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Kinetics and mechanism of the aminolysis of aryl thiocarbamates: effects of the non-leaving group

Hyuck Keun Oh,[a] Young Cheul Jin,[a] Dae Dong Sung[b] and Ikchoon Lee*[b,c]

[a] *Department of Chemistry, Chonbuk National University, Chonju 560-756, Korea*
[b] *Department of Chemistry, Dong-A University, Busan 604-714, Korea*
[c] *Department of Chemistry, Inha University, 253 Yonghyungdong Namgu, Inchon 402-751, Korea. E-mail: ilee@inha.ac.kr; Fax: +82-32-865-4855; Tel: +82-32-860-7681*

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The kinetics of the aminolysis of aryl thiocarbamates [ATC: $H_2NC(=O)SC_6H_4Z$] with benzylamines ($XC_6H_4CH_2NH_2$) in acetonitrile at 10.0 °C have been studied. The rate order with variation of the non-leaving amino group, RNH, in $RNHC(=O)SC_6H_4Z$ is NH_2 < PhNH < EtNH indicating that the polar (σ^*) and steric (E_s) effects of the RNH group are insignificant, and the strength of push to expel the leaving group in the tetrahedral transition state is the sole, important effect. The strong push provided by the NH_2 group, the negative ρ_{XZ} (−0.38) value, the size of β_Z (−0.54), and failure of the reactivity–selectivity principle are all consistent with the concerted mechanism. The kinetic isotope effects involving deuterated amine nucleophiles ($XC_6H_4CH_2ND_2$) are normal ($k_H/k_D \approx 1.40$–1.73) suggesting a hydrogen-bonded cyclic transition state.

Introduction

The kinetics and mechanisms of the aminolysis of aryl esters and carbonates have been widely investigated.[1,2] For example, there is abundant literature on the mechanistic studies of the aminolysis of aryl thiocarbonates,[3] **2a**, with R = alkyl or aryl group. Kinetic studies on the aminolysis mechanisms of aryl carbamates, **1**, are, however, relatively scarce,[4] albeit they (**1**) are structurally similar to the corresponding esters and carbonates. Recent works on the

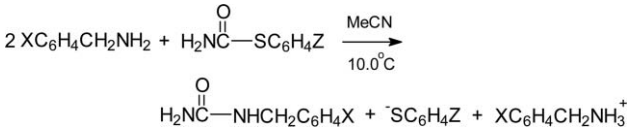
1a **2a**

1. Carbamate: Leaving group: **a**. $^-SC_6H_4Z$

2. Carbonate: **b**. $^-OC_6H_4Z$

aminolysis of aryl thiocarbamates, **1a**, with R = Et[4e] and Ph[4d] have indicated that the aminolysis rates with benzylamines in acetonitrile are more than three times faster with R = Et than with R = Ph in concerted processes. This rate enhancement with R = Et relative to R = Ph has been attributed mainly to a stronger push to expel the thiophenoxide leaving group by EtNH than by PhNH in the tetrahedral transition state.

It is, however, not well understood (i) exactly what type of electronic effect is responsible for this push, *e.g.* is it a polar or a charge-transfer effect?,[2] and (ii) whether there is a steric inhibition effect operative with a bulkier phenyl group relative to an ethyl group or not. In order to shed more light on the aminolysis mechanism of aryl thiocarbamates by elucidating effects of the non-leaving (RNH) group in **1a**, we carried out kinetic studies on the aminolysis of aryl thiocarbamates (ATC; R = H in **1a**) with benzylamines in acetonitrile, eqn. (1).



