Spectral and photochemical properties of bifunctional compounds and their charge-transfer complexes. Derivatives of diphenylamine

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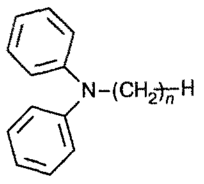
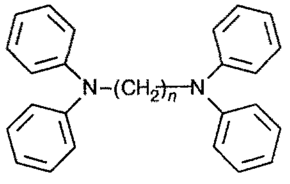
Spectral properties of diphenylamine (DPA) derivatives $Ph_2N-(CH_2)_n-NPh_2$ (n = 1, 3, 5, and 9) and their charge-transfer complexes with CBr_4 have been studied. The interaction of two Ph_2N groups results in hypsochromic shifts of absorption bands and changes in their intensities in spectra of diamines when n = 1 and 3 compared to the spectra of *N*-alkyl-substituted derivatives of DPA. The spectrum of the diamine complex when n = 1 is shifted hypsochromically, while those of the other diamine complexes are shifted bathochromically relative to the spectrum of the *N*-methyldiphenylamine complex. The positions of absorption maxima in the spectra correlates with the values of redox potentials of amines. Irradiation at the charge-transfer band ($\lambda \approx 365$ nm) of complexes between diamines and CBr_4 results in the formation of dyes, which absorb at 550 to 700 nm and presumably have di- and triphenylmethane structures.

Key words: bifunctional compounds, diphenylamine derivatives, CBr_4, charge-transfer complexes; orbital interactions; photochemical reactions.

Compounds containing two and more equivalent substituents with unshared electron pairs (UEP) or π-electronic systems separated by several σ-bonds have recently attracted attention of researchers.[1,2] Orbitals of these substituents are able to interact through space or *via* σ-bonds, and depending on the geometry of a molecule, interactions of both types can either amplify or counteract each other. This results in splitting of energy levels, which appears in the change in physical and chemical properties of compounds compared to those of model molecules in which there are no orbital interactions. For example, in absorption spectra of bifunctional (or bichromophoric[2]) compounds the resonance (exciton) splitting of electron transitions results in the splitting of absorption bands of the corresponding monochromic compounds.

In this work, the manifestation of orbital interactions is studied in absorption spectra of phenyl-substituted derivatives of α,ω-diaminoalkanes **2a—d** (n = 1, 3, 5, and 9), in which the UEP of each N atom is conjugated with π-systems of two benzene rings. DPA (**1a**) and its *N*-alkyl-substituted derivatives **1b,c** (n = 1 and 4) were used as model monofunctional compounds.


1a—c


2a—d

1: n = 0 (**a**), 1 (**b**), 4 (**c**)

2: n = 1 (**a**), 3 (**b**), 5 (**c**), 9 (**d**)

The study of complexing properties of diamines was the purpose of this work as well. It has been shown previously[3] that DPA can form charge-transfer complexes (CTC) of the 2 : 1 composition with such an acceptor as CBr_4. Since molecules of diamines **2a—d** contain two structural DPA fragments retained by the methylene bridge close to each other, it is assumed that at some n values the formation of the CTC of the "two donors—one acceptor" functional composition at the 1 : 1 molecular ratio will be facilitated. According to the published data,[3] the absorption spectrum of such a complex is bathochromically shifted relative to the spectrum of the "one donor—one acceptor" complex.

Experimental

Amines **1a—c** and **2a—d** were synthesized by alkylation of DPA by the corresponding mono- and dibromo- or diiodoalkanes according to the procedures described previously.[5—7] Prior to recording spectra amines were recrystallized from hexane or ethanol, and CBr_4 was recrystallized from aqueous toluene.

