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Regiospecific Synthesis and Structural Study of Some Trifluoromethyl Substituted Dibenzosemibullvalenes**

Klaudio Otočan[1], **Mladen Mintas**[1,*], **Fritz Kastner**[2], **Albrecht Mannschreck**[2], **James A. Golen**[3,***], and **Paul G. Williard**[3]

[1] Department of Organic Chemistry, University of Zagreb, 41000 Zagreb, Croatia
[2] Institute of Organic Chemistry, University of Regensburg, D-W-8400 Regensburg, Federal Republic of Germany
[3] Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

Summary. Preparation of the regiospecifically trifluoromethyl substituted dibenzosemibullvalenes **3** and **5** is described. An unequivocal proof of chirality of **3** and **5** was obtained by enrichment of their enantiomers using liquid chromatography on triacetyl- or tribenzoylcellulose. The stereostructure of compounds **3** to **5** was proved by their ^{1}H-NMR spectra and confirmed by X-ray crystallographic analysis. The geometrical data from X-ray structural analyses showed that five-membered rings involved in the skeleton of **3** and **5** adopt flattened envelope conformations. These results indicate also a significant substituent-induced bond length asymmetry in the cyclopropane rings of **3** and **5**.

Keywords. Dibenzobarrelene; Dibenzosemibullvalene; Enantioselective chromatography; Trifluoromethylation; Photochemical rearrangement; X-ray crystal structures.

Regiospezifische Synthese und Strukturuntersuchung einiger Trifluormethyl-substituierter Dibenzosemibullvalene

Zusammenfassung. Es wird die Herstellung der Trifluormethyl-substituierten Dibenzosemibullvalene **3** und **5** beschrieben. Der eindeutige Beweis ihrer Chiralität wurde durch Anreicherung der Enantiomeren mittels Flüssigchromatographie an Triacetyl- bzw. Tribenzoylzellulose erbracht. Die Stereochemie der Verbindungen **3** und **5** wurde mittels ^{1}H-NMR und Röntgenstrukturanalyse geklärt. Die Röntgenstrukturdaten zeigten, daß der Fünfring in **3** und **5** eine abgeflachte Briefumschlagkonformation einnimmt. Es zeigt sich auch eine signifikante substituentenbedingte Asymmetrie in den Bindungslängen der Cyclopropanringe von **3** und **5**.

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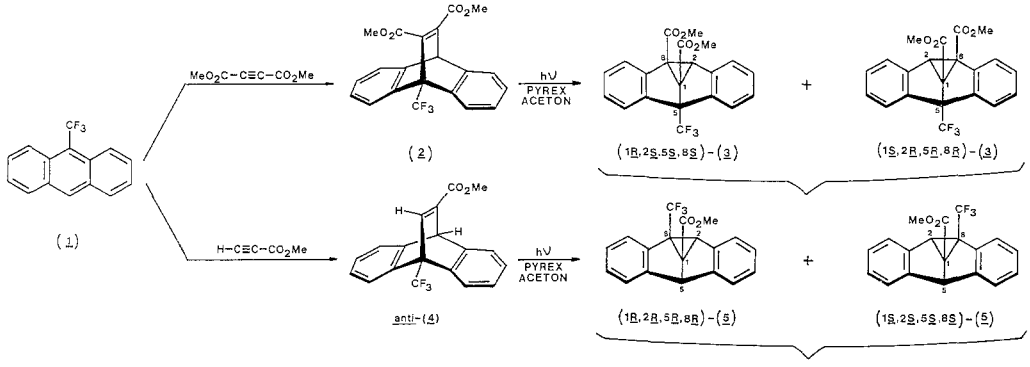
*** Permanent address: Department of Chemistry, Southeastern Massachusetts University, North Dartmouth, MA 02747, USA

Introduction

Our previous study on 9-trifluoromethylanthracene [1] as well as the work of Scheffer and coworkers on dibenzosemibullvalenes [2, 3] led us to investigate the possibility that might lead to specifically trifluoromethyl-substituted derivatives of dibenzosemibullvalenes. The present study was additionally stimulated by the fact that some dibenzosemibullvalene derivatives (dibenzotricyclo[3. 3. 0. 0. ^{2,8}]octa-3, 6-diene) possess antidepressive activities [4]. This work resulted in discovery of the novel dibenzobarrelenes dibenzobicyclo[2. 2. 2]octa-2, 5, 7-triene **2** and **4** and dibenzosemibullvalenes **3** and **5** which we now report.

Results and Discussion

Diels-Alder (DA)-cycloaddition of dimethyl acetylene dicarboxylate and methyl propiolate to 9-trifluoromethylanthracene (**1**) gave dibenzobarrelenes **2** and **4** re-



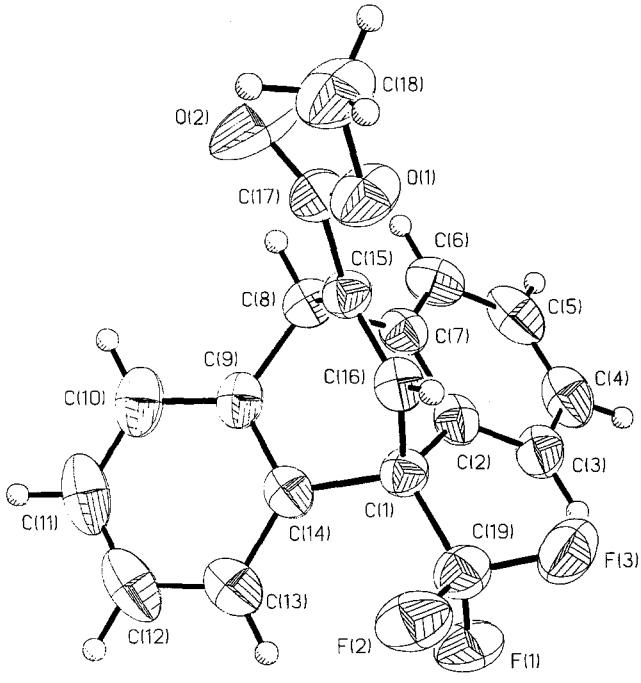


Fig. 1. Stereo-drawing of dibenzobarrelene (**4**) showing the atomic numbering and the *anti*-relationship of the trifluoromethyl and methyl ester groups

spectively, whose structures were proven by ^{1}H-NMR spectra. The cycloadduct **4** is formed in a regiospecific manner in which the trifluoromethyl and methyl ester groups are disposed in *anti* relationship. This stereostructure was confirmed by X-ray crystal structure analysis of **4** (Fig. 1). Irradiation of dibenzobarrelenes **2** and **4** in acetone as sensitizer led to formation of **3** and **5** respectively. The formation of the photoproduct **3** may be explained by the generally accepted mechanism for di-π-methane rearrangement [5]. However, the observed structure of the photoproduct **5** cannot be explained without bond rearrangements in the proposed biradical intermediate for such a process [5]. This result therefore calls for further mechanistic studies.

