Basicity of Nitrogen–Sulphur(VI) Compounds. Part 6.[1] Ionization of *NN'*-Di- and *N*-Mono-substituted Sulphamides and Dihydro-2,1,3-benzothiadiazoline and Benzothiadiazine 2,2-Dioxides (Cyclic Sulphamides)

Padraig O. Burke, Séan D. McDermott, Thomas J. Hannigan, and William J. Spillane*
Department of Chemistry, University College, Galway, Ireland

36 Di- and mono- and two tri-substituted sulphamides have been synthesised and their ionization equilibria in base (Schemes 1—3) have been studied. Many of the sulphamides are new materials. The pK_a values obtained for each series have been correlated in Hammett and Taft plots. The Hammett ρ values obtained for the ionization of the proximate hydrogen are *ca.* 2.3. The Taft ρ* value obtained for ionization of the 'remoter' hydrogen is 1.68. The six-membered cyclic sulphamides are more acidic than their acyclic analogues by *ca.* 2.5 pK_a units and the five-membered cyclic sulphamides are *ca.* 4 pK_a units more acidic than model open-chain counterparts. Sulphur *d*-orbital involvement and ring-strain are suggested as possible sources of this 'acid-strengthening' effect.

In previous papers we have looked at the ionization equilibria of several series of trisubstituted[1,2] and a series of *NN'*-diarylsulphamides.[2] In the present paper we have measured pK_a values for several series of *N*-aryl-*N'*-alkyl (alicyclic) sulphamides, for some *N*-aryl, and for a series of cyclic sulphamides. The effects of substituents in all series have been correlated in a number of Hammett and Taft equations.

Six-membered cyclised sulphamide[3,4] and sulphonamide[5,6] systems are known to exhibit enhanced acidities compared with their acyclic counterparts. We have provided further examples of this in this paper and we also show that the 'acid-strengthening' effect is further enhanced possibly due to ring strain in a series of five-membered cyclic sulphamides.

Experimental

Potentiometric measurements were made with a Pye-Unicam 290 MK2 pH meter standardized with buffers at pH 4.0, 7.0, 10.0, and 12.0. U.v. measurements were made at 25 °C on a Perkin-Elmer 124 spectrophotometer. ^{13}C N.m.r. spectra were recorded on a JEOL JNM FX 60 spectrometer and ^1H n.m.r. spectra on a JEOL MH 100 MHz spectrometer.

Materials.—Liquid amines were distilled prior to use and solid amines were recrystallized from appropriate solvents. Sulphamide (Alfa Inorganics) was used as obtained. Diglyme was distilled from calcium hydride before use. Other materials were commercially available and used as obtained. The potassium hydroxide solutions for the pK_a determinations were made up and checked as before.[1]

N-Cyclohexyl- [b.p. 136—140 °C at 0.22 mmHg (lit.,[7] 120 °C at 0.1 mmHg)], *N*-n-butyl- [b.p. 84—86 °C at 0.1 mmHg (lit.,[8] 80 °C at 0.11 mmHg)], *N*-phenyl[9] [b.p. 130 °C at 2.5 mmHg], and *N*-benzyl- [b.p. 113 °C at 0.1 mmHg (Found: C, 40.4; H, 4.0; N, 6.9. $C_7H_7ClNO_2S$ requires C, 40.9; H, 3.9; N, 6.8%)] sulphamoyl chlorides were prepared as before,[1,9] yields being 75, 89, 71, and 87%, respectively (undistilled). In the case of the synthesis of n-butylsulphamoyl chloride the n-butylsulphamate salt mixture was not isolated but was reacted *in situ* to form the chloride. *N*-Benzylsulphamoyl chloride did not decompose[7] on distillation in our hands. All the sulphamoyl chlorides were used without distillation in subsequent reactions to form the sulphamides.

