Extended-Hückel Energy Band Structures of Organometallic Compounds with One-Dimensional Crystal Geometries

Computational Results for Bis(2,5-dimethyl-N,N′-dicyanoquinonediimine)copper, -silver, and -lithium

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In order to rationalize the high electrical conductivity of 2,5-dimethyl-N,N′-dicyanoquinonediimine radical anion salts (2,5-DM-DCNQI) of copper, silver, and lithium, we performed one-dimensional energy band structure calculations of extended-Hückel type (namely Self-Consistence of Charge, SCC) for one-dimensional models of these "organic conductors". In each case, SCC yields two overlapping incompletely occupied valence bands, which give rise to some evidence for the observed high electrical conductivity, in spite of the one-electron nature of the method. Furthermore, these two frontier energy bands do not contain any metallic orbital contribution, which suggests that the electron transport takes place in the organic stack of the 2,5-DM-DCNQI ligands only.

1. Introduction

The highly conducting organometallic compounds bis(2,5-dimethyl-N,N′-dicyanoquinonediimine)copper, -silver, and -lithium $(2,5\text{-DM-DCNQI})_2\text{Me}$ (Me = Cu, Ag, Li) fulfil two basic requirements for an investigation of their interesting electronic properties by means of a one-dimensional energy band structure calculation:

- Single crystals, appropriate to examine their spatial structure by X-ray diffraction methods, can be grown.
- These single crystals are built up of parallel molecular stacks. Distances between the molecules within the stacks are short compared to those between neighboring stacks [1].

To describe the electronic structure of such anisotropic systems, the interactions between the stacks are completely ignored. From the entire crystal one stack can be taken to represent its geometric and chemical composition.

Furthermore, we assume that such one-dimensional crystals are chemically homogeneous and have no defects. In order to introduce cyclic (Born-v. Kármán-) boundary conditions (cf. [4]) they are regarded as consisting of an infinite number of one-dimensional unit cells; any different geometries and compositions of the terminating cells will be ignored.

In this paper, we report the Self-Consistence of Charge (SCC) energy band structure for one-dimensional crystals of $(2,5\text{-DM-DCNQI})_2\text{Me}$ (Me = Cu, Ag, Li). All basic equations of this extended-Hückel type method have been summarized earlier in [2]. Although the SCC procedure is methodically simple, a considerable amount of computer time and storage capacity is required since the number of electrons per unit cell is rather big. Ab-initio methods based on the Hartree-Fock approximation cannot be applied in such cases, in spite of our restriction to one-dimensional model geometries.

Recently, Vela and Gázquez proposed new SCC parameter sets, derived non-empirically from density functional theory for s, p, and d valence electrons (in the so-called transition state) for all atomic numbers up to 85 (excluding noble gases and rare earth elements) [3]. We used this new parametrization scheme developed from one single theoretical source in order to obtain comparable results for the three closely related compounds under consideration.

2. One-Dimensional Energy Band Structures of $(2,5\text{-DM-DCNQI})_2$ Radical Anion Stacks with Copper, Silver, and Lithium as Counter Ions

2.1. Model Geometries

Since the spatial structures of all three compounds look very similar, for illustrative purposes we only

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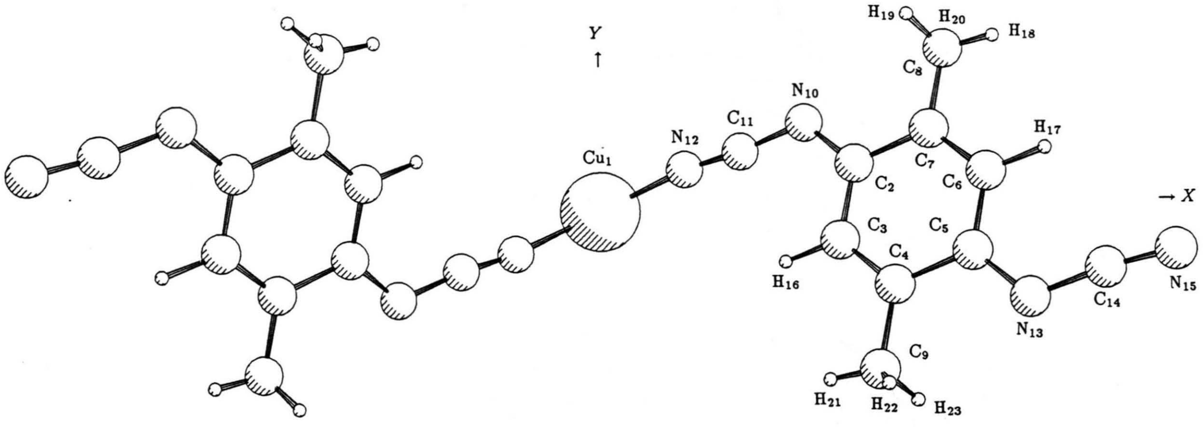

Fig. 1. One-dimensional unit cell of $(2,5\text{-DM-DCNQI})_2\text{Cu}$.

plotted the chosen one-dimensional unit cell of $(2,5\text{-DM-DCNQI})_2\text{Cu}$ (Figure 1).