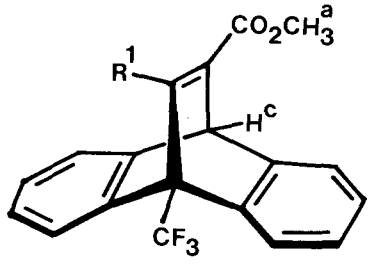
^{1}H-*NMR Studies*

In order to establish the stereostructure of the isolated dibenzobarrelenes **2** and **4** and dibenzosemibullvalenes **3** and **5**, their ^{1}H-NMR spectra were examined in detail to see if a correlation of chemical shifts and coupling constants with stereochemistry would be apparent. The spectral assignments are given in Table 1.

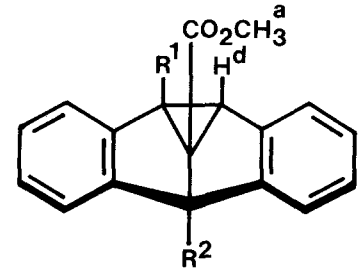
The methyl resonances of the nonequivalent ester substituents $CH_3{}^a$ and $CH_3{}^b$ in the cycloadduct **2** appear as singlets at 3.77 and 3.80 ppm. We assign the resonance at slightly lower field (i. e., $\delta = 3.80$) to the $CH_3{}^b$ group due to the deshielding effect of the adjacent trifluoromethyl group.

The bridgehead methine signal H^c and vinyl hydrogen signal H^e in the compound **4** at 5.65 and 7.76 ppm occur as mutually coupled doublets as confirmed by spin

Table 1. ^{1}H-NMR chemical shifts (δ)/ppm and coupling constants ^nJ/Hz for protons a – d*



2 and 4



3 and 5

Compound	R^1	R^2	δ($CH_3{}^a$)	δ($CH_3{}^b$)	δ(> C-H^c)	δ(▽H^d)	δ(=CH^e)	δ(benzo)
(2)	$CO_2CH_3{}^b$	-	3.77(s)	3.80(s)	5.65(s)	-	-	6.99 – 7.62(m)
(4)	H^e	-	3.75(s)	-	5.65(d)	-	7.76(d)	7.02 – 7.54(m)
					$^4J = 2$ Hz	-	$^4J = 2$ Hz	
(3)	$CO_2CH_3{}^b$	CF_3	3.87(s)	3.75(s)		4.38(s)	-	7.10 – 7.74(m)
(5)	CF_3	H^c	3.77	-	4.26(d)	5.04(s)	-	7.05 – 7.52(m)

* Peak multiplicities are represented by s (singlet), d (doublet), and m (multiplet). Chemical shift assignments in (**2**) and (**5**) were confirmed by spin decoupling and Nuclear Overhauser Enhancement experiments, respectively.

decoupling experiments. The coupling constant between H^c and H^e is 2 Hz which is consistent with the magnitude of coupling constants through four bonds and the stereostructure of the cycloadduct, **4** in which protons H^c and H^e are disposed in *anti*-relationship (Table 1). If those groups had been *syn*-disposed in the other possible regioisomer, the coupling constant of H^c to the adjacent bridgehead proton

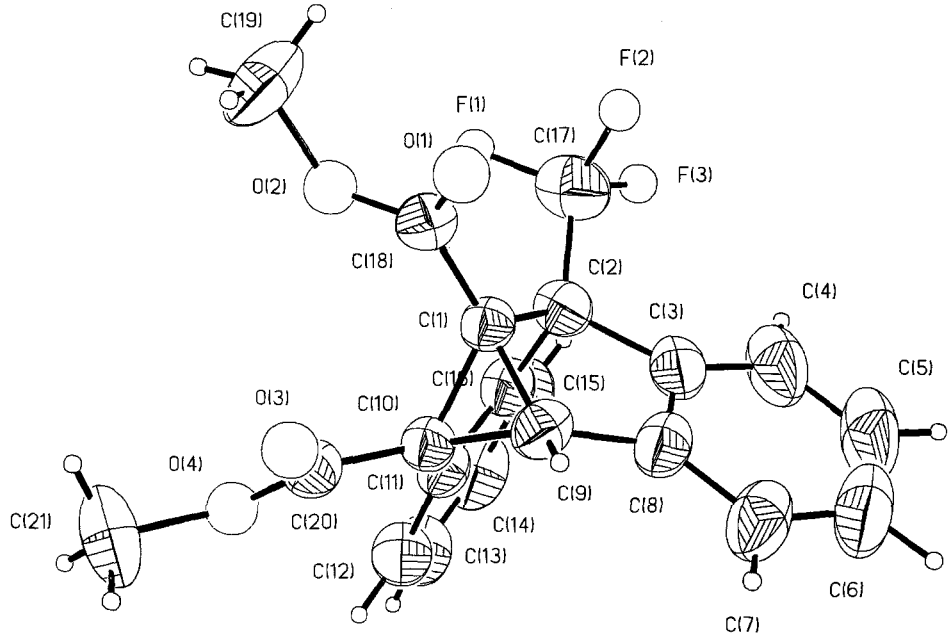


Fig. 2. Stereo-drawing and atomic numbering for dibenzosemibullvalene (**3**)

