equilibrium for $Copy_2Cl_2$ system. Half conversion of td-$Co(dpa)\,Cl_2$ to oh-$Co(dpa)_2Cl_2$ occurs with 0.157 $M$ of 2,2′-dipyridylamine at 25°C, while that of td-$Copy_2Cl_2$ occurs with 1.18 $M$(in $CH_3NO_2$) or 1.52–2.17 $M$ (in pyridine) of pyridine. Although the effect of different solvents on the equilibria is uncertain, binding of 2,2′-dipyridylamine, a chelating ligand, appears to result in 4–7 times (with statistical correction) more effective formation of the octahedral complex than binding of a nonchelating ligand, pyridine. The "chelate effect"[18, 19] is further supported by the values of $\Delta H^0$ and $\Delta S^0$. The greater $\Delta H^0$ for $Co(dpa)Cl_2$ system may be attributed to the greater steric strain resulting from the presence of two chelate rings in $Co(dpa)_2Cl_2$. On the other hand, the greater $\Delta S^0$ for $Co(dpa)Cl_2$ system reflects the smaller number of the reacting ligand. Thus, the more favorable formation of oh-$Co(dpa)_2Cl_2$ compared with oh-$Copy_2Cl_2$ is caused by the greater $\Delta S^0$ value.

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# The Crystal and Molecular Structures of Sulfametrole

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Sulfametrole, $C_9H_{10}N_4O_3S_2$, crystallizes in the monoclinic system, space group $P2_1/n$, with $a=8.145(2)$, $b=16.505(4)$, $c=9.637(1)$ Å, $\beta=103.72(1)°$, $D_m=1.52$ $gcm^{-3}$, $Z=4$. Intensities for 3594(2143 observed) unique reflections were measured on a four-circle diffractometer with Mo $K_\alpha$ radiation ($\lambda=0.71069$ Å). The structure was solved by direct method and refined by full-matrix least squares to a final $R$ of 0.070. The geometrical features of the thiadiazole ring indicate some $\pi$-electron delocalization inside the ring. The least squares planes defined by the benzene and thiadiazole rings are nearly perpendicular to each other(dihedral angle; 93.9°). All the potential hydrogen-bond donor atoms in the molecule, N(1) and N(2), are included in the hydrogen bonding. The molecules through hydrogen bonding form three dimensional network.

## Introduction

The study of sulfametrole was undertaken as a part of a program of structure analysis of the therapeutically useful, sulfonyl-group containing compounds being pursued in this laboratory.

The stereochemical structure of a molecule can supply useful information about the relationship between structure and activity. And the geometrical parameters determined can be correlated with the molecular electronic structure. From these facts sulfametrole which is a new antibacterial agent is of particular interest in the $\pi$-electron delocalization inside the thiadiazole ring and in the conjugation between the thiadiazole ring and its substituents.

In this paper, the geometrical parameters will be discussed in comparison with those of other related compounds[1-5] and the hydrogen bonding scheme also discussed.

## Experimental

3-methoxy-4-sulfanilamido-1,2,5-thiadiazole was crystallized by slow evaporation from aqueous ethanol solution in the form of colorless transparent prisms. Rotation and Weissenberg photographs showed the monoclinic symmetry of the crystals and yielded approximate lattice constants. The density was measured by flotation in a mixture of carbon tetrachloride and benzene. The space group $P2_1/n$ was indicated by the absence of reflections $h0l$ with $(h+l)$ odd and $0k0$ with $k$ odd.

A crystal with approximate dimensions 0.2×0.2×0.3mm was selected for the data collection. The intensities of 3594 unique reflections with $0<2\theta\leq60°$ were measured using a Rigaku four-circle diffractometer with graphite-monochromatized Mo $K_\alpha$ radiation in the $\omega$-$2\theta$ scan mode, with a scan speed of 4 °min$^{-1}$ in $2\theta$ and a scan width of $(1.2+0.5\tan\theta)°$ in $\omega$. At both ends of the scan range 10 sec background counts were taken for each reflection. Three standard reflections, measured after every 50 reflections during the data collection, showed only small random deviations about their mean intensities. The lattice constants were refined by least-squares from the measured $\theta$ values for 30 well centered reflections, lying in the $2\theta$ range 10-40°. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied. 2143 reflections had $F_0\geq3\sigma(F_0)$ and were considered to be observed.

