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NON-BONDED INTERACTIONS BETWEEN PROXIMATE PHENYL AND POLYFLUOROPHENYL RINGS? THE REGIOSPECIFIC SYNTHESIS OF THE FACIAL TETRAFLUOROJANUSENE*

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SUMMARY

Cycloadditions of anthracenes to dibenzobarrelenes, with at least one C_6F_4 moiety in either reactant, afford the janusenes 2 and 3, in which phenyl and tetrafluorophenyl rings are disposed in a close facial relationship. Compound 3, which is formed in a regiospecific manner, exhibits an ultraviolet spectrum that suggests a donor-acceptor interaction between the proximate $-C_6H_4-$ and $-C_6F_4-$ rings.

INTRODUCTION

We are interested in non-bonded interactions between proximate phenyl and polyfluorophenyl rings in sterically constrained systems, e.g., the [2.2] cyclophanes [1,2]. Janusene (1), first described [3] by Cristol and coworkers, possesses two lateral (L) and two parallel facial (F) rings ca. 2.5Å apart; it is a [3.3] orthocyclophane having vis-à-vis benzene rings [4].

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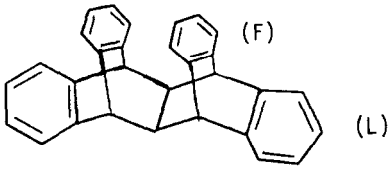

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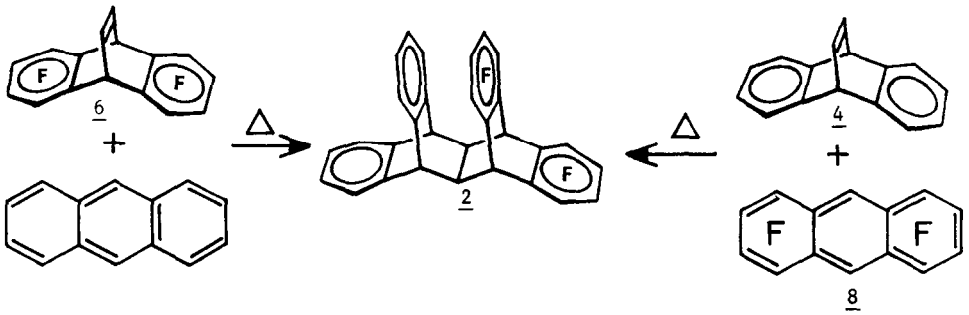
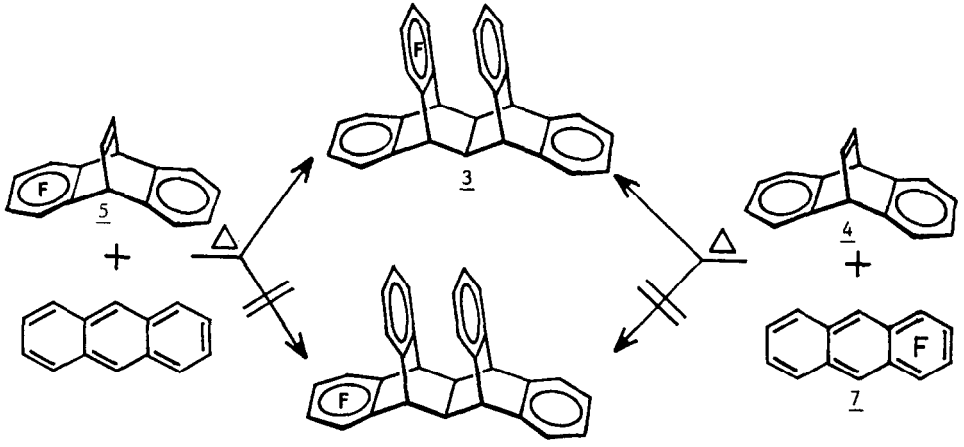
In this paper we report the preparation and spectral properties of the octafluorojanusene 2 (Scheme 1) and the regiospecific synthesis of the facial isomer of tetrafluorojanusene, 3 (Scheme 2). In both compounds, a facial tetrafluorophenyl ring lies parallel and in close proximity to a facial phenyl ring.

