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# CROSS-INTERACTION CONSTANTS AS A MEASURE OF THE TRANSITION STATE STRUCTURE. PART 8. MECHANISM OF THE REACTION OF 2-PHENYLETHYL BENZENESULPHONATES WITH BENZYLAMINE IN ACETONITRILE

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**The kinetics of reactions between 2-phenylethyl benzenesulphonates (2-PEB) and benzylamines in acetonitrile at 65·0 °C have been studied; the mechanism was examined on the basis of the sign and magnitude of cross-interaction constants $\rho_{ij}$ and $\beta_{ij}$. In contrast to the reactions of 2-PEB with anilines in methanol, participation of the aryl-assisted pathway was negligible, with a strong indication that the reaction proceeds largely by an intermolecular $S_Ni$ mechanism with a four-centre transition state (TS). The effect of substituents on the TS variation was in accord with the predictions of the quantum mechanical model.**

## INTRODUCTION

The nucleophilic displacement reactions of 2-phenylethyl compounds have attracted considerable attention in connection with the involvement of an aryl participation.[1] In such reactions there is a three-way competition in the rate-determining displacement of the leaving group by the solvent ($k_s$), nucleophiles other than the solvent ($k_N$) and neighbouring aryl groups ($k_\Delta$), as shown in Scheme 1.[1]

In previous work,[1] we reported the results of kinetic studies of the reactions between 2-phenylethyl benzenesulphonates (2-PEB) with anilines in methanol at 65·0 °C, showing that the overall reaction proceeded by a dissociative $S_N2$ mechanism with a relatively small degree of aryl participation and the possibility of four-centre transition state (TS) in an intermolecular $S_Ni$ mechanism[2] for the aryl-unassisted pathway. These conclusions were based on the magnitude of the cross-interaction constants $\rho_{ij}$ defined by[3]

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

The magnitude of the cross-interaction constants reflect the strength of the indirect interaction between substituents $i$ and $j$ through reaction centres $R_i$ and $R_j$ when both substituents interact with their respective centres simultaneously in the TS (Scheme 2), and provides a useful measure of bond length, $r_{ij}$.[3]

It has been shown that $r_{ij}$ is linearly related to $\log(|\rho_{ij}|^{-1})$:

$$r_{ij} = \alpha + \beta\ \log(|\rho_{ij}|^{-1}) \qquad (2)$$

where $\alpha$ and $\beta$ are constants which depend on the rows of the Periodic Table for the two atoms being bonded at constant temperature.[4] We have since introduced the Brønsted type of cross-interaction constant $\beta_{ij}$:

$$\log(k_{ij}/k_{HH}) = \beta_i\Delta pK_i + \beta_j\Delta pK_j + \beta_{ij}\Delta pK_i\Delta pK_j \qquad (3)$$

and applied them to the rationalization of mechanistic details involved in a variety of reactions.

In this paper, we report the results of kinetic studies of the reactions between 2-PEB and benzylamines (BA) in acetonitrile at 65·0 °C, equation (4), elaborating on the mechanism based on various cross-interaction constants $\rho_{ij}$ and $\beta_{ij}$ determined from $k_{ij}$ values by multiple linear regressions using equations (1) and (3).

$$2XC_6H_4CH_2NH_2 + YC_6H_4CH_2CH_2OSO_2C_6H_4Z \xrightarrow[65\cdot0\,^\circ C]{MeCN} YC_6H_4CH_2CH_2NHCH_2C_6H_4X + XC_6H_4CH_2NH_3^+ + {}^-OSO_2C_6H_4Z \qquad (4)$$

$X = p\text{-}CH_3O,\ p\text{-}CH_3,\ H \text{ or } p\text{-}Cl$
$Y = p\text{-}CH_3O,\ p\text{-}CH_3,\ H,\ p\text{-}Br \text{ or } p\text{-}NO_2$
$Z = p\text{-}CH_3,\ H,\ p\text{-}Cl \text{ or } p\text{-}NO_2$

## RESULTS AND DISCUSSION

Second-order rate constants, $k_2$, for the reaction of 2-PEB with benzylamines [equation (4)] were obtained from slopes of pseudo-first-order rate constants, $k_1^{obs}$,

