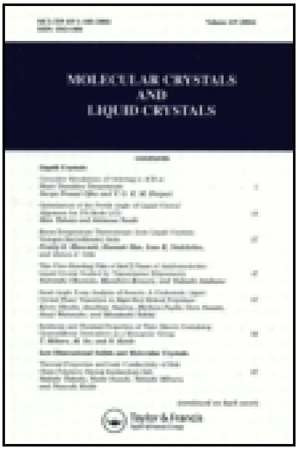

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Kuhn Periodicity in Oligoanilines and Oligoaniline-Iodine Complexes

R. G. Patel [a] , G. K. Solanki [a] , S. M. Prajapati [a] & A. T. Oza [a]

[a] Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

To cite this article: R. G. Patel, G. K. Solanki, S. M. Prajapati & A. T. Oza (2005): Kuhn Periodicity in Oligoanilines and Oligoaniline-Iodine Complexes, Molecular Crystals and Liquid Crystals, 442:1, 167-180

To link to this article: http://dx.doi.org/10.1080/154214090964924

Mol. Cryst. Liq. Cryst., Vol. 442, pp. 167–180, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090964924

Kuhn Periodicity in Oligoanilines and Oligoaniline–Iodine Complexes

R. G. Patel
G. K. Solanki
S. M. Prajapati
A. T. Oza
Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

Spectroscopic work on eight-ring oligoanilines, namely emeraldine, nigraniline, and pernigraniline, has been performed. Infrared spectra are obtained with and without iodine to study the effect of complexation with iodine. Spectra of these even-numbered systems show Kuhn periodicity (paired rings). The number of Gaussian curves shows the delocalized charge between two or more consecutive rings. Thus, emeraldine shows three Gaussian curves. As the quinonoid resonance is established, it electronically shorts two neighboring rings. This leads to two Gaussian curves in nigraniline and one Gaussian curve in pernigraniline. Thus, the quinonoid resonance suppresses Kuhn periodicity and establishes long-range order.

Keywords: Gaussian distributions; iodine complexes; oligoanilines; quinonoid resonances

INTRODUCTION

In charge-transfer complexes with iodine, usually the stacks of organic donors conduct electricity. A large number of oligoanilines are reviewed elsewhere [1]. $(DPPD)_5I_{12}$ (DPPD is N,N′-diphenyl-p-phenylene diamine) was crystallized and studied with X-ray diffraction [2]. It was found to be a small band gap semiconductor [3]. The electron-spin resonance study indicates that the thermally excited spins are the charge carriers. There is also a change in the sign of the thermoelectric power. The infrared spectra of $(DPPD)_5I_{12}$ were studied in detail

---

Address correspondence to A. T. Oza, Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India.

recently [4]. The electrical resistivity of a series of oligoaniline–iodine complexes are known [5–10]. The resistivity and activation energy decrease systematically as the number of atomic units increases from three to seven. There is a slight mismatch between the number of iodine atoms and the number of NH groups. Activation energy changes at low temperature because of partial degeneracy of electron gas and worsening of charge transfer. Emeraldine doped with the HSO_4 group is a semiconductor [11]. There is a series of three oligoanilines not differing in the number of phenyl rings but differing in the number of quinonoid rings [12,13]. These are precursors of aniline black dye, which has been previously studied [14]. Three eight-ring oligomers with iodine were studied with resistivity measurements down to a low temperature [15]. Poly(diphenylamine) was also explained with tetracyanoethylene (TCNE) and halogens [16]. Emeraldine, nigraniline, and pernigraniline were also studied with infrared spectroscopy [17]. These oligoanilines are prepared here by a different method, and iodine complexes are also prepared in the present study. The transmittance spectra between $400\,cm^{-1}$ and $4000\,cm^{-1}$ have been studied with and without iodine.

Kuhn periodicity is observed in even-membered polymers where the activation energy does not tend to zero, as it does in odd-membered cases. In the latter, high polarization develops and the dielectric constant increases. Kuhn periodicity is a pairwise periodicity along a carbon chain that occurs both in the ground state as well as in the excited state. It is very similar to the Peierls transition in a one-dimensional conductor. High electrondensity shortens a bond and low density lengthens it. The ground state is lowered with an associated distortion in the chain. It is a kind of one-dimensional Jahn–Teller effect that occurs in molecules and crystals. The probability density maxima are in the interatomic space, unlike these maxima at the atomic centers in the odd-membered systems. Further details can be seen in an earlier review article [18]. Iodine complexes of oligoanilines have not been studied until now. This is the first report of oligomer–iodine complexes.

