502 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (2), 502—506 (1977) [Vol. 50, No. 2

Condensed State Spectra and Phase Transitions of Charge Transfer Autocomplexes

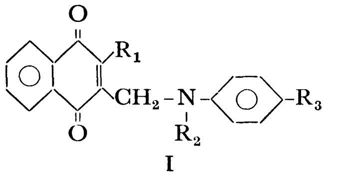
Jānis Freimanis, Andrejs Mālmanis, and Jānis Drēgeris
Institute of Organic Synthesis, Latvian Academy of Sciences, Riga 226006, U. S. S. R.

(Received January 8, 1976)

The results of a spectroscopic study of super-cooled melts and crystalline layers of charge-transfer autocomplexes are reported. Samples obtained by sublimation *in vacuo* or by melting of the complex between transparent plates undergo a "liquid-solid" phase transition. Amorphous films produce absorption bands identical with those obtained from solutions, whereas crystalline layers are colored depending on intermolecular CT interaction. In some cases transparent crystalline films with pronounced optical anisotropy were obtained.

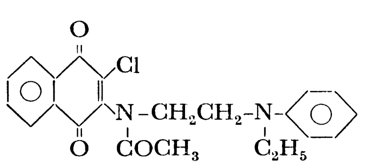
Vacuum-sublimed solid thin films are widely used for studying optical and electrophysical properties of organic compounds. Difficulties encountered in such studies are connected with the fact that the state of organic matter changes with time. Polychromism and polymorphism in donor–acceptor compounds (also in monomolecular ones) have been reported in a number of cases.[1–11] Only few of these have, however, been analysed from a structural point of view.[3,6,7,10] Another difficulty arises in connection with the fact that thin-layer samples are liable not only to polymorphic transitions of the "crystal-crystal" type, but also to "supercooled amorphous phase - crystal" transitions. Melting has been also found to produce considerable changes in the optical properties of certain donor–acceptor compounds.[12,15]

Polychromic changes of 2,4-dinitro-4′-diethylaminodiphenylamine and 2,4,6-trinitro-4′-diethylaminodiphenylamine have been reported previously.[2] The present work deals with a spectroscopic study of phase states, as well as of charge-transfer phenomena of molecular donor–acceptor autocomplexes (AC), particularly in thin-layer condensed films. Molecular autocomplexes of the naphthoquinone and nitroaryl series I,II,III have been investigated.

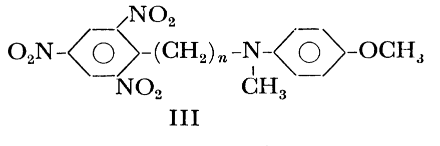


I

a) $R_1=Cl$; $R_2=C_2H_5$; $R_3=Br$.
b) $R_1=Cl$; $R_2=C_2H_5$; $R_3=H$.
c) $R_1=Cl$; $R_2=CH_3$; $R_3=CH_3$.
d) $R_1=CH_3$; $R_2=CH_3$; $R_3=OCH_3$.
e) $R_1=CH_3$; $R_2=CH_3$; $R_3=CH_3$.



II



III

a) $n=1$, b) $n=2$.

Thin layers of these compounds were obtained by sublimation or melting *in vacuo*.[3] In this procedure the majority of compounds condense on the base in an unstable form, deposited as an amorphous, usually sticky, transparent and homogeneous film. Mechanical interference or standing leads to transition of the layers in to a final, stable form. Both forms have been examined by means of electron diffraction pattern.

Amorphous layers have been recently obtained even for naphthacene,[16] whereas production of so-called specular non-crystalline dye layers from solution is well known. In our case the amorphous layers obtained may be considered as unstable supercooled melts. The optical density and hence the extinction coefficient of such layers can be calculated within a certain error, accounting for a 1.1-fold expansion of most cyclic organic compounds on melting (Ref. 17 as well as calculations based on available data on specific volume changes of many substances on melting).

