

MESOIONIC COMPOUNDS. SYDNONES AND THEIR PHOTOCHROMIC PROPERTIES

M. ŠORM and S. NEŠPŮREK

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

Received September 25th, 1974

The paper is dealing with the preparation and characterization of some new sydnones. The NMR, infrared and ultraviolet spectra and general photochromic properties of these compounds are discussed.

The photochromic behaviour of sydnones was first observed by Tien and Hunsberger¹ with 3-(3-pyridyl)sydnone in the solid state. It was assumed from the chemical standpoint that photochromism could be a general property of sydnones. However, later on it was found that none of the large number of sydnones²⁻⁴ prepared exhibited any important degree of photochromism.

The mechanism of photochromism in organic compounds is based on the existence of the heterolytic and homolytic cleavage of bonds, *cis-trans*-isomerization, tautomerism, free radical formation, oxidation-reduction processes, activation of triplet states⁵ *etc.* None of the above principles, however, could be employed for the interpretation of the photochromism of 3-(3-pyridyl)sydnone. Some authors^{6,7} believe that the photochromism of this compound is due to the formation of colour centres, similarly to alkali halides. Mitsui and Ehara⁸ assume that the photochromism is caused rather by the intermolecular transition of the charge-transfer type than by the colour centres. The sydnone ring seems to be the necessary but not the single condition of the photochromism in sydnones. An important role will probably be played also by the effects of the structural and steric nature, crystal lattice and its defects, material purity *etc.* In order to investigate some of these effects in greater detail, we tried to prepare some further new photochromic sydnones.

Greco and O'Reilly⁹ prepared several alkenylsydnones, in three of which they observed photochromism in the solid state. In our preceding communication¹⁰ we mentioned the preparation and properties of two other photochromic sydnones. Some of the compounds prepared by us exhibited rather strong photochromism not only in the solid crystalline state, but also in solid organic glasses at the liquid nitrogen temperatures. A more detailed description of their preparation, characterization and discussion of the NMR, infrared and ultraviolet spectra and general photochromic properties are the subject of this paper.

EXPERIMENTAL

The melting points were determined with a Kofler block and were not corrected. The infrared spectra were recorded with a Perkin-Elmer 457 spectrometer in KBr discs. The ultraviolet spectra

TABLE I
Hydroxysydnone II

II	Compound		M.p., °C (solvent)	Yield ^a %
	R ¹	R ²		
a	phenyl	H	97–99 (benzene–hexane)	42.5
b	pyridyl	CH ₃	143–145 (benzene)	64.3
c	cyclohexyl	CH ₃	150–151.5 (methanol)	57.4
d	phenyl	CH(CH ₃)	95–97 ^e (benzene–hexane)	38.5

^a Related to initial sydnone I (cf. Scheme A). ^b s = singlet, d = doublet, q = quartet. ^c NMR spectra of compounds were recorded in CDCl₃. ^d Spectrum contains also chemical shifts of syd-

in the solid state were obtained with a Carry 14 spectrophotometer, spectra in solutions were determined with an Optica Milano CF-4 spectrophotometer. The NMR spectra were recorded with a JEOL PS 100 apparatus at a frequency 100 mc/s with hexamethyldisilocene as the internal standard. The mass spectra were obtained with an AEI MS 902 spectrometer.

3-Phenylsydnone¹¹, 3-(3-pyridyl)-sydnone³ and 3-cyclohexylsydnone⁴ were prepared according to the literature and kept in the dark. The stock solution of n-C₄H₉Li in benzene was prepared by a reaction of butyl bromide with lithium powder and its concentration (0.855 mol/l) was determined by double titration. All reactions with n-C₄H₉Li were carried out in an argon atmosphere. Ether and benzene were dried with sodium, ketones were dried with calcium chloride and redistilled.

