

Calculations of transfer integrals for tetracyanoquinodimethane salts

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Calculations of the transfer integral for the one-dimensional electron band of 7,7,8,8-tetracyanoquinodimethane (TCNQ) salts are presented. A critical discussion of the method is given, from which it follows that accurate estimates of these quantities are hard to obtain. However, relative values are expected to be more reliable. For the series of N-substituted morpholinium TCNQ salts a qualitative agreement between dc electrical conductivity and calculated transfer integral was found. For 1,2,6-trimethylpyridinium TCNQ, a counter-intuitive result is obtained, the "crystallophic" dimer and the "electronic" dimer being different.

I. INTRODUCTION

Quasi-one-dimensional compounds, like many TCNQ salts, have electrons which are delocalized mainly in one direction. The appropriate description for delocalized electrons in solids is band theory. This theory is often used in the tight-binding approximation, i.e., for a one-dimensional chain of equivalent molecules, a Hamiltonian is used of the form

$$H = t \sum_{i,\sigma} c_{i+1,\sigma}^\dagger c_{i,\sigma}, \quad (1.1)$$

where $c_{i,\sigma}^\dagger$ is the creation operator for an electron with spin σ on site i ; t is the transfer integral. The summation runs over the chain on which the delocalized electrons reside. In pure one-electron theory the transfer integral is given by

$$t = \langle \Psi_{i+1}^w | H(1) | \Psi_i^w \rangle \quad (1.2)$$

with Ψ_i^w the Wannier function on site i and $H(1)$ the one-electron operator, which incorporates interactions with all electrons except the band electrons in a Hartree-Fock way.

In the tight-binding theory all correlation effects are neglected. A Hamiltonian which accounts for part of the correlation was proposed by Hubbard:¹

$$H = t \sum_{i,\sigma} c_{i+1,\sigma}^\dagger c_{i,\sigma} + U \sum_i c_{i,\sigma}^\dagger c_{i,\sigma} c_{i,\bar{\sigma}}^\dagger c_{i,\bar{\sigma}}, \quad (1.3)$$

where U is the on-site electron-electron repulsion; again the transfer integral is given by (1.2).

If the Hamiltonian (1.1) or (1.3) is used to describe some properties of real compounds, the transfer integral and the on-site repulsion parameter will assume effective values. For example, U will be affected by the correlation terms neglected, the polarization of the embedding lattice,² and the band filling.³ These effects can be large enough to alter the values of U with a factor between 1 and 10.^{2,3} The same mechanisms will influence the effective value of the transfer integral. However, in the Hubbard Hamiltonian, part of the correlation (and also of the other effects) is incorporated in the parameter U . There-

fore, the effective transfer integral will be different in the tight-binding model and in the Hubbard Hamiltonian.

Nevertheless several attempts have been made to calculate the transfer integral in simple one-electron theory,⁴⁻⁷ i.e., by evaluation of (1.2). In view of the foregoing discussion, one cannot expect to obtain reliable values for the transfer integral by such a calculation, as was also noted by Berlinsky *et al.*⁴ However, for a series of similar compounds it might be expected that the relative values of the transfer integrals as obtained by evaluation of (1.2) will be quite reliable.

The values of the transfer integrals depend in a sensitive way on the interatomic distances between molecules, and these depend in turn on the precise geometrical arrangement of the molecules in the crystal. This explains at least qualitatively, that physical properties can vary very strongly in a series of similar compounds, such as the N-substituted morpholinium TCNQ salts.

This paper reports on detailed calculations for a number of these compounds, taking full account of the crystal structure. It will be shown that the variations in the values of the calculated transfer integrals explain the surprisingly large variations observed in the electrical conductivity, i.e., the observation of metals and semiconductors of widely differing conductivities.

In Sec. II the method for evaluation of the transfer integral (1.2) is described. A discussion is given of the most important factors influencing its value. In Sec. III the results are presented and the application to conductivity measurements is discussed.

