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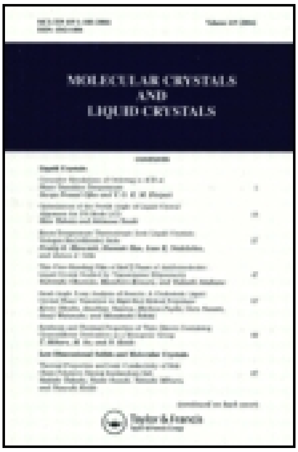

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Spectroscopic Study of Charge Transfer Complexes of Biphenyl

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Biphenyl is a well-known photoconductor with a band gap of 0.16 eV lying in the infrared range. In the present work, the charge transfer complexes of biphenyl with the acceptors such as 7,7,8,8-tetracyano-p-quinodimethane, N,N,N′,N′-tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), Chloranil, and iodine have been studied with ultraviolet-visible near infrared and infrared spectroscopy. Biphenyl-TCNE and biphenyl-DDQ show spin-orbit splitting of valence band and consequently show three optical transitions. Biphenyl-iodine and biphenyl-chloranil show nondegenerate semiconducting nature. The charge transfer complexes (CTCs) show an asymmetric Gaussian band associated with small polaron model. Many of the CTCs also show a scattering of charge carriers by light particles as expected in photoconductors.

Keywords Biphenyl; charge transfer complexes; IR spectroscopy; UV-VIS-NIR spectroscopy

1. Introduction

Biphenyl, the molecular structure of which is shown (Fig. 1) is a C–C bridged benzene rings which resonate as a whole. It is symmetric molecule and its resonance structures are defined through the Kekule structures of benzene rings. Only asymmetric molecule has a dipole moment. So biphenyl does not have an appreciable dipole moment but resonance structures are closely spaced in energy and undergo quantum mechanical resonances. It has good photoconductivity and consequently known as a good photoconductor. Here, for the first time, we study charge transfer complexes of biphenyl with the help of ultraviolet-visible near infrared and infrared (IR) spectroscopies. Biphenyl is a well-known photoconducting material and has white color [1] Although it gives photocurrent in nanoamperes, it has only a very small value of activation energy of 0.07 eV [2]. It is expected that photocurrent can be enhanced in its charge transfer complexes with organic acceptors. Biphenyl can work as an electron donor because of a large number of C–H groups, which are electron donating as in the cases of, condensed hydrocarbons like pyrene and perylene [3]. Also resonance like Kekule structures of benzene probably leads to a small value of activation energy. It is our curiosity and interest to see whether photoconductivity increases or decreases upon the formation of charge transfer complexes with organic acceptors. Photoconductivity is a dc response when visible light falls on a photoconductor [4]. Its UV-visible spectrum should

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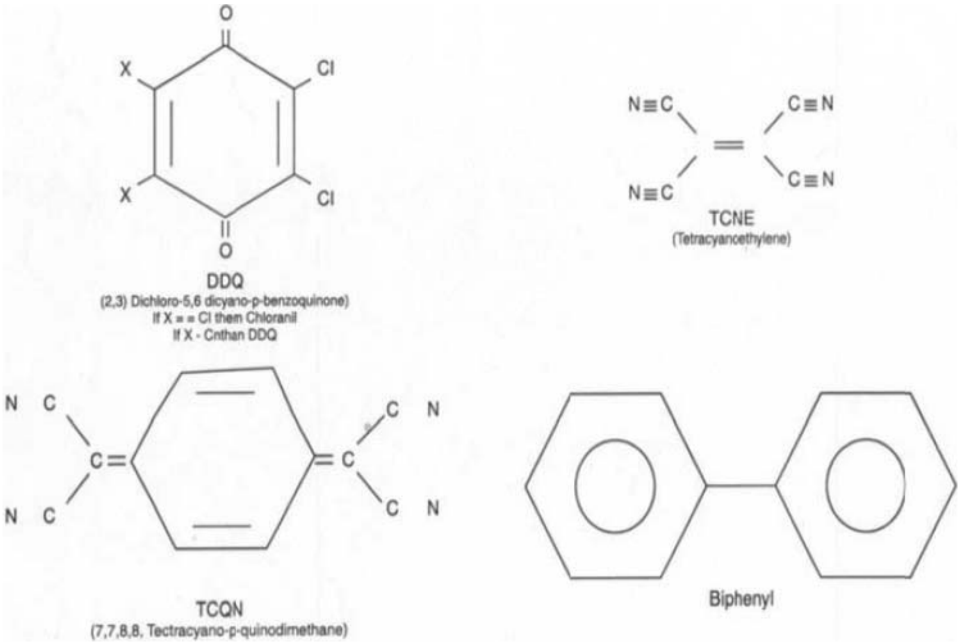

Figure 1. Molecular structures of biphenyl and organic acceptors.

be related with electrical conductivity. Therefore, we study UV-visible-near IR spectra of five charge transfer complexes of biphenyl. There is voluminous old literature on charge transfer complexes and organic semiconductors [2,5,6]. There are large amount of data available on organic, organometallic, and polymeric photoconductors reviewed elsewhere [2]. But these were all homomolecular photoconductors. Photoconductivity studies on charge transfer complexes have only recently begun. Here, we take a different approach that is how systematic effect of charge transfer on those homomolecular photoconductors occurs, when a bimolecular complex is formed. In this regard, we study the infrared spectra of biphenyl as an example and its charge transfer complexes with organic acceptors. The thermal activation energy of biphenyl is 0.08 eV [2] and therefore, the forbidden energy gap between valence and conduction band which $E_g = 2E_a$ for intrinsic semiconductor is about 0.16 eV, which lies in the infrared range of 0.05–0.5 eV (400–4000 cm^{-1}).

2. Experimental

Biphenyl and organic acceptors like TCNQ (7,7,8,8-tetracyano-p-quinodimethane), TCNE (N,N,N′,N′-tetracyanoethylene), DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone), chloranil (2,3,5,6-tetrachloro-p-benzoquinone), and iodine were mixed one by one in equal molecular weight proportions in a mortar and grinded to form five deeply colored charge transfer complexes. Remarkable change in color and characteristic colors different from the colors of the mixtures clearly indicated the formation of charge transfer complexes. Molecular structures of biphenyl and organic acceptors used in the present work are shown in Fig. 1.