Absorption spectra of free amines (in hexane, with the concentration of $0.5 \cdot 10^{-4}$ mol L^{-1}) and complexes (in toluene,

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Table 1. Parameters of mono- and diamines

Amine	λ_{max} /nm	ε_{max} /10^3 L mol^{-1} cm^{-1}	$\varepsilon_1/\varepsilon_2$	E_{ox}/V
1a	284	18.0	—	0.96
1b	299, 249	10.6, 9.1	1.16	0.93
1c	300, 250	15.2, 13.1	1.16	0.90
2a	284, 245	24.5, 14.5	1.69	0.99
2b	297, 247	22.8, 11.0	2.07	0.82
2c	298, 250	21.8, 19.6	1.11	0.90
2d	300, 250	21.7, 18.9	1.15	0.90

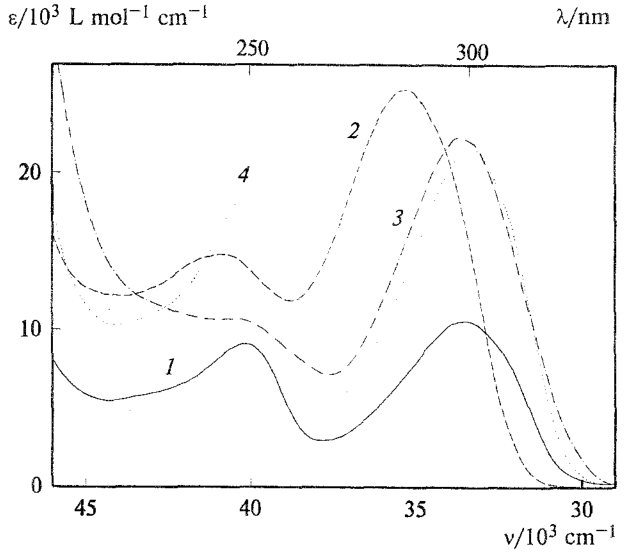


Fig. 1. Absorption spectra of amines **1b** (*1*), **2a** (*2*), **2b** (*3*), and **2d** (*4*) in hexane.

concentrations of CBr_4 and monoamines were 0.07 mol L^{-1} and the concentration of diamines was 0.035 mol L^{-1}) were recorded on a Specord M40 spectrophotometer in 1- and 0.1-cm quartz cells; measurement accuracy was 100 cm^{-1}.

A PI-50-1 potentiostat with a PR-8 programmer was used for electrochemical measurements by cyclic voltammetry. A disk platinum electrode 1 mm in diameter served as the working electrode, acetonitrile was used as a solvent, Et_4NClO_4 ($5 \cdot 10^{-4}$ mol L^{-1}) was used as the supporting electrolyte, and the concentration of amines was $2 \cdot 10^{-3}$ mol L^{-1}. All amines studied were irreversibly oxidized, and the potentials of anodic peaks E_{ox} (Table 1) are presented with the accuracy of 0.01 V relative to an aqueous saturated calomel electrode, which was separated from the system studied by the bridge filled with an acetonitrile solution of the supporting electrolyte. The value of the ferrocene/ferricinium transition relative to this electrode was 0.42 V.

Irradiation was carried out with the light of a DRSh-50 lamp through UFS-6 and BS-7 (365 nm) filters, and the power of the light beam was $1.3 \cdot 10^{-3}$ W cm^{-2}. All experiments were carried out at room temperature in air-saturated solutions.

Results and Discussion

Absorption spectra

As compared to nonsubstituted DPA, whose absorption spectrum (within the 220 to 330 nm range) contains a single band at 284 nm (see Table 1), *N*-alkylated derivatives are characterized by two bands: a long-wave band at 300 nm and a short-wave band at 250 nm with a ratio of intensities $\varepsilon_1/\varepsilon_2 \approx 1.16$. The two-band character of the spectrum is retained in diamines **2a—d** (Fig. 1); however, the position of bands and the ratio of their intensities depend on the length of the methylene bridge.

