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Nucleophilic Substitution Reactions of Aryl *N*-Phenyl Thiocarbamates with Benzylamines in Acetonitrile

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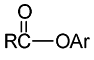
Received January 27, 2004

The aminolysis reactions of aryl *N*-phenythiocarbamates ($PhNHC(=O)SC_6H_4Z$; **3b**) with benzylamines ($XC_6H_4CH_2NH_2$) in acetonitrile are studied. Rates are much faster than the corresponding reactions of aryl *N*-phenylcarbamates ($PhNHC(=O)OC_6H_4Z$; **3a**). The rate increase from **3a** to **3b** is greater than that expected from substitution of thiophenoxide for phenoxide leaving group in the stepwise aminolysis reactions of esters. This large rate increase and the similar change in the aminolysis rates that are reported to occur from aryl ethyl carbonate ($EtOC(=O)OC_6H_4Z$; **2a**) to aryl ethylthiocarbonate ($EtOC(=O)SC_6H_4Z$; **2b**) lead us to conclude that the aminolysis of **3b** proceeds by a concerted mechanism in contrast to a stepwise process for **3a**. The negative ρ_{XZ} values (−0.63) and violation of the reactivity−selectivity principle (RSP) support the proposed mechanism. The large β_X values (1.3−1.5) obtained are considered to indicate a large degree of bond making in the transition state, which is consistent with the relatively large kinetic isotope effects ($k_H/k_D > 1.0$) observed.

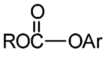
Introduction

Aryl esters **1**, carbonates **2**, and carbamates **3** are three classes of compounds that differ only in the acyl part, R, RO, and RNH, where R is alkyl or aryl. The aminolysis



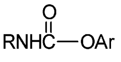
$RC(=O){-}OAr$

1



$ROC(=O){-}OAr$

2



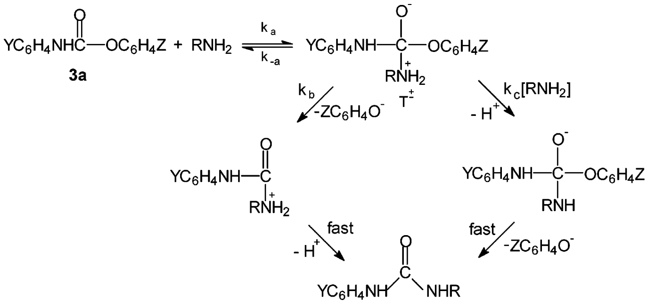
$RNHC(=O){-}OAr$

3

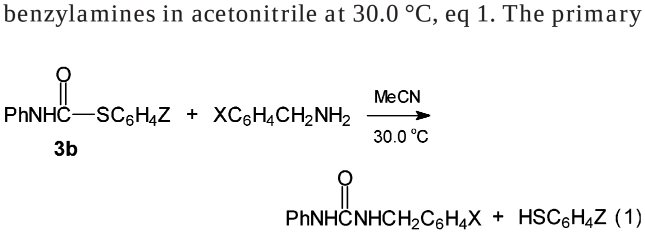
mechanism of the carbonates is quite similar to that of esters **1** and carbonates **2**, especially to the latter. For example, the aminolysis of aryl *O*-ethyl carbonates[1] (**2a**; R = Et) and aryl *N*-phenylcarbamates[2] (**3a**; R = C_6H_4Y) was found to proceed via two reaction pathways, uncatalyzed (k_b) and catalyzed ($k_c[RNH_2]$), Scheme 1 (shown for **3a**), through a zwitterionic tetrahedral intermediate, $T^{\pm}$. For the two (**2a** and **3a**) aminolysis reactions with benzylamines, the β_X values are large ($\beta_X > 1.0$) and the signs of ρ_{XY} (+1.10 for **3a**) and ρ_{XZ} (+0.16 for **2a**) are positive with adherence to the reactivity−selectivity principle (RSP).[3]