II. METHOD

In evaluating the transfer integral we start from Eq. (1.2). The first approximation made is to assume that the electron band is formed by the lowest unoccupied molecular orbital (LUMO) of the free TCNQ molecule. Interaction between different molecular orbitals is neglected. Then, up to first order in the intermolecular overlap S , the (orthonormal) Wannier functions are

$$\Psi_i^w = \Psi_i - \frac{1}{2} S (\Psi_{i-1} + \Psi_{i+1}), \quad (2.1)$$

where Ψ_i is the LUMO of TCNQ on site i . The intermolecular overlap integral is defined by

$$S = \int \Psi_{i+1}(r)\Psi_i(r)dr . \quad (2.2)$$

After substitution of (2.1) in (1.2) and use of the Mulliken approximation^{4,7,8} for the resulting matrix element of the one-electron operator between the functions Ψ_i , the following expression is obtained:

$$t = h_{ii}(K - 1)S . \quad (2.3)$$

K is a constant between 1 and 2, generally^{4,7} taken to be 1.75; h_{ii} is the orbital energy of the LUMO.

Note that it is important to substitute orthogonal functions in Eq. (1.2). Berlinsky *et al.*⁴ realized this too and arrived at (2.3) by using the analog of (1.2) for nonorthogonal functions. Grant,^{6,7} however, used (1.2) directly, but substituted the nonorthogonal functions Ψ_i . It is easily seen that one then obtains an expression similar to (2.3), but with $K - 1$ replaced by K . Consequently, values for the transfer integral are then obtained twice as large as the "true" ones.

If one is only interested in the relative values for the transfer integral, the only important outcome of (2.3) is that the transfer integral is proportional to the overlap. The total prefactor can then be considered as an adjustable parameter. Because for N-methyl-N-ethylmorpholinium di-tetracyanoquinodimethane [MEM(TCNQ)₂] and Rb(TCNQ) experimental values are available, it was possible to determine this prefactor, as will be described in the next section.

To evaluate the overlap integral S , the LCAO approximation for the wave function is used. Use is made of the self-consistent-field (SCF) Hartree-Fock wave function determined by Jonkman *et al.*⁹ (Fig. 1), where the multi-GTO (Gaussian-type orbital) basis set is replaced by one STO fitted to it by a least-squares procedure. The exponents are 1.568 for carbon and 1.917 for nitrogen. The formulas necessary for evaluation of the resulting integrals are given by Roothaan.¹⁰

The effects of different choices for the wave function were studied by Grant.¹¹ He showed that the choice of better SCF approximations, i.e., more STO's in the expansion of the atomic orbitals, for the Hartree-Fock wave function leads to much larger values for the overlap. This observation gave rise to the conclusion that one should use the best Hartree-Fock function available, for the evaluation of the transfer integral. Strictly speaking, the important observation is that the electron density outside the vicinity of the nucleus is most important in determination of the transfer integral. This electron density can be described with a single- ζ basis set nearly as well as with the exact Hartree-Fock function. However, it is necessary to adopt the exponent (ζ) to this density and not to use the exponent following from a single- ζ SCF approximation for the Hartree-Fock function. Therefore, we assert here that it is justified to use a single- ζ basis set, when an appropriate value for the exponent is chosen. For the relative values of the transfer integrals this approximation is still better: The differences for different wave functions will then be canceled to a large extent, although not completely.

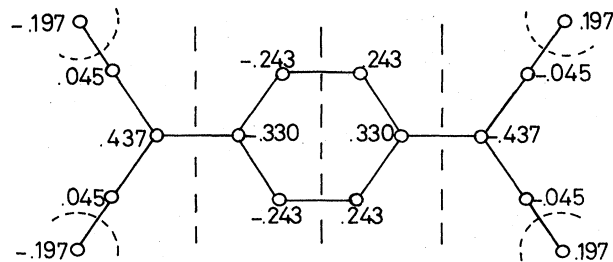


FIG. 1. The TCNQ molecule. The numbers are the coefficients of the AO's in the LCAO approximation for the LUMO. The dashed lines denote the nodal planes of the LUMO.

Finally, it is mentioned that the calculation of the overlap does reflect the most important dependence of the transfer integral on crystal geometry, in the sense that it takes the nodal structure of the molecular-orbital properly into account. It is this structure which makes the transfer integral very sensitive to the geometry.

