MOLECULAR COMPLEXES OF 3,3',5,5'-TETRAHALO-4,4'-DIPHENOQUINONES. 1. SYNTHESIS AND PROPERTIES OF 3,3',5,5'-TETRAHALO-4,4'-DIPHENOQUINONES

> Yu. P. Popov, V. P. Litvinov, and I. L. Sokol'skaya

Compounds such as charge-transfer complexes (CTC) and radical-ion salts have several unusual properties, including relatively high photosensitivity over a wide spectral range, clear anisotropy of their properties, a wide range of electrical conductivity, and interesting luminescence properties [1-3].

Various halogen derivatives of benzoquinone and diphenoquinone are quite strong π acceptors [4]; the CTC's of varied stoichiometry of tetrahalo-p- and -o-benzoquinones are best known and most widely used. Their synthesis and properties have been rather extensively described in the literature [1-7]. Information on tetrahalodiphenoquinones (I) is lacking or extremely limited and contradictory.



Magatti [8] prepared 3,3',5,5'-tetrachloro- and 3,3',5,5'-tetrabromodiphenoquinones (Ia) and (Ib) by halogenation of 4,4'-diphenol and oxidation of the synthetic product with concentrated HNO_3 . The report omitted any description of the course of the reaction, data on the yields of the intermediates and final products, and information on the physical properties [8]. Attempts to use this method for the preparation of 3,3',5,5'-tetraiododiphenoquinone (Ic) were unsuccessful because of the problem of separating the difficultly separable oxidation products [9, 10].

On the basis of analysis of the iodination products of phenols in alkaline medium [11], Kammerer and Benzinger assigned the product, which has received the name "Lautemann red," the structure (Ic) [12]. In support they gave an analysis of the reaction schemes rather than a specific description of their course and characterization of the products. Hunter and Morse [9] have questioned their work [12] and reported the preparation of (Ic) by rapid oxidation of potassium triiodophenolate in 5.6% yield. Woollett et al. prepared 3,3',5,5'tetraiodo-4,4'-diphenol in 31% yield by rapid oxidation of 2,6-diiodophenol in weakly alkaline medium, using Cr_2O_3 as oxidant [10].

Our intention in the work reported here was to synthesize the new acceptor 3,3',5,5'tetrafluoro-4,4'-diphenoquinone (Id) and to make a complex study of the properties of 3,3',5,5'-tetrahalodiphenoquinones (Ia-d) by various physicochemical techniques.

DISCUSSION

Analysis of the electronic absorption spectra (EAS) of the synthetic acceptors in films, the fluorescence excitation spectra (FES) of their radical anions in films, and the EAS of the radical anions generated polarographically in solution (Figs. 1 and 2 and Table 1) revealed some of their distinctive features.

The EAS from 200 to 1587 nm contain three relatively intense bands and a long-wavelength tail at 667-1587 nm. The most intense long-wavelength band undergoes a bathochromic

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2279-2283, October, 1980. Original article submitted November 28, 1979.

1597

UDC 541.49:542.91:547.567.3

Com- pound	Color	E_A, eV	Film absorp- tion, nm		Fluorescence excitation spectrum of radical anion, nm		Absorption spec- trum of radical anion, nm long-wave-			Absorp- tion threshold,
			IMCT	p- band	IMCT	p- band	ima I	III II	IMCT	eV
(Id) (Ia) (Ib) (Ic)	Lilac Purple Criinson Dark green	$2,78 \\ 2,80 \\ 2,82 \\ 2,85 $	440 459 488 524	411 427 449 476	453 475 496 535	$410 \\ 427 \\ 446 \\ 476$	772 887 984 1149	682 781 842 962	455 475 498 535	1,32 1,09 0,97 0,78

TABLE 1. Luminescence Properties of 3,3',5,5'-Tetrahalo-4,4'-diphenoquinones



Fig. 1. Electronic spectra of a) (Id), b) (Ia), c) (Ib), and d) (Ic): 1) absorption of a thin film of the acceptor; 2) absorption of the radical anion of the acceptor in CHCl₃ solution; and 3) fluorescence excitation of the radical anion of the acceptor in a thin film.

shift in accordance with the polarizing effect of the halo substituent: 411 nm (Id), 427 nm (Ia), 449 nm (Ib), and 476 nm (Ic). The nature of the polarization of this band (polarized roughly perpendicular to the long axis of the molecule) and the low sensitivity to excitation suggest assignment as the p-band, using Clar's classification for heterosubstituted compounds.