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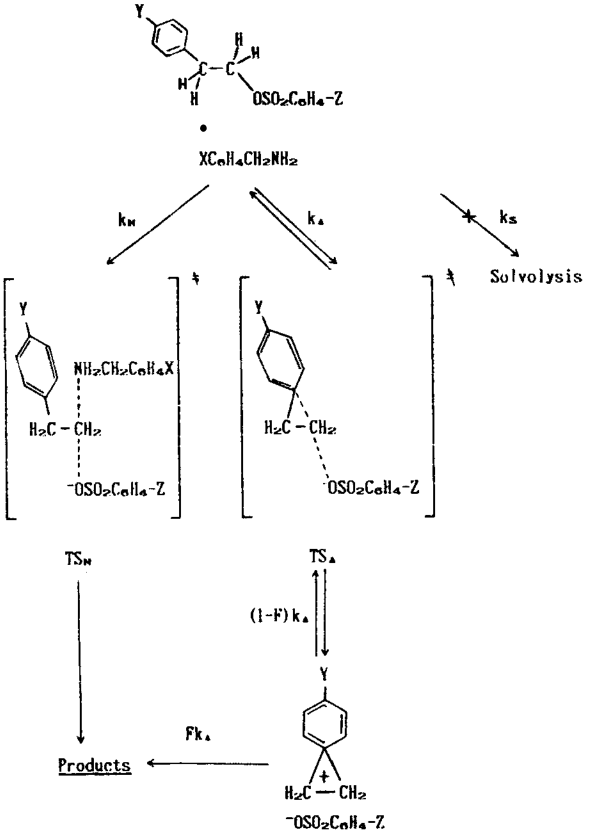
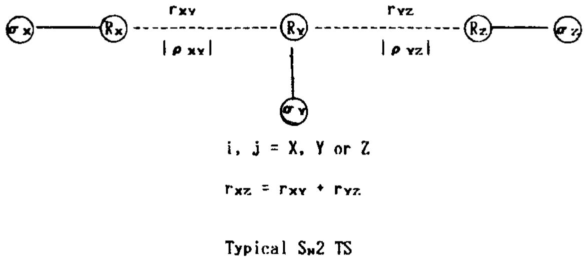


Scheme 1



Scheme 2

versus benzylamine concentration, [BA] [equation (5), Table 1].

$$k_1^{obs} = k_1 + k_2[BA] \qquad (5)$$

Solvolysis of 2-PEB in acetonitrile[5] can be safely ruled out from zero intercepts, $k_1 \approx 0$, in equation (5) in all cases. The magnitudes of $k_2$ are approximately twice those for the corresponding reactions of 2-PEB with anilines in methanol at the same temperature.[1] The rate increases with a more electron-withdrawing substituent in the leaving group (Z = EWS) and with a more electron-dominating substituent in the nucleophile (X = EDS).

Table 1. Second-order rate constants ($k_2 \times 10^4$ l mol$^{-1}$ s$^{-1}$) for the reactions between $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ and $XC_6H_4CH_2NH_2$ in acetonitrile at 65·0 °C

| | | Y | | | | |
|---|---|---|---|---|---|---|
| Z | X | *p*-CH₃O | *p*-CH₃ | H | *p*-Br | *p*-NO₂ |
| *p*-NO₂ | *p*-CH₃O | 55·3 | 56·2 | 56·9 | 56·5 | 56·2 |
| | *p*-CH₃ | 48·3 | 48·9 | 51·0 | 50·2 | 50·4 |
| | H | 36·9 | 38·2 | 39·0 | 37·9 | 37·4 |
| | *p*-Cl | 25·9 | 26·9 | 27·5 | 26·1 | 25·9 |
| *p*-Cl | *p*-CH₃O | 12·3 | 12·6 | 12·8 | 12·8 | 12·1 |
| | *p*-CH₃ | 10·7 | 10·8 | 11·1 | 10·8 | 10·2 |
| | H | 8·39 | 8·45 | 8·69 | 8·39 | 8·13 |
| | *p*-Cl | 6·02 | 6·10 | 6·25 | 6·17 | 5·83 |
| H | *p*-CH₃O | 6·46 | 6·53 | 6·61 | 6·64 | 6·17 |
| | *p*-CH₃ | 5·69 | 5·79 | 6·03 | 5·97 | 5·43 |
| | H | 4·47 | 4·57 | 4·75 | 4·51 | 4·27 |
| | *p*-Cl | 3·31 | 3·37 | 3·47 | 3·51 | 3·24 |
| *p*-CH₃ | *p*-CH₃O | 3·89 | 3·89 | 4·01 | 3·98 | 3·80 |
| | *p*-CH₃ | 3·47 | 3·48 | 3·63 | 3·63 | 3·47 |
| | H | 2·84 | 2·88 | 2·98 | 2·91 | 2·69 |
| | *p*-Cl | 2·11 | 2·16 | 2·24 | 2·19 | 2·04 |