Because of their twofold rotation axes C_2 in Z direction (identical with the invariant lines), all three one-dimensional crystals belong to line group symmetry $\mathbf{L}2$ (cf. [4]) with translational periods a of 3.8870 Å, 3.8360 Å, and 3.8320 Å for the Cu, Ag, and Li compound, respectively. The two irreducible representations of the point subgroup $\mathbf{C}_2$ of $\mathbf{L}2$ are labelled A_0 and A_1. To avoid band-indexing difficulties [5], we used symmetry-adapted linear combinations of Bloch sums as basis functions.

All atomic coordinates (cf. Tables 2, 4, and 6) have been taken from crystallographic data [6]; equivalent atomic families have been labelled according to Figure 1.

2.2. Parametrization

All details of the one-dimensional SCC energy band structure calculations reported here are identical with those documented in [2]. The exceptions (in parts aforementioned) are:

- Initial valence orbital ionization potentials (VOIP) as well as all SCC interpolation parameters A, B, and C (=VOIP) were taken from [3] (cf. Table 1). Unlike in [2], the Self-Consistence of Charge and Configuration (SCCC) procedure has not been applied for any atomic family.
- Orbital exponents ζ have been derived according to Burns' rules [8] from valence-state configurations which also underlie the density functional approach for the SCC parameter determination of Vela and Gázquez. These valence-state configurations are listed in Table II of [3]. For electrons in d valence orbitals, two valence-state configurations are specified in this table; in these cases, the arithmetic mean of the corresponding two Burns orbital exponents have been used.
- Finally, in order to construct a sufficiently resolved density of states histogram, we set the grid parameter n_E equal to 3000 (cf. (54) and (55) of [2]).

2.3. Computational Results for $(2,5\text{-DM-DCNQI})_2\text{Cu}$

With the chosen set of valence orbitals (cf. Table 1) each model unit cell of $(2,5\text{-DM-DCNQI})_2\text{Cu}$ contains 147 valence electrons. The summation (4) of [2] included overlap integrals of 15 unit cells ($N_{\max}=7$). The SCC procedure converged after 8 iteration cycles. Using symmetry adapted linear combinations of Bloch sums, the eigenvalue problem (2) of [2] can be split into two matrix equations with dimensions $\dim V_{k,\mathrm{A}_0} = 69$ and $\dim V_{k,\mathrm{A}_1} = 68$, respectively.

In Table 2, valence orbital ionization potentials V, populations Δ, Σ, and Π, as well as atomic charges q of the last iteration step have been listed. The 3d orbitals of copper are nearly completely filled whereas its 4s and especially 4p orbitals are only slightly populated, yielding a net positive charge of 0.31 a.u. As expected, the most electronegative nitrogens all are negatively charged.

Figure 2 shows the one-dimensional energy band structure and the corresponding density of states histogram in the energy range between −17 eV and −5 eV. A starred (∗) little circle represents the energy of an occupied crystal orbital; unoccupied band orbital circles remain unstarred. Within the new parametriza-