(1)

We varied the substitutents in the nucleophile (X) and the leaving group (Z), and subjected the second-order rate constants (k_2) to multiple regression analysis and determined the cross-interaction constant,[5] ρ_{XZ}, as defined by eqns. (2a) and (2b):

$$\log(k_{XZ}/k_{HH}) = \rho_X\sigma_X + \rho_Z\sigma_Z + \rho_{XZ}\sigma_X\sigma_Z \quad (2a)$$

$$\rho_{XZ} = \partial\rho_Z/\partial\sigma_X = \partial\rho_X/\partial\sigma_Z \quad (2b)$$

Results and discussion

The reactions of aryl thiocarbamates [ATC; $H_2NC(=O)SC_6H_4Z$] with X-benzylamines (BA) in acetonitrile follow clear, second-order kinetics, eqns. (3a) and (3b).

$$\text{rate} = k_{obs}[\text{ATC}] \quad (3a)$$

$$k_{obs} = k_2[\text{BA}] \quad (3b)$$

Unlike in the aminolysis of aryl *N*-phenylcarbamates[4c] [**1b** with R = Ph; $PhNHC(=O)OC_6H_4Z$] we found no base catalysis by the amine. The rate constants, k_2, determined are summarized in Table 1 together with selectivity parameters ρ_X, β_X, ρ_Z, and β_Z. The β_X (β_{nuc}) values are obtained by using the pK_a values of benzylamines in water. This procedure was found to be reliable since the pK_a values in acetonitrile and in water vary in parallel, although the absolute values are different.[1h,6] For the β_Z (β_{LG}; LG = leaving group) values, a factor of 0.62 was multiplied to all the β_Z values determined using the pK_a (H_2O) values.[4d,7]

The rate constant, k_2, estimated using the absolute rate expression[8] for X = *p*-MeO and Z = *p*-Me at 30.0 °C is 0.205 M^{-1} s^{-1} for ATC (R = H in **1a**) which is slower by more than an order of magnitude than those of the corresponding reactions for *N*-phenyl[4d] (R = Ph in **1a**; k_2 = 2.18 M^{-1} s^{-1}) and *N*-ethyl[4e] (R = Et in **1a**; k_2 = 6.96 M^{-1} s^{-1}) carbamates. Various substituent constants and relevant selectivity parameters are compared in Table 2. We note that the order observed, NH_2 < NHPh < NHEt, is not followed by the *polar* substituent constants, σ^*, since the order would be (i) NHEt < NH_2 < NHPh if the initial state of the substrate is important, *i.e.* the more positive the carbonyl carbon center, the faster is the rate, and (ii) NHPh < NH_2 < NHEt if the electron donating *polar* effect is important in the tetrahedral transition state (TS). Again, the order expected from the *steric* substituent constant, E_s, NHPh < NHEt < NH_2, is not consistent with the observed rate order. These comparisons clearly show that the polar and steric effects of the

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Table 1 The second-order rate constants, k_2 ($\times 10^2$ dm^3 mol^{-1} s^{-1}), for the reactions of Z-aryl thiocarbamates with X-benzylamines in acetonitrile at 10.0 °C

	Z					
X	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[b]
p-OMe	8.79			71.7	2.24 ± 0.12	−0.58 ± 0.02
	4.85[c]	18.5	62.0	40.6[c]		
	2.72[d]			23.4[d]		
p-Me	6.20	13.1	41.6	47.8	2.17 ± 0.10	−0.56 ± 0.02
H	4.12	8.16	25.8	29.0	2.09 ± 0.11	−0.54 ± 0.01
p-Cl	2.41			16.7	2.05 ± 0.11	−0.53 ± 0.01
	1.36[c]	4.69	14.6	9.72[c]		
	0.779[d]			5.73[d]		
m-Cl	1.67	3.29	9.62	10.4	1.97 ± 0.07	−0.51 ± 0.01
ρ_X[e]	−1.10 ± 0.04	−1.15 ± 0.04	−1.22 ± 0.05	−1.27 ± 0.05	ρ_{XZ}[f] = −0.38 ± 0.05	
β_X[g]	1.07 ± 0.02	1.13 ± 0.03	1.20 ± 0.03	1.24 ± 0.04		

[a] The σ values were taken from ref. 11. Correlation coefficients were better than 0.997 in all cases. [b] Ref. 7. The pK_a(H_2O) values were taken from the *Dictionary of Organic Compounds*, J. Buckingham and F. Macdonald, eds., Chapman and Hall, New York, 5th edn., 1982. Correlation coefficients were better than 0.999 in all cases. [c] At 0 °C. [d] At −10 °C. [e] The source of σ is same as for footnote *a*. Correlation coefficients were better than 0.998 in all cases. [f] Calculated using eqn. (2b). Correlation coefficient was 0.980 and $F_{cal} = 36.4$ ($F_{tab} = 19$ at the 95% confidence level). [g] The pK_a values were taken from: A. Streitwieser, Jr. and H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, 3rd edn., 1989, p. 693. Correlation coefficients were better than 0.999 in all cases.

