SHORT-WAVE BAND IN THE ELECTRONIC SPECTRA OF SYDNONES AND SYDNONIMINES

V. V. Ogorodnikova, I. S. Slyusarenko,
and V. G. Yashunskii

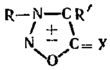
UDC 547.793.3:543.422.6

A new absorption maximum was observed in the UV spectra of sydnones and sydnonimines at 200 nm, and the effect of substituents and solvents on its position was studied.

The UV spectra of sydnones, sydnonimines, and their N-exocyclic derivatives have been studied quite extensively. The effect of substituents and solvents on the shift of the absorption maxima has been investigated [1-4]. An intense absorption maximum at 290-340 nm is characteristic for these heterocycles, which are representatives of the class of the so-called mesoionic compounds. Another single maximum at 220-240 nm appears in the spectra of compounds with aryl substituents in the 3-position of the ring.

We have observed a new absorption maximum in the UV spectra of sydnones, sydnonimine salts, and their N-exocyclic derivatives at 200 nm, the intensity of which is lower than that of the long-wave absorp-

TABLE 1



R	R′	X	λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε
$(CH_3)_2CH$	H	O	205	3,44			293	3,82
$(CH_3)_2CH$	CH_2COOH	O	203	3,53			302	3,90
C_6H_5	H	O	205	4,09	238	3,96	316	3,71
$C_6H_5CH_2CHCH_3$	CH_3	O	207	3,98	210	sh	305	3,87
$C_6H_5CH_2CHCH_3$	C_6H_5	O	206	4,17	245	3,62	316	3,86
$C_6H_5CH_2CHCH_3$	Br	O	207,5	4,00	210	sh	312	3,87
C_6H_5	CH_3	O	204,5	4,04	237	3,80	313	3,84
C_6H_5	$CONH_2$	O	205,5	3,95	225	3,95	315	3,80
C_6H_5	COOH	O	206	3,90	223	3,94	313	3,75
Ethylenebissydnone			202,5	3,43			298	3,68
CH_3	H	$\overset{+}{N}H_2\overset{-}{Cl}$	205	3,61			300	3,62
cyclo-C_6H_{11}	H	$\overset{+}{N}H_2\overset{-}{Cl}$	205,5	3,87			299	3,87
C_4H_9	H	$\overset{+}{N}H_2\overset{-}{Cl}$	205	4,21			300	4,22
C_6H_5	CH_3	$\overset{+}{N}H_2\overset{-}{Cl}$	207	3,92			308	3,91
$CH_3OC_6H_5$	H	$\overset{+}{N}H_2\overset{-}{Cl}$	206,5	4,08			323	4,06
C_6H_5	C_6H_5	$\overset{+}{N}H_2\overset{-}{Cl}$	207,5	4,25	245	4,02	327	3,92
$C_6H_5CH_2CHCH_3$	C_6H_5	$\overset{+}{N}H_2\overset{-}{Cl}$	205,5	4,26	245	3,96	313	4,02
$C_6H_5CH_2CHCH_3$	H	$\overset{+}{N}H_2\overset{-}{Cl}$	208	4,11			303	3,74
Ethylenebissydnonimine hydrochloride			205	4,00			305	3,95
C_4H_9	H	$NCOCH_3$	202,5	3,85	243	3,85	323	3,74
$(CH_3)_2CH$	H	$NCOCH_3$	196,5	3,43	243	3,70	327	3,97
C_6H_5	H	$NCOCCl_3$	204	4,04	267	4,16	344	4,15
$C_6H_5CH_2CHCH_3$	H	$NCONH_2$	207,5	4,02	235	4,11	332	3,97
$C_6H_5CH_2CHCH_3$	H	$NSO_2C_6H_5$	208	4,35	237	4,12	318	4,03

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 464-465, April, 1972. Original article submitted July 12, 1971.

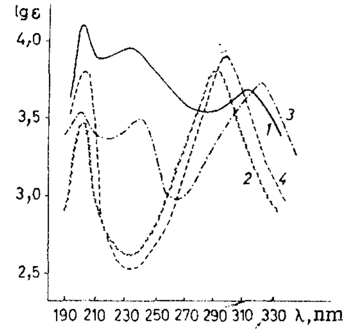


Fig. 1. UV spectra of ethanol solutions of: 1) 3-phenylsydnone; 2) 3-isopropylsydnone; 3) 3-butyl-N-exo-acetylsydnonimine; 4) 3-butylsydnonimine hydrochloride.

tion. N-Substituted glycines and acetonitriles and their N-nitro derivatives, which are the starting materials in the synthesis of sydnones and sydnonimines, are optically transparent in this region. The observed short-wave maximum is constantly observed in the studied heterocycles with the most diverse substituents. As an example, the absorption curves of typical representatives of this series are presented in Fig. 1, while the data from the UV spectra of some of them, recorded from anhydrous ethanol solutions, are presented in Table 1. It is seen that the character of the substituent in the 3 and 4 positions of the ring and of the exocyclic group attached to the 4-carbon atom has virtually no effect on the position of this maximum, in contrast to the long-wave absorption, where the shifts are of considerable magnitude.

In the case of 3-phenylsydnone, it has been demonstrated that the polarity of the solvent has an effect on the absorption in the short-wave region of the spectrum. While this maximum is found at 200 nm in the spectra of aqueous solutions, it is situated at 205 and 212 nm, respectively, in the spectra of alcohol and hexane (or dioxane) solutions. Thus the short-wave absorption undergoes a "blue shift" as the solvent polarity increases, while a "red shift" is characteristic for the long-wave maximum [4]. This makes it possible to assume that, in contrast to the long-wave absorption caused by $\pi-\pi^*$ transitions, the short-wave maximum is associated with an $n-\pi^*$ transition of the $N_{(2)}$ or $O_{(1)}$ atoms of the ring. However, the high intensity and the position of this maximum correspond more to the bands of a $\pi-\pi^*$ transition. Additional investigations are necessary for a clarification of the nature of the short-wave absorption maximum of sydnones and sydnonimines.

The UV spectra of $1 \cdot 10^{-4}$ M absolute ethanol solutions of the substances were recorded with a Shimadzu MPS-50L spectrometer in a quartz cuvette with $l = 1$ cm.

LITERATURE CITED

1. F. I. Metz, W. C. Servoss, and F. E. Welsh, J. Phys. Chem., 66, 2446 (1962).
2. V. G. Yashunskii, "Investigation of sydnones and sydnonimines," Doctoral Dissertation [in Russian], Moscow (1964).
3. V. G. Yashunskii and E. M. Peresleni, Zh. Obshch. Khim., 32, 1687 (1962).
4. P. B. Talukdar and S. K. Senqupta, J. Ind. Chem. Soc., 46, 182 (1969).