromosuccinimide (CCl_4, reflux, $h\nu$) left **3** untouched. (In contrast, similar treatment of dihydro product **4** with NBS led to its smooth, quantitative conversion to **1**.)

Unexpectedly, when simply heated to 170 °C in the absence of a suitable atom-transfer agent, both *d,l*- and *meso*-**3** underwent quantitative reversion to two molecules of AF4, along with presumed expulsion of two $CF_3^\bullet$ radicals! Evidence that this process did indeed involve the generation of free $CF_3^\bullet$ radicals was obtained by carrying out the thermolysis in benzene solution, with the result that trifluoromethylbenzene was formed, much as was observed by Sawada in his study of the reaction of $(CF_3CO_2)_2$ with benzene.[9]

Clean sources of $CF_3^\bullet$ radicals are quite rare. The remarkable "persistent" radical, $CF_3CF_2(i\text{-}C_3F_7)_2C^\bullet$, known as Scherer's radical, is such a source.[11] It is known to slowly and cleanly fragment to generate $CF_3^\bullet$ radicals at 100 °C. Probably the most commonly used source of $CF_3^\bullet$ radicals, as mentioned above, is $(CF_3CO_2)_2$, but it is a potentially hazardous, thermally unstable precursor that decomposes slowly at room temperature (half-life 6 h at 50 °C).[9,12] In contrast, *meso*- and *d,l*-**3** are crystalline compounds, stable indefinitely at room temperature, but remarkably capable of safely and quantitatively[13,14] generating $CF_3\bullet$ radicals at temperatures of >150 °C, with the only side product being the effectively inert AF4. Among other possible applications, *meso*- and *d,l*-**3** appear to have potential utility as high-temperature, free-radical initiators of polymerization.

Table 1. Activation Parameters for Homolysis of *meso*- and *d,l*-**3**.

compound	log *A*	$E_a{}^a$	$\Delta H^{\ddagger a,b}$	$\Delta S^{\ddagger b,c}$	$\Delta G^{\ddagger a,b}$
meso-**3**	17.3 ± 0.8	42.8 ± 1.9	41.9	18	34.7
d,l-**3**	18.2 ± 1.3	44.8 ± 3.0	43.9	22	34.9

[a] In kcal/mol. [b] $T = 177.0$ °C. [c] In cal/deg·mol.

Table 2. Polymerization of VDF Using Initiator *d,l*-**3**. Experimental Conditions and Results

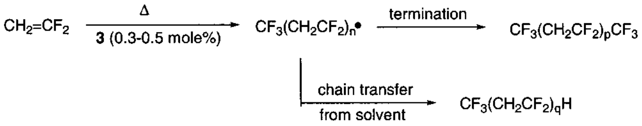
$[VDF]_0/[3]_0$	*T*, °C	*t* (h)	VDF, % conversion	$\overline{DP_n}$ (by ^{19}F NMR)	% normal VDF Units[a]
356	175 (then 180)	15.5 (then 4.0)	55	220 ± 15	95.8
242	170	14	34	58 ± 3	95.3
196	170	14	47	113 ± 8	96.7

[a] "Normal" VDF units are those joined in head-to-tail ($-CH_2CF_2CH_2CF_2-$) sequences (as opposed to head-to-head ($-CH_2CF_2CF_2CH_2-$) sequences.)

Table 3. Rate Constants (k/s^{-1}) for Homolysis of *meso*- and *d,l*-**3**

	temp, °C				
	165.4	169.0	181.0	186.7	190.3
meso-**3**	9.7×10^{-5}	1.6×10^{-4}	6.5×10^{-4}	1.0×10^{-3}	1.3×10^{-3}
d,l-**3**	6.9×10^{-5}	1.5×10^{-4}	5.6×10^{-4}	8.7×10^{-4}	1.2×10^{-3}

Consistent with such expectations, it was possible to use **3** to initiate polymerization of vinylidene fluoride (VDF) in sealed Carius tubes at 150−180 °C, leading to CF_3 end-capped PVDF, as shown below:



In our initial, preliminary examination of this polymerization, ^1H and particularly ^{19}F NMR spectra provided unambiguous evidence regarding the efficacy of PVDF formation, with signals at −91 to −95 ppm being assigned to normal head-to-tail $-CH_2CF_2CH_2CF_2-$ PVDF units (with I_1 integrals) and those at −113 and −116 ppm being attributed to reversed $-CH_2CF_2CF_2CH_2-$ and $-CH_2CF_2CF_2CH_2CH_2-$ PVDF units (with I_2 and I_3 integrals), respectively.[15−18] Furthermore, the quintet ($^3J_{F,F} = {}^4J_{F,H} = 10.0$ Hz) centered at − 60.8 ppm (I_4 integral) and assigned to $CF_3CH_2CF_2-$ permitted assessment of the average degree of polymerization, $\overline{DP_n}$ of such original PVDF−CF_3 from the following equation: $\overline{DP_n} = 3(I_1 + I_2 + I_3)/2I_4$. The results of the polymerization study are given in Table 2.

One could assess the defects of chaining of the macromolecular chain, using the following ratio of integrals: % defect $= (I_2 + I_3)/(I_1 + I_2 + I_3)$. The observed proportion of defect (3.3−4.7%) is surprisingly small for experiments performed at 170−180 °C. Values of the reversed VDF adduct are reported to range between 5 and 9%,[19] although there are values as low

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(11) Scherer, K. V., Jr.; Ono, T.; Yamanouchi, K.; Fernandez, R.; Henderson, P.; Goldwhite, H. *J. Am. Chem. Soc.* **1985**, *107*, 718−719.

(12) Zhao, C.; Zhou, R.; Pan, H.; Jin, X.; Qu, Y.; Wu, C.; Jiang, X. *J. Org. Chem.* **1982**, *45*, 2009−2013.

(13) Although it is difficult to get a quantitative measure of the yield of CF_3 radicals in the thermal decomposition of **3**, because of the propensity of **3** itself to be trapped by atom-transfer agents, when the analogous C_2F_5 dimer was heated at 155 °C in the presence of I_2, a quantitative yield of C_2F_5I was obtained.[14]

(14) Dolbier, W. R., Jr.; Duan, J.-X.; Ameduri, B.; Pooput, C., unpublished results.

(15) ^1H NMR: broad multiplet in the 2.6−3.3 ppm range; the ^1H and ^{19}F NMR spectra are consistent with values in the literature.

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Table 4. Crystal Data and Structure Refinement[a]

identification code	*d,l*-**3**	*meso*-**3**
empirical formula	$C_{37}H_{22}F_{22}O$	$C_{37}H_{22}F_{22}O$
formula weight	900.55	900.55
temperature	173(2) K	173(2) K
wavelength	0.710 73 Å	0.710 73 Å
crystal system	monoclinic	triclinic
space group	*P*2(1)/*c*	*P*-1
unit cell dimensions	$a = 8.6334(1)$ Å $b = 13.4174(2)$ Å $c = 29.2213(2)$ Å	$a = 11.0134(3)$ Å $b = 12.1014(3)$ Å $c = 15.0438(4)$ Å
α	90°	74.890(1)°
β	98.390(1)°	76.423(1)°
γ	90°	63.931(1)°
volume, *Z*	3348.75(7) Å^3, 4	1721.98(8) Å^3, 2
density (calcd)	1.786 Mg/m^3	1.737 Mg/m^3
absorption coefficient	0.192 mm^{-1}	0.186 mm^{-1}
F(000)	1800	900
crystal size	0.19 × 0.13 × 0.13 mm^3	0.34 × 0.19 × 0.19 mm^3
θ range for data collection	1.67−27.50°	1.90−24.99°
reflections collected	23 962	9620
independent reflections	7672 [*R*(int) = 0.0367]	5993 [*R*(int) = 0.0168]
completeness to θ	27.50° (99.7%)	24.99° (98.8%)
absorption correction	integration	empirical
max and min transmission	0.9801, 0.9658	0.811, 0.977
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	7672/0/542	5993/0/636
goodness-of-fit on F^2	1.002	1.025
final *R* indices [$I > 2s(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0879$ [5264]	$R_1 = 0.0388$, $wR_2 = 0.1031$ [4617]
R indices (all data)	$R_1 = 0.0613$, $wR_2 = 0.0938$	$R_1 = 0.0508$, $wR_2 = 0.1076$
extinction coefficient	0.0029(4)	0.0061(10)
largest diff peak and hole	0.289 and −0.240 e·Å^{-3}	0.295 and −0.212 e·Å^{-3}

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, where $p = [\max(F_o^2,0) + 2F_c^2]/3$.

as 2.4% reported under Ziegler-Natta conditions at temperatures below room temperature.[20,21]

Although requiring high temperatures, the above polymerizations of VDF using initiation by **3** leads to highly isoregic PVDF with CF_3 end groups which allow ready determination of the degree of polymerization. Furthermore, such CF_3 end groups could lead to polymers with novel properties.