It should be expected that the strongest interaction of two diphenylamine groups is observed for the minimum chain length in compound **2a**. Both bands are hypsochromically shifted relative to the absorption maximum of the model monofunctional compound **1b** (the shift of the long-wave band reaches 1840 cm^{-1}), and the $\varepsilon_1/\varepsilon_2$ ratio increases to 1.69. Almost no shifts of bands occur in the spectrum of **2b**; however, the difference in their intensities still more increases (see Table 1). The further increase in *n* does not result in a change in the position of bands, while the ratio of intensities decreases and takes almost the initial value at *n* = 9. In fact, spectrum of **2d** is the arithmetic sum of two spectra of **1b**, *i.e.*, when the chain consists of 9 methylene groups, two Ph_2N groups almost do not interact.

It is interesting to compare the spectral behavior of bichromophoric DPA derivatives, in which the UEP of the N atom is conjugated with the aromatic π-system, to similar compounds, in which only atomic orbitals of nitrogen (as, for example, in α,ω-bis(dimethylamino)-alkanes[8]) or only π-electrons of aromatic ring (as in dinaphthyl derivatives[9]) interact. The position of absorption bands of tetramethyl analogs of compounds **2a—d** are almost unchanged compared to the spectrum of model trimethylamine (λ_{max} = 198 nm); for example, in the case of the analog of **2a**, the 2-nm bathochromic shift relative to the model compound[8] was found (the 15-nm hypsochromic shift relative to the absorption of **1b** was observed for the band of **2a**). The intensity of bands of methylated diamines are approximately twice as large as that in the spectra of monoamines, which also testifies that there is no interaction of two UEP.[8] An increase in the intensity is greater than the arithmetic sum only for the analog of **2a**.

Dinaphthyl derivatives, in which two naphthalene cores are separated by a rigid norbornyl bridge,[9] differ more substantially from compounds **2a—d**. In these compounds, the absorption band of naphthalene at 230 nm is split to two bands (the long-wave band and the short-wave band), and the splitting value decreases rapidly as the length of the linking chain increases. It is likely that the difference between the two types of bichromophoric compounds is determined, first, by the nonplanar structure of Ph_2N groups and, second, by the flexibility of the linking polymethylene chain in compounds **2a—d**.

Charge-transfer complexes

Since the excitation of the CTC is accompanied by electron transfer from the highest occupied MO (HOMO) of a donor to the lowest unoccupied MO (LUMO) of an acceptor, the proportionality between the energy of the CT band ($h\nu_{CT}$) and the energy of the HOMO (E_{HOMO}) should be fulfilled in the series of complexes of one acceptor (A) with the homologic series of donors (D).[10] The value of E_{HOMO} can be estimated experimentally, measuring ionization or oxidation potentials (E_{ox}) of the donor.[11]

$$h\nu_{CT} = c_1E_{HOMO} + c_2 \quad (1)$$

It has been shown theoretically and by the example of several bifunctional compounds that if unsaturated systems are separated by the even number of σ-bonds, as in diamines **2a—d**, orbital interactions of these systems through the space and σ-bonds enhance one another; the splitting is exponentially decreased as the distance between chromophores increases.[1,2] In this connection it could be expected that the maximum splitting of the HOMO should be observed for compound **2a**, then the effect gradually attenuates and becomes minimum in the case of **2d**. As a result, it has been assumed that the highest increase in E_{HOMO} in the molecule of **2a** results in the maximum bathochromic shift of the CT band of its complex compared to the spectrum of the complex of compound **1b**, and then this shift decreases as *n* increases.

Parameters of complexes between amines and CBr_4 are presented in Table 2: the position of the CT band (λ_{CT}), the optical density in the maximum of the band (D_{max}), the half-width of the band at the half-height ($\Delta\nu_{1/2}$) measured from the position of the maximum toward the long-wave decrease of the band, and the shift of the CT band relative to the long-wave absorption maximum of amine ($\Delta\nu_A = \nu_1 - \nu_{CT}$). The data were obtained under the condition that concentrations of an acceptor and a donor were equal; for diamines this condition was fulfilled relative to the concentration of functional groups.

