Molecular Interaction between 1,4-Benzenedithiol and 1,4-Diethynylbenzene

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(Received July 28, 1990)

ABSTRACT: Molecular interactions of 1,4-benzenedithiol (BDT) and 1,4-diethynylbenzene (DEB) were studied in hexane or in toluene at 23—25°C by a UV-spectroscopy to elucidate the mechanism for the polyaddition of BDT to DEB. The solution containing both BDT and DEB showed a broad absorption at 280—380 nm. The magnitude of the absorbance gradually increased during storage of the solution. Both BDT and DEB may have molecular interactions in solution and also in the solid state to make complexes of the charge-transfer (CT) type. The equilibrium constant (K) and extinction coefficient (ϵ) were tentatively estimated to be about 40 and 8000—15000 at 310 nm in hexane or 5.8 and 8000 in toluene, respectively, at 5 s after mixing the component solutions. As a model system, spectroscopic investigation was also made with systems of thiophenol (TP)—phenylacetylene (PA), TP—DEB and BDT—PA in hexane. These systems exhibited a large equilibrium constant and large extinction coefficient as well as BDT and DEB. Consequently, CT interactions seem to control the polyaddition of BDT to DEB in solution and also in solid state.

KEY WORDS 1,4-Benzenedithiol / 1,4-Diethynylbenzene / Polyaddition / Model Addition Compounds / UV-Spectroscopy / Charge-Transfer Interaction / Equilibrium Constant (K) / Extinction Coefficient (ϵ) / Continuous-Variation Method / Ketelaar Method /

When strong electron-donating monomers are mixed with strong electron-accepting ones, regular alternating copolymers may be formed either by spontaneous initiation or more commonly in the presence of a free radical initiator.

Previously, the authors found a novel polymer of BDT and DEB in solution¹ or in solid state² under UV- or γ -ray irradiation. In the case of solid state polymerization, thin layer crystals of the 1:1 mixture of BDT and DEB are mounted on a glass plate by sublimation of a 1:1 mixture of BDT and DEB. The thin layer crystals are readily polymerized under UV-irradiation in high yield.² Both BDT and DEB are assumed to be arranged alternately

in the thin layer crystals perhaps induced by molecular interaction between BDT and DEB.

This report deals with molecular interactions of BDT and DEB studied by UV-spectroscopy in solution.

EXPERIMENTAL

BDT and DEB

BDT and DEB were prepared by the previous method.^{1,2} BDT was recrystallized from the ethyl acetate solution, and then sublimed at 70°C under reduced pressure prior to use, mp 97—98°C (97—98°C¹). DEB was purified by sublimation at 60°C under reduced pressure prior to use, mp 96.5°C (96.5°C¹).

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Procedures

The mixture of BDT and DEB in hexane was rapidly polymerized in the presence of a trace amount of oxygen in the solution. Therefore, the solvents, BDT, and DEB must be carefully purified to exclude any oxygen. Hexane (special grade, Wako Pure Chemical Industries) was purified through a column chromatograph packed with Al_2O_3 activated at 200°C for 12 h *in vacuo*, degassed and bubbled with purified nitrogen, and then distilled under atmosphere of the purified nitrogen. Here, the purified nitrogen was prepared by deoxygenation of four nine nitrogen ($\text{O}_2 < 2$ ppm) through a reduced copper column, silica gel, calcium chloride, molecular sieves 4A, and then a column packed with cooled molecular sieves 5A^3 at about -150°C . Solutions of BDT or DEB were prepared by adding the calculated amount of the purified hexane measured by a burette into the degassed BDT or DEB under atmosphere of the purified nitrogen. Each solution was transferred to a rubber-capped UV cell by a stainless steel tube syphon and admixed for 5 s by a magnetic stirrer under atmosphere of the purified nitrogen. According to the above semi-closed method the mixed solution containing both BDT and DEB was fairly stable for several hours without the formation of dimers, trimers and so on, a turbidity or a precipitation of polymers.

UV Measurement

UV spectra were recorded on a Shimadzu UV-260 spectrophotometer under atmosphere of the purified nitrogen.

