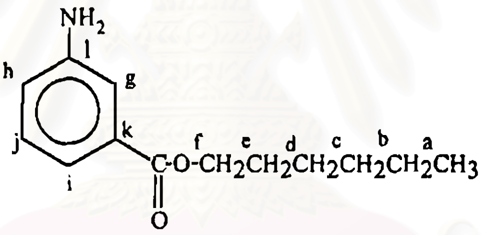
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization and physical properties

4.1.1 Characterization of hexyl-3-aminobenzoate

Hexyl-3-aminobenzoate prepared from esterification of 3-aminobenzoic acid with 1-hexanol was a dark brown liquid, insoluble in water, soluble in methanol, chloroform and toluene. The yield of product was 69%. The structure was shown below.



Structure of hexyl-3-aminobenzoate

The FT-IR spectrum of hexyl-3-aminobenzoate (Fig.4-1) could be assigned as shown in Table 4-1. Its FT-IR spectrum showed the important absorptions at 3466, 3376 cm^{-1} (N-H stretching vibration of primary amine), 2956 - 2858 cm^{-1} (C-H stretching vibration of aliphatic), 1708 cm^{-1} (C=O stretching vibration of ester), 1606,1589,1492 and 1462cm^{-1}(C=C stretching vibration of aromatic), 1290 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1240, 1105cm^{-1}(C-O-C stretching vibration).

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Table 4-1 The FT-IR absorption band assignments of hexyl-3-aminobenzoate

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3466, 3376	w, m	N-H stretching vibration of primary amine
2956 - 2858	m-s	C-H stretching vibration of aliphatic
1708	v.s.	C=O stretching vibration of ester
1624	m	N-H in-plane bending
1606, 1589,1492,1462	m	C=C stretching vibration of aromatic
1291	s	C-N stretching vibration of primary amine
1240, 1105	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-2) could be assigned as shown in Table 4-2. Its spectrum showed carbon signals which one carbon signal at 13.9 ppm belonged to -$\underline{C}H_3$, five methylene carbons at 22.5, 25.6, 28.6, 31.4 and 65.0 ppm, six aromatic carbons at 115.7,119.2,119.6,129.1, 131.4 and 146.4 ppm. The last signal at 166.8 ppm was carbonyl carbon.

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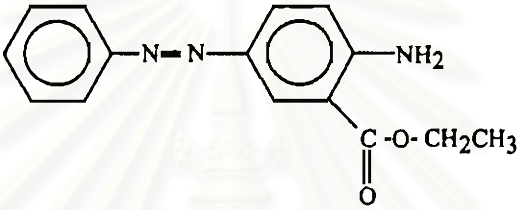
Table 4-2 The ^{13}C- NMR spectrum assignments of hexyl-3-aminobenzoate

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	13.9	h	119.2
b	22.5	i	119.6
c	25.6	j	129.1
d	28.6	k	131.4
e	31.4	l	146.4
f	65.0	m	166.8
g	115.7	--	--

The ^{1}H- NMR spectrum (Fig.4-3) showed the signals at 0.87-1.72 ppm, which were the signals of methyl and methylene protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the triplet at 4.25 ppm. The protons of amino group showed the signal at 3.37 ppm and the signals at 6.80-7.40 ppm belonged to aromatic protons. Additional signals at 3.09 and 3.60 ppm were from excess alcohol.

4.1.2 Characterization of ethyl-2-aminobenzoate phenyl azo

Ethyl-2-aminobenzoate phenyl azo prepared from coupling reaction of aniline diazonium salt and ethyl-2-aminobenzoate was a reddish-brown liquid, insoluble in water, soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate phenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate phenyl azo (Fig.4-4) could be assigned as shown in Table 4-3. Its FT-IR spectrum showed the important absorptions at 3481, 3372 cm^{-1} (N-H stretching vibration of primary amine), 2981 cm^{-1} (C-H stretching vibration of aliphatic), 1689 cm^{-1} (C=O stretching vibration of ester), 1616 cm^{-1} (N=N stretching vibration of azo compound), 1588, 1488 and1454 cm^{-1} (C=C stretching vibration of aromatic), 1293 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1246, 1103 cm^{-1}(C-O-C stretching vibration).

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Table 4-3 The FT-IR -absorption band assignments of ethyl-2-aminobenzoate-phenyl azo

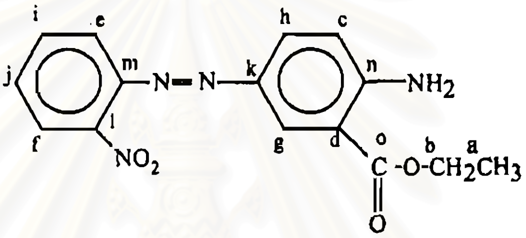
Frequency (cm^{-1})	Peak intensity	Tentative assignments
3481, 3372	m	N-H stretching vibration of primary amine
2981	w	C-H stretching vibration of aliphatic
1689	s	C=O stretching vibration of ester
1616	s	N=N stretching vibration
1588, 1487, 1454	m	C=C stretching vibration of aromatic
1293	s	C-N stretching vibration of primary amine
1246,1103	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-5) showed carbon signals which one signal at 14.3 ppm belonged to methyl carbon, one methylene carbon at 60.2 ppm, the aromatic carbon signals at 111.0, 116.1, 116.6, 122.3, 131.1, 133.9 and 150.4 ppm. The last carbon signal at 168.1 ppm was carbonyl carbon.

The ^{1}H- NMR spectrum (Fig.4-6) showed the triplet at 1.37 ppm, which was the signal of methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet at 4.32 ppm. The protons of amino group showed the singlet at 5.72 ppm and the signals at 6.61-7.88 ppm belonged to aromatic protons.

4.1.3 Characterization of ethyl-2-aminobenzoate-2-nitrophenyl azo

Ethyl-2-aminobenzoate-2-nitrophenyl azo prepared from coupling reaction of o-nitroaniline diazonium salt and ethyl-2-aminobenzoate was a yellow solid. It was recrystallized from hot acetone to give a yellow crystal with a m.p. of 147-148 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-2-nitrophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-2-nitrophenyl azo (Fig.4-7) could be assigned as shown in Table 4-4. Its FT-IR spectrum showed the important absorptions at 3216 cm^{-1} (N-H stretching vibration of primary amine), 2985 cm^{-1} (C-H stretching vibration of aliphatic), 1682 cm^{-1} (C=O stretching vibration of ester), 1604, 1586, 1505 and 1442 cm^{-1} (C=C stretching vibration of aromatic), 1535 and 1364 cm^{-1} (N =O stretching vibration of nitro compound) and 1261, 1159 cm^{-1}(C-O-C stretching vibration).

Table 4-4 The FT-IR -absorption band assignments of ethyl-2-aminobenzoate-2-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3216	m	N-H stretching vibration of primary amine
2985	w	C-H stretching vibration of aliphatic
1682	s	C=O stretching vibration of ester
1604, 1586,1505, 1442	w-s	C=C stretching vibration of aromatic
1535, 1364	m	N=O stretching vibration of nitro compound
1318	m	C-N stretching vibration of primary amine
1261,1159	v.s., s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-8) could be assigned as shown in Table 4-5. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.4 ppm and aromatic carbons at 114.8, 118.5, 120.9, 122.3, 123.9, 127.3, 129.3, 131.2, 132.5, 134.4, 143.2 and 146.1 ppm. The last signal at 167.2 ppm was carbonyl carbon.

Table 4-5 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-2-nitrophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	i	129.3
b	61.4	j	131.2
c	114.8	k	132.5
d	118.5	l	134.4
e	120.9	m	143.2
f	122.3	n	146.1
g	123.9	o	167.2
h	127.3	---	---

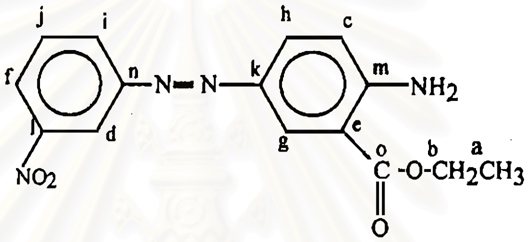
The ^{1}H- NMR spectrum (Fig.4-9) showed the triplet at 1.39 ppm, belonged to methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet at 4.38 ppm. The protons of amino group showed the singlet at 5.60 ppm and the signals at 7.09-7.99 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	57.88	4.19	17.52
Calculation	57.32	4.46	17.83
% Different	0.56	0.27	0.31

4.1.4 Characterization of ethyl-2-aminobenzoate-3-nitrophenyl azo

Ethyl-2-aminobenzoate-3-nitrophenyl azo prepared from coupling reaction of m-nitroaniline diazonium salt and ethyl-2-aminobenzoate was a yellow solid. It was recrystallized from hot acetone to give a yellow crystal with a m.p. of 130-131 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-3-nitrophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-3-nitrophenyl azo (Fig.4-10) could be assigned as shown in Table 4-6. Its FT-IR spectrum showed the important absorptions at 3226 cm^{-1} (N-H stretching vibration of primary amine), 3096 cm^{-1} (C-H stretching vibration of aromatic), 2981 cm^{-1} (C-H stretching vibration of aliphatic), 1684 cm^{-1} (C=O stretching vibration of ester), 1604, 1585, 1505 and 1456 cm^{-1} (C=C stretching vibration of aromatic), 1523 and 1344 cm^{-1} (N =O stretching vibration of nitro compound) and 1258, 1172 cm^{-1} (C-O-C stretching vibration).

Table 4-6 The FT-IR –absorption band assignments of ethyl-2-aminobenzoate-3-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3226	m	N-H stretching vibration of primary amine
3096	w	C-H stretching vibration of aromatic
2981	w	C-H stretching vibration of aliphatic
1684	v.s.	C=O stretching vibration of ester
1604, 1585,1505, 1456	w-v.s.	C=C stretching vibration of aromatic
1523, 1344	s	N=O stretching vibration of nitro compound
1258, 1172	v.s., s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-11) could be assigned as shown in Table 4-7. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.4 ppm and aromatic carbons at 112.9, 114.7, 115.7, 121.8, 122.1, 128.2, 129.8, 131.2, 134.6, 143.2 149.0 and 150.7 ppm. The last carbon signal at 167.3 ppm was carbonyl carbon.

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Table 4-7 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-3-nitrophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	i	129.8
b	61.4	j	131.2
c	112.9	k	134.6
d	114.7	l	143.2
e	115.7	m	149.0
f	121.8	n	150.7
g	122.1	o	167.3
h	128.2	---	---

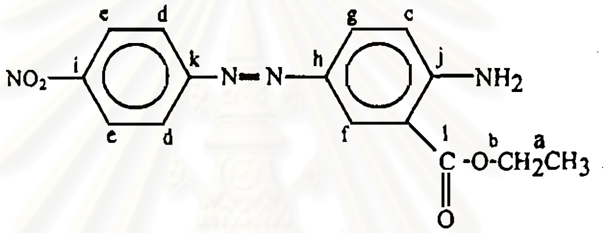
The ^{1}H- NMR spectrum (Fig.4-12) showed the triplet at 1.42 ppm, which was the signal of methyl protons. The methylene protons attached to ester (C$\underline{H}_2$-O) appeared as the quartet 4.39 ppm. The signals at 7.06-8.42 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	57.40	4.40	17.81
Calculation	57.32	4.46	17.83
% Different	0.08	0.06	0.02

4.1.5 Characterization of ethyl-2-aminobenzoate-4-nitrophenyl azo

Ethyl-2-aminobenzoate-4-nitrophenyl azo prepared from coupling reaction of p-nitroaniline diazonium salt and ethyl-2-aminobenzoate was an orange solid. It was recrystallized from hot acetone to give a yellow crystal with a m.p. of 154-155 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-4-nitrophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-4-nitrophenyl azo (Fig. 4-13) could be assigned as shown in Table 4-8. Its FT-IR spectrum showed the important absorptions at 3238 cm^{-1}(N-H stretching vibration of primary amine), 3078 cm^{-1} (C-H stretching vibration of aromatic), 2983 cm^{-1} (C-H stretching vibration of aliphatic), 1684 cm^{-1} (C=O stretching vibration of ester), 1605, 1584, 1504 and 1458 cm^{-1} (C=C stretching vibration of aromatic), 1515 and 1341cm^{-1} (N =O stretching vibration of nitro compound) and 1268, 1160 cm^{-1}(C-O-C stretching vibration).