Samples for UV-visible-near IR spectra were pastes of the complexes sticking on semitransparent strips with the help of paraffin oil. The spectra were recorded between 200

Table 1. IR transmission in biphenyl complexes

Name of the complex	Range of IR transmission (cm^{-1})	Maximum transmission (%)
Biphenyl-TCNE	1800–2800	98
Biphenyl-DDQ	1750–2800	98
Biphenyl-TCNQ	1800–2800	97
Biphenyl-I_2	1800–2800	97
Biphenyl-chloranil	1700–3000	97

and 1600 nm using a standard spectrophotometer of Perkin Elmer Company. Biphenyl was grinded in a mortar with TCNE. Biphenyl was white and TCNE was black in color. The grinding led to a change in color. The final color was very much different from a neutral mixture of the two. Similarly, TCNQ, chloranil, DDQ, and molecular iodine (I_2) were grinded with biphenyl to form charge transfer complexes of specific and distinct colors (Table 1).

3. Results and Discussion

First, we consider biphenyl-iodine (Fig. 2(a)). Two sharp peaks near 375 nm and an intense peak at 395 nm can be ascribed to local excitation and a $\pi \rightarrow \pi^*$ transition across biphenyl molecule, respectively. The broad and intense transmission dip at 480 nm is the strong absorption of well-known iodine band which lies at 540 nm. Thus this band is blueshifted by 60 nm. This cannot happen if iodine gets polarized and I-I distance increases. The blue shift is very peculiar here which should be ascribed to the interaction of iodine with biphenyl. The transmission above 65%, above 600 nm and becoming constant above 820 nm near 83% indicate that biphenyl-iodine is a transparent dielectric in the near IR range. The increase in transmission, i.e., the decrease in absorption, as the frequency decreases in the region 600–820 nm seemed nearly parabolic horizontally and, therefore, was analyzed to follow the relation.

$$A = A_0(h\nu - E_g)^{1/2} \tag{1}$$

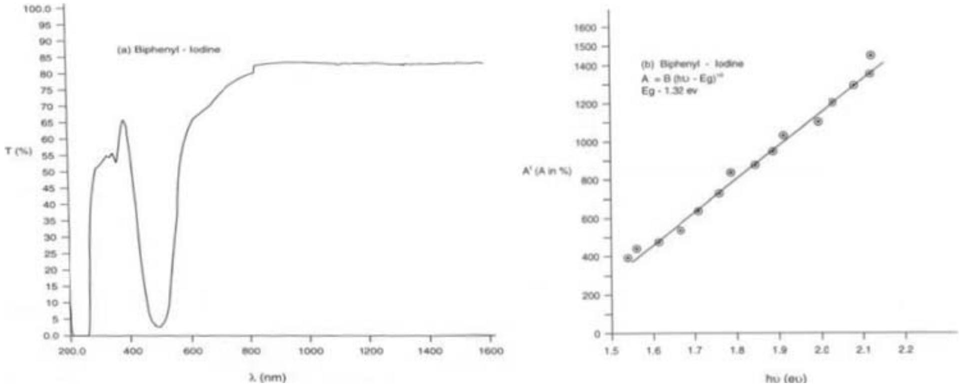

Figure 2. (a). UV-visible-near IR spectrum of biphenyl-iodine. (b). Allowed direct transition in biphenyl-iodine.

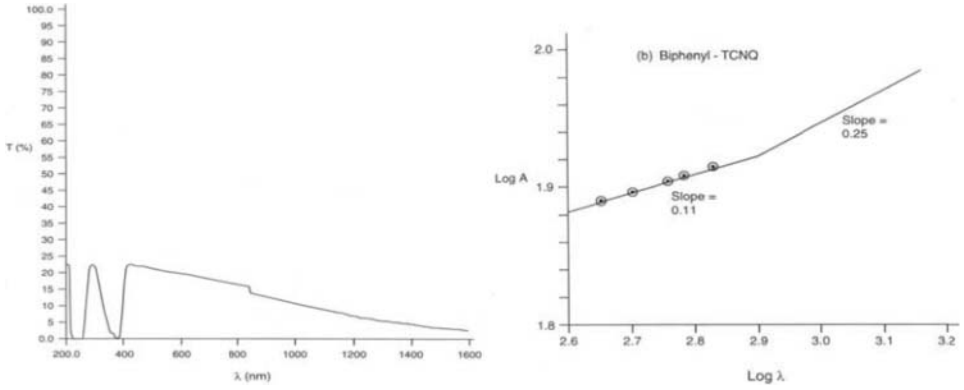

Figure 3. (a). UV-visible-near IR spectrum of biphenyl-TCNQ. (b). Free-carrier absorption (log A versus log λ) in biphenyl-TCNQ.

Where A is absorbance, ν frequency, and E_g is the band gap [7] indicating an allowed direct transition. The optical absorption edge $E_g = 1.32$ eV was found if extrapolated to give $A = 0$. If a step function near 600 nm was assumed, this edge was $E_g = 1.50$ eV (Fig. 2(b)).

Next is biphenyl-TCNQ (a red-colored charge transfer complex) which showed a simple spectrum (Fig. 3(a)). The peak in transmission at 300 nm can be ascribed to electronic excitation of biphenyl molecule. The transmission dip (absorption peak) near 390 nm can be assigned to the absorption by TCNQ molecule. The featureless regions between 400 and 820 nm and between 820 and 1600 nm can be ascribed to free-carrier absorption [8] corresponding to $h\nu > E_g$, where E_g is a photoconducting gap in the infrared range. The slopes of log A versus log λ in the two regions were found to be very small 0.11 and 0.25, respectively (Fig. 3(b)). This reveals a transition in a two-dimensional system [1].