Model Addition Compounds

As model addition compounds for spectroscopic investigation, compounds (A-*cis*), (A-*trans*), (B), and (C) were synthesized as follows: TP (bp $47.4\text{--}48.0^\circ\text{C}/8\text{ mmHg}$, Wako Pure Chemical Industries) and PA (bp $47.8\text{--}48.2^\circ\text{C}/25\text{ mmHg}$, Wako Pure Chemical Industries) were distilled before use, and subjected to the reactions.

(A-*cis*) Compound

PA (40.8 mmol) was added dropwise with stirring to a solution of TP (27 mmol) in heptane (5 ml) at -30°C and then allowed to react for 6 h at -30°C under atmosphere of nitrogen. The reaction mixture was washed to exclude residual TP with 4% aqueous sodium hydroxide solution followed by water. The organic layer was dried with MgSO_4 and then cooled with ice-water bath at 0°C for 6 h. The precipitates were filtered off and recrystallized from the heptane solution⁴; yield 38.6%, mp $48.9\text{--}49.2^\circ\text{C}$ ($41.5\text{--}42.5^\circ\text{C}^4$), ^1H NMR in CDCl_3 7.2 ppm (m, 10H), 6.3 ppm (AB quartet, 2H), $J(\text{CH}=\text{CH})$ 10.5 cps (10.0 cps^4).

(A-*trans*) Compound

The *trans* adduct was prepared by adding TP (27 mmol) to PA (29 mmol) in bulk and the reaction continued for 7 h at 40°C under atmosphere of nitrogen. Benzene (10 ml) was added to the reaction mixture. The reaction mixture of the benzene solution was washed to exclude residual TP with 4% aqueous sodium hydroxide solution followed by water. The organic layer was dried with MgSO_4 and cooled with ice-salt bath at -20°C for 6 h. The precipitates were filtered off and recrystallized from the ether solution; yield 44.9%, mp $38.6\text{--}39.5^\circ\text{C}$ ($35\text{--}36^\circ\text{C}^4$), ^1H NMR in CDCl_3 7.2 ppm (m, 10H), 6.6 ppm (AB quartet, 2H), $J(\text{CH}=\text{CH})$ 15.5 cps (17.0 cps^4).

(B-*trans-trans*) Compound

DEB (5 mmol) in a benzene solution (10 ml)

was added dropwise with stirring to a solution of TP (11 mmol) in benzene (5 ml) at 20°C and allowed to react for 4 h at 20°C under atmosphere of nitrogen. The reaction mixture was washed to exclude residual TP with 4% aqueous sodium hydroxide solution and water. The organic layer was dried with MgSO_4 and then benzene was evaporated. The residue was washed with Et_2O and dried *in vacuo*. The crude product was dissolved in a small amount of benzene (*ca.* 8 ml) and purified through a column chromatograph packed with Al_2O_3 . Benzene was used as the eluent; yield 73%, mp. 122.7–123.0°, ^1H NMR in CDCl_3 7.1 ppm (m, 14H), 6.7 ppm (AB quartet, 4H), $J(\text{CH}=\text{CH})$ 15.5 cps (see Figure 1), S-contents 18.5–18.6 wt% (calcd. 18.5 wt%).

(*C-cis-cis*) Compound

BDT (5 mmol) in a benzene solution (10 ml) was added dropwise with stirring to a solution of PA (10 mmol) in benzene (5 ml) at 20°C and allowed to react for 4 h at 20°C under atmosphere of nitrogen. The reaction mixture was washed to exclude residual BDT with 4% aqueous sodium hydroxide solution and water. The organic layer was dried with MgSO_4 and then benzene was evaporated. The residue was recrystallized three times from the benzene solution; yield 71%, mp 130.5–131.0°C, ^1H NMR in CDCl_3 7.1 ppm (m, 14H), 6.4 ppm (AB quartet, 4H), $J(\text{CH}=\text{CH})$ 10.5 cps (see Figure 1), S-contents 18.5–18.6 wt% (calcd. 18.5 wt%).

^1H NMR spectra of the compounds (*B-trans-trans*) and (*C-cis-cis*) are shown in Figure 1.