Table 2 Selected substituents and selectivity parameters

R (in RNH)	k_2[a]/M^{-1} s^{-1}	σ_m[b]	σ_p^+[b]	σ_p^+[b]	σ^*[c]	E_s[c]	β_X[d]	β_Z[e]	ρ_{XZ}
H	0.205	−0.16	−0.66	−1.30	0	0	1.13	−0.54	−0.38
Et[f]	6.96	−0.24	−0.61	−1.80	−1.00	−0.36	0.87	−0.32	−0.86
Ph[g]	2.18	−0.02	−0.56	−1.40	+0.600	−0.38	1.31	−0.48	−0.63

[a] For X = *p*-MeO and Z = *p*-Me at 30.0 °C. [b] For RNH, ref. 10. [c] From R. C. D. Johnson, *The Hammett Equation*, Cambridge University Press, Cambridge, 1973, ch. 3. [d] For Z = H. [e] For X = H. [f] Ref. 4*e*. [g] Ref. 4*d*.

amino non-leaving group (RNH) on the rates of aminolysis are insignificant. As we have stressed in the previous reports,[4d,e] the effect of the amino non-leaving group can only be rationalized by the strength of push provided to expel the leaving group in the tetrahedral TS. It seems that the polar and steric effects are swamped out, or overwhelmed, by the strong push of the amino non-leaving group. The σ_p^+ constants can be a measure of the charge transfer since they represent proximate charge transfer through the π* orbital of benzene ring to an electron deficient center. The strength of push represented by the σ_p^+ constant parallels well with the rate order observed, NH_2 < NHPh < NHEt. This is quite reasonable since the lone pair on the nitrogen atom, n_N, can be antiperiplanar to,[9] and can vicinally overlap with, the σ* bond orbital of the C–S bond,[10] σ^*_{C-S}, and the $n_N \rightarrow \sigma^*_{C-S}$ charge-transfer interaction can be efficient in the tetrahedral TS, but not in the initial state where the two orbitals, n_N and σ^*_{C-S}, are nearly orthogonal and can scarcely interact (or overlap). The charge transfer becomes stronger, the higher the n_N and the lower the σ^*_{C-S}, since the second-order perturbation stabilization energy, $\Delta E^{(2)}$, is inversely related to the energy gap between the two interacting orbitals,[10] $\Delta\varepsilon = \varepsilon_{\sigma*} - \varepsilon_n$ [eqn. (4)],

$$\Delta E^{(2)} = -\frac{2F^2_{n\sigma*}}{\Delta\varepsilon} \quad (4)$$

where $F_{n\sigma*}$ is the Fock matrix element which is propotional to the overlap, $S_{n\sigma*}$, of the two interacting orbitals.

The electron donating ability of the amino group is dependent on the level of n_N orbitals, the higher the n_N level the greater is the electron donating effect. The level of the n_N is in the order $\varepsilon_N(NH_2) < \varepsilon_N(NHPh) < \varepsilon_N(NHEt)$ since the electron releasing effect of R in RNH (σ_p^+ is 0, −0.18 and −0.30 for R = H, Ph, and Et)[11] is in the same order, and the greater the electron releasing ability of R, the higher the n_N is elevated.[10c] Likewise, in general RNH groups are stronger electron donors than the corresponding RO groups since the level of n_N is higher than that of n_O.[10a] The stronger electron donating effect of RNH than RO is reflected in the σ_p^+ constant, *e.g.* for EtO and EtNH the σ_p^+ values are −0.81 and −1.80, respectively.[11]