Table 4-8 The FT-IR - absorption band assignments of ethyl-2-aminobenzoate-4-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3238	m	N-H stretching vibration of primary amine
3078	w	C-H stretching vibration of aromatic
2983	w	C-H stretching vibration of aliphatic
1684	s	C=O stretching vibration of ester
1605, 1584,1504, 1458	w-s	C=C stretching vibration of aromatic
1515, 1341	s, v.s.	N=Ostretching vibration of nitro compound
1268, 1160	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-14) could be assigned as shown in Table 4-9. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.5 ppm and aromatic carbons at 113.1, 114.7, 121.9, 122.4, 124.7, 131.2, 134.4, 142.8, 146.3 and 154.3 ppm. The last carbon signal at 167.2 ppm was carbonyl carbon.

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Table 4-9 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-4-nitrophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	h	131.2
b	61.5	i	134.4
c	113.1	j	142.8
d	114.7	k	146.3
e	121.9	l	154.2
f	122.4	m	167.2
g	124.7	---	---

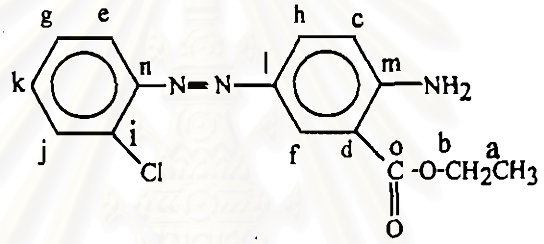
The ^{1}H- NMR spectrum (Fig.4-15) showed the triplet at 1.41 ppm, which belonged to methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet 4.39 ppm. The signals at 7.06-8.24 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	56.61	4.46	17.49
Calculation	57.32	4.46	17.83
% Different	0.71	0.00	0.34

4.1.6 Characterization of ethyl-2-aminobenzoate-2-chlorophenyl azo

Ethyl-2-aminobenzoate-2-chlorophenyl azo prepared from coupling reaction of 2-chloroaniline diazonium salt and ethyl-2-aminobenzoate was a yellow solid. It was recrystallized from hot acetone to give a yellow crystal with a m.p. of 121-122 °C. It was soluble in chloroform, toluene and partly soluble in xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-2-chlorophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-2-chlorophenyl azo (Fig.4-16) could be assigned as shown in Table 4-10. Its FT-IR spectrum showed the important absorptions at 3249 cm^{-1}(N-H stretching vibration of primary amine), 3070 cm^{-1} (C-H stretching vibration of aromatic), 2989 cm^{-1} (C-H stretching vibration of aliphatic), 1694 cm^{-1} (C=O stretching vibration of ester), 1604, 1584, 1512 and 1461 cm^{-1} (C=C stretching vibration of aromatic) and 1266, 1170 cm^{-1}(C-O-C stretching vibration).

Table 4-10 The FT-IR–absorption band assignments of ethyl-2-aminobenzoate-2-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3249	m	N-H stretching vibration of primary amine
3070	w	C-H stretching vibration of aromatic
2989	w	C-H stretching vibration of aliphatic
1694	v.s.	C=O stretching vibration of ester
1604, 1584,1512, 1461	w-m	C=C stretching vibration of aromatic
1266, 1170	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-17) could be assigned as shown in Table 4-11. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.3 ppm and aromatic carbons at 114.6,117.6, 121.6, 125.5, 127.2, 128.3, 130.4, 131.1, 134.3, 143.5,146.1 and 153.2 ppm. The last carbon signal at 167.2 ppm was carbonyl carbon.

Table 4-11 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-2-chlorophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	i	130.4
b	61.3	j	131.1
c	114.6	k	134.3
d	117.6	l	143.5
e	121.6	m	146.1
f	125.5	n	153.2
g	127.2	o	167.2
h	128.3	--	--

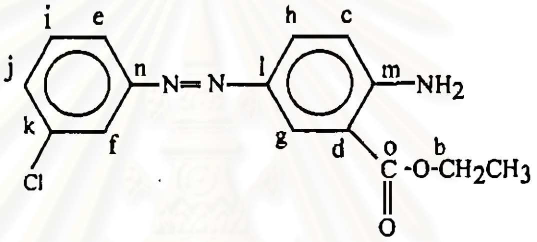
The ^{1}H- NMR spectrum (Fig.4-18) showed the triplet at 1.40 ppm, which belonged to methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet 4.38 ppm. The signals at 7.02-8.56 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	60.10	4.97	12.89
Calculation	59.31	4.61	13.84
% Different	0.79	0.36	0.95

4.1.7 Characterization of Ethyl-2-aminobenzoate-3-chlorophenyl azo

Ethyl-2-aminobenzoate-3-chlorophenyl azo prepared from coupling reaction of 3-chloroaniline diazonium salt and ethyl-2-aminobenzoate was a yellow solid. It was recrystallized from hot acetone to give an orange crystal with a m.p. of 100-101 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-3-chlorophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-3-chlorophenyl azo (Fig.4-19) could be assigned as shown in Table 4-12. Its FT-IR spectrum showed the important absorptions at 3224 cm^{-1}(N-H stretching vibration of primary amine), 3055 cm^{-1} (C-H stretching vibration of aromatic), 2991 cm^{-1}(C-H stretching vibration of aliphatic), 1683 cm^{-1} (C=O stretching vibration of ester), 1603, 1583, 1502 and 1452cm^{-1} (C=C stretching vibration of aromatic) and 1265, 1158 cm^{-1}(C-O-C stretching vibration).

Table 4-12 The FT-IR -absorption band assignments of ethyl-2-aminobenzoate-3-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3224	m	N-H stretching vibration of primary amine
3055	w	C-H stretching vibration of aromatic
2991	w	C-H stretching vibration of aliphatic
1683	s	C=O stretching vibration of ester
1603, 1583, 1502, 1452	m-s	C=C stretching vibration of aromatic
1265, 1158	v.s.	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-20) could be assigned as shown in Table 4-13. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.3 ppm and aromatic carbons at 112.4, 114.5, 120.7, 120.9, 121.4, 127.5, 130.0, 131.1, 134.4, 134.8, 143.5 and 150.8 ppm. The last carbon signal at 167.3 ppm was carbonyl carbon.

Table 4-13 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-3-chlorophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	i	130.0
b	61.3	j	131.1
c	112.4	k	134.4
d	114.5	l	134.8
e	120.7	m	143.5
f	120.9	n	150.8
g	121.4	o	167.3
h	127.5	--	--

The ^{1}H- NMR spectrum (Fig.4-21) showed the triplet at 1.40 ppm, which belonged to methyl protons. The methylene protons attached to ester (C$\underline{H}_2$-O) appeared as the quartet 4.38 ppm. The signals at 7.01-8.02 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	60.18	4.28	13.23
Calculation	59.31	4.61	13.84
% Different	0.87	0.33	0.61

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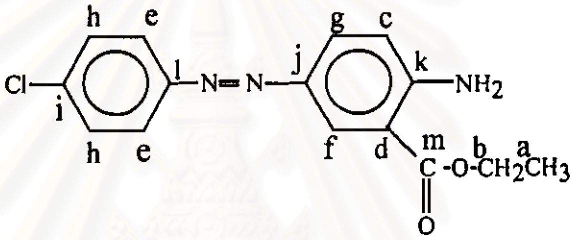
4.1.8 Characterization of ethyl-2-aminobenzoate-4-chlorophenyl azo

Ethyl-2-aminobenzoate-4-chlorophenyl azo prepared from coupling reaction of 4-chloroaniline diazonium salt and ethyl-2-aminobenzoate was a yellow solid. It was recrystallized from hot acetone to give a yellow crystal with a m.p. of 120-121 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-4-chlorophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-4-chlorophenyl azo (Fig.4-22) could be assigned as shown in Table 4-14. Its FT-IR spectrum showed the important absorptions at 3249 cm^{-1} (N-H stretching vibration of primary amine), 3099 cm^{-1} (C-H stretching vibration of aromatic), 2989 cm^{-1} (C-H stretching vibration of aliphatic), 1694 cm^{-1} (C=O stretching vibration of ester), 1604, 1584, 1512 and 1461cm^{-1} (C=C stretching vibration of aromatic) and 1265, 1170 cm^{-1}(C-O-C stretching vibration).

Table 4-14 The FT-IR -absorption band assignments of ethyl-2-aminobenzoate-4-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3249	m	N-H stretching vibration of primary amine
3099	w	C-H stretching vibration of aromatic
2989	w	C-H stretching vibration of aliphatic
1694	v.s.	C=O stretching vibration of ester
1604, 1584, 1512, 1462	w-m	C=C stretching vibration of aromatic
1265, 1170	v.s.	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-23) could be assigned as shown in Table 4-15. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.2 ppm and aromatic carbons at 112.3, 114.4, 121.2, 122.8, 129.1, 131.1, 133.2, 134.4, 143.7 and 148.2 ppm. The last carbon signal at 167.3 ppm was carbonyl carbon.

Table 4-15 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-4-chlorophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	h	131.1
b	61.2	i	133.2
c	112.3	j	134.4
d	114.4	k	143.7
e	121.2	l	148.2
f	122.8	m	167.3
g	129.1	--	---

The ^{1}H- NMR spectrum (Fig.4-24) showed the triplet at 1.40 ppm, which belonged to methyl protons. The methylene protons attached to ester ($\mathrm{C\underline{H}_2}$-O) appeared as the quartet 4.38 ppm. The signals at 6.99-8.02 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	59.66	4.41	13.08
Calculation	59.31	4.61	13.84
% Different	0.35	0.21	0.76

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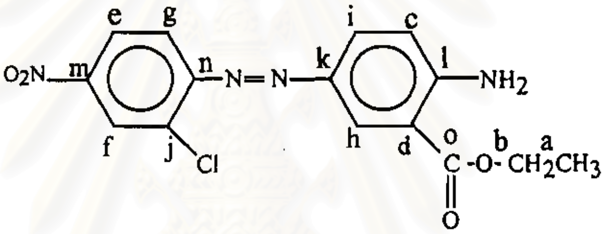
4.1.9 Characterization of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

Ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo prepared from coupling reaction of 2-chloro-4-nitroaniline diazonium salt and ethyl-2-aminobenzoate was an orange solid. It was recrystallized from hot acetone to give an orange crystal with a m.p. of 146-147 °C. It was soluble in chloroform, toluene and partly soluble in xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo (Fig.4-25) could be assigned as shown in Table 4-16. Its FT-IR spectrum showed the important absorptions at 3220 cm^{-1} (N-H stretching vibration of primary amine), 3094 cm^{-1} (C-H stretching vibration of aromatic), 2991 cm^{-1} (C-H stretching vibration of aliphatic), 1680 cm^{-1}(C=O stretching vibration of ester), 1604, 1583, 1500 and 1450cm^{-1} (C=C stretching vibration of aromatic), 1517 and 1344 cm^{-1} (N=O stretching vibration of nitro compound) and 1251,1164 cm^{-1}(C-O-C stretching vibration).