Crystal data of 3-methoxy-4-sulfanilamido-1,2,5-thiadiazole

$C_9H_{10}N_4O_3S_2$
Monoclinic
M.W. ; 286.33
$a$; 8.145(2) Å
$b$; 16.505(4)
$c$; 9.637(1)
$\beta$; 103.72(1)°
$\mu$; 3.72 mm$^{-1}$
mp ; 153-154 °C
Space group ; $P2_1/n$
$Z$ : 4
$F(000)$; 592
$V$; 1258.8 Å$^3$
$D_c$; 1.511 g cm$^{-3}$
$D_m$; 1.52 g cm$^{-3}$
$\lambda(M_0\ K_\alpha)$; 0.71069 Å

**TABLE 1(a): Fractional Atomic Coordinates for the Non-Hydrogen Atoms in Sulfametrole. The e.s.d's are Given in Parentheses**

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| S(1) | 0.3290(2) | 0.3942(1) | 0.0368(1) |
| S(2) | 0.8792(2) | 0.4290(1) | 0.3346(2) |
| O(1) | 0.1664(5) | 0.4296(2) | −0.0167(4) |
| O(2) | 0.4347(6) | 0.3782(2) | −0.0595(4) |
| O(3) | 0.5434(5) | 0.5677(3) | 0.3791(4) |
| N(1) | 0.2906(7) | 0.1060(3) | 0.3880(6) |
| N(2) | 0.4219(6) | 0.4594(4) | 0.1590(5) |
| N(3) | 0.7020(6) | 0.4058(3) | 0.2147(6) |
| N(4) | 0.8079(7) | 0.5061(4) | 0.4113(6) |
| C(1) | 0.2958(7) | 0.1723(3) | 0.2995(6) |
| C(2) | 0.1695(7) | 0.2301(3) | 0.2795(6) |
| C(3) | 0.1776(7) | 0.2972(3) | 0.1936(6) |
| C(4) | 0.3105(7) | 0.3053(3) | 0.1293(6) |
| C(5) | 0.4339(7) | 0.2463(3) | 0.1441(7) |
| C(6) | 0.4255(8) | 0.1801(4) | 0.2299(7) |
| C(7) | 0.5873(7) | 0.4570(3) | 0.2350(6) |
| C(8) | 0.6492(7) | 0.5140(4) | 0.3471(6) |
| C(9) | 0.6164(9) | 0.6244(4) | 0.4923(6) |

**TABLE 1(b): Anisotropic Thermal Parameters $u_{ij}$ (X10$^4$) for the Non-Hydrogen Atoms in Sulfametrole. The e.s.d's are Given in Parentheses**

The $u_{ij}$ values given are defined by the temprcature factor: $\exp\{-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}klb^*c^*)\}$

| | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{23}$ | $u_{13}$ | $u_{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 294(6) | 172(5) | 257(5) | −1(5) | 70(4) | −18(5) |
| S(2) | 338(8) | 653(12) | 607(11) | −147(9) | −33(7) | 135(8) |
| O(1) | 326(19) | 240(17) | 387(22) | 26(16) | 0(16) | −10(16) |
| O(2) | 484(29) | 289(21) | 341(21) | 16(16) | 226(20) | 8(19) |
| O(3) | 462(24) | 454(24) | 328(22) | −123(19) | 35(18) | 63(20) |
| N(1) | 346(25) | 299(23) | 442(28) | 129(23) | 96(23) | −4(21) |
| N(2) | 293(22) | 198(20) | 353(24) | −68(17) | 6(18) | −10(17) |
| N(3) | 308(23) | 356(28) | 512(30) | −114(23) | 17(21) | 37(20) |
| N(4) | 376(28) | 556(34) | 401(28) | −125(25) | −30(22) | 36(25) |
| C(1) | 295(25) | 244(25) | 342(27) | 32(20) | 43(21) | −47(20) |
| C(2) | 262(25) | 270(27) | 447(32) | 52(23) | 147(23) | −16(21) |
| C(3) | 307(26) | 185(22) | 438(30) | 9(21) | 127(23) | 32(20) |
| C(4) | 307(27) | 214(22) | 306(25) | 7(19) | 108(22) | −52(19) |
| C(5) | 335(29) | 286(25) | 484(34) | 115(26) | 225(26) | 41(22) |
| C(6) | 380(32) | 303(28) | 532(37) | 139(23) | 175(29) | 131(25) |
| C(7) | 331(27) | 255(24) | 280(26) | 29(19) | 73(21) | 5(20) |
| C(8) | 366(29) | 359(29) | 271(27) | −36(22) | 42(23) | −42(23) |
| C(9) | 748(44) | 448(35) | 356(28) | −191(24) | 25(28) | 20(32) |

