# **Reference Data**

## Substituent Effects on the <sup>13</sup>C NMR Spectra of Ethyl *cis-* and *trans-2-(p*substituted - phenyl) - 1 - cyclopropanecar boxylates

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KEY WORDS <sup>13</sup>C NMR Substituted cyclopropanes

#### **INTRODUCTION**

The direction of the influence of para substit-

uents for substituent-induced chemical shifts (SCS,  $\delta_x - \delta_H$ ) of C- $\beta$  in *para*-substituted cyclopropylbenzenes is normal (i.e. electronattracting groups such as NO<sub>2</sub> give a low-field shift), as for the SCS (C- $\beta$ ) of *para*-substituted styrenes, since the C--C bonds of cyclopropane have, to a higher or lower degree,  $\pi$ -bonding character.<sup>1-3</sup> The trend and the magnitude of SCS (C- $\beta$ ) vary, however, with replacement of the hydrogens on the cyclopropane ring with other groups.<sup>4-6</sup> We report here <sup>13</sup>C NMR chemical shift data for 28 geometric isomers of

# Table 1. Substituent-induced chemical shifts ( $\delta_x - \delta_H$ , ppm) for ethyl 2-(*p*-substituted-phenyl)-1-cyclopropanecarboxylates in chloroform- $d_1$

	Carbon									
Substituent	1	2	3	4	5	6	7	8	9	10
cis (A)										
Hª	0	0	0	0	0	0	0	0	0	0
	(21.81)	(25.45)	(11.10)	(170.89)	(60.13)	(14.00)	(136.50)	(127.78)	(129.20)	(126.53)
NH <sub>2</sub>	-0.11	-0.17	0	0.33	0	ь	ь	b	ь	ь
CH <sub>3</sub> O	-0.11	-0.57	0.12	0.06	-0.05	0.12	-8.03	2.39	-15.94	31.71
C₂H₅O	-0.11	-0.62	0.06	0.05	-0.05	0.07	-8.21	2.34	-15.37	31.0 <del>9</del>
CH3	-0.17	-0.28	0.06	0.05	-0.05	0.07	-3.14	0.74°	-0.11°	9.45
$C_2H_5$	-0.06	-0.22	0.06	0.05	-0.05	0.01	-2.85	0.46	-0.05	15.89
$CH(CH_3)_2$	0	-0.28	0	0.05	-0.11	~0.05	-2.68	1.37°	−3.35°	20.50
$C(CH_3)_3$	0	-0.39	0	0	-0.11	-0.11	-3.08	1.08	-4.49	22.77
F	-0.11	-0.78	0.23	-0.18	0.06	0.07	-4.27 <sup>d</sup>	2.94 <sup>d</sup>	-14.56 <sup>d</sup>	35.05 <sup>d</sup>
							3.43 <sup>e</sup>	7.71°	21.41°	245.80°
CI	0	-0.68	0.17	-0.23	0.12	0.07	-1.49	2.74	-1.30	5.81
Br	0	-0.57	0.17	-0.35	0.12	0.07	~0.97	3.13	1.71	-6.10
COOC <sub>2</sub> H <sub>5</sub>	0.34	-0.11	0.24	-0.51	0.12	0.12	5.46	1.42°	-0.16°	2.10
CN	0.46	-0.17	0.40	-0.63	0.29	0.07	5.75	2.22°	2.34°	-16.17
NO <sub>2</sub>	0.63	-0.34	0.74	-0.58	0.40	0.12	8.02	2.28	-6.20	19.93
trans (B)										
Hª	0	0	0	0	0	0	0	0	0	0
	(24.20)	(26.19)	(17.03)	(173.28)	(60.65)	(14.29)	(140.02)	(126.07)	(128.41)	(126.36)
$NH_2$	-0.51	-0.34	-0.46	2.39	-0.12	-0.05	b	1.14	-13.33	b
CH <sub>3</sub> O	-0.34	-0.56	-0.35	0.11	-0.12	-0.05	-8.02	1.20	-14.58	31.88
C <sub>2</sub> H <sub>5</sub> O	-0.34	-0.56	-0.35	0.11	-0.12	0	-8.20	1.14	-13.95	31.26
CH <sub>3</sub>	-0.17	-0.28	-0.17	0.06	-0.12	-0.05	-3.01	-0.06°	0.63°	9.56
$C_2H_5$	0.17	-0.22	-0.12	0.06	-0.12	-0.05	-2.78	0°	-0.57°	16.06
$CH(CH_3)_2$	-0.17	-0.22	-0.12	0.06	-0.06	0	-2.62	0.35°	−2.34°	20.73
$C(CH_3)_3$	-0.11	-0.39	-0.17	0	-0.18	-0.05	-3.02	−0.34°	-3.19°	22.94
F	-0.23	-0.79	-0.17	-0.17	0.05	-0.05	-4.37 <sup>d</sup>	1.63 <sup>d</sup>	-13.24 <sup>d</sup>	35.13ª
							3.43 <sup>e</sup>	7.71°	21.41°	244.94°
CI	-0.06	-0.74	-0.06	-0.29	0.11	-0.05	-1.48	1.43	0.06	5.75
Br	-0.06	-0.68	-0.12	-0.34	0.11	-0.05	-0.91	1.77	3.02	-6.32
COOC₂H₅	0.46	-0.22	0.45	-0.46	0.17	-0.05	5.42	-0.22	1.25	2.27
CN	0.68	-0.33	0.51	-0.85	0.33	-0.05	5.87	0.69	3.81	-16.32
NO <sub>2</sub>	0.91°	-0.51°	0.79	-0.92	0.39	-0.05	8.09	0.63	-4.73	20.16

