ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 556−562. © Pleiades Publishing, Ltd., 2009.
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PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Hydrogen Transfer in the Reaction of *p*-Phenylenediamine with Chloranil

K. K. Kalninsh and G. M. Makhov

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

Received January 21, 2008

Abstract—Stage of electron transfer between *p*-phenylenediamine and chloranil in methanol was studied and a strictly reversible redox conversion of reagents was observed at low temperatures of –50 to –90°C. At positive temperatures, the proton transfer initiates a polycondensation yielding a polyaminoquinone of brown color. The nature of the absorption bands of charge-transfer complexes in the visible spectral range is discussed. Quantum-chemical calculations of excited reaction complexes and of absorption spectra of polyaminoquinone were performed.

DOI: 10.1134/S1070427209040053

Direct experimental observation of the stage of electron transfer in reaction of primary aromatic amines containing a mobile hydrogen atom N–H is complicated by the rapidly occurring succeeding stage of proton transfer, which ends in the formation of the reaction product. To reactions of this kind belong reactions of aromatic amines with anhydrides and quinones [1–3], in whose course no radical species are commonly formed. In contrast to primary amines, N-substituted amines can be oxidized to the corresponding cation-radicals, which can be detected spectrophotometrically or by the EPR technique. The best known of these amines, *N,N,N*',*N*'-tetramethyl-*p*-phenylenediamine (TMPD), one of the strongest organic electron donors with an ionization potential of 6.4 eV [4], easily loses an electron to be converted into a cation-radical $\mathrm{TMPD}^{\cdot+}$, known as “Wurster’s blue.” The $\mathrm{TMPD}^{\cdot+}$ cation-radical in a polar medium, e.g., in acetonitrile, is stable during a long time at room temperature.

Oxidation of primary amines as a successive transfer of an electron and a proton (in all, a hydrogen atom) was considered by Terenin for the example of *p*-phenylenediamine or benzidine [5]. Separate stages of electron and proton transfer can be observed under deep cooling, when cation-radicals formed in the primary stage spontaneously abstract a proton. In later years, this standpoint concerning the mechanism of hydrogen transfer has been confirmed in studies of photochemical reactions. It has been demonstrated by means of time-resolved pulsed spectroscopy that hydrogen phototransfer occurs in excited complexes, exciplexes. Transfer of an electron in the first stage leads to formation of ion-radicals, and, further, these species are converted in the stage of proton transfer to free radicals. In a particular case of crystalline quinone–hydroquinone complexes (quinhydrones), the thermal transfer of hydrogen can also be justly regarded as an excited-state reaction [8–10], because the activation energy of the thermal reaction, E_a, is close to the energy of optical charge transfer. The role of the hydrogen bond in the huge decrease in the energy of the excited state of the molecular complex was discussed in [11, 12].

Dimers of the cation-radicals $p\mathrm{PD}^{\cdot+}$ and $\mathrm{TMPD}^{\cdot+}$ are converted to diamagnetic complexes via electron pairing [13]. The dimerization gives rise to a new band of intermolecular charge transfer in the low-frequency part of the electronic spectrum and to a blue shift of intramolecular transitions [14]. It has been found that the dimerization reaction is characterized by a small heat (5–8 kcal mol^{-1}) and, for this reason, can only be recorded at low temperatures (in methanol or ether).

In this study, the reaction of electron-and-proton transfer between *p*-phenylenediamine (*p*PD) and chloranil (Chl) was analyzed experimentally and by means of quantum-chemical calculations, and the dimerization of the cation-radicals $p\text{PD}^{\cdot+}$ and $\text{TMPD}^{\cdot+}$ was considered.

EXPERIMENTAL

The electronic absorption spectra were obtained on an M-40 spectrometer with the use of a low-temperature setup in which an evacuated quartz cuvette with a thickness of 1 cm was cooled with a liquid nitrogen vapor. The reagents used were purified by sublimation.

The quantum-chemical calculations were made using RHF, ROHF, B3LYP/6-31G*, and DH methods by GAMESS software [15]. The procedure employed in the quantum-chemical calculations of molecules in the ground and excited S1 and T1 states was described in [16]. In calculations of the full energies, a correction was made for the energy of zero vibrations.