EXPERIMENTAL

Emeraldine, nigraniline, and pernigraniline were prepared earlier by peroxydisulfate synthesis [17]. This study did not change the strength of the oxidizing agents. Here, we synthesized these three oligomers by changing the oxidizing strengths of the chemical reagents. Hydrogen peroxide, perchoric acid, and potassium permanganate were used along with sulfuric acid rather than copper sulfate. Copper sulfate is a weaker oxidizing agent, which was used in the preparation of four-ring Willstater's emeraldine [13]. Also, copper sulfate can form

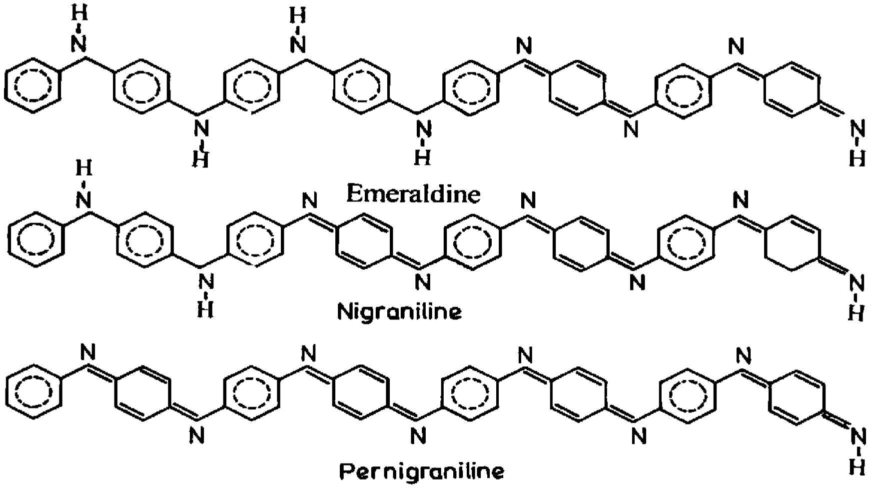

FIGURE 1 Molecular structure of oligoaniline.

polymeric species of coordination polymers in which copper remains bonded. Thus, this was not used in the present work. Only a few drops of hydrochloric acid were used to partially form aniline hydrochloride in the rest of the aniline medium in the following process.

Emeraldine was prepared by oxidation of aniline hydrochloride by hydrogen peroxide in the presence of sulfuric acid. Nigraniline was prepared in the form of single crystals by oxidation of aniline hydrochloride by perchloric acid in the presence of sulfuric acid. Pernigraniline (fully oxidized) was prepared by oxidation of aniline hydrochloride by potassium dichloromate or potassium permanganate in the presence of sulfuric acid. Emeraldine was green, nigraniline was blue, and pernigraniline was violet. The molecular structure of these oligoanilines are shown (Fig. 1). Their iodine complexes were prepared by grinding the oligomers (finite polymers) with molecular iodine in a mortar.

The oligoanilines and iodine complexes were ground with KBr and pellets were prepared. The KBr mull absorption spectra were obtained in a standard spectrophotometer (Perkin-Elmer). The spectra are shown in Figs. 2, 3, and 4.

RESULTS AND DISCUSSION

There are large number of bands in the spectra of oligoanilines in the infrared range. These bands are ascribed to various stretching and

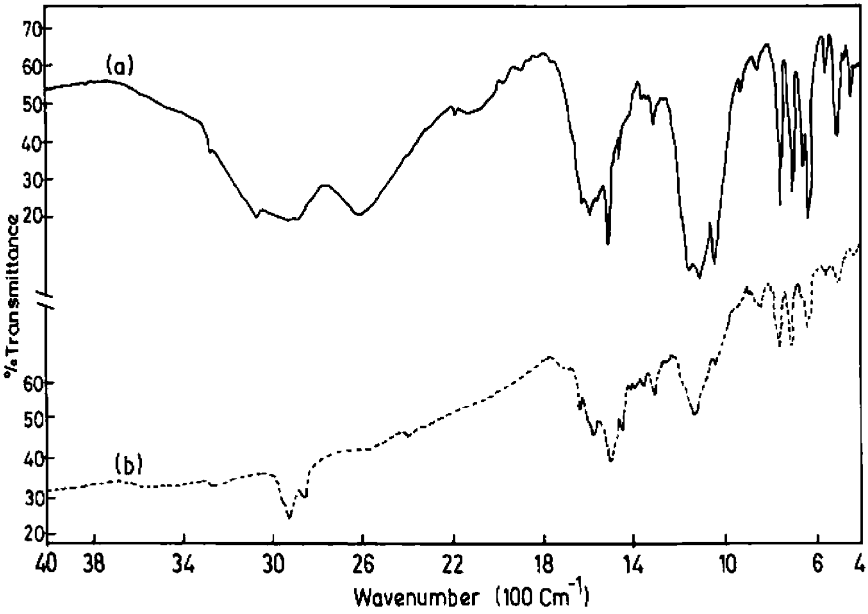

FIGURE 2 Infrared spectra of (a) emeraldine and (b) emeraldine–iodine.