The stepwise aminolysis mechanism of **2a** through a tetrahedral intermediate, however, shifts to a concerted process when the leaving group is changed to a thiophenoxide[4] (**2b**; EtOC(=O)SAr) instead of a phenoxide ($^{-}$O-Ar). The push provided by an EtO group to expel $^{-}$SAr in $T^{\pm}$ is now strong enough to make the intermediate so unstable that the intermediate cannot exist. In view of the similar strong push expected from a PhNH group to expel the $^{-}$SAr group in $T^{\pm}$, it is of interest to see whether the aminolysis mechanism of the thiol analogue of aryl *N*-phenylthiocarbamates, $C_6H_5NHC(=O)SC_6H_4Z$ (**3b**), also shifts to a concerted mechanism or not.

SCHEME 1



In this work, we carried out kinetic studies on the aminolysis of aryl *N*-phenylthiocarbamates (**3b**) with benzylamines in acetonitrile at 30.0 °C, eq 1. The primary



$$PhNHC(=O){-}SC_6H_4Z + XC_6H_4CH_2NH_2 \xrightarrow[30.0\ ^{\circ}C]{MeCN} PhNHC(=O)NHCH_2C_6H_4X + HSC_6H_4Z \quad (1)$$

3b

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10.1021/jo049845+ CCC: $27.50

TABLE 1. Second-Order Rate Constants, k_2 ($dm^3\ mol^{-1}\ s^{-1}$), for the Reactions of Z-Phenyl *N*-Phenyl Thiocarbamates with X-Benzylamines in Acetonitrile at 30.0 °C

	Z					
X	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Z[a]	β_Z[b]
	3.95[c]			26.9		
p-OMe	2.18	3.97	13.0	15.1	2.07 ± 0.17	−0.55
	1.19[d]			8.43		
p-Me	1.44	2.77	7.60	8.84	1.92 ± 0.11	−0.51
H	0.959	1.75	4.40	5.51	1.81 ± 0.15	−0.48
	0.822			4.24		
p-Cl	0.451	0.805	2.03	2.33	1.74 ± 0.10	−0.46
	0.243			1.27		
m-Cl	0.311	0.558	1.26	1.47	1.62 ± 0.09	−0.43
ρ_X[e]	-1.30 ± 0.05	-1.33 ± 0.04	-1.54 ± 0.07	-1.54 ± 0.07		
					ρ_{XZ}[f] =	−0.63
β_X[g]	1.28 ± 0.02	1.31 ± 0.02	1.50 ± 0.03	1.51 ± 0.03		

[a] The σ values were taken from: Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Table 7-1. Correlation coefficients were better than 0.994 in all cases. [b] The pK_a values were taken from: Buckingham, J., Ed. *Dictionary of Organic Chemistry*, 5th ed.; Chapman and Hall: New York, 1982. Z = *m*-Cl was excluded from the Brönsted plot for β_Z due to an unreliable pK_a value. Correlation coefficients were better than 0.993 in all cases. [c] At 40 °C. [d] At 20 °C [e] The σ values were taken from: McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420. Correlation coefficients were better than 0.997 in all cases. [f] Correlation coefficients were 0.997. [g] The pK_a values were taken from: Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588. Correlation coefficients were better than 0.999 in all cases. X = *p*-CH_3O were excluded from the Brönsted plot for β_X (benzylamine) due to an unreliable pK_a value listed.

purpose of the present work is to establish the aminolysis reaction mechanism for eq 1 and to see whether the mechanistic change from a stepwise to a concerted by the change **2a** → **2b** is also carried on to the change **3a** → **3b** or not. In this work, we invoke the mechanistic criteria based on the sign of cross-interaction constants,[5] ρ_{XZ} (eq 2) where X and Z are the substituents in the nucleophile and leaving group, respectively; for a stepwise mechanism the sign of ρ_{XZ} was invariably positive and the RSP was found to hold.[5d,6]