In the electronic absorption spectra of solutions of an equimolar mixture (2.5×10^{-4} M) of *p*PD and Chl in methanol at low temperature (–94°C), we observed immediately after mixing an absorption band at 13600 cm^{-1}, whose frequency satisfies the known relation

$$E_{\text{CT}} = I - E_{\text{A}} - W, \tag{1}$$

where E_{CT} is the charge-transfer energy; I_{D}, donor ionization potential; E_{A}, electron affinity of the acceptor; and W, coulomb term equal to approximately 3–3.5 eV.

If we use the tabulated values of I_{D} and E_{A} for *p*PD and Chl [4], we obtain $E_{\text{CT}} = 6.9 - 2.5 - 3 = 1.4$ eV or 11285 cm^{-1}, which gives reason to attribute this band to charge (electron) transfer between *p*PD and Chl. In the first stage, the interaction of the strong electron donor *p*PD and strong electron acceptor Chl has a typically donor-acceptor nature and is accompanied by the appearance of a charge-transfer band in electronic spectra.

A short-time heating of a solution of the complex in methanol to –20°C activates an electron transfer

$$p\text{PD} = \text{Chl} \overset{K_{\text{eq}}}{\rightleftarrows} p\text{PD}^{\cdot+}...\text{Chl}^{\cdot-} \tag{2}$$

If the mixing is made at room temperature, a group of bands immediately appears in the absorption spectrum. These bands are related to $p\text{PD}^{\cdot+}$cation-radicals (20200, 21600 cm^{-1}) and $\text{Chl}^{\cdot-}$ cation-radicals (22200 and 23600 cm^{-1}) and are components of the corresponding electronic-vibrational bands (Fig. 1). The high electron-transfer rate is accounted for by the low energy of the excited level, equal to 1.69 eV (13600 cm^{-1}) for the vertical transition in the absorption spectra. To estimate the energy of the equilibrium state, this value should be diminished by the vibrational relaxation energy (~0.5 eV) and by the energy of solvation of the polar excited state by methanol molecules $(p\text{PD}^{\cdot+}...\text{Chl}^{\cdot-})^*$ (~0.8 eV). As a result, we obtain a low-lying excited level below 0.4 eV, of the type of an ion-radical pair, which is effectively occupied under standard conditions.

At low temperatures, a strictly reversible equilibrium is observed in a certain temperature interval (Fig. 1) between the starting molecules and their ion-radical forms [Eq. (1)], which is indicated by the existence of two isosbestic points at frequencies of 19400 and 22000 cm^{-1}. At these points, the rate of variation of the optical density with temperature is zero. On lowering the temperature, the intensity of the absorption bands of the ion-radicals at 20000–24000 cm^{-1} decreases, and, consequently, their concentration becomes lower. Simultaneously increases the intensity of two other bands, at 26000 and 15000 cm^{-1}, which can be attributed with confidence to dimers of ion-radical pairs:

$$2(p\text{PD}^{\cdot+}...\text{Chl}^{\cdot-}) \overset{K_{\text{eq}}}{\rightleftarrows} (p\text{PD}^{\cdot+}...\text{Chl}^{\cdot-})_2, \tag{3}$$

According to a study in which ion-radical salts of *p*-phenylenediamine and its methylated analogs were

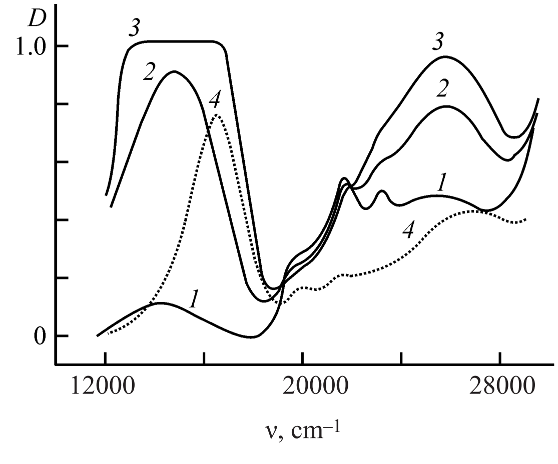


Fig. 1. Absorption spectra of a solution of an equimolar mixture of chloranil with *p*-phenylenediamine (2.5×10^{-4} M) in methanol. (*D*) Optical density and (ν) wave number; the same for Fig. 2. *T* (°C): (*1*) –53, (*2*) –78, (*3*) –94, and (*4*) –88 (Chl + *p*PD + acetic acid).

