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Combined Sensitisation of Benzaldehyde Diphenylhydrazones: Effect of Hydrazone Structure on Sensitization Efficiency

E.V. Mikubayeva*, N.S. Kobotayeva and E.E. Sirotkina

Institute of Petroleum Chemistry, Siberian Branch of Russian Academy of Sciences,
3, Academichesky Ave., 634021, Tomsk, Russia

Abstract

Injection, spectral and combined (injection-spectral) sensitisations of several benzaldehyde diphenylhydrazones have been studied using the layers of amorphous selenium and complex compounds based on pyril dyes to broaden photosensitivity spectrum of electrophotographic carrier and to study sensitisation mechanism. Two photogeneration mechanisms for charge carriers have been shown to exist at a combined sensitisation, *i.e.* generation in the injection layer followed by the injection into a transport layer and generation in a transport layer on a dye. The excited dye molecules have been established to create hole strapping sites in a transport layer: it is exhibited in a different nature of photodischarge curves in selenium- and dye-absorbing regions at the negative surface potential. The effect of the substituent in a benzaldehyde fragment on the efficiency of injection, spectral and combined sensitisations of benzaldehyde diphenylhydrazones has been studied. The ionization potentials of hydrazones were determined by the two following methods: according to the charge transfer band of hydrazone-chloranil charge transfer complexes and by means of quantum-chemical calculations of hydrazone molecules to interpret the results obtained. In the course of quantum-chemical calculations the conjugation character was also determined in the molecules of benzaldehyde diphenylhydrazones.

Introduction

The problem of improving of photosensitivity of organic carriers based on organic semiconductors may be solved by applying the sensitisation of different types [1]. The application of two types of sensitisation simultaneously, *i.e.* spectral and injection, on the one hand, allows broadening of the photosensitivity spectrum, on the other hand, it makes feasible a more detailed study of the sensitisation mechanism [2,3]. Injection, spectral and combined (injection-spectral) sensitisation of benzaldehyde diphenylhydrazones has been studied. One has revealed the effect of the substituent in a benzaldehyde fragment of the molecule on sensitisation.

It is known that the efficiency of injection sensitisation strongly depends on the co-ordination of energy levels of the compounds generating and transporting the charge carriers. In particular, the efficiency of hole injection is as higher as lower ionization potential (IP) of the compound transporting the holes [4,5]. One of the methods for IP determination is based on the ability of compounds to form the charge transfer complexes (CTC) with electron acceptors. The interaction of the highest occupied molecular orbital (HOMO) of the donor and the lowest vacanced molecular orbital (LVMO) of the acceptor takes place in CTC, as a result a certain redistribution of the electron density occurs characterised by the degree of the charge transfer. A new long-wave absorption band, called as a charge transfer band (CTB) is observed. The charge transfer energy both depends on donor IP and acceptor electron affinity [6]. Thus, it is possible to determine donor IP by CTB position. We have obtained CTC of benzaldehyde diphenylhydrazones with chloranil and have determined hydrazones IP by electron absorption spectra of the complexes.

Hydrazones IP were also determined using quantum-chemical calculations of benzaldehyde diphenylhydrazones molecules. Quantum-chemical calculations allowed obtaining the data on the conjugation in hydrazones molecules. It is known that the mobility of holes strongly depends on the feasibility of the intramolecular mobility, *i.e.* transfer of a minimum

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*corresponding author. E-mail: see@ipc.tsc.ru unit with a hole to the longest possible distances owing to intramolecular resonance structures [7]. Such a transfer is determined by the length of the conjugation chain in the molecule of a compound transporting the holes.

Experimental

Benzaldehyde diphenylhydrazones (hereafter called hydrazones) of the general formula R-C_6H_4-CH=N-N$(C_6H_5)_2$, where R = H (H-1), *p*-N$(C_2H_5)_2$ (H-2), *p*-OCH_3 (H-3), *p*-Cl (H-4), *p*-Br (H-5), *o*-I (H-6) and *p*-NO_2 (H-7) were prepared as described in [8] and doubly recrystallized from ethanol. The purity of the products was controlled by thin-layer chromatography on Silufol.

