BRIEF COMMUNICATIONS

CORRELATION EQUATION FOR THE ACTIVATION FREE ENERGY OF THE INVERSION OF CONFIGURATION IN THE CLOSED FORM OF INDOLINOSPIROPYRANS

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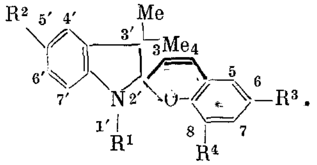
Dynamic NMR spectroscopy was used to determine the activation free energy ΔG# of the thermally induced inversion of configuration of the closed form of spiropyrans (SP), which involves cleavage of the S_{spiro}–O bond, rotation about the two orthogonal molecular fragments and closure of the spiro bond with the generation of a form enantiomeric to the starting molecule [1, 2]. In our previous work [2], the experimental dependence of the ΔG# values on the substituent donor–acceptor properties was explained using the concept of orbital interactions of the unshared electron pairs (UEP) of the nitrogen and oxygen heteroatoms with the σ* antibonding orbitals, σ^*_{CO} and σ^*_{CN}, respectively. A Hammett equation was obtained for molecules having substituents in the ortho and para positions relative to the oxygen atom which satisfactorily describes the quantitative data.

In the present work, we obtained an analogous equation for SP molecules having different substituents and $N^{1'}$ and $C^{5'}$ ((I)-(XXV), Table 1) and using our previous data [2], a general correlation equation for ΔG# for SP with donor–acceptor substituents in both the benzopyran and indoline molecular fragments. The structural formula for the SP studied is as follows:



EXPERIMENTAL

Samples of SP (I)-(XXV) were prepared and purified according to reported procedures [3, 4]. The PMR spectra were taken on a Bruker WP-80-SY spectrometer in deuterated DMSO. The method of determining ΔG# relative to the coalescence temperature for the signals of the geminal groups in the SP was described in our previous work [1, 2]. When heating to 185°C does not lead to coalescence of these signals as in the case of (XIV), (XVIII), and (XX)-(XXII), the rate constant for inversion of configuration of the closed form of the SP was determined using the formula $k = \pi(\omega_a - \omega_0)$, where ω_a and ω_0 are the line halfwidth in the NMR spectrum upon slot and zero exchange, respectively [5] and then ΔG# was calculated using the Eyring equation [6]. The substituent constants σ_p and σ^* were taken from the work of Becker [7] and Pal'm [8]. The experimental data are given in Table 1. The error in the determination of ΔG# was ±0.3 kcal/mole for the SP, with signal coalescence below 185°C and ±0.5 kcal/mole for the remaining SP.

RESULTS AND DISCUSSION

The following equation was obtained for the quantitative description of the substituent effect in the benzopyran fragment of the SP molecules on the ΔG# value in our previous work [2]:

$$\Delta G^{\#} = A + \rho_b (0{,}6\sigma_p + 0{,}4\sigma^*) \tag{1}$$

where $\rho_b = -3.6$ and σ_p and σ^* are the Hammett and Taft constants characterizing the effect of substituents in the para and ortho positions relative to the pyran oxygen atom, respectively.

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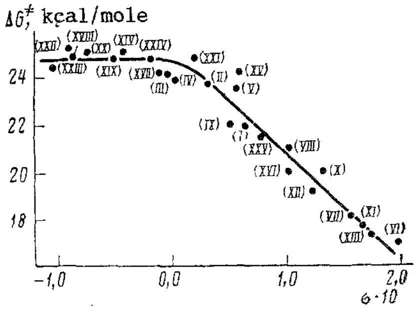

Fig. 1. General correlation equation for ΔG≠ for SP with substituents both in the indoline and benzopyran molecular fragments. The numbers corresponds to the listing of the SP in Table 1.

In order to obtain an analogous correlation equation for substituents in the indoline fragment, we synthesized and studied SP (I), (XIV), (XVI), (XVII), (XXIV), and (XXV) having the identical benzopyran fragment and different R^1 and R^2 substituents. The experimental data for these compounds conform best to the correlation equation

$$\Delta G^{\neq} = B + \rho_i (0{,}5\sigma_p + 0{,}5\sigma^*) \qquad (2)$$

where σ_p is the Hammett constant for the substituents at $C^{5'}$ (R^2) and σ^* is the Taft constant for the substituents at $N^{1'}$ (R^1), while the slope $\rho_i = 10.2$. A detailed qualitative explanation for the effect of the substituents in the indoline fragment in the SP molecule was given in our previous work [2]. According to this explanation, electron-withdrawing substituents lead to competitive conjugation of the nitrogen UEP with the π-conjugated system of the substituted indoline, thereby decreasing the $n_N-\sigma^*_{CO}$ orbital interaction, leading to strengthening of the C^2—O bond and an increase in ΔG≠. The effect of electron-donor substituents is the opposite.