Amorphous films of complexes I and II crystallize after a certain time. A change of color of the film can be observed with phase transition and formation of fissures. Free parts of the base appearing between crystallites can be observed by means of a microscope. This necessitates in some cases great care in securing conditions for minimum light scattering in the final crystalline layer (*cf.* Experimental).

Let us first consider visible absorption in naphthoquinone AC. Figure 1a and Table 1, as well as the shape of experimental curves[18] show close similarity between the absorption curves of solutions and those of amorphous layers of the substances. It can be inferred that the long wavelength band of amorphous films is most likely due to intermolecular n-π^* or π-π^* (in the case of II) charge transfer, as is in the case for liquid[18,19] or solid[20] solutions of these compounds. There is, however, a general increase in intensity ever the whole visible spectrum in the case of non-crystalline layers.

This is apparently due to the fact that in sublimed layers the molecules are free from a solvent shell and thus may possess a somewhat different donor or acceptor ability of their molecular fragments, as well as different conditions of intermolecular orbital overlap.

The spectra of crystalline naphthoquinone autocomplex films show further increase in visible absorption (Figs. 2—3 and Table 1). X-Ray data on complex Ic[21] and on the prototype of autocomplexes

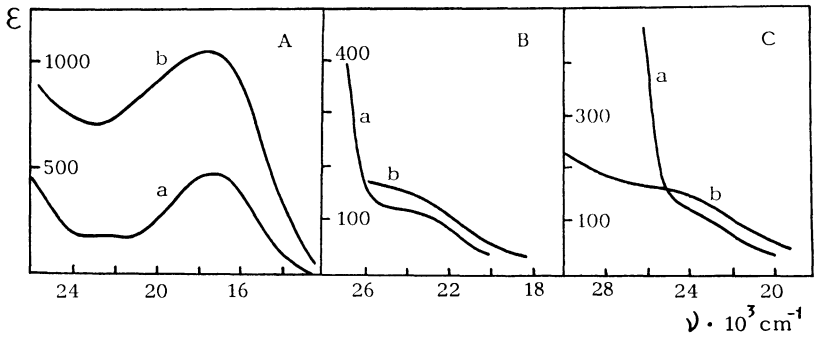


Fig. 1. Absorption of naphthoquinone-type AC Ia and some model compounds.
A, curves: a—Ia in benzene, b—sublimed amorphous film.
B, C—accordingly 2-methyl-1,4-naphthoquinone and 2-chloro-1,4-naphthoquinone, a—in benzene, b—crystalline layer from a melt.

Table 1. OPTICAL CHARACTERISTICS OF THE SOLUTIONS AND SUBLIMATED LAYERS OF AUTOCOMPLEXES

Compound	Solution		Amorphous layer		Crystalline layer	
	ν_{max}	ε	ν_{max}	ε	ν_{max}	ε
Ia	17.3	490	17.5	≈1050[a]	of Fig. 3B	
Ib	16.7	410	17.0	≈680	16.0	≈1160
Ic	16.7	410	16.8	≈890	18.7	≈4000
Id	18.4	185	19.0	≈600	19.0	≈850
	≈23.5	150	23.0	≈600		
Ie	18.5	225	19.0	≈550	17.8	≈810
	≈23.5	170	23	≈530		
II	18.8	1700	18.3	≈1850	17.8	≈3650
IIIa	≈27 i	1250	24.0	≈2800		
IIIb	20.6	1490	19.8	≈6060[b]	19.3	≈7070[b]

ν_{max} in cm^{-1}×10^{-3}, ε—molar extinction coefficient. i—inflexion. Bands with ν_{max} 27×10^3 cm^{-1} are cited only.
a) Supercooled melt between two glass plates. b) Sublimed films with a different degree of crystallinity.

Id, e[22] show a packing of molecular donor and acceptor fragments in infinite stacks of type DADADA..., as is usual for binary CTC. This leads to the conclusion that the observed changes in absorption with phase transition of the autocomplexes is due to the appearance of an additional band of intermolecular charge transfer (ICT). A phase transition alone could not have produced such considerable changes in visible absorption. This is seen clearly from a comparison of UV spectra obtained from solutions and from solid layers of 2-chloro- and 2-methyl-1,4-naphthoquinones which correspond to the acceptor fragments of autocomplexes Ia—e (Fig. 3B, C). Some possible differences in simple van der Waals intermolecular interactions in amorphous and crystalline states should not be neglected, but these would be considerably small.