RESULTS AND DISCUSSION

Compound 1 is constructed by [4π + 2π] cycloaddition of anthracene to dibenzobicyclo(2.2.2)octatriene(dibenzobarrelene) 4, a compound somewhat difficult to prepare. We recently described a novel and superior route to both 1 and 4 via an acetylene transfer between anthracene and 1,2,3,4-tetrafluorobenzobarrelene [5]. For the synthesis of 2 and 3, we first prepared the pivotal compounds tetrafluoro- and octafluorodibenzobarrelenes 5 and 6 [6], obtained by reaction of tetrafluorobenzyne (from C_6F_5MgBr) with naphthalene and 1,2,3,4-tetrafluoronaphthalene, respectively. Compounds 5 and 6 serve not only as activated dienophiles in the [4+2] cycloadditions to form 2 and 3, but as key reactants for the preparation, via



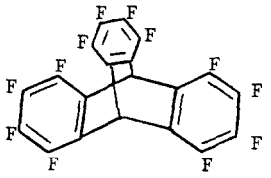
Scheme 1



Scheme 2

cycloaddition-reversion, of the dienes, 1,2,3,4-tetrafluoro- and 1,2,3,4,5,6,7,8-octafluoroanthracenes, 7 and 8 [6].

Two approaches to 2 and 3 are available. Thus, heating a 1:1 molar mixture of 6 and anthracene at 220°C in a sealed ampoule for 2.5 days provided 2 in 67% yield. Alternatively, 2 was obtained in 59% yield from 4 and 8, under the same conditions. The relative reactivity of 8 as a diene, even under these conditions, is somewhat unexpected, since we anticipated considerable deactivation by the two flanking tetrafluorophenyl rings. Indeed, attempts to prepare dodecafluorotriptycene 9, albeit under milder conditions, by reaction of 8 with tetrafluorobenzyne, were unsuccessful. However, octafluorotriptycene 10, not previously characterized, was obtained from 7 and tetrafluorobenzyne.



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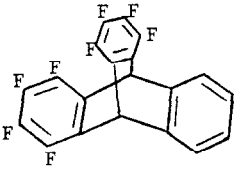

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Mention should be made of difficulties in preparing pure samples of 2 and 10, owing to problems in removing traces of bromine-containing contaminants in precursor compounds, e.g., 6 and 8 [6], which arise from the generation of small quantities of bromotrifluorobenzyne in the decomposition of C_6F_5MgBr.

Compound 2 necessarily possesses a facial tetrafluorophenyl ring and thus, serves as a model for establishing the structure of the tetrafluorojanusene 3. Cycloaddition of anthracene to 5 at 220° for 2.5 days gave only one product, in 67% yield. Reaction of 7 with 4 afforded the identical compound in 63% yield. Despite careful scrutiny, no other addition products could be detected. Two isomers are possible from either combination of reactants (Scheme 2). From Cristol's work [3,7] and the ultraviolet spectra (vide infra), we suggest that the sole product isolated possesses structure 3, the tetrafluorophenyl facial isomer. We hope that X-ray crystallographic analysis will provide confirmation of this assignment.

Ultraviolet Spectra

Comparison of the u.v. spectrum of 1 with those of the fluoro analogs, reveals a common absorption maximum for 2 and 3, absent in 1 (Fig. 1) and the dibenzobarrelenes. We ascribe the presence of the bands near 283-284 nm to donor-acceptor interactions between the facial π-electron-demanding tetrafluorophenyl and the facial π-electron-donating phenyl rings.