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

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

Results and Discussion

The reactions of aryl *N*-phenylthiocarbamates (**3b**; $C_6H_5NHC({=}O)SC_6H_4Z$) with benzylamines

$$\text{rate} = k_{obs}[\text{substrate}] \qquad (3a)$$

$$k_{obs} = k_2[\text{benzylamine}] \qquad (3b)$$

follow a clean second-order kinetics, eq 3. Unlike in the aminolysis of aryl *N*-phenylcarbamate (**3a**), no base catalysis by the amine was noted. The rate constants, k_2, determined are summarized in Table 1 together with the selectivity parameters ρ_X, β_X, ρ_Z, and β_Z. For the determination of β_X (β_{nuc}), the pK_a values of benzylamines in H_2O are used. This procedure was found to be reliable since the pK_a values in MeCN and in H_2O vary in parallel, although the absolute values are different.[7] For the β_Z (β_{lg}) values, a factor of 0.62[8] was multiplied to all the β_Z values determined using the pK_a(H_2O) values.[8] We note in Table 1 that the rates are substantially faster than those for the corresponding aminolysis of thio esters, **1b**, which are reported to be in the order of 10^{-3} M^{-1} s^{-1} at 45−55 °C for R = Me,[9] Et,[10] Ph,[11] and $PhCH_2$.[12] For example, the estimated k_2 value for $PhCH_2C({=}O)SC_6H_4$-4-NO_2 at 55.0 °C[12] is 9.78×10^{-2} M^{-1} s^{-1}, whereas that for the aminolysis of the corresponding thiocarbonate, $PhNHC({=}O)SC_6H_4$-4-NO_2, at 25.0 °C is 6.55×10^{-1} M^{-1} s^{-1}. This rate enhancement by substitution of R = PhNH for R = $PhCH_2$ is no doubt due to a stronger push provided by the PhNH group to expel the leaving group, $^{-}$SAr, as a result of the vicinal charge-transfer interaction of the lone-pair electron on the nitrogen atom (n_N) with the σ^* orbital of the C−S bond (σ^*_{C-S}), $n_N \rightarrow \sigma^*_{C-S}$ interaction. This interaction is especially strong due to the lower σ^*_{C-S} level, compared with the σ^*_{C-O} level[13] in the substrates with phenoxide leaving group ($^{-}$OAr). This is evident by comparing the rates of the aminolysis of **3a** ($k_2 = 0.655$ M^{-1} s^{-1} at 25.0 °C with X = H and Z = 4-NO_2) with **3b** ($k_2 = 45.2$ M^{-1} s^{-1} at 30.0 °C with X = H and Z = 4-NO_2 (estimated)). The lone-pair electrons on N can also delocalize into the π^* orbital of the carbonyl group by an $n_N \rightarrow \pi^*_{C=O}$ interaction. This will facilitate the formation of a tetrahedral structure, which can be a transition state in the concerted reaction or an intermediate in the stepwise reaction.

The situation is quite similar to that observed between *O*-ethyl carbonate[1] (**2a**; $EtOC({=}O)OAr$) and *O*-ethyl thiocarbonates[4] (**2b**; $EtOC({=}O)SAr$). The aminolysis rates of the latter were faster than the former, $k_2 = 0.455$

