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Organic Semiconductors. II.* The Electrical Resistivity of Organic Molecular Complexes

MORTIMER M. LABES, ROBERT SEHR, AND MONISHA BOSE†

The Franklin Institute, Laboratories for Research and Development, Philadelphia 3, Pennsylvania

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Thirty molecular complexes involving quinones, halogens, polynitroaromatics, or tetracyanoethylene as electron acceptors and aromatic hydrocarbons or substituted aromatics as electron donors have been prepared and the room temperature electrical resistivities measured on compressed microcrystalline material. A lowering of electrical resistivity is generally associated with complex formation. The results are discussed in terms of crystal structure and charge transfer complex theory.

I. INTRODUCTION

MOLECULAR complexes can be formed from the interaction of a wide variety of molecules, primarily aromatics which can behave as electron donors (*D*) with electron acceptors (*A*) such as quinones, halogens, and nitro-compounds.¹ The present concept of the nature of these complexes, based on the charge transfer or donor acceptor interaction theory, was developed by Mulliken.² This theory has recently been reviewed by McGlynn^{1b}; briefly, the ground state of a 1:1 complex can be described by a wave function ψ_n , given by

$$\psi_n(D, A) = a\psi_0(D, A) + b\psi_1(D^+A^-). \quad (1)$$

ψ_0 designates a no-bond wave function; ψ_1 represents a "dative bond" wave function, corresponding to a transfer of an electron from *D* to *A*. The excited state wave function ψ_E is given by

$$\psi_E(D, A) = a^*\psi_1(D^+A^-) - b^*\psi_0(D, A). \quad (2)$$

For weak molecular complexes $a \gg b$, $|a| \cong 1$, $|b| \cong 0$, so that ψ_n has essentially no bond character and ψ_E has essentially ionic character. For primarily ionic complexes, the ground state wave function is given by Eq. (1), with $b > a$.

A few of these molecular complexes have been observed to have resistivities many decades lower than conventional organic materials. Our investigation has concerned itself with examining the generality of this observation, a thorough study of several semiconductor parameters on some typical representatives, and a contribution to an understanding of the mechanism of semiconduction in organic molecular solids. This paper concerns itself with the first of these questions.

* These results were presented at the Princeton University Conference on Semiconduction in Molecular Solids, February 16-17, 1960.

† Visiting Research Associate from the Department of Chemistry, University of Calcutta, India.

¹ For recent reviews see (a) L. J. Andrews, *Chem. Revs.* **54**, 713 (1954); (b) S. P. McGlynn, *ibid.* **58**, 1113 (1958).

² R. S. Mulliken, *Rec. trav. chim.* **75**, 845 (1956), and earlier papers cited therein.

II. EXPERIMENTAL

Apparatus

The apparatus employed in performing the electrical measurements has already been described³; the most convenient sample holder which we have devised is pictured in Fig. 1.

Materials

The following materials were purified by simple recrystallizations to constant melting point; hexamethylbenzene, dimethoxybenzene, *p*-anisidine, *p*-phenylenediamine, quinhydrone, chloranil, 1,3,5-trinitrobenzene, picric acid, 2,4,7-trinitrofluorenone. Tetracyanoethylene was kindly supplied by E. I. Dupont de Nemours & Company. 1,5-Diaminonaph-

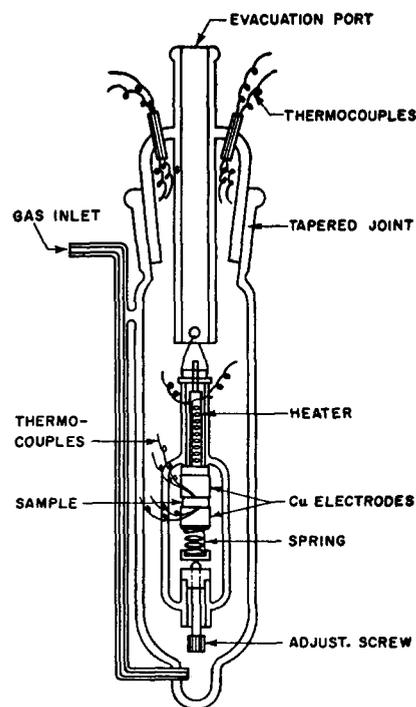


FIG. 1. Sample holder.