The aminolysis of *S*-aryl *O*-ethyl thiocarbonates [**2a** with R = Et; EtO–C(=O)SC_6H_4Z] with secondary alicyclic amines in water is reported to proceed concertedly only when nucleofugality of the leaving group is strong enough [with Z = 2,4-$(NO_2)_2$ and Z = 2,4,6-$(NO_2)_3$][3a,b] to sufficiently destabilize the putative zwitterionic tetrahedral intermediate, $T^{\pm}$, so that it cannot exist. This is in contrast to a stepwise mechanism for other compounds with poor leaving groups[3e] (Z = 4-NO_2, 4-Cl, H, 4-Me, or 4-MeO). Similarly, the corresponding aminolysis with anilines is concerted with Z = 2,4,6-$(NO_2)_3$ but is stepwise with Z = 2,4-$(NO_2)_2$.[12]

The nucleofugality of the leaving group can be enhanced by a strong $n_{NLG} \rightarrow \sigma^*_{C-LG}$ charge transfer from the non-leaving group (NLG) with appropriate lone pair orbital(s) (n_{NLG}) to the σ* anti-bonding orbital of the carbonyl carbon-leaving group bond (σ^*_{C-LG}). When this enhancement is strong enough, the putative tetrahedral intermediate $T^{\pm}$ is destabilized to such an extent that the aminolysis of carbonates and carbamates containing a relatively strong leaving group can lead to a concerted process. For example, a mechanistic change occurs from a stepwise process with a phenoxide[4c,13] (**b**: $^-$OAr) to a concerted process with a thiophenoxide leaving group[3f,4d] (**a**: $^-$SAr) as the charge-transfer electron donating ability of the non-leaving group is increased by the change from alkyl or aryl (R) to EtO or RNH group. This is due to the greater nucleofugality of $^-$SAr than $^-$OAr; the σ^*_{C-S} orbital is lower than the σ^*_{C-O} level and hence is a better electron acceptor with a smaller energy gap,[9,10a] $\Delta\varepsilon$ in eqn. (4), leading to a more facile bond scission of C–S than C–O. For example, the aminolysis of *N*-phenyl aryl carbamates (R = Ph in **1b**) with benzylamines in acetonitrile is stepwise[4c] ($\beta_X = 1.6$ with Z = 4-NO_2, $\rho_{XZ} = +1.10$) in contrast

to a concerted process[4d] ($\beta_X = 1.3$ with Z = H, $\rho_{XZ} = -0.63$) for the thiocarbamates (R = Ph in **1a**). Similar mechanistic change is also observed with *O*-ethyl arylcarbonates[13] (stepwise) and thiocarbonates[3f] (concerted).

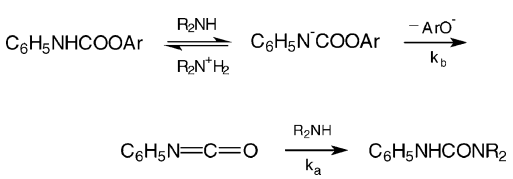
Since such strong destabilization of $T^{\pm}$ should be provided by a stronger push to expel the leaving group by the amino non-leaving group, R = H in **1a** ($\sigma_p^+ = -0.81$ and -1.30 for EtO and NH_2 groups,[11] respectively), the aminolysis of ATC (**1a** with R = H) with benzylamines in acetonitrile is proposed to proceed concertedly. The β_Z values in Table 1 are within the range of values that are expected for a concerted mechanism.[14] Further support for the concerted mechanism is provided by a negative ρ_{XZ} (-0.38) obtained,[5,9] and failure of the reactivity–selectivity principle (RSP).[9] The selectivities (ρ and β values in Table 1) are greater for the faster reactions. This type of anti-RSP is considered another criterion for the concerted aminolysis.[9]

Reference to Table 1 reveals that the β_X values are *ca.* 1.07–1.24 which are rather larger than the values normally expected for the concerted aminolysis processes, $\beta_X \approx 0.4$–0.7.[3a,12,14a] However, β_X values smaller than 0.4[15] as well as those larger than 0.7[16] have also been observed for the concerted reactions. Especially in solvents less polar than water, larger β_X values (*ca.* 1.3–1.6)[17] are often obtained for the concerted processes. Thus the large β_X values in the present work may be due to the less polar solvent used, acetonitrile. The relatively large β_X values may reflect rather tight bond formation in the TS.