Table 2. Parameters of complexes between amines and CBr_4

Amine	λ_{CT}/nm	D_{max}	$\Delta\nu_{1/2}$/cm^{-1}	$\Delta\nu_A$/cm^{-1}
1b	352	0.22	2880	5030
1c	360	0.21	2720	5580
2a	341	0.19	2610	5880
2b	363	0.15	3040	6120
2c	355	0.18	3040	5350
2d	356	0.15	3040	5270

It can be seen from the data in Table 2 that the effect observed in the case of compound **2a** is opposite to the expected effect, *i.e.*, an 11-nm hypsochromic shift of the CT band relative to the band of **1b** is observed instead of the bathochromic shift. It turned out that complex **2b** has the longest-wave absorption (Fig. 2, for convenience of comparison the differential spectra are normalized to a maximum), and further increase in *n* results in a decrease in the shift of the CT band relative to **1b**. As a result, the ν_{CT}—*n* dependence is not monotonic, but zigzag-like (Fig. 3, curve *1*). The same effect can be observed (although in a smoother form)

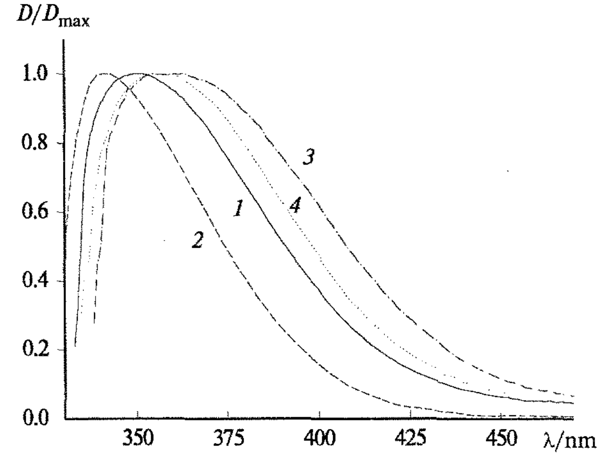


Fig. 2. Differential absorption spectra of complexes of amines **1b** (*1*), **2a** (*2*), **2b** (*3*), and **2d** (*4*) with CBr_4 in toluene normalized to a maximum ($[CBr_4]$ = [**1b**] = 0.07 mol L^{-1}, [**2a—d**] = 0.035 mol L^{-1}).

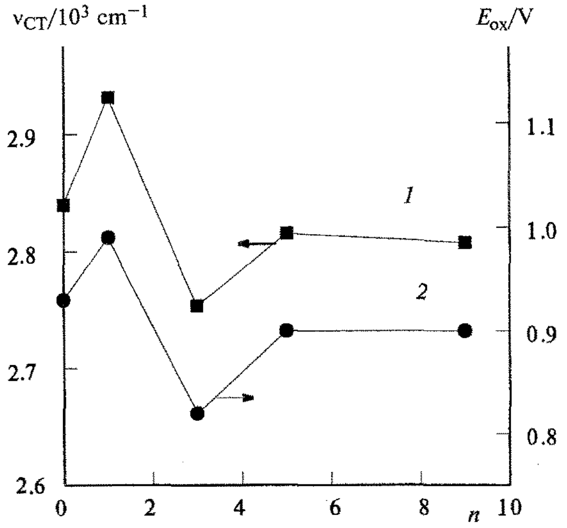


Fig. 3. Dependence of the frequency of the charge-transfer band ν_{CT} (*1*) and the oxidation potential of the amine E_{ox} (*2*) on the number of methylene groups in diamines **2a—d** (the value for monoamine **1b** is accepted as the zero point).

when the position of the CT band of the CT complex relative to the long-wave absorption band of the amine itself ($\Delta\nu_A$) is used as a parameter for comparison (see Table 2). An increase in n results in a smooth decrease in the $\Delta\nu_A$ value; however, the value for **2a** drops out of this regularity.

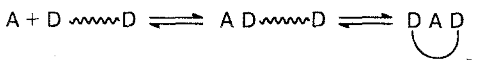
Two reasons are possible for such a deviation: the proportionality between $h\nu_{CT}$ and E_{HOMO} is not fulfilled or the proportionality between the value of the HOMO splitting (ΔE_{HOMO}) and the length of the methylene bridge is distorted. The first reason can be excluded, because the $h\nu_{CT}$ and E_{ox} values are linearly correlated according to the following equation: $h\nu_{CT} = 1.28E_{ox} + 2.35$ ($r = 0.95$).