NMR Studies

Comparison of the 300 MHz ^{1}H nmr spectra of 1, 2, and 3 also suggests the tetrafluorophenyl "face" structure for 6. In the spectrum of 1, the two multiplets at upper field have been assigned to the protons of the "face" rings, which are shielded by 0.35 ppm compared with those of the lateral rings [8]. The spectra of 2 and 3 (Fig. 2) show that the resonances attributed

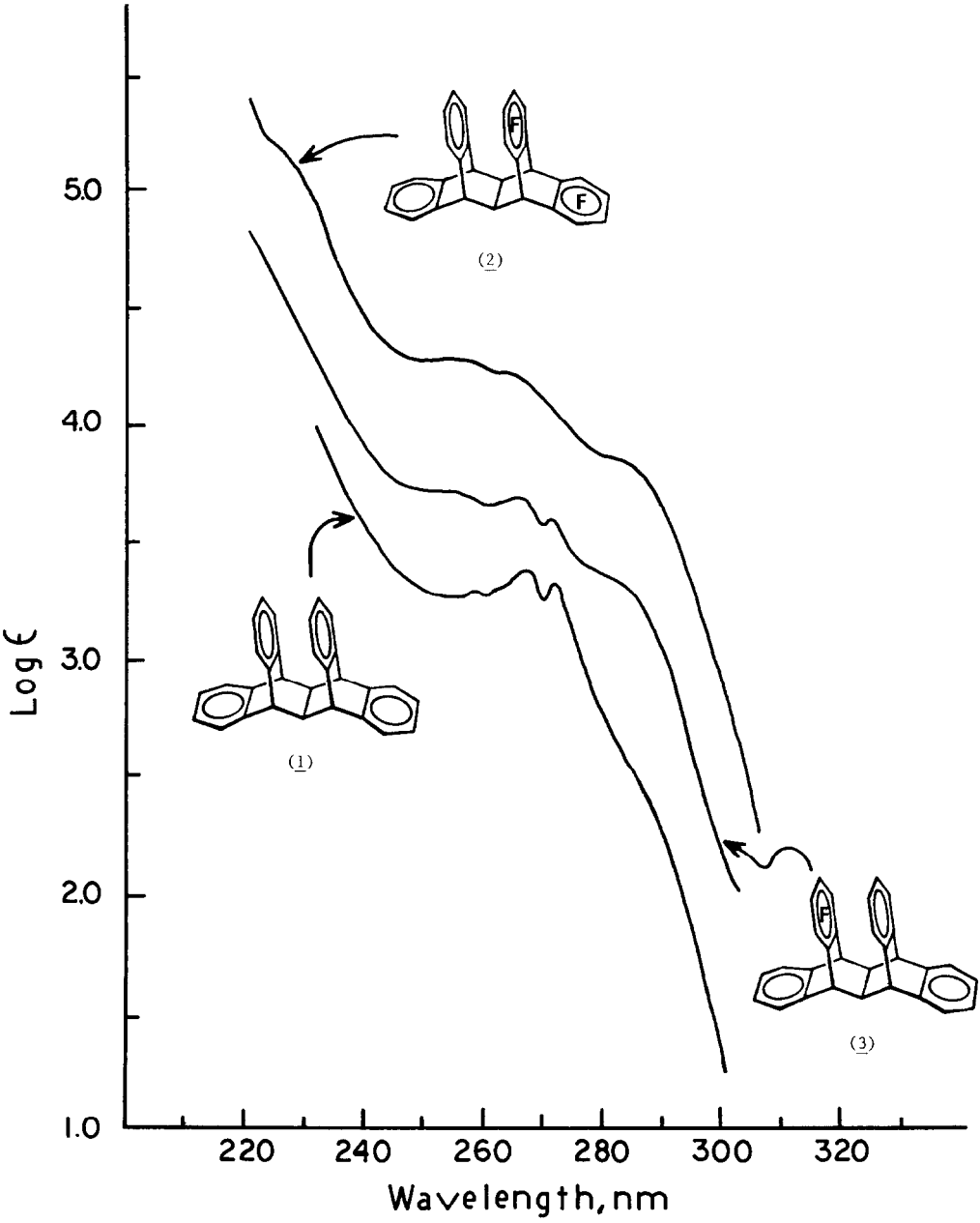

Fig. 1. Ultraviolet Absorbances of Janusene, F-Tetrafluorojanusene (Log ε+½), and Octafluorojanusene (Log ε+1) in Cyclohexane.