The three series of *NN'*-disubstituted sulphamides (**1**)—(**20**) were prepared by one of the procedures of Wheeler and Degering.[10] The *N*-monosubstituted sulphamides (**21**), (**22**), and (**24**)—(**29**) were prepared by reaction of the appropriate amines with sulphamide employing methods described in the literature.[11-13] Compound (**23**) was prepared by the method of Catt and Matier[14] by stirring for 12 h at room temperature a solution of *N*-3-chlorophenyl-*N'*-t-butylsulphamide (0.76 mmol) in trifluoroacetic acid (15 ml). The acid was removed under reduced pressure and the crude sulphamide recrystallized from benzene–chloroform to give pure (**23**) in 71% yield. In general, and unless otherwise stated, all the sulphamides prepared were recrystallized from aqueous ethanol. Cyclic sulphamides (**32**)—(**34**) have been prepared previously.[15-17] Compounds (**35**)—(**37**) were prepared by reacting the appropriate *o*-phenylenediamine with sulphamide in dry refluxing diglyme.[15,16] 4,5-Dimethyl- (Fluka) and 3-methyl-1,2-phenylenediamines (SSF) were used as obtained and 4-nitro-1,2-phenylenediamine was recrystallized from ligroin prior to use.

Preparation of Acetylated Sulphamide.—Compound (**38**) was prepared by stirring compound (**32**) (1.1 mmol) with an equimolar quantity of acetic anhydride to which a few drops of concentrated sulphuric acid had been added. The crude product thus obtained was recrystallized from ethanol (0.17 g, 68%), m.p. 174—176 °C (Found: C, 45.1; H, 3.7; N, 12.8. $C_8H_8N_2O_3S$ requires C, 45.3; H, 3.8; N, 13.2%). In a separate experiment using (**32**) (0.5 g, 2.9 mmol) and acetic anhydride (1 ml) and a few drops of concentrated sulphuric acid two products were formed. Compound (A) (0.144 g), m.p. 172—174 °C, was identified as (**38**) from i.r., ^1H n.m.r., and elemental analysis. Compound (B) (0.396 g), m.p. 103—105 °C, was recrystallized from benzene–light petroleum (b.p. 40—60 °C) and identified as (**32**) (diacetylated) from i.r. and ^1H n.m.r. spectra.

Preparation of Methylated Sulphamide.—Compound (**31**) was prepared by stirring MeI (5.4 mmol) with a solution of (**30**) (5.4 mmol) and powdered NaOH (0.22 g) in 60% v/v ethanol–water (*ca.* 12 ml) at 18 °C for 30 h. The solid which fell out of solution was filtered, washed with distilled water, and recrystallized slowly from aqueous ethanol to yield pure (**31**) (0.33 g, 31%), m.p. 114 °C (Found: C, 48.3; H, 5.2; N, 14.4. $C_8H_{10}N_2O_2S$ requires C, 48.5; H, 5.05; N, 14.1%).

Alternative routes were available to some of the sulphamides used in these studies. For example, (**15**) was prepared by a 'reverse procedure' involving the reaction of phenylsulphamoyl chloride and benzylamine in the presence of triethylamine (all

$XC_6H_4NHSO_2NHR \rightleftharpoons XC_6H_4\bar{N}SO_2NHR$

(1) R = cyclo-C_6H_{11}, X = 4-Me
(2) R = cyclo-C_6H_{11}, X = 3-Me
(3) R = cyclo-C_6H_{11}, X = H
(4) R = cyclo-C_6H_{11}, X = 3-Cl
(5) R = cyclo-C_6H_{11}, X = 4-NO_2
(6) R = Bu^n, X = 4-Me
(7) R = Bu^n, X = 3-Me
(8) R = Bu^n, X = H
(9) R = Bu^n, X = 3-MeO
(10) R = Bu^n, X = 3-Cl
(11) R = Bu^n, X = 4-Br
(12) R = Bu^n, X = 3-NO_2
(13) R = Bu^n, X = 4-EtO
(14) R = $C_6H_5CH_2$, X = 4-Me
(15) R = $C_6H_5CH_2$, X = H
(16) R = $C_6H_5CH_2$, X = 3-MeO
(17) R = $C_6H_5CH_2$, X = 3-Cl
(18) R = $C_6H_5CH_2$, X = 4-Cl
(19) R = $C_6H_5CH_2$, X = 4-Br
(20) R = $C_6H_5CH_2$, X = 3-NO_2

Scheme 1.

2.6 mmol) in dry ether (20 ml). Work-up yielded pure (**15**), m.p. 86—88 °C.[18]

Characterization of Sulphamides.—About one third of the sulphamides used in the present study were previously reported. In the Table comparison between recorded m.p.s and the literature values is made in the footnotes. ^{1}H N.m.r. ($CDCl_3$ or $CDCl_3$–[$^2H_6$]DMSO) spectra were recorded for those sulphamides not previously reported and were readily interpreted on the basis of the structures outlined.