Strong destabilization incurred by powerful nucleofugality of benzylamines from $T^{\pm}$ is known to cause the aminolysis to proceed by a concerted mechanism.[1h] The order of the increasing rate of expulsion of amines from $T^{\pm}$ is reported as[9] pyridines < anilines < secondary alicyclic amines < quinuclidines < benzylamines. Moreover, it has been shown that carbonyl (C=O) has a greater proclivity for the concerted mechanism than the thiocarbonyl (C=S) group[18] due to a narrower energy gap between π^* and σ^* levels, $\Delta\varepsilon = \varepsilon(\pi^*_{C=O}) - \varepsilon(\sigma^*_{C-S}) < \Delta\varepsilon = \varepsilon(\pi^*_{C=S}) - \varepsilon(\sigma^*_{C-S})$, enabling efficient mixing of the two anti-bonding orbitals.[9,19] Thus, concerted mechanisms are found for the aminolyses of *S*-(2,4-dinitrophenyl)[18] and *S*-(2,4,6-trinitrophenyl)[3b] *O*-ethyl thiocarbonates in contrast to the stepwise mechanisms for the corresponding dithiocarbonates.[20] Less polar solvents are also conducive to a concerted mechanism as observed for the aminolysis of carbonates from stepwise in water to concerted in acetonitrile.[3f,21,22] For example, the aminolysis of 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates is stepwise[20] (biphasic Brønsted plot) in water, but is concerted ($\beta_X = 0.53$) in a less polar solvent (44 wt% aqueous EtOH).[23] The change of solvent from water to a less polar solvent such as MeCN destabilizes the zwitterionic intermediate by enhancing the rate of expulsion of the amine from $T^{\pm}$, and renders the intermediate, $T^{\pm}$, more unstable kinetically so that a concerted mechanism is enforced.[21c,23]

In summary, the strong push provided by the amino non-leaving group, the less polar solvent, MeCN than water, carbonyl rather than a thiocarbonyl group, and the strong nucleofugality of benzylamines from $T^{\pm}$ are all conducive to the concerted mechanism.

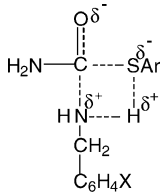
The E1cB mechanism, Scheme 1, proposed by Menger and Glass[4a] for the reaction of *p*-nitrophenyl *N*-phenyl carbamate with diethylamine in toluene can be ruled out based on our results, especially with the non-zero cross-interaction constant observed $\rho_{XZ} = -0.38$. In the leaving group departure, k_b, and amine addition, k_a, processes, there can be no interaction between the nucleophile (X) and leaving group (Z) so that ρ_{XZ} should vanish[5] ($\rho_{XZ} = 0$) which is not consisted with our result, $\rho_{XZ} \neq 0$. In the deprotonation equilibrium, the forward rate, k_f, will be retarded by a stronger electron donor R in RNH, due to a greater basicity of the amine, *i.e.* k_f (EtNH) < k_f (NH_2), rather than accelerated as observed (Table 2).



Scheme 1

We note in Table 2 that the leaving group departure in the TS is the least ($\beta_Z = -0.32$) for the fastest reaction with EtNH and the greatest ($\beta_Z = -0.54$) for the slowest reaction with NH_2. This is in agreement with the Bell–Evans–Polanyi (BEP) principle[24] and reflects the importance of bond cleavage in the TS, since the faster the reaction the earlier is the progress of the reaction in the TS. It is also noteworthy that the magnitude of ρ_{XZ} is the largest, *i.e.* the TS is the tightest, for NHEt and the smallest, *i.e.* the TS is the loosest,[5] for NH_2. This is also a manifestation of the importance of leaving group departure in the TS, since the degree of bond cleavage evidenced by the magnitude of β_Z reflects the overall tightness (or looseness) of the TS.