Recently, the absorption bands due to intramolecular charge transfer (IMCT) have been conventionally set in a special category (they can be identified with the scheme of intermolecular charge-transfer bands) [13]. By this criterion, we can assign the longer wavelength and less intense (in the ground state) band located next to the p-band with maximum at 440 nm (Id), 459 nm (Ia), 478 nm (Ib), and 524 nm (Ic), both from the polarization and the sensitivity to excitation, to the IMCT band due to the electronic transitions of the halogen lone pair in the diphenoquinone π system (Fig. 1). In the fluorescence excitation spectrum (with λ_{ex} 239 nm) λ_{max} of the IMCT undergoes a slight long-wavelength shift (greatest in (Ia)) and the intensity of the IMCT band generally increase. Since for electronic transitions of this type [13] the involvement of the ground and first IMCT excited states is most probable [14], we would expect that the weight of each state would substantially affect the position, shape, and intensity of the IMCT band. Moreover, we cannot discount the effect of the vibronic states of the molecule. Both these factors seem to be involved, together with the electronic structure of the of the 3,3',5,5'-tetraholodiphenoquinones, with the interaction in the extended m-conjugated system, the increase in the inductive effect in the order F > C1 > Br > I, and the IMCT of the halogen lone pair in the diphenoquinone π system. These features of the electronic structure of 3, 3', 5, 5'-tetrahalodiphenoquinone in turn determine the ease of conversion to the radical-anion state. The film FES of the synthetic radical anions of the acceptors are almost identical in the short-wavelength region with the EAS of these radical anions of the acceptors generated polarographically in solution. The long-wavelength absorption maxima of the radical anions in solution are localized in the region of the long-wavelength tail of the film absorption of the acceptor, which is also the case for the radical anion of the strong π -acceptor 7,7',8,8'-tetracyanoquinodimethane. This seems to be a typical feature of extended quinoid systems. Moreover, in the long-wavelength region the film absorption thresholds of the acceptor and its radical anion in solution are identical. This could be used to identify the absorption threshold of compounds of related series in the solid state.

Polarography of (Ia)-(Id) gave the half-wave redox potentials $E_{1/2}$, V: +0.32 (Id), +0.34 (Ia), +0.36 (Ib), and +0.39 (Ic), which are in good agreement with the values of $E_{1/2}$ found earlier for (Ia) and (Ib) [2, 3]. Figure 3 shows the dependence of $E_{1/2}$ on the electron affinity of (I). If we consider the absolute value of $E_A = 2.80$ eV for (Ia) to be accurate [2], we can easily find E_A for the other (I) from the linear dependence (Table 1). In general the polarographic behavior of the series (Ie), (Id), (Ia), (Ib), (Ic) is typical of halo anils [15].

The EAS of (Ie) shows a very big long-wavelength shift relative to the diphenol (Figs. 1d and 2). The absorption of the diphenols in the shorter-wavelength region relative to the diphenoquinones is caused by the reduction in the π conjugation as a result of the exclusion of the 0 atom from the conjugated system.

When the phenols contain groups with opposed strong donor (hydroxyl or amino) and acceptor (nitro) functions, the EAS in solution and in films generally show a very long-wavelength absorption band due to the intermolecular donor-acceptor interaction of these groups,



Fig. 2. Electronic absorption spectra in solution: 1) phenol in cyclohexane; 2) p-nitrophenol in iscoctane; 3) 2,6-diiodo-4-aminophenol in ethanol; 4) 2,6diiodo-4-nitrophenol in ethanol; 5) 2,6-diiodophenol in ethanol; and 6) 3,3',5,5'-tetraiodo-4,4'-diphenol in ethanol.



and $E_{1/2}$ for (Ia-e): 1) (Id); 2) (Ia); 3) (Ib); 4) (Ic); and 5) (Ie).

i.e., an intermolecular charge-transfer band (Fig. 2, curves 2-4) in the intermediates in the synthesis of the acceptors: 380 nm in 2,6-diiodo-4-nitrophenol, 370 nm in 2,6-diiodo-4-amino-phenol, and 372 nm in p-nitrophenol. The appearance of the maxima in the 240-340 nm region in the EAS typifies the characteristic absorption of functionally substituted benzenes.

EXPERIMENTAL

The electronic absorption spectra in solution or of films deposited on quartz glasses by vacuum sublimation (10^{-6} torr) were recorded on Unicam SP-700 or Specord UV-VIS spectrophotometers. The luminescence spectra of the films were recorded on a Hitachi MPF-3 twobeam instrument. Polarographic measurements were carried out on a PP1-1 polarograph with an electrolysis cell suitable for EAS and ESR measurements with a Hg dropping electrode under N₂ in CH₂Cl₂ or in CHCl₃. The physical and luminescence properties of the 3,3',5,5'-tetrahalo-4,4'-diphenoquinones are summarized in Table 1.

<u>3,3',5,5'-Tetrachloro-4,4'-diphenol (IIa) and 3,3',5,5'-Tetrabromo-4,4'-diphenol (IIb).</u> The starting 4,4'-diphenol was prepared by the improved method [16]. Compounds (IIa) and (IIb) were prepared by halogenation of (Ie) in glacial AcOH [8]. The yield of (IIa) was 60%, mp 233°C; the yield of (IIb) was 60%, mp 264°C (mp 264°C [8]).