The position of the ICT band of the crystal can be determined from differential spectra and depends only very little on absorption background (Figs. 2 and 3A). The intensity of the ITC band peak which characterizes electronic transitions in the crystal can only be approximately estimated, owing to different light scattering in the crystalline and the corresponding amorphous film. Each sample may also contain, in addition to its basic phase, inclusion of the other phase. Thus the accuracy of intensity measurements is estimated to be within ±5%. Intermolecular charge

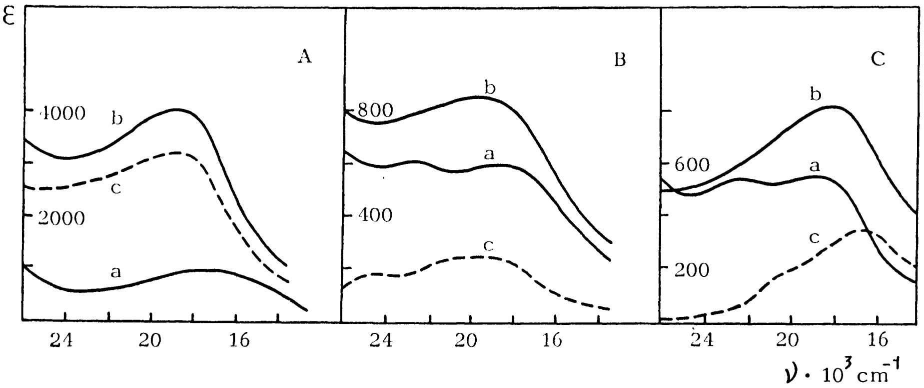


Fig. 2. Absorption of crystalline and amorphous films of naphthoquinone autocomplexes.
A—Ic; B—Id; C—Ie.
Curves: a—amorphous film, b—crystalline layer, c—differential curves "b"—"a". For Ic ν_{max}=19000 cm^{-1}, ε=3200; for Id ν_{max}=20000 cm^{-1}, ε=260; Ie—ν_{max}=16600 cm^{-1}, ε=350. All the samples were obtained by sublimation technique.