Table 4-16 The FT-IR - absorption band assignments of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3220	m	N-H stretching vibration of primary amine
3094	w	C-H stretching vibration of aromatic
2991	w	C-H stretching vibration of aliphatic
1680	v.s.	C=O stretching vibration of ester
1604, 1583, 1500, 1450	w-s	C=C stretching vibration of aromatic
1517, 1344	v.s.	N=O stretching vibration
1252, 1164	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-26) could be assigned as shown in Table 4-17. Its spectrum showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 61.6 ppm and aromatic carbons at 113.8, 115.0, 119.3, 122.6, 123.1, 126.1, 130.9, 131.2, 134.5, 142.6. 146.1 and 150.9 ppm. The last carbon signal at 167.2 ppm was carbonyl carbon.

Table 4-17 The ^{13}C- NMR spectrum assignments of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.2	i	130.9
b	61.6	j	131.2
c	113.8	k	134.5
d	115.0	l	142.6
e	119.3	m	146.1
f	122.6	n	150.9
g	123.1	o	167.2
h	126.1	--	--

The ^{1}H- NMR spectrum (Fig.4-27) showed the triplet at 1.42 ppm, which belonged to methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet 4.41 ppm. The signals at 7.12-8.31 ppm belonged to aromatic protons.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	50.74	4.72	15.75
Calculation	51.65	3.73	16.07
% Different	0.91	0.99	0.32

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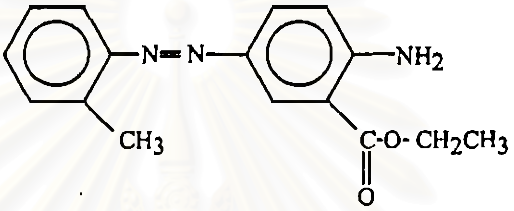
4.1.10 Characterization of ethyl-2-aminobenzoate-2-methylphenyl azo

Ethyl-2-aminobenzoate-2-methylphenyl azo prepared from coupling reaction of o-toluidine diazonium salt and ethyl-2-aminobenzoate was a dark reddish brown. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-2-methylphenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-2-methylphenyl azo (Fig.4-28) could be assigned as shown in Table 4-18. Its FT-IR spectrum showed the important absorptions at 3481 and 3372 cm^{-1}(N-H stretching vibration of primary amine), 2981 cm^{-1} (C-H stretching vibration of aliphatic), 1689 cm^{-1} (C=O stretching vibration of ester), 1617 cm^{-1}(N=N stretching vibration of azo compound), 1588, 1488 and 1455 cm^{-1} (C=C stretching vibration of aromatic), 1294 cm^{-1} (C-N stretching vibration of primary aryl amine), and 1246, 1103 cm^{-1} (C-O-C stretching vibration).

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Table 4-18 The FT-IR absorption band assignments of ethyl-2-aminobenzoate-2-methylphenyl azo

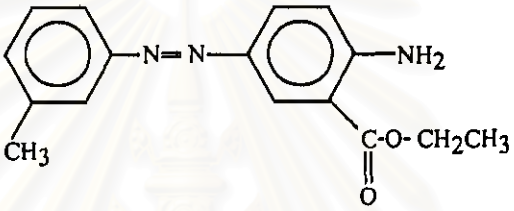
Frequency (cm^{-1})	Peak intensity	Tentative assignments
3481, 3372	m	N-H stretching vibration of primary amine
2981	w	C-H stretching vibration of aliphatic
1689	s	C=O stretching vibration of ester
1617	s	N=N stretching vibration of azo compound
1588, 1488, 1455	w-s	C=C stretching vibration of aromatic
1294	s	C-N stretching vibration of primary amine
1245, 1103	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-29) showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 60.1 ppm and aromatic carbons at 110.9, 116.0, 116.5, 131.1, 133.8 and 150.4 ppm. The last carbon signal at 168.0 ppm was carbonyl carbon.

The ^{1}H- NMR spectrum (Fig.4-30) showed the triplet at 1.37 ppm, which belonged to methyl protons. The methylene protons attached to ester ($C\underline{H}_2$-O) appeared as the quartet 4.32 ppm. The protons of amino group showed the one signal at 5.74 ppm and the signals at 6.62-7.89 ppm belonged to aromatic protons.

4.1.11 Characterization of ethyl-2-aminobenzoate-3-methylphenyl azo

Ethyl-2-aminobenzoate-3-methylphenyl azo prepared from coupling reaction of m-toluidine diazonium salt and ethyl-2-aminobenzoate was a dark reddish brown. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-3-methylphenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-3-methylphenyl azo (Fig.4.31) could be assigned as shown in Table 4-19. Its FT-IR spectrum showed the important absorptions at 3483 and 3372 cm^{-1} (N-H stretching vibration of primary amine), 2981 cm^{-1} (C-H stretching vibration of aliphatic), 1689 cm^{-1} (C=O stretching vibration of ester), 1617 cm^{-1}(N=N stretching vibration of azo compound), 1588, 1488 and 1454 cm^{-1} (C=C stretching vibration of aromatic), 1293 cm^{-1} (C-N stretching vibration of primary aryl amine), and 1246, 1103 cm^{-1} (C-O-C stretching vibration).

Table 4-19 The FT-IR-absorption band assignments of ethyl-2-aminobenzoate-3-methylphenyl azo

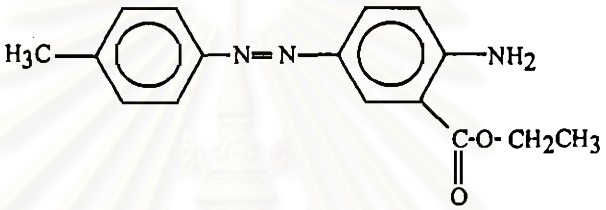
Frequency (cm^{-1})	Peak intensity	Tentative assignments
3483, 3372	m	N-H stretching vibration of primary amine
2981	w	C-H stretching vibration of aliphatic
1689	s	C=O stretching vibration of ester
1617	s	N=N stretching vibration
1588, 1488, 1454	w-s	C=C stretching vibration of aromatic
1293	m	C-N stretching vibration of primary amine
1246, 1103	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-32) showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 60.2 ppm and aromatic carbons at 110.7-150.3 ppm. The last carbon signal at 168.1 ppm was carbonyl carbon.

The ^{1}H- NMR spectrum (Fig.4-33) showed the triplet at 1.37 ppm, belonged to methyl protons. The methyl protons attached aromatic carbon showed the signal at 2.26 ppm. The methylene protons attached to ester ($C\underline{H_2}$-O) appeared as the quartet 4.33 ppm. The protons of amino group showed the one signal at 5.70 ppm . The signals at 6.62-7.89 ppm belonged to aromatic protons.

4.1.12 Characterization of ethyl-2-aminobenzoate-4-methylphenyl azo

Ethyl-2-aminobenzoate-4-methylphenyl azo prepared from coupling reaction of p-toluidine diazonium salt and ethyl-2-aminobenzoate was a dark reddish brown It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of ethyl-2-aminobenzoate-4-methylphenyl azo

The FT-IR spectrum of ethyl-2-aminobenzoate-4-methylphenyl azo (Fig.4-34) could be assigned as shown in Table 4-20. Its FT-IR spectrum showed the important absorptions at 3482 and 3372 cm^{-1} (N-H stretching vibration of primary amine), 2981 cm^{-1}(C-H stretching vibration of aliphatic), 1689 cm^{-1} (C=O stretching vibration of ester), 1617 cm^{-1}(N=N stretching vibration of azo compound), 1588, 1488 and 1455 cm^{-1} (C=C stretching vibration of aromatic), 1294 cm^{-1} (C-N stretching vibration of primary aryl amine), and 1246, 1103 cm^{-1}(C-O-C stretching vibration).

Table 4-20 The FT-IR –absorption band assignments of ethyl-2-aminobenzoate-4-methylphenyl azo

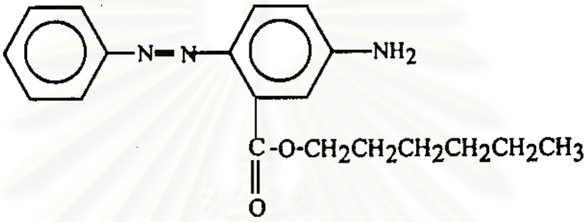
Frequency (cm^{-1})	Peak intensity	Tentative assignments
3482, 3372	m	N-H stretching vibration of primary amine
2981	w	C-H stretching vibration of aliphatic
1689	s	C=O stretching vibration of ester
1617	s	N=N stretching vibration of azo compound
1588, 1488, 1455	w-s	C=C stretching vibration of aromatic
1294	s	C-N stretching vibration of primary amine
1246, 1103	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-35) showed one methyl carbon signal at 14.2 ppm, one methylene carbon at 60.1 ppm and aromatic carbons at 110.9-150.4 ppm. The last carbon signal at 168.0 ppm was carbonyl carbon.

The ^{1}H- NMR spectrum (Fig.4-36) showed the triplet at 1.37 ppm, which belonged to methyl protons. The methylene protons attached to ester ($C\underline{H_2}$-O) appeared as the quartet 4.32 ppm. The protons of amino group showed the one signal at 5.74 ppm. The signals at 6.62-7.89 ppm belonged to aromatic protons.

4.1.13 Characterization of hexyl-3-aminobenzoate phenyl azo

Hexyl-3-aminobenzoate phenyl azo prepared from coupling of aniline diazonium salt and hexyl-3-aminobenzoate was a reddish-brown liquid. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate phenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate phenyl azo (Fig.4-37) could be assigned as shown in Table 4-21. Its FT-IR spectrum showed the important absorptions at 3375 cm^{-1}(N-H stretching vibration of primary amine), 2956-2858 cm^{-1}(C-H stretching vibration of aliphatic), 1709 cm^{-1}(C=O stretching vibration of ester), 1604, 1491 and 1462 cm^{-1} (C=C stretching vibration of aromatic), 1291 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1240, 1104 cm^{-1}(C-O-C stretching vibration).

Table 4-21 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate phenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3375	m	N-H stretching vibration of primary amine
2956-2858	m-s	C-H stretching vibration of aliphatic
1709	v.s.	C=O stretching vibration of ester
1604, 1491, 1462	w-m	C=C stretching vibration of aromatic
1291	s	C-N stretching vibration of primary amine
1240, 1104	v.s., m	C-O-C stretching vibration

The ^{13}C-NMR spectrum (Fig.4-38) showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.0 ppm, the aromatic carbon signals at 113.6-146.2 ppm. The last carbon signal at 166.8 ppm was carbonyl carbon.

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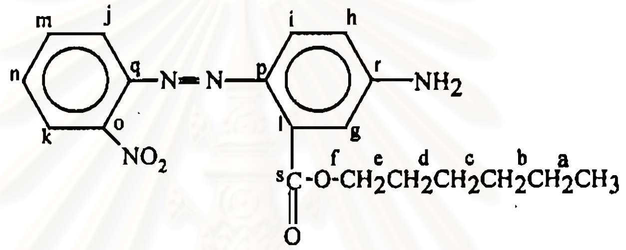
4.1.14 Characterization of hexyl-3-aminobenzoate-2-nitrophenyl azo

Hexyl-3-aminobenzoate-2-nitrophenyl azo prepared from coupling reaction of o-nitroaniline diazonium salt and hexyl-3-aminobenzoate was a yellow solid. It was recrystallized from hot methanol to give a yellow solid with a m.p. of 77-78 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-2-nitrophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-2-nitrophenyl azo (Fig.4-39) could be assigned as shown in Table 4-22. Its FT-IR spectrum showed the important absorptions at 3309 cm^{-1}(N-H stretching vibration of primary amine), 2953 cm^{-1} (C-H stretching vibration of aliphatic), 1726 cm^{-1} (C=O stretching vibration of ester), 1614 cm^{-1} (N=N stretching vibration of azo compound), 1578, 1502 and 1448 cm^{-1} (C=C stretching vibration of aromatic), 1520 and 1339 cm^{-1}(N=O stretching vibration of nitro compound) and 1269, 1156 cm^{-1}(C-O-C stretching vibration).