RESULTS AND DISCUSSION

UV spectra of BDT and DEB in hexane are shown in Figure 2. According to a separate experiment, λ_{max} of BDT and DEB was 280 nm (260, 284 nm in ethanol⁵) and 270, 290 nm (270 nm in heptane⁶) in hexene, respectively, whereas the mixture of BDT and DEB in

a)

b)

Figure 1. ^1H NMR spectra of the model addition compounds in CDCl_3 (JEOL JNM FX 270): a) (*B-trans-trans*); b) (*C-cis-cis*).

hexane exhibits a broad absorption at 280–380 nm as shown in Figure 3. The dotted line in Figure 3 is the arithmetic mean of the

Figure 2. UV spectra of BDT and DEB in hexane at 23°C: $[BDT] = [DEB] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$.

Figure 3. UV spectra of the mixture of BDT and DEB at 5 s after mixing in hexane at 23°C: $[BDT] = 1.04 \times 10^{-3} \text{ mol l}^{-1}$; $[DEB] = 0.97 \times 10^{-3} \text{ mol l}^{-1}$; ----, arithmetic mean of the absorption spectra of each compound.

Figure 4. UV spectra of the mixture of BDT and DEB in hexane at 24°C: $[BDT] = 1.2 \times 10^{-3} \text{ mol l}^{-1}$; $[DEB] = 0.8 \times 10^{-3} \text{ mol l}^{-1}$. Storage time of the mixed solution: 5 s (a), 30 s (b), 90 s (c), 3 min (d), 5 min (e), and 30 min (f).

absorption spectra of each compound taken with the data in Figure 2.

A similar broad absorption of the 1:1 mixture of BDT and DEB has been also recognized in solid state by measurement of the diffuse reflectance spectrum.² This behavior on UV spectra suggests a formation of charge-transfer complexes between BDT and DEB in the solution and also in the solid state.

A characteristic absorption of the complex can be monitored by varying the reagent concentration, and stoichiometry can be determined from the composition at which maximum absorption occurred.⁷ Figure 4 shows the original absorption spectra in the course of storage of the mixed solution. In the case of the mixed solution, a maximum absorption at 320 nm appeared at 5 s after mixing. The absorbance gradually increased with increasing storage time of the solution

Figure 5. Continuous-variation curves of BDT and DEB at 5 s after mixing in hexane at 24°C: $[BDT] + [DEB] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$.

Figure 6. Continuous-variation curves of BDT and DEB at 5 min after mixing in hexane at 24°C: $[BDT] + [DEB] = 2.0 \times 10^{-3} \text{ mol l}^{-1}$.

and the broad absorption diffused to longer wavelength than 400 nm. However, there were no observable dimers, trimers and so on, and a turbidity or precipitation of polymers. Hereafter, spectroscopic measurements were carried out at 5 s after the mixing of the solutions except for the data in Table II with the model compounds, because the model compounds showed well optical stability.

As shown later, spectroscopic changes may result from the formation of 1:2, 2:1, and finally $m:n$ complexes. That is, CT-complexes induce a large cluster formation. This speculation is partly supported by the following evidence. Absorbance markedly decreased with dilution by adding the solvent. However, polymerization occurred frequently by contamination of a trace amount of oxygen. Accordingly, the dilution effect cannot be discussed quantitatively by experimental data.

Figure 5 shows the continuous-variation curves of the mixed solution between BDT and DEB, where the total monomer concentration is fixed on $2.0 \times 10^{-3} \text{ mol l}^{-1}$ in hexane. The

maximum absorbance appears at a molar fraction of 0.5, indicating the formation of molecular complexes at a 1:1 composition with respect to BDT and DEB. However, as shown in Figure 6, it is expected that composition changes of complexes already occur in the region of the dotted line in Figure 5. Previously, the authors reported a bimodal curve with continuous-variation taken with a mixed solution at 10 min or more than 10 min after mixing of the solutions.⁸ For instance, Figure 6 shows curves at 5 min. Absorbance considerably increased and absorbance at the mixing ratio of 0.3 and 0.65 increased about twice as much compared with the corresponding mixing ratio shown in Figure 5. During the storage of the mixed solution the contribution of 1:2 and 2:1 complexes may have marked effect on the observed spectra.