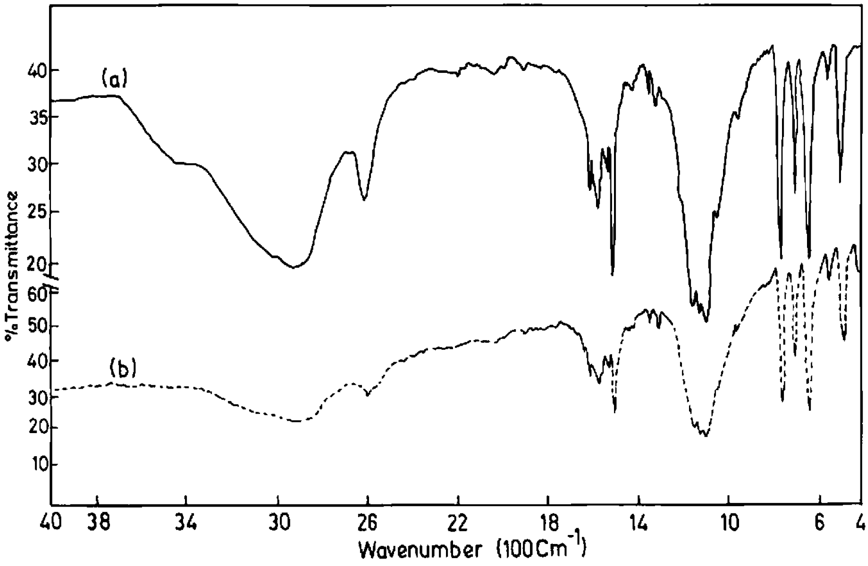

FIGURE 3 Infrared spectra of (a) nigraniline and (b) nigraniline–iodine.

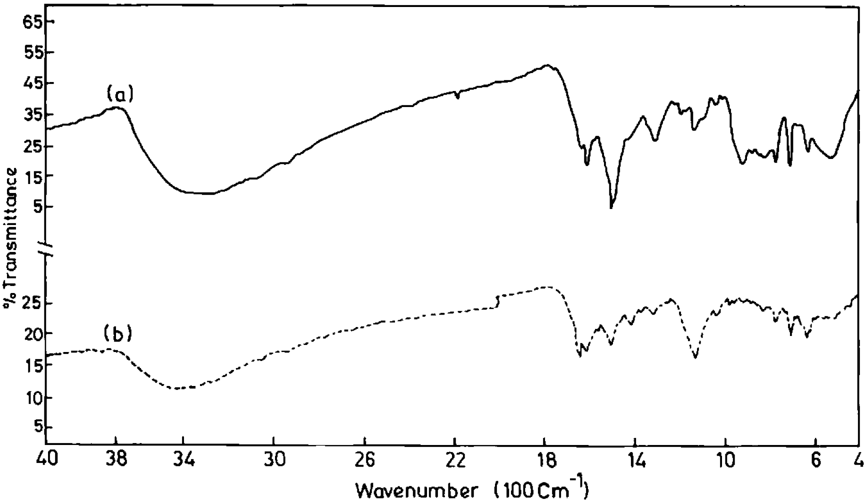

FIGURE 4 Infrared spectra of (a) pernigraniline and (b) pernigraniline–iodine.

deformation vibrations using guidance from elsewhere [19,20] (Table 1). Below 800 cm^{-1}, Raman active modes are observed. In the spectra of iodine complexes, no new bands are observed. Only intensities of bands and location (wavenumbers) of the bands are affected. Medium and weak bands are ascribed to nondegenerate vibrations and quinonoid resonances.

TABLE 1 Band Assignments in the Infrared Range Wavenumber (cm^{-1})

Em	Em-I_2	Nig	Nig-I_2	Pernig	Pernig-I_2	Assignments
3280	3280	—	—	—	—	N–H stretching
3080	3080	—	—	—	—	C–H stretching
2600	2600	2600	2600	—	—	Crystallinity
2200	2200	2180	2180	2480	—	C=C stretching
1670	1670	—	—	1640	1660	C–C bending
1600	1600	1600	1600	1600	1600	C=N stretching
1580	1580	1580	1580	1500	1500	N–H bending
1300	1300	1300	1300	1310	1290	C–H bending
1180	1180	1160	1160	1190	1170	Ring C–C vibrations
1100	1150	1120	1120	1130	1130	Ring C–C vibrations
1020	1040	1100	1060	1100	—	Ring C–C vibrations
850–400	850–400	800–400	800–400	—	—	Raman active modes

A comparison of the spectra of emeraldine and its iodine complex shows that there is a blue shift of C–C vibrations and increase in intensity of these vibrations. Moreover, there is a decrease in the intensities of Raman active modes.