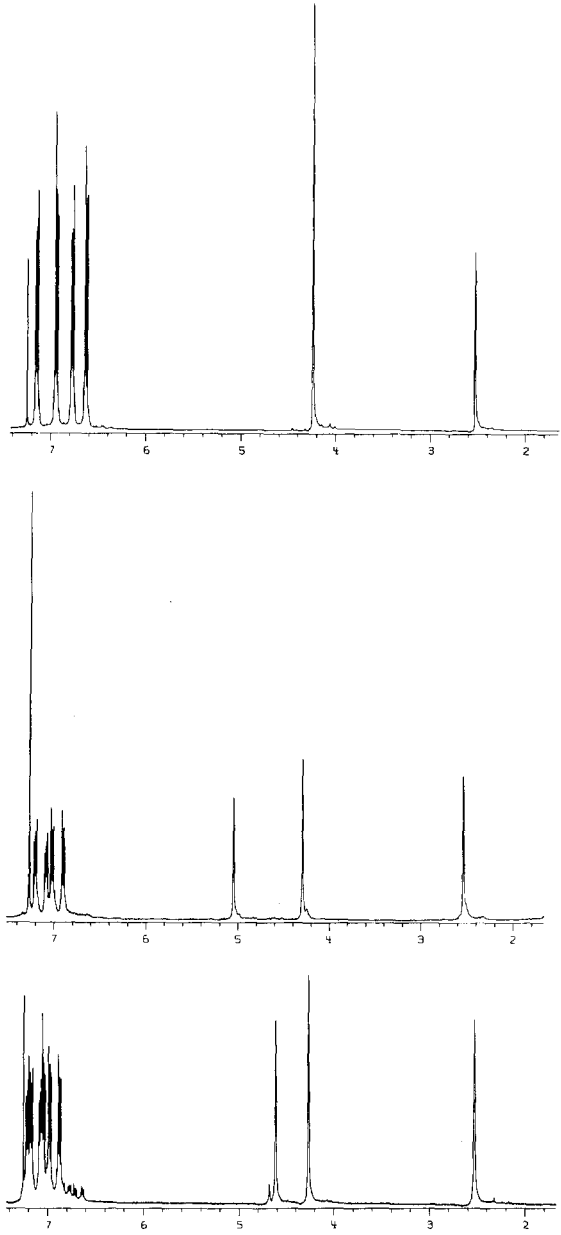

Fig. 2. ^{1}H nmr spectra of janusenes. Chemical shifts ($CDCl_3$), δ ppm from TMS. The peaks at ca. δ 7.30 are due to presence of $C\underline{H}Cl_3$.

to their facial protons occur at 0.25 ppm lower field than in 1. The reduced carbon-hydrogen polarization caused by the proximate fluorinated ring results in deshielding. This effect has also been noted in the ^1H nmr spectrum of tetrafluoro[2.2]paracyclophane relative to [2.2]paracyclophane [2].

Regioselectivity

Studies by Cristol [3] revealed strong regioselectivity toward electrophilic substitution on a facial phenyl ring in janusene (1) and in the predominant formation of janusenes whose facial rings possess the nitro or methyl group of the precursor substituted anthracene [7]. The regiospecific formation of 3 from either of two pairs of reactants strongly suggests that substantial attractive electronic interactions between closely disposed and parallel C_6H_4 and C_6F_4 rings play a crucial role in stabilizing the transition state and thereby, determining the structure, as proposed, for the cycloaddition product [9].

