Kinetics and Mechanism of the Aminolysis of Cycloalkyl Arenesulfonates

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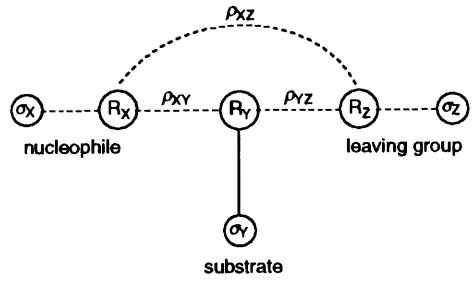
Nucleophilic substitution reactions of cycloalkyl arenesulfonates ($C_nH_{2n-1}OSO_2C_6H_4Z$) with anilines in acetonitrile at 65.0 °C are studied. The reactivity decreases in the order n = 5 > 7 > 4 > 6, which is influenced by angular deformation energies in the transition state (TS), steric effect and exoergicity of the reaction. The cross-interaction constants, ρ_{XZ}, between substituents in the nucleophile (X) and nucleofuge (Z) for all the cycloalkyl compounds, irrespective of the ring size, are uniformly the same (0.11) as those observed for isopropyl arenesulfonates. This indicates that the TS for S_N2 processes at a secondary carbon atom is substantially looser than that at a primary carbon for which a greater ρ_{XZ} value (0.33) has been reported, regardless of the size of the group attached to the reaction centre. The TS shifts toward an earlier position along the reaction coordinate, and becomes more asymmetric, as the ring size decreases, n = 7→4, in accordance with the Bell–Evans–Polanyi principle.

For the past several years, we have been engaged in developing the cross-interaction constants, ρ_{ij} [eqn. (1)] as a mechanistic

$$\log\left(\frac{k_{ij}}{k_{HH}}\right) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

tool for organic reactions in solution;[1] in this equation, i and j represent substituents X, Y or Z in the nucleophile, substrate and leaving group, respectively (Scheme 1).



Scheme 1

Our endeavour has led us to postulate some useful generalizations for the nucleophilic substitution reactions. (*i*) The magnitudes of ρ_{XY} and ρ_{YZ} are directly proportional to the degree of bond-making and -breaking, respectively, in the transition state (TS), provided the fall-off effect of $|\rho_{ij}|$ (by *ca.* 2.8), due to an intervening non-conjugative group, *e.g.* CH_2 or CO, between the substituent and the reaction centre, is accounted for.[2] (*ii*) A positive (negative) ρ_{XZ} leads to an earlier (later) TS along the reaction coordinate for a stronger nucleophile ($\delta\sigma_X < 0$) and/or a stronger nucleofuge, *i.e.*, a better leaving group ($\delta\sigma_Z > 0$).[1] (*iii*) The magnitude of ρ_{XZ} is a measure of the TS tightness; the greater the $|\rho_{XZ}|$ the tighter is the TS.[1] During the course of our studies we found interesting results regarding the TS tightness: for S_N2 processes at a primary carbon centre ρ_{XZ} is a relatively large positive constant value, *ca.* 0.33 in MeCN at 65.0 °C, irrespective of the size of the group attached to the reacting carbon centre.[3]

This is in contrast with a smaller value, *ca.* one-third (ρ_{XZ} = 0.10), observed for isopropyl arenesulfonates,[4] a secondary alkyl substrate, under similar reaction conditions. It is, therefore, of much interest to test whether other S_N2 processes at a secondary carbon centre also have a looser TS with an approximately constant, smaller ρ_{XZ} value ($\rho_{XZ} \simeq 0.10$) regardless of the size of the group attached to the secondary carbon centre. To this end, we carried out kinetic studies of the aminolysis of cycloalkyl arenesulfonates, eqn. (2), and

$$2\,XC_6H_4NH_2 + C_nH_{2n-1}\cdot OSO_2C_6H_4Z \xrightarrow[65.0\,^\circ C]{MeCN} C_nH_{2n-1}\cdot NHC_6H_4X + XC_6H_4NH_3^+ + {}^-OSO_2C_6H_4Z \qquad (2)$$

X = *p*-CH_3O, *p*-CH_3, H or *p*-Cl;
Z = *p*-CH_3, H, *p*-Cl or *p*-NO_2; n = 4–7

determined the ρ_{XZ} values by subjecting the rate data to multiple regression analysis using eqn. (1) (with i, j = X, Z).