Table 4-22 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-2-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3309	m	N-H stretching vibration of primary amine
2953	m	C-H stretching vibration of aliphatic
1726	v.s.	C=O stretching vibration of ester
1614	s	N=N stretching vibration of azo compound
1578, 1502, 1448	m-v.s.	C=C stretching vibration of aromatic
1520, 1339	m	N=O stretching vibration of nitro compound
1298	v.s.	C-N stretching vibration of primary amine
1269, 1156	v.s.	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-40) could be assigned as shown in Table 4-23. Its spectrum showed carbon signals which one signal at 13.9 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.6, 28.6, 31.4 and 65.4 ppm, the aromatic carbon signals at 116.4, 121.7, 122.7, 126.0, 126.1, 129.1, 129.5, 131.6, 132.8, 135.9, 137.9 and 148.8 ppm. The last carbon signal at 166.0 ppm was carbonyl carbon.

Table 4-23 The ^{13}C- NMR spectrum assignments of hexyl-3-aminobenzoate-2-nitrophenyl azo

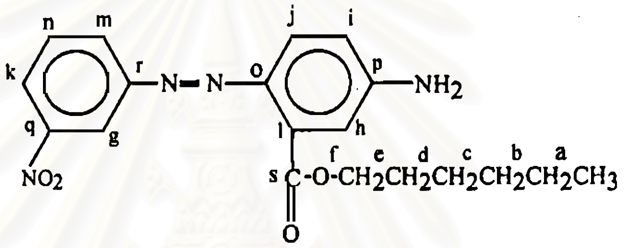
Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	13.9	k	126.1
b	22.5	l	129.1
c	25.6	m	129.5
d	28.6	n	131.6
e	31.4	o	132.8
f	65.4	p	135.9
g	116.4	q	137.9
h	121.7	r	148.8
i	122.7	s	166.0
j	126.0	--	---

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	61.92	6.02	15.66
Calculation	61.62	5.95	15.14
% Different	0.30	0.07	0.52

4.1.15 Characterization of hexyl-3-aminobenzoate-3-nitrophenyl azo

Hexyl-3-aminobenzoate-3-nitrophenyl azo prepared from coupling reaction of m-nitroaniline diazonium salt and hexyl-3-aminobenzoate was a yellow solid. It was recrystallized from hot methanol to give a yellow solid with a m.p. of 98-99 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-3-nitrophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-3-nitrophenyl azo (Fig.4-41) could be assigned as shown in Table 4-24. Its FT-IR spectrum showed the important absorptions at 3222 cm^{-1}(N-H stretching vibration of primary amine), 2954-2861 cm^{-1} (C-H stretching vibration of aliphatic), 1702 cm^{-1} (C=O stretching vibration of ester), 1618 cm^{-1}(N=N stretching vibration of azo compound), 1591 and 1457 cm^{-1} (C=C stretching vibration of aromatic), 1531 and 1350 cm^{-1} (N=O stretching vibration of nitro compound) and 1281, 1162 cm^{-1} (C-O-C stretching vibration).

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Table 4-24 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-3-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3222	m	N-H stretching vibration of primary amine
2954-2861	m	C-H stretching vibration of aliphatic
1702	v.s.	C=O stretching vibration of ester
1618	m	N=N stretching vibration of azo compound
1591, 1457	w-v.s.	C=C stretching vibration of aromatic
1531, 1350	v.s., s	N=O stretching vibration of nitro compound
1281, 1162	s, m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-42) could be assigned as shown in Table 4-25. Its spectrum showed carbon signals which one signal at 13.9 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.6, 28.6, 31.4 and 65.5 ppm, the aromatic carbon signals at 112.8, 115.7, 119.6, 121.8, 123.7, 126.6, 129.1, 129.4, 129.9, 131.6, 146.4 and 149.0 ppm. The last carbon signal at 166.3 ppm was carbonyl carbon.

Table 4-25 The ^{13}C- NMR spectrum assignments of hexyl-3-aminobenzoate-3-nitrophenyl azo

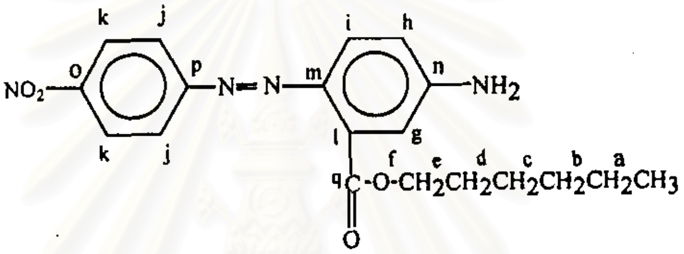
Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	13.9	k	123.7
b	22.5	l	126.6
c	25.6	m	129.1
d	28.6	n	129.4
e	31.4	o	129.9
f	65.5	p	131.6
g	112.8	q	146.4
h	115.7	r	149.0
i	119.6	s	166.3
j	121.8	--	---

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	62.28	5.44	14.99
Calculation	61.62	5.95	15.14
% Different	0.66	0.51	0.15

4.1.16 Characterization of hexyl-3-aminobenzoate-4-nitrophenyl azo

Hexyl-3-aminobenzoate-4-nitrophenyl azo prepared from coupling reaction of p-nitroaniline diazonium salt and hexyl-3-aminobenzoate was an orange solid. It was recrystallized from hot methanol to give an orange solid with a m.p. of 121-122 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-4-nitrophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-4-nitrophenyl azo (Fig.4-43) could be assigned as shown in Table 4.26. Its FT-IR spectrum showed the important absorptions at 3242 cm^{-1}(N-H stretching vibration of primary amine), 3047 cm^{-1} (C-H stretching vibration of aromatic), 2958-2858 cm^{-1} (C-H stretching vibration of aliphatic), 1705 cm^{-1} (C=O stretching vibration of ester), 1598, 1506 and 1456 cm^{-1} (C=C stretching vibration of aromatic), 1528 and 1329 cm^{-1}(N=O stretching vibration of nitro compound) and 1250, 1168 cm^{-1}(C-O-C stretching vibration).

Table 4-26 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-4-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3242	m	N-H stretching vibration of primary amine
3047	w	C-H stretching vibration of aromatic
2958-2858	w	C-H stretching vibration of aliphatic
1705	v.s.	C=O stretching vibration of ester
1598, 1506, 1456	s	C=C stretching vibration of aromatic
1528, 1329	m, s	N=O stretching vibration of nitro compound
1250, 1168	v.s., m	C-O-C stretching vibration

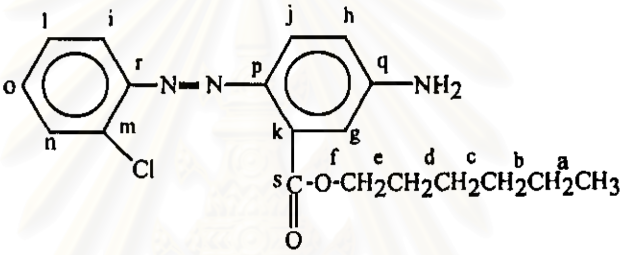
The ^{13}C- NMR spectrum (Fig.4-44) showed carbon signals which one signal at 13.9 ppm belonged to methyl carbon, five methylene carbons at 22.4, 25.6, 28.6, 31.3 and 65.5 ppm, the aromatic carbon signals at 115.2, 119.6, 121.8, 124.1, 125.6, 128.4, 129.2, 131.6, 143.3 and 155.0 ppm. The last carbon signal at 166.2 ppm was carbonyl carbon.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	61.74	5.59	15.27
Calculation	61.62	5.95	15.14
% Different	0.12	0.36	0.13

4.1.17 Characterization of hexyl-3-aminobenzoate-2-chlorophenyl azo

Hexyl-3-aminobenzoate-2-chlorophenyl azo prepared from coupling reaction of 2-chloroaniline diazonium salt and hexyl-3-aminobenzoate was a yellow solid. It was recrystallized from hot methanol to give a yellow solid with a m.p. of 109-110 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-2-chlorophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-2-chlorophenyl azo (Fig.4-45) could be assigned as shown in Table 4-27. Its FT-IR spectrum showed the important absorptions at 3253, 3213 cm^{-1}(N-H stretching vibration of primary amine), 3062 cm^{-1} (C-H stretching vibration of aromatic), 2956-2858 cm^{-1} (C-H stretching vibration of aliphatic), 1698 cm^{-1} (C=O stretching vibration of ester), 1611 cm^{-1} (N=N stretching vibration of azo compound), 1591 and 1523 cm^{-1} (C=C stretching vibration of aromatic) and 1290, 1195 cm^{-1}(C-O-C stretching vibration).

Table 4-27 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-2-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3253-3213	m	N-H stretching vibration of primary amine
3062	w	C-H stretching vibration of aromatic
2956-2858	m	C-H stretching vibration of aliphatic
1698	v.s.	C=O stretching vibration of ester
1611	m	N=N stretching vibration of aromatic
1591, 1523	m	C=C stretching vibration of aromatic
1290, 1195	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-46) could be assigned as shown in Table 4-28. Its spectrum showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.4 ppm, the aromatic carbon signals at 116.0, 118.9, 121.6, 124.2, 124.6, 127.9, 128.1, 129.2, 131.7, 138.4 and 148.0 ppm. The last carbon signal at 166.3 ppm was carbonyl carbon.

Table 4-28 The ^{13}C- NMR spectrum assignments of hexyl-3-aminobenzoate-2-chlorophenyl azo

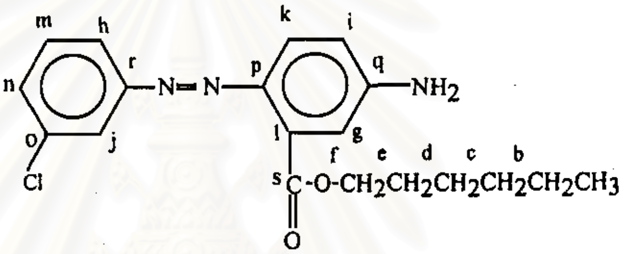
Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.0	k	124.6
b	22.5	l	127.9
c	25.7	m	128.1
d	28.6	n	129.2
e	31.4	o	129.7
f	65.3	p	131.7
g	116.0	q	138.4
h	118.9	r	148.0
i	121.6	s	166.3
j	124.2	--	---

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	63.57	6.73	11.50
Calculation	63.42	6.12	11.68
% Different	0.15	0.61	0.18

4.1.18 Characterization of hexyl-3-aminobenzoate-3-chlorophenyl azo

Hexyl-3-aminobenzoate-3-chlorophenyl azo prepared from coupling reaction of 3-chloroaniline diazonium salt and hexyl-3-aminobenzoate was a yellow solid. It was recrystallized from hot methanol to give a yellow solid with a m.p. of 100-102 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-3-chlorophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-3-chlorophenyl azo (Fig.4-47) could be assigned as shown in Table 4-29. Its FT-IR spectrum showed the important absorptions at 3229 cm^{-1}(N-H stretching vibration of primary amine), 3073 and 3033 cm^{-1} (C-H stretching vibration of aromatic), 2957-2854 cm^{-1} (C-H stretching vibration of aliphatic), 1700 cm^{-1} (C=O stretching vibration of ester), 1612 cm^{-1} (N=N stretching vibration of azo compound), 1590, 1491 and 1451 cm^{-1} (C=C stretching vibration of aromatic) and 1300, 1195 cm^{-1} (C-O-C stretching vibration).

