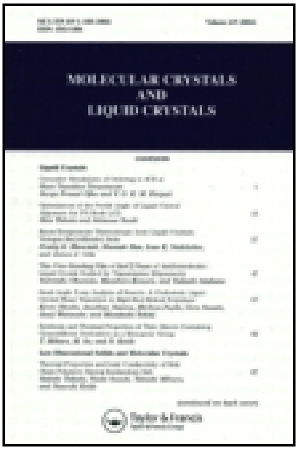

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Substituent Effects on Thermochromism of N-Salicylide-NE-2-Aminopyridines in the Solid State

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SUBSTITUENT EFFECTS ON THERMOCHROMISM OF N-SALICYLIDENE-2-AMINOPYRIDINES IN THE SOLID STATE

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Abstract The substituent effect on thermochromism of the isostructural N-salicylidene-2-aminopyridines series has been investigated in the solid state. It was found that the substituents affect the thermochromic phenomenon mainly in low temperatures and in a stronger way when the substitution takes place in the pyridine ring than in the salicylaldehyde ring.

I. INTRODUCTION

Crystalline salicylidene-2-aminopyridine (Fig. 1) and its derivatives exhibit thermochromic phenomena, i.e. they show a reversible colour change, mostly from yellow to red, as a result of a variation in temperature.[1] Photochromism, reversible colour change on ultraviolet irradiation, is not observed in this class of compounds.

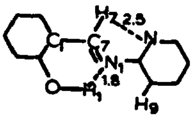

FIGURE 1. Intramolecular distances (Å) and atom numbering system for salicylidene-2-aminopyridine.

The appearance of the thermochromic phenomenon and its generality depends upon the crystal structure and the molecular orientation of the compounds.[1] Thus, an investigation by X-ray diffraction shows that the molecules are essentially planar[2] ; the flat molecules are arranged in stacks along the shortest crystal axis with mean interplanar distance of 3.5 Å and the hetero-nitrogen atom always at the cis position with respect to the H(7) hydrogen atom. The distance between these atoms, 2.5 Å , corresponds to normal van der Waals contact. The lone pair of the imino nitrogen atom in this planar molecular structure does not overlap with the electrons of the pyridine ring, and consequently the basicity of the bridge N atom and hence the strength of the hydrogen bond between the OH group and the imino N atom is higher.[3] In addition, all the examined structures show a strong intramolecular hydrogen bond with a mean H(1)--N(1) distance of 1.95 Å and the appropriate geometry, so that the hydrogen atom points toward the lone pair of the N(1) atom. Therefore, the proton transfer shown in Fig. 2 is favoured in the planar as against a non-planar conformation and thermochromism can be interpreted with this shift in the tautomeric equilibrium as in the case of thermochromic N-salicylideneanilines for which a similar interpretation was given.[4]

FIGURE 2. Thermochromic mechanism in N-salicylidene-2-aminopyridine.

Since it was argued that the phenomenon of photochromism in the N-salicylideneaniline series is a topochemically determined phenomenon, i.e., there seems to be no correlation of activity with substituents, but the packing arrangement in the crystal is of importance,[4] we decided to examine the effects of substituents on thermochromism in solid N-salicylidene-2-aminopyridines which are planar molecules and exhibit exclusively thermochromic phenomena[1]. Electron-donating and withdrawing groups were placed in various positions of the two rings to achieve an increase of the electron density at the nitrogen atom of the bridge or decrease of the electron density at the oxygen atom of the OH group of the aldehyde ring, since these processes facilitate the approach of protons according to the mechanism of Fig. 2 and consequently the thermochromic phenomenon. The extent of tautomerism, as measured by the absorbance at the maximum of the termochromic band around 480nm and taking the moler absorptivity for all the quinoid tautomers equal to 1.5 X 10^4 lit/moleXcm[5] , is then used to calculate equilibrium constants (K) and attempt a more generalized correlation analysis.

II. EXPERIMENTAL

The compounds were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate 2-aminopyridine in ethanol, followed by repeated recrystallization from the same solvent. The prepared compounds employed in the present work are shown in Table 1. In this table the indices of the vertical columns correspond to ij where i denotes substitution in the pyridine ring (1 = ortho-CH_3, 2 = H , 3 □ para-Cl and 4 = ortho-Cl + para-Cl) and j substitution in the salicylaldehyde ring (1 = H , 2 = para-Br, 3 □ para-OCH_3 and 4 = ortho-CH_3). The ortho-position for the pyridine ring is considered to be at the H_9 of Fig. 1 and for the salicylaldehyde ring next to the OH-group.