In addition, we performed MO theoretical computations to shed more light on the elucidation of the mechanism of S_N2 processes at secondary carbon centres.

Results and Discussion

The second order rate constants, k_2, for the reactions of cycloalkyl Z-arenesulfonates with X-anilines in acetonitrile at 65.0 °C are summarized in Table 1. The rate is faster with a stronger nucleophile ($\delta\sigma_X < 0$) and nucleofuge ($\delta\sigma_Z > 0$) as expected from a typical S_N2 process. In agreement with the I-strain theory[5] the rate is seen to decrease for n in the order 5 > 7 ≫ 4 > 6; for the reactions of a stronger nucleophile (X = *p*-CH_3O) and the cycloalkyl derivatives with a stronger nucleofuge (Z = *p*-NO_2), however, the reactivity order reverses to n = 7 > 5.

The activation barrier, $\Delta E^{\ddagger}$ (and hence the reactivity), for a relatively wide range of S_N2 reactions has been shown to be given adequately by the Marcus equation,[6] eqn. (3), where $\Delta E_o^{\ddagger}$

$$\Delta E^{\ddagger} = \Delta E_o^{\ddagger} + \frac{\Delta E^{\circ}}{2} + \frac{\Delta E^{\circ 2}}{16\Delta E_o^{\ddagger}} \qquad (3)$$

and ΔE° are the intrinsic and thermodynamic barrier, respectively. For non-identity processes, $\Delta E_o^{\ddagger}$ is given by the average of the two $\Delta E_o^{\ddagger}$ values involving the forward and reverse thermoneutral (or identity) processes. The intrinsic barrier $\Delta E_o^{\ddagger}$, is mainly determined by the overall deformation energy required for the substrate to reach its TS, which in turn can

Table 1 Second order rate constants, k_2 (10^5 dm^3 mol^{-1}), for reactions of Z-substituted cycloalkyl benzenesulfonates with X-substituted anilines in MeCN at 65.0 °C

		Z			
Substrate	X	*p*-Me	H	*p*-Cl	*p*-NO_2
Cyclobutyl	*p*-MeO	2.26	3.07	5.79	20.51
	p-Me	1.76	2.40	4.62	16.67
	H	1.20	1.69	3.27	12.02
	p-Cl	0.728	1.06	2.12	7.57
Cyclopentyl	*p*-MeO	12.9	17.2	34.5	133
	p-Me	8.49	12.5	26.2	96.5
	H	5.01	7.41	15.5	58.2
	p-Cl	2.56	3.95	8.01	31.3
Cyclohexyl	*p*-MeO	1.24	1.96	4.08	19.1
	p-Me	0.855	1.33	2.81	13.1
	H	0.445	0.707	1.49	7.42
	p-Cl	0.209	0.331	0.749	3.57
Cycloheptyl	*p*-MeO	10.8	17.2	36.1	174
	p-Me	7.45	12.4	25.9	126
	H	3.91	6.51	13.7	68.5
	p-Cl	1.72	2.89	6.17	31.3

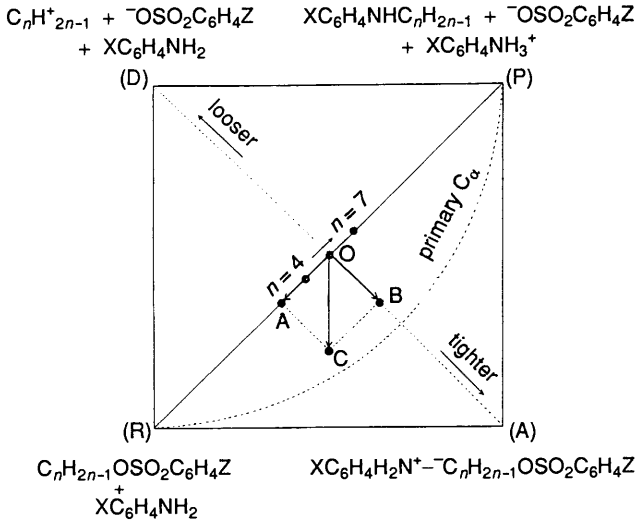


Fig. 1 Potential energy surface diagram. R→P: reaction coordinate diagonal. A→D: tightness diagonal.