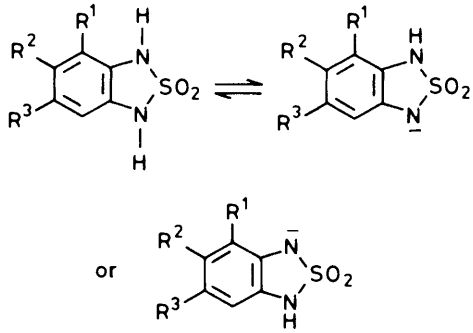
I.r. spectra (Nujol mull) of all new sulphamides were recorded and the characteristic bands[1,19] of substituted sulphamides were observed. Satisfactory C, H, and N (± 0.5) analyses were obtained for all new sulphamides except for compound (**37**) (Found: C, 46.0; H, 4.4; N, 15.9. $C_7H_8N_2O_2S$ requires C, 45.7, H, 4.4; N, 15.2%). Compound (**36**) gave a satisfactory C, H, and N analysis but had a poor sulphur analysis (Found: S, 15.5. $C_8H_{10}N_2O_2S$ requires S, 16.2%). ^{13}C N.m.r. spectra ([$^2H_6$]-DMSO or $CDCl_3$–[$^2H_6$]DMSO) were recorded for (**3**), (**4**), (**6**)—(**12**), (**14**)—(**20**), and (**32**)—(**37**). These confirmed the assigned structures. Chemical shift data (in p.p.m.) for compounds (**32**)—(**37**) were as follows: δ_C ([$^2H_6$]DMSO; Me_4Si) (**32**) 110.2, 121.4, 129.5; (**33**) 110.3, 110.8, 121.7, 127.3, 129.9, 130.7; (**34**) 109.9, 111.2, 120.9, 125.1, 128.2, 130.5; (**35**) 104.6, 108.8, 118.5, 128.9, 135.2, 141.0; (**36**) 111.8, 127.8, 129.1; (**37**) 108.1, 120.7, 121.8, 123.1, 128.6, 129.9.

pK_a *Determinations.*—These were carried out as previously described.[1,20] The initial substrate concentration was 0.0033M in all cases and the strength of the base used was 0.055M-KOH. The volume at 'half-neutralization' was 38.7 ml and pK_a values were calculated within a 30—85% range of ionization. In calculating a_{OH^-}, the hydroxyl ion activity, a value for pK_s of 15.1[21] was used for the 60% v/v EtOH–H_2O system where a_{OH^-} = antilog (pH − pK_s). As a test of our method we determined the pK_a of sulphanilamide as 12.05 ± 0.09 (n = 5) compared with the literature value of 12.04.[22c] The u.v. measurement on (**13**) was carried out as before.[1]

$Ar\ (or\ R)NHSO_2NH_2 \rightleftharpoons Ar\ (or\ R)\bar{N}SO_2NH_2$

(21) Ar = 4-MeC_6H_4
(22) Ar = C_6H_5
(23) Ar = 3-ClC_6H_4
(24) Ar = 3-$NO_2C_6H_4$
(25) Ar = 4-$EtOC_6H_4$
(26) R = Bu^n
(27) R = cyclo-C_6H_{11}
(28) R = n-C_6H_{13}
(29) R = $C_6H_5CH_2$

Scheme 2.



or

(32) R^1, R^2, R^3 = H
(33) R^1, R^3 = H, R^2 = Me
(34) R^1, R^3 = H, R^2 = Cl
(35) R^1, R^3 = H, R^2 = NO_2
(36) R^1 = H, R^2, R^3 = Me
(37) R^1 = Me, R^2, R^3 = H

Scheme 3.