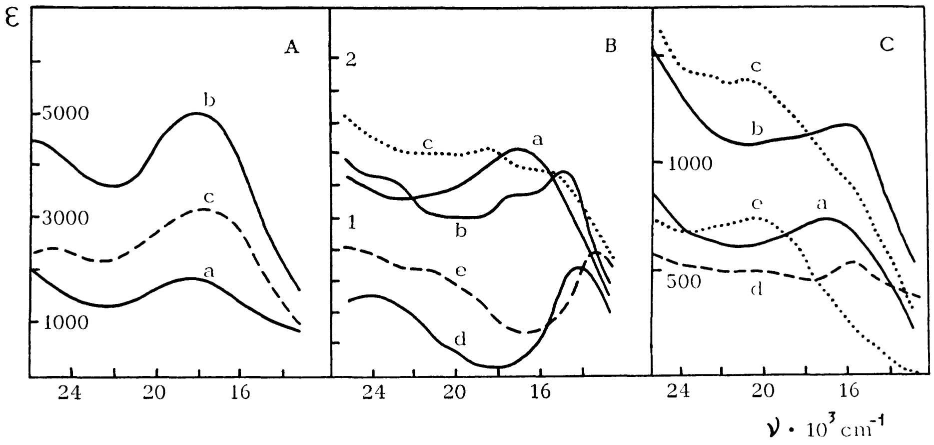


Fig. 3. Absorption of crystalline and amorphous films of naphthoquinone autocomplexes.
A—layers from II obtained by sublimation.
Curves: a—amorphous film, b—crystalline layer, c—differential spectrm "b"—"a", $\nu_{max}=17800\ cm^{-1}$, $\varepsilon=3100$.
B—from layers Ia obtained by melting.
Curves: a—amorphous film, b—the same film in a day, c—absorption of the large-grained layer, d—differential spectrum "b"—"a", $\nu_{max}=14000\ cm^{-1}$, e—differential spectrum "c"—"a". Ordinate in arbitrary units.
C—layers from Ib.
Curves: a—amorphous sublimed layer, b—fine-crystalline sublimed layer, c—large-grained layer from the melt, d—differential spectrum "b"—"a", $\nu_{max}=\approx 15800\ cm^{-1}$, e—differential spectrum "c"—"a". For curves a, b, d on the ordinate—extinction coefficient, for curves c, e the absorption is given in arbitrary units.

transfer in AC Ic is primarily caused crystallographically. It was shown that[23,24] in crystalline autocomplex II we might expect intramoleclar donor–acceptor interaction but the orientation of the nearest planes of donor and acceptor fragments of adjoining molecules in the crystal should not favor intermolecular charge transfer. Hence, the very high intensity of the CTC band in the differential spectrum (Fig. 3A, curve c) may be due either to compression of the horseshoe-shaped molecules II in the process of crystallization of the amorphous phase, or to additional intermolecular interaction within the crystal, *e. g.* through contacts C–O . . . Cl. In the case of Ic and II the interatomic distances of adjacent molecules in the lattice are practically equal to those caused by van der Waals interaction[21,23]; nevertheless distinct n-π* charge transfer is suggested for analogous halogenquinones by de Gaultier *et al.*[25]

It could be shown in the case of autocomplexes Ia,b that the optical properties of crystalline films largely depend on the mode of preparation. Crystallization of a melt of Ia between glass plates, or fast sublimation of Ib leads to the formation of blue microcrystalline layers. Their spectra clearly show an ICT band in the region of $(14-16)\times 10^3\ cm^{-1}$ (Figs. 3 B, C, curves b, d).

A crystalline melt of quinone Ia between a quartz and a mica plate, or that of an analogue of Ib between glass plates has much larger crystalline particles. These particles are, in the case of a layer of Ia, distributed non-homogeneously, and the sample is always unevenly colored. Violet and blue patches can be observed simultaneously. The resultant spectrum is shown in Fig. 3Bc. These shades merge into each other on a change in the angle of vision, or on observing the film through a polarizing microscope with a white light source and a rotating object-table. Quinone Ib produces a more homogeneous layer, and change of the angle of vision leads to a change of shade of the whole sample. At the same time, the band in the region $(14-16)\times 10^3\ cm^{-1}$ is less characteristic of this compound, unlike the other analogue of Ia, as can be seen from curves "c" in Figs. 3B, C and from the corresponding differential spectra "c"—"a".

It follows that in microcrystalline samples of AC Ia,b the orientation of separate single crystals, and, hence, that of the planes of molecular donor–acceptor pairs, with respect to the plane of the base is essentially different from the one in the macrocrystalline sample of quinone Ib. The inhomogeneous macrocrystalline sample of Ia shows a non-uniform distribution of single crystals both with respect to orientation and to location within the area of the film.

The absorption spectrum of a siblimed nitroaryl AC IIIa film has a bathochromically shifted long wave (length) edge, as compared to that of solution (Fig. 4A, curves a, b). Analysis of first Gaussian components shows that the low-frequency absorption edge is shifted towards lower energy values by at least $4\times 10^3\ cm^{-1}$. This indicates a high microcrystal inclusion or oligomolecular associate percentage in a "freshly" sublimed film, intermolecular interaction taking place between each part of such inclusions. Thus the well defined $22.5\times 10^3\ cm^{-1}$ band in the differential spectrum of amorphous phase *vs.* solution indicates not only changes in intermolecular interaction between