General procedure of preparation of hydroxysydnone (II). A suspension of sydnone I (cf. Scheme 1) in ether and of n-C₄H₉Li (1.1 molar excess) in benzene were mixed and stirred at –20°C for 1 h; the respective ketone was added in a two-molar excess to the solution, and after stirring at room temperature for two hours the insoluble fraction was filtered off, washed with dilute hydrochloric acid and water and dried. Alcohol *Iib* remains dissolved in the reaction mixture and was isolated from its evaporation residue. The results are summarized in Table I. The same procedure was used for the preparation of sydnones *Iie* (R¹ = phenyl, R² = CH₃), *Iif* (R¹ = phenyl, R² = CH₂CH₃), *Iig* (R¹ = phenyl, R² = cyclohexyl) and *Iih* (R¹ = phenyl, R² = cyclopentyl), the physical values of which and the results of spectral measurements are in good accord with the data described elsewhere⁹.

General procedure of preparation of sydnones III, IV, and V. Benzene solution of hydroxysydnone II was refluxed (1 h) with P₂O₅ (1.1 molar excess) in the dark (in the cases of *Iia* and *Iic* the reaction time was 15 min, for *Iib* it was 5 h). The reaction mixture was filtered off while still hot, the

TABLE I
 (Continued)

NMR (p.p.m.) τ (multiplicity ^b , No of protons, assignments)	IR: $\tilde{\nu}$, cm ⁻¹	
	OH	m/e
2.20—2.82 (m, 5, phenyl), 5.40 (q, 1, $\underline{\text{CH}}-\text{CH}_3$), 6.20 (s, 1, OH), 8.50 (d, 3, $\underline{\text{CH}}_3-\text{CH}$) ^c	3 400 1 700	206
1.05—2.57 (m, 4, pyridyl), 7.09 (s, 1, OH), 8.50 (s, 6, CH_3)	3 400 1 720 1 735 sh	221
7.26 (s, 1, OH), 7.70—8.90 (m, 10, cyclohexyl), 5.52 (m, 1, CH-cyclohexyl), 8.40 (s, 6, CH_3) ^d	3 350 1 716	226
2.36—2.62 (m, 5, phenyl), 6.97 (s, 1, OH), 7.99 (septet, 1, $\text{CH}(\text{CH}_3)_2$), 8.70 (s, 3, CH_3), 9, 17 (d, 3, $\underline{\text{CH}}_3\text{CH}$), 9.22 (d, 3, $\underline{\text{CH}}_3\text{CH}$)	3 410 1 720	230 ^f

none *IIIc* (Table II). ^e in ref.⁹ m.p. 113—114°C. ^f Fragment formed by splitting-off of water from molecular ion.

insoluble inorganic residue was washed with benzene, the joined benzene filtrates were evaporated and the evaporation residue was crystallized from the respective solvent (Table II).

The evaporation residue after the dehydration of *IId* was chromatographed on a silicagel column (a hundredfold excess of silicagel), with a mixture of benzene and ether (7 : 3) as the elution solvent. The first fraction yielded sydnone *IIIe*, the second fraction gave sydnone *IIIc*. The evaporation residue after the dehydration of *IId* was extracted with benzene and sydnone *IIIa* was isolated from the benzene filtrate by repurification by way of chromatography on a silicagel column with ether as the eluent. Dimer *IV* was obtained from the insoluble fraction in benzene.

Sydnone *V*, which was formed in a c. 5% yield during the dehydration of *IIIe* and was isolated similarly to *IV*, was prepared on a major scale by the dimerization of sydnone *IIIc* in a solution of dichloromethane by treating it with a 96% sulphuric acid (two-molar excess) at -70°C in an argon atmosphere. After three hours of stirring the solvent was evaporated, the evaporation residue was washed with ethanol and crystallized. Sydnones *IIIe* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{CH}(\text{CH}_3)_2$), *IIIc* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{CH}_3$), *IIIg* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{R}^4 = \text{CH}_3$), *IIIh* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{H}$, $\text{R}^3-\text{R}^4 = (\text{CH}_2)_4$), *IIIi* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{H}$, $\text{R}^3-\text{R}^4 = (\text{CH}_2)_3$) and *IIIj* ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{CH}_2\text{CH}_3$) have been described earlier by Greco and O'Reilly; their physical values and spectral data (NMR and ultraviolet spectra of ethanolic solutions) determined in this study are in good accord with the literature data.

