

**An Evidence of the Substituent Induced Electronic Interplay. The Effect of the Remote Aromatic Ring Substituent of Phenyl Benzoates on the Sensitivity of the Carbonyl Unit to Electronic Effects of Phenyl or Benzoyl Ring Substituents.**

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**Melting point range and  $^{13}\text{C}$  NMR data (125.78 MHz,  $\text{CDCl}_3$ ) for the prepared substituted phenyl benzoates**

**4-nitrophenyl 4-nitrobenzoate (1a):** mp 156.5–157.5 °C (lit.<sup>1,2</sup> 158.5–159.5 °C),  $^{13}\text{C}$  NMR  $\delta$  162.5, 155.1, 151.2, 145.8, 133.9, 131.5, 125.5, 123.9, 122.5.

**4-cyanophenyl 4-nitrobenzoate (1b):** mp 190.5–191.5 °C (lit.<sup>2</sup> 189–191 °C),  $^{13}\text{C}$  NMR  $\delta$  162.5, 153.6, 151.2, 134.0, 133.9, 131.5, 123.9, 122.7, 118.0, 110.5.

**4-chlorophenyl 4-nitrobenzoate (1c):** mp 171.5–172.5 °C (lit.<sup>1</sup> 171–172 °C; lit.<sup>2</sup> 171.5–172.5 °C),  $^{13}\text{C}$  NMR  $\delta$  163.1, 151.0, 148.9, 134.6, 131.9, 131.3, 129.8, 123.8, 122.8.

**4-bromophenyl 4-nitrobenzoate (1d):** mp 183–184 °C,  $^{13}\text{C}$  NMR  $\delta$  163.0, 151.0, 149.5, 134.5, 132.7, 131.3, 123.8, 123.2, 119.6.

**phenyl 4-nitrobenzoate (1e):** mp 127.5–128.0 °C (lit.<sup>1,2</sup> 128–129 °C),  $^{13}\text{C}$  NMR  $\delta$  163.3, 150.9, 150.5, 135.0, 131.3, 129.7, 126.4, 123.7, 121.4.

**4-methylphenyl 4-nitrobenzoate (1f):** mp 98–99 °C (lit.<sup>1</sup> 98–99 °C),  $^{13}\text{C}$  NMR  $\delta$  163.5, 150.9, 148.3, 136.1, 135.1, 131.3, 130.2, 123.7, 121.06, 20.9.

**4-methoxyphenyl 4-nitrobenzoate (1g):** 114.0–114.5 °C (lit.<sup>3</sup> 114 °C),  $^{13}\text{C}$  NMR  $\delta$  163.7, 157.7, 150.9, 144.0, 135.1, 131.3, 123.7, 122.2, 114.7, 55.7.

**4-nitrophenyl 4-chlorobenzoate (2a):** 134.5–135.0 °C (lit.<sup>1</sup> 137–138.5 °C; lit.<sup>2</sup> 138–139 °C),  $^{13}\text{C}$  NMR  $\delta$  163.4, 155.5, 145.5, 140.9, 131.7, 129.2, 126.9, 125.3, 122.6.

**4-cyanophenyl 4-chlorobenzoate (2b):** 115–116 °C,  $^{13}\text{C}$  NMR  $\delta$  163.5, 154.0, 140.8, 133.8, 131.6, 129.2, 127.1, 122.8, 118.2, 110.0.

**4-chlorophenyl 4-chlorobenzoate (2c):** 96.5–96.0 °C (lit.<sup>4</sup> 96 °C, lit.<sup>1</sup> 96–96.5 °C),  $^{13}\text{C}$  NMR  $\delta$  164.1, 149.2, 140.4, 131.5, 131.6, 129.6, 129.0, 127.6, 123.0.

**4-bromophenyl 4-chlorobenzoate (2d):** mp 102–104 °C (lit.<sup>5</sup> 100–104 °C; lit.<sup>6</sup> 105–106 °C),  $^{13}\text{C}$  NMR  $\delta$  164.0, 149.8, 140.4, 132.6, 131.6, 129.0, 127.6, 123.4, 119.2.

**phenyl 4-chlorobenzoate (2e):** mp 103–104 °C (lit.<sup>1</sup> 103.5–104.5; lit.<sup>5</sup> 100.5–101.5 °C),  $^{13}\text{C}$  NMR  $\delta$  164.3, 150.8, 140.2, 131.5, 129.5, 129.0, 128.0, 126.0, 121.6.

**4-methylphenyl 4-chlorobenzoate (2f):** mp 96.0–96.5 °C (lit.<sup>1</sup> 97.5–98.5 °C; lit.<sup>4</sup> 98 °C),  $^{13}\text{C}$  NMR  $\delta$  164.5, 148.5, 140.0, 135.7, 131.5, 130.1, 128.9, 128.1, 121.3, 20.9.