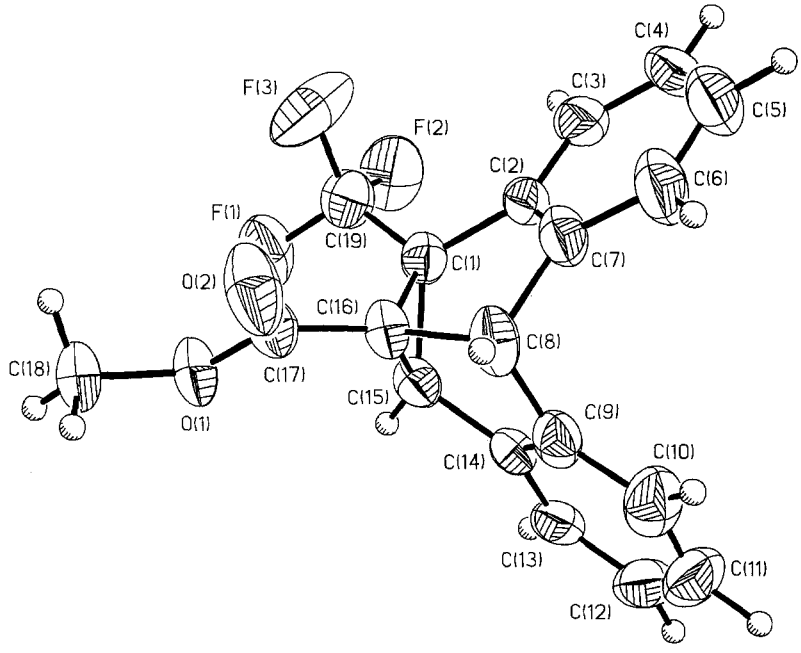


Fig. 3. Stereo-drawing and atomic numbering for dibenzosemibullvalene (**5**)

H^e would have been greater than that value. The coupling constants between *cis* vicinal protons in a similar dibenzobarrelene derivative is found to be $^3J_{cis} = 3$ Hz [6]. In addition proton H^e in **4** appears at an appreciable low field ($\delta = 7.76$) which may be explained by the deshielding effect of two adjacent trifluoromethyl and methyl ester groups.

Examination of the ^{1}H-NMR spectra of dibenzosemibullvalenes **3** and **5** showed the following features: The two methyl ester groups in **3** are nonequivalent and the $CH_3{}^a$ signal appears at lower field ($\delta = 3.87$) than protons of $CH_3{}^b$ group ($\delta = 3.75$) probably due to the deshielding effect of the adjacent trifluromethyl group. Comparison of the spectra of **3** and **5** shows that the $CH_3{}^a$ group in **3** occurs at lower field ($\delta = 3.87$) than in **5** ($\delta = 3.77$) owing to the proximity of that group to both trifluoromethyl and other carboxymethyl group ($CH_3{}^b$) in **3**. Similarly, proton H^d in **5** appears at lower field ($\delta = 5.04$) than H^d in **3** ($\delta = 4.38$) which may be explained again by the deshielding effect of trifluoromethyl group which is a stronger electron withdrawing group than the carboxymethyl one and closer to the proton H^d in **5** than in **3**. Comparison with the ^{1}H-NMR spectra of the corresponding structurally related dibenzobarrelenes and dibenzosemibullvalenes [3, 7] is consistent with that assignment.

These facts were also in accord with the proposed structures of the regioisomeric dibenzosemibullvalenes **3** and **5** which were subsequently confirmed by X-ray crystallographic analysis (Fig. 2 and 3).

Separation of Enantiomers

The chromatographic parameters for the separation of enantiomers are summarized in Table 2.

Dibenzosemibullvalene (±)-**3** showed only marginal resolution of enantiomers by liquid chromatography (*LC*) on triacetylcellulose (*TAC*) as well as by high performance liquid chromatography (*HPLC*) on tribenzoylcellulose (*TBC*) [10,

Table 2. Chromatographic parameters for separation of enantiomers by liquid chromatography

	R^1	R^2	k^a	Polarimetric detection[b]
(±)-**3**	CO_2CH_3	CF_3	0.57[c]	(−), (+)
			1.7[d]	(−), (+)
			1.45[e]	(+), (−)
(±)-**5**	CF_3	H	0.71[c, f]	(−), (+)

[a] Mean capacity factor [8.9]

[b] Sign of rotation at 365 nm

[c] Triacetylcellulose [8] as a sorbent and *Et*OH:H_2O (96 : 4, v/v) as an eluent

[d] Tribenzoylcellulose [10, 11] as a sorbent and *Me*OH as an eluent

[e] (+)-Poly(tritylmethacrylate)/SiO_2 [12] as a sorbent and *Me*OH as an eluent

[f] See Fig. 4

11]. *HPLC* on silica, coated with (+)-poly(trityl/methacrylate) [12], yielded also a slight separation of enantiomers of (±)-**3**. However, an enrichment of enantiomers was achieved for (±)-**5** by *LC* on *TAC* at 20°C (Fig. 4).

Admittedly, the comparison of the chromatographic behaviour of these two molecules is hardly enough to warrant any firm conclusions about structure-enantioselectivity relationship in that class of molecules. However, these preliminary results prove chirality of **3** and **5** and show that, in spite of incomplete separation of enantiomers, *LC* on *TAC* or *TBC* could be applied for the preparation of

(1R,2R,5R,8R)- 5 (1S,2S,5S,8S)- 5

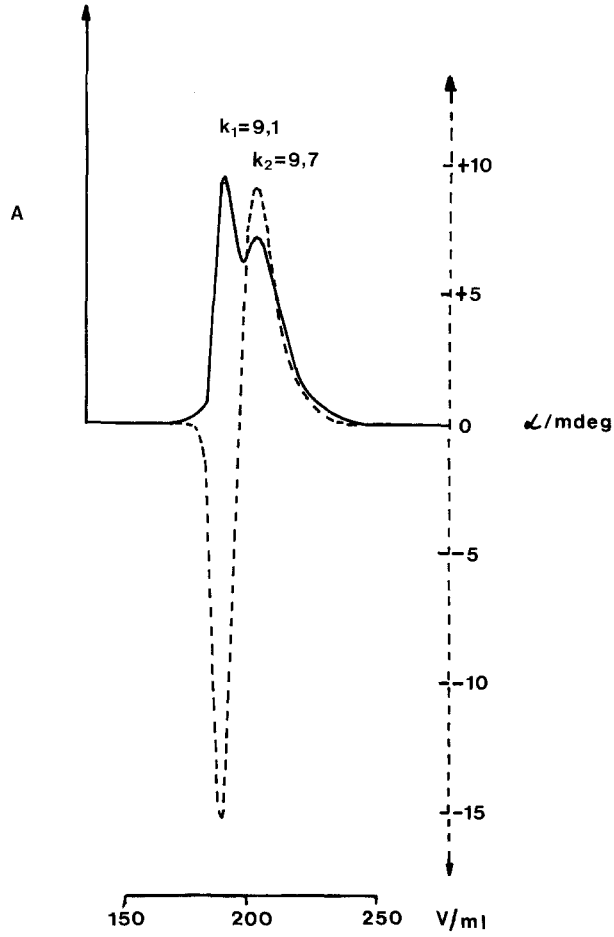
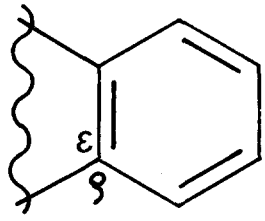