The rate is almost insensitive, however, to substituent changes in the substrate (Y). A slight decrease in rate (<7%) is observed with both Y = EWS and Y = EDS. This is in contrast with a slight increase in rate induced by Y = $CH_3O$ in the reaction of 2-PEB with anilines in methanol[1] and the relatively strong rate enhancement in solvolysis in ethanol acetic acid and formic acid.[6] Since the *p*-$CH_3O$ substituent is considered to be a strong phenyl group activator for the aryl-assisted process, $k_\Delta$,[6] such an insensitivity of substituents (Y) in the substrate indicate that the aryl-assisted pathway is less important in the nucleophilic substitution reaction (4) than in solvolysis. This may be especially true when the rate of the nucleophilic pathway, $k_N$, is fast enough that the competition of the aryl-assisted path becomes negligible.[1]

Variations of Hammett $\rho_X$ and Brønsted $\beta_X(\beta_N)$ parameters (obtained by varying substituent X in the nucleophile) with substituents Y in the substrate and Z in the leaving group (LG) are summarized in Table 2.

The $\rho_X$ values are negative and approximately half those for the reaction with aniline[1] owing to an intervening $CH_2$ group in benzylamine.[7] The magnitudes of $\rho_X$ and $\beta_X$ increase with a better LG (Z = *p*-$NO_2$), but vary very little with the substituent in the substrate (Y). It is barely observable that both Y = EWS and Y = EDS tend to have slightly greater $|\rho_X|$ and $|\beta_X|$.

The $\rho_Z$ and $\beta_Z$ ($\beta_{LG}$) values (obtained by varying substituent Z in the LG) are shown in Table 3. The magnitudes of $\rho_Z$ and $\beta_Z$ increase with a more EDS in the nucleophile (X = *p*-$CH_3$) and again vary very little with the substituent Y in the substrate. $\beta_X$ is greater

Table 2. Hammett $\rho_X$[a] and Brønsted $\beta_X$[a] values for reaction (4)[b]

| | | Y | | | | |
|---|---|---|---|---|---|---|
| Z | Parameter | *p*-CH₃O | *p*-CH₃ | H | *p*-Br | *p*-NO₂ |
| *p*-NO₂ | $\rho_X$ | −0·67 | −0·65 | −0·65 | −0·69 | −0·69 |
| | $\beta_X$ | 0·67 | 0·65 | 0·67 | 0·71 | 0·72 |
| *p*-Cl | $\rho_X$ | −0·63 | −0·63 | −0·63 | −0·64 | −0·63 |
| | $\beta_X$ | 0·62 | 0·62 | 0·62 | 0·61 | 0·61 |
| H | $\rho_X$ | −0·59 | −0·58 | −0·58 | −0·57 | −0·57 |
| | $\beta_X$ | 0·59 | 0·59 | 0·60 | 0·57 | 0·56 |
| *p*-CH₃ | $\rho_X$ | −0·54 | −0·51 | −0·51 | −0·53 | −0·56 |
| | $\beta_X$ | 0·54 | 0·52 | 0·52 | 0·55 | 0·57 |

[a] Correlation coefficients are better than 0·998 at the 99% confidence level in all cases.

[b] The p$K_a$ values of BA were taken from Ref. 13.