be partitioned into a component associated with the bond stretch (ΔE_r), and a component associated with the angular deformation (ΔE_θ).[7] It has been shown that the contribution of the former (ΔE_r) is larger than that of the latter (ΔE_θ).[7] In addition to these deformation energies, the steric effect can also contribute to $\Delta E^{\ddagger}_{o}$.

Molecular models[8a] indicate that the bulky leaving group, $OSO_2C_6H_4Z$, should prefer the equatorial position in all the reactants.* For cyclobutyl and cyclohexyl, however, this equatorial leaving group must be rotated to the axial position prior to displacement, which takes place axially, in order to ease excessive steric inhibition in the TS; for cyclopentyl and cycloheptyl the rotation to axial position may not be required since equatorial displacement can be sterically preferred. This angular deformation (ΔE_θ) at the reacting carbon centre in the TS must result in a greater overall deformation energy and hence lower rates for $n = 4$ and 6 than for $n = 5$ and 7. Steric inhibition in the S_N2 displacement becomes increasingly greater with the ring size as Taft's steric constant, E_s,[9] indicates; E_s values are −0.06, −0.51, −0.79 and −1.10 for $n = 4$, 5, 6 and 7, respectively. Purely on steric grounds, the reactivity is expected to be in the order, $n = 4 > 5 > 6 > 7$. Thus the order, 4 > 6 and 5 > 7, must be deemed in line with the steric effect.

* This was confirmed by our AM1 calculations.

Table 2 Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z) coefficients[a] for reactions of Z-substituted cycloalkyl benzenesulfonates with X-substituted anilines

Substrate	Z	ρ_X	β_X	X	ρ_Z	β_Z
Cyclobutyl	*p*-Me	−0.99	0.36	*p*-MeO	1.03	−0.28
	H	−0.92	0.33	*p*-Me	1.05	−0.28
	p-Cl	−0.88	0.32	H	1.07	−0.29
	p-NO_2	−0.87	0.31	*p*-Cl	1.08	−0.29
Cyclopentyl	*p*-Me	−1.39	0.50	*p*-MeO	1.09	−0.30
	H	−1.29	0.47	*p*-Me	1.12	−0.31
	p-Cl	−1.28	0.46	H	1.13	−0.31
	p-NO_2	−1.26	0.46	*p*-Cl	1.15	−0.31
Cyclohexyl	*p*-Me	−1.57	0.56	*p*-MeO	1.26	−0.34
	H	−1.56	0.56	*p*-Me	1.27	−0.34
	p-Cl	−1.49	0.54	H	1.30	−0.35
	p-NO_2	−1.47	0.53	*p*-Cl	1.31	−0.36
Cycloheptyl	*p*-Me	−1.61	0.58	*p*-MeO	1.28	−0.35
	H	−1.58	0.57	*p*-Me	1.29	−0.35
	p-Cl	−1.56	0.56	H	1.31	−0.36
	p-NO_2	−1.51	0.55	*p*-Cl	1.33	−0.36

[a] Correlation coefficients were greater than 0.995 in all cases.