RESULTS AND DISCUSSION

Sydnones *I* yield by reacting with $n\text{-C}_4\text{H}_9\text{Li}$ and the respective ketones hydroxy derivatives *II*. The intermediates of these reactions were lithium salts of sydnones *I*

TABLE II
Sydnones III–V

Compound	R ¹	R ²	R ³	R ⁴	M.p., °C (solvent)
<i>IIIa</i>	phenyl	H	H	H	76–79 (methanol) ^b
<i>IIIb</i>	pyridyl	H	H	CH ₃	98–99.5 (ethanol)
<i>IIIc</i>	cyclohexyl	H	H	CH ₃	51–53.5 (ether, –70°C)
<i>III_d</i>	phenyl	CH ₃	CH ₃	CH ₃	85–87 (methanol, –70°C) ^b
<i>IV</i>	—	—	—	—	206–207.5 (acetone)
<i>V</i>	—	—	—	—	236–238.5 (acetone)

^a Related to initial sydnone *II*. ^b Isolated by chromatography. ^c Fragment due to splitting-off of CO from molecular ion.

which were used directly without isolation in a further reaction. The dehydration of alcohols *II* yielded alkenylsydnones *III* (Scheme 1). The dehydration of *IIa* and *IIe* via the above procedures gave sydnones *IIIa*, *III_f* and sydnones *IV*, *V* as side products arising from the former two by dimerization catalyzed by the *in situ* forming phosphoric acid. The dimerization took place also with other catalysts (H₂SO₄, H₃PO₄, TiCl₄ · H₂O *etc.*) in nonpolar and chlorinated solvents at room temperature and below (–70°C), as has been proved¹⁰ for *III_f*. In the other cases the formation of analogous dimeric products was not observed. Attempts at the dimerization of sydnones *IIIb* and *IIIg* under the same conditions as for *III_f* were also unsuccessful. Steric effects and the basicity of substituents seem to play the decisive role here.

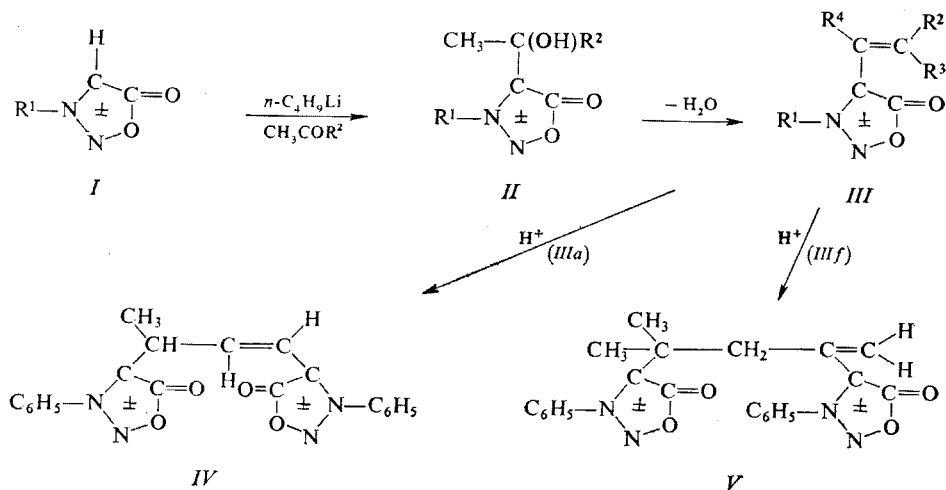
On dehydration, sydnones *III_d* and *III_f* yielded a mixture of two isomeric sydnones differing in the position of the double bond. The dehydration of *III_d* gave rise to sydnones *III_d* and *III_e* in a ratio 4 : 5, which were separated by chromatography. If sydnone *III_d* was dehydrated in an aqueous medium with acetic acid, only isomer *III_e* was formed⁹. In the case of *III_f*, *III_g* was formed as the main product together with a low amount of sydnone *III_j*. Compounds *III_g*, *III_j* could not be isolated in the pure state.