In a normal photoconductor, the material is having considerably reduced exponents than 1.5, 2.5, and 3.5 proposed for scattering by acoustic phonons, optical phonons, and ionized impurities, respectively. This can have two reasons; first is the exponents may be depending on dimensionality like in the case of nature of transitions and second is the coulomb repulsive effect changing the nature of scattering in nearly degenerate photoconductors. Biphenyl-TCNE (Fig. 4(a)) shows a different type of spectrum. This shows that the UV-visible-near IR spectra of five complexes are governed by absorption among electronic levels of acceptor molecules as well as depend on the donor-acceptors interactions and not on biphenyl molecules. The shoulders at 375 nm can be ascribed to $\sigma \rightarrow \pi^*$ transition. Peak at 420 nm can be ascribed to $\pi \rightarrow \pi^*$ transition and peak at 580 nm can be ascribed to a charge transfer band. The transmittance is constant between 620 and 820 nm which show dielectric nature. The drops in transmission between 820 and 1200 nm and between 1350 and 1480 nm correspond to free-carrier absorption with reduced power compared to ordinary semiconductors. The sharp transmission dip at 1520 nm is due to a Raman active mode or a dispersion shape showing resonance and anti-resonance spike (one of the Hanle curves) due to the real part of dielectric constant.

A vigilant observation of the entire UV-visible-near IR spectrum has lead to analysis of the transmission profile as four different optical or electronic transitions having different absorption functions having in the range 300–800 nm (Fig. 4(b)). The optical absorption edges can be summarized as follows:

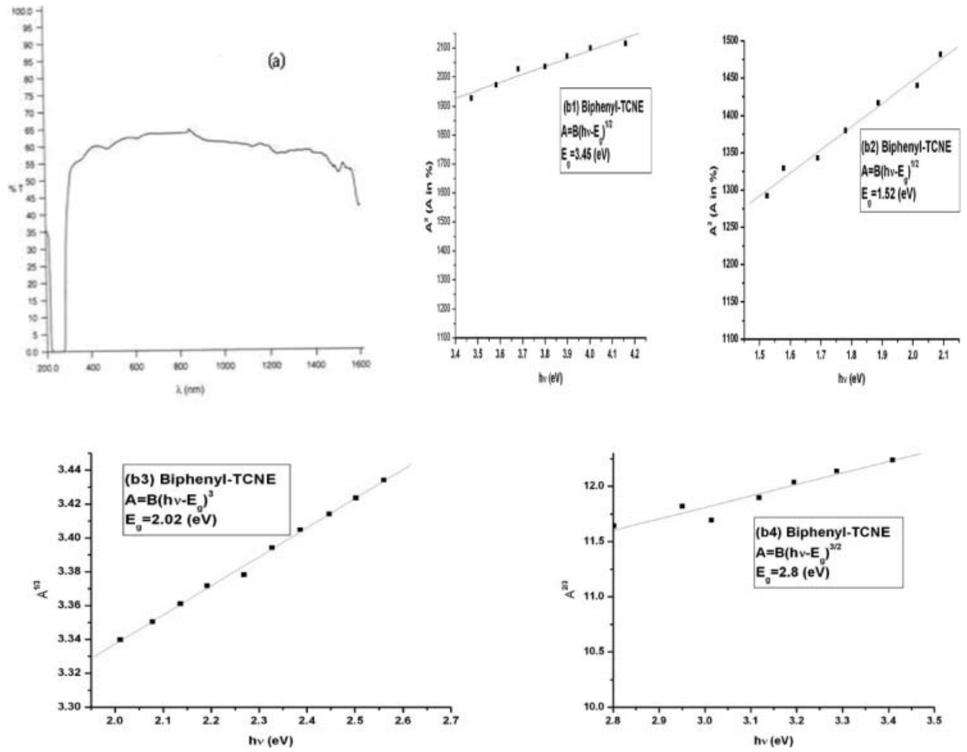

Figure 4. (a). UV-visible-near IR spectrum of biphenyl-TCNE. (b1–b4). Different optical absorption edges showing different types of of biphenyl-TCNE.

It is quite complex to understand the reason and significance of these transitions in biphenyl-TCNE only. This may be related with intraband transitions among spin-orbit split valence subbands.

The free-carrier absorptions are analyzed in two regions (Fig. 4(c)) and are found to obey the relation:

$$\alpha_f = A\lambda^{0.75} \text{ and } \alpha_f = A\lambda^{0.8} \tag{2}$$

The scattering seems to be due to acoustic phonons. The reduction of the exponent from 1.5 may be due to coulomb repulsion in photoconductors or due to two phonon process.

Next is biphenyl-DDQ which shows stepwise increase in transmission (Fig. 5(a)) between 280 and 850 nm. Here also as in the case of biphenyl-TCNE, three different optical or electronic transitions among subbands or valleys are observed and optical absorption edges are evaluated by analyzing nature of transitions (Figs. 5(b) and (c)). The major transition between 2.0 and 3.5 eV is an indirect transition showing a large change in absorption. The spin-orbit splitting at the center of the Brillouin zone [9] is found of the order of 0.2 eV in the same manner as phonon energy. At lower energy ranges, i.e., 2.05–1.5 eV and 1.1–0.9 eV, a direct allowed and indirect allowed transitions are found which give two band gaps $E_g = 1.5$ eV and $E_g = 0.92$ eV (Fig. 5(c)). These transitions can be due to intraband transitions among spin-orbit split valence bands.

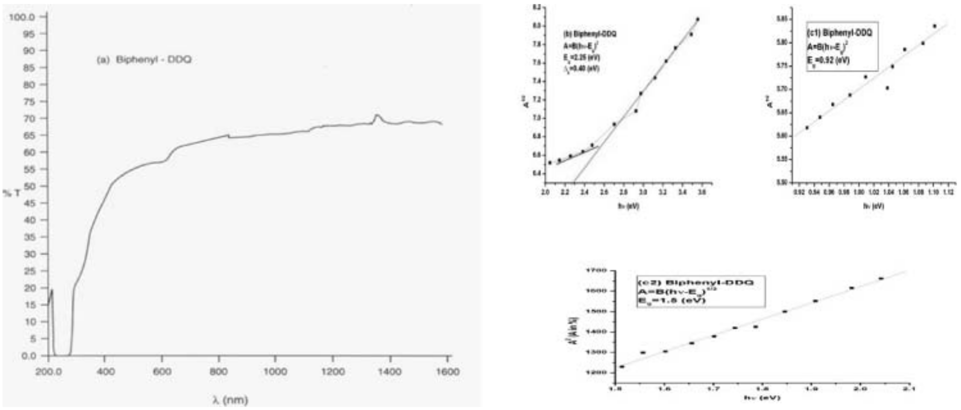

Figure 5. (a). UV-visible-near IR spectrum of biphenyl-DDQ. (b). Major allowed indirect transition with spin-orbit splitting of valance band in biphenyl-DDQ. (c1–c2). Two other electronic transitions at low energies – one direct and other indirect – in biphenyl-DDQ.