Relaxation of this steric requirement in the TS should lead to an increase in the rate, and the effect of this relaxation on the rate is expected to be greater in the TS with a greater steric inhibition. Since for the reactions in this study [eqn. (2)] the ρ_{XZ} values are all positive (*vide infra*) a stronger nucleophile and/or a stronger nucleofuge should lead to an earlier TS,[1] which is in accord with the TS variation predicted by the potential energy surface (PES) diagram,[10] Fig. 1. Thus, in the reactions involving a stronger nucleophile (X = *p*-CH_3O) and nucleofuge (Z = *p*-NO_2) the TS should shift toward an earlier position along the reaction coordinate, O→A or O→C (= $\vec{OA}$ + $\vec{OB}$). The shift of the TS toward an earlier position should lead to a greater release of the steric strain in the TS for the more sterically crowded system, *i.e.*, for $n = 7$ rather than for $n = 5$; this could be the reason why the reactivity order reverses to $n = 7 > 5$ for the reactions involving a stronger nucleophile and nucleofuge.

The Hammett (ρ_X and ρ_Z) and Brönsted (β_X and β_Z) coefficients are summarized in Table 2. The magnitudes of both types of coefficients, ρ_X ($|\beta_X|$) and ρ_Z ($|\beta_Z|$), in all cases decrease with a stronger nucleophile and/or nucleofuge reflecting correctly the TS shift toward an earlier position on the reaction coordinate. We note a quite interesting trend in Table 2: the magnitudes of the two coefficients, ρ_X (β_X) and ρ_Z (β_Z), become successively greater as the ring size grows, $n = 4 \rightarrow 7$. This can be interpreted as a trend that the TS shifts successively toward a later position on the reaction coordinate, as schematically presented in Fig. 1 ($n = 4 \rightarrow 7$). This interpretation is supported by the results of the secondary kinetic isotope effect (SKIE) studies involving deuteriated nucleophiles ($XC_6H_4ND_2$), shown in Table 3.

Reference to this Table reveals that the SKIEs (k_H/k_D) are inverse type, *i.e.*, $k_H/k_D < 1.0$, reflecting an increase in steric crowding, and hence a vibrational frequency (N–H stretching as well as bending) increase,[11] in the TS as the aniline–substrate bond is formed. Moreover, the k_H/k_D value becomes smaller as the ring size increases, $n = 4 \rightarrow 7$, indicating that a greater degree of bond formation (a later TS) is obtained with a greater ring size.

Finally, the rate data in Table 1 were subjected to multiple regression analysis using eqn. (1) and the cross-interaction constants, ρ_{XZ} were determined as shown in Table 4.

Table 3 Kinetic isotope effects observed for the reaction of *p*-methyl substituted cycloalkyl benzenesulfonates with *p*-chloro substituted *N*-deuteriated aniline nucleophiles in MeCN at 65.0 °C

Substrate	k_H/dm^3 mol^{-1} s^{-1}	k_D/dm^3 mol^{-1} s^{-1}	k_H/k_D
Cyclobutyl	$7.28_3(\pm 0.00_2)^a \times 10^{-6}$	$7.97_4(\pm 0.00_9)^a \times 10^{-6}$	$0.91_3 \pm 0.01_1^b$
Cyclopentyl	$2.56_0(\pm 0.00_3)^a \times 10^{-5}$	$2.82_6(\pm 0.03_0)^a \times 10^{-5}$	$0.90_5 \pm 0.00_8^b$
Cyclohexyl	$2.09_1(\pm 0.00_1)^a \times 10^{-6}$	$2.34_9(\pm 0.00_6)^a \times 10^{-6}$	$0.89_0 \pm 0.00_6^b$
Cycloheptyl	$1.72_1(\pm 0.01_0)^a \times 10^{-5}$	$1.96_0(\pm 0.03_0)^a \times 10^{-5}$	$0.87_8 \pm 0.01_4^b$

[a] Standard deviation. [b] Standard error.[20]

Table 4 Cross interaction constants, ρ_{XZ} and β_{XZ}, for reactions of Z-substituted cycloalkyl benzenesufonates with X-anilines in MeCN at 65.0 °C

Substrate	ρ_{XZ} (cc)[a]	β_{XZ} (cc)[a]
Cyclobutyl	0.11 (0.999)	0.06 (0.994)
Cyclopentyl	0.11 (0.999)	0.06 (0.993)
Cyxlohexyl	0.11 (0.999)	0.07 (0.994)
Cycloheptyl	0.11 (0.999)	0.06 (0.994)

[a] cc = correlation coefficient.