Fig. 4. Chromatogram of (±)-**5** in *Et*OH:H_2O (96:4) after chromatography through a column of triacetylcellulose (particle size 0.02 – 0.03 mm), 20°C; (—) rotation angle (α) at 365 nm; (?) absorbance (*A*) at 278 nm; *V* volume of eluate; *k* capacity factor [8, 9]

enantiomerically enriched samples of these molecules. That might be of importance because of (i) possible pharmacological activities of these molecules and (ii) demands for comparative evaluations of the activities and toxicities of the enantiomers of racemic drugs [13].

X-Ray Crystallographic Study

Single crystals of **3**, **4**, and **5** suitable for X-ray structure analysis were prepared by growth under slow evaporation at room temperature of a very dilute solution of ethyl acetate-ethanol mixture (1 : 3). A perspective view of the molecules with atom numbering is shown in Figures 1 – 3. The dibenzobarrelene skeleton in **4** is similar to that of isopropyl methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**6**) [5] and dibenzo-barrelene itself [14]. The skeleton in **4** (Fig. 1) contains two nearly planar aromatic rings and an isolated C = C double bond. The bridging double bond C(15) = C(16) in **4** [1.327(4) Å] is shorter than the corresponding bridge bond in **6** amounting 1.334(4) Å [5], but longer than in dibenzobarrelene itself [1.316(4)] [14]. The dihedral angle C(16)-C(15)-C(17)-O(2) (φ) in **4** is 166.9(3)°, i. e. the stereostructure of the C = C-C = O system is *anti*. The ester group is conjugated to the central double bond ($\cos^2\varphi = 0.949$). This conjugation is reflected in the sp^2-sp^2 [C(15)-C(17)] single bond length of 1.470(4) Å. The values of the bond lengths reasonably suggest the extent of electron delocalization over the α, β unsaturated carbonyl systems [5]. The value found for the C(15)-C(17) single bond in **4** is in accord with the bond length of 1.470(2) Å [15], which is expected for complete delocaliation for such a system. The angles external to the benzene rings, ρ, mean 127.3° and the intraannular benzene-barrelene angles ε, mean 112.6°, are distorted to about the same extent as in the related bridge double bond substituted dibenzobarrelene (6) [5] and dibenzobarrelene itself [14].



Scheme 2: Definition of extra- and intra-annular angles ρ and ε:

This is consistent with the general observation that strain induced by ring fusion is reflected in systematic angular deformations [16]. In spite of these systematic distortions in the bond angles, the bond lengths are generally as expected and similar to those of the related dibenzobarrelene derivative **6** [5] and dibenzobarrelene itself [14]. The dibenzosemibullvalene ring skeleton in **3** and **5** are similar. The corresponding mean values for ρ and ε in the product molecules where the ring fusion is between benzene and cyclopropane ring are 129.3° and 110.1°, respectively. The values of these angles are consistent with the corresponding values found in related dibenzosemibullvalenes [5]. The dihedral angles between the plane C(1)-C(2)-C(9) and the least-square (l. s.) plane defined by atoms C(2)-C(3)-(8)-C(9) and between the plane C(1)-C(2)-C(10) and l. s. plane C(10)-C(11)-C(16)-C(2)

in (3) are 159.4(2)° and 161.0(2)°, respectively. In **5** the corresponding dihedral angle values are similar, amounting 158.2(2)° and 160.3(3)°. Accordingly the two five-membered rings C(1)-C(2)-C(3)-C(8)-C(9) and C(1)-C(2)-C(16)-C(11)-C(10) in **3** and C(16)-C(8)-C(9)-C(14)-C(15) and C(16)-C(1)-C(2)-C(7)-C(8) in **5** exhibit flattened envelope conformations (Fig. 5).

It has been shown by Allen [15] that many properties of the cyclopropane ring are more similar to those of the vinyl group. In particular, the hybrid orbitals are closer to sp^2 than sp^3, while a conformation-dependent conjugative ability is exhibited with π-acceptor substituents [15]. In connection with those studies we have examined the geometrical data of the cyclopropane ring and its substituent groups

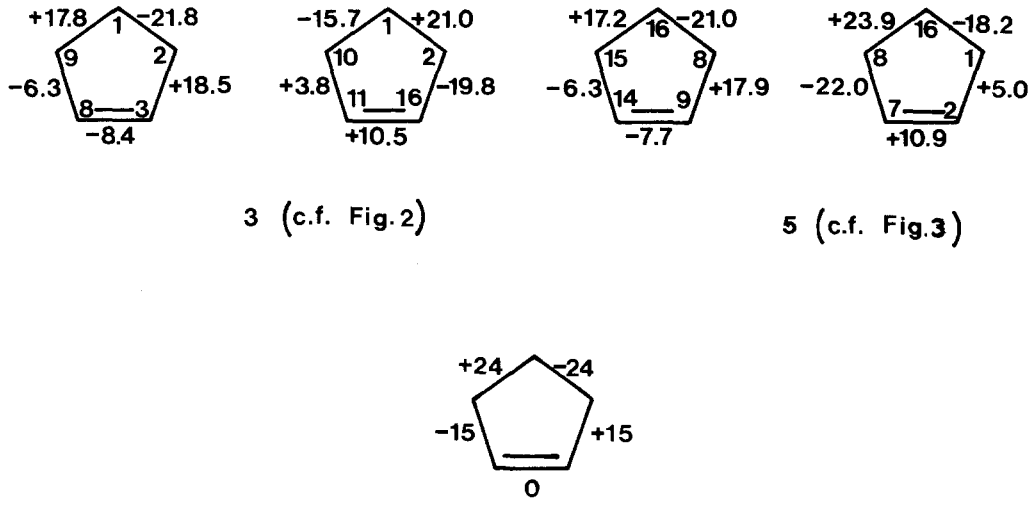


Fig. 5. Torsional angles of **3** and **5** in comparison with the ideal values for the cyclopentene envelope [17]