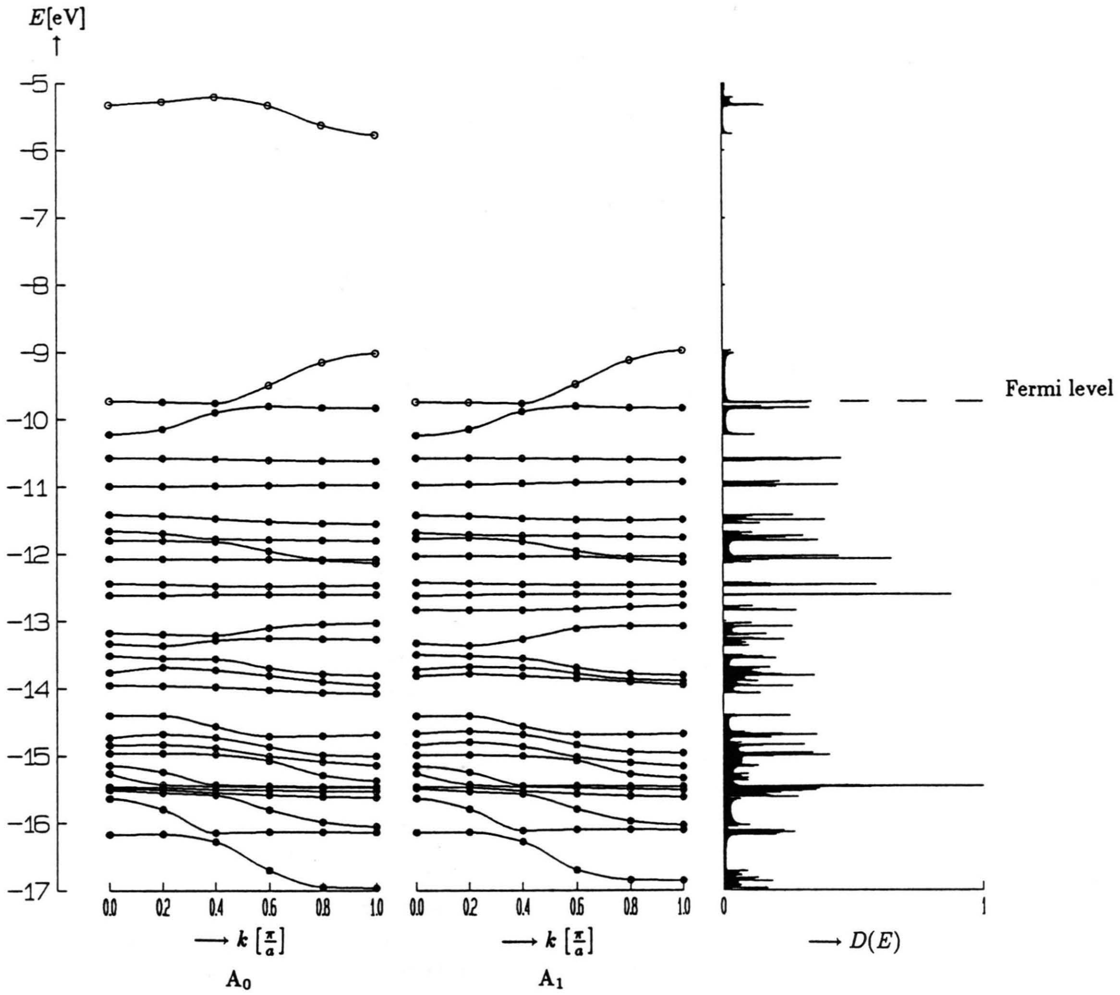

Fig. 2. One-dimensional energy band structure and density of states histogram for $(2,5\text{-DM-DCNQI})_2Cu$.

Table 1. Valence orbitals, orbital exponents, and SCC interpolation parameters (in eV).

Atom	Valence orbital	ζ	A	B	C VOIP
H	1s	1.0000	0.125	14.089	12.565
Li	2s	0.6000	0.031	5.388	5.439
Li	2p	0.5000	0.031	4.296	3.610
C	2s	1.5500	0.031	12.926	19.654
C	2p	1.3250	0.031	11.305	11.129
N	2s	1.8750	0.031	15.341	25.366
N	2p	1.6500	0.031	13.575	13.900
Cu	3d	3.7500	0.014	19.306	13.162
Cu	4s	1.9250	0.008	6.424	8.345
Cu	4p	1.1500	0.008	4.593	4.216
Ag	4d	3.0625	0.008	13.648	14.884
Ag	5s	1.5400	0.005	5.684	7.664
Ag	5p	0.9200	0.005	4.200	4.071

tion scheme, the energy band structure of our model $(2,5\text{-DM-DCNQI})_2Cu$ looks somewhat different from that published earlier [2]. In addition to a pair of overlapping incompletely filled frontier bands, we find another two overlapping bands separated from the former by a very small energy gap of 0.040 eV. These four highest (partially) occupied bands together cover an energy range of 1.263 eV. A dashed line marks the occupation limit (−9.735 eV). All occupied crystal orbitals together sum up to an SCC total energy $\mathscr{E}$ of −2480.560 eV.

Table 3 shows the dominant percental composition (eq. (50) of [2]) of two crystal orbitals (with wavenumbers $k=0$ and $k=\pi/a$) of the four frontier energy bands labelled 37 A_0, 38 A_0, 36 A_1, and 37 A_1. None of

Table 2. Cartesian coordinates X, Y, and Z, valence orbital ionization potentials V, configurations $d^{\Delta} s^{\Sigma} p^{\Pi}$, and charges q for all representative atoms of (2,5-DM-DCNQI)$_2$Cu.

Atomic family	X (Å)	Y (Å)	Z (Å)	V (d) (eV)	V (s) (eV)	V (p) (eV)	Δ	Σ	Π	q (a.u.)
Cu$_1$	0.0000	0.0000	−3.8870	15.456	9.109	4.761	9.99	0.47	0.23	0.31
C$_2$	4.5493	0.7718	−1.2676		20.869	12.191		1.10	2.76	0.14
C$_3$	4.2308	−0.5855	−0.9194		19.455	10.955		1.07	2.93	0.00
C$_4$	5.0613	−1.3554	−0.1786		20.081	11.502		1.10	2.84	0.06
C$_5$	6.3057	−0.7718	0.2958		20.868	12.191		1.10	2.76	0.14
C$_6$	6.6242	0.5855	−0.0523		19.474	10.972		1.07	2.92	0.01
C$_7$	5.7938	1.3554	−0.7931		20.074	11.496		1.10	2.84	0.06
C$_8$	6.1231	2.7954	−1.1338		18.429	10.058		1.01	3.17	−0.18
C$_9$	4.7319	−2.7954	0.1620		18.429	10.057		1.01	3.17	−0.18
N$_{10}$	3.7511	1.5507	−2.0188		23.238	12.017		1.29	3.96	−0.26
C$_{11}$	2.5978	1.0627	−2.4992		21.225	12.504		1.11	2.79	0.09
N$_{12}$	1.5837	0.7657	−2.9714		22.990	11.798		1.39	3.86	−0.25
N$_{13}$	7.1039	−1.5507	1.0470		23.168	11.955		1.30	3.97	−0.26
C$_{14}$	8.2572	−1.0627	1.5275		21.047	12.348		1.12	2.88	0.01
N$_{15}$	9.2713	−0.7657	1.9997		22.093	11.004		1.42	3.97	−0.39
H$_{16}$	3.3004	−0.9622	−1.3454		12.944			0.92		0.08
H$_{17}$	7.5546	0.9622	0.3737		12.958			0.92		0.08
H$_{18}$	6.9327	2.9866	−0.7951		13.138			0.90		0.10
H$_{19}$	5.4236	3.3772	−0.6969		13.106			0.91		0.09
H$_{20}$	6.1201	2.9437	−2.0715		13.168			0.89		0.11
H$_{21}$	3.9223	−2.9866	−0.1766		13.137			0.90		0.10
H$_{22}$	4.7350	−2.9437	1.0997		13.168			0.89		0.11
H$_{23}$	5.4314	−3.3772	−0.2748		13.107			0.91		0.09