³ M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.* **32**, 1570 (1960).

TABLE I. Literature data on electrical resistivity of molecular complexes.

Compound (A-B)	Molar ratio A:B	dc Room temp. resistivity ohm cm	Temp. range °C	E^a ev	Compounding conditions	Reference
Perylene-Br ₂	1:2.2	7.8	-20 to -170	0.13	g	13
Pyranthrene-Br ₂	1:1.7	220	-20 to -170	0.20	g	13
Violanthrene-Br ₂	1:2.3	66	-20 to -170	0.20	g	13
Violanthrene-I ₂	1:2	45	-20 to -170	0.15	g	13
Violanthrene-I ₂	1:2	45	10 to 60	0.14	g	13
Pyrene-I ₂	1:2	75	...	0.22	g	14a
Perylene-I ₂	2:3	8	...	0.03	g	14a
Dimethylaniline-chloranil	...	10 ⁹	...	0.45 ^b	...	f
Dimethylaniline-bromanil	...	10 ⁹	...	0.45 ^b	...	f
Dimethylaniline-iodanil	...	10 ⁸	...	0.45 ^b	...	f
<i>p</i> -Phenylenediamine-chloranil	...	10 ^{6c}	-10 to 20	0.50	...	12
<i>p</i> -Phenylenediamine-chloranil	3:2 5:3	10 ⁷	-25 to 55	1.15	h	3
Li Anthracene ^d	1.16:1	10 ¹¹	25 to 50	1.34	i	11a
K-anthracene ^d	1.18:1	10 ¹¹	25 to 50	1.12	i	11a
Na-anthracene ^d	2.12:1	10 ⁸	25 to 50	0.63	i	11a, 11b
Na-3:4 benzoquinoline ^e	1.5:1	10 ¹⁰	...	0.35	j	11e
3:4-benzoquinoline-Br ₂ ^e	1:2.8	10 ⁶	...	0.37	j	11e

^a Calculated from $\rho = \rho_0 \exp(E/2kT)$.

^b This value given in a private communication cited in footnote 12.

^c Resistivity at 0°.

^d Reference gives data at other metal concentrations and also for Na-anthracene which retains ether.

^e Reference gives data on other benzoquinoline isomers and complex compositions.

^f D. D. Eley and H. Inokuchi, *Proceedings of the Third Conference on Carbon* (Pergamon Press, New York, 1959), p. 91.

^g Compressed at 200 kg/cm² using silver coated metallic cap electrodes.

^h Compressed at 42 000 psi (3000 kg/cm²) using Cu or Pt foil electrodes.

ⁱ Compressed at 20 kg/cm² using Cu or stainless steel electrodes.

^j Compressed at 8-12 kg/cm² using Cu electrodes fitted with Pt caps.

thalene, 1,8-diaminonaphthalene, *p*-aminodiphenylamine, and acridine were obtained from Aldrich Chemical Company and used without purification. Iodine was Merck reagent grade; iodine monochloride was Eastman practical. *N,N*-dimethylamine was freshly distilled *in vacuo* immediately prior to use. Pyrene, perylene, and coronene were purified by the continuous adsorption purification technique of Sangster and Irvine.⁴ *N,N,N',N'*-tetramethyl-*p*-phenylenediamine was obtained as the dihydrochloride from B.D.H.; the free base was liberated with ammonia and the washed solid dissolved in benzene. The benzene solution was dried, filtered, and used immediately in complex formation.

3,8- and 3,10-diaminopyrene were prepared by the procedure of Vollman *et al.*⁵ 3,8-Diaminopyrene was crystallized 3 times from xylene, mp 226-27°; 3,10-diaminopyrene was crystallized 3 times from xylene, and 2 times from toluene, mp 160-62°.