 $\frac{3,3',5,5'-\text{Tetrachloro}-4,4'-\text{diphenoquinone (Ia) and 3,3',5,5'-\text{Tetrabromo}-4,4'-\text{diphenoquinone}}{(Ib). Oxidation of (IIa) and (IIb) with concentrated HNO₃ in glacial AcOH [8] gave (Ia) and (Ib) in 70% yield, decomposition point > 500°C; (Ib) mol. wt. 499.94 (ebullioscopy in CHCl₃).$

<u>3,3',5,5'-Tetraiodo-4,4'-diphenoquinone (Ic)</u>. 3,3',5,5'-Tetraiodo-4,4'-diphenol (IIc) was oxidized with freshly prepared Cr_2O_3 in ethyl acetate [10]. The product was distilled under vacuum (10⁻⁴ torr) until the photosensitivity was unchanged (the photocurrent exhancement factor k = I_{phot}/I_{dark} under constant illumination L = 0.015 W/cm with identical applied field 100 V/cm). The yield of (Ic) was 21%, decomposition point > 500°C. Found: C 21.03; H 0.61; I 73.75%. C₁₂H₄O₂I₄. Calculated, %: C 20.96; H 0.59; I 73.80%.

<u>3,3',5,5'-Tetrafluoro-4,4'-diphenol (IId)</u>. To a suspension of NaF (1.68 g, 0.04 mole) in purified sulfolane (10 ml) [7] was added slowly with stirring (IIb) (5.01 g, 0.01 mole) in sulfolane (150 ml). The mixture was stirred at 100°C for 2 h. The temperature was slowly raised to 150-160°C, kept constant for 1 h, and then raised to 200°C for 3 h. The solution was evaporated to $^{1}/_{6}$ of the original volume and kept at 200°C for 1 h. After cooling, the solvent was stripped under vacuum, and the precipitate was washed with water and with ether, and dried. Vacuum distillation (10⁻⁴ torr) gave (IId) (0.4 g. 16%) as white crystallina powder, mp 267°C. Found: C 55.75; H 2.42; F 29.27%. C₁₂H₆O₂F₄. Calculated: C 55.83; H 2.34; F 29.44%.

3,3',5,5'-Tetrafluoro-4,4'-diphenoquinone (Id). To a solution of (IId) (2.58 g, 0.01 mole) in glacial AcOH (40 ml) was added dropwise with stirring concentrated HNO₃ (0.56 ml).

The mixture was heated on a water bath for 40 min. The precipitate was washed with water and with ether and dried to constant weight at 100°C. The product was purified in the same way as (Ic) to give (Id) (1.72 g, 67%) as a lilac crystalline powder, decomposition point > 500°C. Found: 56.23; H 1.62; F 29.71%. $C_{12}H_4O_2F_4$. Calculated: C 56.27; H 1.57; F 29.67%.

CONCLUSIONS

1. We have synthesized 3,3',5,5'-tetrafluoro-4,4'-diphenoquinone and examined its luminescence spectra.

2. We have made a comparative analysis of the luminescence properties of the 3,3',5,5'tetrahalo-4,4'-diphenoquinones.

3. We have measured the electron affinities of the 3,3',5,5'-tetrahalo-4,4'-diphenoquinones.

LITERATURE CITED

- 1. Zh. Vses. Khim. Obshch., 23, 482 (1978).
- 2. V. Kampars and O. Neilands, Usp. Khim., <u>46</u>, 945 (1977).
- 3. G. Briegleb, Electron Donor-Acceptor Complexes, Springer, Berlin (1961).
- 4. R. Foster, Organic Charge-Transfer Complexes, Academic Press, New York (1969).
- A. V. Airapetyants, Organic Semiconductors [in Russian], Izd. Akad. Nauk SSSR (1963), p. 207.
- 6. M. Slifkin, Physicochemical Properties of Nucleic Acids [Russian translation], Mir (1976), p. 77.
- 7. L. F. Fieser and M. Fieser, Reagents for Organic Synthesis, Vols. 1-7, Interscience, New York.
- 8. G. Magatti, Ber., <u>13</u>, 224 (1880).
- 9. W. H. Hunter and M. L. Morse, J. Am. Chem. Soc., 55, 3701 (1933).
- 10. G. H. Woollett, F. M. Davis, C. N. Jones, and M. Neill, J. Am. Chem. Soc., <u>59</u>, 861 (1937).
- 11. H. Kolbe and E. Lautemann, Lieb. Ann. Chem., 119, 136 (1861).
- 12. H. Kammerer and E. Benzinger, Ber., <u>11</u>, 557 (1878).
- 13. G. V. Saidov, O. V. Sverdlova, and N. G. Bakhishev, Dokl. Akad. Nauk SSSR, <u>182</u>, 638 (1968).
- S. P. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall, Englewood Cliffs (1969).
- C. L. Perrin, New Problems in Physical Organic Chemistry [Russian translation], Mir (1965), p. 95.
- 16. R. Hirsch, Ber., 21, 335 (1889).