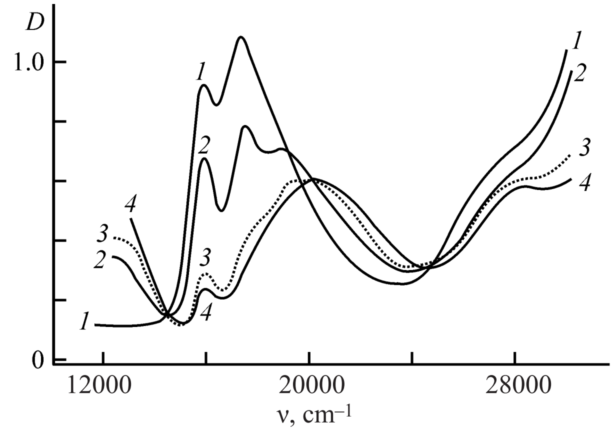


Fig. 2. Absorption spectra of an equimolar mixture of chloranil with TMPD in tetrahydrofuran. T (°C): (*1*) 0, (*2*) –63, (*3*) –85, and (*4*) –97.

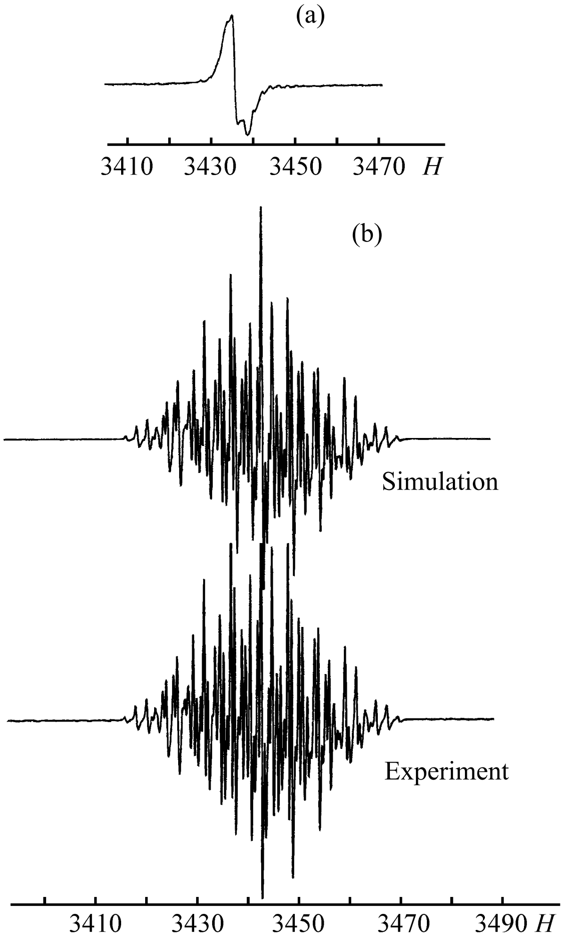


Fig. 3. EPR spectra of a mixture of chloranil and p-phenylenediamine in methanol at (a) –103 and (b) +17°C.

examined [14], to pPD$^{\cdot+}$ cation-radicals is related, in addition to the structured absorption at 20000 cm^{-1} (R band), a strong band at 31000 cm^{-1} (Y band). The dimers (pPD$^{\cdot+}$)$_2$ absorb at 16500 (C band), 26000 (R' band), and 36000 cm^{-1} (Y' band) and have the form of pairs of radical molecules in a plane-parallel arrangement, surrounded by Cl$^-$, Br$^-$, or ClO$_4^-$ anions. Of particular interest is the C band in the near-IR region, which is attributed to charge transfer between π-systems of two pPD$^{\cdot+}$ molecules. The increase in the intensity of this band upon solution cooling is accompanied by a decrease in the paramagnetism of the system [13], which points to pairing of electrons of two radical species to give a diamagnetic π-complex (pPD$^{\cdot+}$)$_2$.