⁴ R. C. Sangster and J. W. Irvine, Jr., *J. Chem. Phys.* **24**, 670 (1956).

⁵ H. Vollman, H. Becker, M. Corell, H. Streeck, and G. Langbein, *Ann.* **531**, 1 (1937).

Bromanil and iodanil were prepared according to the procedure described by Jackson and Bolton.⁶ Bromanil was recrystallized twice from benzene, mp 299-299.5°. Iodanil was recrystallized twice from ethyl acetate, mp 265-268°. Octoiodo-*p*-benzoquinhydrone was also prepared by Jackson and Bolton's method.⁶

The complexes were then prepared by mixing the ingredients separately dissolved in solvent, usually benzene; *s*-tetrachloroethane was a convenient solvent for the iodine complexes of coronene and perylene. The complexes formed immediately from cold solutions, or upon cooling in the cases where hot solvents were used, and were obtained as microcrystalline solids. Occasionally, slow cooling would yield crystals of reasonable size to attempt single crystal measurements (see Table II), but these results are not as yet considered reliable. The complexes were not routinely submitted for analyses except in those cases where detailed study of the temperature dependence of resistivity and other semi-

⁶ C. L. Jackson and E. K. Bolton, *J. Am. Chem. Soc.* **36**, 301 (1914).

TABLE II. Room temperature electrical resistivities of molecular complexes.

Acceptor	Donor	Resistivity ohm-cm
Tetracyanoethylene	Pyrene	10 ^{8a} , 10 ¹⁰
Tetracyanoethylene	Perylene	10 ^{8a} , 10 ¹¹
Tetracyanoethylene	Hexamethylbenzene	10 ¹¹
Tetracyanoethylene	Dimethoxybenzene	10 ¹¹
Chloranil	Pyrene	10 ¹¹
Chloranil	Perylene	10 ⁸
Chloranil	Hexamethylbenzene	10 ¹¹
Chloranil	<i>N,N</i> -Dimethylaniline	10 ¹⁰
Chloranil	<i>p</i> -Phenylenediamine	10 ⁷
Chloranil	1,5-Diaminonaphthalene	10 ¹¹
Chloranil	1,8-Diaminopapthalene	10 ¹¹
Chloranil	<i>p</i> -Aminodiphenylamine	10 ¹⁰
Chloranil	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine	10 ⁹
Chloranil	3,8-Diaminopyrene	10 ⁴
Chloranil	3,10-Diaminopyrene	10 ⁶
Chloranil	<i>p</i> -Anisidine	10 ¹¹
Bromanil	<i>p</i> -Phenylenediamine	10 ¹⁰
Bromanil	3,8-Diaminopyrene	10 ⁸
Iodanil	<i>p</i> -Phenylenediamine	10 ¹¹
Iodanil	3,8-Diaminopyrene	10 ⁶
Iodine	Coronene	10 ⁹
Iodine	Perylene	10
Iodine	Acridine	10 ¹³
Iodine monochloride	Acridine	10 ¹³
1,3,5-Trinitrobenzene	<i>N,N</i> -Dimethylaniline	10 ^{8a} , 10 ¹¹
1,3,5-Trinitrobenzene	Coronene	10 ¹³
Picric acid	Coronene	10 ¹²
2,4,7-Trinitrofluorenone	Coronene	10 ¹²
	Quinhydrone	10 ¹¹
	Octoiodo- <i>p</i> -benzquinhydrone	10 ¹¹

* Initial attempts at single crystal measurements; we do not as yet consider these values reliable.

conductor properties were undertaken. Hence the values should be considered and are given as order of magnitude values.