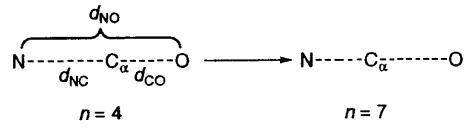
Table 5 AM1 heats of formation, $\Delta_f H$, and the thermodynamic barriers ($\Delta E°$) for the reactions of $C_nH_{2n-1}OSO_2C_6H_5$ with aniline (kcal mol^{-1})[a]

	$\Delta_f H$		
n	$C_nH_{2n-1}OSO_2C_6H_5$	$C_nH_{2n-1}NHC_6H_5$	$\Delta E°$[b]
4	−79.70	+33.16	−8.8
5	−106.64	+8.40	−6.7
6	−116.02	+0.23	−5.5
7	−118.23	−1.45	−5.0

[a] 1 cal = 4.184 J. [b] $\Delta E° = \Delta H° - RT$ at 65.0 °C.

Surprisingly the ρ_{XZ} (β_{XZ}) values are constant, $\rho_{XZ} = 0.11$ ($\beta_{XZ} = 0.06$–0.07), irrespective of the ring size. Moreover, the magnitude is quite similar to that for the reactions of isopropyl arenesulfonates ($\rho_{XZ} = 0.10$ and $\beta_{XZ} = 0.06$) under similar reaction conditions.[4] Thus, we conclude that the TS tightness for S_N2 processes at the secondary carbon centre is similar regardless of the size of the group attached to the reacting carbon centre (α-substituent). This is in accord with exactly the same trend found for the TS tightness at the primary carbon centre;[3] the difference between the TSs for the two types of carbon centres is that the TS is much looser for the S_N2 processes occuring at the secondary rather than the primary carbon centres. On the PES diagram, Fig. 1, this difference can be represented by a curve which is more deflected toward corner D, *i.e.*, a shift downward on the tightness diagonal.

The overall TS variation for the cycloalkyl systems can be given schematically as shown in Fig. 2 for $n = 4$ and 7. Wolfe *et al.*[8b] have shown that the tightness (or looseness) and the asymmetry of the S_N2 TS can be correlated with the magnitude of the intrinsic barrier, $\Delta E_o^‡$ (barrier for the thermoneutral process), and the thermodynamic barrier, $\Delta E°$ (reaction energy), respectively. This means that $|\rho_{XZ}|$ can be correlated with $\Delta E_o^‡$, since $|\rho_{XZ}|$ is a measure of the TS tightness and hence the similar magnitude of ρ_{XZ} should be an indication of the approximately constant $\Delta E_o^‡$. Thus, the relatively constant $|\rho_{XZ}|$ values obtained for the primary ($\rho_{XZ} = 0.33$) and secondary ($\rho_{XZ} = 0.11$) carbon centres reflect that an α-alkyl substituent has little effect on the intrinsic barrier. The greater ρ_{XZ} value, *i.e.*, a tighter TS, for the primary series also reflects that the intrinsic barrier, $\Delta E_o^‡$, is lower for the primary series than for the secondary series since the intrinsic barrier is primarily a



$d^‡_{NO}(n = 4) = d^‡_{NO}(n = 7)$; $d^‡_{CN}(n = 4) > d^‡_{CN}(n = 7)$; $d^‡_{CO}(n = 4) < d^‡_{CO}(n = 7)$

Fig. 2 Schematic illustration of the TS tightness for $n = 4$ and 7

function of bond stretching energy,[7] ΔE_r, in the TS; *i.e.*, the smaller the $d^‡_{NO}$, the lower the $\Delta E_o^‡$, and hence the faster is the intrinsic rate. The actual reactivity ($\Delta E^‡$) is affected also by the angular deformation, ΔE_θ, and the steric effect in addition to the thermodynamic barrier, $\Delta E°$, as we have discussed above. However, as already mentioned above, the contribution of ΔE_θ is relatively small and the stretching deformation, ΔE_r, is the dominant contribution to $\Delta E_o^‡$.[7]