Table 4-29 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-3-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3229	s	N-H stretching vibration of primary amine
3073-3033	w	C-H stretching vibration of aromatic
2957-2854	m	C-H stretching vibration of aliphatic
1700	v.s.	C=O stretching vibration of ester
1612	m	N=N stretching vibration of azo compound
1590, 1491, 1451	m-s	C=C stretching vibration of aromatic
1300, 1195	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-48) could be assigned as shown in Table 4-29. Its spectrum showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.4 ppm, the aromatic carbon signals at 116.4, 117.8, 119.2, 122.0, 125.3, 126.4, 129.3, 130.3, 131.7, 135.1, 145.0 and 146.1 ppm. The last carbon signal at 166.3 ppm was carbonyl carbon.

Table 4-30 The ^{13}C- NMR spectrum assignments of hexyl-3-aminobenzoate-3-chlorophenyl azo

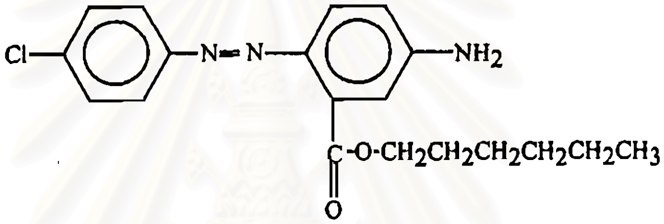
Carbon position	Chemical shift (ppm)	Carbon position	Chemical shift (ppm)
a	14.0	k	125.3
b	22.5	l	126.4
c	25.7	m	129.3
d	28.6	n	130.3
e	31.4	o	131.7
f	65.4	p	135.1
g	116.4	q	145.0
h	117.8	r	146.1
i	119.2	s	166.3
j	122.0	--	---

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	62.52	6.43	10.75
Calculation	63.42	6.12	11.68
% Different	0.10	0.31	0.93

4.1.19 Characterization of hexyl-3-aminobenzoate-4-chlorophenyl azo

Hexyl-3-aminobenzoate-4-chlorophenyl azo prepared from coupling reaction of 4-chloroaniline diazonium salt and hexyl-3-aminobenzoate was a yellow solid. It was recrystallized from hot methanol to give a yellow solid with a m.p. of 111-112 °C. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-4-chlorophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-4-chlorophenyl azo (Fig.4-49) could be assigned as shown in Table 4-31. Its FT-IR spectrum showed the important absorptions at 3235 cm^{-1}(N-H stretching vibration of primary amine), 3062 and 3023 cm^{-1} (C-H stretching vibration of aromatic), 2960-2870 cm^{-1} (C-H stretching vibration of aliphatic), 1699 cm^{-1} (C=O stretching vibration of ester), 1610 cm^{-1} (N=N stretching vibration of azo compound), 1589, 1482 and 1452 cm^{-1} (C=C stretching vibration of aromatic) and 1301, 1192 cm^{-1}(C-O-C stretching vibration).

Table 4-31 The FT-IR –absorption band assignments of hexyl-3-aminobenzoate-4-chlorophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3235	s	N-H stretching vibration of primary amine
3062, 3023	w	C-H stretching vibration of aromatic
2960-2870	m	C-H stretching vibration of aliphatic
1699	v.s.	C=O stretching vibration of ester
1610	m	N=N stretching vibration of azo compound
1589, 1482, 1452	m-s	C=C stretching vibration of aromatic
1301, 1192	s	C-O-C stretching vibration

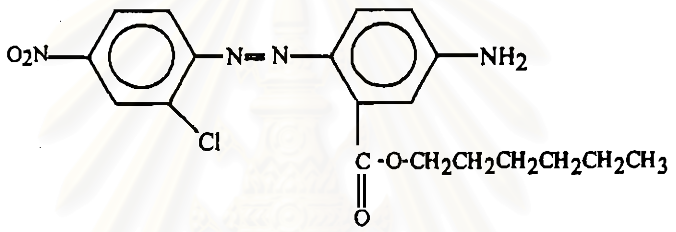
The ^{13}C- NMR spectrum (Fig.4-50) showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.4 ppm, the aromatic carbon signals at 113.3-148.5 ppm. The last carbon signal at 166.3 ppm was carbonyl carbon.

Elemental analysis determination showed the elements as the following.

Source	Carbon, % wt.	Hydrogen, % wt.	Nitrogen, % wt.
Testing	63.27	6.97	11.62
Calculation	63.42	6.12	11.68
% Different	0.15	0.85	0.06

4.1.20 Characterization of hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo

Hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo prepared from coupling reaction of 2-chloro-4-nitroaniline diazonium salt and hexyl-3-aminobenzoate was an orange semisolid. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo (Fig.4-51) could be assigned as shown in Table 4-32. Its FT-IR spectrum showed the important absorptions at 3228 cm^{-1}(N-H stretching vibration of primary amine), 2930 cm^{-1} (C-H stretching vibration of aliphatic), 1692 cm^{-1} (C=O stretching vibration of ester), 1607 cm^{-1} (N=N stretching vibration of azo compound), 1590, 1490 and 1447 cm^{-1} (C=C stretching vibration of aromatic), 1528 and 1340 cm^{-1} (N=O stretching vibration of nitro compound) and 1287 cm^{-1} (C-O-C stretching vibration).

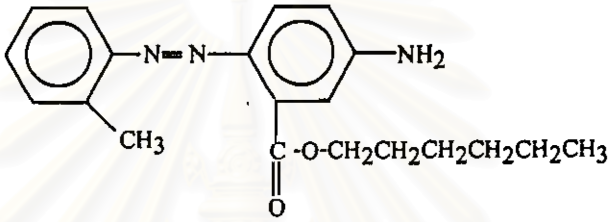
Table 4-32 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3228	s	N-H stretching vibration of primary amine
2930	m	C-H stretching vibration of aliphatic
1692	s	C=O stretching vibration of ester
1607	m	N=N stretching vibration of azo compound
1590, 1490, 1447	m-s	C=C stretching vibration of aromatic
1528, 1340	s	N=O stretching vibration of nitro compound
1287	s	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-52) showed carbon signals which one signal at 13.9 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.6, 28.6, 31.4 and 65.5 ppm, the aromatic carbon signals at 114.5- 147.8 ppm. The last carbon signal at 166.2 ppm was carbonyl carbon.

4.1.21 Characterization of hexyl-3-aminobenzoate-2-methylphenyl azo

Hexyl-3-aminobenzoate-2-methylphenyl azo prepared from coupling reaction of o-toluidine diazonium salt and hexyl-3-aminobenzoate was a dark reddish-brown liquid. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-2-methylphenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-2-methylphenyl azo (Fig.4-53) could be assigned as shown in Table 4-33. Its FT-IR spectrum showed the important absorptions at 3454 and 3375 cm^{-1} (N-H stretching vibration of primary amine), 2956-2858 cm^{-1}(C-H stretching vibration of aliphatic), 1708 cm^{-1} (C=O stretching vibration of ester), 1606, 1589, 1491 and 1462 cm^{-1} (C=C stretching vibration of aromatic), 1291 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1240, 1104 cm^{-1}(C-O-C stretching vibration).

Table 4-33 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-2-methylphenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3454, 3375	m	N-H stretching vibration of primary amine
2956-2858	m-s	C-H stretching vibration of aliphatic
1708	v.s.	C=O stretching vibration of ester
1606, 1589, 1491, 1462	w-m	C=C stretching vibration of aromatic
1291	s	C-N stretching vibration of primary amine
1240, 1104	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-54) showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.0 ppm, the aromatic carbon signals at 113.6 – 146.3 ppm. The last carbon signal at 166.8 ppm was carbonyl carbon.

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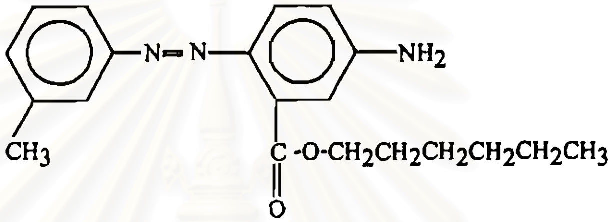
4.1.22 Characterization of hexyl-3-aminobenzoate-3-methylphenyl azo

Hexyl-3-aminobenzoate-3-methylphenyl azo prepared from coupling reaction of m-toluidine diazonium salt and hexyl-3-aminobenzoate was a dark reddish-brown liquid. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-3-methylphenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-3-methylphenyl azo (Fig.4-55) could be assigned as shown in Table 4-34. Its FT-IR spectrum showed the important absorptions at 3461 and 3375 cm^{-1}(N-H stretching vibration of primary amine), 2956-2858 cm^{-1} (C-H stretching vibration of aliphatic), 1708 cm^{-1} (C=O stretching vibration of ester), 1604, 1587, 1491 and 1459 cm^{-1} (C=C stretching vibration of aromatic), 1291 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1240, 1105 cm^{-1}(C-O-C stretching vibration).

Table 4-34 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-3-methylphenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3461, 3375	m	N-H stretching vibration of primary amine
2956-2858	m-s	C-H stretching vibration of aliphatic
1708	v.s.	C=O stretching vibration of ester
1604, 1587,1491,1458	w-m	C=C stretching vibration of aromatic
1291	s	C-N stretching vibration of primary amine
1240, 1105	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-56) showed carbon signals which one signal at 14.0 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.7, 28.6, 31.4 and 65.1 ppm, the aromatic carbon signals at 115.8 – 146.3 ppm. The last carbon signal at 166.9 ppm was carbonyl carbon.

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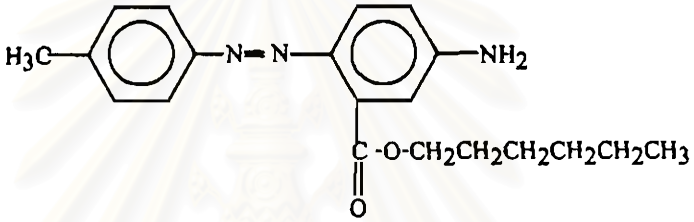
4.1.23 Characterization of hexyl-3-aminobenzoate-4-methylphenyl azo

Hexyl-3-aminobenzoate-4-methylphenyl azo prepared from coupling reaction of p-toluidine diazonium salt and hexyl-3-aminobenzoate was a dark reddish-brown liquid. It was soluble in chloroform, toluene and xylene. The structure was shown below.



Structure of hexyl-3-aminobenzoate-4-methylphenyl azo

The FT-IR spectrum of hexyl-3-aminobenzoate-4-methylphenyl azo (Fig.4-57) could be assigned as shown in Table 4-35. Its FT-IR spectrum showed the important absorptions at 3461 and 3375 cm^{-1}(N-H stretching vibration of primary amine), 2956-2858 cm^{-1}(C-H stretching vibration of aliphatic), 1708 cm^{-1}(C=O stretching vibration of ester), 1605, 1589, 1491 and 1462 cm^{-1} (C=C stretching vibration of aromatic), 1291 cm^{-1}(C-N stretching vibration of primary aryl amine) and 1240, 1104 cm^{-1}(C-O-C stretching vibration).

Table 4-35 The FT-IR -absorption band assignments of hexyl-3-aminobenzoate-4-methylphenyl azo

Frequency (cm^{-1})	Peak intensity	Tentative assignments
3461, 3375	m	N-H stretching vibration of primary amine
2956-2858	m-s	C-H stretching vibration of aliphatic
1708	v.s.	C=O stretching vibration of ester
1605, 1589, 1491, 1462	w-m	C=C stretching vibration of aromatic
1291	s	C-N stretching vibration of primary amine
1240, 1104	v.s., m	C-O-C stretching vibration

The ^{13}C- NMR spectrum (Fig.4-58) showed carbon signals which one signal at 13.9 ppm belonged to methyl carbon, five methylene carbons at 22.5, 25.6, 28.6, 31.4 and 65.0 ppm, the aromatic carbon signals at 113.7-146.2 ppm. The last carbon signal at 166.8 ppm was carbonyl carbon.