III. RESULTS AND DISCUSSION

Transfer integrals, i.e., overlaps, were calculated for a series of closely related N-substituted morpholinium TCNQ (1:2) salts, for which conductivities were measured.¹²

For one of the compounds, MEM(TCNQ)₂, the transfer integral was determined from optical reflectance experiments by Rice *et al.*¹³ This gives us a scaling point, in order to obtain absolute values for the transfer integral. Rice *et al.*¹³ give as a value for the largest transfer integral, 0.195 eV. We calculate an overlap of 2.19×10^{-2} . This gives $t_0 = 8.90$ eV, where $t = t_0 S$. All quantities given in Tables I–III will refer to this value for t_0 .

Another scaling point is provided by Rb(TCNQ) for which Hoekstra *et al.*¹⁴ determined the crystal structure and Hibma *et al.*¹⁵ determined the transfer integral from the triplet excitation energies as determined by ESR and the activation energy of the conductivity.

Calculation of the two different overlaps give $S_1 = 2.81 \times 10^{-2}$ and $S_2 = 1.18 \times 10^{-2}$. Using the equations derived by Hibma *et al.*,¹⁵ a value of 15.3 eV is obtained for t_0 . Although an appreciable difference is found in t_0 , this should not worry us too much. The measured transfer integrals come from two completely different kinds of experiments, for which there are many uncertainties in the interpretation. Also the difference in band-filling [half-filled for Rb(TCNQ) and quarter-filled for the other compounds] can be a cause for the discrepancy found.

In all members of the series of morpholinium TCNQ salts the TCNQ ions are stacked, but many types of overlap occur.¹⁶ Because of the stoichiometry and the extension of the morpholinium ions there are two TCNQ ions per unit cell along the stack. Therefore, neighboring ions are always translationally inequivalent. That, however, does not necessarily mean that the inter-TCNQ transfer integrals differ. In fact, it turned out that about half of the compounds have but one value for the transfer integral. In this case the materials showed metallic behavior (high conductivity and a very small or zero ac-

TABLE I. Transfer integrals and conductivities for a series of N-substituted morpholinium di-tetracyanoquinodimethane salts.

Compound ^a	t_1 (eV) ^b	t_2 (eV)	t_3 (eV)	$t_1 - t_2$ (eV)	σ [$(\Omega \text{ cm})^{-1}$]	E_a (eV)
MEM(TCNQ) ₂ (350 K)*	0.17	0.16		0.01	30.0	0.0
MBTM(TCNQ) ₂ [†]	0.17	0.17		0.01	9.0	0.0
METM(TCNQ) ₂ [†]	0.18	0.18		0.00	2.7	0.0
HBTM(TCNQ) ₂ [†]	0.17	0.15		0.03	1.9×10^{-1}	0.11
HMM(TCNQ) ₂ [‡]	0.17	0.16		0.01	1.7×10^{-1}	0.17
EBM(TCNQ) ₂ [‡]	0.16	0.15	0.17	0.01	3.5×10^{-2}	0.06
HEM(TCNQ) ₂ [‡]	0.19	0.10	0.19	0.09	3.2×10^{-2}	0.37
DMTM(TCNQ) ₂ [†]	0.18	0.04		0.14	2.2×10^{-3}	0.25
DMM(I)(TCNQ) ₂ [§]	0.18	0.06		0.12	2.0×10^{-3}	0.23
MEM(TCNQ) ₂ **	0.20	0.06		0.14	1.5×10^{-3}	0.23
EBTM(TCNQ) ₂ [†]	0.21	0.02	0.13	0.19	1.7×10^{-4}	0.20