Last is biphenyl-chloranil which shows a spectrum different from even biphenyl-DDQ (Fig. 6(a)). The 360 nm peak in transition can be assigned to $\sigma \rightarrow \pi^*$ transition. A broad and asymmetric peak around 500 nm is a special characteristic of symmetric chloranil molecule and probably it is a charge transfer band. But it is possible to analyze this region (2.0–3.6 eV) as an electronic transition giving rise to monotonic profile rather than a peak-showing band and is fitted here (Fig. 6(b)). It follows an allowed indirect transition function, i.e., $A = B(h\nu - E_g + \Delta_0)^2$, where $E_g = 2.4$ eV and $\Delta_0 \cong 0.7$ eV. Δ_0 is the spin-orbit splitting parameter near the center of the Brillouin zone [9]. It is evaluated in the same

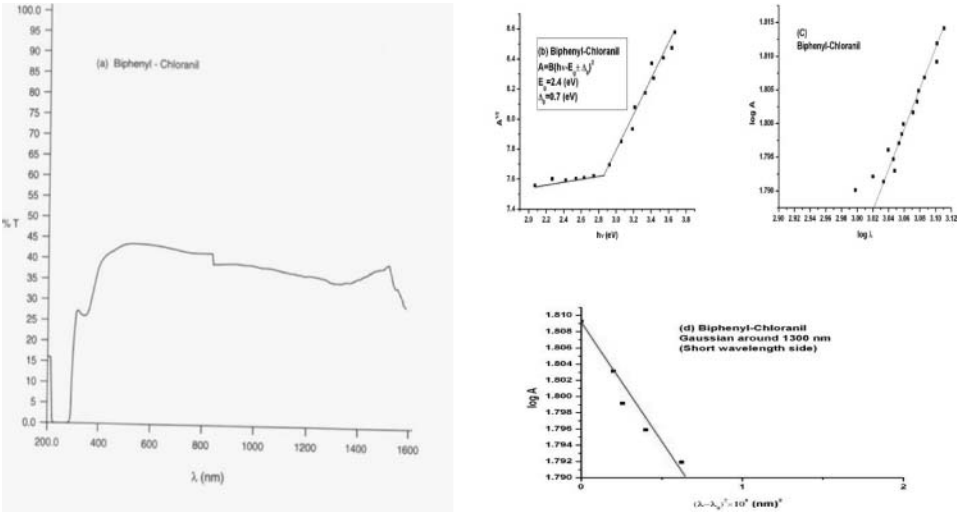

Figure 6. (a). UV-visible-near IR spectrum of biphenyl-chloranil. (b). Major allowed indirect transition with spin-split valence band in biphenyl-chloranil. (c). Free carrier absorption logA vs. logλ in biphenyl-chloranil. (d). Broad and weak Gaussian band centered in biphenyl-chloranil around λ = 1300 nm fitted by plotting logA vs. $(\lambda\text{-}\lambda_0)_2$.

manner as phonon energy distinguishing between emission or absorption of a phonon or here, an elementary excitation like exciton or polaron.

Above 820 nm up to 1300 nm it is a free-carrier absorption which is analyzed by plotting log A versus log λ (Fig. 6(c)). Here too, the slope is 0.19 revealing a low-dimensional nature or reduction due to columbic scattering. A sharp peak in transmission at 1550 nm is related with a molecular exciton on chloranil molecule.

Consider the infrared spectrum of biphenyl. Biphenyl is a semiconductor and has two benzene rings joined by C–C bond (Fig. 1). The strong and broad band around 3434 cm^{-1} is due to C–H stretching mode of a large number of C–H bonds. It is broad because of statistical distributions of maxima and solid-state effects. There is a small doublet around 3032 cm^{-1} and one more doublet near 2364 cm^{-1}, both can correspond to impurity levels within the forbidden gap region. It is transmitting with constant transmission near 90% over a broad range between 1800 and 3000 cm^{-1}. This transparent IR range is affected normally by the donor-acceptor interactions (charge transfer interactions) and the complex obeys $\alpha \sim (h\nu - E_g)^n$ or $\alpha h\nu \sim (h\nu - E_g)^n$, where n depends on the type of transition, after developments of the absorption [3,7,10–14]. But this is not found here in the charge transfer complexes of biphenyl (Figs 7 and 8). CT complexes remain almost transmitting in this range.

The electrical and optical conductivity (σ) are related to absorption coefficient (α) as follows:

$$\sigma = \frac{\alpha n_1 c}{4\pi} = \frac{\omega \varepsilon_2}{4\pi} = \frac{2\omega\, n_1 n_2}{4\pi} \tag{3}$$

and so

$$\alpha = \frac{2\omega}{c} n_2 \tag{4}$$

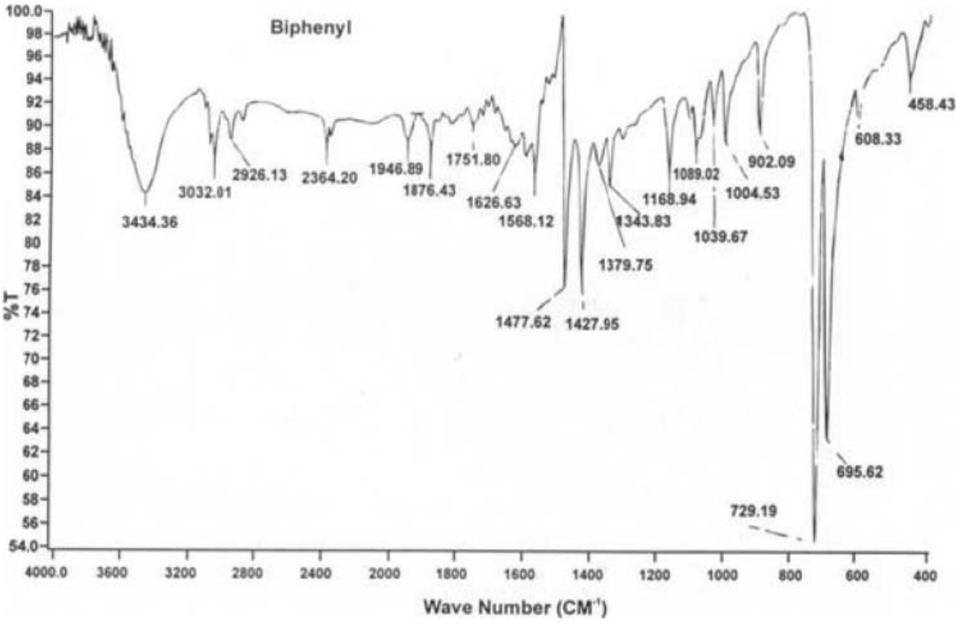

Figure 7. IR spectrum of biphenyl.