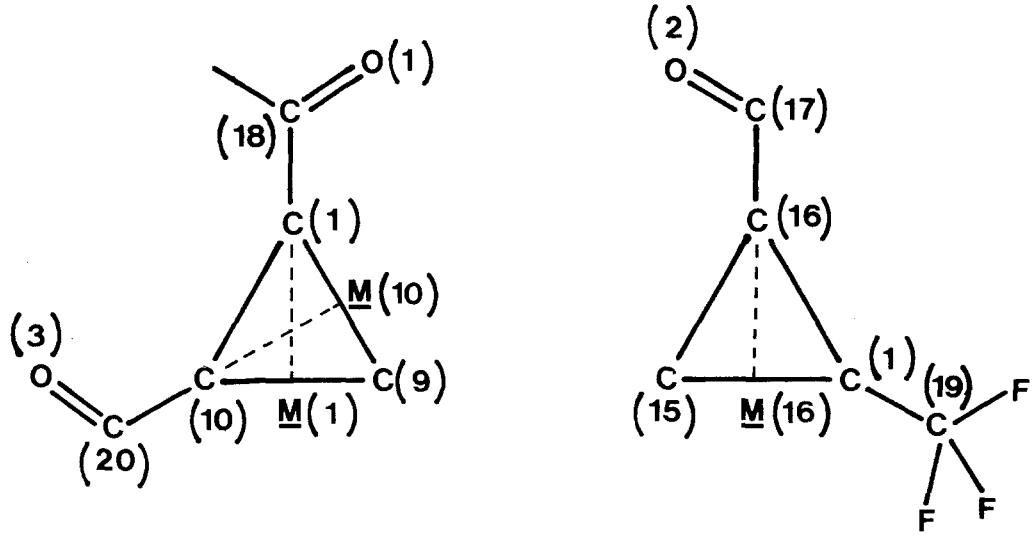


Fig. 6. Geometry of the cyclopropane substructure in **3** and **5** (M_{ij} are the midpoints of the cyclopropane ring bonds opposite atoms C_{ij})

in **3** and **5**. The analysis shows that the dihedral angles between the plane of the cyclopropane ring C(1)-C(9)-C(10) and the lines through atoms C(1)-C(18) and C(10)-C(20) in **3** amount 142.7(2)° and 150.8(2)°, respectively. These markedly wide angles could be due to the steric repulsion between the two adjacent methyl ester groups on the cyclopropane rings. Accordingly, the O(1)...O(3) non-bonded distance [i. e. the distance between the oxygen atoms in **3**] is significantly increased, 3.406(3) Å. On the contrary, the O(2)...F(1) distance of 2.831(3) Å indicates close contact between those atoms. The torsion angles $\tau_1[M(10)\text{-}C(10)\text{-}C(20)\text{-}O(3)]$ and $\tau_2[M(1)\text{-}C(1)\text{-}C(18)\text{-}O(1)]$ are $-13.4(4)°$ and $77.8(4)°$ for **3**. Accordingly, C(20)=O(3) and C(18)=O(1) bonds adopt nearly *cis*-bisected and perpendicular conformations with respect to the cyclopropane ring (Fig. 6).

The bond lengths C(1)-C(9) [1.477(5) Å] and C(9)-C(10) [1.586(5) Å] for **3** show that C(20)=O(3) is conjugated to the cyclopropane ring while C(18)=O(1) is not. This is consistent with the torsion angles τ_1 and τ_2 and the corresponding values found for these bond lengths in conjugated and non-conjugated systems of 1.484(4) and 1.506(6) Å, respectively [18]. The dihedral angles between the cyclopropane ring C(1)-C(15)-C(16) and the lines through atoms C(16)-C(17) and C(1)-C(19) in **5** are 135.2(2)° and 145.6(2)°. These markedly large angles may be attributed to the steric congestion in the cyclopropane ring which thus forces the two vicinal trifluoromethyl and carboxymethyl groups to be remote from each other. The torsion angle $[M(16)\text{-}C(16)\text{-}C(17)\text{-}O(2)]$ is $-148.1(4)$ for **5**. This value deviates by 32° from the *trans*-bisected conformation (180°) of the C(17)=O(2) bond with respect to the cyclopropane ring. Furthermore, the cyclopropane ring C(1)-C(15)-C(16) is asymmetrical, the two C-C bonds being of significantly different lengths: 1.497(3) and 1.554(3) Å for C(15)-C(16) and C(1)-C(15), respectively. Thus, the C(15)-C(16) bond, which is *vicinal* to the C(17)-O(2) group but *distal*, i. e. opposite to the CF_3 group (c. f. Fig. 4), is shortened for 0.012(3) Å relative to the individual mean C-C (cyclopropane ring) length of 1.509(2) Å. Analogously, the C(1)-C(15) bond, *distal* to the C(17)=O(2) and *vicinal* to the CF_3 group is lengthened for 0.045(3) Å. Although the *distal*-bond shortening for the CF_3 group is quantitatively small, it is in agreement with the expected effect of fluorine to accept electron density from the cyclopropane ring. The C(1)-C(15) bond lengthening may be qualitatively explained by the cooperative electronic action of CF_3 and methyl ester groups on that bond. Therefore the conformation of the C(17)=O(2) group appears not to be effective enough for interactions with 3e′ orbitals [18] of the cyclopropane ring. These results indicate that the π-electron acceptor ability of the trifluoromethyl group compared to the carboxymethyl one is predominant.