The structures of sydnones *II* prepared by us are in good accord with the results of

TABLE II
(Continued)

Yield ^a %	Calculated/Found			$\bar{\nu}$, cm ⁻¹ C=O	<i>m/e</i>
	% C	% H	% N		
30.0	63.79	4.28	14.89	1 750	188
	63.67	4.55	14.59		
82.0	59.15	4.47	20.71	1 740	203
	59.14	4.64	20.46		
61.8	63.41	7.73	13.46	1 730	208
	63.68	7.91	13.28		
38.6	67.83	6.13	12.17	1 738	230
	67.96	6.42	12.09		
14.0	63.79	4.28	14.89	1 760	376
	63.72	4.32	14.43		
80.0	65.40	4.95	13.86	1 738	360 ^c
	65.18	5.13	13.94		

elemental analysis. In the infrared spectra of sydnones *II* (Table I) the band of the hydroxyl group was observed in the region 3350–3410 cm⁻¹ and the characteristic



SCHEME 1

TABLE III
NMR and UV Spectra of Sydnones III—V

Compound	NMR (p.p.m.)		UV: λ max, nm (log ϵ)	
	Solvent	τ (multiplicity ^a , No of protons, assignments)	nonpolar ^b	polar ^c
IIIa	CDCl ₃	2.25—2.65 (m, 5, phenyl), 3.80 (m, 2, $\underline{\text{CH}}=\underline{\text{CH}}\text{H}$),	e	207 (3.92)
		4.70 (m, 1, $\underline{\text{CH}}=\underline{\text{CH}}\text{H}$) ^d		224 (3.76) 252 (3.73) 329 (3.82)
IIIb	DMSO-D ₆	1.12—2.28 (m, 4, pyridyl), 4.66 (m, 1, $\text{CH}_2=\text{C}$),	204 (4.04)	343
		4.80 (m, 1, $\text{CH}_2=\text{C}$), 8.62 (s, 3, CH_3)	233 (3.93) 257 (3.81) 342 (3.83)	
IIIc	CCl ₄	4.79 (m, 1, $\text{CH}_2=\text{C}$), 4.91 (m, 1, $\text{CH}_2=\text{C}$),	200 (~3.60)	204 (3.36)
		5.53 (m, 1, cyclohexyl), 7.79—8.92 (m, 10, cyclohexyl),	229 (3.61)	234 (3.53)
		7.98 (s, 3, CH_3)	236 (3.68) 252 (3.52) 322 (3.88)	310 (3.76)
III d	CCl ₄	2.36—2.62 (m, 5, phenyl), 8.26 (s, 3, CH_3),	206 (4.08)	207 (4.08)
		8.43 (s, 6, $(\text{CH}_3)_2\text{C}=\text{}$)	233 (3.94) 343 (3.69)	232 (3.95) 326 (3.76)
IIIe	CCl ₄	2.39—2.60 (m, 5, phenyl), 4.90 (m, 1, $\text{CH}_2=\text{C}$),	205 (~4)	206 (~4.11)
		5.09 (m, 1, $\text{CH}_2=\text{C}$), 7.36 (septet, 1, $\underline{\text{CH}}(\text{CH}_3)_2$), 8.98 (d, 6, CH_3) ^f	233 (3.93) 340 (3.85)	230 (4.04) 324 (3.90)