In summary, novel radical addition chemistry of AF4 leads to formation of an unprecedented new class of dimeric CF_3-substituted AF4 derivatives. These highly sterically constrained compounds undergo clean two-step thermal homolytic processes to form trifluoromethyl radicals in a process that is amenable to their use as free-radical initiators, as is shown by a study of the polymerization of vinylidene fluoride.

Experimental Section

Reaction of Trifluoromethyl Radical with AF4. Into a 100-mL three-necked, round-bottomed flask was added a mixture of AF4 (10 g, 30 mmol), methylene chloride (40 mL), and H_2O_2 (50%) (1.2 g, 30 mmol). The mixture was cooled to −40 °C, and under vigorous stirring, $(CF_3CO)_2O$ (18.6 g, 90 mmol) was slowly added. After the addition was complete, the mixture was allowed to slowly warm to room temperature and then heated to reflux for 12 h. The product precipitated during this time. After cooling to 0 °C, the crude product was obtained by filtration. Recrystallization from methylene chloride gave pure product **3** (6.1 g, 50%) as a 57:43 mixture of diastereoisomers (as determined by ^{19}F NMR). Separation of diastereomers, *d,l*- and *meso*-**3**, was obtained by recrystallization from ethyl acetate, wherein each isomer gave different shaped crystals, which could be separated by picking out each one manually. Crystals obtained in this manner were used for the X-ray analysis, which indicated that the major isomer was the *d,l*.

^{19}F NMR for *meso*-3: δ −64.27 (m, 6F), −109.7 (AB, J = 242.0 Hz, 2F), −110.71 (AB, J = 246.9 Hz, 2F), −112.43 (AB, J = 242.0 Hz, 2F), −112.92 (AB, J = 60.4 Hz, 2F), −113.82 (AB, J = 60.4 Hz, 2F), −114.51 (AB, q, J = 246.9, 19.5 Hz, 2F), −116.32 (AB, q, J = 242.04, 9.9 Hz, 2F), 116.62 (AB, J = 242.0 Hz, 2F) ppm; ^{1}H NMR δ 2.53 (br, 2H), 3.76 (m, J = 9.0 2H), 6.12 (d, 6.9 Hz, 2H), 6.32 (br, 2H), 7.50 (AB, J = 8.10 Hz, 2H), 7.69 (AB, J = 8.4 Hz, 2H), 7.75 (AB, J = 8.4 Hz, 2H), 7.84 (AB, J = 8.1 Hz, 2H).

^{19}F NMR for *d,l*-3: δ −64.56 (m, 6F), −108.8 (AB, J = 244.5 Hz, 2F), −109.45 (AB, J = 244.5 Hz, 2F), −111.53 (AB, J = 244.5 Hz, 2F), −113.87 (AB, J = 14.4, 244.5 Hz, 2F), −114.65 (AB, J = 239.7 Hz, 2F), −114.85 (AB, J = 239.7 Hz, 2F), −116.38 (AB, q, J = 239.7, 7.9 Hz, 2F), 116.40 (AB, J = 239.7 Hz, 2F) ppm; ^{1}H NMR δ 2.61 (br, 2H), 3.79 (m, J = 8.4 Hz, 2H), 6.17 (d, 7.2 Hz, 2H), 6.25 (br, 2H), 7.47 (AB, J = 8.10 Hz, 2H), 7.67 (AB, J = 8.4 Hz, 2H), 7.72 (AB, J = 8.4 Hz, 2H), 7.81 (AB, J = 8.1 Hz, 2H)

Kinetic Experiments. Either *meso*- or *d,l*-**3** (0.2 mg, 2.38 × 10^{-4} mmol) was added to an NMR tube containing 0.5 mL of CD_3CN and 0.1 mL of 1,4-cyclohexadiene. After the tube was degassed in vacuo for 5 min at − 78 °C, the NMR tube was immersed in a constant-temperature bath for an appropriate time, then removed, cooled, and analyzed by ^{19}F NMR, with the concentration of **3** being measured versus internal standard, trifluoromethylbenzene. In this manner were rates determined for the homolysis of each isomer at five different temperatures, with the observed rate constants being given in Table 3, and plots of the data being shown in Figure 1.