Experimental Part

Melting points were determined on a Kofler micro hot-stage (Reichert, Wien) and are not corrected. UV spectra were recorded on a Hitachi Perkin-Elmer 124 spectrometer. The ^{1}H-NMR spectra of **2** and **3** were recorded on Jeol JNM FX (PFT mode, 8 K data points 90 MHz). The ^{1}H-NMR spectra, selective decoupling and Nuclear Overhauser Enhancement (NOE) experiments of **4** and **5** were performed on a Bruker WH 250 (PFT mode, 32 K data points, 250 MHz) spectrometer. The electron impact mass spectra (EIMS) of **2** and **3** were recorded on a Varian MAT CH7 instrument with ionizing energy 70 eV and emission current 0.1 mA. The EIMS of **4** was recorded on a Varian MAT 711 double focussing mass spectrometer with ionizing energy 80 eV and emission current 0.8 mA. The exact mass

measurement of the molecular ion of **4** was performed by using the same instrument at resolution 10 000 (10% relative value definition). Low and high resolution EIMS of **5** were recorded on Varian MAT 90 spectrometer with a ionizing of energy 70 eV. Elemental analyses were performed by the Central Analytical Service, Ruder Bošković Institute, Zagreb.

Chromatography

Low-pressure liquid chromatography (column 300 – 200 nm) at a flow rate of 3.3 – 3.9 $cm^3 min^{-1}$, $\Delta p = 2.0 - 2.5$ bar* on *TAC* [8] as a stationary phase with particle diameter of 0.02 – 0.03 mm and ethanol:water, 96 : 4 (v/v) as the eluent at 22 – 25°C was used for separation of enantiomers of (±)-**3** and (±)-**5**. High performance liquid chromatography (*HPLC*) at a flow rate of 0.5 $cm^3 min^{-1}$, $\Delta p = 54$ bar* on *PTMA* [12] as a stationary phase and *Me*OH as the eluent at +15°C was used for separation of enantiomers of (±)-**3**. *HPLC* at a flow rate of 1.0 $cm^3 min^{-1}$, Δp 21 bar* on *TBC* [10, 11] as a stationary phase with methanol as the eluent at 22 – 25°C was also used for separation of (±)-**3**.

Dimethyl-1-trifluoromethyl-dibenzobicyclo[2.2.2]octa-2,5,7-triene-7,8-dicarboxylate (**2**)

A stirred mixture of **1** (0.6 g, 0.0025 mol), dimethyl acetylene dicarboxylate (5 cm^3, 0.04 mol) and anhydrous aluminium chloride (2 g, 0.0015 mol) was heated under reflux at 130 – 140°C for 4 h. After filtration, the crude oily product was purified by column chromatography on silica gel (0.063 – 0.200 mm) using light petroleum (40 – 70°C)-chloroform in volume ratio 1 : 3 as the solvent. Recrystallization of the solidified product from methanol gave colourless crystals of **2**; yield 31%; m.p. 177.8°C. $C_{21}H_{15}F_3O_4$ requires C 64.95, H 3.89; found C 65.14, H 4.15; MS (70 eV) *m/z* (rel. intensity): 389 (24), 388 (M^+, 100), 360 (40), 357 (17), 356 (14), 330 (22), 329 (86), 301 (41), 285 (13), 271 (10), 270 (38), 269 (11), 260 (25), 246 (14), 217 (15), 216 (14), 202 (15), 201 (14), 200 (13), 59 (11); UV (methanol): $\lambda_{max} = 212$ nm ($\log \varepsilon = 4.25$). For ^{1}H-NMR spectrum see Table 1.

1,8-Dimethyl-5-trifluoromethyl-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-dien-1,2-dicarboxylate (**3**)

A $3 \cdot 10^{-3}$ molar solution of **2** in acetone was irradiated for 23 h through Pyrex glass with a high pressure mercury immersion lamp. Oxygen was excluded during the irradiation by bubbling nitrogen through the solution. Removal of acetone by evaporation under reduced pressure gave a crude residue which was purified by column chromatography on silica gel (0.063 – 0.200 mm) with light petroleum (40 – 70°C) chloroform (3 : 1) as a solvent and subsequent recrystallization of the solidified product from ethyl acetate-ethanol (1 : 3). Colourless crystals of **3**; yield 55%; m.p. 130 – 132°C; $C_{12}H_{15}F_3O_4$ requires C 64.95, H 3.89; found C 64.88. H 4.0; MS (70 eV) *m/z* 404 (11%), 389 (26), 388 (M^+, 84), 361 (10), 360 (33), 357 (18), 356 (16), 345 (17), 330 (26), 329 (100), 313 (12), 302 (11), 301 (48), 269 (10), 268 (12), 261 (12), 260 (37), 256 (13), 232 (11), 229 (12), 217 (26), 202 (22), 201 (25), 200 (18), 64 (12); UV (methanol): $\lambda_{max} = 217$ nm ($\log \varepsilon = 4.49$). For ^{1}H-NMR spectrum see Table 1.

Methyl-1-trifluoromethyl-dibenzobicyclo[2.2.2]octa-2,5,7-triene-8-carboxylate (**4**)

A mixture of **1** (0.6 g, 0.0025 mol) and methyl propiolate (2.2 cm^3, 0.0125 mol) was heated under reflux and nitrogen at 103 – 105°C for 4 h. The excess of methyl propiolate was then removed by evaporation and the oily residue solidified by trituration with ethanol. After filtration and recrystallization of the solidified product from ethanol colourless crystals of **4**, yield 39%, m.p. 166-167°C were obtained. MS (80 eV) *m/z* (rel. intensity): 331 (20), 330 (M^+, 100), 315 (11), 272 (13), 271 (70), 270 (30), 261 (19), 251 (13), 203 (12), 202 (61) and 101 (17); found M^+ 330.086761; calc. for $C_{19}H_{13}F_3O_2$: $M^+ = 330.08677$. For ^{1}H-NMR spectrum see Table 1.