^aMEM is N-methyl-N-ethylmorpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]^+$; MBTM is N-methyl-N-(*n*-butyl)thiamorpholinium, or $\text{S}(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{C}_4\text{H}_9)^+$; METM is N-methyl-N-ethylthiamorpholinium, or $\text{S}[(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)(\text{CH}_3)]^+$; HBTM is N-(*n*-butyl)thiamorpholinium, or $\text{S}[(\text{CH}_2)_4\text{N}(\text{C}_4\text{H}_9)]^+$; HMM is N-methylmorpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)]^+$; EBM is N-ethyl-N-(*n*-butyl)morpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)]^+$; HEM is N-ethylmorpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)]^+$; DMTM is [di-(N-methyl)]thiamorpholinium, or $\text{S}[(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{CH}_3)]^+$; DMM is [di-(N-methyl)]morpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{CH}_3)]^+$; EBTM is N-ethyl-N-(*n*-butyl)thiamorpholinium, or $\text{S}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)^+$; morpholine $[\text{O}(\text{CH}_2)_4\text{NH}]$ is also known as tetrahydro-*p*-isoxazine. All quantities refer to room temperature, except the first one, MEM(TCNQ)₂ in its uniform phase, which is at 350 K. Structures are from *, B. van Bodegom and A. Bosch, Acta Crystallogr. Sect. B 37, 863 (1981); †, Ref. 16; ‡, B. van Bodegom and J. L. de Boer, Acta Crystallogr. Sect. B 37, 119 (1981); §, P. Kamminga and B. Bodegom, Acta Crystallogr. Sect. B 37, 114 (1981); **, B. van Bodegom, Acta Crystallogr. Sect. B 37, 857 (1981).

^bGiven is t_0S , where S is the calculated overlap and $t_0 = 8.7$ eV. t_1 is the intradimer overlap; t_2 is the interdimer overlap and for tetramerized compounds the intertetramer overlap; t_3 is the intratetramer overlap.

tivation energy). On the other hand, if $t_1 \neq t_2$ the materials behave like semiconductors. These results are summarized in Table I. As can be seen, there is a very rough correlation between the room-temperature conductivity, its activation energy, and the difference in the transfer integrals.

In summary it seems that the calculations provide a manner to globally divide a series of closely-related TCNQ salts into classes, but so far the calculations appear to be insufficient to account more quantitatively for the conductivity. This may, amongst other things, be caused by the effect of the unequal Madelung potentials on inequivalent TCNQ molecules. This effect is clearly operative in the "inverse" Peierls transition,¹⁷ where through the inequivalence of two TCNQ chains arising in a phase

transition, electrons flow from one chain to the other, leading to a considerable increase in conductivity (going to lower temperature).

Therefore, in Table II the conductivity and the transfer integrals for three compounds with such inequivalent chains are given. In MPM(TCNQ)₂ the transfer integrals clearly differentiate between the chains. It is most likely that chain *A* is responsible for the conductivity.

Finally, it should be mentioned that these calculations can lead to counterintuitive results. Transfer integrals were also calculated for 1,2,4-trimethylpyridinium di-tetracyanoquinodimethane (using the structure from Ref. 18), denoted in short form as N-Me-2,4-Me-Py-(TCNQ)₂ and N-Me-2,6-Me-Py-(TCNQ)₂ (structure from Ref. 19). From a structural point of view two different overlap

TABLE II. Transfer integrals and conductivities for some N-substituted morpholinium di-tetracyanoquinodimethane salts, with two inequivalent stacks.

Compound ^a	t_1 (eV) ^b	t_2 (eV)	$t_1 - t_2$ (eV)	σ [$(\Omega \text{ cm})^{-1}$]	E_a (eV)
MBM(TCNQ) ₂ * (<i>A</i>)	0.17	0.15	0.02	5.0	0.0
(<i>B</i>)	0.16	0.16	0.00		
MPM(TCNQ) ₂ * (<i>A</i>)	0.18	0.16	0.02	1.2×10^{-1}	0.05
(<i>B</i>)	0.20	0.12	0.08		
DEM(TCNQ) ₂ [†] (<i>A</i>)	0.19	0.04	0.15	3.7×10^{-3}	0.09
(<i>B</i>)	0.22	0.03	0.18		

^aMBM is N-methyl-N-(*n*-butyl)morpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{C}_4\text{H}_9)]^+$; MPM is N-methyl-N-(*n*-propyl)morpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{CH}_3)(\text{C}_3\text{H}_7)]^+$; DEM is [di-(N-ethyl)]morpholinium, or $[\text{O}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)_2]^+$. Structures are from *, Ref. 16; †, H. Morssink and B. van Bodegom, Acta Crystallogr. Sect. B 37, 107 (1981); *A* and *B* denote the two different stacks. See also Table I.

^bSee Table I.

TABLE III. Transfer integrals for two substituted pyridinium TCNQ salts.