**TABLE 2: Fractional Atomic Coordinates and Isotropic Thermal Parameters u $(X10^3)$ for the Hydrogen Atoms in Sulfametrole. The e.s.d's are Given in Parentheses**

| | *X/a* | *Y/b* | *Z/c* | *u* |
|---|---|---|---|---|
| H'(N1) | 0.235(7) | 0.114(4) | 0.454(6) | 39(15) |
| H''(N1) | 0.385(12) | 0.089(6) | 0.441(10) | 93(35) |
| H(C2) | 0.068(9) | 0.223(4) | 0.313(7) | 50(21) |
| H(C3) | 0.085(9) | 0.339(5) | 0.183(8) | 42(23) |
| H(C5) | 0.532(11) | 0.254(6) | 0.099(10) | 42(31) |
| H(C6) | 0.508(7) | 0.147(4) | 0.235(6) | 45(16) |
| H(N2) | 0.375(10) | 0.493(5) | 0.176(9) | 66(28) |
| H'(C9)* | 0.521 | 0.666 | 0.510 | 90 |
| H''(C9)* | 0.716 | 0.658 | 0.462 | 96 |
| H'''(C9) | 0.668 | 0.591 | 0.589 | 134 |

*Hydrogen atoms with positions geometrically fixed.

**TABLE 3(a): Bond Lengths (Å) in Sulfametrole. The e.s.d's are Given in Parentheses**

| | | | |
|---|---|---|---|
| C(1)-N(1) | 1.393(8) | C(1)-C(2) | 1.383(8) |
| C(2)-C(3) | 1.394(8) | C(3)-C(4) | 1.376(9) |
| C(4)-C(5) | 1.382(8) | C(5)-C(6) | 1.382(9) |
| C(6)-C(1) | 1.385(9) | S(1)-C(4) | 1.742(5) |
| S(1)-O(1) | 1.427(4) | S(1)-O(2) | 1.433(5) |
| S(1)-N(2) | 1.641(4) | N(2)-C(7) | 1.374(6) |
| C(7)-N(3) | 1.308(8) | N(3)-S(2) | 1.665(5) |
| S(2)-N(4) | 1.646(6) | N(4)-C(8) | 1.300(7) |
| C(8)-C(7) | 1.431(7) | C(8)-O(3) | 1.322(8) |
| O(3)-C(9) | 1.454(7) | N(1)-H'(N1) | 0.87(7) |
| N(1)-H''(N1) | 0.87(9) | C(2)-H(C2) | 0.97(8) |
| C(3)-H(C3) | 1.01(8) | C(5)-H(C5) | 1.01(10) |
| C(6)-H(C6) | 0.86(6) | N(2)-H(N2) | 0.72(9) |