The fact that Eq. (1) is fulfilled for amines studied testifies that, first, when the CTC is formed an acceptor interacts with the generalized HOMO of diamine and, second, the distortion of the monotonic character of the dependence of ΔE_{HOMO} on n is the reason for the hypsochromic shift of the CT band of complex **2a**. Since the value of splitting of interacting MO depends substantially on their orientation, it can be assumed that in the case of **2a** it is difficult to achieve a conformation favorable for the maximum interaction due to a small length of the bridge and bulky chromophoric groups. It is evident that this is an effect of the nonplanar structure of diphenylamine fragments, as in absorption spectra. In addition, peculiarities of the molecular structure of compound **2a** are also manifested in the fact that its complex has the narrowest CT band (see Table 2).

Now let us consider how the data obtained agree with the results of Ref. 4, which show that complexes of 2 : 1 composition have a lower energy of the CT band compared to that of complexes containing the same components but of 1 : 1 composition. Since the optical density of the CT band at the maximum, D_{max}, is proportional to the product of the concentration of the complex and its molecular absorption index (m.a.i.), assuming that variations of m.a.i. are not too large in the series of related complexes, analysis of the values of D_{max} measured under the same conditions (see Table 2) allows one to conclude that concentrations of the complexes are comparable. Therefore, stages of complex formation processes in reactions of mono- and bifunctional donors can be compared.

In the first case, the 1 : 1 complex is formed first, and the presence of a sufficient amount of a donor is needed for the formation of the 2 : 1 complex. Both of the stages of the reaction are bimolecular. When the concentration of a donor increases, *i.e.*, under the conditions which favor the formation of the 2 : 1 complex, the shift of the CT band toward lower wavelengths is observed.[3]

$$\mathrm{A + D \rightleftharpoons AD \overset{D}{\rightleftharpoons} DAD}$$

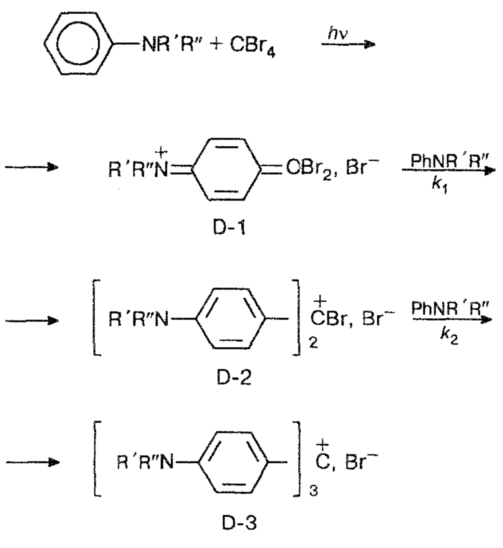


It is likely that in the second case the coordination of an acceptor with one of a donating groups occurs first as well. The formation of the complex of the 2 : 1 functional composition requires the intramolecular interaction, which is hindered for diamine **2a** due to a short bridge and becomes unfavorable at $n > 3$ because of entropy restrictions. Therefore, it turned out that the structure of diamine **2b** is the optimum for the formation of the intramolecular complex of the 2 : 1 composition, and the absorption spectrum of this complex exhibits the maximum bathochromic shift relative to the absorption maximum of **1b**. The similarity of the values of the bathochromic shift of complexes of two types also corresponds to the general character of complex formation processes: 900 cm^{-1} for the intramolecular complex of the 2 : 1 composition and 1000 cm^{-1} for the intermolecular complex.[3]

Thus, in the 2 : 1 complex with a monofunctional donor, an acceptor is the main component, which provides interaction of the MO of two donors resulting in an increase in the energy of the HOMO of the molecular system formed,[4] and this interaction disappears when the complex is decomposed. In the 2 : 1 complex with a bifunctional donor, an acceptor only facilitates the splitting of the MO of two covalently linked groups, which already occurs independently of an acceptor. Nevertheless, both cases result in bathochromic shift of the CT band of the 2 : 1 complex relative to the band of the similar or model complex of 1 : 1 composition.