A similar comparison for nigraniline shows that there is a decrease in intensity of a band at 1500 cm^{-1} when an iodine complex is formed. Also, ring C–C vibrations are suppressed. Here, Raman active modes are affected.

In the case of pernigraniline, there are intensity changes in the vibrations near 1640 cm^{-1}. The vibration at 1500 cm^{-1} is suppressed in the spectrum of iodine complexes. Ring C–C vibrations are enhanced in the spectra of iodine complexes.

A comparison of the spectra of three oligoanilines shows that the strong bands are similar. The difference lies in diminution of ring C–C vibrations in the spectrum of pernigraniline because of quinonoid resonance. A C=N stretching vibration should emerge in pernigraniline, but this band is not observed because of increased continuous background absorption.

In the spectra of emeraldine and nigraniline, a special band is observed at 2600 cm^{-1}, which can be assigned to crystallinity. In the spectrum of nigraniline, it is sharp and intense because of highly crystalline nigraniline. It is broad in the spectrum of emeraldine.

The nigraniline was precipitated in a liquid medium in the form of large crystals. Emeraldine formed flakes, which are flat platelets. Pernigraniline formed films on the side of beakers. It was the least crystalline material because the films were disordered or amorphous.

The absorption increases as wavenumber increases in the range of 3200 cm^{-1} in the spectra of all three oligoanilines. This transition can be ascribed to an impurity level.

This type of increase in absorption as wavenumber increases can be attributed to the transition to an impurity level, particularly above the band gap [21,22]. Free-carrier absorption has a reverse trend [23]. This has also been found in elemental or inorganic compound semiconductors [21]. It could be impurities such as sulfuric acid or an oxidizing agent left unreacted in the present study. Iodine suppresses this transition and this increase is not observed in the spectra of iodine complexes. Rather, it is intercalation or an inclusion compound with iodine in each case.

However, iodine changes the band gap of all three oligomers. When continuous and featureless absorption in the range 1800 cm^{-1} to 2600 cm^{-1} is analyzed, it is found that iodine decreases band gap (Table 2). Pernigraniline shows the least band gap in the series of the three oligoanilines.

TABLE 2 Optical Absorption Edges

Compound	Frequency of minimum absorption (cm^{-1})	Optical absorption edge (eV)
Emeraldine	2200	0.265
Emeraldine–iodine	1790	0.215
Nigraniline	2300	0.277
Nigraniline–iodine	1750	0.211
Pernigraniline	1800	0.217
Pernigraniline–iodine	1770	0.213

In the case of emeraldine–iodine, there is no change in the frequency or intensity of any band in the range 400–1800 cm^{-1}. Iodine increases the background absorption above 1800 cm^{-1}. There is a change in the nature and in the type of transition from the valence band to the conduction band (Table 2). The spectrum of emeraldine shows three Gaussian curves at 2850 cm^{-1}, 2920 cm^{-1}, and 3450 cm^{-1} (Figs. 2 and 5). The two Gaussian curves at 2850 cm^{-1} and 2920 cm^{-1} turn into an oscillator model in the spectrum of its iodine complex (Fig. 2) and both the bands become sharp. However, the Gaussian at 3450 cm^{-1} broadens and smears out (Fig. 2).

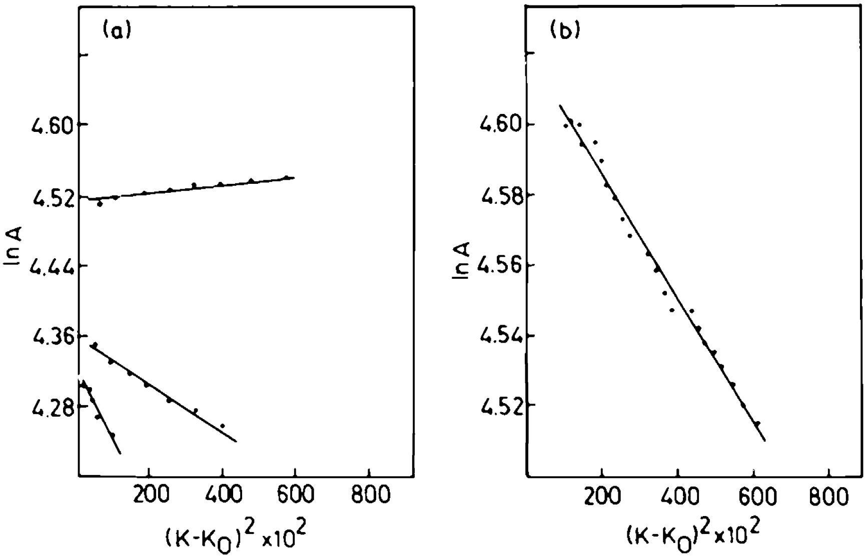

FIGURE 5 Gaussian fitted in the spectra of (a) emeraldine and (b) emeraldine–iodine.