Crystalline films were prepared from the melt of a known quantity of the compound {10^{-6}(M.W.)g/cm^2} between two quartz plates under pressure, their quality was examined under a polarized microscope and their spectra were recorded at various temperatures.

Table I contains also the optical densities measured at the maximum of the thermochromic band for each compound at various temperatures.

III. CORRELATION ANALYSIS

For equilibria, like those in Fig. 2, equation 1 applies, from which we calculate the standard free enthalpy ΔG^o_{ij}

$$\log K_{ij} = - \frac{\Delta G^o_{ij}}{2.303\ RT} \tag{1}$$

as a function of temperature, since as it was mentioned earlier K's are evaluated from the optical densities at various temperatures. Therefore, the values ΔG^o_{ij} may be considered to have the form of the equation 2 for which the

$$\Delta G^o_{ij} = A_{ij} + B_{ij}\ T + C_{ij}\ T^2 \tag{2}$$

correlation coefficient is greater than 0.99.

From these values we can deduct the standard enthalpy difference, the standard entropy difference and the standard heat capacity difference:

$$\Delta H^o_{ij} = \left\{\frac{\partial(\Delta G^o_{ij}/T)}{\partial(1/T)}\right\}_p = A_{ij} - C_{ij}\ T^2 \tag{3}$$

$$\Delta S^o_{ij} = -\left(\frac{\partial \Delta G^o_{ij}}{\partial T}\right)_p = - B_{ij} - 2C_{ij}T \tag{4}$$

$$\Delta C^o_{pij} = -T\left(\frac{\partial^2 \Delta G^o_{ij}}{\partial T^2}\right)_p = - 2C_{ij}T \tag{5}$$

Based on previous assumptions[6,7,8] we consider the substituent effect to be a combination of the "field" (including the "induction" effect as well), the "resonance"

TABLE I Optical Densities of N-Salicylidene-2-aminopyridines at Various Temperatures

T	11	12	13	14	21	22	23	24	31	32	33	34	41	42	43	44
110	0.019	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
120	0.030	0.017	-	0.018	-	-	-	-	-	-	-	-	-	-	-	-
130	0.045	0.028	-	0.028	-	-	-	0.018	-	-	-	-	-	-	-	-
140	0.062	0.042	-	0.043	0.016	0.014	-	0.028	-	-	-	-	-	-	-	-
150	0.082	0.060	0.014	0.060	0.024	0.022	-	0.040	-	-	-	-	-	-	-	-
160	0.106	0.082	0.021	0.082	0.036	0.033	0.016	0.056	0.014	0.014	0.017	0.014	-	-	-	-
170	0.133	0.108	0.029	0.107	0.050	0.047	0.023	0.076	0.024	0.021	0.027	0.022	-	0.014	-	0.016
180	0.162	0.139	0.039	0.136	0.068	0.0.65	0.032	0.098	0.033	0.032	0.040	0.033	-	0.022	-	0.025
190	0.195	0.192	0.052	0.167	0.089	0.086	0.044	0.123	0.048	0.045	0.056	0.046	0.013	0.032	0.016	0.036
200	0.229	0.212	0.066	0.202	0.111	0.101	0.057	0.152	0.067	0.061	0.077	0.063	0.021	0.045	0.025	0.051
210	0.268	0.253	0.082	0.239	0.141	0.141	0.073	0.183	0.090	0.081	0.102	0.083	0.031	0.061	0.037	0.068
220	0.308	0.299	0.100	0.278	0.172	0.175	0.091	0.217	0.117	0.105	0.129	0.105	0.044	0.081	0.051	0.089
130	0.350	0.348	0.120	0.319	0.206	0.210	0.112	0.254	0.147	0.132	0.161	0.131	0.061	0.104	0.069	0.112
240	0.393	0.399	0.141	0.362	0.245	0.249	0.126	0.292	0.183	0.162	0.197	0.160	0.080	0.130	0.090	0.139
250	0.438	0.453	0.164	0.406	0.286	0.292	0.158	0.333	0.221	0.217	0.232	0.191	0.103	0.159	0.113	0.166
260	0.487	0.504	0.188	0.451	0.328	0.338	0.185	0.374	0.261	0.232	0.272	0.224	0.128	0.191	0.139	0.196
270	0.536	0.560	0.213	0.496	0.376	0.387	0.212	0.418	0.306	0.272	0.313	0.258	0.156	0.226	0.167	0.228
280	0.585	0.622	0.240	0.541	0.427	0.437	0.242	0.462	0.351	0.315	0.355	0.294	0.186	0.262	0.196	0.260
290	0.637	0.678	0.267	0.592	0.475	0.489	0.272	0.508	0.399	0.359	0.398	0.331	0.216	0.301	0.226	0.293
300	0.691	0.739	0.294	0.634	0.531	0.544	0.305	0.555	0.448	0.404	0.441	0.369	0.248	0.341	0.258	0.323
310	0.746	-	0.325	0.680	0.587	0.601	0.338	0.601	0.499	0.454	0.484	0.405	0.281	0.382	0.296	0.359
320	0.797	-	0.356	0.725	0.647	0.659	0.372	0.649	0.549	0.500	0.526	0.442	0.313	0.423	0.316	0.390
330	0.852	-	0.384	0.770	0.711	0.718	0.406	0.696	0.599	0.549	0.565	0.479	0.345	0.465	0.344	0.421
340	0.910	-	0.414	0.815	-	0.775	0.441	0.744	0.647	0.599	0.605	0.515	0.374	0.507	0.369	0.450
350	0.972	-	-	0.857	-	0.836	-	0.792	0.698	0.647	0.636	0.554	0.403	0.549	0.393	0.477
360	-	-	-	0.901	-	0.901	-	0.839	0.746	0.699	0.678	0.583	0.429	0.589	0.419	0.502
370	-	-	-	0.943	-	0.962	-	0.886	0.790	0.746	0.710	0.615	0.453	0.628	0.433	0.526