To carry out the injection sensitisation of hydrazones we used the amorphous selenium layers obtained by vacuum evaporation. To carry out the spectral sensitisation we used complex compounds based on pyryl dyes: D-500 – bis(2,6-diphenylpyrylo-4)monomethinecyanine, D-600 – 2,6-diphenyl(2,6-diphenyl-4-methylidenepyrano)thiapyrylium, D-700 – bis(2,6-diphenylselenpyrylo-4)monomethinecyanine, D-700 Cl – 6(chlorthiaflavynilidene-4)methyl-6-chlorthiaflavylium, D-800 – 4-[3-(6-tretbutylthiaflavynilidene-4)propenyl]6-tretbutylthiaflavylium.

The samples of spectrally sensitised electrophotographic carriers represented the layers of hydrazone in a polycarbonate binder (3:2) with a dye (1.5%) deposited on the lavsan support metallised by titanium. The samples sensitised by injection were produced by depositing hydrazone layers in a binder (3:2) without a dye (transport layer) on a titanium-metallised lavsan support pre-coated by selenium layer (injection layer). The samples with a combined sensitisation differed from the samples with an injection sensitisation by the presence of a dye in the transport layer (1.5%). Hydrazones layers were 2.5-5 μm thick, the selenium layer was 0.3 μm thick.

The thickness of transport and injection layers were measured using Linnik interference micro-scope MII-4. Absorption spectra of the following solutions: complex dyes, hydrazones, CTC of hydrazone and chloranil, as well as the spectra of the samples of electrophotographic carriers were recorded with spectrophotometer "Specord M-40".

The samples of electrophotographic carriers were tested under electrophotographic mode at negative and positive surface potentials. The photosensitivity was determined by the rate of the photoinduced discharge under the action of the monochromatic light of a known intensity using the formulas (1) and (2):

$$S_\alpha^\lambda = (H\cdot\tau_\alpha)^{-1} \quad (1)$$

$$\alpha = \frac{V_d(t) - V_S(t)}{V_d(t)} \quad (2)$$

where S_α^λ is the photosensitivity, m^2/J; λ is the wave length, nm; α is the level of the photosensitivity measurement; H is the illumination intensity, W/m^2; τ_a is the time required to reach specified electrostatic contrast, s; $V_d(t)$ is the dark discharging, V/s; $V_S(t)$ is the photoinduced discharging, V/s.

To obtain CTC, equimolar solutions of hydrazone and chloranil in chloroform were mixed at the room temperature. An additional maximum absorption appeared in the absorption spectrum of the prepared solution, which was absent in the individual spectra of the donor and acceptor. IP were calculated by the formula (3) proposed for CTC of phenylhydrazones with chloranil [9]:

$$\mathrm{IP} = 5.00 + 1.50\cdot10^{-4}\nu \quad (3)$$

where ν is CTB, cm^{-1}.

Quantum-chemical calculations of hydrazones were performed by the MNDO semiempirical method [10] using the MNDO-85 program [11]. The geometry of the H-2 molecule was selected with the use of the X-ray structural data on *p*-diethylaminobenzaldehyde diphenylhydrazone [12]. For H-1, the structure was optimized in *ab initio* restricted Hartree-Fock calculations with the STO-3G basis set (Slater-type atomic orbitals approximated by three Gauss-type functions) [13]. The geometry of the other hydrazones was constructed based on the geometry of H-1, and the structural parameters of the substituents were set equal to the handbook values [14,15]. No geometry optimization was performed during calculations.

Results and Discussion

When studying the samples with spectral, injection and combined sensitisations of hydrazones the main regularities were established as follows. In the absence of an injection selenium layer the spectrum of hydrazones photosensitivities sensitised by the complexes of pyrylium dyes corresponds to the absorption spectra of these dyes both at the positive and negative surface potentials. In case of the injection sensitisation the photosensitivity is observed only at the negative surface potential. In this case the photosensitivity spectrum corresponds to the spectrum of selenium absorption. In case of the combined sensitisation at the negative surface potential the photosensitivity spectrum corresponds to the absorption spectrum of the sample. There takes place either the broadening of the photosensitivity spectrum into the long-wave region (D-500 dye) or the appearance of extra photosensitivity peaks corresponding to long-wave peaks of dye absorption (D-600, D-700, D-700 Cl, D-800). At the positive surface potential in case of the samples with a combined sensitisation the photosensitivity is observed only in the range of the dye absorption: the photosensitivity spectrum corresponds to the absorption spectrum of the dye used.