The absorption of the Gaussian form is described by

$$A = A_0 \exp\left[-\left(\frac{(\omega - \omega_0)^2}{2M_2}\right)\right]$$

where A is absorbance, A_0 is the maximum absorbance, ω_0 is the central frequency, and M_2 is the second moment related with the band width according to

$$M_2 = \frac{W^2}{8 \ln 2}$$

where W is the full width at half maximum.

In the case of nigraniline–iodine, the spectrum reveals reduction in the maximum intensities of bands between 400–1800 cm^{-1}. There is also a broadening of bands of nigraniline between 800 cm^{-1} and 1800 cm^{-1}. There are two envelopes centered around 1100 cm^{-1} and 1550 cm^{-1}. Both are broadened in the spectrum of the iodine complex. This shows that the electron–phonon constant increases by complexation with iodine. The charge transfer from nigraniline to iodine increases this coupling constant. In the spectrum of nigraniline, there are two Gaussian curves centered around 2900 cm^{-1} and 3000 cm^{-1}. The Gaussian distributions remain Gaussian in the spectrum of its iodine complex (Fig. 3). These Gaussian curves are shown in Fig. 6. Iodine slightly increases the background absorption in the range of 1800 cm^{-1} to 2400 cm^{-1} as the frequency increases. This absorption remains almost constant in the spectrum of pure nigraniline in that particular range.

In the case of pernigraniline–iodine, an increase in background absorption compared to the full infrared spectrum of pernigraniline is observed (Fig. 7). The intensity of a broad band at 1120 cm^{-1} increases because of complexation with iodine, whereas there is a reduction in the intensity of a band at 1510 cm^{-1} in the spectrum of pernigraniline. There is also a doublet centered around 1610 cm^{-1}, which is modified in the spectrum of the iodine complex. The nature and type of transition from the valence to the conduction band do not change because of complexation with iodine as it does in the case of emeraldine. There is only one broad Gaussian band at 3300 cm^{-1} in the spectrum of its iodine complex (Fig. 4). These Gaussian curves are presented in Fig. 4. The central frequencies, absorption maxima, and the widths of the Gaussian bands are calculated from the Gaussian curve fits and tabulated (Table 3).

In a semiconducting material there can be a direct or indirect transition between the valence band and conduction band depending on

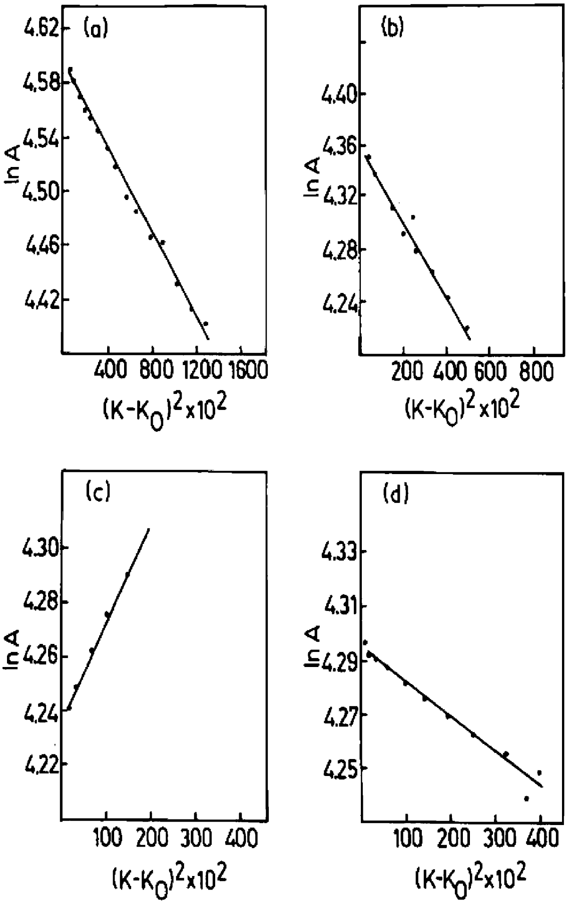

FIGURE 6 Gaussian fitted in the spectra of (a, b) nigraniline and (c, d) nigraniline–iodine.

whether the band structures have valleys in three dimensions, which in turn depends on the crystal structure and bonding interactions [24]. In a direct transition, there is no momentum change and the transition occurs from the top of the valence band to the bottom of the conduction band. Electrons do not require a momentum change. In an indirect transition, when there is more than one conduction band minima, electrons have to take help from phonons (quantized lattice vibration) with a transient coupling leading to a transition. After a transition, momentum is required to lower the minimum of the

