

equilibrium for $\text{Co(dpa)}_2\text{Cl}_2$ system. Half conversion of $\text{td-Co(dpa)}_2\text{Cl}_2$ to $\text{oh-Co(dpa)}_2\text{Cl}_2$ occurs with 0.157 M of 2,2'-dipyridylamine at 25°C, while that of $\text{td-Copy}_2\text{Cl}_2$ 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 ΔH° and ΔS° . The greater ΔH° for $\text{Co(dpa)}_2\text{Cl}_2$ system may be attributed to the greater steric strain resulting from the presence of two chelate rings in $\text{Co(dpa)}_2\text{Cl}_2$. On the other hand, the greater ΔS° for $\text{Co(dpa)}_2\text{Cl}_2$ system reflects the smaller number of the reacting ligand. Thus, the more favorable formation of $\text{oh-Co(dpa)}_2\text{Cl}_2$ compared with $\text{oh-Copy}_2\text{Cl}_2$ is caused by the greater ΔS° value.

Acknowledgement. One of the authors (M. H. Paik Suh) expresses appreciation for financial support to Korea Science and Engineering Foundation.

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The Crystal and Molecular Structures of Sulfametrole

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Sulfametrole, $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_3\text{S}_2$, crystallizes in the monoclinic system, space group $P2_1/n$, with $a=8.145(2)$, $b=16.505(4)$, $c=9.637(1) \text{ \AA}$, $\beta=103.72(1)^\circ$, $D_w=1.52 \text{ gcm}^{-3}$, $Z=4$. Intensities for 3594(2143 observed) unique reflections were measured on a four-circle diffractometer with Mo K_α radiation ($\lambda=0.71069 \text{ \AA}$). 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 thiaziazole ring indicate some π -electron delocalization inside the ring. The least squares planes defined by the benzene and thiaziazole 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 π -electron delocalization inside the thiaziazole ring and in the conjugation between the thiaziazole ring and its substituents.

In this paper, the geometrical parameters will be discussed in comparison with those of other related compounds¹⁻⁵ and the hydrogen bonding scheme also discussed.

Experimental

3-methoxy-4-sulfanilamido-1,2,5-thiaziazole 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 $0.2 \times 0.2 \times 0.3$ mm was selected for the data collection. The intensities of 3594 unique reflections with $0 < 2\theta \leq 60^\circ$ were measured using a Rigaku four-circle diffractometer with graphite-monochromatized Mo K_α radiation in the ω - 2θ scan mode, with a scan speed of 4°min^{-1} in 2θ and a scan width of $(1.2 + 0.5 \tan \theta)^\circ$ in ω . 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 θ values for

30 well centered reflections, lying in the 2θ 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 $F_0 \geq 3\sigma(F_0)$ and were considered to be observed.

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

$\text{C}_9\text{H}_{10}\text{N}_4\text{O}_3\text{S}_2$	mp ; 153–154 °C
Monoclinic	Space group ; $P2_1/n$
M.W. ; 286.33	Z : 4
a ; 8.145(2) Å	$F(000)$; 592
b ; 16.505(4)	V ; 1258.8 Å ³
c ; 9.637(1)	D_c ; 1.511 g cm ⁻³
β ; 103.72(1)°	D_m ; 1.52 g cm ⁻³
μ ; 3.72 mm ⁻¹	$\lambda(M_0 K_\alpha)$; 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} ($\times 10^4$) 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 temperature factor: $\exp\{-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}k lb^*c^*)\}$

	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 (\AA^2) 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 (\AA) 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 ($^\circ$) 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)	170(6)	H(N2)-N(2)-C(7)	114(6)

Structure Determination and Refinement

The direct methods program MULTAN⁶ 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 \AA . 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 \AA which is slightly less than the mean C-C bond length in crystalline benzene⁸ of 1.392 \AA . The atoms of the benzene ring are coplanar within 0.02 \AA . 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 \AA , respectively.

The C(1)-N(1) bond length of 1.393 \AA is in the usual range found in *p*-amino-substituted benzene (e.g. 1.385 \AA in β -sulphanilamide², 1.401 \AA 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 $^\circ$ while the O(1)-S(1)-N(2) angle narrows to 102.8 $^\circ$. The average value of the angles around the S(1) atom, 109.3 $^\circ$, 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 \AA } are similar to those found in tolazamide³.