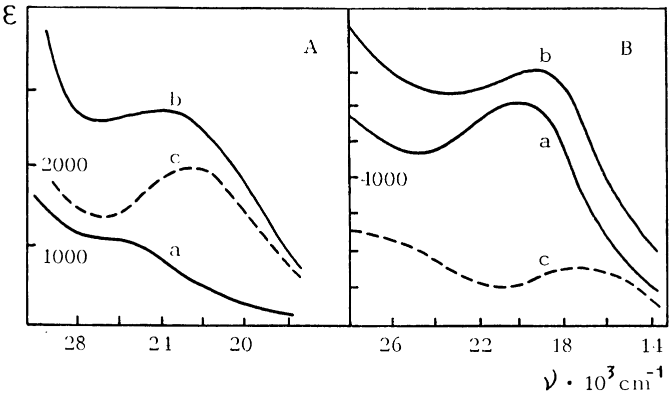


Fig. 4. Absorption of nitroaryl autocomplexes.
A—spectra of IIIa.
Curves: a—in benzene solution, b—"amorphous" sublimed layer, c—differential spectrum "b"—"a".
B—spectra of IIIb.
Curves: a—freshly sublimed film, b—the same sample after a 15 day storage, c—differential spectrum "b"—"a", $\nu_{\max}\approx 18000\ \text{cm}^{-1}$, $\varepsilon=1500$.

functional groups in the absence of solvent, but also contribution of the intermolecular charge transfer, as demonstrated by X-ray studies.[24,26]

A freshly sublimed film of the three-member-bridged autocomplex IIIb hardly differs optically from a film that has been kept for several weeks. Only a considerable intensity increase of the CT band and a slight bathochromic peak shift can be observed, as compared with that of solution (Fig. 4B and Table 1). In this case the differential spectrum also shows an absorption component due to intermolecular interaction; both samples are likely to contain both the amorphous and the crystalline phases, only in different proportions. The ICT band is estimated to be in the region $(17—18)\times 10^3\ \text{cm}^{-1}$ in this case.

As expected, owing to different polarization values of the molecules and their fragments in the solid phase the variochromic ICT band shift do not always follow the simple Mulliken relations (spectra of pairs of compounds differing only in one structural element, such as IIIa, b; Id, e; Ie, c; Ia, b). This, too, can be easily explained by the fact that the differential spectra can demonstrate only intermolecular CT absorption as a whole, which undoubtedly depends on the different grain orientation at the base for different compounds.

Experimental

Compounds I—III were synthesized according to the methods reported.[27—30] Samples for absorption measurements were prepared by sublimation of AC I—III *in vacuo* on a glass base at room temperature. The sublimation process is controlled visually. The heater of the evaporator is switched off[31] as soon as the melting point of the autocomplex has been reached. A thermogravimetric experiment on Ib demonstrated that this substance is not decomposed by melting. The heating rate of a compound in the evaporator varied from 3 to 20 min, the vacuum being about 10^{-5} Torr, depending on the desired type of film. For the preparation of an amorphous coating, comparatively rapid sublimation is usually necessary; only in the case of complex Ib and amorphous layer could be prepared by slow sublimation. However, in this case the film itself must be sufficiently thick. Microcrystalline layers were obtained immediately in the course of sublimation from substances Ic and II only if the evaporator was heated very slowly. A microcrystalline film from AC Ib is formed only by very rapid sublimation of a small sample.

The method of melting the sample *in vacuo* between transparent windows was used when the vacuum-deposited films turned out to scatter light after crystallization (Ib, and sometimes Ia). For this purpose a supercooled amorphous layer is prepared between two glass plates. In a few hours the melt crystallizes into a microcrystalline (Ia) or a large-grained sample (Ib). Large-grained samples of Ia could be obtained by melting the complex between a glass and a mica plate. Films of AC IIIa, b could not be obtained by the melting procedure owing to decomposition.

The authors express their gratitude to E. Chirkowa and M. Kaminsky for thermographic analysis of AC Ib; to J. Kalnačs for structure analysis by electron diffraction; to L. Berzina, D. Novicka, E. Siliņš for their assistance and to Ya. Eiduss for valuable advice.