and the "steric" effects. Thus, the ΔG^{o}_{ij} value for the reaction can be written as follows:

$$\Delta G^{o}_{ij} = \Delta G^{o}_{pij} + \Delta G_{eij} + \Delta G_{Rij} + \Delta G_{Sij} \qquad (6)$$

where $\Delta G_{Sij} = \Delta G_{Si} + \Delta G_{Sj}$ and the term ΔG^{o}_{pij} is the standard free enthalpy difference not due to the substituents or the interaction with the neighbouring molecules.

The contribution of the resonance in the standard free enthalpy is set as a product of a constant of the substituent (a_r) multiplied by a transmission coefficient t_r. We thus have:

$$\Delta G_{Rij} = a_{ri} \cdot t_{r1} + a_{rj} \cdot t_{r2} \qquad (7)$$

It should be pointed here that we have two terms since we expect contribution from both rings of the molecule.

The substituent constant a_{ri} or a_{rj} depends only on the substituent while the transmission coefficient depends on the parent skeleton of the molecule and on the ability of the substituent to conjugate with the basic site of the reaction.

Correspondingly, the contributions of the "field" is set as a product of the substituent constant (a_e) and the transmission coefficient of the electrostatic field, t_e.

Thus, taking care again for contributions from both rings, we have:

$$\Delta G_{eij} = a_{ei} \cdot t_{e1} + a_{ej} \cdot t_{e2}. \qquad (8)$$

Combining equations (6), (7) and (8) we get :

$$\Delta G^{o}_{ij} = \Delta G^{o}_{pij} + a_{ri} \cdot t_{r1} + a_{ei} \cdot t_{e1} + a_{rj} \cdot t_{r2} + a_{ej} \cdot t_{e2} + \Delta G_{Sij} \qquad (9)$$

$$\Delta C^{o}_{pij} = -T\{a_{ri}\left(\frac{\partial^2 t_{r1}}{\partial T^2}\right)_p + a_{ei}\left(\frac{\partial^2 t_{e1}}{\partial T^2}\right)_p + a_{rj}\left(\frac{\partial^2 t_{r2}}{\partial T^2}\right)_p +$$

$$+ a_{ej}\left(\frac{\partial^2 t_{e2}}{\partial T^2}\right)_p + \frac{\partial^2 G_{sij}}{\partial T^2}\} \qquad (10)$$

and combining equations (5) and (10) we get:

$$C_{ij} = \frac{1}{2}\{\left(\frac{\partial^2 t_{r1}}{\partial T^2}\right)_p a_{ri} + a_{e1}\left(\frac{\partial^2 t_{ei}}{\partial T^2}\right)_p + a_{rj}\left(\frac{\partial^2 t_{r2}}{\partial T^2}\right)_p +$$

$$+ a_{ej}\left(\frac{\partial^2 t_{e2}}{\partial T^2}\right)_p + \frac{\partial^2 G_{sij}}{\partial T^2}\} \qquad (11)$$