EXPERIMENTAL

Melting points (uncorrected) were determined on a Mel-Temp capillary apparatus. A Pye-Unicam 3-300 spectrophotometer was used to record infrared spectra of samples in KBr. Ultraviolet spectra were measured on a Cary Model 15 spectrophotometer. The routine ^1H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer, while high resolution ^1H NMR was performed on a Nicolet spectrometer at 300 MHz. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, while ^{19}F NMR spectra were recorded on a JEOL FX-90Q spectrometer with chemical shifts reported in ppm relative to $CFCl_3$. Mass spectra were measured

with a Finnigan TSQ 45A MS at an ionizing energy of 70 eV. Microanalytical determinations were conducted by MicroTech Laboratories of Skokie, Illinois.

The following compounds were prepared, according to previously described procedures.

9,10-Dihydro-9,10-ethenoanthracene (Dibenzobarrelene)(4) [5]

5,5a,6,11,11a,12-Hexahydro-5,12:6,11-di-o-benzenonaphthacene (Janusene) (1) [5]

5,6,7,8-Tetrafluoro-9,10-ethenoanthracene(5,6,7,8-tetrafluorodibenzobarrelene) (5) [10].

1,2,3,4,5,6,7,8-Octafluoro-9,10-ethenoanthracene (1,2,3,4,5,6,7,8-octafluorodibenzobarrelene)(6) [6].

1,2,3,4-Tetrafluoroanthracene(7) and 1,2,3,4,5,6,7,8-octafluoroanthracene (8) [6].

13,14,15,16-Tetrafluoro-5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-o-benzenonaphthacene (F-Tetrafluoroianusene) (nc) (3). Method A

To a 1 mL ampoule was added dibenzobarrelene (4) (255 mg, 1.25 mmol) and 1,2,3,4-tetrafluoroanthracene (313 mg, 1.25 mmol), and 10 mg of hydroquinone. The ampoule was sealed under nitrogen. The contents were heated in a tube furnace at 220°C for 2.5 days. At the end of this period, the dark brown solid was dissolved in dichloromethane and treated with activated charcoal (100 mg). After filtration, the light brown liquid was concentrated in a sublimation apparatus. No starting materials were recovered by sublimation. A white solid sublimed at 185°C (0.1 mm Hg) The material was further purified on TLC using hexanes/benzenes (9:1) as the solvent system. The UV active band

was separated and extracted with dichloromethane. After filtration and removal of the solvent, tetrafluorojanusene (381 mg, 0.84 mmol, 67%) remained as a white solid with the following physical and spectral characteristics: mp 239°C (ethanol); IR (KBr) 3019, 3008, 2940, 2920, 1500-1440, 1380, 1330, 1320, 1280, 1160, 1100, 1090, 1080, 1020, 985, 920, 905, 760-730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.27-6.85 (m, 12H), δ 4.61 (s, 2H), δ 4.26 (s, 2H), δ 2.53 (s, 2H); ^{19}F NMR ($CDCl_3$) 148.87-148.64 (m, 2F), 161.12-160.72 (m, 2F); ^{13}C NMR ($CDCl_3$) 144.81, δ 143.21, δ 140.12, δ 126.36, δ 126.01, δ 125.83, δ 124.70, δ 123.59, δ 123.21, δ 48.51, δ 44.27, δ 40.90; mass spectrum m/e calcd (M^+) 454, obsd 454. Fragments obsd.: 250 (tetrafluoroanthracene), 204 (dibenzobarrelene), and 178 (anthracene). Anal calcd for $C_{30}H_{18}F_4$: C, 79.29%; H, 3.99%; F, 16.72%. Found: C, 78.85%; H, 4.00%; F, 16.79%.

Method B. To a 1 mL ampoule was added 1,2,3,4-tetrafluorodibenzobarrelene (5) (304 mg, 1.10 mmol), anthracene (196 mg, 1.10 mmol), and hydroquinone (10 mg). The sample was heated in a tube furnace at 220°C for 2.5 days. After the same workup as that used in Method A, the F-tetrafluorojanusene (315 mg, 0.69 mmol, 63%) was isolated. The physical and spectral characteristics were identical to those recorded in Method A.