Table 3. Composition of the four frontier energy bands 37 A$_0$, 38 A$_0$, 36 A$_1$, and 37 A$_1$ of (2,5-DM-DCNQI)$_2$Cu.

37 A$_0$										
k=0.0:	22% N$_{13}$ p	18% N$_{15}$ p	16% N$_{10}$ p	12% N$_{12}$ p	7% C$_2$ p	6% C$_4$ p	6% C$_5$ p	4% C$_7$ p	3% C$_6$ p	2% C$_3$ p
k=1.0:	14% N$_{13}$ p	9% C$_5$ p	9% C$_6$ p	8% N$_{15}$ p	8% C$_8$ p	7% N$_{10}$ p	7% C$_9$ p	7% C$_2$ p	7%C$_4$ p	6% C$_7$ p
38 A$_0$										
k=0.0:	15% N$_{13}$ p	9% C$_5$ p	8% N$_{10}$ p	8% C$_6$ p	7% C$_9$ p	7% C$_8$ p	7% C$_2$ p	7% N$_{15}$ p	7% C$_4$ p	6% C$_7$ p
k=1.0:	19% N$_{13}$ p	15% N$_{10}$ p	13% C$_2$ p	11% C$_5$ p	7% C$_4$ p	7% N$_{15}$ p	6% C$_7$ p	6% C$_6$ p	5% N$_{12}$ p	4% C$_3$ p
36 A$_1$										
k=0.0:	22% N$_{13}$ p	18% N$_{15}$ p	15% N$_{10}$ p	11% N$_{12}$ p	7% C$_2$ p	6% C$_4$ p	5% C$_5$ p	4% C$_7$ p	3% C$_6$ p	2% C$_3$ p
k=1.0:	14% N$_{13}$ p	9% C$_5$ p	8% C$_{15}$ p	8% C$_6$ p	8% C$_8$ p	7% N$_{10}$ p	7% C$_9$ p	7% C$_2$ p	7% C$_4$ p	6% C$_3$ p
37 A$_1$										
k=0.0:	14% N$_{13}$ p	9% C$_5$ p	8% N$_{10}$ p	8% C$_6$ p	7% C$_9$ p	7% C$_2$ p	7% C$_8$ p	7% N$_{15}$ p	7% C$_4$ p	6% C$_3$ p
k=1.0:	19% N$_{13}$ p	16% N$_{10}$ p	12% C$_2$ p	11% C$_5$ p	7% C$_4$ p	7% N$_{15}$ p	7% C$_7$ p	6% N$_{12}$ p	5% C$_6$ p	4% C$_3$ p

them contains any significant Cu orbital contribution. Consequently, Cu should not play any role in the mechanism of electronic conductivity, so that it can be expected to be replaceable by similarly sized counter ions with the same charge.

2.4. *Computational Results for (2,5-DM-DCNQI)$_2$Ag*

For the Ag compound (147 valence electrons per unit cell, dim $V_{k,\mathrm{A}_0} = 69$ and dim $V_{k,\mathrm{A}_1} = 68$) the SCC procedure converged after 8 iteration steps. 17 unit cells were included in the summation of the overlap integrals (4) of [2] ($N_{\max} = 8$).

Table 4 lists valence orbital ionization potentials V, populations Δ, Σ, and Π, as well as atomic charges q of the last iteration step. Ag 4d orbitals are nearly completely filled and Ag 5p orbitals are nearly unpopulated. The net positive charge of silver amounts to 0.60 a.u.