Table 3. Hammett $\rho Z$[a] and Brønsted $\beta_Z$[a] values for reaction (4)[b]

| | | Y | | | | |
|---|---|---|---|---|---|---|
| X | Parameter | *p*-CH₃O | *p*-CH₃ | H | *p*-Br | *p*-NO₂ |
| *p*-CH₃O | $\rho_Z$ | 1·21 | 1·22 | 1·21 | 1·21 | 1·21 |
| | $\beta_Z$ | −0·40 | −0·41 | −0·40 | −0·40 | −0·41 |
| *p*-CH₃ | $\rho_Z$ | 1·20 | 1·20 | 1·20 | 1·20 | 1·23 |
| | $\beta_Z$ | −0·40 | −0·40 | −0·40 | −0·40 | −0·41 |
| H | $\rho_Z$ | 1·18 | 1·18 | 1·18 | 1·18 | 1·21 |
| | $\beta_Z$ | −0·39 | −0·40 | −0·39 | −0·39 | −0·40 |
| *p*-Cl | $\rho_Z$ | 1·15 | 1·16 | 1·15 | 1·13 | 1·16 |
| | $\beta_Z$ | −0·38 | −0·39 | −0·38 | −0·38 | −0·39 |

[a] Correlation coefficients are better than 0·998 at the 99% confidence level in all cases.

[b] The p$K_a$ values were taken from Ref. 14.

than $\beta_Z$, suggesting a greater degree of bond formation than bond breaking in the TS.

In this reaction, a stronger nucleophile ($\sigma_X < 0$) and/or nucleofuge ($\sigma_Z > 0$) lends to a greater degree of bond breaking ($\Delta r_{YZ} > 0$) and/or formation ($\Delta f_{XY} < 0$), resulting in a 'late' TS conforming to the predictions by the quantum mechanical (QM) model.[3g,8] This means that reaction (4) constitutes an intrinsically controlled series following the relationships

$$\begin{gathered} \Delta r_{XY} = \lambda \sigma_Z \\ \Delta r_{YZ} = \lambda \sigma_X \\ \lambda < 0 \text{ and } \lambda' < 0 \end{gathered} \tag{6}$$

where λ and λ′ are negative constants.[1,3g,i,p,9]

The $\rho_Y$ values for reaction (4) are summarized in Table 4. Their sign is mostly negative, indicating a slightly greater degree of bond breaking than of bond formation, in contrast to the conclusion above based on the magnitudes of $\rho_X$ and $\beta_Z$. However, the magnitude is very small indeed, as we expected from the insensitivity of $\rho_X$ and $\rho_Z$ with the substituent Y in the substrate. One reason for this negligible $|\rho_Y|$ is the fall-off of the substituent effect susceptibility by a factor of 2·4–2·8 owing to an intervening CH₂ group (β-CH₂) in the substrate,[7] and another may well be a near charge balance owing to approximately the same degree of bond formation and breaking. These two factors immediately rule out any significant participation of the aryl group ($k_\Delta$) in the rate-determining step, since the aryl-assisted pathway has the TS structure which is not consistent with the two factors; the aryl-assisted intermediate has no CH₂ group corresponding to β-CH₂ with a unit positive charge.

Table 4. Hammett $\rho_Y$ values for reaction (4)[a]

| | X | | | |
|---|---|---|---|---|
| Z | *p*-CH₃O | *p*-CH₃ | H | *p*-Cl |
| *p*-NO₂ | 0·00 | 0·01 | 0·00 | −0·01 |
| *p*-Cl | −0·01 | −0·02 | −0·02 | −0·02 |
| H | −0·02 | −0·02 | −0·03 | −0·01 |
| *p*-CH₃ | −0·01 | 0·00 | −0·03 | −0·02 |

[a] The linearities of the plots were unsatisfactory in most cases since there were tendencies to form two branches by EWS and EDS. The values are therefore only approximate guides.

The $k_2$ values in Table 1 were subjected to a multiple linear regression analysis[11] using equations (1) and (3), and cross-interaction constants $\rho_{XY}$, $\rho_{YZ}$, $\rho_{XZ}$ and $\beta_{XZ}$ were determined.[3] The results are summarized in Table 5. The signs of these parameters are consistent with those expected from the predictions of TS variation by the QM model.[8] The very small magnitudes of $\rho_{XY}$ and $\rho_{YZ}$ are again partly due to the intervening CH₂ groups in the nucleophile, BA, and substrate, 2-PEB.[7] Since the fall-off factor for one CH₂ group is in the range 2·4–2·8, $|\rho_{XY}|$ should decrease by a factor of $(2{\cdot}4\text{–}2{\cdot}8)^2$ in comparison with those for the reactions of anilines with 1-phenylethyl (1-PEB), ($|\rho_{XY}| \approx 0{\cdot}21$)[3h,i] or the benzyl series ($|\rho_{XY}| \approx 0{\cdot}70$).[3i] Rough estimates give 0·03 for 1-PEB and 0·10 for the benzyl series when the fall-off of $(2{\cdot}6)^2$ is applied, showing that the degree of bond formation is small, being approximately the same as that of the 1-PEB series.[3h] However $|\rho_{YZ}|$ is smaller than that for the reaction of 1-PEB[3h] when the fall-off factor is allowed for. Since the reaction conditions, i.e. solvent and temperature, are different,[3] these comparisons are only approximate.