<i>IIIg</i>	CDCl_3	2:25—2:80 (m, 5, phenyl) 4:60 (m, 1, $\text{CH}_2=\text{C}$), 4:80 (m, 1, $\text{CH}_2=\text{C}$), 8:32 (s, 3, CH_3)	206 (~4) 230 (3:94) 260 (3:72) 340 (3:81)	208 (~4) 231 (3:93)	235
<i>IIIg + j^g</i>	CDCl_3	2:34—2:56 (m, 5, phenyl), 4:04 (q, 1, $=\text{CHCH}_3$), 8:35 (d, 3, $\text{CH}_3\text{CH}=\text{C}$), 8:52 (s, 3, CH_3), 4:78 (m, 1, $\text{CH}_2=\text{C}$), 4:88 (m, 1, $\text{CH}_2=\text{C}$), 7:92 (q, 2, CH_2CH_3), 9:10 (t, 3, CH_3CH_2)	206 (4:04) 230 (4:04) 342 (3:75)	206 (4:02) 222 (3:98) 332 (3:91)	333 335
<i>IIIh</i>	CDCl_3	2:36—2:64 (m, 5, phenyl), 3:83 (m, 1, $\text{CH}=\text{C}$), 7:98 (m, 2, CH_2), 8:24 (m, 2, CH_2), 8:52 (m, 4, CH_2CH_2)	205 (4:05) 232 (3:85) 340 (3:73)	206 (3:97) 234 (3:92) 333 (3:89)	365 ± 5
<i>IIIi</i>	CCl_4	2:33—2:56 (m, 5, phenyl), 3:78 (m, 1, $\text{CH}=\text{C}$), 7:69 (m, 2, $\text{CH}_2\text{C}=\text{C}$), 8:00 (m, 2, $\text{CH}_2\text{C}=\text{C}$), 8:32 (m, 2, CH_2)	205 (4:08) 235 (4:04) 344 (3:98)	206 (4:11) 237 (4:08) 341 (4:08)	324
<i>IV</i>	DMSO-D_6	2:08—2:44 (m, 10, phenyl), 3:56 (m, 1, $\text{CH}-\text{CH}=\text{CH}$), 4:68 (m, 1, $\text{CH}=\text{CH}$, $J_{\text{HH}} = 16 \text{ Hz}$), 6:56 (m, 1, $\text{CH}-\text{CH}=\text{C}$, $J_{\text{HH}} = 8 \text{ Hz}$), 8:69 (m, 3, CH_3)	— ^e	206 (4:11) 228 (3:91) 253 (3:87) 331 (4:08)	
<i>V</i>	DMSO-D_6	2:20—2:40 (m, 10, phenyl), 4:64 (s, 1, $\text{CH}_2=\text{C}$), 4:72 (s, 1, $\text{CH}_2=\text{C}$), 7:62 (s, 2, CH_2), 9:10 (s, 6, CH_3)	— ^e	208 (4:41) 236 (4:15) 314 (4:20)	380 ^h

^a The same meaning as in Table I. ^b Heptane. ^c Ethanol. ^d Other data: ABX ; $J_{\text{AX}} = 9:1$; $J_{\text{BX}} = 3:8$; $J_{\text{AB}} = 17:0 \text{ Hz}$; $\delta_{\text{AB}} = 5:25 \text{ Hz}$. ^e Inso-
luble. ^f $J = 7:0 \text{ Hz}$. ^g Mixture of 93% *IIIg* and 7% *IIIj*. ^h At 8K.

singlet band of the carbonyl group of the sydnone ring was observed at 1700 to 1735 cm^{-1} . The carbonyl band of *IIb* appeared as a doublet. In the spectra of alkenylsydnones *III*, *IV* and *V* (Table III) the carbonyl groups again appeared as singlet bands in the region 1731–1760 cm^{-1} . The shift of the bands of the carbonyls of sydnone *II* by 10–50 cm^{-1} towards lower wave frequencies compared to the bands of the carbonyls of sydnones *III*, *IV* and *V* can be explained by the formation of a hydrogen bridge between the hydroxyl group and the oxygen atom of the carbonyl group.