Photochemical reactions

It is known that UV irradiation of complexes between CBr_4 and DPA derivatives, whose molecules contain benzene rings unsubstituted at the *para*-position, results in the subsequent formation of mono-, di-, and then triphenylmethane dyes (D-1, D-2, and D-3, respectively); the two latter dyes exhibit absorption bands in the 650—670 and 580—610 nm ranges.[12]



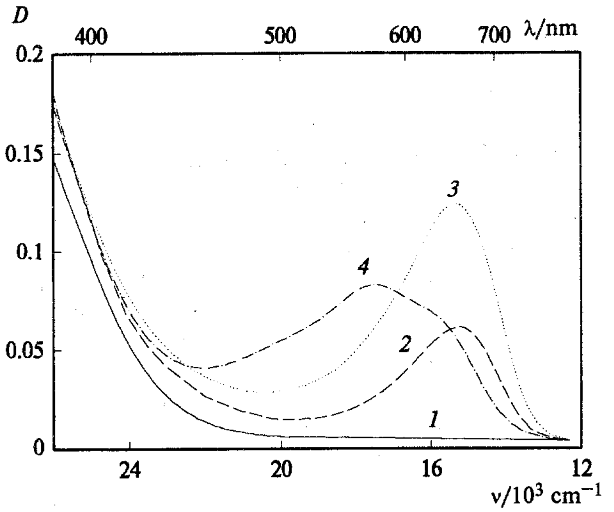


Fig. 4. Absorption spectra of the mixture of **2c** (0.035 mol L^{-1}) and CBr_4 (0.07 mol L^{-1}) in toluene: *1,* initial; *2,* after irradiation at λ = 365 nm (40 mJ cm^{-2}); *3,* spectrum *2* in 30 min; *4,* spectrum *3* in 3 h.

Spectral changes observed during irradiation (λ = 365 nm) of the diamine—CBr_4 CTC are shown in Fig. 4 by the example of compound **2c**. Spectrum *1* characterizes the integral absorption of the reaction mixture before irradiation and corresponds to the sum of spectra of the initial components and the complex between them. Spectrum *2* was recorded immediately after irradiation, then (in dark) during 30 min it was transformed to spectrum *3* with the absorption maximum at 655 nm, and then (in 3.5 h) it was transformed to spectrum *4* with the main maximum at 570 nm.

The photoinduced reaction of formation of the "Opal blue" (OB) triphenylmethane dye upon irradiation of the DPA—CBr_4 CTC has previously[13,14] been studied in detail. The kinetics of the formation of the intermediate D-2 and its further transformation to the final OB (D-3) have been studied. Since the reaction occurs in an excess of amine, the formation of the D-2 dye and its transformation to OB correspond to the kinetics of the pseudo-first order, and the calculated values of bimolecular constants are 3.5 and 0.014 L mol^{-1} s^{-1} (toluene, 25 °C), respectively.[14] The study of the kinetics of spectral changes in the case of the **2c**—CBr_4 complex shows that both an increase in the optical density at 655 nm and its subsequent decrease accompanied by the parallel increase in D_{570} are exponential. Taking into account, first, the analogy of the photochemical behavior of complexes between DPA and **2c**; second, the similarity of spectral parameters of photogenerated dyes; and, third, the fact that the spectral changes observed obey the same kinetic law, it can be suggested that spectrum *3* (see Fig. 4) relates to the D-2 type dye, while spectrum *4* relates to the D-3 type dye, and reactions of their formation are also bimolecular and involve additional amine molecules. In this case, the estimations of the corresponding bimolecular constants give the values $k_1 \approx 4 \cdot 10^{-2}$ L mol^{-1} s^{-1} and $k_2 \approx 8 \cdot 10^{-3}$ L mol^{-1} s^{-1} (toluene, 22 °C). The comparison with the rate constants of the formation of OB shows that in the case of **2c** both thermal reactions are retarded, and the retardation of the formation of D-2 is especially substantial.