TABLE 3 Gaussian Bands Fitted in Oligoanilines and Their Iodine Complexes

Compound	Maximum absorption A (%)	Central frequency wavenumber K_0 (cm^{-1})	Full width at half maximum W (cm^{-1})
Emeraldine	(1) 93.31	2100	294.864
	(2) 77.32	2600	104.880
	(3) 74.291	3000	58.86
Emeraldine–I_2	99.982	2600	12.769
Nigraniline	(1) 98.297	2900	140.718
	(2) 77.478	3400	88.994
Nigraniline–I_2	(1) 74.291	2600	86.67
	(2) 73.332	2900	141.72
Pernigraniline	93.316	3400	103.254
Pernigraniline–I_2	93.690	3400	134.251

conduction band, and reemission of a phonon occurs. The absorption coefficient is given by

$$\alpha = A(h\nu - E_g)^r$$

where $r = 1/2$ for a direct transition and $r = 2$ for an indirect transition (for transitions that are not allowed at $k = 0$, $r = 3/2$, and

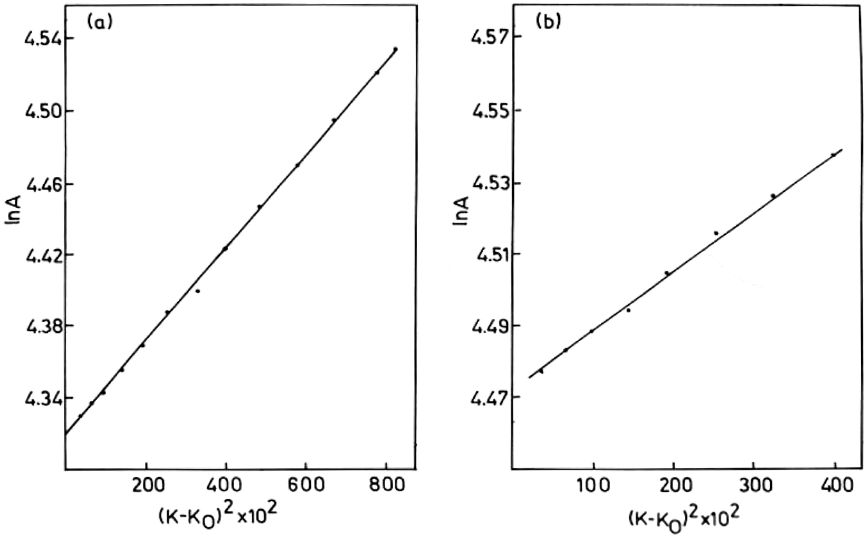

FIGURE 7 Gaussian fitted in the spectra of (a) pernigraniline and (b) pernigraniline–iodine.

$r = 3$ for the direct and an indirect cases). This equation is for crystalline media. For disordered or amorphous media, the absorption coefficient is given by

$$\alpha h\nu = A(h\nu - E_g)^r$$

where r varies in the same manner as before, but $\alpha h\nu$ is used instead of α (i.e., a weaker dependence of absorption on frequency). All these cases have been discussed in detail earlier [21,25]. These models particularly apply to elemental or compound semiconductors and have been applied to organic, organometallic, or polymeric semiconductors except by one of the authors and his group [26–32].

The types of transitions were identified by calculation and plotting $(Ah\nu)^{1/2}$, $(Ah\nu)^2$, $(Ah\nu)^{1/3}$, and $(Ah\nu)^{2/3}$ vs. $h\nu$ for powder samples (obtained during grinding with KBr). The best fits are shown in Figs. 8, 9, and 10. This shows forbidden direct transitions in all oligoanilines and their iodine complexes.

There is Kuhn periodicity [18] (pairwise periodicity) observed in the emeraldine eight-ring oligomer. This should show four Gaussian bands, but three Gaussian bands are observed because the quinonoid resonance of two rings in which there is a π-cloud in the excited state