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M^{-1} s^{-1} for X = H and Z = 3-NO_2 at 45.0 °C and k_2 = 6.30 × 10^{-2} M^{-1} s^{-1} for X = H and Z = 3-NO_2 at 45.0 °C (estimated)[1], for **2b** and **2a**, respectively. The rate enhancement due to an increased nucleofugality with SAr compared to OAr is ca. 7 times for R = EtO, while it is much greater, at least 50 times for R = PhNH. This suggests that the rate increase is not completely due to the substitution of SAr for OAr, but the mechanistic change from stepwise to concerted is partly responsible. In fact, the substitution of SAr for OAr was found to result in only ca. 2−3 times the rate increase when there is no mechanistic change. The aminolysis of 2,4-dinitrophenyl thioacetate,[14] $CH_3C(=O)SC_6H_3(NO_2)_2$, with alicyclic secondary amines is only ca. 2−3 times faster than those corresponding rates of 2,4-dinitrophenyl acetate,[15] $CH_3C(=O)OC_6H_3(NO_2)_2$, in aqueous solution at 25.0 °C. These two reactions were found to proceed stepwise with rate-limiting expulsion of the leaving group, $^{-}$SAr in the former and $^{-}$OAr in the latter. The unusually large aminolysis rate increase from **3a** to **3b** is therefore most likely caused partly by a change of mechanism from a stepwise (for **3a**) to a concerted (for **3b**), similar to the rate increase accompanied by a mechanistic change observed from **2a** to **2b**.

Further important mechanistic criteria for the concerted reaction with **3b** rather than the stepwise reaction (as with **3a**) is that the sign of cross-interaction constant ρ_{XZ} is negative for **3b** (rather than positive as with **3a**) and the reactivity−selectivity principle (a stronger reactivity is accompanied by a lower selectivity; RSP) fails with **3b**.[5d,6] The stepwise mechanism is not favored for the present reactions, since for the stepwise aminolysis of esters, carbonates and carbamates, the sign of ρ_{XZ} (and ρ_{XY}) is positive and the RSP holds.[5d,6]

The magnitude of β_X is, however, large ($\beta_X \cong 1.3-1.5$), which is normally considered to indicate a stepwise reaction.[16] For concerted aminolysis reactions, the β_X values were found to range from 0.4−0.8.[17] It is, however, well-known that the large magnitude of the Brönsted slope alone is not sufficient to decide the aminolysis mechanism as stepwise. Jencks and co-workers reported concerted acyl-transfer reactions with large β_X values, β_X = 0.6−0.9 for the reactions of phenyl formates with substituted *O*-chlorophenolate anions[18] and β_X = 0.7−1.0 for the reactions of a series of nucleophilic reagents with substituted *N*-acetylpyridinium ions.[19] Williams and co-workers[20] reported even larger β_X values (β_X = 1.3 and 1.6) for the concerted acyl-transfer reactions. Thus, the large β_X values observed in the present work may be taken as an indicative of a stepwise mechanism but cannot provide conclusive evidence for a stepwise mechanism.

TABLE 2. Kinetic Isotope Effects for the Reactions of Z-Phenyl *N*-Phenyl Thiocarbamates with X-Benzylamines in Acetonitrile at 30.0 °C

X	Z	k_H (M^{-1} s^{-1})	k_D (M^{-1} s^{-1})	k_H/k_D
p-OMe	*p*-Me	2.18 (±0.05)	1.70 (±0.02)	1.28 ± 0.03[a]
p-OMe	H	3.97 (±0.06)	2.96 (±0.06)	1.34 ± 0.08
p-OMe	*p*-Cl	13.0 (±0.1)	9.35 (±0.08)	1.39 ± 0.02
P-OMe	*p*-Me	15.1 (±0.2)	10.6 (±0.09)	1.43 ± 0.02
p-Cl	*p*-Br	0.451 (±0.004)	0.364 (±0.002)	1.24 ± 0.01
p-Cl	H	0.805 (±0.008)	0.615 (±0.005)	1.31 ± 0.02
p-Cl	*p*-Cl	2.03 (±0.04)	1.48 (±0.02)	1.37 ± 0.03
p-Cl	*p*-Br	2.33 (±0.05)	1.65 (±0.02)	1.41 ± 0.03

[a] Standard deviations.