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* 1 bar = 10^5 Pa

Table 3. Bond lenghts/Å and valence angles/° for **3**, **4**, and **5** with e. s. d.'s in the least significant digits in parentheses

Bond distances/Å

3		4		5	
O(1)-C(18)	1.193(4)	C(1)-C(2)	1.543(4)	C(1)-C(2)	1.503(3)
O(2)-C(19)	1.445(5)	C(1)-C(16)	1.526(3)	C(1)-C(16)	1.521(3)
O(4)-C(20)	1.327(4)	C(2)-C(3)	1.385(4)	C(2)-C(3)	1.385(4)
F(1)-C(17)	1.358(5)	C(3)-C(4)	1.380(4)	C(3)-C(4)	1.402(4)
F(3)-C(17)	1.345(5)	C(5)-C(6)	1.382(4)	C(5)-C(6)	1.364(5)
C(1)-C(9)	1.477(5)	C(7)-C(8)	1.521(4)	C(7)-C(8)	1.507(4)
C(1)-C(18)	1.502(5)	C(8)-C(15)	1.528(4)	C(8)-C(16)	1.546(3)
C(2)-C(16)	1.524(5)	C(9)-C(14)	1.395(4)	C(9)-C(14)	1.392(3)
C(3)-C(4)	1.378(5)	C(11)-C(12)	1.373(5)	C(11)-C(12)	1.365(5)
C(4)-C(5)	1.399(6)	C(13)-C(14)	1.390(4)	C(13)-C(14)	1.390(4)
C(6)-C(7)	1.381(6)	C(15)-C(17)	1.470(4)	C(15)-C(16)	1.497(3)
C(8)-C(9)	1.480(5)	C(17)-O(2)	1.193(4)	C(17)-O(1)	1.315(3)
C(10)-C(11)	1.498(4)	C(19)-F(1)	1.339(3)	C(18)-O(1)	1.449(3)
C(11)-C(12)	1.378(5)	C(19)-F(3)	1.346(3)	C(19)-F(2)	1.333(3)
C(12)-C(13)	1.383(5)	C(1)-C(14)	1.544(4)	C(1)-C(15)	1.554(3)
C(14)-C(15)	1.384(5)	C(1)-C(19)	1.504(4)	C(1)-C(19)	1.484(4)
O(2)-C(18)	1.319(4)	C(2)-C(7)	1.395(4)	C(2)-C(7)	1.385(4)
O(3)-C(20)	1.204(4)	C(4)-C(5)	1.376(5)	C(4)-C(5)	1.370(6)
O(4)-C(21)	1.456(5)	C(6)-C(7)	1.388(4)	C(6)-C(7)	1.383(4)
F(2)-C(17)	1.402(5)	C(8)-C(9)	1.521(4)	C(8)-C(9)	1.525(4)
C(1)-C(2)	1.578(5)	C(9)-C(10)	1.384(4)	C(9)-C(10)	1.378(4)
C(1)-C(10)	1.518(5)	C(10)-C(11)	1.378(4)	C(10)-C(11)	1.386(5)
C(2)-C(3)	1.545(5)	C(12)-C(13)	1.388(4)	C(12)-C(13)	1.378(4)
C(2)-C(17)	1.518(5)	C(15)-C(16)	1.327(4)	C(14)-C(15)	1.482(3)
C(3)-C(8)	1.401(5)	C(17)-O(1)	1.333(3)	C(16)-C(17)	1.485(3)
C(5)-C(6)	1.368(8)	C(18)-O(1)	1.439(3)	C(17)-O(2)	1.197(3)
C(7)-C(8)	1.394(5)	C(19)-F(2)	1.339(3)	C(19)-F(1)	1.323(3)
C(9)-C(10)	1.586(5)			C(19)-F(3)	1.316(3)
C(10)-C(20)	1.489(5)				
C(11)-C(16)	1.392(5)				
C(13)-C(14)	1.376(6)				
C(15)-C(16)	1.388(5)				