The magnitudes of $\rho_{XZ}$ and $\beta_{XZ}$ are strikingly large, however; again, if we apply the fall-off factor to $|\rho_{XZ}|$, the magnitude amplifies to nearly that for the reaction of aniline and 1-PEB ($|\rho_{XZ}| \approx 0{\cdot}50$).[3h,j] Since we are free from the fall-off factors in the Brønsted-type coefficients, $\beta_{XZ}$ values can be directly compared.[3n] Some examples of $\beta_{XZ}$ values are given in Table 6.

Table 5. Hammett and Brønsted (in parentheses)[a] type cross-interaction constants for reaction (4)

| Z | $\rho_{XY}$ | Correlation coefficient | X | $\rho_{YZ}$ | Correlation coefficient | Y | $\rho_{XZ}$ | Correlation coefficient |
|---|---|---|---|---|---|---|---|---|
| *p*-$NO_2$ | −0·04 | 0·997 | *p*-$CH_3O$ | 0·02 | 0·999 | *p*-$CH_3O$ | −0·13<br>(−0·22) | 1·000<br>(0·992) |
| *p*-Cl | −0·01 | 0·997 | *p*-$CH_3$ | 0·02 | 0·999 | *p*-$CH_3$ | −0·12<br>(−0·19) | 1·000<br>(0·992) |
| H | −0·02 | 0·994 | H | 0·03 | 1·000 | H | −0·13<br>(−0·21) | 1·000<br>(0·992) |
| *p*-$CH_3$ | −0·03 | 0·994 | *p*-Cl | 0·01 | 0·999 | *p*-Br | −0·16<br>(−0·29) | 0·999<br>(0·992) |
|  |  |  |  |  |  | *p*-$NO_2$ | −0·15<br>(−0·30) | 1·000<br>(0·993) |

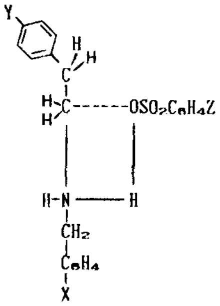
[a] The $pK_a$ values of sulphonic acids were taken from Ref. 15 and the $pK_a$ values for BA from Ref. 13.

Table 6. Comparison of Brønsted type cross-interaction constants

| Reaction | Reactants |  | $\beta_{XZ}$ | Correlation coefficient | Ref. |
|---|---|---|---|---|---|
| A | $XC_6H_4NH_2$ + $YC_6H_4COCH_2OSO_2C_6H_4Z$ | MeOH<br>40·0 °C | 0·19 | 0·995 | 3g |
| B | $XC_6H_4CH_2NH_2$ + $YC_6H_4COCH_2OSO_2C_6H_4Z$ | MeOH<br>45·0 °C | 0·17 | 0·995 | 3m |
| C | $XC_6H_4NH_2$ + $YC_6H_4CH_2OSO_2C_6H_4Z$ | MeOH<br>35·0 °C | −0·06 | 0·996 | 3a |
| D | $XC_6H_4N(CH_3)_2$ + $YC_6H_4CH(CH_3)OSO_2C_6H_4Z$ | MeOH<br>35·0 °C | −0·11 | 0·989 | 3l |
| E | $XC_6H_4NH_2$ + $YC_6H_4CH(CH_3)OSO_2C_6H_4Z$ | MeOH<br>25·0 °C | −0·32 | 0·987 | 3h |
| F | $XC_6H_4NH_2$ + $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ | MeOH<br>65·0 °C | −0·28 | 0·995 | 1 |
| G | $XC_6H_4CH_2NH_2$ + $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ | MeOH<br>65·0 °C | −0·21 | 0·992 | This work |