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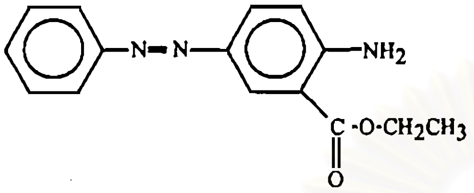
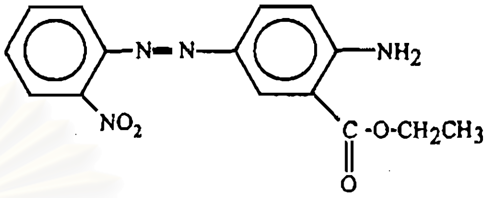
4.1.24 Structures of all markers

The structures of markers in this study were shown as follows:



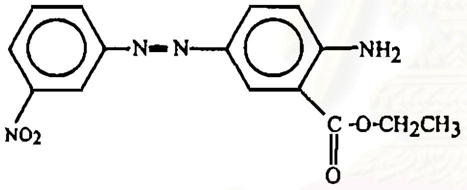
Ethyl-2-aminobenzoate phenyl azo

(Compound 1)



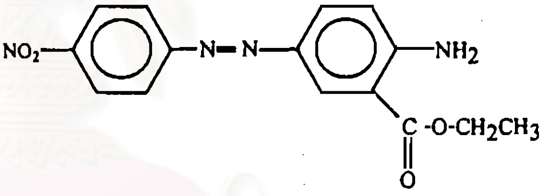
Ethyl-2-aminobenzoate-2-nitrophenyl azo

(Compound 2)

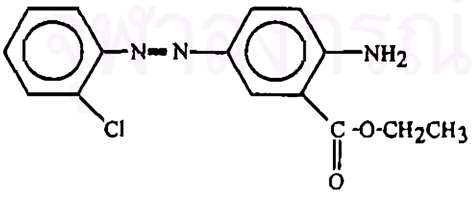


Ethyl-2-aminobenzoate-3-nitrophenyl azo

Compound 3)

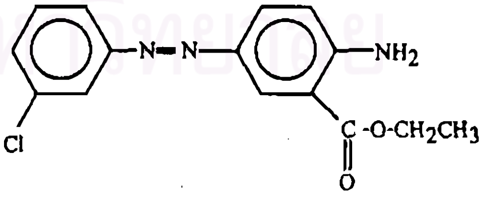


Ethyl-2-aminobenzoate-4-nitrophenyl azo **(Compound 4)**



Ethyl-2-aminobenzoate-2-chlorophenyl azo

(Compound 5)



Ethyl-2-aminobenzoate-3-chlorophenyl azo **(Compound 6)**

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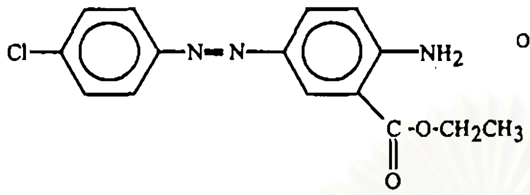
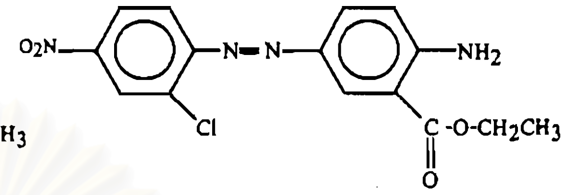
(cont.)



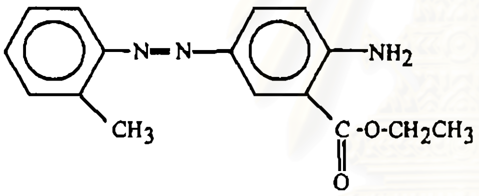
Ethyl-2-aminobenzoate-4-chlorophenyl azo

(Compound 7)



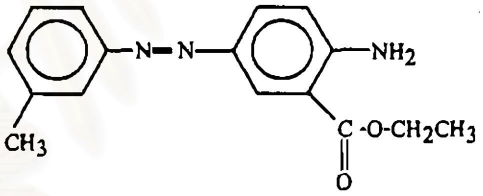
Ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

(Compound 8)



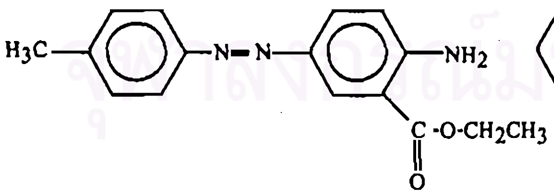
Ethyl-2-aminobenzoate-2-methylphenyl azo

(Compound 9)



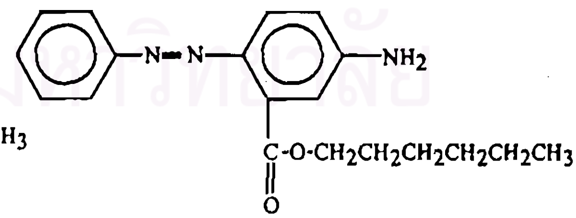
Ethyl-2-aminobenzoate-3-methyl-phenyl azo

(Compound 10)



Ethyl-2-aminobenzoate-4-methylphenyl azo

(Compound 11)



Hexyl-3-aminobenzoate phenyl azo

(Compound 12)

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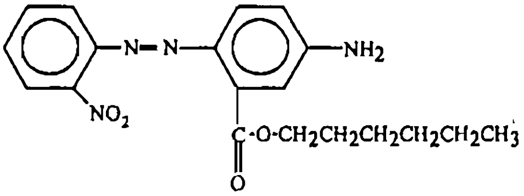
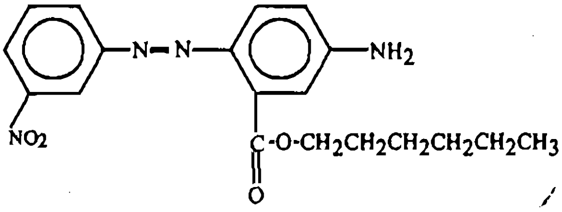
(cont.)



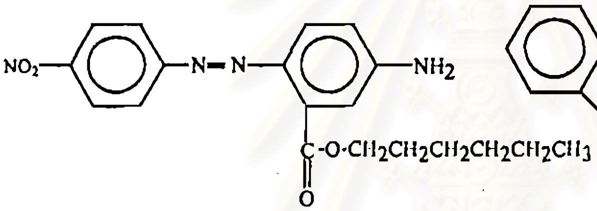
Hexyl-3-aminobenzoate-2-nitrophenyl azo

(Compound 13)



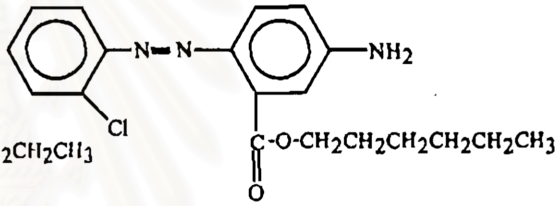
Hexyl-3-aminobenzoate-3-nitrophenyl azo

(Compound 14)



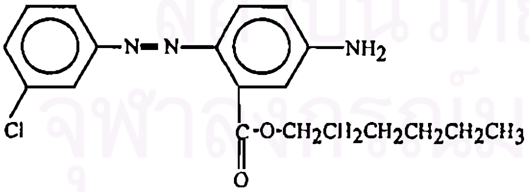
Hexyl-3-aminobenzoate-4-nitrophenyl azo

(Compound 15)



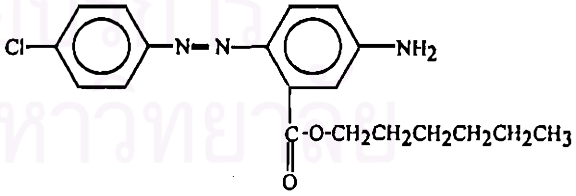
Hexyl-3-aminobenzoate-2-chlorophenyl azo

(Compound 16)



Hexyl-3-aminobenzoate-3-chlorophenyl azo

(Compound 17)



Hexyl-3-aminobenzoate-4-chlorophenyl azo

(Compound 18)

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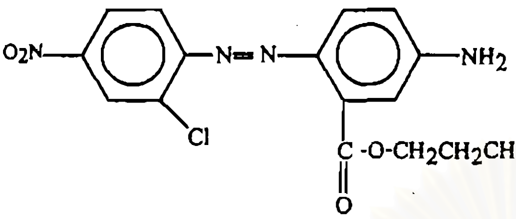
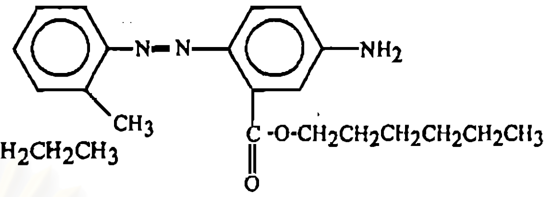
(cont.)



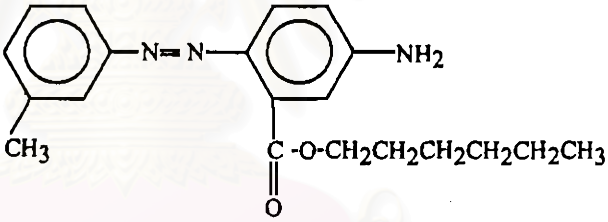


Hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo

(Compound 19)

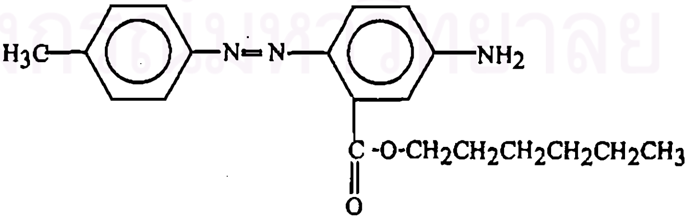
Hexyl-3-aminobenzoate-2-methylphenyl azo

(Compound 20)



Hexyl-3-aminobenzoate-3- methylphenyl azo

(Compound 21)



Hexyl-3-aminobenzoate-4-methylphenyl azo

(Compound 22)

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4.2 Suitable extraction solutions

The different extraction solutions were used to extract the marker from marked HSD into the extracted phase. The color and color intensity of the extracted lower phase were observed and compared with unmarked extracted phase. The results were given in Table 4-36.

Table 4-36 The color and color intensity of the extracted lower phase at the 10 ppm of markers.

Markers	7%KOH in H_2O	7%KOH in MeOH	10%KOH in 90%MeOH-EG	5%KOH in EG	10%HCl in MeOH
Unmarked	colorless	Pale yellow	Pale yellow	colorless	Pale yellow
Compound 1	Pale yellow	Pale yellow	Pale yellow	Fair yellow	Fair yellow
Compound 2	Pale orange	***Strong reddish-orange***	Fair reddish-orange	Fair yellow	Dark yellow
Compound 3	Pale yellow	strong yellow	Pale yellow	Fair yellow	Dark yellow
Compound 4	Fair red	***Strong red***	Fair red	Fair orange	Dark yellow
Compound 5	Pale yellow	Pale yellow	Pale yellow	Fair yellow	Dark yellow
Compound 6	Pale yellow	Pale yellow	Pale yellow	Fair yellow	Dark yellow
Compound 7	Pale yellow	Pale yellow	Pale yellow	Fair yellow	Dark yellow
Compound 8	Pale orange	***Strong red***	Fair red	Fair reddish-orange	Dark yellow
Compound 9	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Compound 10	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale orange
Compound 11	Pale yellow	Pale yellow	Pale yellow	Pale yellow	Pale yellow

Table 4-36 (cont.)