TABLE 3. Activation Parameters[a] for the Reactions of Z-Phenyl *N*-Phenyl Thiocarbamates with X-Benzylamines in Acetonitrile

X	Z	$\Delta H^{\ddagger}$/kcal mol^{-1} [b]	$-\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
p-OMe	*p*-Me	10.5	22
p-OMe	*p*-Br	10.1	20
p-Cl	*p*-Me	9.4	29
p-Cl	*p*-Br	10.5	22

[a] Calculated by use of the Eyring equation with the k_2 values at three temperatures: 20, 30, and 40 °C. The maximum errors calculated (by the method of: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; p 378) are ±1.0 kcal mol^{-1} and ±4 eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. [b] Correlation coefficients were better than 0.9996 in all cases.

The kinetic isotope effects (k_H/k_D) involving deuterated benzylamines[5c] ($XC_6H_4CH_2ND_2$) are presented in Table 2. We note that the isotope effects are normal with k_H/k_D > 1.0 suggesting there is a hydrogen bond formed by the amino proton (N−H or N−D) in the TS, most probably with the negatively charged S atom in the leaving group. Since the large β_X and β_Z values suggest that the TS is a late type with a large degree of bond formation and bond cleavage, the hydrogen bonding seems to be rather strong with relatively large values of k_H/k_D > 1.0. This is supported by a larger k_H/k_D value for a stronger nucleophilie ($\delta\sigma_X < 0$) and a stronger nucleofuge ($\delta\sigma_Z > 0$), which will lead to a later TS in accordance with the negative ρ_{XZ}; a stronger nucleophile, $\delta\sigma_X < 0$, gave a larger ρ_Z value $\delta\rho_Z > 0$ so that $\rho_{XZ} = \delta\rho_Z/\delta\sigma_X < 0$, while a stronger nucleofuge, $\delta\sigma_Z > 0$, gave a larger negative ρ_X value ($\delta\rho_X < 0$) leading to $\rho_{XZ} < 0$.

The activation parameters determined with the rate data at three temperatures are summarized in Table 3. The values are well within the ranges obtained for the concerted reactions. However, it is difficult to distinguish by the magnitude of the activation parameters a stepwise from a concerted process. For example, the $\Delta H^{\ddagger}$ and $-\Delta S^{\ddagger}$ values for the aminolysis reactions of **2a** (stepwise)[1] and **2b** (concerted)[4] are 14.4−15.0 kcal mol^{-1}, 17−21 eu and 12.5−16.3 kcal mol^{-1}, 15−28 2 eu, respectively.

In summary, the nucleophilic substitution reactions of aryl *N*-phenylthiocarbamates (**3b**) with benzylamines in acetonitrile proceed by a concerted mechanism, which is in contrast to the stepwise mechanism of the corresponding reactions of aryl *N*-phenylcarbamates (**3a**). The mechanistic change occurred by substitution of SAr (**3b**) for OAr (**3a**) is quite similar to the mechanistic change

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reported from aryl ethyl carbonate (**2a**) to aryl ethylthiocarbonate (**2b**).

Experimental Section

Materials. GR acetonitrile was used after three distillations. The benzylamine nucleophiles were used after recrystallization.

Substrates. Phenyl *N*-Phenyl Thiocarbamate. A solution of thiophenol (0.01 mol) in dry toluene (10 mL) was added to a solution of phenyl isocyanate (0.01 mol). A catalytic quantity (0.5 mL) of pyridine was added and the solution refluxed for 1 h. On evaporation of the solvent in vacuo, the thiocarbamate precipitated and was recrystallized from chloroform−pentane. The other substituted phenyl *N*-phenyl thiocarbamates were prepared in an analogous manner and recrystallized from chloroform−pentane. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

$C_6H_5NHC({=}O)SC_6H_4$-*p*-CH_3: mp 129−131 °C; ^1H NMR (400 MHz, $CDCl_3$), δ 2.41 (3H, s, CH_3), 6.4 (1H, s, NH), 7.08−7.51 (9H, m, C_6H_5, C_6H_4); ^{13}C NMR (100.4 MHz, $CDCl_3$), δ 178.1, 140.5, 135.6, 130.4, 129.1, 125.6, 124.5, 119.5, 21.4; ν_{max} (KBr) 3296 (NH), 3045−3202 (CH), 2844 (CH, aromatic), 1663 ($C{=}O$), 638 (C−S); MS *m*/*z* 243 (M^+). Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.1; H, 5.41. Found: C, 69.3; H, 5.43.