To minimize overlapping effect of absorbance between CT complexes and each monomer, the Ketelaar method is used to estimate the K value by assuming the formation of the 1:1 complex.⁹ The absorbance d_c at a

Figure 7. Ketelaar plots of BDT and DEB at 310 nm in hexane at 25°C: $[BDT] = 5.2\text{--}8.1 \times 10^{-3} \text{ mol l}^{-1}$; $[DEB] = 1.1\text{--}3.9 \times 10^{-4} \text{ mol l}^{-1}$.

Figure 8. Ketelaar plots of BDT and DEB at 310 nm in hexane at 25°C: $[BDT] = 1.1\text{--}4.1 \times 10^{-4} \text{ mol l}^{-1}$; $[DEB] = 6.9\text{--}9.0 \times 10^{-3} \text{ mol l}^{-1}$.

given wavelength is related to K by the equations,

$$[DEB]l/(d_c - d_m) = 1/[BDT]K(\epsilon_c - \epsilon_m) + 1/(\epsilon_c - \epsilon_m), \quad [BDT] \gg [DEB]$$

$$[BDT]l/(d_c - d_m) = 1/[DEB]K(\epsilon_c - \epsilon_m) + 1/(\epsilon_c - \epsilon_m), \quad [DEB] \gg [BDT]$$

where l is the optical path length (1 cm), ϵ_c and ϵ_m are the extinction coefficient of the 1:1 complex and BDT or DEB, respectively. Here, to minimize minor contributions of the absorbance of addition compounds, absorbance d was measured at 310 nm, but not $\lambda_{\max}$ of the CT-complex at 320 nm, since, $\lambda_{\max}$ of the model addition compounds such as B-*trans-trans* compound and C-*cis-cis* compound are 344 nm and 312 nm, respectively (see Table II). $\lambda_{\max}$ of CT-complexes at 320 nm may be somewhat influenced by the absorption of the addition compounds, but not so much. d_m is the absorbance of BDT or DEB at 310 nm. Figures 7 and 8 show the Ketelaar plots for BDT-DEB complex in hexane. The linearity of the plots is good in spite of the optical instability of the mixed solutions. Consequently, apparent K are acceptable for dis-

cussion.

Table I summarizes the spectroscopic data. Generally, K and ϵ mean values at equilibrium state. Here, the constants obtained may have no quantitative significance. However, the model compound system shown in Table II exhibits large K and ϵ values with good optical stability. Consequently, the authors expect that the optical instability of BDT-DEB system may be caused by a large cluster formation between BDT and DEB in the course of the storage time of the solution, since BDT and DEB have two functional groups inducing molecular interactions. The values of K are of higher order than the conventional CT systems, for instance, styrene-maleic anhydride has 0.34 in hexane.¹⁰ BDT may act as an electron-donor and DEB as an electron-acceptor, since the ionization potential of TP and PA is 8.54 eV¹¹ and 9.15 eV,¹² respectively. The authors also estimated the orbital energy by the simple HMO method.¹³ The LUMO and HOMO of BDT are $\alpha - 0.2728\beta$ and $\alpha + 1.0000\beta$, respectively, and those of DEB are $\alpha - 0.4009\beta$ and $\alpha + 0.5455\beta$. In such a case of a strong donor-acceptor system, the dative bond is known to induce an ionic polymerization of

Table I. Spectroscopic data of binary mixed system in hexane or toluene at 23–25°C at 5 s after mixing