1,2,3,4,13,14,15,16-Octafluoro-5,5a,6,11,11a,12-hexahydro-5,12;6,11-di-o-benzenonaphthacene (Octafluorojanusene) (nc) (2)

Method A

Using the procedure described for the tetrafluorojanusene, octafluorodibenzobarrelene (6) (217 mg, 0.624 mmol), anthracene

(111 mg, 0.625 mmol), and hydroquinone reacted at 220°C for 2.5 days in a 1 mL ampoule. After sublimation (185°C, 0.1 mm Hg) and TLC (hexanes/benzene), the product (220 mg, 0.419 mmol, 67%) was isolated as a white solid which was characterized as follows: mp 168-170°C; IR(KBr) 3060, 3015, 2970, 2940, 1500, 1480, 1460, 1375, 1295, 1120, 1050, 940, 918, 770, 750, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.21-6.87 (m, 8H), δ 5.04 (s, 2H), δ 4.28 (s, 2H), δ 2.53 (s, 2H); ^{19}F NMR ($CDCl_3$) 146.94-146.39 (m, 4F), 158.23 (m, 4F); ^{13}C δ NMR 144.27, 139.68, 126.26, 126.12, 124.78, 48.04, 43.36, 33.55 ppm; mass spectrum m/e calcd (M^+) 526, obsd 526, Fragments obsd.: 322 (octafluoroanthracene), 204 (dibenzobarrelene) and 178 (anthracene).

Method B. When 1,2,3,4,5,6,7,8-octafluoroanthracene (containing a small amount of bromo contaminant) (107 mg, 0.332 mmol), dibenzobarrelene (68 mg, 0.33 mmol), and hydroquinone (10 mg) reacted at 220°C for 2.5 days, workup, as in Method A, afforded octafluorojanusene (103 mg, 0.196 mmol, 59%). The mass spectrum, ^{1}H and ^{13}C NMR and IR were identical to those obtained by Method A.

1,2,3,4,5,6,7,8-Octafluoro-9,10-dihydro-9,10-o-benzenoanthracene (1,2,3,4,5,6,7,8-Octafluorotriptycene) (nc) (10)

Tetrafluorobenzyne was prepared by a modified procedure of Heaney [12]. To a suspension of magnesium turnings (40 mg, 1.6 mmol) in anhydrous diethyl ether (2 mL), under nitrogen, activated by a crystal of iodine, was added bromopentafluorobenzene (0.20 mL, 1.60 mmol). Reflux was maintained until the metal was consumed. 1,2,3,4,-Tetrafluoroanthracene (7) (401 mg,

1.60 mmol) in 10 mL of dry cyclohexane was introduced. The mixture was distilled under nitrogen until the distillation head temperature reached 76°C. The residual mixture was refluxed for 9 h and the salts were filtered and washed with 5 mL of dichloromethane. The solvent was removed under reduced pressure and unreacted tetrafluoroanthracene (113 mg, 0.45 mmol) was recovered by fractional sublimation. The crude octafluorotriptycene sublimed at 170°C (0.1 mm Hg) as an oily solid. The mass spectrum indicated the presence of a bromine-containing analog as a contaminant: m/e calcd (M^+) 398, obsd. 398. The mixture was dissolved in 5 mL of hexanes and treated with n-butyllithium (1.80 mL), 2.5 M in hexanes) at 0°C. After quenching with carbon dioxide (g) and hydrolyzing with a 5% ammonium chloride solution, the solvent was removed and the oil chromatographed using TLC (hexanes). The recovered white solid (243 mg) had a melting range of 108-113°C and gave the following spectral data: ^{1}H NMR ($CDCl_3$) δ 7.54-7.43 (m, 2H), δ 7.25-7.06 (m, 2H), δ 6.16 (m, 2H); ^{19}F NMR ($CDCl_3$) 146.93-146.12 (m, 4F), 158.81-157.91 (m, 4F); IR (KBr) 2965, 2930, 2850, 1495, 1468, 1400, 1112, 1080, 1020, 995, 934, 761, 739, 665, 618 cm^{-1}.

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