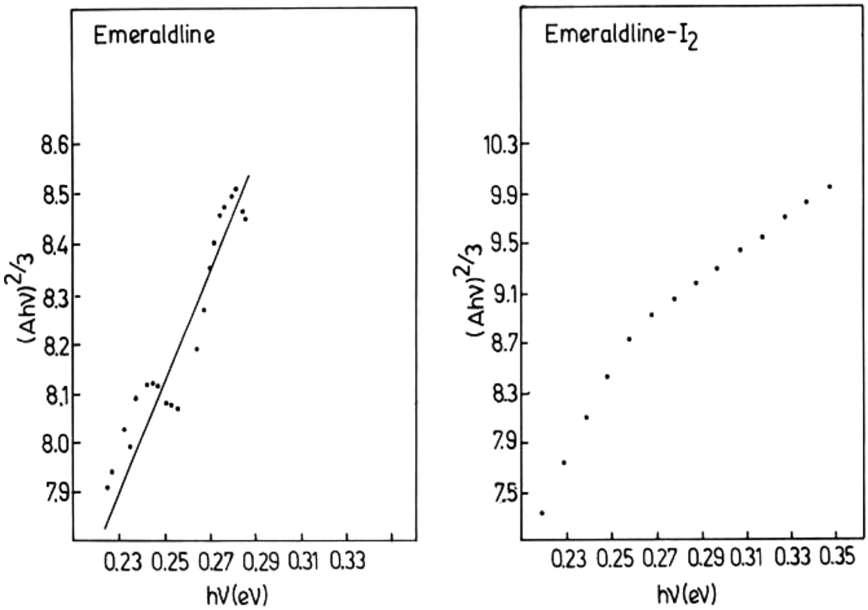

FIGURE 8 Transition in (a) emeraldine and (b) emeraldine–iodine.

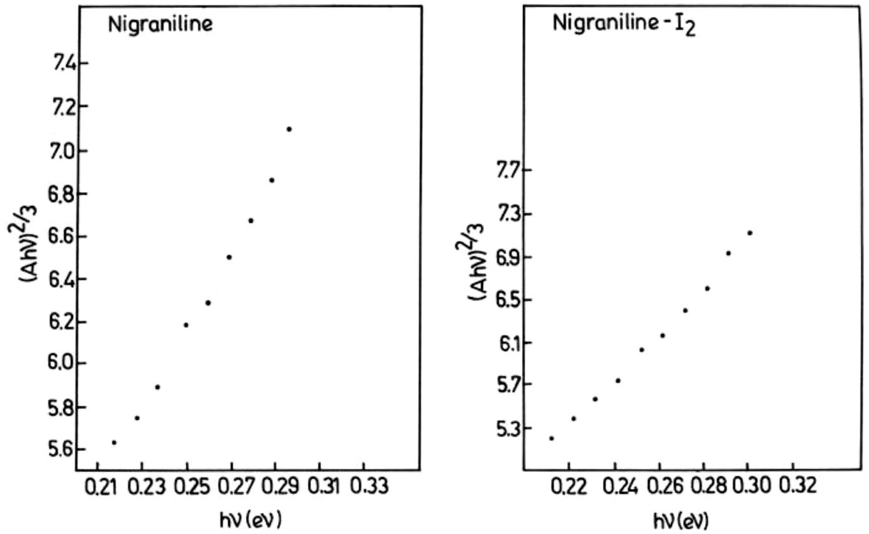

FIGURE 9 Transition in (a) nigraniline and (b) nigraniline–iodine.

shorts four rings electronically. In nigraniline, only two Gaussians bands are observed because there are three paired rings that short six rings. In the case of pernigraniline all the rings are electrically

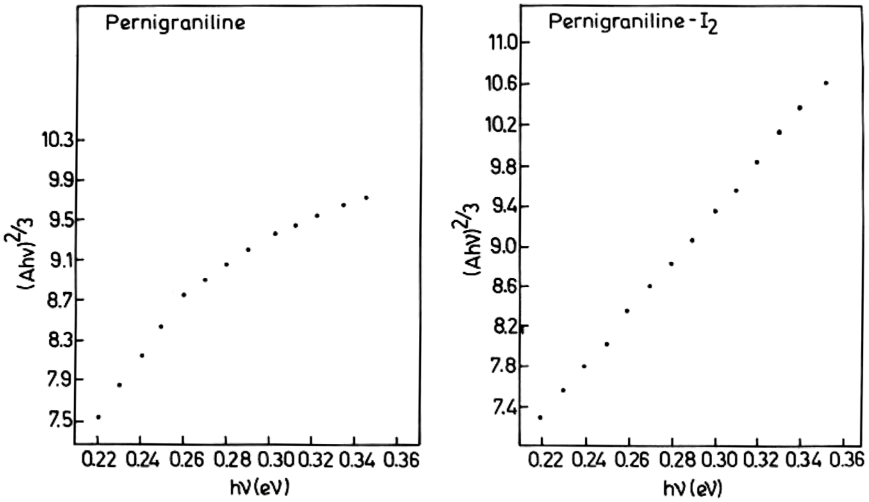

FIGURE 10 Transition in (a) pernigraniline and (b) pernigraniline–iodine.

shorted by four aromatic rings undergoing quinonoid resonances. Thus, quinonoid resonance suppresses Kuhn periodicity and establishes long-range order.