**TABLE 3(b): Bond Angles(°) in Sulfametrole. The e.s.d's are Given in Parentheses**

| | | | |
|---|---|---|---|
| C(2)-C(1)-N(1) | 119.9(6) | C(6)-C(1)-N(1) | 120.4(5) |
| C(6)-C(1)-C(2) | 119.7(5) | C(3)-C(2)-C(1) | 119.5(6) |
| C(4)-C(3)-C(2) | 119.8(5) | C(5)-C(4)-C(3) | 121.1(5) |
| C(6)-C(5)-C(4) | 118.8(6) | C(5)-C(6)-C(1) | 121.0(6) |
| O(1)-S(1)-C(4) | 110.1(2) | O(2)-S(1)-C(4) | 108.3(3) |
| O(2)-S(1)-O(1) | 119.3(2) | N(2)-S(1)-C(4) | 105.5(2) |
| N(2)-S(1)-O(1) | 102.8(2) | N(2)-S(1)-O(2) | 109.9(3) |
| C(7)-N(2)-S(1) | 126.2(4) | N(3)-C(7)-N(2) | 125.7(5) |
| C(8)-C(7)-N(2) | 120.6(5) | C(8)-C(7)-N(3) | 113.7(5) |
| C(7)-N(3)-S(2) | 106.3(4) | N(4)-C(2)-N(3) | 98.6(3) |
| C(8)-N(4)-S(2) | 106.3(4) | N(4)-S(8)-O(3) | 125.9(5) |
| C(7)-C(8)-O(3) | 118.9(5) | C(7)-C(8)-N(4) | 115.2(5) |
| C(9)-O(3)-C(8) | 115.7(5) | S(1)-C(4)-C(3) | 119.0(4) |
| S(1)-C(4)-C(5) | 119.8(5) | H'(N1)-N(1)-C(1) | 115(4) |
| H''(N1)-N(1)-C(1) | 118(7) | H''(N1)-N(1)-H'(N1) | 99(8) |
| H(C2)-C(2)-C(1) | 122(4) | H(C2)-C(2)-C(3) | 118(4) |
| H(C3)-C(3)-C(2) | 118(5) | H(C3)-C(3)-C(4) | 123(5) |
| H(C5)-C(5)-C(4) | 120(5) | H(C5)-C(5)-C(6) | 121(5) |
| H(C6)-C(6)-C(5) | 113(4) | H(C6)-C(6)-C(1) | 126(4) |
| H(N2)-N(2)-S(1) | 120(6) | H(N2)-N(2)-C(7) | 114(6) |

## Structure Determination and Refinement

The direct methods program MULTAN[6] was used to calculate phases for the 259 *E* values greater than 1.25. The phase set with the largest combined figure of merit was selected, and the *E* map calculated with these phases revealed the positions of all the non-hydrogen atoms. After several cycles of isotropic and anisotropic refinement of these non-hydrogen atoms, the R value was 0.106. A difference map obtained at this stage revealed the positions of 7 H atoms. The positions of the remaining 3 H atoms in the methyl group were generated assuming regular tetrahedral C atom with C—H=1.08 Å. Two final least-squares cycles in which the non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically reduced *R* to 0.070. All refinements were carried out by the full matrix least-squares method using SHELX 76.[7]

The fractional atomic coordinates and thermal parameters are listed in Tables 1(a), 1(b) and 2, together with the estimated standard deviations. The bond lengths and angles with the estimated standard deviations are given in Tables 3(a) and 3(b). The observed and calculated structure factors are listed in Table 4.

## Description and Discussion of the Structure

The bond lengths and angles are given in Figure 1. The equations of the least squares planes of the benzene and thiadiazole rings, and the deviations of the various atoms from these planes, are given in Table 5.

The mean value found for the C-C bond lengths in the benzene ring is 1.384 Å which is slightly less than the mean C-C bond length in crystalline benzene[8] of 1.392 Å. The atoms of the benzene ring are coplanar within 0.02 Å. The N(1) atom also lies approximately on the same plane, but the S(1) atom is markedly displaced from this plane; the displacements are 0.046 and 0.183 Å, respectively.

The C(1)-N(1) bond length of 1.393 Å is in the usual range found in *p*-amino-substituted benzene (*e.g.* 1.385 Å in *β*-sulphanilamide[2], 1.401 Å in sulphathiazole II)[1].