However, it should be taken into account that assignment of spectra *3* and *4* to the corresponding dyes and consideration of reactions of their formation as bimolecular reactions are only preliminary. Since in the molecule of **2c** two diphenylamine functional groups are separated by the flexible and rather long chain of bonds, not only the intermolecular mechanism of the reaction discussed (involving the second amine molecule) takes place, but the intramolecular mechanism (involving the second amine residue of the same molecule of **2c**) is possible as well. To elucidate the real nature of photoinduced thermal transformations of complexes between diamines and CBr_4, more detailed studies of the kinetics of these reactions and the structures of dyes formed are necessary.

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Thus, the study of absorption spectra, oxidation potentials, and spectra of CTC with diphenylamine derivatives shows that when the linking chain contains more than five methylene groups, two Ph_2N fragments almost do not interact. It is noteworthy that all these parameters are related in fact to chromophores in the ground electron state. The interaction of such chromophores in the excited state is of doubtless interest. It is likely that, as in the case of other intramolecular exciplexes,[15] manifestation of the "rule of number 3" should be expected (*i.e.,* an especially strong interaction of a bichromophoric compound with three methylene groups). It is unambiguous that steric hindrance created by functional groups in a compound with one methylene group will appear for excited states. In addition, an excited state usually exhibits a farther interaction than a ground state. For example, an electron is transferred within 13 Å with a rate of up to 10^{11} s^{-1} (Ref. 2). These problems will be the subject of our further investigation.

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References

1. E. I. Brodskaya, G. V. Ratovskii, and M. G. Voronkov, *Usp. Khim.*, 1993, **62**, 975 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
2. M. N. Paddon-Row, *Acc. Chem. Res.*, 1994, **27**, 18.
3. M. F. Budyka, A. G. Rachinsky, and M. V. Alfimov, *Chem. Phys. Lett.*, 1991, **181**, 59.
4. M. F. Budyka and N. D. Sokolov, *Khim. Fiz.*, 1994, **13**, No. 12 [*Russ. Chem. Phys.*, 1994, **13**, No. 12 (Engl. Transl.)].

5. Brit. Pat. No. 1452318, Cl. C07C 85/00, 1976.
6. J. Forest, D. A. Lidell, and S. H. Tucker, *J. Chem. Soc.*, 1946, 454.
7. D. Steinborn, *J. Organomet. Chem.*, 1979, **182**, 313.
8. A. M. Halpern, M. W. Legenza, and B. R. Ramachandran, *J. Am. Chem. Soc.*, 1979, **101**, 5736.
9. G. D. Scholes, K. P. Chiggino, A. M. Oliver, and M. N. Paddon-Row, *J. Am. Chem. Soc.*, 1993, **115**, 4345.
10. R. J. Mulliken and W. B. Person, *Molecular Complexes. A Lecture and Reprint Volume,* Wiley, New York, 1969, 498.
11. *Organic Electrochemistry,* Ed. M. M. Blaizer and H. Lund, Marcel Dekker, New York, 1983.
12. M. F. Budyka and M. V. Alfimov, *Usp. Nauchnoi Fotografii* [*Advances in Scientific Photography*], 1989, **25**, 97 (in Russian).
13. R. H. Sprague, H. L. Fichter, and E. Wainer, *Photogr. Sci. Eng.*, 1961, **5**, 98.
14. M. F. Budyka and O. D. Laukhina, *Kinet. Katal.*, 1989, **30**, 1293 [*Kinet. Catal.*, 1989, **30** (Engl. Transl.)].
15. E. I. Kapinus, *Fotonika molekulyarnykh kompleksov* [*Photonics of Molecular Complexes*], Naukova Dumka, Kiev, 1988, 256 (in Russian).

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