In the NMR spectrum of sydnone *IIIa* a system ABX of three olefinic protons at 3.80 and 4.70 τ was observed, besides the multiplet of aromatic protons. The two-proton multiplet at a lower magnetic field was assigned to the hydrogens in the α - and β -*cis* configuration with respect to the phenylsydnone substituent, while the sextet at 4.70 τ was ascribed to the β -*trans* proton. By using atomic models it was shown that the most advantageous arrangement of the molecule is reached if the olefinic bond lies in the plane of the molecule and the α -proton is situated near the phenyl ring. The substitution of α -proton with a bulkier methyl, e.g. for *IIIg*, causes the double bond to twist out of the plane of phenylsydnone, which has as a consequence a decrease in the “deshielding” effect of both the carbonyl group and the two aromatic rings, as well as a chemical shift of the β -*cis* proton towards higher values (4.60 τ). The methyl group also participates by its shielding effect in the change of the chemical shifts of both geminal β -protons¹². If α -proton is substituted by a still bulkier alkyl, such as ethyl (*IIIj*) or isopropyl (*IIIe*), the changes in the chemical shifts of both geminal protons are even more pronounced.

The effect of substituents in position 3 of the sydnone ring on the chemical shifts of both geminal β -protons is insignificant. By substituting the phenyl substituent of sydnone *IIIg* for the pyridyl (*IIIb*) or cyclohexyl (*IIIc*) one the chemical shifts of β -*cis* protons will be increased by only 0.06 and 0.19 τ , while a change in the chemical shifts of β -*trans* protons is even smaller (0 and 0.11 τ).

Sydnones *IIIg* and *IV* can – in addition to the formation of isomers differing in the position of the double bond – also form isomers differing in the configuration of substituents on the double bond. In the NMR spectrum of sydnone *IIIg* the signal of the olefinic proton was observed at 4.04 τ and compared to the chemical shifts of the geminal protons of *IIIg* it was decreased by 0.6–0.8 τ . Bearing in mind the known fact that methyl group reduces the signal of the geminal proton of the olefinic bond by its “deshielding” effect¹² (but not more than by 0.44 τ), it is rather the structure of the compound with the *cis*-configuration of the proton towards the phenylsydnone substituent than the structure with the *trans*-configuration that corresponds to this value of the chemical shift. Such assignment is further corroborated by the NMR spectra of sydnones *IIIh* and *IIIi*, in which the olefinic proton cannot occupy any other configuration than β -*cis* with phenylsydnone⁹. A similar structure with the *cis*-configuration can also be assumed for sydnone *IV*, mainly for steric reasons.

In all ultraviolet spectra of sydnones *III*–*V* in ethanol three characteristic bands were observed with the exception of sydnones *IIIa*, *IIIb* and *IV* for which also bands at λ 250 nm are observed. The same bands can also be observed for sydnones *IIIb* (257 nm), *IIIc* (252 nm) and *IIIf* (260 nm) in nonpolar solvents. At the first absorption band a comparatively strong shift in the position of the maximum towards shorter wavelength can be seen with increasing polarity of the solvent. The nature of this shift has been investigated in more detail for *IIIf* in the mixture heptane–ethanol. With increasing dielectric constant of the solvent the maximum of this band is gradually shifted into the blue region by as much as 11 nm. The shift could be due to the hydrogen bond of the n -electrons of sydnone with the hydroxyl groups of the solvent, which has as its consequence an increase in the stability of the basic state compared to the excited state of the molecule. However, fluorescence measurements did not confirm the existence of the n - π^* transition. It seems more likely that the excited state is less polar than the basic one.