The kinetic isotope effects, k_H/k_D, involving deuterated benzylamines ($XC_6H_4CH_2ND_2$)[25] in Table 3 are larger than unity (*ca.* 1.40–1.73) indicating that a proton transfer is involved in the TS, which in turn suggests a hydrogen-bonded cyclic TS. The relatively low $\Delta H^{\neq}$ with large, negative $\Delta S^{\neq}$ values in Table 4 are consistent with this proposed TS structure. The $\Delta H^{\neq}$ values are small due to a large energy gain in C–N bond formation relative to energy loss in C–S bond cleavage in the TS and also to the assistance in the C–S bond cleavage by the hydrogen bonding, and the $\Delta S^{\neq}$ values are large and negative due to the strained, cyclic, four-membered TS structure.



TS

Table 3 Kinetic isotope effects for the reactions of Z-aryl thiocarbamates with deuterated X-benzylamines ($XC_6H_4CH_2ND_2$) in acetonitrile at 10.0 °C

X	Z	k_H ($\times 10^2$ M^{-1} s^{-1})	k_D ($\times 10^2$ M^{-1} s^{-1})	k_H/k_D
p-OMe	*p*-Me	8.79 (±0.07)[a]	5.32 (±0.05)[a]	1.65 ± 0.02[a]
p-OMe	H	18.5 (±0.2)	11.8 (±0.1)	1.57 ± 0.02
p-OMe	*p*-Cl	62.0 (±1.0)	41.9 (±0.7)	1.49 ± 0.04
p-OMe	*p*-Br	71.7 (±1.2)	51.2 (±0.8)	1.40 ± 0.03
p-Cl	*p*-Me	2.41 (±0.03)	1.39 (±0.02)	1.73 ± 0.03
p-Cl	H	4.69 (±0.04)	2.86 (±0.02)	1.64 ± 0.02
p-Cl	*p*-Cl	14.6 (±0.1)	9.36 (±0.08)	1.56 ± 0.02
p-Cl	*p*-Br	16.2 (±0.2)	11.2 (±0.1)	1.45 ± 0.02

[a] Standard deviations.

Table 4 Activation parameters[a] for the reactions of Z-aryl thiocarbamates with X-benzylamines in acetonitrile

X	Z	$\Delta H^{\neq}$/kcal mol^{-1}	$-\Delta S^{\neq}$/cal mol^{-1} K^{-1}
p-OMe	*p*-Me	8.1	35
p-OMe	*p*-Br	7.6	32
p-Cl	*p*-Me	7.6	38
p-Cl	*p*-Br	7.3	36

[a] Calculated using the Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964, p. 378) are ±0.4 kcal mol^{-1} and ±2 e.u. for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

Experimental

Materials

GR grade acetonitrile was used after three distillations. The benzylamine nucleophiles were used without further purification. GR grade thiophenols and potassium cyanate were used.

Preparations of aryl thiocarbamates. The aryl thiocarbamates were prepared by the literature method of Al-Rawi and Williams.[26] These substrates were prepared by adding acetic acid (1 mL) over a period of 5 min to a stirred suspension of thiophenol (1 g) and potassium cyanate (0.8 g) in water (10 mL). After about 15 min, a precipitate formed which was filtered and recrystallized. Melting point, IR (Nicolet 5BX FT-IR) and ^{1}H and ^{13}C NMR (JEOL 400 MHz) data were found to agree well with the literature values.[26]

Kinetic measurement

Rates were measured conductometrically at 10.0 ± 0.05 °C. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge.[27] Pseudo-first-order rate constants, k_{obs}, were determined by the Guggenheim method[28] with large excess of benzylamine. Second-order rate constants, k_2, were obtained from the slope of a plot of k_{obs} *vs.* benzylamine with more than five concentrations. The values reported are averages of more than three runs and were reproducible to within ±3%.