References

1) J. F. Freimanis and L. E. Berzina, *Dokl. Akad. Nauk SSSR*, **185**, 139 (1969).

2) J. F. Freimanis, J. J. Drēgeris, L. E. Berzina, A. J. Mālmanis, and E. J. Neimanis, *Zh. Obshch. Khim.* **42**, 603 (1972).

3) J. F. Freimanis, A. J. Mālmanis, J. J. Drēgeris, and S. J. Bitte, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, **1973**, 333.

4) V. A. Ismailsky and V. I. Stavrovskaya, *Zh. Obshch. Khim.*, **9**, 1006 (1939).

5) V. A. Ismailsky and V. E. Limanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1959**, 1500.

6) R. L. Hansen and J. J. Neumayer, *J. Phys. Chem.*, **71**, 3047 (1967).

7) E. Hertel and M. Schinzel, *Z. Elektrochem.* **45** (5), 51 (1939).

8) Sh. Koizumi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **45**, 423 (1972).

9) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **44**, 2868 (1971).

10) J. Aihara, G. Kushibiki, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **46**, 3584 (1973).

11) Y. Matsunaga, VII Molecular Crystal Symposium, NIKKO, Japan, 1975, Abstracts, p. 173.

12) G. Saito and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **44**, 3328 (1971).

13) N. Inoue and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **46**, 3345 (1973).

14) J. Aihara, A. Sasaki, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **43**, 3323 (1970).

15) J. Aihara, *Bull. Chem. Soc. Jpn.*, **47**, 2063 (1974).

16) Y. Maruyama, K. Machida, and N. Iwasaki, VII Molecular Crystal Symposium, NIKKO, Japan, 1975, Abstracts, p. 49.

17) E. A. Melwyn-Hughes, "Physical Chemistry," (Russ. ed), Moscow (1962), p. 663.

18) J. F. Freimanis, J. J. Drēgers, L. E. Berzina, I. V. Turovsky, S. J. Bitte, L. M. Blynov, and V. G. Rumiancev, *Adv. Mol. Rel. Processes*, **5**, 33 (1973).

19) V. G. Rumiancev, L. M. Blynov, J. F. Freimanis, and J. J. Drēgeris, *Zh. Strukt. Khim.*, **16**, 223 (1975).

20) J. F. Freimanis, S. V. Titarenko, V. A Gailite, and J. J. Drēgeris, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, **1975**, 216.

21) A. E. Shvets, J. J. Bleidelis, and J. F. Freimanis, *Zh. Strukt. Khim.*, **16**, 417 (1975).

22) C. K. Prout and E. E. Castellano, *J. Chem. Soc.*, *A*, **1970**, 2775.

23) A. E. Shvets, J. J. Bleidelis, and J. F. Freimanis, *Zh. Strukt. Khim.*, **16**, 640 (1975).

24) A. E. Shvets, J. J. Bleidelis, and J. F. Freimanis, *Acta Crystallogr.*, **A31**, Part S3, p. S129 (1975).

25) J. Gaultier, Ch. Hauw, and M. Schvoerer, *Acta Crystallogr.*, **B27**, 2199 (1971).

26) A. E. Shvets, J. J. Bleidelis, and J. F. Freimanis, *Zh. Strukt. Khim.*, **16**, 98 (1975).

27) J. J. Drēgeris, D. J. Murniece, and J. F. Freimanis, *Zh. Obshch. Khim.*, **42**, 600 (1972).

28) J. J. Drēgeris, S. J. Bitte, J. F. Freimanis, and A. J. Spārina, *Zh. Obshch. Khim.*, **45**, 123 (1975).

29) L. E. Berzina, J. J. Drēgeris, J. F. Freimanis, and I. V. Turovsky, *Zh. Obshch. Khim.*, **42**, 2719 (1972).

30) L. E. Berzina, D. J. Murniece, J. J. Drēgeris, and J. F. Freimanis, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, **1971**, 460.

31) A. K. Gailis, A. E. Siliņš, and J. F. Freimanis, *Elektrokhimiya*, **1966**(2), 1420.