<sup>a</sup> Values in parentheses are chemical shifts ( $\delta$ ) in ppm from internal TMS.

<sup>b</sup> Assignments were impossible because of contamination by impurities.

<sup>c</sup> Assignments may be exchangeable.

<sup>d</sup> Centre of doublet.

• "J(C,F).

# **Reference Data**

ethyl 2-(p-substituted-phenyl)-1-cyclopropanecarboxylate (cis, A; trans, B).



#### **RESULTS AND DISCUSSION**

The <sup>13</sup>C NMR chemical shift data for series A and B are given in Table 1.

The assignments of the most of the <sup>13</sup>C signals were made by comparison of the measured chemical shifts with those reported for para-disubstituted benzenes<sup>2</sup> and substituted cyclopropylbenzenes.<sup>7</sup> The signals of C-1, C-2, C-3 and C-4 exhibit upfield shifts on going from the trans to the cis configuration. SCS(C-1, C-2, C-3 and C-4) for B are larger than the corresponding SCS(C-1, C-2, C-3 and C-4) for A. These phenomena arise from the repulsive interaction between the ortho hydrogen and the ethoxycarbonyl group, and from the subsequent deceleration of the overlapping of the  $\pi$  bonds of the phenyl and carbonyl groups with the C-C bonds of cyclopropane ring in A.8



The SCS(C-1 and C-3) trends are normal, whereas the magnitudes are smaller than those observed for the  $SCS(C-\beta)$  of parasubstituted cyclopropylbenzenes owing to a decrease in the polarizability of the C-1-C-2 and the C-2-C-3 bonds.5 SCS(C-2) is normal for electron-donating groups and for the *a*-carbons of *para*-substituted cyclopropylbenzenes and isopropylbenzenes.1 For electron-accepting groups, however, SCS(C-2) has an inverse trend compared with the

### Total Assignment of the <sup>1</sup>H and <sup>13</sup>C Spectra of Peridinin

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a-carbons of para-substituted cyclopropylbenzenes and isopropylbenzenes.<sup>1</sup> SCS(C-4) also has an inverse trend, which is the same as that observed for the carbonyl carbons of 2-substituted 1-cyclopropanecarboxylates.9,10