$C_6H_5NHC({=}O)SC_6H_5$: mp 110−112 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.3 (1H, s, NH), 7.09−7.63 (10H, m, C_6H_5, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 179.8, 137.5, 135.6, 135.5, 129.9, 129.5, 129.1, 127.9, 124.6; ν_{max} (KBr) 3253 (NH), 3048−3201 (CH), 2849 (CH, aromatic), 1661 ($C{=}O$), 649 (C−S); MS *m*/*z* 229 (M^+). Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.1; H, 4.80. Found; C, 68.3; H, 4.82.

$C_6H_5NHC({=}O)SC_6H_4$-*p*-Cl: mp 158−160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.6 (1H, s, NH), 7.10−7.58 (9H, m, C_6H_5, C_6H_4); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 177.8, 138.1, 135.3, 135.2, 139.9, 129.8, 129.7, 128.2, 126.5; ν_{max} (KBr) 3293 (NH), 3047−3205 (CH), 2846 (CH, aromatic), 1659 ($C{=}O$), 624 (C−S); MS *m*/*z* 263 (M^+). Anal. Calcdfor $C_{13}H_{10}ClNOS$: C, 59.2; H, 3.81. Found: C, 59.4; H, 3.83.

$C_6H_5NHC({=}O)SC_6H_4$-*p*-Br: mp 146−148 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.5 (1H, s, NH), 7.11−7.53 (9H, m, C_6H_5, C_6H_4); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 176.9, 136.7, 136.3, 134.3, 130.0, 129.6, 129.2, 126.3, 124.8; ν_{max} (KBr) 3291 (NH), 3045−3209 (CH), 2845 (CH, aromatic), 1660 ($C{=}O$), 629 (C−S); MS *m*/*z* 308 (M^+). Anal. Calcd $C_{13}H_{10}BrNOS$: C, 50.7; H, 3.30. Found: C,50.9; H, 3.32.

Kinetic Measurement. Rates were measured conductometrically in acetonitrile. The conductivity bridge used in this work was a homemade computer-automatic A/D converter conductivity bridge. Good linearities were found between conductance and concentration of product ions ($XC_6H_4CH_2NH_3^+$ and −SPh). Pseudo-first-order rate constants, k_{obsd}, were determined by the Guggenheim method with large excess of benzylamine. Second-order rate constants, k_2, were obtained from the slope of a plot of k_{obsd} vs [benzylamine] with more than five concentrations of benzylamine. The k_2 values in Table 1 are the averages of more than three runs and were reproducible to within ±3%. Product analysis. The substrate phenyl *N*-phenyl thiocarbonate (0.05 mol) was reacted with excess benzylamine (0.5 mol) with stirring for more than 15 half-lives at 30.0 °C in acetonitrile, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate-*n*-hexene). Analysis of the product gave the following results.

$C_6H_5NHC({=}O)NHCH_2C_6H_5$: mp 169−171 °C; ^1H NMR-(400 MHz, $CDCl_3$) δ 4.3 (2H, d, CH_2), 6.5 (1H, s, NH), 7.22−7.32 (10H, m, C_6H_5); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 155.8, 138.7, 138.2, 129.2, 128.5, 127.3, 127.2, 123.8, 121.1, 44.4; ν_{max} (KBr) 3293 (NH), 3048−3205 (CH), 2842 (CH, aromatic), 1669 ($C{=}O$), 629 (C−S); MS *m*/*z* 226 (M^+). Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.21. Found: C, 74.5; H, 6.23.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2002-070-C00061).

JO049845+