Markers	7%KOH in H_2O	7%KOH in MeOH	10%KOH in 90%MeOH-EG	5%KOH in EG	10%HCl in EG
Compound 12	Colorless	Pale yellow	Pale yellow	Fair yellow	Pale yellow
Compound 13	Pale yellow	Fair reddish - orange	***Strong reddish orange***	Strong yellow	Fair yellow
Compound 14	Pale yellow	Fair yellow	Fair yellow	Strong yellow	Fair yellow
Compound 15	Pale orange	Fair red	Fair red	***Strong red***	Fair yellow
Compound 16	Colorless	Pale yellow	Pale yellow	Fair yellow	Pale yellow
Compound 17	Colorless	Pale yellow	Pale yellow	Fair yellow	Pale yellow
Compound 18	Colorless	Pale yellow	Pale yellow	Fair yellow	Pale yellow
Compound 19	Colorless	Fair red	Fair red	***Strong red***	Pale yellow
Compound 20	Colorless	Pale yellow	Pale yellow	Colorless	Pale yellow
Compound 21	Colorless	Pale yellow	Pale yellow	Colorless	Pale yellow
Compound 22	Colorless	Pale yellow	Pale yellow	Colorless	Pale yellow

When the color of extracted marker was compared with the extracted unmarked HSD, it was found that the color and color intensity would vary, depending on the substituent group and the extraction solution. The colors of extracted unmarked HSD, developed in all solvent systems were colorless to pale yellow. While the markers having the substituent group as hydrogen in compounds 1(Fig.4-59) and 12 (Fig.4-60), as chloro group in compounds 5, 6, 7 (Fig.4-59), 16, 17 and 18(Fig.4-60), as well as methyl group in compounds 9, 10, 11 (Fig. 4-61), 20, 21 and 22(Fig.4-62) gave the same color of extracted phase as that of the extracted phase of unmarked HSD. However, some markers such as compounds 2, 4 (Fig.4-63), 8(Fig.4-65), 13, 15(Fig.4-64) and 19(Fig.4-66) could produce the different color in the extracted phase when compared with the extracted phase of unmarked HSD. These markers could provide clearly chemical distinction between marked HSD and unmarked HSD.

The suitable extraction solutions of above mentioned markers, developed the stronger and different color in the extracted phase include as follows:

1.The solution of 7%KOH in methanol was suitable for compounds 2, 4 and 8.

2.The solution of 10%KOH in mixture of 90% methanol-ethylene glycol was suitable for compound 13.

3.The solution of 5%KOH in ethylene glycol was suitable for compounds 15 and 19.

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Figure 4-59 The color of extracted lower phase of ethyl-2-aminobenzoate azo dyes having substituent group as chloro group.

1. Unmarked HSD	2. Compound 1 (aniline)
3. Compound 5 (o-chloroaniline)	4. Compound 6 (m-chloroaniline)
5. Compound 7 (p-chloroaniline)	

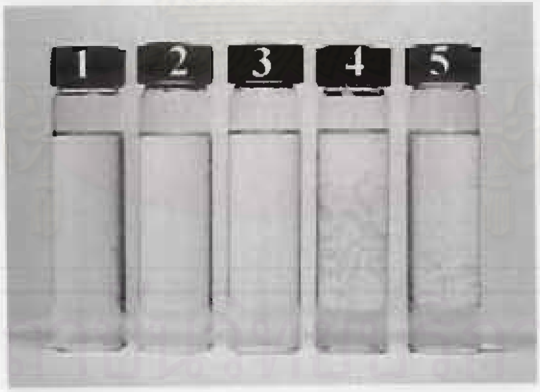

Figure 4-60 The color of extracted lower phase of hexyl-3-aminobenzoate azo dyes having substituent group as chloro group.

1. Unmarked HSD	2.Compound 12 (aniline)
3. Compound 16 (o-chloroaniline)	4. Compound 17 (m-chloroaniline)
5. Compound 18 (p-chloroaniline)	

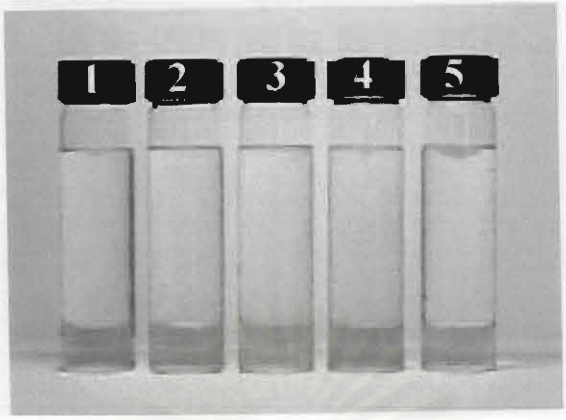

Figure 4-61 The color of extracted lower phase of ethyl-2-aminobenzoate azo dyes having substituent group as methyl group.

1. Unmarked HSD	2.Compound 1 (aniline)
3. Compound 9 (o-toluidine)	4. Compound 10 (m-toluidine)
5. Compound 11 (p-toluidine)	

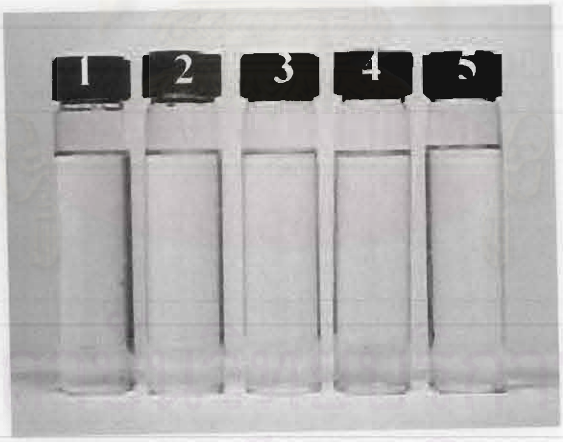

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Figure 4-62 The color of extracted lower phase of hexyl-3-aminobenzoate azo dyes having substituent group as methyl group.

1. Unmarked HSD	2.Compound 12 (aniline)
3. Compound 20 (o-toluidine)	4. Compound 21 (m-toluidine)
5. Compound 22 (p-toluidine)	

Figure 4-63 The color of extracted lower phase of ethyl-2-aminobenzoate azo dyes having substituent group as nitro group.

1. Unmarked HSD
2.Compound 1 (aniline)
3. Compound 2 (o-nitroaniline)
4. Compound 3 (m-nitroaniline)
5. Compound 4 (p-nitroaniline)

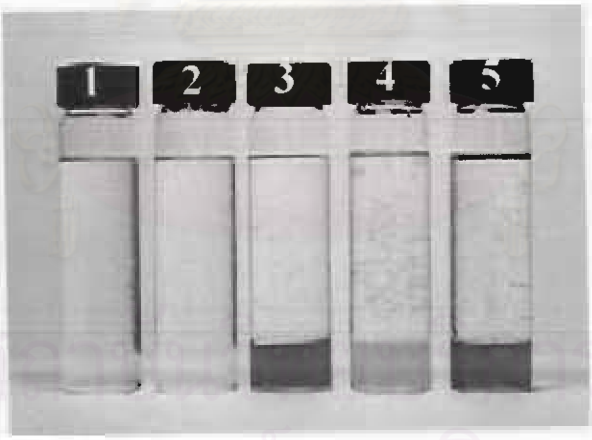

Figure 4-64 The color of extracted lower phase of hexyl-3-aminobenzoate azo dyes having substituent group as nitro group.

1. Unmarked HSD
2.Compound 12 (aniline)
3. Compound 13 (o-nitroaniline)
4. Compound 14 (m-nitroaniline)
5. Compound 15 (p-nitroaniline)

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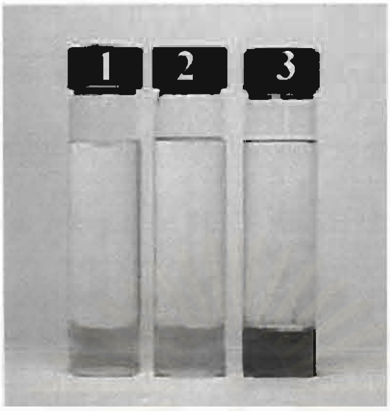

Figure 4-65 The color of extracted lower phase of ethyl-2-aminobenzoate azo dyes having substituent group as 2-chloro-4-nitro group.

1. Unmarked HSD 2.Compound 1 (aniline)

3. Compound 8 (2-chloro-4-nitroaniline)

Figure 4-66 The color of extracted lower phase of hexyl-3-aminobenzoate azo dyes having substituent group as 2-chloro-4-nitro group.

1. Unmarked HSD 2.Compound 12 (aniline)

3. Compound 8 (2-chloro-4-nitroaniline)

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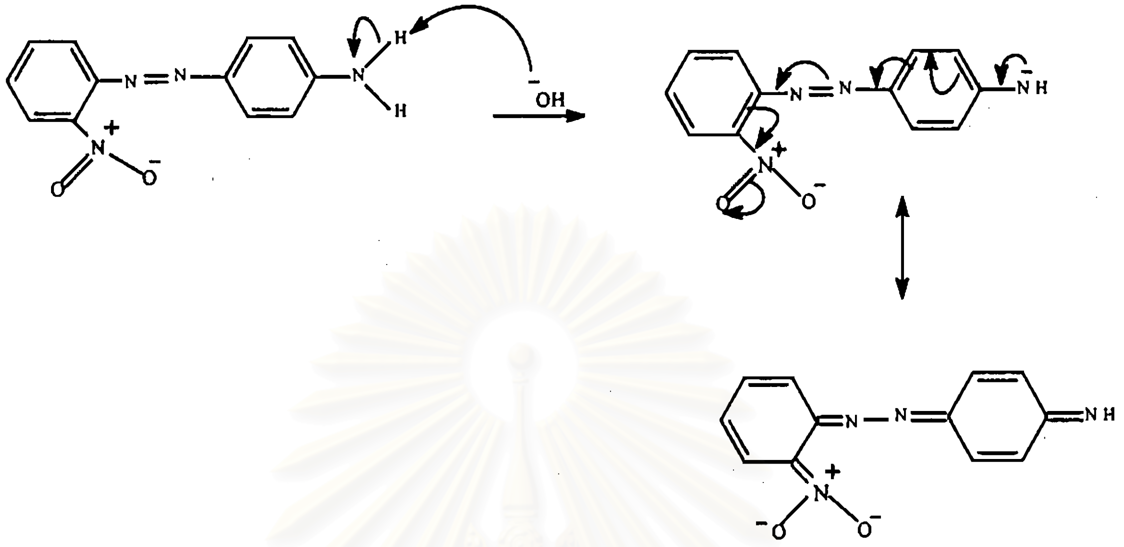
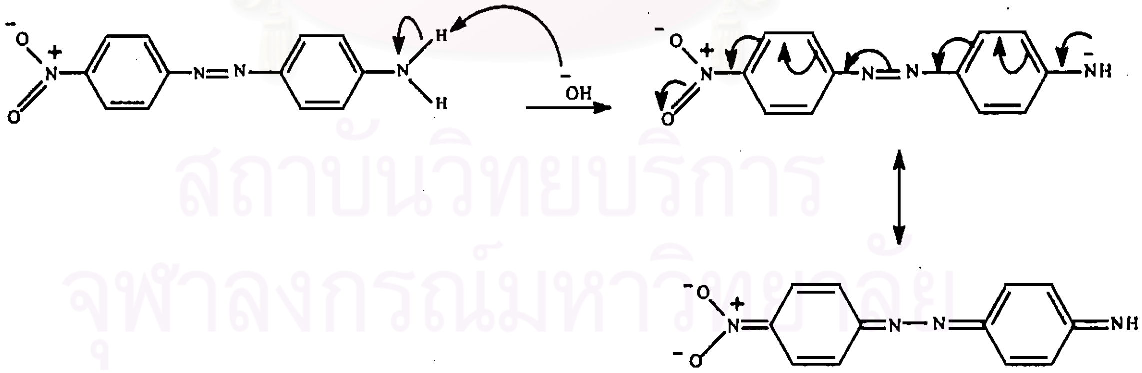
In the extraction of markers containing amino group the procedure could be carried out in both acidic and basic condition. For this present invention an alkaline extraction solution was suitable due to the production of a different color when the marker was present in HSD. While the marker was extracted with an alkaline solution, base could easily abstract proton of primary amino group. Amino group was ionized and then formed the negative charge. If the azo dye was containing nitro group (electron withdrawing) in o- and p-position to azo group in the benzene ring, the negative charge formed could be distributed more effectively into benzene ring with the resonance effect of nitro group (Schemes 4-1 to 4-2). This could increase electron mobility, resulting in a bathochromic shift. Absorption would shift to longer wavelengths, the color visualised was deeper passing from yellow-green to blue-green. Therefore, markers compounds 2, 4, 8, 13, 15 and 19, having substituent group as nitro group in o- and p- positions could be developed different color from reddish orange to red when extracted with a suitable alkaline solution. The marker not only reacted with base but also became more soluble in extraction solvent and less soluble in oil. Thus, the suitable solvent that provides the stronger color was required.