### **EXPERIMENTAL**

2-(p-Substituted-phenyl)-1-cyclopropanecarboxylates were synthesized by the reaction of para-substituted styrenes with ethyl diazoacetate in the presence of palladium(II) acetate.11 The geometric isomers were obtained by the method described in the literature.11 The boiling and melting points of the esters thus obtained were as follows [substituent, b.p. (°C)/mmHg) or m.p. (°C)]: H(cis), 98-99/3; H(trans), 99/2.5, 33; CH<sub>3</sub>(cis), 103/2; CH<sub>3</sub>(trans), 113/2.5; C<sub>2</sub>H<sub>5</sub>(cis), 117-118/4;  $C_2H_5(trans)$ , 137/4;  $(CH_3)_2CH(cis)$ , 127/4; (CH<sub>3</sub>)<sub>2</sub>CH(trans), 128-131/3; (CH<sub>3</sub>)<sub>3</sub>C(cis), 122/2; (CH<sub>3</sub>)<sub>3</sub>C(trans), 138/3; F(cis), 126-129/10; F(trans), 132/10; Cl(cis), 110-113/2; Cl(trans), 125/3; Br(cis), 128-130/ 3; Br(trans), 133-138/3; CH<sub>3</sub>O(cis), 125-129/ 3; CH<sub>3</sub>O(trans), 83; C<sub>2</sub>H<sub>5</sub>O(cis), 135/7; C<sub>2</sub>H<sub>5</sub>O(*trans*), 83; NO<sub>2</sub>(*cis*), 153–155/2; NO<sub>2</sub>(trans), 155-158/1.5.

Ethyl 2-(p-cyanophenyl)-1-cyclopropanecarboxylate was prepared by the reaction of 2-(p-bromophenyl)-1-cyclopropaneethvl carboxylate with copper(I) cyanide in pyridine. The p-ethoxycarbonyl derivative was obtained by the esterification of the corresponding dicarboxylic acid, itself prepared by the hydration of ethyl 2-(p-cyanophenyl)-1cyclopropanecarboxylate. Ethyl 2-(p-aminophenyl)-1-cyclopropanecarboxylate was obtained by the reduction of the corresponding ethvl 2-(p-nitrophenyl)-1-cyclopropanecarboxylate using sodium sulphide and sulphur in aqueous ethanol. The boiling and melting points of these esters were as follows [substituent, b.p. (°C/mmHg) or m.p. (°C)]: CN(cis), 140-145/2; CN(trans), 150/2;C<sub>2</sub>H<sub>5</sub>OCO(cis), 160/3; C<sub>2</sub>H<sub>5</sub>OCO(trans), 160/2.5; NH<sub>2</sub>(cis), 165/3, 45; NH<sub>2</sub>(trans), 69-70.

Typically, <sup>13</sup>C NMR spectra were recorded

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Complete <sup>1</sup>H and <sup>13</sup>C spectral assignments are reported for peridinin, the major dino-

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for ca 100 mg of A or B in 2 ml of CDCl<sub>3</sub> using a 10 mm sample tube at 28 °C on a JEOL FX 60Q spectrometer; broadband decoupled spectra were obtained from 3000 transients using 8K memory points, 3.5 kHz spectral width, a flip angle of  $45^{\circ}$  (5 µs) and a pulse interval of 5 s. The chemical shifts were measured relative to internal TMS. The reproducibility was at least  $\pm 0.1$  ppm.

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flagellate carotenoid responsible for 'red tides' in the ocean. These assignments were made with the aid of HETCOR, FLOCK and COSY 2D spectra and NOE difference spectra.

KEY WORDS <sup>1</sup>H NMR <sup>13</sup>C NMR Total spectral assignment Peridinin

#### **INTRODUCTION**

Peridinin, the major dinoflagellate carot-