The sign and magnitude of $\beta_{XZ}$ for reaction (4), i.e. G, are nearer to those of reactions E and F but much greater than those of reactions C and D. This unusually large $|\rho_{XZ}|$ (corrected for the fall-off factor) and $|\beta_{XZ}|$ are indeed an indication that reaction (4) also proceeds largely by an intermolecular $S_{Ni}$ mechanism with a four-centre TS, (Scheme 3), as we concluded for reactions E and F in previous papers;[1,3h] the magnitude of cross-interaction is inversely proportional to the distances between reaction centres (Scheme 2), equation (2),[4] so that $|\rho_{XZ}|$ should be the smallest instead of the greatest found since $r_{XZ}$ $(= r_{XY} + r_{YZ})$ is greater than either $r_{XY}$ or $r_{YZ}$.[3h]

Hence of the three reaction paths conceivable for reaction (4), direct displacement, $k_N$, aryl-assisted, $k_\Delta$, and intermolecular, $S_{Ni}$, the last mechanism with a four-centre TS is the most likely based on the sign and magnitude of the cross-interaction constants. In this mechanism the nucleophile is required to approach from the front, forming a by-pass hydrogen bridge, which greatly enhances the interaction between the substituent in the nucleophile (X) and in the LG (Z).[3c,h]



Scheme 3

## EXPERIMENTAL

*Materials.* Benzylamines[3i,p] and acetonitrile[3p] were used after appropriate purification as described previously. 2-Phenylethyl benzenesulphonates were prepared and purified as described.[1]

*Rate constants.* Rates were measured conductimetrically[1] at 65·0 °C in acetonitrile. Pseudo-first-order rate constants, $k_1^{\text{obs.}}$, were determined by the Guggenheim method[10] with a large excess of benzylamine; [2-PEB] $\approx 10^{-3}$ M and [BA] $\approx 0{\cdot}06$–$0{\cdot}15$ M. Second-order rate constants, $k_2$ were obtained from the slope of equation (5). The absence of solvolysis[5] in acetonitrile was confirmed by zero intercepts, $k_1 = 0$ in equation (5), in all cases. No elimination products of 2-PEB were found in the preliminary tests. These are also evident from the large values of $|\rho_{XZ}|$ since if there were any of these complications, the magnitude of $\rho_{XZ}$ would be small.

The linearity of the plot [equation (5)] was good, with correlation coefficients of better than 0·998 with a 99% confidence limit[12] (more than four [BA] values were used). The $k_2$ values listed in Table 1 are averages obtained by more than two runs, and were reproducible to within ±5%.

*Product analysis.* Products of the reagent of 2-PEB with BA ($PhCH_2CH_2NHCH_2Ph$ and $PhCH_2NH_3^+$ $^-SO_3PhCH_3$) were identified by thin-layer chromatography, IR and NMR spectrometry and elemental analysis.

*N*-(2-Phenylethyl)benzylamine showed $\nu_{max}$ 3400 (secondary aromatic amine) and 1360 $cm^{-1}$ (CN of secondary aromatic NH); $\delta$ 7·3 (Ph, 10H, m), 3·7 ($\alpha$-$CH_2$, 4H, s), 2·8 ($\beta$-$CH_2$, 2H, s) and 1·9 (NH, 1H, s). $R_F = 0{\cdot}55$ [developing solvent, cyclohexane–ethyl acetate (5 : 1)]. Found: C, 85·14; H, 8·19; N, 6·55. $C_{14}H_{17}NO_3S$ requires C, 85·26; H, 8·11; N, 6·63%.

Benzylammonium toluene-*p*-sulphonate was insoluble in organic solvents and had m.p. 198–200 °C; $\nu_{max}$ 3400, 2600, 1600 and 1495 ($NH_3^+$) and 1210, 1170, 565 and 490 $cm^{-1}$ ($SO_3^-$); $\delta$ 7·5 (Ph, 9H, m), 4·2 ($CH_2$, 2H, s), 3·1 ($NH_3^+$, 3H, s) and 2·4 ($CH_3$, 3H, s). Found: C, 60·05; H, 6·21; N, 5·16. $C_{14}H_{17}NO_3S$ requires C, 60·19; H, 6·13; N, 5·01%.

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