Having obtained correlation equations separately for the indoline and benzopyran SP fragments, we attempted to combine these equations to obtain a general expression describing the overall effect of donor—acceptor substituents at $N^{1'}$, $C^{5'}$, C^6, and C^8 on the ΔG≠ value. It is natural to assume that

$$\Delta G^{\neq} = \Delta G^{\neq}_0 + \rho_b \Sigma\sigma_b + \rho_i \Sigma\sigma_i \qquad (3)$$

where $\Sigma\sigma_b = 0.6\sigma_n + 0.4\sigma^*$ (benzopyran fragment) and $\Sigma\sigma_i = 0.5\sigma_n + 0.5\sigma^*$ (indoline fragment), $\rho_b = -3.6$ and $\rho_i = 10.2$. Equation (3) may be given as

$$\Delta G^{\neq} = \Delta G_0^{\neq} + \rho\sigma \qquad (4)$$

where $\rho = \rho_i \rho_b$ and $\sigma = (\Sigma\sigma_b/\rho_i + \Sigma\sigma_i/\rho_b)$. The experimental data for the different SP treated by Eq. (4) are given in Table 1 and in Fig. 1. For $\sigma > 0$, Eq. (4) holds rather well and the ρ value found (−40) is in accord with the value of $\rho_i \rho_b = -37$. For $\sigma < 0$, a plateau is found with ΔG≠ ∿ 25 kcal/mole. In order to interpret this result, we should consider the observation that SP either unsubstituted or having electron-donor substituents in the indoline fragments are in the region with $\sigma > 0$, while only those SP with strong electron-withdrawing substituents as NO_2 and CF_3 in the indoline fragment are found in the region with $\sigma < 0$. In this case, the nature of the substituents in the benzopyran fragment holds no importance. Hence, when the nitrogen UEP is conjugated with the π-electron system of the indoline fragment and does not participate in an $n_N-\sigma^*_{CO}$ interaction, the effect of the substituents in the benzopyran fragment on the ΔG≠ and thus, on the strength of the C^2—O bond is negligible although we might have expected that the $n_O-\sigma^*_{CN}$ interaction whose contribution depends on the donor—acceptor properties of the substituents in the benzopyran fragment would play the major role in this case as a result of a lowering of the level of the σ^*_{CN} antibonding orbital (due to an increase in the effective electronegativity of the nitrogen atom) [2]. However, the existence of a plateau indicates that the role of this interaction

TABLE 1. Activation Free Energy ΔG≠ for the Inversion of Configuration of the Closed Form of Substituted Indolinospiropyrans

Compound	R^1	R^2	R^3	R^4	$\Delta G^{\neq}_{25}$, kcal/mole	σ·10 *
(I)	CH_3	H	NO_2	H	21,9	0,65
(II)	»		COH	H	23,7	0,32
(III)	»		OH	H	24,1	−0,02
(IV)	»		OCH_3	H	23,9	0,03
(V)	»		H	OCH_3	23,5	0,57
(VI)	»		NO_2	NO_2	<17	1,99
(VII)	»		NO_2	Br	18,1	1,56
(VIII)	»		NO_2	OCH_3	21,0	1,03
(IX)	»		NO_2	CH_2CHCH_2	22,0	0,51
(X)	»		$COOCH_3$	Br	20,0	1,32
(XI)	»		$COOCH_3$	NO_2	17,7	1,67
(XII)	»		NO_2	CO_2CH_3	19,2	1,24
(XIII)	»		COOH	NO_2	17,3	1,75
(XIV)	»	NO_2	NO_2	H	25,0	−0,42
(XV)	»	NO_2	Br	NO_2	24,2	0,60
(XVI)	»	OCH_3	NO_2	H	20,0	1,02
(XVII)	»	CF_3	NO_2	H	24,1	−0,09
(XVIII)	C_6H_5	NO_2	NO_2	OCH_3	24,8	−0,86
(XIX)	CH_3	NO_2	H	OCH_3	24,7	−0,50
(XX)	»	NO_2	Br	H	25,0	−0,74
(XXI)	»	H	H	H	24,8	0,20
(XXII)	»	NO_2	H	H	25,2	−0,87
(XXIII)	»	NO_2	OCH_3	H	24,4	−1,04
(XXIV)	C_6H_5	H	NO_2	H	24,8	−0,17
(XXV)	C_2H_4OH	H	NO_2	H	21,4	0,79

$^*\sigma = (\Sigma\sigma_b)/\rho_i + (\Sigma\sigma_i)/\rho_b$; $\rho_b = -3.6$; $\rho_i = 10.2$.

in the determination of ΔG≠ relative to the $n_N-\sigma^*_{CO}$ interaction is small. Therefore, the dependence of ΔG≠ on σ when σ > 0 is mainly a function of the efficiency of the $n_N-\sigma^*_{CO}$ orbital interaction.

CONCLUSIONS

1. A correlation equation was obtained for the active free energy ΔG≠ for the thermal inversion of configuration of the closed form of spiropyrans substituted both in the indoline and benzopyran fragments.

2. The $n_N-\sigma^*_{CO}$ orbital interaction plays the major role in determining the magnitude of ΔG≠ and the strength of the C^2–O bond.

LITERATURE CITED

1. V. S. Marevtsev, N. L. Zaichenko, V. D. Ermakova, et al., Izv. Akad. Nauk SSR, Ser. Khim., 2272 (1980).
2. N. L. Zaichenko, V. S. Marevtsev, V. D. Arsenov, and M. I. Cherkashin, Khim. Fiz., No. 6 (1987).
3. A. Hinnen, C. Audic, and R. Gautron, Bull. Soc. Chim. France, 2066 (1968).
4. V. D. Arsenov, V. D. Ermakova, M. I. Cherkashin, and P. P. Kisilitsa, Izv. Akad. Nauk SSSR, Ser. Khim., 452 (1972).
5. G. Binch, Top. Stereochem., 3, 97 (1968).
6. J. M. Lehn, Top. Curr. Chem., 15, 311 (1970).
7. G. Becker, Introduction to the Electronic Theory of Organic Reactions [Russian translation], Mir, Moscow (1977), p. 87.
8. V. A. Pal'm, Usp. Khim., 30, 1069 (1961).