The highest occupied energy bands of one-dimensional (2,5-DM-DCNQI)$_2$Ag show a similar shape to those of the corresponding Cu compound (cf. Fig-

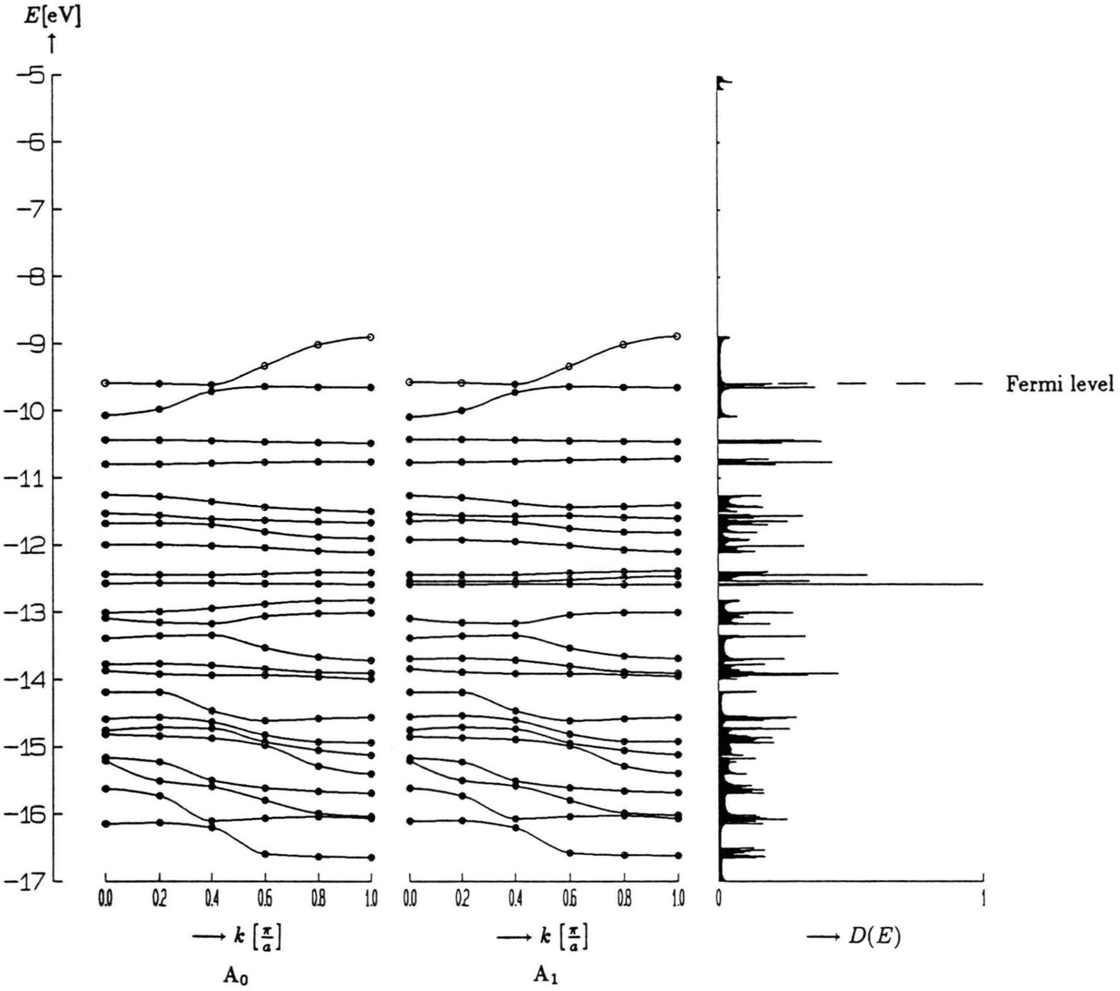

Fig. 3. One-dimensional energy band structure and density of states histogram for $(2,5\text{-DM-DCNQI})_2Ag$.

ure 3). The gapless energy range between −8.876 eV and −10.084 eV is covered by the energy bands $37\,A_0$, $38\,A_0$, $36\,A_1$, and $37\,A_1$. The occupation limit (identified with the Fermi level) occurs at −9.589 eV. The SCC total energy $\mathscr{E}$ amounts to −2493.033 eV. Orbital compositions calculated according to (50) of [2] for these four frontier bands are summarized in Table 5. As in the case of the copper compound, there is no significant transition metal contribution at all.

2.5. Computational Results for $(2,5\text{-}DM\text{-}DCNQI)_2Li$

Model unit cells of $(2,5\text{-DM-DCNQI})_2Li$ contain only 137 electrons. The matrix dimensions dim V_{k,A_0} and dim V_{k,A_1} are equal to 66 in both cases. The SCC procedure (including 23 unit cells in (4) of [2], i.e. $N_{max} = 11$) converged after 9 iteration cycles.

Table 6 indicates that among the three compounds under consideration, $(2,5\text{-DM-DCNQI})_2Li$ (with a charge of 0.71 a.u.) is the most ionic one. Li s and p orbitals therefore are only slightly occupied.

The qualitative shape of the frontier energy band structure remains similar to that of the transition metal species even though lithium has no d orbitals (cf. Figure 4). But also s and p orbital contributions do not occur in the four highest (partially) occupied energy bands $34\,A_0$, $35\,A_0$, $34\,A_1$, and$35\,A_1$, as can be read from Table 7. Together, these four bands cover a range of 1.218 eV. The occupation limit (Fermi level) occurs at −9.646 eV. The SCC total energy amounts to −2309.534 eV.