Compound ^a	Overlap type ^b	t^c (eV)	d^d (Å)
N-Me-2,4Me-Py	(1)-(2)	0.07	4.78
	(1)-(3)	0.03	5.00
N-Me-2,6Me-Py	(4)-(5)	0.02	3.35
	(4)-(6)	0.06	5.18

^aN-Me-2,4Me-Py(TCNQ)₂, structure from Ref. 18; N-Me-2,6Me-Py(TCNQ)₂, structure from Ref. 19.

^bFor N-Me-2,4Me-Py(TCNQ)₂: (1) is molecule on (x, y, z) ; (2) on $(-x, -y, -z)$; (3) on $(x, -y + \frac{1}{2}, z - \frac{1}{2})$; (1)-(2) is the structural dimer. For N-Me-2,6Me-Py(TCNQ)₂: (4) is molecule on (x, y, z) ; (5) $(-x, -y, -z)$; (6) on $(-x, -y + 1, -z)$; (4)-(5) is the structural dimer.

^cSee footnote b, Table I.

^dThe distance between the centers of mass of the two TCNQ molecules.

types can be distinguished. One large overlap, with the molecules almost on top of each other and a small overlap, where the molecules have a larger shift with respect to each other (Fig. 2). The former can be considered as the dimer, from a structural point of view. The transfer integrals for each of the two overlap types and each of the compounds are given in Table III. It appears that for N-Me-2,4Me-Py all things are as one would expect: The structural dimer has the largest transfer integral. However, for N-Me-2,6Me-Py the structural dimer has the smaller transfer integral. Apparently for the latter compound the electronic dimer is different from the structural dimer.

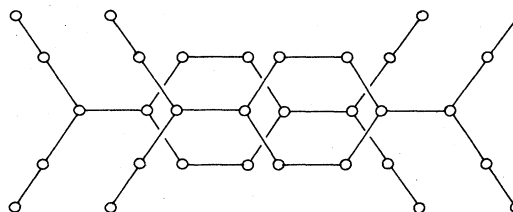
These results show that the details of the molecular orbital, especially its nodal structure, are important in determination of the transfer integral. It is not sufficient to just look at the structure to determine whether a particular overlap is large or small. Calculations of overlap integrals are clearly an aid to that purpose.

IV. CONCLUSIONS

In the one-electron approximation for the band structure of TCNQ salts, as well as in applications of the Hubbard Hamiltonian to these materials, the transfer integral plays a major role.

In this paper, it is shown that quantum-chemical calculations yield rather arbitrary values for this quantity, since it is critically dependent on the "tail" of the wave function. Generally, this part is not known very well, because when, for organic molecules, wave functions are calibrated against experiment, this is usually done with optical transitions or spin densities as found by ESR. These experiments calibrate the wave function around the nucleus

(a)



(b)

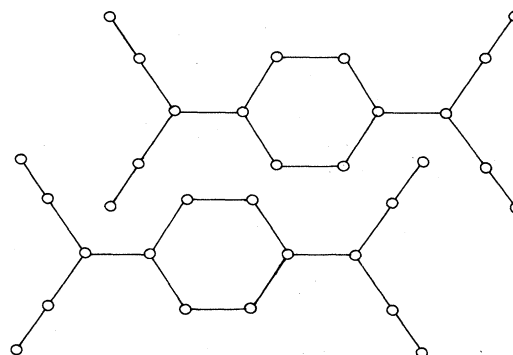


FIG. 2. The two structural overlaps for N-Me-2,6Me-Py(TCNQ)₂. The figures are taken from Ref. 19. (a) Structural dimer [overlap type (4)-(5) in Table III]; (b) interdimer overlap [overlap type (4)-(6) in Table III].

and not their "tails," therefore the latter part remains rather arbitrary.

The only way out appears to be to take the transfer integral to be proportional to the intersite orbital overlap. Then their geometric dependence is correctly accounted for and at least relative values of transfer integrals can be relied on. In this respect the symmetry of the relevant molecular orbital plays a dominant role.

Sometimes, inspection of the crystal structure can give quite erroneous estimates for even the relative values of the transfer integrals. For N-Me-2,6-Me-Py-(TCNQ)₂ the structural dimer, as estimated from crystal packing, is different from the electronic dimer. For N-Me-2,4-Me-Py-(TCNQ)₂ the structural dimer and the electronic dimer do coincide.

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