The temperature dependence of the spectrum in Fig. 1 indicates that both radical species are involved in the dimerization of the ion-radical pair pPD$^{\cdot+}$...Chl$^{\cdot-}$: on cooling the solution, the intensities of the bands of pPD$^{\cdot+}$ at 20000 cm^{-1} and Chl$^{\cdot-}$ at 23000 cm^{-1} are redistributed in favor of two broad bands having no vibrational structure, at 15000 and 26000 cm^{-1}. This case differs from that considered in [14], in which dimerization of the ion-radical salt pPD$^{\cdot+}$X$^-$ leads to pairing of cation-radicals, and counter ions X$^-$ only form an ionic "coat" and diminish the electrostatic repulsion between pPD$^{\cdot+}$ molecules. It can be assumed that the dimers (pPD$^{\cdot+}$... Chl$^{\cdot-}$) are constituted by [(pPD$^{\cdot+}$)$_2$...(Chl$^{\cdot-}$)$_2$] pairs bound together by electrostatic forces, with a plane-parallel arrangement of ion-radical molecules. This provides both pairing of ion-radicals, with transformation of radical complexes to a diamagnetic structure, and weakening of the electrostatic repulsion in the ion-radical pairs (pPD$^{\cdot+}$)$_2$ and (Chl$^{\cdot-}$)$_2$.

The broad strong band at 15000 cm^{-1} in low-temperature spectra of the pPD + Chl system (Fig. 1) should apparently be attributed to an intermolecular charge-transfer transition by analogy with (pPD$^{\cdot+}$)$_2$ dimers absorbing at a frequency of 16530 cm^{-1}. However, it was noted in [14] that the absorption spectrum is independent of the type of a counter ion: Cl$^-$, Br$^-$, or ClO$_4^-$. Therefore, the lower frequency (15000 cm^{-1}) for the dimeric complex (pPD$^{\cdot+}$...Chl$^{\cdot-}$)$_2$ is possibly due to interaction of two intermolecular transitions in the dimers (pPD$^{\cdot+}$)$_2$ and (Chl$^{\cdot-}$)$_2$. Another strong band at 26000 cm^{-1} (Fig. 1), which appears in low-temperature spectra of the pPD + Chl solution, is specific to the given system and cannot be unambiguously assigned. It can be assumed that this band is related to an electron transition in a complex of ion-radical species, associated with excitation of the anion-radical Chl$^{\cdot-}$.

It is of interest to consider low-temperature spectra of chloranil complexes with TMPD containing no mobile hydrogen atoms (Fig. 2). Mixing of solutions of a strong electron donor and electron acceptor, TMPD and chloranil, in tetrahydrofuran leads to almost instantaneous formation of equimolar concentrations of the corresponding ion-radicals, whose absorption spectra are known [14] and can be recorded at room temperature:

$$\mathrm{TMPD} + \mathrm{Chl}^{-} \overset{K_{\mathrm{eq}}}{\rightleftarrows} \mathrm{TMPD}^{\cdot+}...\mathrm{Chl}^{\cdot-} \qquad (4)$$

As temperature is lowered, the structured band of $\mathrm{TMPD}^{\cdot+}$ cation-radicals at 16000 cm^{-1} is shifted to 20000 cm^{-1}, thereby a weakly pronounced vibrational structure preserved. The blue-shifted band at 20000 cm^{-1} should be attributed, in accordance with the data of [14], to the dimers:

$$2(\mathrm{TMDP}^{\cdot+}...\mathrm{Chl}^{\cdot-}) \overset{K_{\mathrm{eq}}}{\rightleftarrows} (\mathrm{TMDP}^{\cdot+}...\mathrm{Chl}^{\cdot-})_2, \qquad (5)$$

Of particular interest is the low-frequency band peaked at 13000 cm^{-1}, which appears at low temperatures (Fig. 2) and obeys a strictly reversible equilibrium (two isosbestic points at 145000 and 24500 cm^{-1}) between the associates and monomeric forms. This band of intermolecular charge transfer should be attributed to a dimer of the cation-radical, $(\mathrm{TMPD}^{\cdot-})_2$ or to a dimer of the ion-radical pair, $(\mathrm{TMPD}^{\cdot+}...\mathrm{Chl}^{\cdot-})_2$.