Bond angles/°

3		4		5	
C(18)-O(2)-C(19)	115.3(2)	C(2)-C(1)-C(14)	105.7(2)	C(2)-C(1)-C(15)	121.8(2)
C(2)-C(1)-C(9)	105.8(2)	C(14)-C(1)-C(16)	105.5(2)	C(15)-C(1)-C(16)	58.2(2)
C(9)-C(1)-C(10)	63.9(2)	C(14)-C(1)-C(19)	114.3(2)	C(15)-C(1)-C(19)	116.2(2)
C(9)-C(1)-C(18)	120.5(2)	C(1)-C(2)-C(3)	128.5(3)	C(1)-C(2)-C(3)	129.5(2)
C(1)-C(2)-C(3)	102.3(2)	C(3)-C(2)-C(7)	120.0(2)	C(3)-C(2)-C(7)	120.4(2)
C(3)-C(2)-C(16)	105.4(2)	C(3)-C(4)-(5)	120.7(3)	C(3)-C(4)-C(5)	121.3(3)
C(3)-C(2)-(17)	114.8(3)	C(5)-C(6)-C(7)	119.5(3)	C(5)-(6)-C(7)	118.5(3)
C(2)-C(3)-C(4)	130.1(3)	C(2)-C(7)-C(8)	113.7(2)	C(2)-(7)-C(8)	109.9(2)
C(4)-C(3)-C(8)	120.9(3)	C(7)-C(8)-C(9)	105.5(2)	C(7)-8)-C(9)	104.9(2)
C(4)-C(5)-C(6)	120.7(4)	C(9)-C(8)-C(15)	105.4(2)	C(9)-C(8)-C(16)	103.5(2)
C(6)-(7)-(8)	118.2(4)	C(8)-C(9)-C(14)	113.1(2)	C(8)-C(9)-C(14)	109.4(2)
C(3)-C(8)-C(9)	111.1(3)	C(9)-C(10)-C(11)	119.5(3)	C(9)-C(10)-C(11)	118.7(3)
C(1)-C(9)-C(8)	107.3(2)	C(11)-C(12)-C(13)	121.0(3)	C(11)-C(12)-C(13)	120.7(3)
C(8)-C(9)-C(10)	121.2(2)	C(1)-C(14)-C(9)	112.1(2)	C(9)-C(14)-(13)	120.3(2)
C(1)-C(10)-C(11)	107.0(2)	C(9)-C(14)-C(13)	119.7(2)	C(13)-C(14)-C(15)	129.4(2)
C(1)-C(10)-C(20)	116.7(2)	C(8)-C(15)-C(17)	121.0(2)	C(1)-C(15)-C(16)	59.8(2)
C(11)-C(10)-C(20)	122.3(2)	C(1)-C(16)-C(15)	114.4(2)	C(1)-C(16)-C(8)	104.6(2)
C(10)-C(11)-C(16)	110.4(2)	C(15)-C(17)-O(2)	124.1(3)	C(8)-C(16)-C(15)	105.3(2)
C(11)-C(12)-C(13)	118.7(3)	C(1)-C(19)-F(1)	113.4(2)	C(2)-C(1)-C(16)	105.9(2)
C(13)-C(14)-C(15)	120.7(3)	F(1)-C(19)-F(2)	106.6(2)	C(2)-C(1)-C(19)	118.1(2)
C(2)-C(16)-C(11)	109.9(2)	F(1)-C(19)-F(3)	106.1(2)	C(16)-C(1)-C(19)	122.2(2)
C(11)-C(16)-C(15)	120.4(3)	C(2)-C(1)-C(16)	105.6(2)	C(1)-C(2)-C(7)	110.0(2)
F(1)-C(17)-F(3)	105.0(3)	C(2)-C(1)-C(19)	114.6(2)	C(2)-C(3)-C(4)	117.4(3)
F(1)-C(17)-C(2)	111.1(3)	C(16)-C(1)-C(19)	110.5(2)	C(4)-C(5)-C(6)	121.1(3)
F(3)-C(17)-C(2)	111.2(3)	C(1)-C(2)-C(7)	111.5(2)	C(2)-C(7)-C(6)	121.3(3)
O(1)-C(18)-C(1)	124.2(3)	C(2)-C(3)-C(4)	119.5(3)	C(6)-C(7)-C(8)	128.4(3)
O(3)-C(20)-O(4)	123.7(3)	C(4)-C(5)-(6)	120.4(3)	C(7)-C(8)-C(16)	103.7(2)
O(4)-C(20)-C(10)	112.3(2)	C(2)-C(7)-C(6)	119.9(2)	C(8)-C(9)-C(10)	129.9(2)
C(20)-O(4)-C(21)	116.9(2)	C(6)-C(7)-C(8)	126.5(3)	C(10)-C(9)-C(14)	120.2(2)
C(2)-C(1)-C(10)	104.5(2)	C(7)-C(8)-C(15)	106.2(2)	C(10)-C(11)-C(12)	121.1(3)
C(2)-C(1)-C(18)	124.7(2)	C(8)-C(9)-C(10)	126.4(3)	C(12)-C(13)-C(14)	118.8(3)
C(10)-C(1)-C(18)	121.4(2)	C(10)-C(9)-C(14)	120.5(3)	C(9)-C(14)-C(15)	110.2(2)
C(1)-C(2)-C(16)	103.5(2)	C(10)-C(11)-C(12)	120.3(3)	C(1)-C(15)-C(14)	120.6(2)
C(1)-C(2)-C(17)	114.0(3)	C(12)-C(13)-C(14)	119.0(3)	C(1)-C(16)-C(15)	62.0(2)
C(14)-C(15)-C(16)	107.1(2)	C(1)-C(14)-C(13)	128.3(2)	C(1)-C(16)-C(17)	126.5(2)
C(16)-C(2)-C(17)	115.5(3)	C(8)-C(15)-C(16)	113.7(2)		
C(2)-C(3)-C(8)	108.6(3)	C(16)-C(15)-C(17)	125.0(2)		
C(3)-C(4)-C(5)	118.2(4)	C(15)-C(17)-O(1)	112.6(2)		
C(5)-C(6)-(7)	121.7(4)	O(1)-C(17)-O(2)	123.2(3)		
C(3)-C(8)-C(7)	120.1(3)	C(1)-C(19)-F(2)	112.3(2)		
C(7)-(8)-C(9)	128.6(3)	C(1)-C(19)-F(3)	112.1(2)		
C(1)-C(9)-C(10)	59.3(2)	F(2)-C(19)-F(3)	105.8(2)		
C(1)-C(10)-C(9)	56.8(2)				
C(9)-C(10)-C(11)	121.1(2)				
C(9)-C(10)-C(20)	114.0(2)				
C(10)-C(11)-C(12)	129.0(3)				
C(12)-C(11)-C(16)	120.6(3)				
C(12)-C(13)-C(14)	121.0(3)				
C(14)-C(15)-C(16)	118.6(3)				
C(2)-C(16)-C(15)	129.2(3)				
F(1)-C(17)-F(2)	109.9(3)				
F(2)-C(17)-F(3)	106.5(3)				
F(2)-C(17)-C(2)	112.8(3)				
O(1)-C(18)-O(2)	124.2(3)				
O(2)-C(18)-C(1)	111.7(2)				
O(3)-C(20)-C(10)	124.0(3)				

Methyl-8-trifluoromethyl-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-dien-1-carboxylate (**5**)

A solution containing 0.280 g (0.00079 mol) of **4** in 265 cm^3 of acetone was degassed with nitrogen and irradiated through a pyrex glass for 40 h. After evaporation of acetone an oily residue formed which crystallized from ethanol in the refrigerator. Recrystallization of the solidified product from ethanol gave colourless crystals of **5**; yield 51%; m. p. 88-89°C; MS (70 eV) *m/z* (rel. intensity): 330 (M^+, 47), 319 (33), 317 (12), 310 (25), 305 (21), 293 (54), 282 (13), 281 (99), 272 (18), 271 (100), 270 (27), 269 (62), 267 (15), 255 (24), 251 (34), 243 (64), 236 (10), 217 (12), 213 (11), 212 (12), 205 (23), 203 (13), 202 (72), 201 (10); found $M^+ = 330.0877$; calc. for $C_{19}H_8F_3O_2$: $M^+ = 330.0868$. For ^{1}H-NMR spectrum see Table 1.

X-Ray Crystal Structure Study

X-ray structure determinations of **3** and **5** were performed with a Nicolet R^{3}m/E crystallographic system using the Wyckoff scan routine. After Lorentz and polarisation correlations, the structures were solved by the SHELXTL 5.1 programs. All non-hydrogens atoms were refined anisotropically. The approximate location of all hydrogen atoms was determined by Fourier difference synthesis. In the final stages of refinement the hydrogen atoms were placed in calculated positions and allowed to ride with the atom to which they are attached. Bond lengths and valence angles for **3**–**5** are given in Table 3; additional experimental details of the structure determination are deposited at the Fachinformationszentrum Karlsruhe. Further X-ray crystallographic data details of the structure determination, tables of atome coordinates, anisotropic temperature factors, hydrogen coordinates with temperature factors and torsion angles along with computer generated plot with atom labels (15 pages), are available from the authors.

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