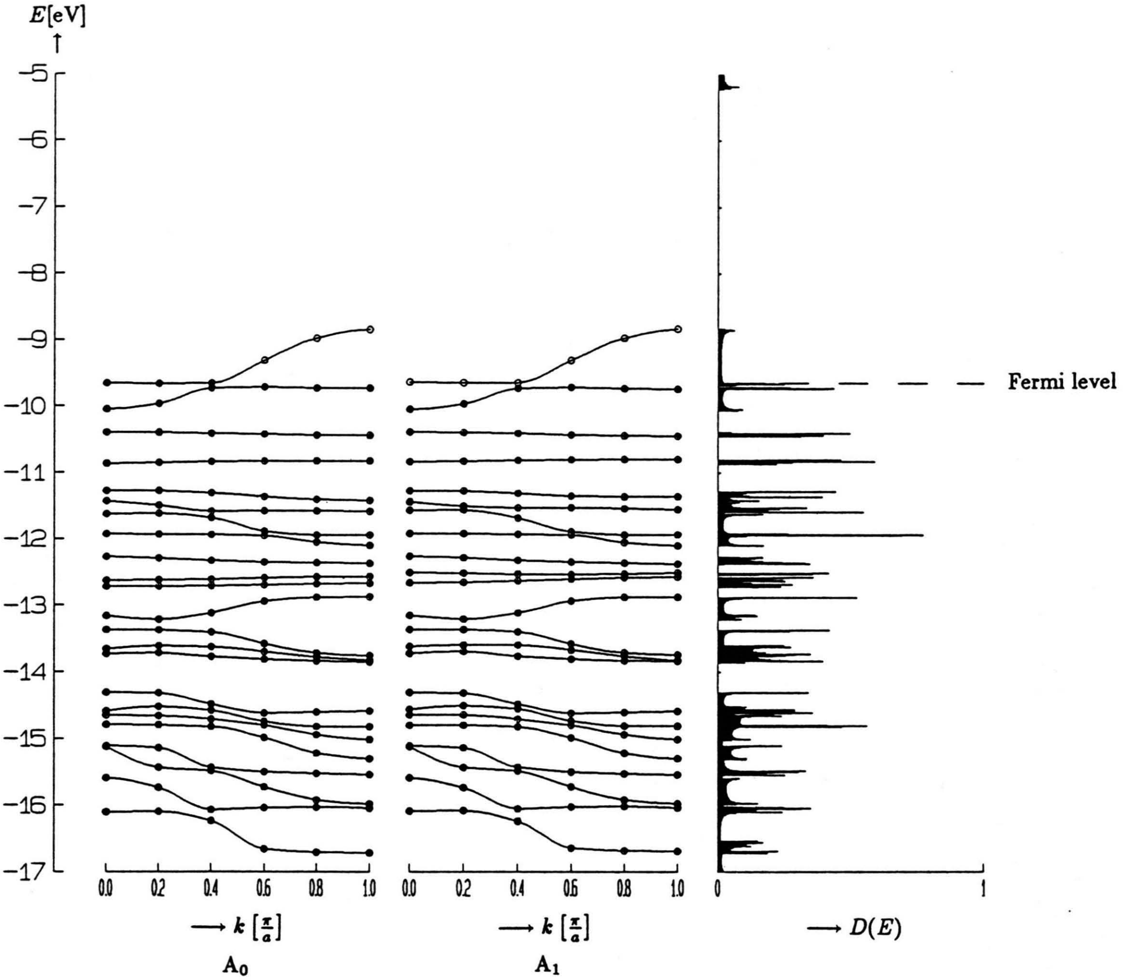

Fig. 4. One-dimensional energy band structure and density of states histogram for $(2,5\text{-DM-DCNQI})_2Li$.

3. Conclusion

The purpose of one-electron band structure calculations can only be to gain some insight from a theoretical (or semiempirical) point of view as a supplementary tool in order to rationalize experimentally well-known properties.

In particular, the three organometallic compounds under consideration are excellent "organic conductors". From temperature dependent conductivity measurements it is known that the Cu compound shows an overall metallic behaviour, whereas in Ag and Li 2,5-DM-DCNQI at low temperatures a metal-semiconductor transition takes place [1].

These important properties can never be predicted seriously within one-electron energy band theories. The predictory ability of such theoretical models is rather limited; results obtained from a band structure calculation of extended-Hückel type should not be overestimated, since exchange, correlation, and spin effects are not at all explicitly included [9].

The documented SCC energy band structures are not contradictory to the high electronic conductivity of the three 2,5-DM-DCNQI salts, since we found two incompletely filled overlapping energy bands in each case [10]. From the frontier band occupancy alone, however, we cannot answer the crucial question, wheather metallic or semiconduting (insulating) behaviour should be expected.

Table 4. Cartesian coordinates X, Y, and Z, valence orbital ionization potentials V, configurations $d^{\Delta} s^{\Sigma} p^{\Pi}$, and charges q for all representative atoms of $(2,5\text{-DM-DCNQI})_2Ag$.