This shows that the rings are arranged perpendicular to the plane of the diagram (Fig. 1), that is, there is stacking of aromatic rings. The out-of-phase ring-puckering vibrations occur in such a manner that there is pairwise periodicity unless there is quinonoid resonance. In the case of quinonoid resonance, the aromatic rings become perfectly planar and ring-puckering vibrations cease. Actually there should be localization of charge carriers because the π-cloud is in an excited state and it shifts toward the neighboring rings, leading to electronic shorting of the rings and leading to delocalization.

REFERENCES

[1] Perlstein, J. H. (1997). *Chem. Int. Ed. Engl.*, *16*, 519.
[2] Huml, K. (1967). *Acta Cryst.*, *22*, 29.
[3] Hadek, V. (1968). *J. Chem. Phys.*, *49*, 5202.
[4] Patel, K. D. & Oza, A. T. (1997). *Indian J. Phys.*, *71B*, 161.
[5] Honzl, J., Ulbert, K., Hadek, V., Tiustakova, M., & Metalove, M. (1969). *J. Poly. Sci.*, *C16*, 4465.
[6] Honzl, J. & Thustakove, M. (1968). *J. Poly. Sci.*, *C22*, 451.
[7] Honzl, J., Ulbert, K., Hadek, V., & Tiustakova, M. (1965). *Chem. Commun.* (London), *19*, 440.
[8] Hadek, V., Zach, P., Ulbert, K., & Honzl, J. (1969). *Collect. Czech. Chem. Commun.*, *34*, 3139.
[9] Hadek, V. & Ulbert, K. (1967). *Collect. Czech. Chem. Commun.*, *32*, 1118.
[10] Hadek, V. (1968). *Physica Status Solidi*, *1*, 930.
[11] Keneto, K., Tanimatra, K., Vashino, K., & Inushed, Y. (1977). *Solid State Commun.*, *22*, 383.
[12] Kerrar, P. (1950). In: *Organic Chemistry*, A. J. Mcc (Trans.), Elsevier: New York, 585.
[13] Von Ritcher, V. (1946). The chemistry of carbon compounds. In: *The Aromatic Compounds*, A. J. Mcc (Trans.), Elsevier: New York, Vol. 3, 76, 107, and 248.
[14] Pohl, H. A. & Engelhardt, E. M. (1962). *J. Phys. Chem.*, *66*, 2085.
[15] Oza, A. T. (1980). Ph. D. Thesis, Indian Institute of Science, Bangalore.
[16] Kuwata, K., Sato, Y., & Hirota, K. (1964). *Bull. Chem. Soc. Jpn.*, *37*, 1391.
[17] Quillard, S., Louarn, G., Buisson, J. P., Lefrant, S., Master, J., & Macdiamird, A. G. (1992). *Syn. Metals*, *49*, 525.
[18] Pohl, H. A. (1968). In: *The Monographs in Macromolecular Chemistry*, *Organic Semiconducting Polymers*, Katon, J. E. (Ed.), Marcel-Dekker: New York, 51, and references therein.
[19] Drago, R. *Physical methods in inorganic chemistry*, East-West Press: New Delhi, 222.
[20] Sindhu, P. S. (1985). *Molecular spectroscopy*, Tata McGraw-Hill, 104.
[21] Pankove, J. A. (1965). *Optical processes in semiconductors*, Prentice-Hall: Englewood Cliffs, NJ.
[22] Burstein, E., Picus, G. S., & Sclar, N. (1965). *Proc. Photoconductivity Conference*, p. 353, Wiley.

[23] Fan, H. Y., Spitzer, W. G., & Collins, R. J. (1956). *Phys. Rev.*, *101*, 556.

[24] Johnson, E. J. In: *Semiconductors and Semi-Metals*, Willardson, R. K. & Beer, A. C. (Eds.), Academic press: New York, Vol. 3, 200.

[25] Kireev, P. S. (1975). *Semiconductor physics*, Mir Publishers: Moscow, 527.

[26] Oza, A. T. (1989). *Solid State Commun.*, *71*, 1005.

[27] Patel, K. D. & Oza, A. T. (1997). *Ind. J. Phys.*, *71B*, 161.

[28] Patel, R. G. & Oza, A. T. (2000). *Ind. J. Phys.*, *74B*, 31.

[29] Patel, M. B., Patel, S. G., Vaidya, R., & Oza, A. T. (2003). *Ind. J. Phys.*, *77B*, 199.

[30] Oza, A. T., Solanki, G. K., Patel, R. G., & Prajapati, S. M. (2004). *Ind. J. Phys.*, *78*, 591.

[31] Oza, A. T., Patel, S. G., Patel, R. G., Prajapati, S. M., & Vaidya, R. *Thin Solid Films* (accepted).

[32] Patel, M. B., Patel, S. G., Mehul, D., & Oza, A. T. (2004). *Ind. J. Pure Appl. Phys.*, *42*, 79.