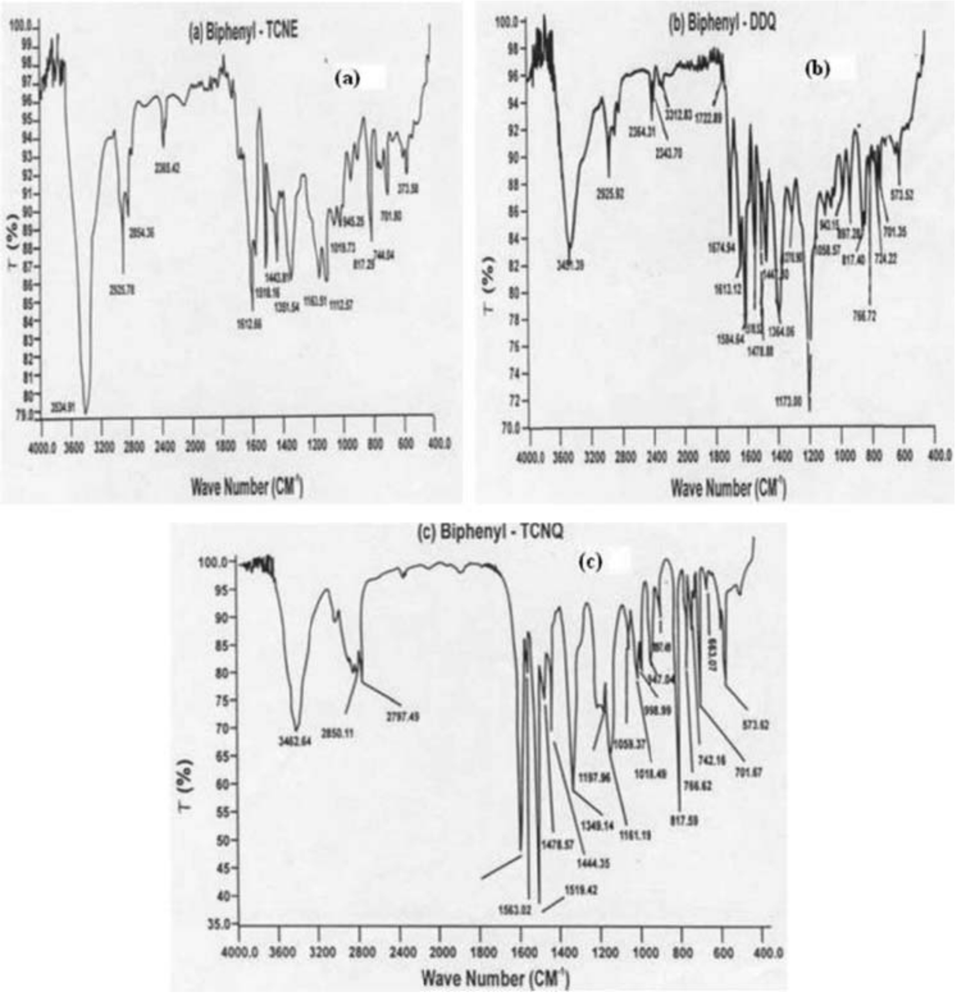

Figure 8. (a)–(c). IR spectrum of biphenyl-TCNE IR spectrum of biphenyl-DDQ and IR spectrum of biphenyl-TCNQ.

where n_1 and n_2 are real and imaginary parts of refractive index and ε_2 is the imaginary part of dielectric constant.

A Gaussian band is centered around 1430 cm^{-1} with fine structure. An average or smooth Gaussian curve can be plotted leaving out one strong dip in transmission at 1428 cm^{-1} and one sharp dispersion line-shape around 1478 cm^{-1}. The sharp dip is the transmission at 1428 cm^{-1} can be related with Gaussian split in the center when the density of states and the Fermi level both changing while varying energy [15]. The sharp dispersion line shape should not be observed in the absorption or transmission because α is proportional to n_2 and not to n_1, the later is likely to have dispersion shape. This proves that the sharp dispersion comes from reflectivity of the sample.

The Gaussian around 1430 cm^{-1} is similar to the one observed in $(DPPD)_5I_{12}$ which has photoconductivity [16,17]. In photoconductors, either a sharp step found in conductivity which shifts when light is incident [4,18] or a peak (either Gaussian shape or other shape) is

Table 2. Gaussian distributions in biphenyl complexes

Name of the complex	Absorption	Wave number of maximum absorption	Full width at half maximum (cm^{-1})
Biphenyl	10	1900	670
	15	1480	350
Biphenyl-TCNE	7.5	1400	200
	7.5	1100	220
Biphenyl-DDQ	8.7	1180	270
	5.5	650	450
Biphenyl-TCNQ	6.0	1380	250
	6.8	1100	210
	6.0	750	600
Biphenyl-iodine	5.3	1350	190
	6.0	1100	200
	6.5	680	340

observed [19,20]. Both types of photoconductors, intrinsic or extrinsic lead to a symmetric band in spectrum [21,22]. There are many studies on inorganic photoconductors like ZnSe, CdSe, many alloys, PbS, SiC, CdS, PbS, and wide literature is available from old time [4]. There is a symmetric fine structure in the Gaussian curves in biphenyl and $(DPPD)_5I_{12}$. This fine structure can be ascribed to exciton-photon or exciton-phonon coupling [23]. There is a long tail of Gaussian profile in low-frequency range 1200–800 cm^{-1} making the Gaussian curve asymmetric. Such asymmetric Gaussian bands are expected within optical properties within a small polaron model [24]. The parameters of Gaussian distributions found in the present study are all summarized (Table 2).