Results and Discussion

pK_a *Values.*—For reasons of solubility the pK_a values of all the sulphamides in the Table were determined in 60% v/v EtOH–H_2O. In the potentiometric method pK_a values were calculated using equation (1) which includes a correction for hydroxyl ion activity. In the u.v. method equation (2) was used, as before,[1] to calculate pK_a.

$$pK = pH + \log_{10}\frac{[HA] + a_{OH^-}}{[A^-] - a_{OH^-}} \quad (1)$$

$$pK_a = pH + \log_{10}\frac{d_i - d}{d - d_m} \quad (2)$$

pK_a Values have been determined (Table) for the compounds shown in Schemes 1—3 and for compounds (**30**), (**31**), and (**38**). pK_a Determinations on compounds (**26**)—(**29**) were not made. The observed pH values at 'half-neutralization' were between 11.90 and 12.34 for each of these four compounds and, thus, reliable pK_a values could not be obtained by potentiometry. These compounds are not amenable to pK_a determination by spectrophotometry due to the absence of a chromophore.

Table. Yield (%), m.p., and pK_a value at 25 °C in 60% v/v EtOH–H_2O for disubstituted, monosubstituted, and cyclic sulphamides

Compound	Yield (%)	M.p. (C)	pK_a[a]	Spread (±)[b]	n[c]
(1)	65	93—95	11.83	0.06	7
(2)	44	79—80	11.70	0.06	6
(3)	47	71—72	11.40	0.08	6
(4)	55	70—72	10.77	0.06	7
(5)	67	118—120	9.11	0.06	7
(6)	56	54—55	11.42	0.02	8
(7)	44	43—44	11.29	0.03	7
(8)	56	44—45[d]	11.34	0.04	7
(9)	42	48—49	10.98	0.04	8
(10)	40	53—54	10.35	0.06	6
(11)	34	69—71	10.71	0.05	6
(12)	38	101	9.42	0.04	6
(13)	40	107—109	12.05[e]	0.04	5
(14)	37	106—107	11.31	0.03	7
(15)	71	86—89	11.04	0.04	7
(16)	56	75—78	10.83	0.04	8
(17)	50	74—75	10.14	0.05	7
(18)	53	101—103	10.41	0.06	6
(19)	38	112—113	10.34	0.03	7
(20)	36	108—109	9.35	0.04	7
(21)	22	129—131[f]	11.20	0.04	7
(22)	28	104—106[g]	11.10[h]	0.02	6
(23)	71	110—112	10.12	0.03	6
(24)	8	158—162[i]	9.22	0.08	8
(25)	4	126—129[j]	11.28	0.02	8
(30)	[k]	190—192	8.79	0.03	6
(31)	31	114	10.66	0.03	8
(32)	64	175—177[l]	6.41	0.05	8
(33)	34	169—170[m]	6.70	0.03	10
(34)	5	199—200[n]	5.06	0.07	8
(35)	8	190	2.85	0.03	7
(36)	20	148	6.88	0.03	9
(37)	15	153—155	6.62	0.04	8
(38)	68	174—176	3.40	0.07	7

[a] Some pK_a measurements were repeated and in such cases agreement was good. [b] The spread or scatter was calculated as described in ref. 20 ch. 1. [c] n = No. of pK_a values averaged to obtain the value given. [d] Lit.,[7] 66 °C. [e] pK_a determined by u.v. spectrophotometry using 245 nm as analytical wavelength. [f] Lit.,[12] 123—125 °C. [g] Lit.,[12] 105—107 °C. [h] This pK_a was measured previously.[2] [i] Lit.,[12] 149—150 °C. [j] Lit.,[12] 125—126 °C. [k] This compound was a gift (M. Knollmüller, *Monatsch. Chem.*, 1971, **102**, 1055). [l] Lit.,[16] 175—177 °C; lit.,[15] 181—183 °C. [m] Lit.,[17] 169—170 °C. [n] Lit.,[15] 199 °C.

In Scheme 2, for convenience (**26**)—(**29**) are also represented as ionizing at the substituted nitrogen. Compound (**13**), which was expected to have a larger pK_a, had its pK_a determined by u.v. since potentiometry would be unlikely to give a reliable value.[20]

Because compounds (**32**)—(**37**) have two possible sites for ionization [these are the same in (**32**) and (**36**)] the possibility of overlapping pK_a values was considered. However, when the ionization of (**34**) was followed by spectrophotometry it was seen that only two species, *i.e.* the neutral molecule and the monoanion, were present in buffered solutions[20] between pH values 2.90 and 8.21. Furthermore the differences of *ca.* 5 pK_a units between the first and second pK_a values for the related open-chain compounds of type $RNHSO_2NHR$ suggest the absence of overlapping ionization processes.[2] The above two considerations taken in conjunction with the good precision obtained for the pK_a values indicates that there is no overlap.