Atomic family	X (Å)	Y (Å)	Z (Å)	V(d) (eV)	V(s) (eV)	V(p) (eV)	Δ	Σ	Π	q (a.u.)
Ag_1	0.0000	0.0000	−3.8360	17.778	8.869	4.962	9.98	0.42	0.01	0.60
C_2	4.7413	0.8433	−1.2200		20.825	12.153		1.10	2.77	0.13
C_3	4.3633	−0.5048	−0.8972		19.313	10.831		1.05	2.97	−0.02
C_4	5.1549	−1.3349	−0.1951		20.041	11.467		1.10	2.85	0.05
C_5	6.4427	−0.8433	0.2610		20.845	12.171		1.10	2.77	0.13
C_6	6.8207	0.5048	−0.0618		19.338	10.853		1.05	2.97	−0.01
C_7	6.0291	1.3349	−0.7639		20.042	11.468		1.10	2.85	0.05
C_8	6.4187	2.7528	−1.0785		18.496	10.116		1.02	3.15	−0.17
C_9	4.7653	−2.7528	0.1195		18.495	10.115		1.02	3.15	−0.17
N_{10}	3.9893	1.6736	−1.9331		23.220	12.001		1.29	3.97	−0.26
C_{11}	2.8087	1.2745	−2.3822		21.133	12.423		1.12	2.82	0.06
N_{12}	1.7794	1.0560	−2.8385		22.650	11.497		1.39	3.90	−0.29
N_{13}	7.1947	−1.6736	0.9741		23.191	11.976		1.29	3.98	−0.27
C_{14}	8.3753	−1.2745	1.4232		21.059	12.358		1.11	2.88	0.01
N_{15}	9.4046	−1.0560	1.8795		22.063	10.977		1.41	3.98	−0.40
H_{16}	3.5024	−0.8551	−1.1580		13.052			0.90		0.10
H_{17}	7.6816	0.8551	0.1990		13.102			0.89		0.11
H_{18}	7.1866	2.9998	−0.5755		13.077			0.91		0.09
H_{19}	5.7067	3.4011	−0.7342		13.116			0.91		0.09
H_{20}	6.3505	2.9519	−2.0617		13.136			0.90		0.10
H_{21}	3.9974	−2.9998	−0.3835		13.069			0.91		0.09
H_{22}	4.8335	−2.9519	1.1027		13.134			0.90		0.10
H_{23}	5.4773	−3.4001	−0.2248		13.117			0.91		0.09

Table 5. Composition of the four frontier energy bands 37 A_0, 38 A_0, 36 A_1, and 37 A_1 of $(2,5\text{-DM-DCNQI})_2Ag$.

37 A_0										
$k=0.0$:	20% N_{13}p	17% N_{10}p	16% N_{15}p	13% N_{12}p	7% C_2p	6% C_5p	6% C_4p	5% C_7p	2% C_3p	2% C_6p
$k=1.0$:	12% N_{13}p	9% N_{10}p	9% C_5p	8% C_6p	8% C_2p	7% C_4p	7% C_7p	7% C_3p	6% C_9p	6% C_8p
38 A_0										
$k=0.0$:	13% N_{13}p	9% C_5p	8% N_{10}p	8% C_4p	8% C_2p	8% C_6p	7% N_{15}p	7% C_3p	6% C_9p	6% C_8p
$k=1.0$:	19% N_{13}p	16% N_{10}p	12% C_2p	11% C_5p	7% N_{15}p	7% C_4p	6% N_{12}p	6% C_7p	5% C_6p	4% C_3p
36 A_1										
$k=0.0$:	20% N_{13}p	16% N_{10}p	16% N_{15}p	12% N_{12}p	7% C_2p	6% C_5p	6% C_4p	5% C_7p	3% C_6p	2% C_3p
$k=1.0$:	12% N_{13}p	9% N_{10}p	9% C_5p	8% C_2p	7% C_6p	7% C_3p	7% C_7p	7% C_4p	6% C_9p	6% C_8p
37 A_1										
$k=0.0$:	12% N_{13}p	10% N_{10}p	9% C_5p	8% C_2p	7% C_6p	7% C_3p	7% C_7p	7% C_4p	6% N_{15}p	6% C_8p
$k=1.0$:	19% N_{13}p	17% N_{10}p	12% C_2p	11% C_5p	7% C_4p	7% N_{15}p	7% C_7p	6% N_{12}p	5% C_3p	5% C_6p

Population analyses, on the other hand, may be regarded as useful tools in order to introduce some chemical intuition into the numerical quantum chemical output. Our most important result seems to be that in all three compounds the metallic component does not influence directly the electronic conduction mechanism, due to the fact that there is no orbital contribution to one of the frontier bands which originated from the metal counter ions. This result is in agreement with the interpretation of the XPS and UPS photoelectron spectra of $(2,5\text{-DM-DCNQI})_2Ag$ and -Li [11]. For the copper compound, however, an admixture of Cu 3d states had been expected [12], in contradiction to our findings.