The above regularities allow making a conclusion that at the combined sensitisation of hydrazones two mechanisms of the generation of the charge carriers take place: generation in the selenium layer is followed by the injection into the transport layer and generation in the bulk of the transport layer on the dye. At the negative surface potential both mechanisms work, in this case in the short-wave region the holes are injected from the injection layer into the transport one. At the positive surface potential the electrons are not injected from the selenium layer into the transport layer, and an insignificant increase of the photosensitivity in the short-wave region corresponds to the short-wave peak of the dye absorption.

In addition, the character of the photodischarge curve for the samples with a combined hydrazones sensitisation possessing a sufficient depth of transport layers (3.5 μm and more) at the negative surface potential differs in the region of selenium absorption and in the region of the dye absorption. Figure 1 shows the photosensitivity spectra measured using several levels for a sample with H-1 hydrazone and D-700 Cl dye in the transport layer (the transport layer was 4.67 μm thick). The $S_{0.1}^{\lambda}$ spectrum (curve 1) corresponds to the absorption spectrum of the sample, whereas the $S_{0.5}^{\lambda}$ spectrum (curve 5) corresponds rather to the dye absorption spectrum.

This phenomenon is probably connected to the fact that in the region of the wavelength of 440-550 nm there takes place the photogeneration of the charge carriers on the dye preventing the holes injection from the selenium layer into the transport layer. Moreover, at a low electric field strength the holes injection is probably completely suppressed because the curve 5 coincides by its character with $S_{0.1}^{\lambda}$ spectrum obtained for the same sample at a positive surface potential when the electron injection from selenium into the transport layer is absent. We assume that the excited dye molecules create the sites of the holes capture in the transport layer.

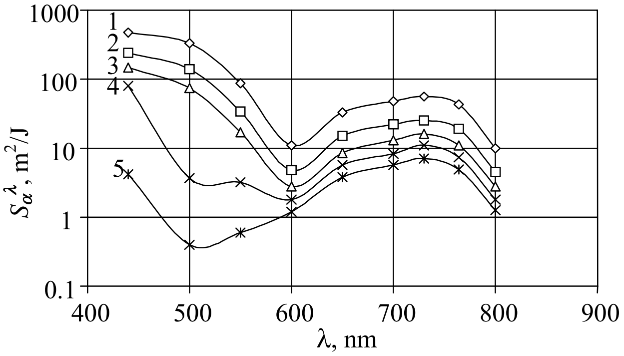

Fig. 1. Photosensitivity spectrum of the sample with H-1 hydrazone and D-700 Cl dye in the transport layer measured at a negative surface potential (1 – α = 0.1; 2 – α = 0.2; 3 – α = 0.3; 4 – α = 0.4; 5 – α = 0.5).

As far as concerns the influence of the substituent in the benzaldehyde molecule fragment on the efficiency of the injection, spectral and combined sensitisations of benzaldehyde diphenylhydrazones, one may note the following. The samples with H-2 hydrazone possess the best electrophotographic characteristics. The lowest photosensitivity values and the worst dark characteristics were obtained for the samples with H-7 hydrazone. Electrophotographic characteristics of the samples with the other hydrazones differ little from each other.

Table 1 shows λ_{max} values of the charge transfer bands of hydrazones-chloranil CTC and IP calculated by the formula (3) as well as the IP values obtained using quantum-chemical calculations.

It was impossible to determine CTB position of CTC of H-7 hydrazone with chloranil because the peak of CTC absorption interflow with the absorption edge of the hydrazone itself. In the case of H-2 hydrazone possessing the lowest IP, CTB is recorded incompletely in the visible region, that is why a precise λ_{max} is hindered. Presumably, λ_{max} of CTC of H-2 hydrazone with chloranil is within the range of 910-930 nm, whereas "Specord M40" spectrophotometer allows recording the absorption spectra within 200-900 nm.

It should be noted that IP values obtained by quantum-chemical calculations are overestimated. Ionization potentials were estimated by the MNDO method in the Koopmans theorem approximation. According to this theorem, the ionization potential equals the energy of the highest occupied molecular orbital taken with the opposite sign [10,16]. The MNDO method, as a rule, exaggerates ionization potentials because it uses the valence approximation and neglects the minteractions between valence and core *s* and *p* atomic orbitals (AOs) [10]. The ionization potentials of molecules containing different functional groups can be unequally exaggerated. We, however, obtained a satisfactory dependence of ionization potentials on the character of the substituent in the hydrazone molecule (Table 1). According to our calculations, the ionization potentials of molecules with electron-donor substituents were lower than those of molecules with electron-acceptor groups. The lowest ionization potential was obtained for H-2 with a strong electron-donor substituent, and the highest ionization potential was that of H-7 containing a strong electron-acceptor substituent.