The last range to be discussed in Fig. 7 is between 400 and 800 cm^{-1}. Biphenyl contains sharp vibrational bands around 729 cm^{-1}, 695 cm^{-1}, and some small bands. Only when charge transfer interactions are strong as in TCNE complex (Fig. 8(a)) and in DDQ complex (Fig. 8(b)) that these bands merge into a long tail of Gaussian curves. Now consider the effect of charge transfer on the spectrum of biphenyl. The first point to be mentioned is about the transparency of infrared light in the range of 1800–3000 cm^{-1}. Many organic donors show a development of absorption while interacting with acceptors at various sites and the analysis of the increased but featureless absorption leads to the determination of band gap and phonon energy, later in the case of an indirect transition [25–27]. However, this is completely not found in any complex of biphenyl (Figs 8 and 9).

This is related with photoconducting nature of biphenyl. Charge transfer does occur with all five acceptors used in the present cases as it is revealed by strong color difference from a color of mixtures, e.g., biphenyl-TCNQ was red, not green like TCNQ nor like biphenyl, nor a color of mixture. It may be that the electrons (or holes) involved in photoconduction repel acceptor electrons and therefore, do not interact in 1800–3000 cm^{-1} range. The changes in the spectral features in rest of the range below 1800 cm^{-1} are remarkably different from a spectrum of mere superposition.

Consider biphenyl-TCNE (1:1) complex. Its infrared spectrum is shown in Fig. 8. The dispersion line shape discussed above in the biphenyl gets inverted (or 180° out of phase) in the spectrum of biphenyl-TCNE (see the band marked as 1587 cm^{-1}). The Gaussian band at 1430 cm^{-1} in biphenyl show a redshift to about 1403 cm^{-1}. The background absorption,

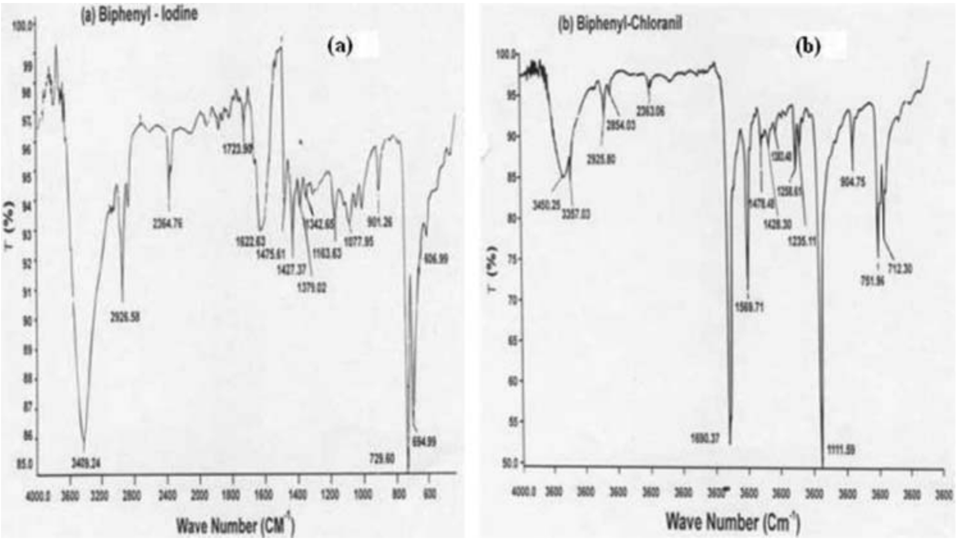

Figure 9. (a) and (b). IR spectrum of biphenyl-iodine and IR spectrum of biphenyl-chloranil.

which developed in the range 800–1800 cm^{-1} in biphenyl, is extended to 400 cm^{-1} still keeping two sharp vibrational bands distinct. Overall background absorption is increased and oscillator strength can be determined by the area under the featureless background. The vibrational and rotational band sharpens in CT complexes rather than broadening. This shows that the electron-phonon coupling consents reduce upon the formation of a CT complex. The background absorption borrows intensity from the individual vibrational and rotational modes. This is contrary to what happens in a normal CT complex. The Gaussian bands of biphenyl and its CT complexes are fitted (Figs 10(a)–(e)).

Among all the complexes, biphenyl-TCNE shows the largest change in the oscillator strength of background absorption. There is a range between 1800 and 2800 cm^{-1}. When α increases as λ (wavelength) increase. Here, free carrier absorption [7] is fitted which is given by

$$\alpha_{\mathrm{f}} = \mathrm{A}\lambda^{1.5} + \mathrm{B}\lambda^{2.5} + \mathrm{C}\lambda^{3.5} \tag{5}$$

log α versus log λ can be plotted and if slope is 1.5, it is scattering by acoustic phonons, if it is 2.5, it is scattering by optical phonons and if it is 3.5, it is scattering by ionized impurities. It can also be analyzed by using

$$\left(\frac{\alpha_f}{\lambda^{1.5}}\right) = A + B\lambda + C\lambda^2 \tag{6}$$

and

$$\frac{d}{d\lambda}\left(\frac{\alpha_f}{\lambda^{1.5}}\right) = B + 2C\lambda \tag{7}$$

If all types of scattering are not present log α versus log λ are plotted (Fig. 11) for both biphenyl-TCNQ and biphenyl-TCNE. The graphs clearly show that there is scattering by acoustic phonons in biphenyl-TCNE and biphenyl-TCNQ. The infrared spectrum of