RESULTS AND DISCUSSION

The literature concerned with measurements of electrical resistivity for molecular complexes is summarized in Table I. Some of the reports do not give details of measuring apparatus, condition of compression, or electrode materials, making comparison of results rather difficult. Table II lists 30 complexes we have studied. Our values agree within an order of magnitude with the literature values for the three compounds we have reinvestigated: perylene-*I*₂, dimethylaniline-chloranil, *p*-phenylenediamine-chloranil. It can be seen that a lowering of electrical resistivity is generally associated with complex formation. We have not been able to find any new donor-acceptor systems with resistivities as low as the aromatic amine-tetrahalogen-*p*-benzoquinone or aromatic hydrocarbon-halogen systems, and most of our work involved the preparation and screening of a series of amino substituted hydrocarbons complexed with the tetrahalogen-*p*-benzoquinones. In addition to having low resistivities, these complexes appear to be more stable than the tetracyanoethylene or halogen complexes.

It is important to consider whether there are any changes in the molecular crystal of an aromatic charge

transfer complex as compared with the parent hydrocarbon. In hydrocarbons like coronene and ovalene, the perpendicular distance between successive molecular planes is very close to the interplanar distance found in graphite, 3.4 Å, the normal van der Waals approach. This also applies to other large molecules with aromatic character such as the phthalocyanines. In the case of smaller aromatic molecules, the distances are a little greater, varying from about 3.5 to 3.7 Å.⁷

A good possibility is that the basic structural feature which differentiates a molecular complex crystal having resistivities lower than conventional organic materials from a pure hydrocarbon crystal is a chain-like structure with large regions of parallel positioning of molecular planes, and an alternation of sites with donor (positive) and acceptor (negative) character. There is not a significant decrease in interatomic distances between molecular planes in general but the molecular planes are much closer to having a common chief axis. In the complexes which exhibit the lowest resistivities, there may, however, be some decrease in distance between planes. We still consider two types of complexes which seem to have a chain-like structure; aromatic hydrocarbon-halogen complexes, and an aromatic hydrocarbon-quinone complex.

⁷J. M. Robertson, *Organic Crystals and Molecules* (Cornell University Press, Ithaca, New York, 1953).

Hassel^{8a} has succeeded in determining the crystal structure of the 1:1 benzene-bromine charge transfer complex at -40° to 50°C . Here the bromine atoms are symmetrically situated on the common chief axis of two neighboring benzene rings. The crystal is built up of chains consisting of alternating benzene and bromine molecules. No change in the Br—Br distance (2.36 Å) is found. The distance to the center of the nearest benzene ring is 3.36 Å. Each bromine atom is symmetrically situated with respect to all C—C bonds. A steep fall in x-ray intensities at increasing reflection angles is observed indicating the weakness of the bond. The benzene-chlorine complex^{8b} has a similar structure, the Cl—Cl distance being 1.99 Å, and the distance from one particular chlorine atom to the nearest benzene plane (3.28 Å) a little shorter than the corresponding bromine compound.

According to Harding and Wallwork,^{9f} in the chloranil-hexamethylbenzene complex, it is impossible for a pair of hexamethylbenzene molecules, one on either side, both to approach close enough for π orbital overlap to occur over the whole of the area of the C_6 rings. A compromise is made; one-half of the chloranil molecule interacts strongly with the molecule above it; one-half interacts strongly with the molecule below leading to a zig-zag arrangement. The perpendicular spacing between the molecules is about 3.5 Å. Thus the component rings of molecular complexes, although parallel, do not necessarily have coaxial orientations. This picture has, however, been seriously criticized¹⁰ as to structural detail, so that the only clear case of chain-like structure is that of the aromatic hydrocarbon-halogen complexes.

Theoretical evidence shows that the structure with perfect coaxial orientation is not the most favored for the hypothetical benzene-benzene complex.² The more favored structures can be obtained by sliding one ring parallel to the other for a distance of approximately an angstrom. In practice each case must be examined separately since a compromise between polarization bonding and steric repulsion is reached, which may then be further modified by specific interactions such as hydrogen bonding.^{9d}

There are, of course, many complexes in which parallel stacking does not occur or deviations from parallel stacking occur either as a result of steric repulsion or specific interactions. In the *aza*-aromatic-halogen or amine-halogen complexes (“*n*-type” or

“onium” complexes), the charge transfer interaction is localized, leading to primarily an ionic bond between tertiary nitrogen-halogen. X-ray studies⁸ show a very short distance from tertiary nitrogen to directly bonded halogen atoms which is not much longer than an ordinary covalent bond, and the arrangement donor atom-halogen-halogen is linear.