Hammett and Taft Correlations.—A number of Hammett and Taft correlations using the pK_a values in the Table for the compounds represented in Schemes 1—3 were made. The series, ρ value, correlation coefficient, standard error (s), and absolute

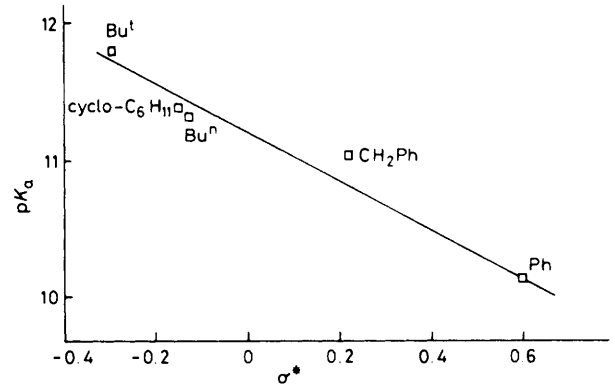


Figure 1. Taft plot for the ionization of $PhNHSO_2NHR$ in 60% v/v ethanol–water

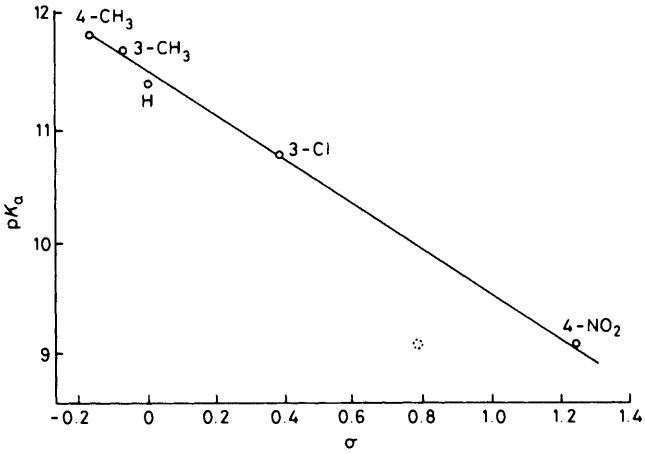


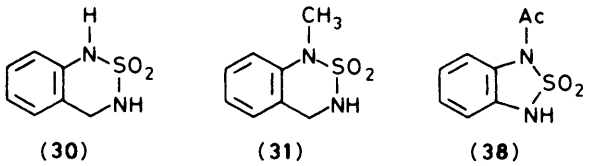
Figure 2. Hammett plot for the ionization of series (**1**)—(**5**) (○ indicates $\sigma_{p\text{-}NO_2}$) in 60% v/v ethanol–water

error (%) were as follows: (**1**)—(**5**), 2.79, 0.983, 0.30, and 10.6; (**6**)—(**13**), 2.51, 0.985, 0.18, and 7.25; (**14**)—(**20**) 2.30, 0.993, 0.12, and 5.2; (**21**)—(**25**), 2.21, 0.987, 0.21 and 9.3; (**32**)—(**37**), 2.80, 0.99, 0.25, and 8.7. A Taft $\rho^*\sigma^*$ correlation for the series $PhNHSO_2NHR$ with R = cyclo-C_6H_{11} (**3**), Bu^n (**8**), $C_6H_5CH_2$ (**15**), Ph (pK_a 10.13[2]), and Bu^t (pK_a 11.74[18]) gave ρ^* 1.68, r = 0.98, s 0.20, and absolute error (%) 11.7 (Figure 1).

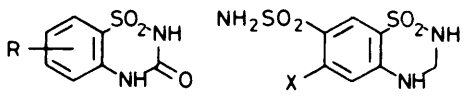
If σ^- is used for *p*-nitro in the cyclohexyl series (**1**)—(**5**) the parameters (ρ, r, s, and absolute error) obtained are: 1.93, 0.990, 0.06, and 3.1 (Figure 2). The ρ value drops considerably and statistical analysis indicates that a better fit of the data is obtained.

In the n-butyl series (**6**)—(**13**) if (**13**), whose pK_a was determined by u.v., is dropped and correlation is carried out with (**6**)—(**12**) the parameters (ρ, r, s, and absolute error) obtained show little change: 2.35, 0.99, 0.17, and 7.1.