The two S-O bonds (1.427 and 1.433 \AA) have comparable and high π -bond character, ~60% according to Cruickshank⁹. The S(1)-C(4) bond length of 1.742 \AA agrees with the S-C_{ph} bond lengths observed in other related compounds¹⁻⁵. In addition, the S(1)-N(2) bond length 1.641 \AA , agrees well with the 1.642 \AA in carbutamide⁴, and the 1.641 \AA in tolazamide(II)⁵. These lengths are considerably shorter than the sum(1.74 \AA) of the Pauling covalent radii¹¹ 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 \AA respectively. The S(2)-N bond lengths (1.665 and 1.646 \AA) in the thiadiazole ring are shorter than a S-N single bond length. The C-N bond lengths

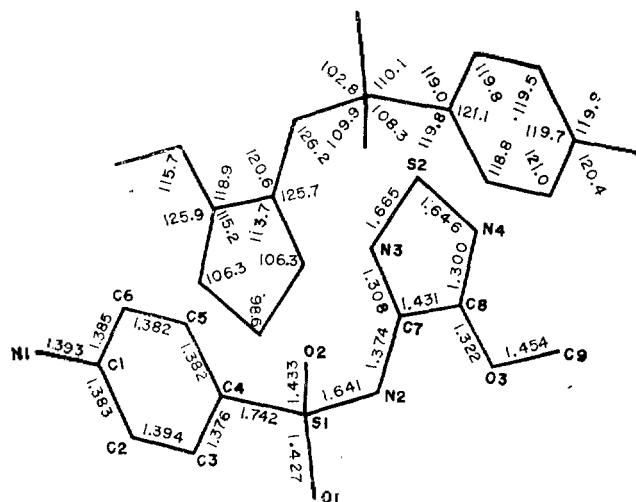


Figure 1. Bond lengths (Å) and angles ($^{\circ}$) in sulfametrole.

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 length¹¹ 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'-hydroxymethanesulfonanilide¹⁰ which is essentially a pure N-C(sp²) 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 π -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°.

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

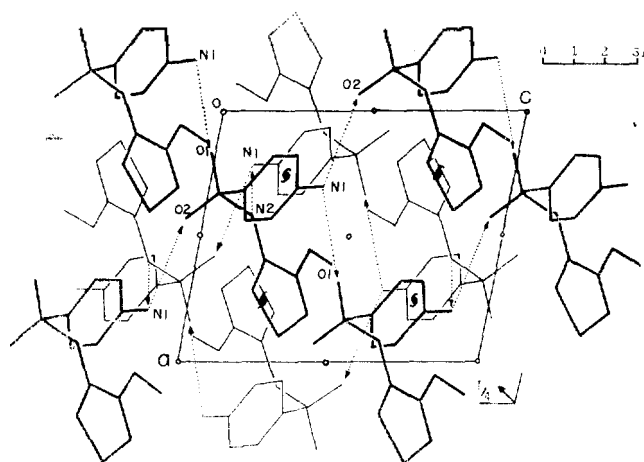


Figure 2. The molecular packing diagram, excluding hydrogen atoms, viewed down the *b*-axis of sulfametrole.

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	\angle 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		

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 acceptor 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 ($C_{methyl}...C_{ph}$) 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.

Acknowledgement. This research was supported by Grant NO. ED80-22 of the Ministry of Education.

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The New Substituent Constants in the Excited States

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The new substituent constants (σ^*) are calculated from the acidity constants (pK^*) of phenol derivatives in the excited state (1L_e). 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 better than that of ground state substituent constants such as σ , σ^+ , and σ^- . From these results, the new substituent constants (σ^*) 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 methods¹. The two of the most widely used methods are Förster cycle² and fluorometric titration^{3,4}. The former makes use of 0-0 electronic transition energy of the acid and 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 $\lambda_{\text{max}}^{\text{ab}}$ from UV-VIS spectra and/or $\lambda_{\text{max}}^{\text{fl}}$ from the fluorescence spectra should be determined.

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

$$= 2.10 \times 10^{-3} (\bar{\nu}_{\text{AH}} - \bar{\nu}_{\text{A}^-}) \text{ at } 25^\circ\text{C}$$

$$\bar{\nu} = \frac{1}{\lambda_{\text{max}}^{\text{ab}}} \text{ or } \frac{1}{\lambda_{\text{max}}^{\text{fl}}} \text{ or } \frac{1}{2} \left(\frac{1}{\lambda_{\text{max}}^{\text{ab}}} + \frac{1}{\lambda_{\text{max}}^{\text{fl}}} \right) \quad (2)$$

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

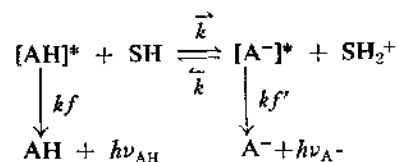
$$pK^* = -\log_{10} K^* \quad (4)$$

Where N is the Avogadro number, R is the gas constant, T is the absolute temperature, h is the Planck constant, $\bar{\nu}_{\text{AH}}$ and $\bar{\nu}_{\text{A}^-}$ 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 $\lambda_{\text{max}}^{\text{ab}}$ and $\lambda_{\text{max}}^{\text{fl}}$ 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, $\lambda_{\text{max}}^{\text{ab}}$ alone is used in the calculation of the 0-0 transition energy. The error can be minimized even in these cases if $\lambda_{\text{max}}^{\text{ab}}$ 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 ($\bar{k} \ll k_f$, $\bar{k}[\text{SH}_2^+] \ll k_f$, $\bar{k} \approx k_f$, $k[\text{SH}_2^+] \approx k_f$) in equation 5. In these cases, incorrect pK^* values are obtained^{3,4}.



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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