The atoms around the S(1) atom are arranged in a distorted tetrahedral configuration. The O(1)-S(1)-O(2) angle increases to 119.3° while the O(1)-S(1)-N(2) angle narrows to 102.8°. The average value of the angles around the S(1) atom, 109.3°, is close to the ideal value. The non-bonded contact lengths {O(1)···O(2) 2.496, O(1)···N(2) 2.402, O(2)···N(2) 2.519 Å} are similar to those found in tolazamide[3].

The two S-O bonds (1.427 and 1.433 Å) have comparable and high $\pi$-bond character, ~60% according to Cruickshank[9]. The S(1)-C(4) bond length of 1.742 Å agrees with the $S–C_{ph}$ bond lengths observed in other related compounds[1-5]. In addition, the S(1)-N(2) bond length 1.641 Å, agrees well with the 1.642 Å in carbutamide[4], and the 1.641 Å in tolasemide(II)[5]. These lengths are considerably shorter than the sum(1.74 Å) of the Pauling covalent radii[11] for sulfur and nitrogen atoms, and indicate a significant degree of double bond character.

The thiadiazole ring is planar(see Table 5). Also N(2), O(3) and C(9) atoms are in the same plane; the displacements are 0.002, 0.035 and 0.006 Å respectively. The S(2)-N bond lengths (1.665 and 1.646 Å) in the thiadiazole ring are shorter than a S-N single bond length. The C-N bond lengths

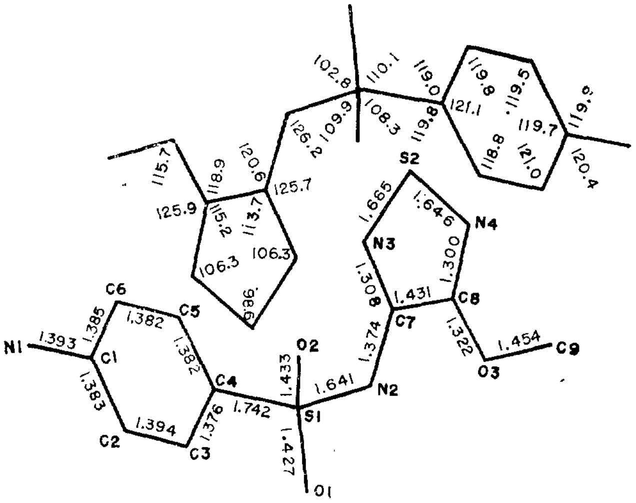

Figure 1. Bond lengths (Å) and angles ( °) in sulfametrole.

TABLE 4: Equations of the Least-Squares Planes and Deviations of the Atoms from the Planes in Sulfametrole

| | | | |
|---|---|---|---|
| (a) LS plane through the atoms of benzene ring | | | |
| $0.3545x+0.4944y+0.6869z=4.2267$ | | | |
| C(1)* | 0.016 Å | S(1) | 0.183 |
| C(2)* | −0.009 | N(1) | 0.046 |
| C(3)* | −0.007 | | |
| C(4)* | 0.017 | | |
| C(5)* | −0.010 | | |
| C(6)* | −0.006 | | |
| (b) LS plane through the atoms of thiadiazole ring | | | |
| $-0.4193x-0.6258y+0.7384z=-5.0571$ | | | |
| S(2)* | 0.004 Å | O(3) | 0.035 |
| N(3)* | −0.004 | C(9) | 0.006 |
| N(4)* | −0.003 | N(2) | 0.002 |
| C(7)* | 0.003 | | |
| C(8)* | 0.001 | | |

*Atoms included in the calculations of the least squares planes.

(mean value 1.304 Å) in the thiadiazole ring are slightly longer than a C–N double bond length[11] of 1.287 Å. Moreover, the N(2)–C(7) bond length of 1.374 Å is significantly shorter than the N–$C_{ph}$ bond length of 1.451 Å in 2′-hydroxymethenesulfonanilide[10] which is essentially a pure N–C($sp^2$) single bond. The same trend is also evident in the C(8)–O(3) and C(7)–C(8) bonds. From the above-mentioned consideration it appears that the thiadiazole ring shows some $\pi$-electron delocalization.

The C–H bond lengths in the benzene ring vary from 0.86 to 1.01 Å with the mean value 0.96 Å. The mean N–H bond length is 0.82 Å.