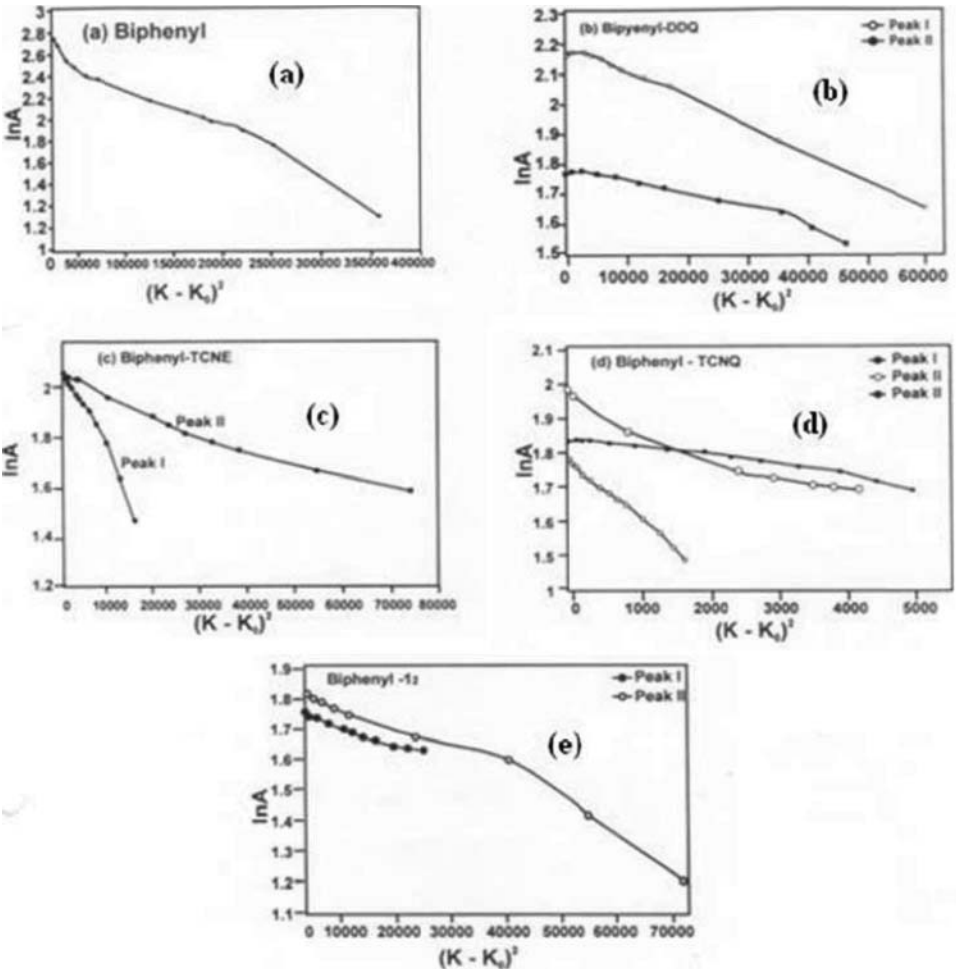

Figure 10. log A versus $(k\text{-}k_o)^2$ for various Gaussian profiles in (a) biphenyl, (b) biphenyl-DDQ, (c) biphenyl-TCNE, (d) biphenyl-TCNQ, and (e) biphenyl-I_2.

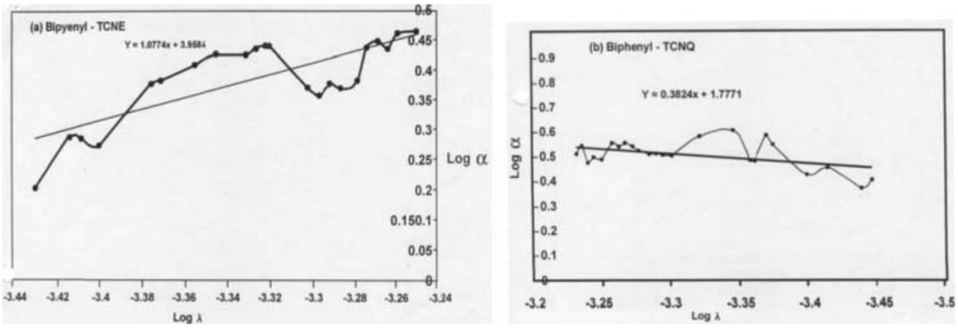

Figure 11. log α versus log λ for (a) biphenyl-TCNE and (b) biphenyl-TCNQ.

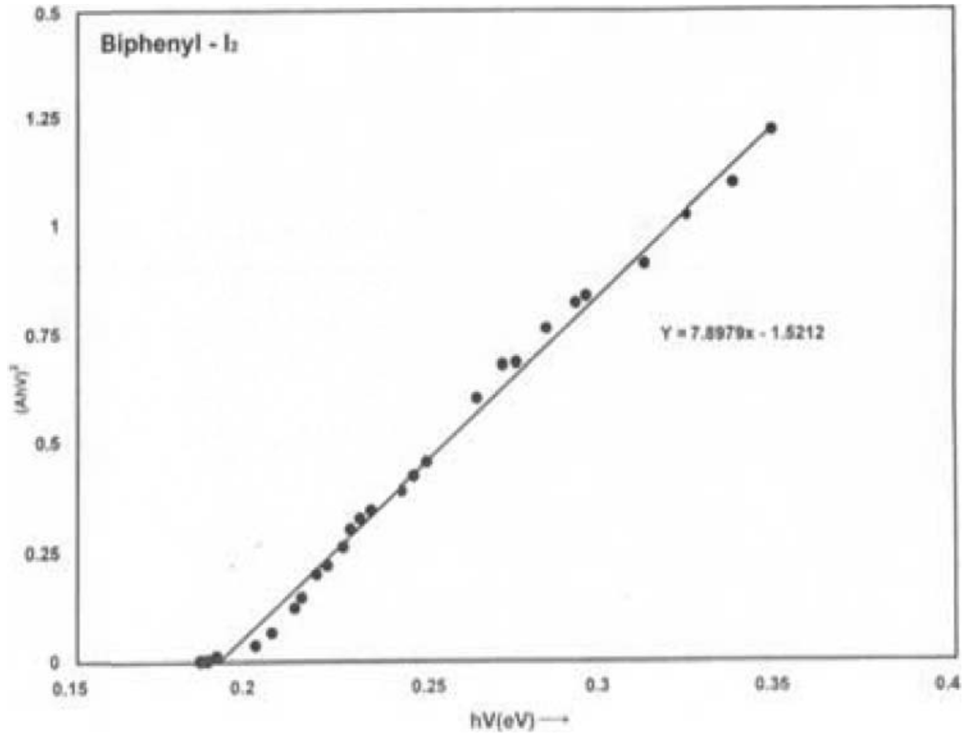

Figure 12. Nature of transition in biphenyl-I_2.

biphenyl-DDQ is shown (Fig. 8(b)). The Gaussian curve is around 1172 cm^{-1} is superposing over a broad flat background between 1800 and 400 cm^{-1}. Low-frequency peaks below 800 cm^{-1} merge in the background. Background absorption obtained by joining transmission peaks has features related with mobility gaps originating from frequency-dependent lifetime, as discussed elsewhere [11]. The infrared spectrum of biphenyl-TCNQ (Fig. 8(c)) contains three Gaussian bands around 1400, 1100, and 696 cm^{-1}. Two of them have sharp absorption maxima superposed over broad Gaussian bands. The infrared spectrum of biphenyl-iodine (Fig. 9(a)) is somewhat of different type than others. It does contain a range 2600–1800 cm^{-1} where nature of transition can be studied. Here $(\alpha h\nu)^{1/2}$,$(\alpha h\nu)^2$, $(\alpha h\nu)^{1/3}$, $(\alpha h\nu)^{2/3}$, and $\ln \alpha$ are calculated and plotted.