Reaction of *d,l*-3 with I_2. Into an NMR tube was added a mixture of 0.5 mL of CD_3CN, I_2 (0.1 g, 0.04 mmol), and *d,l*-**3** (0.2 mg, 2.38 × 10^{-4} mmol). The NMR tube was degassed for 5 min under vacuum (0.4 mm Hg) at −78 °C. After the tube was sealed, it was immersed in a constant-temperature bath maintained at 175 °C and the reaction monitored for 1 h. The ^{19}F NMR spectrum of the solution indicated that both **1** and *meso*-**3** were formed from *d,l*-**3**. When allowed to go to completion (continued heating for 24 h), the reaction produced an 87% yield of **1**, as the only detectable product.

Attempted Aromatization of 3. Refluxing **3** with DDQ in HOAc led to recovery of starting material, as did attempted bromination with

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[20] Liepins, R.; Surles, J. R.; Morosoff, N.; Stannett, V. T.; Timmons, M. L.; Wortman, J. J. *J. Polym. Sc., Polym. Chem. Ed.* **1978**, *17*, 3039−3044.

[21] Cais, R. E.; Kometani, J. M. *Macromolecules* **1984**, *17*, 1887−1889.

Table 5. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg)[a]

d,l-**3**	
C7−C7′	1.576(2)
C6−C7−C8	108.8(1)
C6′-C7′-C8′	108.9(1)
C6−C7−C7′-C6′	−59.9(2)
C8−C7−C7′-C8′	52.6(2)
meso-**3**	
C13−C13#1	1.583(3)
C12−C13−C14	109.4(1)
C12−C13−C13#1-C14#1	−55.8(2)
C13′-C13#2	1.572(3)
C12′-C13′-C14′	109.3(1)
C12′-C13′-C13#2-C14#2	−56.3(2)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 2, -y + 1, -z$. #2: $-x + 1, -y + 1, -z + 1$.

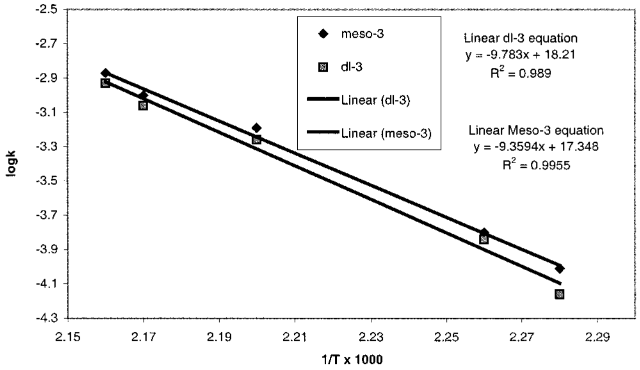

Figure 1. Arrhenius plots of the kinetic data for *meso*- and *d,l*-**3**.

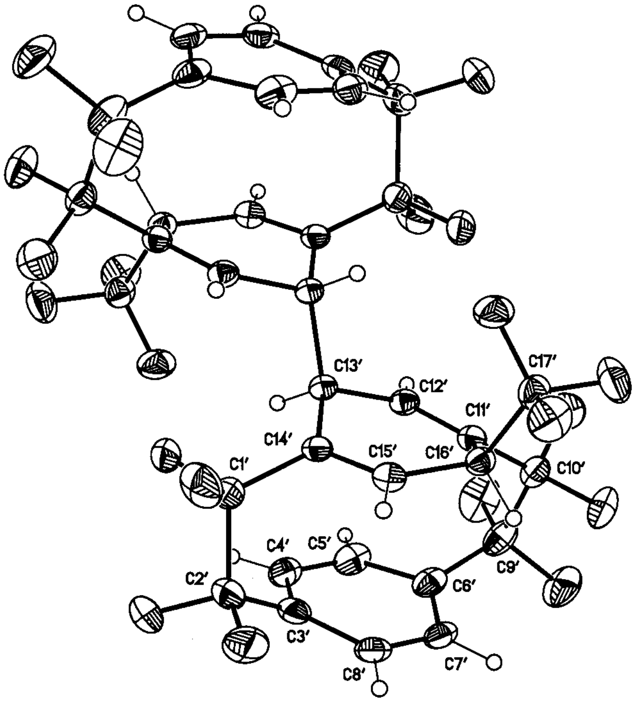

Figure 2. Perspective view (ORTEP) of *meso*-**3**.