According to Wolfe *et al.*,[8b] a greater TS asymmetry for $n = 4$ than for $n = 7$ (Fig. 2) must be due to the greater exoergicity (or lesser endoergicity, $\delta\Delta E° < 0$) of the reaction for $n = 4$ than for $n = 7$. This is indeed borne out in the results of our AM1 calculations[12] on the reaction series, eqn. (2), in Table 5. The reaction becomes successively less endoergic (or more exoergic) as the ring size decreases for $n = 7 \rightarrow 4$, in agreement with an earlier TS for the less endoergic processes for the smaller ring size, Fig. 2; this is in fact consistent with the Bell–Evans–Polanyi (BEP) principle.[13] An interesting aspect emerges from these results: a larger ring size results in a greater steric crowding and to a greater endoergicity for the reaction which in turn leads to a later TS, a greater degree of bond formation. In agreement with this, for a more sterically inhibited system it has been often found that the TS is tighter, *i.e.*, the degree of bond formation is greater,[1b,14] in contrast to a more intuitive concept that a more sterically demanding system should lead to a looser TS, *i.e.*, a lesser degree of bond formation. Indeed, both the experimental ($|\rho_X|$ and k_H/k_D) and theoretical ($\Delta E°$) results lead us to the same conclusion that the TS is located at a later position on the reaction coordinate as the ring size increases, $n = 4 \rightarrow 7$.

There is an important aspect to this conclusion, however. For the systems studied in this work, the conventional view of the SKIE[11] applies: a smaller k_H/k_D (< 1.0) value reflects an increased steric congestion in the TS, *i.e.*, a greater degree of bond formation leading to a tighter TS. This is also true when the k_H/k_D values for the primary carbon centre [*e.g.*, ethyl system with $\rho_{XZ} = 0.33$ and $k_H/k_D = 0.86$ (ref. 15) for Z = *p*-Me and X = *p*-OMe in MeCN at 65.0 °C] and those for the secondary carbon centre (*e.g.*, cyclohexyl system with $\rho_{XZ} = 0.11$ and $k_H/k_D = 0.89$ for Z = *p*-Me and X = *p*-Cl in MeCN at 65.0 °C) are compared; the latter has a greater k_H/k_D value due to a lesser degree of bond formation despite the greater steric crowding (*e.g.*, E_s for ethyl and cyclohexyl are −0.07 and −0.79 respectively) and a greater degree of bond formation (X = *p*-Cl leads to a greater degree of bond formation than for X = *p*-OMe since ρ_{XZ} is positive) expected in the TS. This is, however, at variance with the recent theoretical results of Boyd

et al.[16] They have shown by molecular orbital calculations that a tighter TS leads to a larger theoretical k_H/k_D value for the nonidentity methyl transfer reactions, in contrast to a smaller experimental k_H/k_D (< 1.0) value for a tighter TS obtained in this work. Of course the two systems, *i.e.*, the reactions investigated theoretically, $X^- + CH_3(D_3)Y \longrightarrow XCH_3(D_3) + Y^-$ with X, Y = F, Cl, OH, CN, SH, NC, CCH and the reactions in this work, eqn. (2), are not strictly comparable, but the two conclusions in direct contradiction regarding the tightness of the S_N2 TS and the size of k_H/k_D are nevertheless disturbing. Further experimental and theoretical work is needed to resolve this discrepancy.

Experimental

Materials.—Merck GR acetonitrile was used after three distillations. The aniline nucleophiles, Aldrich GR, were redistilled or recrystallized before use. Preparation of deuteriated anilines were as described previously.[15] The analysis (NMR spectroscopy) of the deuteriated anilines showed more than 99% deuterium content, so no corrections to kinetic isotope effects for incomplete deuterium were made. (*J*-Values in Hz.) The cycloalkyl arenesulfonate substrates were prepared by reacting Aldrich GR cyclobutanol, cyclopentanol, cyclohexanol and cycloheptanol with arenesulfonyl chlorides.[17]

NMR (JEOL 400 MHz) Spectroscopic Data.—*Cyclobutyl benzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.46–2.23 (6 H, m, $-[CH_2]_3-$), 4.76–4.84 (1 H, m, CHO–) and 7.53–7.92 (5 H, m, Ar).