Table 1
The charge transfer bands of hydrazone-chloranil CTC and ionization potentials of hydrazones

Hydrazone	λ_{max}, nm	IP_{CTC}, eV	IP_{MNDO}, eV
H-1	648	7.31	8.21
H-2	> 900	< 6.67	7.98
H-3	645	7.33	8.23
H-4	609	7.46	8.32
H-5	609	7.46	8.32
H-6	597	7.51	8.29
H-7	–	–	8.57

The quantum-chemical calculations of hydrazones allowed us to obtain information about the composition of the highest occupied molecular orbital. A hydrazone molecule is schematically shown in the Fig. 2, where the numbering of atoms is also given. The special features of the geometry of hydrazones [13] should be mentioned. The amine nitrogen atom of the hydrazone frame is in the sp^2 hybridization state, and the =C=N–N= group of atoms is therefore situated almost in one plane. One of the phenyl rings at the amine nitrogen atom lies in the hydrazone fragment plane, whereas the other ring is almost perpendicular to this plane.

The largest coefficients in the expansions of the HOMOs of hydrazones in basis AOs are listed in Table 2, which also contains charges that formally characterize the electron density fraction localized on these AOs ($\sum$) and on the orbitals of the benzaldehyde moiety ($\sum'$). The contributions of the AOs of separate atoms to a molecular orbital are calculated as the sum of the squares of their coefficients in the expansion of this MO [16].

The ionization potentials of hydrazones H-1 and H-3 – H-6 slightly differ from each other. Their HOMOs are largely constructed of the p_z orbitals of the C12, N14, and N15 atoms, which constitute the hydrazone frame, and the p_z orbitals of the C16, C17, C19, C21, C23, and C25 atoms of the phenyl ring that lies in the molecular plane. In addition, the p_z orbitals of the C2, C5, C7, and C8 atoms of the benzaldehyde moiety make certain contributions to the HOMOs. Note that the contribution of the benzaldehyde fragment to the HOMO is determined by the character of the substituent. Depending on the degree of the participation of the benzaldehyde frag-

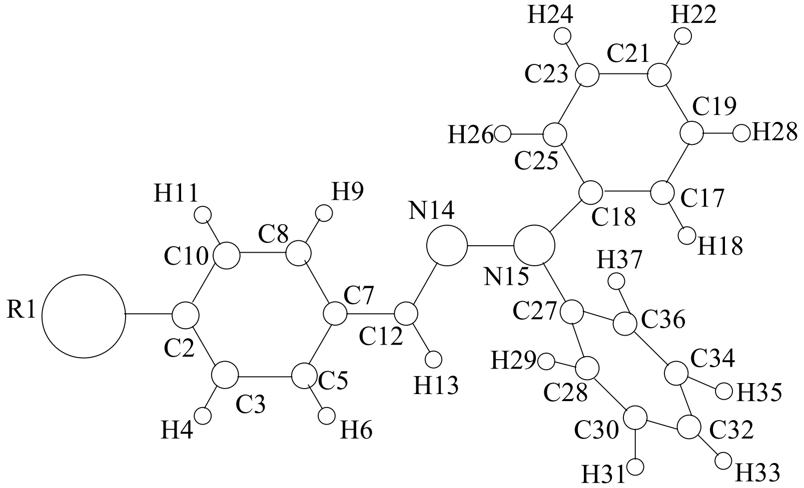

Fig. 2. Structure of hydrazone molecule.

Table 2

Quantum-chemical calculation data on benzaldehyde diphenylhydrazones
(the coefficients of the atomic p_z orbitals that make the largest contributions to the HOMOs)