The dihedral angle between the benzene and thiadiazole planes is 93.9°.

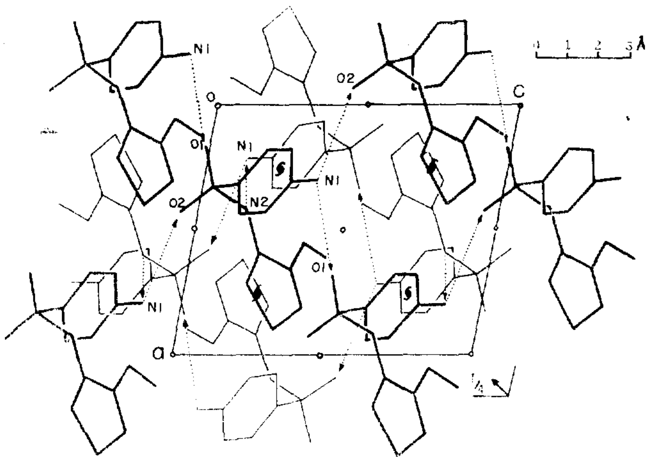

Figure 2. The molecular packing diagram, excluding hydrogen atoms, viewed down the *b*-axis of sulfametrole.

TABLE 5: Details of the Hydrogen Bonds and Other Intermolecular Atomic Contacts(Å) in Sulfametrole

| (a) Hydrogen bonds | | | | | |
|---|---|---|---|---|---|
| D–H···A | Position of A | D–H | H···A | D···A | ∠D–H |
| N(1)–H′(N1)···O(2) | $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ | 0.87 | 2.42 | 0.071 | 132° |
| N(1)–H″(N1)···O(1) | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ | 0.87 | 2.25 | 3.037 | 151° |
| N(2)–H(N2)···N(1) | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ | 0.72 | 2.30 | 2.947 | 151° |
| (b) Intermolecular atomic contacts less than the sum of the van der Waals radii | | | | | |
| S(2)···N(4) | $2-x, 1-y, 1-z$ | | | 3.268 | |
| C(9)···C(2) | $1-x, 1-y, 1-z$ | | | 3.439 | |
| C(9)···C(2) | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ | | | 3.526 | |
| C(9)···C(3) | $1-x, 1-y, 1-z$ | | | 3.353 | |

A projection of the structure down the *b*-axis is shown in Figure 2. The molecules are arranged in pleated sheets which are perpendicular to the *b*-axis; within these sheets, successive molecules are joined by N–H···O hydrogen bonds approximately parallel to the *a*-axis and are related to one another by a ne glide mirror. These sheets are then linked into a three dimensional network by N···H–N hydrogen bonds approximately parallel to the *b*-axis. All the potential hydrogen-bond donor atoms in the molecule, N(1) and N(2), are included in the hydrogen bonding. The nitrogen atom N(1) acts as a donor to the sulfonyl O(1) and O(2), and the N(1)···O(1) and N(1)···O(2) lengths are 3.037 and 3.071 Å respectively. It also acts as an aceptor to N(2), and the N(1)···N(2) length is 2.947 Å. Details of the hydrogen bonds and other intermolecular contact lengths are given in Table 6.

As shown in Table 6, there are three intermolecular atomic contacts ($C_{methyl}\cdots C_{ph}$) significantly less than the sum (3.7 Å) of the van der Waals radii. These may be related to the high thermal vibration amplitude of the terminal atom C(9). There is also a intermolecular atomic contact, 3.268 Å, between S(2) and N(2) which is approximately equal to the sum(3.3 Å) of the van der Waals radii.

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# The New Substituent Constants in the Excited States

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The new substituent constants ($\sigma^*$) are calculated from the acidity constants ($pK^*$) of phenol derivatives in the excited state ($^1L_b$). These substituent constants are applied to the Hammett equations and found good correlation with $pK^*$ of 2,6-di-*tert*-butyl phenol, benzamide, nitroaniline, thiophenol, azobenzene, and benzoic acid derivatives. The correlation was much bettre than that of ground state substituent constants such as $\sigma$, $\sigma^+$, and $\sigma^-$. From these results, the new substituent constants ($\sigma^*$) are proposed to be used for the linear free energy relationship in the $^1(\pi,\pi^*)$ excited states of phenyl compounds.