Cyclobutyl p-*methylbenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.45–2.20 (6 H, m, $-[CH_2]_3-$), 2.44 (3 H, s, CH_3), 4.73–4.80 (1 H, m, CHO–), 7.33 (2 H, d, *m*-H, *J* 8.06) and 7.78 (2 H, d, *o*-H, *J* 8.06).

Cyclobutyl p-*chlorobenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.48–2.24 (6 H, m, $-[CH_2]_3-$), 4.78–4.82 (1 H, m, CHO–), 7.52 (2 H, d, *m*-H, *J* 8.80) and 7.84 (2 H, d, *o*-H, *J* 8.06).

Cyclobutyl p-*nitrobenzenesulfonate.* M.p. 65–66 °C; $\delta_H(CDCl_3)$ 1.51–2.29 (6 H, m, $-[CH_2]_3-$), 4.84–4.92 (1 H, m, CHO–), 8.10 (2 H, d, *m*-H, *J* 8.79) and 8.39 (2 H, d, *o*-H, *J* 8.79).

Cyclopentyl benzenesulfonate. Liquid; $\delta_H(CDCl_3)$ 1.74 (8 H, m, $-[CH_2]_4-$), 4.97 (1 H, m, CHO–) and 7.43–7.93 (5 H, m, Ar).

Cyclopentyl p-*methylbenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.74 (8 H, m, $-[CH_2]_4-$), 2.43 (3 H, s, CH_3), 4.94 (1 H, m, CHO–), 7.32 (2 H, d, *m*-H, *J* 8.1) and 7.78 (2 H, d, *o*-H, *J* 8.1).

Cyclopentyl p-*chlorobenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.74 (8 H, m, $-[CH_2]_3-$), 4.94 (1 H, m, CHO–), 7.50 (2 H, d, *m*-H, *J* 8.5) and 7.84 (2 H, d, *o*-H, *J* 8.5).

Cyclopentyl p-*nitrobenzenesulfonate.* M.p. 48–49 °C; $\delta_H(CDCl_3)$ 1.80 (8 H, m, $-[CH_2]_4-$), 5.10 (1 H, m, CHO–), 8.10 (2 H, d, *m*-H, *J* 8.8) and 8.40 (2 H, d, *o*-H, *J* 8.8).

Cyclohexyl benzenesulfonate. Liquid; $\delta_H(CDCl_3)$ 1.33–1.69 (10 H, m, $-[CH_2]_5$), 4.51 (1 H, m, CHO–) and 7.51–8.03 (5 H, m, Ar).

Cyclohexyl p-*methylbenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.34–1.72 (10 H, m, $-[CH_2]_5-$), 2.44 (3 H, s, CH_3), 4.49 (1 H, m, CHO–), 7.32 (2 H, d, *m*-H, *J* 8.8) and 7.79 (2 H, d, *o*-H, *J* 8.3).

Cyclohexyl p-*chlorobenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.34–1.72 (10 H, m, $-[CH_2]_5-$), 4.53 (1 H, m, CHO–), 7.50 (2 H, d, *m*-H, *J* 8.5) and 7.85 (2 H, d, *o*-H, *J* 8.5).

Cyclohexyl p-*nitrobenzenesulfonate.* M.p. 77–78 °C; $\delta_H(CDCl_3)$ 1.42–1.74 (10 H, m, $-[CH_2]_5-$), 4.65 (1 H, m, CHO–), 8.10 (2 H, d, *m*-H, *J* 9.0), 8.39 (2 H, d, *o*-H, *J* 9.0).