The best fit $\alpha h\nu \sim (h\nu - E_g)^n$ is shown (Fig. 12). This is possible because iodine itself is photoconducting like biphenyl. Remarkable changes are observed below 1800 cm^{-1} in the spectrum of biphenyl. Two Gaussian bands are found with fine structures.

Biphenyl-chloranil has shown small difference in features of the infrared spectrum (Fig. 9(b)) but overall absorption is substantially decreased. So, there is reduction in optical conductivity when charge transfer occurs. The band assignments in the infrared spectra of biphenyl and its five complexes are summarized (Tables 3 and 4). The fine structure of one or more Gaussian profiles can be interpreted in terms of multielectron hopping as discussed elsewhere [28]. Alternative interpretation comes from fine structure of charge density waves or frequency modulation of charge density waves. As charge gets localized due to lattice distortion, number of Gaussian bands increase. One Gaussian curve describes less charge localized rather than two or three Gaussian curves describing more charge getting

Table 3. Band assignments in biphenyl, biphenyl-TCNE, and biphenyl-TCNQ

Biphenyl		Biphenyl-TCNE		Biphenyl-TCNQ	
Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment
3434	ν_{O-H} (water)	3430	ν_{O-H}(water)	3450	ν_{O-H}(water)
3032	Doublet ν_{C-H} (in plane)	2927	ν_{C-H}	2926	ν_{C-H}
2926	ν_{C-H} (out of plane)	2851	ν_{C-H}	2368	$\nu_{C\equiv N}$
2364	doublet (impurity)	2368	$\nu_{C\equiv N}$(TCNE)	2218	$\nu_{C=C}$
1946	Impurity	2208	$\nu_{C=C}$	1926	δ_{N-H}
1876	Impurity	1720	δ_{N-H}	1546	Water
1751	$\nu_{C=C}$	1587	Water	1478	δ_{C-H}
1627	δ_{O-H} (water)	1502	ν_{C-C}	1113	ν_{C-C}
1568	$\nu_{C=C}$	1403	δ_{C-H}	838	π_{C-H}
1478	$n_1(\omega)$	1348	ν_{C-C}	737	π_{C-H}
1379	δ_{C-H}	1154	ν_{C-C}	696	π_{C-H}
1343	ν_{C-C}Nondegenerate ring vibration	1002	ν_{C-C}		
1168	ν_{C-C}	956	π_{C-H}		
1089	ν_{C-C}	732	π_{C-H}		
1039	ν_{C-C}	696	$C-C\equiv N$		
1004	ν_{C-C}	554	$C-C\equiv N$		
902	π_{C-H} and water				
726	π_{C-H}				
695					
608					
458					

Table 4. Band assignments in three complexes of biphenyl

Biphenyl-DDQ		Biphenyl-chloranil		Biphenyl-iodine	
Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment
3427	ν_{O-H} (water)	3450	ν_{O-H} (water)	3409	ν_{O-H} (water)
2926	ν_{C-H}	3357	ν_{C-H}	2926	ν_{C-H}
2855	ν_{C-H}	2926	ν_{C-H}	2364	Impurity
2366	$\nu_{C\equiv N}$	2854	ν_{C-H}	1723	$\nu_{C=C}$
2252	$\nu_{C=C}$	2363	ν_{C-H}	1622	Water
1676	Water	1690	Water	1476	$n_1(\omega)$
1553	$\nu_{C=O}$	1570	$\nu_{C=O}$	1427	
1480	$\nu_{C=N}$	1478	$\nu_{C=C}$	1379	δ_{C-H}
1452	δ_{C-H}	1420	δ_{C-H}	1342	ν_{C-C}
1269	ν_{C-C}	1383	ν_{C-C}	1163	ν_{C-C}
1172	ν_{C-N}	1258	ν_{C-C}	1078	ν_{C-C}
892	$\delta_{C=O}$	1235	ν_{C-O}	901	π_{C-H}
799	π_{C-H}	1112	ν_{C-C}	729	π_{C-H}
736	π_{C-H}	904	π_{C-H}	694	C−Cl
700	C−Cl	752	C−Cl	607	$\pi_{C-H}1$
607	Water	712	C−Cl		

localized. This detail is similar to what is found recently in oligoanilines and their iodine complexes [29]. It is possible that there is Kuhn periodicity in otherwise delocalized electron conduction in photoconductors [30]. It is clear from the present study that the situation is different from the ordinary charge transfer complexes. Charge transfer is detrimental to optical conductivity in the infrared range. However, situation again becomes similar when both the donor and the acceptor are photoconducting, e.g., biphenyl-iodine, where analysis of the nature of transition is possible, i.e., the absorption develops in the gap region.

4. Conclusions

The five complexes of biphenyl show entirely different features from each other in UV-visible-near IR range of electromagnetic spectroscopy. The spectra are governed by acceptor molecules and donor-acceptor interactions. It is far from clear how photoconductivity is related with several optical absorption edges in UV-visible range. Theory for reduction of exponents of free carrier absorption is also unknown. Biphenyl is a well-known photoconductor. Here, five complexes of biphenyl are prepared and studied with infrared spectroscopy. Charge transfer reduces absorption rather than increasing in complete range. No absorption develops in the gap region. The photoconducting band gap is less than usual Peierls gap in one-dimensional conductors. Spectral features do change showing that there is significant effect of charge transfer on the vibrational and rotational bands. Electron-phonon coupling decreases when charge transfer occurs. One or more Gaussian bands are found as in the cases of oligoanilines and their iodine complexes. This predicts Kuhn periodicity in these one-dimensional photoconductors. However, the reduction in optical conductivity does not discard possibility of an increase in dc photoconductivity since dc response of visible light is photoconductivity.

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