Figure 3 shows EPR spectra of a mixture of *p*-phenylenediamine and chloranil in methanol at a temperature of –103°C, which is 6° lower than the melting point of the solvent, –97°C (–96.85°C). In the solid state of the *p*PD–Chl solution, a high-intensity spectrum is observed (Fig. 3a), which mostly constituted by an unresolved line at around 3436 G. Raising the temperature to –53°C leads to an increase in the intensity of the unresolved line and to appearance of a well-resolved spectrum probably belonging to the cation-radical of *p*-phenylenediamine. On raising the temperature further, to +17°C, the unresolved line disappears and the intensity of the resolved spectrum increases.

The conclusion that the spectrum belongs to the cation-radical of *p*-phenylenediamine was based on the group of equidistant lines observed in the peripheral part of the spectrum, with their intensity ratio close to 1 : 4 : 6 : 4 : 1. The spectrum is easily simulated: $a(4\mathrm{H}) = 6.00$, $a(2\mathrm{N}) = 5.30$, $a(4\mathrm{H}) = 2.14$ G. Heating the solution to positive temperatures $T > +50$°C leads to disappearance of the spectrum. The anion-radical of chloranil cannot be precisely identified on the basis of EPR spectra because of the small signal splitting on four chlorine atoms. Possibly, the broad unresolved line at around 3436 Gs related to $\mathrm{Chl}^{\cdot+}$.

An ab initio calculation of the Chl–*p*PD complex in an excited state yields a planar orientation of molecules (Fig. 4) bound by a strong hydrogen bond O...H–N (1.59 Å). In the excited state, there occurs a full electron transfer ($\Delta q = 0.91$) between amine and chloranil molecules, which are thereby transformed to the corresponding ion-radicals. Estimation of the energy of the excited state by the quantum-chemical method RHF, ROHF/DH yields a small negative value of –1.97 kcal mol^{-1}, with the effect of the solvent (methanol) taken into account in terms of the PCM method, which points to an exceedingly easy occurrence of the redox reaction. This value agrees with the above estimate of the energy of the excited state (<0.4 eV) in view of the electron-donor-acceptor properties of the components and the solvation energy of the ion-radical pair.

Thus, the interaction of a strong electron acceptor, chloranil, with a strong electron donor, *p*-phenylenediamine, or its methylated analog TPMD in the polar medium of methanol is accompanied in stage 1 by an intermolecular electron transfer to give ion-radicals $\mathrm{Chl}^{\cdot-}$ and $p\mathrm{PD}^{\cdot+}$ ($\mathrm{TMPD}^{\cdot+}$). At low temperatures (–50 to –90°C), there occurs a strictly reversible equilibrium between the starting reagent and ion-radical species, with new unconventional forms involved in the equilibrium. These are associates of ion-radical species absorbing in the near-IR region and possessing no paramagnetism because of the opposite orientations of spins of unpaired electrons. It is known from the literature that, when an electron donor is simultaneously a proton donor, the electron transfer to give radical species cannot be observed most frequently because of the rapidly succeeding proton transfer. The *p*PD–Chl donor-acceptor pair belongs to not numerous complexes that demonstrate in the pure form the electron transfer that precedes the proton transfer and the formation of a new chemical bond.

On elevating temperature to $T > 0$°C, in stage 2, a proton transfer from the $p\mathrm{PD}^{\cdot+}$ cation radical to $\mathrm{Chl}^{\cdot-}$ is initiated and is accompanied by the formation of a new chemical bond N–C and splitting-off of an HCl molecule. The energy diagram in Fig. 4 shows the spatial structure of the reaction complexes in the excited electron state. It can be seen that largest energy expenditure is required in stage 2, when the N–C bond is formed. It is this value that apparently is the activation energy of the overall