NBS/$h\nu$ in refluxing CCl_4 and attempted oxidation by BuOOH. Heating with Pd/C in refluxing toluene led to formation of a complex mixture of products

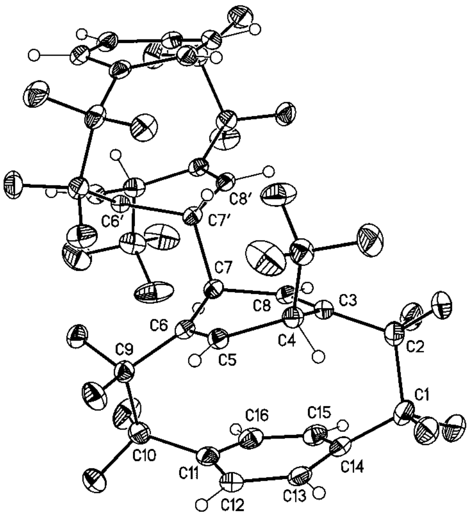

Figure 3. Perspective view (ORTEP) of *d,l*-**3**.

Polymerizations. Bulk polymerizations of VDF (kindly donated by Solvay S. A. (Belgium)) were performed in thick borosilicate Carius tubes in a batch process (length, 130 mm; internal diameter, 10 mm; thickness, 2.5 mm; for a total volume of 8 cm^3). After the initiator was added, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. After five thaw−freeze cycles at least, to get rid of oxygen, VDF was trapped under vacuum in the tube frozen in liquid nitrogen, after its release from an intermediate metallic container calibrated in pressure. The required amount of VDF (0.750 ± 0.008 g) introduced into the tube was assessed by the relative drop of pressure in the release container, initially fed by a cyclinder of 300 g of VDF. A beforehand calibration curve—weight of trapped VDF (in g) versus drop of pressure (in bar)—was determined (for 0.75 g of VDF, a difference in pressure of 0.50 bar being required).

The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed for the required time into the cavity of a shaking oven at the required temperature.

X-ray Experiments. Data were collected at 173 K on a Siemens Smart Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Empirical absorption corrections were applied based on the entire data set.

For *meso*-3: $C_{37}H_{22}F_{22}O$, $M_r = 900.55$, triclinic, $P1$, $a = 11.0134(3)$ Å, $b = 12.1014(3)$ Å, $c = 15.0438(4)$ Å, $\alpha = 74.890(1)°$, $\beta = 76.423(1)°$, $\gamma = 63.931(1)°$, $V = 1721.98(8)$ Å^3, $Z = 2$, $D_{calc} = 1.737$ g cm^{-3}, Mo Kα ($\lambda = 0.710\ 73$ Å), $T = 173$ K.

For *d,l*-3: $C_{37}H_{22}F_{22}O$, $M_r = 900.55$, triclinic, $P2(1)/c$, $a = 8.6334(1)$ Å, $b = 13.4174(2)$ Å, $c = 29.2213(2)$ Å, $\beta = 98.390(1)°$, $V = 3348.75(7)$ Å^3, $Z = 4$, $D_{calc} = 1.786$ g cm^{-3}, Mo Kα ($\lambda = 0.710\ 73$ Å), $T = 173$ K.

The structures were solved by the Direct Methods in SHELXTL5[22] and refined using full-matrix least squares; and the structural data are given in Tables 4 and 5. The ORTEP drawings of *meso*- and *d,l*-**3** are given in Figures 2 and 3, respectively. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. For *meso*-**3**, a total of 636 parameters were refined in the final cycle of refinement using 4617 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.88 and 10.31%, respectively. For *d,l*-**3**, a total of 542 parameters were refined in the final cycle of refinement using 5264 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.74 and 8.79%, respectively. Refinement was done using F^2.

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