Product analysis

Substrate, phenyl thiocarbamates (*ca.* 1.0×10^{-3} mol) was reacted with excess *p*-chlorobenzylamine (*ca.* 1.0×10^{-2} mol) with stirring for more than 15 half-lives at 10.0 °C in *ca.* 200 ml acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 20% ethyl acetate–n-hexane). Analysis of the product gave the following results.

$H_2NC(=O)NHCH_2C_6H_4OCH_3$-*p*. Mp 110–112 °C, yield (47%), IR (KBr), 3435 (N-H), 2836 (C–H, CH_3), 1650 (C=O), 1514 (C–C, aromatic), 1491(C=C, aromatic), 1459 (C–H, CH_2), 703 (C–H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.80 (3H, s, CH_3), 4.29 (2H, s, CH_2), *ca.* 7.21–7.27 (4H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 155.5, 138.4, 132.1, 128.3, 128.1, 55.6, 40.3; Mass, *m*/*z* 180 (M^+). Anal. calc. for $C_9H_{12}N_2O_2$: C, 60.0; H, 6.71. Found: C, 60.2; H, 6.72%.

$H_2NC(=O)NHCH_2C_6H_4CH_3$-*p*. Mp 94–96 °C, yield (45%), IR (KBr), 3432 (N–H), 2852 (C–H, CH_3), 1653 (C=O), 1511 (C–C, aromatic), 1495 (C=C, aromatic), 1463 (C–H, CH_2), 701 (C–H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.95 (3H, s, CH_3), 4.25 (2H, s, CH_2), *ca.* 7.18–7.25 (4H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 154.3, 137.9, 132.3, 128.4, 128.0, 40.5; Mass, *m*/*z* 164 (M^+). Anal. calc. for $C_9H_{12}N_2O$: C, 65.8; H, 7.40. Found: C, 65.6; H, 7.38%.

$H_2NC(=O)NHCH_2C_6H_5$. Mp 72–74 °C, yield (50%), IR (KBr), 3429 (N–H), 1651 (C=O), 1513 (C–C, aromatic), 1489 (C=C, aromatic), 1458 (C–H, CH_2), 702 (C–H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), δ 4.34 (2H, s, CH_2), *ca.* 7.20–7.27 (5H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 155.2, 138.0, 132.2, 128.3, 128.0, 39.9; Mass, *m*/*z* 150 (M^+). Anal. calc. for $C_8H_{10}N_2O$: C, 64.0; H, 6.71. Found: C, 64.2; H, 6.72%.

$H_2NC(=O)NHCH_2C_6H_4Cl$-*p*. Mp 85–87 °C, yield (42%), IR (KBr), 3438 (N–H), 1085 (C–Cl), 1652 (C=O), 1512 (C–C, aromatic), 1492 (C=C, aromatic), 1461 (C–H, CH_2), 705 (C–H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), δ 4.31 (2H, s, CH_2), *ca.* 7.23–7.29 (4H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 154.8, 138.2, 132.2, 128.5, 128.1, 40.1; Mass, *m*/*z* 184 (M^+). Anal. calc. for $C_8H_9ClN_2O$: C, 52.0; H, 4.91. Found: C, 52.1; H, 4.92%.

$H_2NC(=O)NHCH_2C_6H_4Cl$-*m*. Mp 82–84 °C, yield (38%), IR (KBr), 3436 (N–H), 1078 (C–Cl), 1649 (C=O), 1509 (C–C, aromatic), 1490 (C=C, aromatic), 1462 (C–H, CH_2), 703 (C–H, aromatic); ^{1}H NMR (400 MHz, $CDCl_3$), δ 4.28 (2H, s, CH_2), *ca.* 7.24–7.31 (4H, m, aromatic ring); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 154.2, 142.5, 138.1, 132.0, 129.5, 128.2, 127.8, 40.2; Mass, *m*/*z* 184 (M^+). Anal. calc. for $C_8H_9ClN_2O$: C, 52.0; H, 4.91. Found: C, 52.2; H, 4.90%.

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