Of the prepared 12 sydnones of which 6 are compounds not yet described, photochromism at room temperatures in the solid phase was observed for 7 sydnones (*IIIb*, *IIIc*, *IIIe*, *IIIh*, *IIIi*, *IIIj*, and *V*). All are crystalline compounds, stable in the dark. Immediately after irradiation with light having wavelength shorter than λ (410 ÷ 470) nm and according to the type of sydnone there is a change in colour in the solid state. The maximum of this absorption varies within $600 < \lambda < 750$ nm, again according to the type of sydnone. Sydnones *IIIc* and *IIIi* after irradiation with light having wavelength shorter than λ 400 nm quickly undergo photodegradation. This fact was also the cause why Greco and O'Reilly⁹ regarded sydnone *IIIi* as nonphotochromic; they irradiated it with light having wavelengths λ (320 ÷ 400) nm. In contrast with the other sydnones, photochromic sydnones *IIIc* and *IIIi* do not assume colour at the liquid nitrogen temperatures.

The photochromic change of the above sydnones is reversible. Bleaching occurs either thermally or by irradiation with visible or infrared light. The photochromic fatigue of the material depends on the wavelength of the "colouring" light and the irradiation time. For sydnones *IIIe*, *IIIc*, *IIIh* and *V* photochromic changes were still observed after several tens of cycles, while for other compounds (such as *IIIi*) the number of these steps was very low. The quantum yield of the colouration process decreased with the number of cycles; at the same time brown-yellow degradation products were formed. There exists an optimum combination between the irradiation time and the wavelength of the ultraviolet light on the one hand and the change in transmission and the number of cycles (colouration-bleaching) on the other.

In contrast with the existing knowledge of the photochromism of sydnones, when the property is assigned only to the solid state, we were able to detect a reversible change in colour also in solid organic glasses, such as ethanol, methylpentane, in a mixture of ether, isopentane, and ethanol, and in solid polymer solutions at the liquid nitrogen temperatures. This property has not been observed for sydnones *IIIb*

and *IIIi* which are photochromic in the solid state, but it was observed for *IIIe* which is nonphotochromic in the solid state. The maxima of these absorption colour bands were observed according to the type of sydnone within the range 630–670 nm. The colour form can be bleached similarly to crystals by irradiation with visible light. Bleaching also occurs at elevated temperatures in the case of solid polymer solutions, and at the softening point for frozen solutions.

The authors are indebted to Dr J. Exner and Dr K. Ulbert for some valuable comments and discussions, and to Dr D. Doskočilová for the interpretation of the NMR spectra.

REFERENCES

1. Tien J. M., Hunsberger I. M.: *J. Amer. Chem. Soc.* 77, 6604 (1955).
2. Baker W., Ollis W. D., Poole V. D.: *J. Chem. Soc.* 1949, 307.
3. Ohta M., Masaki M.: *Bull. Chem. Soc. Jap.* 33, 649 (1960); Tien J. M., Hunsberger I. M.: *J. Amer. Chem. Soc.* 83, 178 (1961); Greco C. V., Hunsberger I. M.: *J. Heterocycl. Chem.* 7, 761 (1970).
4. Snyder J. P.: *Nonbenzoic Aromatic* Vol. 1, 117 (1969).
5. Brown G. H.: *Photochromism*. Wiley, New York 1971.
6. Mill T., van Roggen A., Wahlig C. F.: *J. Chem. Phys.* 35, 1139 (1961).
7. Gutowsky H. S., Rutledge R. L., Hunsberger I. M.: *J. Chem. Phys.* 29, 1183 (1958).
8. Mitsui A., Ehara N.: *Bull. Chem. Soc. Jap.* 46, 327 (1973).
9. Greco C. V., O'Reilly P.: *J. Heterocycl. Chem.* 9, 207 (1972).
10. Šorm M., Nešpůrek S.: *This Journal* 40, 1534 (1975).
11. Earl J. C., Mackney A. W.: *J. Chem. Soc.* 1935, 899.
12. Jackman L. M., Sternhell S.: *Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Vol. 5, 185 (1969).

Translated by L. Kopecká.