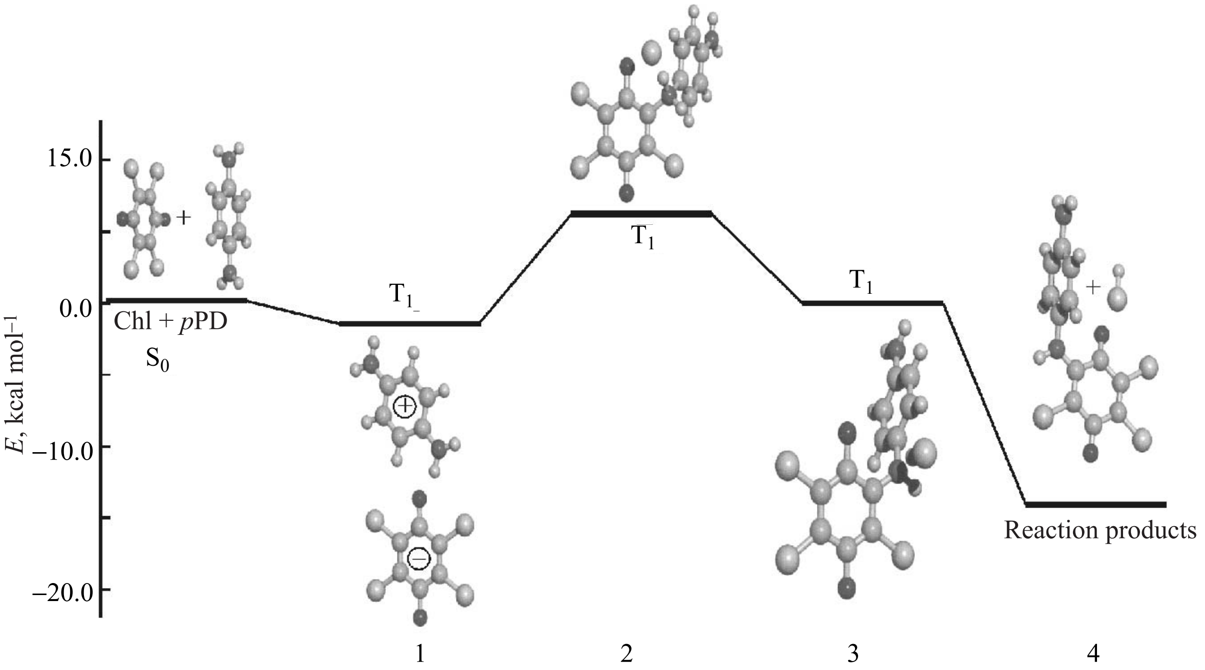
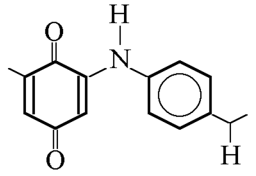


Fig. 4. Energy diagram of the reaction of chloranil with p-phenylenediamine according to the results of an ab initio calculation by the RHF, ROHF/DH method. (E) Full energy relative to the level of free reactants. (1–4) Elementary stages of the reaction.

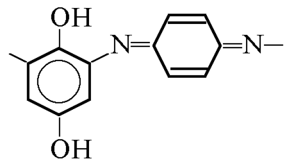
chemical process. Abstraction of a hydrogen atom from the amino group and its binding with a chlorine atom in the third stage does not require any energy expenditure and occurs spontaneously.

The above scheme, which follows from spectroscopic data and is supplemented with a quantum-chemical analysis, gives a semiquantitative description of the reaction between chloranil and p-phenylenediamine. Stage 1 can be clearly distinguished experimentally from the succeeding transformations 2–4. However, this does not mean that stage 2 is necessarily preceded by electron transfer 1. At the level of elementary chemical events, a situation can be imagined in which the formation of a new chemical bond between pPD and Chl molecules and proton transfer constitute, together with the electron transfer, a single process and separate stages 1–4 cannot be distinguished experimentally. At the same time, it is extremely important to note that the experimental observation of ion-radical species demonstrates the fundamental significance of the electron-transfer stage in chemical reactions between reagents whose molecules contain mobile hydrogen atoms N–H or O–H.