## Introduction

The acidity constants in the excited states can be determined by several methods[1]. The two of the most widely used methods are Förster cycle[2] and fluorometric titration[3,4]. The former makes use of O–O electronic transition energy of the aci dand its conjugate base obtained from the UV-VIS spectra as shown in equation 1 and the latter determines the fluorescence quantum yields varying the pH. The 0–0 electronic transition energy in $cm^{-1}$ can be obtained from equation 2. Therefore, the accurate $\lambda^{abs}_{max}$ from UV-VIS spectra and/or $\lambda^{fl}_{max}$ from the fluorescence spectra should be determined.

$$pK-pK^*=\frac{Nh}{2.303RT}(\tilde{\nu}_{AH}-\tilde{\nu}_{A^-}) \qquad (1)$$

$$=2.10\times10^{-3}(\tilde{\nu}_{AH}-\tilde{\nu}_{A^-}) \text{ at } 25°C$$

$$\tilde{\nu}=\frac{1}{\lambda^{abs}_{max}} \text{ or } \frac{1}{\lambda^{fl}_{max}} \text{ or } \frac{1}{2}\left(\frac{1}{\lambda^{abs}_{max}}+\frac{1}{\lambda^{fl}_{max}}\right) \qquad (2)$$

$$pK=-\log_{10}K \qquad (3)$$

$$pK^*=-\log_{10}K^* \qquad (4)$$

Where $N$ is the Avogadro number, $R$ is the gas constant, $T$ is the absolute temperature, $h$ is the Planck constant, $\tilde{\nu}_{AH}$ and $\tilde{\nu}_{A^-}$ are the absorption maximum wavenumber ($cm^{-1}$) of the acid and its conjugate base respectively, $K$ and $K^*$ are the acidity constants in the ground and excited states respectively.

When the $pK^*$ is determined by Förster cycle, the following precautions should be taken: i) It should be checked whether the protonation entropies are equal in the ground and excited states or not. ii) The correct 0–0 electronic transition energy should be used. The correct 0–0 electronic transition energy can ideally be determined by averaging $\lambda^{abs}_{max}$ and $\lambda^{fl}_{max}$ if absorption and fluorescence spectra are mirror images of each other. But the fluorescence spectra are not always available and in many cases, they are not mirror images of absorption spectra. In these cases, $\lambda^{abs}_{max}$ alone is used in the calculation of the 0-0 transition energy. The error can be minimized even in these cases if $\lambda^{abs}_{max}$ of the acid and its conjugate base deviates about the same degree and to the same direction from the true 0-0 electronic transition energy. iii) Förster cycle must be applied to the same kind of protolytic equilibrium and electronic band (state).

When the $pK^*$ is determined by the use of fluorometric titration, the attention must be paid to the proton exchange reaction rate constants in the excited states which are smaller than or similar to the fluorescence rate constants ($\overrightarrow{k} \ll kf$, $\overleftarrow{k}[SH_2^+] \ll kf$, $\overrightarrow{k} \approx kf$, $\overleftarrow{k}[SH_2^+] \approx kf$) in equation 5. In these cases, incorrect $pK^*$ values are obtained[3,4].

$$\begin{tikzcd}
{[AH]^* + SH} \arrow[r, shift left, "\overrightarrow{k}"] \arrow[d, "kf"] & {[A^-]^* + SH_2^+} \arrow[l, shift left, "\overleftarrow{k}"] \arrow[d, "kf'"] \\
{AH + h\nu_{AH}} & {A^- + h\nu_{A^-}}
\end{tikzcd}$$

where SH is the protic solvent.

These difficulties can be overcome by the use of buffer solution, but the usefulness of this method is restricted because fluorescence intensity of some molecules are too weak to determine the fluorescence quantum yields. There are other methods to determine $pK^*$, for example, pho-

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