**4-methoxyphenyl 4-chlorobenzoate (2g)**: mp 101–102 °C,  $^{13}\text{C}$  NMR  $\delta$  164.7, 157.4, 144.2, 140.0, 131.5, 128.9, 128.1, 122.4, 114.6, 55.6.

**4-nitrophenyl benzoate (3a)**: mp 118.5–119 °C (lit.<sup>1,2</sup> 142–143 °C; lit.<sup>4</sup> 142 °C)  $^{13}\text{C}$  NMR  $\delta$  164.2, 155.7, 145.4, 134.3, 130.3, 128.8, 128.5, 125.3, 122.6.

**4-cyanophenyl benzoate (3b)**: mp 91.0–91.5 °C (lit.<sup>7</sup> 91–92 °C),  $^{13}\text{C}$  NMR  $\delta$  164.3, 154.3, 134.2, 133.7, 130.3, 128.8, 128.7, 122.9, 118.3, 109.8.

**4-chlorophenyl benzoate (3c)**: mp 88 – 89 °C (lit.<sup>1</sup> 88–89 °C; lit.<sup>7</sup> 88–90 °C),  $^{13}\text{C}$  NMR  $\delta$  164.9, 149.4, 133.8, 131.3, 130.2, 129.5, 129.2, 128.6, 123.1.

**4-bromophenyl benzoate (3d)**: mp 92 – 93 °C (lit.<sup>5</sup> 104–106 °C),  $^{13}\text{C}$  NMR  $\delta$  164.9, 150.0, 133.8, 132.5, 130.2, 129.2, 128.6, 123.5, 119.0.

**phenyl benzoate (3e)**: mp 69–70 °C (lit.<sup>7</sup> 69–70 °C),  $^{13}\text{C}$  NMR  $\delta$  165.2, 151.0, 133.6, 130.2, 129.5, 129.6, 128.6, 125.9, 121.7.

**4-methylphenyl benzoate (3f)**: mp 71–72 °C (lit.<sup>1</sup> 70.4–71.2 °C; lit.<sup>5</sup> 70–71 °C),  $^{13}\text{C}$  NMR  $\delta$  165.4, 148.7, 135.5, 133.5, 130.2, 130.0, 129.7, 128.5, 121.4, 20.9.

**4-methoxyphenyl benzoate (3g)**: mp 87–88 °C (lit.<sup>5</sup> 84–86 °C),  $^{13}\text{C}$  NMR  $\delta$  165.6, 157.3, 144.4, 133.5, 130.1, 129.7, 128.5, 122.5, 114.5, 55.6.

**4-nitrophenyl 4-methylbenzoate (4a)**: mp 118.5–119.5 °C (lit.<sup>1</sup> 120.3–121.3 °C; lit.<sup>2</sup> 119.5–120 °C),  $^{13}\text{C}$  NMR  $\delta$  164.3, 155.9, 145.33, 145.28, 130.4, 129.5, 125.8, 125.2, 122.7, 21.8.

**4-cyanophenyl 4-methylbenzoate (4b)**: mp 142–143 °C,  $^{13}\text{C}$  NMR  $\delta$  164.4, 154.4, 145.2, 133.7, 130.3, 129.5, 125.9, 123.0, 118.3, 109.7, 21.8.

**4-chlorophenyl 4-methylbenzoate (4c)**: mp 89–90 °C (lit.<sup>1</sup> 89.2–90.7 °C; lit.<sup>4</sup> 91 °C),  $^{13}\text{C}$  NMR  $\delta$  165.0, 149.5, 144.7, 131.2, 130.2, 129.5, 129.4, 126.4, 123.2, 21.8.

**4-bromophenyl 4-methylbenzoate (4d)**: mp 103–104 °C (lit.<sup>5</sup> 94–98 °C),  $^{13}\text{C}$  NMR  $\delta$  164.9, 150.0, 144.7, 132.5, 130.2, 129.4, 126.4, 123.6, 118.9, 21.8.

**phenyl 4-methylbenzoate (4e)**: mp 72.5–73.0 °C (lit.<sup>1</sup> 75–76.5 °C; lit.<sup>5</sup> 70.5–72.5 °C),  $^{13}\text{C}$  NMR  $\delta$  165.3, 151.0, 144.4, 130.2, 129.5, 129.3, 126.8, 125.8, 121.8, 21.8.