Since this value depends only on the substituents we can put: $\left(\frac{\partial^2 t_{r1}}{\partial T^2}\right)_p = 2C_{31}$, $\left(\frac{\partial^2 t_{e1}}{\partial T^2}\right)_p = 2C'_{31}$, $\left(\frac{\partial^2 t_{r2}}{\partial T^2}\right)_p = 2C_{32}$ and

$$\left(\frac{\partial^2 t_{e2}}{\partial T^2}\right)_p = 2C'_{32}$$

where C_{31}, C'_{31}, C_{32} and C'_{32} are constants independent of the particular substituent.[6]

The solutions now of the above differential equations are:

$t_{r1}=C_{11}+C_{21}T+C_{31}T^2$ (12) $t_{r2}=C_{12}+C_{22}T+C_{32}T^2$ (14)

$t_{e1}=C'_{11}+C'_{21}T+C'_{31}T^2$ (13) $t_{e2}=C'_{12}+C'_{22}T+C'_{32}T^2$ (15)

If we consider C analogous to C' then the solutions are written as follows:

$t_{r1}=C_{11}+C_{21}T+C_{31}T^2$ (16) $t_{r2}=C_{12}+C_{22}T+C_{32}T^2$ (18)

$T_{e1}=a(C_{11}+C_{21}T+C_{31}T^2)$ (17) $t_{e2}=a(C_{12}+C_{22}T+C_{32}T^2)$ (19)

A comparison of the equation (9) as a function of the equations (16), (17), (18) and (19) with that of Hammett[8]

$$\log K_{ij} = \rho_1\sigma_i + \rho_2\sigma_j + E_{si} + E_{sj} + C \qquad (20)$$

gives:

$$\rho_1 = \frac{C_{11}}{T} + C_{21} + C_{31}T$$

$$\rho_2 = \frac{C_{12}}{T} + C_{22} + C_{32}\,T$$

$$\left.\begin{aligned} \sigma_i &= -\frac{a_{ri}}{2.3R} - a\,\frac{a_{ei}}{2.3R} = r_iR_i + f_iF_i \\ \sigma_j &= -\frac{a_{rj}}{2.3R} - a\,\frac{a_{ej}}{2.3R} = r_jR_j + f_jF_j \end{aligned}\right\}\ \text{Swain and Lupton}^{6}$$

$$E_{si} = -\frac{\Delta G_{si}}{2.3RT}$$

$$E_{sj} = -\frac{\Delta G_{sj}}{2.3RT}$$

If we replace now the values of f_i, r_i, f_j, r_j, F_i, F_j, R_i and R_j from Swain and Lupton[6] and calculate E_{si} and E_{sj} for the ortho-substituted compounds in comparison with all others without ortho-substituent and make a statistical treatment based on the regression equation 21, we calculate

$$\log K_{ij} - E_{si} - E_{sj} = \rho_1\sigma_i + \rho_2\sigma_j + C \qquad (21)$$

ρ_1 and ρ_2 as a function of temperature as it is shown in Fig. 3.

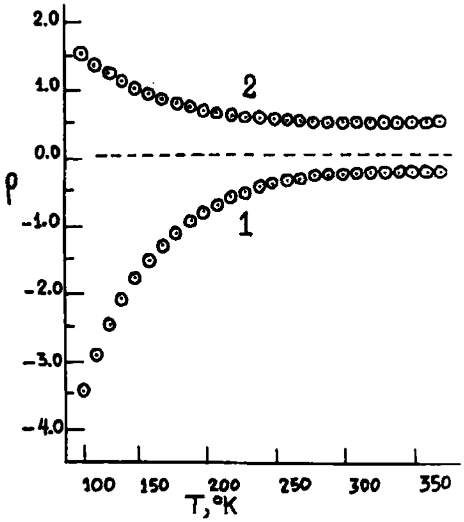

FIGURE 3. ρ vs T for N-salicylidene-2-aminopyridines.

Figure 3 shows that the thermochromic phenomenon is facilitated by substituents in the pyridine ring which decrease the electron density of the nitrogen atom of the bridge (curve 1) and by substituents in the salicylaldehyde ring which reduce the electron density of the oxygen atom of the OH group (curve 2) to a lesser degree, however. It should be noticed also that above ~ 250K the substituents in both rings have a very small effect. These results are in agreement with literature since it is known that a reaction which is facilitated by increasing the electron density at the reaction site has a negative value of ρ , and one facilitated by reducing the electron density at the reaction site has a positive value while ρ-scale covers roughly 0 ± 4.[8]

The above results show that a substituent effect in the thermochromic phenomenon of solid N-salicylidene-2-amimopyridines operates at low temperatures and that a more carefully designed and executed work will bear fruit in the correlation analysis in solid state organic reactions.

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