Although the complexes of diamionaphthalene had higher resistivities than those of *p*-phenylenediamine, diamionpyrene complexes have been found to have quite low resistivities. Thus the fact that one might expect larger aromatic ring systems to interact to give lower resistivity complexes can easily be obscured by possible structural and composition differences. The two isomeric diamionpyrenes, for example, form complexes of quite different composition and have quite different resistivities. Further work on complexes of this type is in progress.

It was our observation that complexes which are primarily ionic in nature and that would be expected to have the linear arrangement of *N*-halogen-halogen atoms discussed above had very high resistivities. This is in disagreement with the results of Ubbelohde *et al.*^{11e}

We also found that complexes involving the polynitroaromatics had, typically, high resistivities. There is evidence that there is deviation from parallel plane stacking with the anthracene-1,3,5-trinitrobenzene complex.^{9g} However, the observation which points out most clearly the difficulties in making generalizations regarding correlations of chemical structure and electrical properties is our study of the coronene-iodine complex. The fact that the resistivity of this halogen-hydrocarbon complex is 7 orders of magnitude higher than halogen complexes of hydrocarbons both smaller and larger than coronene is puzzling. In light of this observation, other results involving measurements of very few compounds with a given electron acceptor must not be considered as necessarily describing that class of complexes. It is clear that crystal structure is of great importance and may profoundly influence the electrical properties.^{11f}

The aromatic amine-tetrahalogen-*p*-benzoquinone complexes have been called biradical molecular compounds, because of their paramagnetism. Bijl, Kainer, and Rose-Innes¹² consider this a case of complexing in which the ionic state is the lowest state because *A* and

⁸ (a) O. Hassel, *J. Mol. Phys.* **1**, 241 (1958); (b) O. Hassel and H. Stromme, *Acta Chem. Scand.* **13**, 1781 (1959).

⁹ (a) J. S. Anderson, *Nature* **140**, 583 (1937); (b) K. Nakamoto, *J. Am. Chem. Soc.* **74**, 1739 (1952); (c) H. M. Powell and G. Huse, *Nature* **144**, 77 (1939); *J. Chem. Soc.* **1943**, 435; (d) H. M. Powell, G. Huse, and P. W. Cooke, *ibid.* **1943**, 153; (e) S. C. Wallwork and T. T. Harding, *Nature* **171**, 40 (1953); (f) T. T. Harding and S. C. Wallwork, *Acta Cryst.* **8**, 787 (1955); (g) S. C. Wallwork, *ibid.* **7**, 648 (1954).

¹⁰ J. Donohue and K. N. Trueblood, *Acta Cryst.* **9**, 960 (1956).

¹¹ (a) W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.* **1954**, 720; (b) J. P. V. Gracey and A. R. Ubbelohde, *ibid.* **1955**, 4089; (c) W. Slough and A. R. Ubbelohde, *ibid.* **1957**, 911; (d) **1957**, 918; (e) **1957**, 982.

¹¹ (f) *Note added in proof*: Preliminary results of a study of the structure of the coronene-iodine complex (R. Pepinsky, private communication) indicate that the crystal does not have alternate coronene and iodine molecules in a stack, but rather may have alternate stacks of coronene and iodine molecules. This would explain the relatively high resistivity. Another paper which also discusses semiconductivity and crystal structure in these complexes has just appeared. See D. D. Eley, H. Inokuchi, and M. R. Willis, *Disc. Faraday Soc.* **28**, 54 (1960).

¹² D. Bijl, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.* **30**, 765 (1959).

D have such greatly different electron affinities. Paramagnetism has also been observed in the aromatic hydrocarbon-iodine complexes.^{13c,d,14} A later paper will

¹³ (a) H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Bull. Chem. Soc. Japan* **29**, 213 (1956); (b) H. Akamatu, Y. Matsunaga, and H. Kuroda, *ibid.* **30**, 618 (1957); (c) Y. Matsunaga, *ibid.* **28**, 475 (1955); (d) Y. Matsunaga, *J. Chem. Phys.* **30**, 855 (1959).