Scheme 4-1 Electron mobility of marker having substituent group as nitro in o-position.



Scheme 4-2 Electron mobility of marker having substituent group as nitro in p-position.

4.3 Suitable concentration of potassium hydroxide

From obtaining of suitable extraction solution for individual marker dye, three concentrations of potassium hydroxide in each solvent system were prepared. Compounds 2, 4, 8, 13, 15 and 19 were extracted and measured the absorption at maximum wavelength. The results were given in Tables 4-37 to 4-39

Table 4-37 Absorbance of the extracted phase of compounds 2, 4 and 8

Solvent system I	Compound 2	Compound 4	Compound 8
5%KOH in MeOH	0.354	0.284	0.340
6%KOH in MeOH	0.408	0.305	0.348
7%KOH in MeOH	***0.443***	***0.400***	***0.350***

Remark: Compounds 2,4 and 8 were measured at λ_{max} = 490.0 (Fig.4-67), 497.0 (Fig.4-69) and 500.9 nm (Fig.4-71) respectively.

Table 4-38 Absorbance of the extracted phase of compound 13

Solvent system II	Compound 13
8%KOH in 90%MeOH-EG	0.417
9%KOH in 90%MeOH-EG	0.439
10%KOH in 90%MeOH-EG	***0.458***

Remark: Compound 13 was measured at λ_{max} = 490.6 nm (Fig.4-73)

Table 4-39 Absorbance of the extracted phase of compounds 15 and 19

Solvent system III	Compound 15	Compound 19
3%KOH in EG	0.412	0.259
4%KOH in EG	0.433	0.307
5%KOH in EG	***0.461***	***0.338***

Remark: Compounds 15 and 19 were measured at λ_{max} = 498.1 (Fig.4-75) and 503.8 nm (Fig.4-77) respectively.

The results in Table 4-37 showed that compounds 2, 4 and 8 gave highest absorbance at λ_{max} when extracted with 7% KOH in MeOH. The results in Table 4- 38 showed that compound 13 gave highest absorbance at λ_{max} when extracted with 10% KOH in 90%MeOH-EG. The results in Table 4-39 showed that compounds 15 and 19 gave highest absorbance at λ_{max} when extracted with 5% KOH in EG. These extraction solutions would be used in further experiment.

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4.4 Quantitative determination

4.4.1 Calibration curve of ethyl-2-aminobenzoate-2-nitrophenyl azo

The calibration data of compound 2 at concentrations of 0, 2, 3, 4 and 5 ppm was shown in Table 4-40 and calibration curve was shown in Figure 4-68.

Table 4-40 Calibration data of compound 2

Concentration (ppm)	Color , ASTM	Absorbance (A) at λ max =490.0 nm
0.0000	L 1.0	0.0000
2.0000	L 1.0	0.2125
3.0000	L 1.0	0.3036
4.0000	L 1.0	0.4091
5.0000	L 1.0	0.5104

Calibration equation: y = 2.494865e-03 +1.016504e-01 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999786

4.4.2 Calibration curve of ethyl-2-aminobenzoate-4-nitrophenyl azo

The calibration data of compound 4 at concentrations of 0, 0.25, 0.5, 1 and 2 ppm was shown in Table 4-41 and calibration curve was shown in Figure 4-70.

Table 4-41 Calibration data of compound 4

Concentration (ppm)	Color, ASTM	Absorbance (A) at λ_{max} = 497.0 nm
0.0000	L 1.0	0.0001
0.2500	L 1.0	0.1223
0.5000	L 1.0	0.2380
1.0000	L 1.0	0.4316
2.0000	L 1.0	0.8972

Calibration equation: y = 5.244750e-03 + 4.434470e-01 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999486

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4.4.3 Calibration curve of ethyl-2-aminobenzoate-2-chloro-4-nitrophenyl azo

The calibration data of compound 8 at concentrations of 0, 0.25, 0.5, 1 and 2 ppm was shown in Table 4-42 and calibration curve was shown in Figure 4-72.

Table 4-42 Calibration data of compound 8

Concentration (ppm)	Color, ASTM	Absorbance (A) at λ_{max} = 500.9 nm
0.0000	L 1.0	0.0001
0.2500	L 1.0	0.1008
0.5000	L 1.0	0.1980
1.0000	L 1.0	0.3926
2.0000	L 1.0	0.8212

Calibration equation: y = - 4.858750e-03 + 4.098410e-01 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999722

4.4.4 Calibration curve of hexyl-3-aminobenzoate-2-nitrophenyl azo

The calibration data of compound 13 at concentrations of 0, 4, 5, 6 and 7 ppm was shown in Table 4-43 and calibration curve was shown in Figure 4-74.

Table 4-43 Calibration data of compound 1

Concentration (ppm)	Color, ASTM	Absorbance (A) at λ_{max} = 490.6 nm
0.0000	L 1.0	-0.000
4.0000	L 1.0	0.3072
5.0000	L 1.0	0.3694
6.0000	L 1.0	0.4562
7.0000	L 1.0	0.5236

Calibration equation: y = 1.126027e-03 + 7.502863e-01 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999647

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4.4.5 Calibration curve of hexyl-3-aminobenzoate-4-nitrophenyl azo

The calibration data of compound 15 at concentrations of 0, 0.5, 1, 2 and 3 ppm was shown in Table 4-44 and calibration curve was shown in Figure 4-76.

Table 4-44 Calibration data of compound 15

Concentration (ppm)	Color, ASTM	Absorbance (A) at λ_{max} = 498.1 nm
0.0000	L 1.0	-0.000
0.5000	L 1.0	0.1327
1.0000	L 1.0	0.2508
2.0000	L 1.0	0.4648
3.0000	L 1.0	0.7158

Calibration equation: y = 7.642500e-03 + 2.346950e-01 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999435

4.4.6 Calibration curve of hexyl-3-aminobenzoate-2-chloro-4-nitrophenyl azo

The calibration data of compound 19 at concentrations 0, 3, 4, 5 and 6 ppm was shown in Table 4-45 and calibration curve was shown in Figure 4-78.

Table 4-45 Calibration data of compound 19

Concentration (ppm)	Color, ASTM	Absorbance (A) at λ_{max} = 503.8 nm
0.0000	L 1.0	0.00014
3.0000	L 1.0	0.2226
4.0000	L 1.0	0.2931
5.0000	L 1.0	0.3743
6.0000	L 1.0	0.4473

Calibration equation: y = -9.841509e-04 + 7.457226e-02 * x

Where x = concentration, y = absorbance (A)

Correlation coefficient = 0.999893

The results in Tables 4-40 to 4-45 showed that markers added in HSD did not alter the color (ASTM) of original HSD or did not alter the appearance of the marked fuel. Therefore, a desirable characteristic of marker was achieved. Moreover, the results showed approximate minimum level of each marker. The minimum concentration of markers that developed the color of the extracted phase visual by the naked eyes and suitable concentration for tagging in HSD were given in Table 4-46. The suitable concentration was a concentration that gave lowest percent error in absorbance of extracted phase. That was absorbance around 0.4 [24].

Table 4-46 Minimum concentrations and suitable concentrations for tagging in HSD.

Markers	Min. concentrations (ppm)	Suitable concentrations (ppm)
Compound 2	2	4
Compound 13	4	6
Compound 4	0.25	1
Compound 15	0.5	2
Compound 8	0.25	1
Compound 19	3	5

On the other hand, from Table 4-46, comparing between suitable concentration of compounds 2 and 13, compounds 4 and 15 as well as compounds 8 and 19 showed that concentrations of hexyl-3-aminobenzoate azo dyes (compounds13, 15 and 19) added in HSD were higher than ethyl-2-aminobenzoate azo dyes (compounds 2, 4 and 8). Thus, increasing longer alkyl chain of hexyl-3-aminobenzoate azo dye to improve solubility of azo dye in fuel oil may give more difficulty in extraction than ethyl-2-aminobenzoate azo dye.

4. 5 Stability of marker dyes in HSD

The stability of marker dyes in fuel oil was studied by monitoring the amount of marker dyes added in HSD every month for the storage period of three months, using UV/VIS-spectrophotometer. The results are shown in Tables 4.47 to 4-52.

Table 4-47 The stability of 4 ppm marker compound 2 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	4.00	3.99	4.00	-
1	3.99	3.98	3.98	0.5
2	4.00	4.02	4.01	0.2
3	4.05	4.04	4.04	1.0

Table 4-48 The stability of 1 ppm marker compound 4 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	0.96	0.95	0.96	-
1	0.89	0.90	0.90	6.2
2	0.93	0.94	0.94	2.1
3	0.91	0.90	0.90	6.2

Table 4-49 The stability of 1 ppm marker compound 8 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	0.97	0.94	0.96	-
1	0.94	0.94	0.94	2.1
2	0.92	0.90	0.91	5.2
3	0.88	0.88	0.88	8.3

Table 4-50 The stability of 6 ppm marker compound 13 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	6.04	6.08	6.06	-
1	6.37	6.40	6.38	5.3
2	7.00	7.03	7.02	15.8
3	7.21	7.24	7.22	19.1

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Table 4-51 The stability of 2 ppm marker compound 15 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	1.95	1.93	1.94	-
1	1.99	1.99	1.99	2.6
2	1.86	1.90	1.88	3.1
3	1.83	1.87	1.85	4.6

Table 4-52 The stability of 5 ppm marker compound 19 in HSD.

Months	Concentration (ppm)			% Difference
	Result 1	Result 2	Average	
0	4.99	5.03	5.01	-
1	5.00	5.06	5.03	0.4
2	5.00	5.01	5.00	0.2
3	5.03	5.02	5.02	0.2

The results in Tables 4-47 to 4-52 except Table 4-50 showed that the concentration of markers could be changed no more than 10% from the original concentration in the storage period of three months. Therefore, the said markers obtained in this study were stable for at least three months, which was enough for the shelf-like of fuel before being consumed on the market. But in the case of marker compound 13, the absorption spectrum (Fig. 4-73) did not clearly show absorption band, so the exact maximum wavelength was not found. The result of stability test in Table 4-50 showed that the concentration of this marker increased more than 10% from the original concentration. Therefore, marker compound 13 was unstable to be used as marker in fuel.

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