Atom	H-1	H-2	H-3	H-4	H-5	H-6	H-7
N1		0.27112					
C2	-0.15177	-0.21968	-0.15598	-0.14163	-0.13971	-0.13286	-0.10752
C3		-0.20337					
C5	0.13026	0.14696	0.13032	0.12261	0.12198	0.11590	0.10589
C7	0.13923	0.29886	0.14741	0.12268	0.11869	0.10693	
C8	0.10892	0.14970	0.10911	0.10378	0.10332	0.10614	
C10		-0.18237					
C12	-0.28235	-0.25866	-0.28101	-0.28098	-0.28111	-0.28381	-0.27849
N14	-0.14280	-0.20398	-0.14362	-0.12994	-0.12829	-0.12318	-0.09646
N15	0.54293	0.46832	0.53977	0.53879	0.53887	0.54159	0.52991
C16	-0.32442	-0.22070	-0.32277	-0.33447	-0.33579	-0.33629	-0.36116
C17	-0.31623	-0.25264	-0.31394	-0.31776	-0.31828	-0.32046	-0.32363
C19	0.15134	0.10303	0.15037	0.15575	0.15641	0.15542	0.16802
C21	0.40806	0.30464	0.40551	0.41470	0.41583	0.41729	0.43379
C23	0.12182		0.12177	0.12745	0.12795	0.12874	0.14174
C25	-0.32022	-0.25705	-0.31776	-0.32158	-0.32219	-0.32349	-0.32680
Σ	0.978	0.940	0.972	0.983	0.977	0.978	0.969
Σ'	0.077	0.256	0.083	0.065	0.063	0.058	0.036

ment in conjugation, hydrazones can be ordered as H-3 > H-1 > H-4 > H-5 > H-6; that is, the introduction of the $–OCH_3$ electron-donor substituent increases the contribution of the atomic orbitals of the benzaldehyde moiety to the HOMO, whereas electron-acceptor substituents (Cl, Br and I) decrease this contribution.

The role played by the orbitals of benzene ring carbon atoms in the HOMO of H-7 with the $–NO_2$ electron-acceptor substituent is insignificant. Conjugation largely involves the hydrazone skeleton atoms and the atoms of the phenyl ring lying in the molecular plane. The contribution of the benzaldehyde fragment AOs to the HOMO increases significantly in the presence of the $–N(C_2H_5)_2$ strong electron donor. The N1 substituent atom, the C2, C3, C5, C7, C8, and C10 benzaldehyde ring atoms, the C12, N14, and N15 hydrazone skeleton atoms, and the C16, C17, C21, C23, and C25 atoms of the phenyl ring lying in the molecular plane participate in conjugation in the H-2 molecule. It follows that H-2 is characterized by the longest conjugation chain and the lowest ionization potential, whereas hydrazone H-7 has the shortest conjugation chain and the highest ionization potential of all hydrazones studied in this work. This conclusion is in accordance with the experimental data obtained during the study of the sensitisation of benzaldehyde diphenylhydrazones, and the ratio between IP values in the series of hydrazones studied coincides with the data calculated by CTC absorption spectra. On the one hand, H-1 hydrazone possesses the best ability to transport the holes owing to a long conjugation chain, on the other hand, the presence of H-1 hydrazone in the transport layer creates the conditions for an effective hole injection from the injection layer to the transport layer due to a low IP value of this hydrazone.

Conclusions

The study of the combined (injection-spectral) sensitisation of benzaldehyde diphenylhydrazones allowed to establish that two mechanisms of charge carrier photogeneration (in the selenium injection layer and in the transport layer on a dye) not only supplement each other: excited molecules of the dye create hole trap sites in a transport layer impeding hole injection from the injection to transport layer.

The efficiency of injection, spectral and combined sensitisation of benzaldehyde diphenylhydrazones depends on hydrazone structure, since substituent character in a hydrazone molecule affects hydrazone ability for charge carrier transport. On the one hand, the character of the substituent influences the ionization potential value, which, as mentioned, determines the effectiveness of the generation and transport of charge carriers [4,5]. On the other hand, the character of the substituent determines the conjugation chain length, which in turn determines intramolecular mobility [7] and, as a consequence, the mobility of holes in the transport layer. The introduction of electron-acceptor substituents (halogens and the nitro group) increases the ionization potential and decreases the contribution of the benzaldehyde moiety to conjugation. The introduction of a weak electron donor (the methoxy group) increases the contribution of the benzaldehyde fragment to conjugation and the ionization potential of the molecule (compared with the unsubstituted hydrazone). The introduction of a strong electron-donor substituent (the diethylamino group) substantially decreases the ionization potential and significantly increases the length of the conjugation chain, which then involves the whole molecule including the nitrogen atom of the substituent. *p*-Diethylaminobenzaldehyde hydrazone should therefore be most capable of transporting charge carriers because of the low ionization potential and the large conjugation chain length.

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