Combination of reagent (solvent)	Reagent $\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$ [$\lambda_{\text{max}}/\text{nm}$]	CT of binary mixture		
		Comp. ratio of CT [λ/nm]	$K/l \text{ mol}^{-1}$	$\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$ at 310 nm
<chem>SHc1ccccc1SH</chem> BDT	13,000 [280]		BDT $\gg$ DEB	
			41	8,000
<chem>HC#Cc1ccccc1C#CH</chem> DEB (hexane)	15,000 [270]	BDT : DEB 1 : 1 [280–380]	BDT $\ll$ DEB	
			40	14,700
BDT	-----		BDT $\ll$ DEB	
		BDT : DEB 1 : 1 [290–370]	5.8	8,000
DEB (toluene)	-----			

vinyl monomers, for instance, homopolymerization of vinylidene cyanide and vinyl ether,¹⁴ although a combination of the strongest donor and acceptor seems to be favorable for formation of stable complexes but not for alternating copolymerization. However, the present system is quite different from the system of the usual vinyl monomers. A part of a thiol compound may be ionized by the aid of acetylenic monomer, but the thiophenyl anion created may react very slowly with the acetylenic bond.¹⁵ Furthermore, λ_{max} of thiophenyl anion (counter cation: Na^+) is 279 nm in dioxane and 292 nm in THF at 20°C.¹⁶ As hexane is a non-polar solvent compared with dioxane and THF, λ_{max} of thiophenyl anion in hexane may shift to a shorter wavelength, if it exists. Consequently, absorption at 300–350 nm assigned for CT-complexes of BDT and DEB. Therefore, direct attack of thiophenyl anion may be a minor contribution compared with the present radical polyaddition through the CT-complex.

Consequently, spectroscopic investigation supports strongly the existence of CT-complexes in the polyaddition system as an inter-

mediate state, although detailed study on the spectroscopic investigation would be needed.

The value of K in toluene is lower order than that in hexane. Toluene (dipole moment 0.37D¹⁷) is polar solvent comparing with hexane (dipole moment 0.08D¹⁸). Formation of the CT complex may be inversely dependent on the polarity of solvents, suggesting the formation of non-ionic complexes. Toluene may simply act as a donor instead of BDT.¹⁴

As the model system, combinations between TP-PA, TP-DEB, and BDT-PA are studied as shown in Table II. Here, the spectroscopic data of addition compounds are also appended. K and ϵ of the model systems are very large, indicating special molecular interactions between thiol compounds and acetylenic ones.

The spectroscopic data obtained were scarcely affected by the addition compounds. The minor absorbance due to the addition compounds at the initial stage of the mixing of both solutions may be subtracted from the observed spectra of BDT-DEB system, but the present spectroscopic data of the K and ϵ shown in Table I are uncorrected ones.

Consequently, CT interaction seems to par-

Table II. Spectroscopic data of binary mixture of model compounds and those of addition compounds in hexane at 21–24°C

Reagent $\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$ [$\lambda_{\text{max}}/\text{nm}$]	CT of binary mixture		Addition Compounds ^a	
	Comp. ratio of CT [λ/nm]	$K/l \text{ mol}^{-1}$ $\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$ [λ/nm]	$\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$ [$\lambda_{\text{max}}/\text{nm}$]	
TP 12500 [236]	TP:PA 1:1 [280–370] d	760 400 d	TP $\ll$ PA 5000 [290] 4500 [300] d	
PA 11000 [206]			(A- <i>cis</i>) 21000 ^b [296] (A- <i>trans</i>) 20000 ^c [307]	
d				
TP	TP:DEB 2:1 [290–370]	93 260	TP $\gg$ DEB 7700 [300] 5700 [310]	
DEB 15000 [270]			(B- <i>trans-trans</i>) 44000 [344]	
PA	PA:BDT 2:1 [280–370]	75	PA $\gg$ BDT 7300 [290]	
BDT 13000 [280]			(C- <i>cis-cis</i>) 48000 [312]

^b *cis* compound: ϵ 19600/l mol⁻¹ cm⁻¹ [λ_{max} 296 nm¹⁹].

^c *trans* compound: ϵ 18800/l mol⁻¹ cm⁻¹ [λ_{max} 306 nm¹⁹].

^d 30–33°C.

participate in the polyaddition of BDT to DEB in solution and also in solid state. In the case of solid state polymerization, the arrangement of monomers of BDT and DEB may be caused by CT interaction during the sublimation of the equimolar mixture of BDT and DEB under reduced pressure. X-Ray study of the monomer arrangement in the solid state is now being conducted.

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