- 4-methylphenyl 4-methylbenzoate (4f):** mp 89.0–89.5 °C (lit.<sup>1</sup> 89.0–90.5 °C), <sup>13</sup>C NMR δ 165.4, 148.8, 144.3, 135.4, 130.2, 130.0, 129.2, 126.9, 121.4, 21.7, 20.9.
- 4-methoxyphenyl 4-methylbenzoate (4g):** mp 93–94 °C (lit.<sup>9</sup> 93–95 °C), <sup>13</sup>C NMR δ 165.6, 157.3, 144.5, 144.3, 130.2, 129.3, 126.9, 122.5, 114.5, 55.6, 21.8.
- 4-nitrophenyl 4-methoxybenzoate (5a):** mp 164.5–165.5 °C (lit.<sup>7</sup> 164–165 °C; lit.<sup>2</sup> 165–166 °C), <sup>13</sup>C NMR δ 164.4, 163.9, 155.9, 145.3, 132.5, 125.2, 122.7, 120.7, 114.1, 55.6.
- 4-cyanophenyl 4-methoxybenzoate (5b):** mp 109–110 °C, <sup>13</sup>C NMR δ 164.3, 164.1, 154.4, 133.7, 132.5, 123.0, 120.9, 118.4, 114.0, 109.6, 55.6.
- 4-chlorophenyl 4-methoxybenzoate (5c):** mp 92.5–93.0 °C (lit.<sup>2</sup> 91.5–92.5 °C), <sup>13</sup>C NMR δ 164.7, 164.1, 149.5, 132.4, 131.1, 129.5, 123.2, 121.5, 113.9, 55.5.
- 4-bromophenyl 4-methoxybenzoate (5d):** mp 104–105 °C (lit.<sup>5</sup> 103–104.5 °C), <sup>13</sup>C NMR δ 164.6, 164.1, 150.1, 132.5, 132.3, 123.6, 121.4, 118.8, 113.9, 55.5.
- phenyl 4-methoxybenzoate(5e):** mp 72–73 °C (lit.<sup>5</sup> 67.5–69 °C; lit.<sup>8</sup> 73.6 °C), <sup>13</sup>C NMR δ 164.9, 163.9, 151.1, 132.3, 129.4, 125.7, 121.9, 121.8, 113.8, 55.5.
- 4-methylphenyl 4-methoxybenzoate (5f):** mp 66–67 °C (lit.<sup>8</sup> 66.9 °C), <sup>13</sup>C NMR δ 165.1, 163.8, 148.8, 135.3, 132.3, 129.9, 122.0, 121.5, 113.8, 55.5, 20.9.
- 4-methoxyphenyl 4-methoxybenzoate (5g):** mp 124.0–124.5 °C, <sup>13</sup>C NMR δ 165.3, 163.8, 157.2, 144.5, 132.2, 122.5, 122.0, 114.5, 113.8, 55.6, 55.5.
- 4-nitrophenyl 4-dimethylaminobenzoate (6a):** mp 195–197 °C (dec.) (lit.<sup>1</sup> 195–196.5 °C), <sup>13</sup>C NMR δ 164.4, 156.4, 154.1, 145.0, 132.2, 125.1, 122.7, 114.6, 110.8, 40.1.
- 4-cyanophenyl 4-dimethylaminobenzoate (6b):** mp 152–153 °C, <sup>13</sup>C NMR δ 164.6, 154.9, 154.0, 133.6, 132.2, 123.1, 118.6, 114.7, 110.8, 109.1, 40.1.
- 4-chlorophenyl 4-dimethylaminobenzoate (6c):** mp 134–135 °C, <sup>13</sup>C NMR δ 165.2, 153.8, 149.9, 132.0, 130.7, 129.3, 123.4, 115.4, 110.8, 40.0.
- 4-bromophenyl 4-dimethylaminobenzoate (6d):** mp 142.5–143.5 °C, <sup>13</sup>C NMR δ 165.2, 153.8, 150.4, 132.3, 132.0, 123.8, 118.4, 115.4, 110.7, 40.0.
- phenyl 4-dimethylaminobenzoate (6e):** mp 179.5–180.5 °C (lit.<sup>1</sup> 180–181 °C), <sup>13</sup>C NMR δ 165.5, 153.7, 151.4, 132.0, 129.3, 125.4, 122.0, 116.0, 110.8, 40.1.

**4-methylphenyl 4-dimethylaminobenzoate (6f):** mp 160–161 °C (dec.) (lit.<sup>1</sup> 160–161 °C), <sup>13</sup>C NMR  $\delta$  165.7, 153.7, 149.1, 134.9, 131.9, 129.8, 121.6, 116.1, 110.7, 40.1, 20.9.

**4-methoxyphenyl 4-dimethylaminobenzoate (6g):** mp 173.0–173.5 °C, <sup>13</sup>C NMR  $\delta$  165.9, 157.0, 153.7, 144.8, 131.9, 122.7, 116.1, 114.4, 110.7, 55.6, 40.1.

### $\sigma$ , $\sigma_F$ and $\sigma_R$ values used in the correlations

Substituent	$\sigma^a$	$\sigma_F^b$	$\sigma_R^b$
NO <sub>2</sub>	0.78	0.65	0.18
CN	0.66	0.60	0.10
Cl	0.23	0.45	-0.17
Br	0.23	0.45	-0.16
H	0	0	0
Me	-0.17	0	-0.08
OMe	-0.27	0.25	-0.42
NMe <sub>2</sub>	-0.83	0.10	-0.64

<sup>a</sup>Ref. 10. <sup>b</sup>Ref. 11, except for Br ref. 10.

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