Cycloheptyl benzenesulfonate. Liquid; $\delta_H(CDCl_3)$ 1.27–1.91 (12 H, m, $-[CH_2]_6-$), 4.71–4.76 (1 H, m, CHO–) and 7.55–7.94 (5 H, m, Ar).

Cycloheptyl p-*methylbenzenesulfonate.* Liquid; $\delta_H(CDCl_3)$ 1.33–1.85 (12 H, m, $-[CH_2]_6-$), 2.44 (3 H, s, CH_3), 4.63–4.99 (1 H, m, CHO–), 7.33 (2 H, d, *m*-H, *J* 8.06) and 7.78 (2 H, d, *o*-H, *J* 8.06).

Cycloheptyl p-*chlorobenzenesulfonate.* M.p. 25–26 °C; $\delta_H(CDCl_3)$ 1.34–1.91 (12 H, m, $-[CH_2]_6-$), 4.69–4.76 (1 H, m, CHO–), 7.51 (2 H, d, *m*-H, *J* 8.79) and 7.84 (2 H, d, *o*-H, *J* 8.80).

Cycloheptyl p-*nitrobenzene sulfonate.* M.p. 71–72 °C; $\delta_H(CDCl_3)$ 1.36–1.93 (12 H, m, $-[CH_2]_6-$), 4.81–4.87 (1 H, m, CHO–), 8.10 (2 H, d, *m*-H, *J* 8.79) and 8.39 (2 H, d, *o*-H, *J* 8.80).

Kinetic Procedures.—Rates were measured conductometrically at 65.0 ± 0.05 °C in acetonitrile. The conductivity bridge used in this work was a computer interface automatic A/D converter conductivity bridge. Substrates were injected with a syringe. Pseudo-first order rate constants, K_{obs}, were determined by the Guggenheim method[18] with a large excess of aniline; [cycloalkyl arenesulfonate] = 10^{-3} mol dm^{-3} and [aniline] = 0.05–0.50 mol dm^{-3}. Second-order rate constants, k_2, are obtained from the slope of k_{obs} *vs.* [aniline] with more than four concentrations of aniline.

Product Analysis.—Cycloalkyl arenesulfonates were reacted with excess of aniline with stirring for more than 48 h at 65.0 °C in acetonitrile and the product mixtures were obtained by removal of the solvent under reduced pressure. The product mixtures were purified by column chromatography. The NMR spectroscopic data are as follows.

$C_6H_5NHC_4H_7$. Liquid; $\delta_H(CDCl_3)$ 1.27–1.84 (6 H, m, $-[CH_2]_3-$), 3.73 (1 H, br, NH), 3.87–3.94 (1 H, m, CH) and 6.60–7.19 (5 H, m, Ar).

$C_6H_5NHC_5H_9$. Liquid; $\delta_H(CDCl_3)$ 1.26–2.03 (8 H, m, $-[CH_2]_4-$), 3.77–3.80 (1 H, m, CH), 3.94 (1 H, br, NH) and 6.59–7.18 (5 H, m, Ar).

$C_6H_5NHC_6H_{11}$. Liquid; $\delta_H(CDCl_3)$ 1.09–2.09 (10 H, m, $-[CH_2]_5-$), 3.21–3.28 (1 H, m, CH), 3.42 (1 H, br, NH) and 6.57–7.17 (5 H, m, Ar).

$C_6H_5NHC_7H_{13}$. Liquid; $\delta_H(CDCl_3)$ 1.19–2.03 (12 H, m, $-[CH_2]_6-$), 3.44–3.49 (1 H, m, CH) and 6.54–7.18 (5 H, m, Ar).

$C_6H_5NH_3^{+-}OSO_2C_6H_4CH_3$. M.p. 226–228 °C; $\delta_H(D_2O)$ 2.14 (3 H, s, CH_3) and 7.12–7.14 (9 H, m, Ar).

AM1 Calculations.—The standard AM1 procedure implemented in the MOPAC version 6.0 program was used throughout in this work. The ground states (geometries and energies) were fully optimized with respect to all geometrical parameters and characterized by all positive eigenvalues in the Hessian matrix.[19]

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