¹⁴ (a) J. Kommandeur and F. R. Hall, *Bull. Am. Phys. Soc.* **4**, 421 (1959); (b) L. S. Singer and J. Kommandeur, *Bull. Am. Phys. Soc.* **4**, 421 (1959).

present measurements of Seebeck coefficient and resistivity as a function of temperature and spin density determinations for several complexes selected from the above screening program.

IV. ACKNOWLEDGMENTS

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Electronic Spectra of Dimers: Derivation of the Fundamental Vibronic Equation*

ANDRZEJ WITKOWSKI† AND WILLIAM MOFFITT

Chemistry Department, Harvard University, Cambridge 38, Massachusetts

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The Hamiltonian describing the vibronic states of a dimer formed by two identical molecules is derived. The monomeric units are assumed to couple by resonance forces only and to have different equilibrium positions in the ground and excited states. The competition of these two effects is formulated mathematically. The strong coupling case occurs when the resonance forces dominate; the weak coupling case arises when the effect of the change of equilibrium positions dominates.

INTRODUCTION

IT has been recognized for some time that the electronic spectra of molecular crystals must be analyzed with some care. For, whereas two molecules which are electronically unexcited attract each other by the familiar dispersion forces of asymptotic dependence R^{-6} , these same forces result in a greater attraction of asymptotic dependence R^{-3} between two identical molecules, only one of which is electronically excited. This so-called resonance coupling has been adduced to explain the long-range transfer of energy between molecules in solution¹; in crystals, it splits the individual molecular energy levels into "exciton" bands but, nevertheless, gives rise to spectra that are often sharp, owing to stringent selection rules.²

Two limiting forms of behavior have been characterized, both empirically and theoretically; in the one case, the resonance coupling is strong and the pattern of vibronic levels is determined in the first place, by electronic considerations;^{2,3} in the other, the resonance coupling is rather weak, and the spectral effects are limited to details in the vibrational structure of band

systems.⁴ Recently, both Simpson and Peterson⁵ and McClure⁶ have investigated the criteria for strong and weak resonance coupling, giving qualitative arguments to cover the treatment of intermediate cases. These authors paid particular attention to the example of a single pair of chromophores, namely that of a dimeric molecule.

We have also been interested in this problem insofar as it involves a coupling between low-frequency electronic motions and nuclear modes, not unlike that encountered in the dynamics of Jahn-Teller instability.⁷ Since our approach is perhaps somewhat different from that of other authors, we are encouraged to report it in the present note. We pay particular attention to a rather idealized dimer in the hope of illustrating as clearly as possible the factors involved in the intermediate coupling case.

GENERAL CONSIDERATIONS

In this section, we derive the basic equations describing the vibronic states of a simple dimer. To avoid complicating the argument unnecessarily, we set up a model which contains the most important features of

* This paper is the first and major part of a preliminary manuscript covering this joint work which was drafted by Professor Moffitt. His death prevented him from putting it in final form.

† Present address: Department of Theoretical Chemistry, Jagellonian University, Kraków, Poland.

¹ Th. Förster, *Ann. Physik* **2**, 55 (1948); A. Gołbiewski and A. Witkowski, *Roczniki. Chem.* **33**, 1443 (1959).

² A. S. Davydov, *Zhur. Eksptl. i Teoret. Fiz.* **18**, 210 (1948).

³ D. P. Craig and P. C. Hobbins, *J. Chem. Soc.* **1955**, 539.

⁴ D. P. Craig, *J. Chem. Soc.* **1955**, 2302; W. A. Bingel, *Can. J. Phys.* **37**, 680, (1959).

⁵ W. T. Simpson and D. L. Peterson, *J. Chem. Phys.* **26**, 588 (1957).

⁶ D. S. McClure, *Can. J. Chem.* **36**, 59 (1958).

⁷ H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)* **A161**, 220 (1937).