The ρ values of 1.93, 2.51, 2.30, and 2.21 for the series (**1**)—(**5**), (**6**)—**13**), (**14**)—(**20**), and (**21**)—(**25**) respectively are in much the same range as those previously reported[1,2] for the various trisubstituted sulphamide series. Each of the present series has at least two ionizable protons but the more acidic is clearly that located between the phenyl ring and the sulphonyl group. The extent of conjugative interaction between a $-M$ substituent, *i.e.* nitro, and the site of ionization was shown to be important in series (**1**)—(**5**) where the use of a σ^- value gave a superior fit (Figure 2). Thus, as before in a sulphamide system[2] and in



(30) (31) (38)



(39) (40)

sulphonamide systems[22] when a $-M$ substituent is situated *para* to an ionizing hydrogen on an aryl nitrogen, it is necessary to use σ^- values.

The Taft plot (Figure 1) for the series $PhNHSO_2NHR$ appears to be reliable since it includes five substituents with a substantial change in σ^* values and a pK_a spread of *ca.* 1.6 pK_a unit. Further the ρ^* value of 1.68 obtained is in excellent agreement with the tentative Hammett ρ value of 1.68 determined previously[1] for the series cyclo-$C_6H_{11}NHSO_2N(Ac)Ar$ (three substituents) in 60% v/v ethanol–water. Of interest in connection with these ρ^* and ρ values are the ρ values of *ca.* 1.6 observed in 50% w/w (*i.e. ca.* 56% v/v) ethanol–water for the ionization of sulphonamides of types NH_2SO_2Ar, $PhNHSO_2Ar$, and $RNHSO_2Ar$[22c] and the ρ of 2.5 reported[23] for the ionization of a series of sulphamate esters, $MeNHSO_2OAr$, in 50% v/v ethanol–water. It thus appears that the sulphamido linkage, $(H)NSO_2N(Ar)$, transmits charge as efficiently as a sulphonamide, $(H)NSO_2(Ar)$, one but not as effectively as a sulphamoyl linkage, $(H)NSO_2O(Ar)$does.

Cyclic Sulphamides.—The hydrogen attached to nitrogen in a cyclised sulphonamide is known to be more acidic than that in an acyclic analogue. Thus, for examples, Girard[5] has reported that the acidity of the 1,2,4-benzothiadiazine dioxides (**39**), which can be regarded as cyclic acylsulphonamides, are *ca.* 2 pK_a units more acidic than their acyclic counterparts. Chatten[6] has shown that even within compounds containing endo- and exo-cyclic sulphonamide moieties there are considerable differences in acidity. Thus, in the medicinally important benzothiadiazines of type (**40**; X = Cl), the pK_a for the ionization of the endocyclic NH is 9.5 and the pK_a for the exocyclic NH is 11.3.

This 'acid-strengthening' effect upon cyclisation of sulphonamides is also found[3,4] for sulphamides when they are cyclised. Thus, compound (**30**) has a pK_a of 8.79 while typical open-chain analogues, *e.g.* compounds (**3**) (pK_a 11.40), (**8**) (pK_a 11.34), and (**15**) (pK_a 11.04) have pK_a values that are on average *ca.* 2.5 pK_a units higher. This difference is maintained on methylation; compound (**31**) has a pK_a *ca.* 2.7 pK_a units lower than the pK_a values of typical acyclic models, *i.e.* cyclo-$C_6H_{11}NHSO_2N(Me)Ph$, $Bu^nNHSO_2N(Me)C_6H_4Me$-4, and $Bu^nNHSO_2N(Me)Ph$.[1] The 'acid-strengthening' effect is greater for sulphamides in a five-membered ring system. Thus, compound (**32**) has a pK_a of 6.41, which may be compared with values of 11.10 for (**22**) and 10.13 for $PhNHSO_2NHPh$,[2] both being suitable models for comparison. Acetylation of (**32**) to give (**38**) raises the acidity considerably.

The origin of this 'acid-strengthening' effect is unclear. Neither Girard[4] nor Chatten[5] have offered explanations for the effect in their six-membered benzothiadiazines. In the case of compounds (**32**)—(**38**) ring-strain may well play a part but for the six-membered sulphonamide and sulphamide systems this seems unlikely to be a major factor. The explanation for the increased acidity of the six-membered rings could lie in sulphur *d*-orbital overlap of the nitrogen lone pair.