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Table 6. Cartesian coordinates X, Y, and Z, valence orbital ionization potentials V, configurations $s^{\Sigma} p^{\Pi}$, and charges q for all representative atoms of $(2,5\text{-DM-DCNQI})_2Li$.

Atomic family	X (Å)	Y (Å)	Z (Å)	V(s) (eV)	V(p) (eV)	Σ	Π	q (a.u.)
Li_1	0.0000	0.0000	−3.8320	6.879	4.760	0.19	0.10	0.71
C_2	4.5806	0.7979	−1.2374	20.882	12.203	1.10	2.77	0.13
C_3	4.2534	−0.5652	−0.9087	19.430	10.933	1.07	2.93	0.00
C_4	5.0812	−1.3559	−0.1867	20.078	11.500	1.10	2.85	0.05
C_5	6.3344	−0.7979	0.2794	20.901	12.220	1.10	2.77	0.13
C_6	6.6616	0.5652	−0.0493	19.458	10.957	1.07	2.92	0.01
C_7	5.8338	1.3559	−0.7713	20.078	11.499	1.10	2.85	0.05
C_8	6.1729	2.7776	−1.0888	18.408	10.039	1.00	3.15	−0.16
C_9	4.7421	−2.7776	0.1308	18.407	10.038	1.00	3.15	−0.16
N_{10}	3.7962	1.5881	−1.9659	23.131	11.922	1.29	3.95	−0.24
C_{11}	2.6532	1.1087	−2.4397	21.058	12.357	1.12	2.84	0.03
N_{12}	1.6462	0.8226	−2.9220	22.339	11.222	1.40	3.91	−0.30
N_{13}	7.1188	−1.5881	1.0079	23.103	11.898	1.29	3.95	−0.24
C_{14}	8.2618	−1.1087	1.4817	21.003	12.309	1.12	2.89	−0.01
N_{15}	9.2688	−0.8226	1.9640	21.905	10.837	1.42	3.95	−0.37
H_{16}	3.3186	−0.9675	−1.3264	12.926		0.94		0.06
H_{17}	7.5964	0.9675	0.3684	12.974		0.93		0.07
H_{18}	6.9710	3.0032	−0.7839	13.185		0.90		0.10
H_{19}	5.4536	3.3959	−0.6871	13.118		0.92		0.08
H_{20}	6.1539	2.9599	−2.0422	13.208		0.90		0.10
H_{21}	3.9440	−3.0032	−0.1741	13.178		0.90		0.10
H_{22}	4.7611	−2.9599	1.0842	13.205		0.90		0.10
H_{23}	5.4614	−3.3959	−0.2709	13.118		0.92		0.08

Table 7. Composition of the four frontier energy bands 34 A_0, 35 A_0, 34 A_1, and 35 A_1 of $(2,5\text{-DM-DCNQI})_2Li$.

34 A_0										
$k=0.0$:	20% N_{13} p	18% N_{15} p	17% N_{10} p	14% N_{12} p	6% C_2 p	5% C_5 p	5% C_4 p	4% C_7 p	3% C_6 p	2% C_3 p
$k=1.0$:	14% N_{13} p	10% N_{10} p	8% C_5 p	8% C_6 p	7% C_2 p	7% N_{15} p	6% C_9 p	6% C_8 p	6% C_3 p	6% C_7 p
35 A_0										
$k=0.0$:	15% N_{13} p	10% N_{10} p	8% C_5 p	8% C_6 p	7% C_2 p	7% N_{15} p	6%C_9 p	6% C_8 p	6% C_3 p	6% C_7 p
$k=1.0$:	19% N_{13} p	17% N_{10} p	12% C_2 p	11% C_5 p	7% C_4 p	7% N_{15} p	7% C_7 p	6% N_{12} p	5% C_6 p	4% C_3 p
34 A_1										
$k=0.0$:	20% N_{13} p	18% N_{15} p	17% N_{10} p	14% N_{12} p	6% C_2 p	5% C_5 p	5% C_4 p	4% C_7 p	3% C_6 p	2% C_3 p
$k=1.0$:	14% N_{13} p	9% N_{10} p	8% C_5 p	8% C_6 p	8% N_{15} p	7% C_2 p	6% C_9 p	6% C_3 p	6% C_8 p	6% C_4 p
35 A_1										
$k=0.0$:	14% N_{13} p	11% N_{10} p	8% C_5 p	7% C_2 p	7% C_6 p	7% N_{15} p	6% C_9 p	6% C_3 p	6% C_8 p	6% C_4 p
$k=1.0$:	19% N_{13} p	18% N_{10} p	11% C_5 p	11% C_2 p	7% C_7 p	7% N_{15} p	7% C_4 p	6% N_{12} p	5% C_3 p	5% C_6 p

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$a=b=21.710$ Å, $c=3.887$ Å for the Cu compound,
$a=b=22.368$ Å, $c=3.836$ Å for the Ag compound,
$a=b=21.830$ Å, $c=3.832$ Å for the Li compound.

Note the refinement compared to the symmetry group ($\mathbf{I}4_1$) stated in [7] for $(2,5\text{-DM-DCNQI})_2Cu$.

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