The reaction of Chl polycondensation with pPD yields as the product a brown polyaminoquinone absorbing in the visible spectral range at a frequency of 22000 cm^{-1}. The IR spectrum of the polymer shows no characteristic carbonyl absorption of quinone at 1630–1650 cm^{-1}. These data indicate that the reaction product has a quinonediimine structure (II) formed from the initial structure (I) via an intramolecular hydrogen transfer:



(I)



(II)

At the same time, according to the results of a semi-empirical calculation (by the PM3 method), isomer (II) is less energetically favorable: by 11.1 kcal mol^{-1} for the 1Chl–2pPD molecule under vacuum conditions as compared with (I), and the difference of the enthalpies of these two forms increases as the polymer chain becomes longer. For example, for 3Chl–4pPD molecules (Fig. 5), this difference in favor of structure (I) is already 33.4 kcal mol^{-1}. It can be assumed that, in a real solution in methanol, the quinonediimine structure (II) is stabilized by interaction with the solvent to a greater extent, compared with structure (I). In addition, analysis of electronic absorption spectra shows that, according to a calculation (see table), transitions associated with both structures fall within the spectral range 22000–24000 cm^{-1}, in which the strong experimental band is observed at 22000 cm^{-1}. However, for one of these, structure (II),

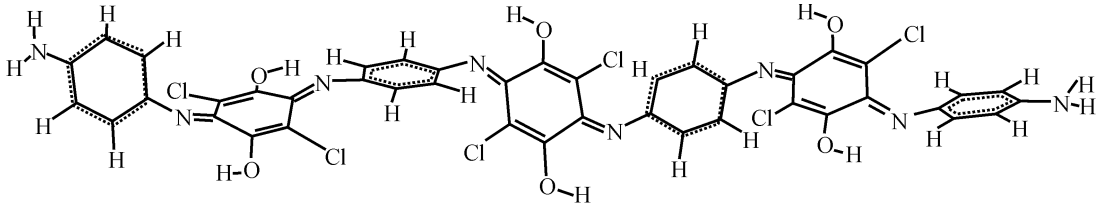


Fig. 5. Calculated structure of the reaction product 3Chl–4*p*PD; PM3 method, GAMESS.

the intensity of transitions is by an order of magnitude higher. These considerations make it possible to assign the band at 22000 cm^{-1} to the quinonediimine structure (II) of the product formed in the reaction of chloranil with *p*-phenylenediamine. In the calculated spectra of this structure (see table), an exceedingly intense electron transition is observed at around 23000 cm^{-1} for oligomeric molecules containing four to five monomer units Chl–*p*PD, whereas structure (I) is characterized by several medium-intensity transitions in the higher-frequency range 25000–28000 cm^{-1}.

CONCLUSIONS

(1) A reversible reaction of electron transfer between a strong electron-and-proton donor *p*-phenylenediamine and a strong electron-and-proton acceptor chloranil was studied. In the course of this reaction, intermediate ion-radical species and their associates are formed in methanol at low temperatures.

(2) At positive temperatures, the proton transfer is activated and the condensation reaction occurs to give a brown polyaminoquinone. The energy diagram of the reaction was constructed on the basis of the results of ab initio quantum-chemical calculations.

Calculated absorption spectra of oligomers of polyaminoquinone *n*Chl–(*n* + 1)*p*PD; ZINDO/S method, configuration optimization by the PM3 semiempirical method, GAMESS

Molecule	ν, cm^{-1}		
	calculation		experiment
Structure (I)			
1Chl-2*p*PD	25807 (0.14)[b]	35168 (0.43)	25400
1Chl-2*p*PD	23866 (0.00)	32051 (0.73)	
2Chl-3*p*PD	25583 (0.21)	26429 (0.15)	
3Chl-4*p*PD	25874 (0.17)	26553 (0.10)	
4Chl-5*p*PD	25830 (0.12)	28022 (0.08)	
5Chl-6*p*PD	25530 (0.07)	26133 (0.14)	
Structure (II)			
1Chl-2*p*PD	22727 (0.01)	32258 (1.37)	22000
1Chl-2*p*PD[a]	20231 (0.47)	31124 (1.32)	
2Chl-3*p*PD	23572 (0.29)	32305 (1.86)	
3Chl-4*p*PD	23264 (1.16)	33456 (1.95)	
4Chl-5*p*PD	23148 (1.54)	33980 (2.77)	
5Chl-6*p*PD	23332 (1.69)	34331 (2.13)	

[a] Configuration optimization by the RHF/DH ab inito method.
[b] In parentheses, oscillator strength.

ACKNOWLEDGMENTS

The authors thank M.P. Bubnov (Nizhni Novgorod State University) for assistance in analysis of EPR spectra.

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