A Hammett plot of the pK_a values of (**32**)—(**37**) using σ_p constants for (**33**) and (**34**), σ_p^- for (**35**), $\sigma_m + \sigma_p$ for (**36**), and σ_m for (**37**) gave ρ, *r*, *s*, and absolute-error (%) of 2.80, 0.985, 0.25, and 8.7, respectively. This ρ value is in good agreement with the ρ value of 2.78 for the first ionization of diphenylsulphamide.[2] However, the data may be providing a fortuitous fit since the site of ionization may change from the 3- to the 1-position, as shown in Scheme 3, for some of the compounds.

Acknowledgements

S. D. McD. and T. J. H. thank the Department of Education for state maintainance Grants for research. We thank Dr. M. Knollmüller, University of Vienna, for a sample of compound (**30**) and SSF, Dottikon, Switzerland, for a sample of 3-methyl-1,2-phenylenediamine and Lt. E. Kiely and Dr. P. Larkin for preparing compounds (**14**)—(**20**) and (**25**), respectively.

References

1 Part 5, S. D. McDermott, P. O. Burke, and W. J. Spillane. *J. Chem. Soc., Perkin Trans. 2*, 1984, 499.
2 T. J. Hannigan and W. J. Spillane, *J. Chem. Soc., Perkin Trans. 2*, 1982, 851.
3 P. F. Degering and J. E. Wilson, *J. Org. Chem.*, 1952, **17**, 339.
4 G. Garcia Munoz, R. Madronero, C. Ochoa, M. Stud, and W. Pfleiderer, *J. Heterocycl. Chem.*, 1976, **13**, 793.
5 Y. Girard, J. G. Atkinson, and J. Rokach. *J. Chem. Soc., Perkin Trans. 1*, 1979, 1043.
6 (*a*) U. G. G. Hennig, L. G. Chatten, R. E. Mosalyk, and C. Eddis, *Analyst (London)*, 1981, **106**, 557; (*b*) U. G. G. Hennig, R. E. Moskalyk, L. G. Chatten, and D. L. Rabenstein, *ibid.*, p. 565.
7 G. Weiss and G. Schulze, *Liebig's Ann. Chem.*, 1969, **729**, 40.
8 N. C. Hansen, *Acta Chem. Scand.*, 1963, **17**, 2141.
9 J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 1976, **41**, 4028.
10 K. W. Wheeler and E. F. Degering, *J. Am. Chem. Soc.*, 1944, **66**, 1242.
11 K. Hamann, Ger. P. 869, 065, 1953.
12 A. V. Kirsanov and I. N. Zolotov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1958, **28**, 340.
13 M. Yamaguchi and K. Nakano, *Hiroshima Daigaku Kogakuba Kenkyu Hokoku*, 1972, **21**, 23.
14 J. D. Catt and W. L. Matier, *J. Org. Chem.*, 1974, **39**, 566.
15 J. Carson, U.S.P., 3, 177, 221, 1965.
16 D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc. C*, 1971, 993.
17 W. J. Spillane and T. J. Hannigan, *J. Chem. Res. (S)*, 1982, 84.
18 S. D. McDermott, Ph.D. Thesis, National University of Ireland, 1983.
19 A. Vandi, T. Moeller, and L. F. Audrieth, *J. Org. Chem.*, 1961, **26**, 1136.
20 A. Albert and E. P. Serjeant 'The Determination of Ionization Constants,' Chapman and Hall, London, 1984.
21 B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, 1953, **75**, 565.
22 (*a*) A. V. Willi, *Helv. Chim. Acta*, 1956, **39**, 46; (*b*) G. Dauphin and A. Kergomard, *Bull. Soc. Chim. Fr.*, 1961, 486; (*c*) G. Dauphin, A. Kergomard, and H. Veschambre, *ibid.*, 1967, 3395; (*d*) D. N. Kravtsov, A. S. Peregudov, E. S. Petrov, M. I. Terekhova, and A. I. Shatenshtein, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 993.
23 A. Williams and K. T. Douglas, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1727.

Received 23rd *March* 1984; *Paper* 4/472