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N,*N′*-Dicyanoquinone Diimines (DCNQIs): Versatile Acceptors for Organic Conductors

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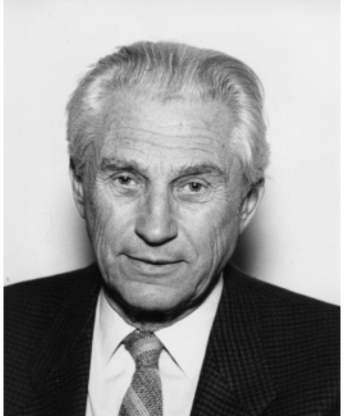
1. Introduction

In 1984, a new type of acceptor was published from our institute: *N*,*N′*-dicyanodiimines derived from benzoquinones (DCNQIs), naphthoquinones (DCNNIs), and anthraquinones (DCNAIs).[1] They were followed in 1986 by conducting charge transfer (CT) complexes[2] and radical anion salts with unprecedented high conductivities.[3,4]



Professor Siegfried Hünig, born in 1921 near Dresden (Germany), studied chemistry at the Technische Hochschule, Dresden, where he was promoted to Dr. Ing in 1943. From 1945 to 1950, he worked at the University of Marburg on his habilitation and stayed there as an assistant professor. In 1960, he moved as an associate professor to the University of Munich. In 1961, he accepted a call as full professor and head of the Chemical Institute where he was active until 1987. Since then, he has been professor emeritus at the Institute of Organic Chemistry. He received honorary doctorate degrees from the Universities of Marburg, Munich, and Halle.

Dr. Edith Herberth, born in 1972 in Agnita (Romania), studied chemistry at the University of Würzburg. In 1997, she spent four months as a research student (founded by an Erasmus scholarship) at Heriot-Watt University in Edinburgh (United Kingdom) in Dr. D. R. Adams group. After she received her diploma degree in 1999, she prepared her Ph.D. thesis in Organic Chemistry in the group of Prof. Dr. M. Christl at the Institute of Organic Chemistry, University of Würzburg.

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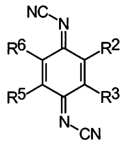
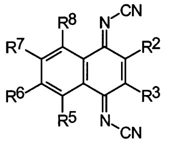
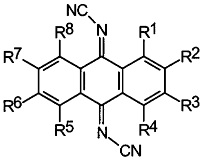


DCNQI



DCNNI



DCNAI

The unique properties of these metal salts, especially the copper DCNQI salts with extremely high conductivities and peculiar temperature/pressure profiles, initiated thorough investigations by several groups. In the meantime, about 480 papers have been published on this subject and the field is still under active investigation.

The topic was briefly reviewed in 1990,[5] 1991,[6] 1994,[7] and 1995.[8] A comparison between DCNQIs and other acceptors determined by CN groups [especially TCNQ (**1**)] has been presented.[9] In 2000, a comprehensive report appeared on DCNQI copper salts and their startling properties.[10]

The intention of this review is (i) to provide collections of all *N,N'*-dicyanodiimines derived from quinones so far published together with the conducting materials involving these acceptors; (ii) to discuss and to highlight the properties of these materials, mainly emphasizing the cooperation of molecular and solid state properties on their conducting behavior; and (iii) to point to some compounds that were designed in analogy to DCNQI chemistry.

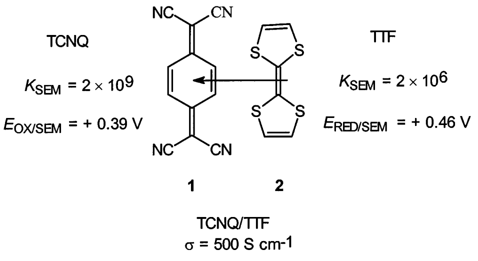
2. Design of DCNQIs

The discoveries of tetrathiafulvalene (**2**)·Cl (TTF·Cl)[11] and especially the CT complex TCNQ/TTF[12,13] as highly conducting materials in the early 1970s opened a new field of material sciences (Scheme 1). Of the various presuppositions for the conducting of low molecular organic compounds,[14] the following two are of primary importance.

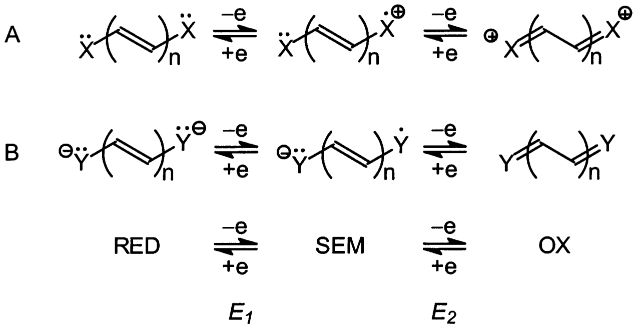
(i) In TCNQ/TTF, for the first time, acceptor and donor molecules are arranged in segregated stacks of equidistant moieties, providing one-dimensional electron transport along the axis of the stacks. (ii) Both TCNQ and TTF are typical examples of the violene type two-step redox systems with stable radical ions, which have been extensively studied since 1964 (Scheme 2).[11−13,15]

The high thermodynamic stability of these violene radical cations and anions expressed as semiquinone formation constants K_{SEM} depend strongly on the planarity of the π-systems. Therefore, it is obvious that TTF will tolerate full substitution by a great variety of even bulky groups without touching the planarity of the core π-system. Consequently, countless TTF derivatives have been and are still published, some leading even to superconducting radical salts (cf. contributions to this issue). In sharp contrast, only a handful of TCNQ derivatives have been described, most of them with worse acceptor properties as compared to the parent TCNQ system. Obviously, already one substituent of the size of a methyl group (but not fluorine)[16,17] will distort the neighboring rigid, Y-shaped $=C(CN)_2$ group. Therefore, it was anticipated that substituting $=C(CN)_2$ in TCNQ by the more flexible, bent $=N-CN$ moiety in DCNQI should overcome these limitations, especially since chemical[16,17] and spectroscopic[18] analogies between these two groups were already known.

Scheme 1. CT Complex TCNQ (1)/TTF (2) Together with Semiquinone Formation Constants K_{SEM} and the Corresponding Redox Potentials of the Components



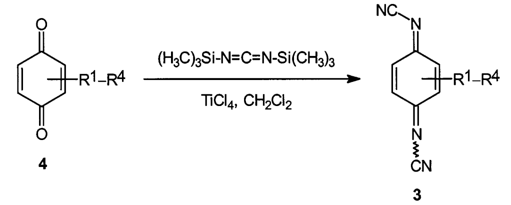
Scheme 2. General Structures for Reversible Two-Step Redox Systems of the Violene Type[a]



$$E_1 - E_2 = 0.059 \lg K_{SEM}\ [V]\ (25\ °C);$$
$$K_{SEM} = [SEM]^2/[OX][RED]$$

[a] RED = reduced form; SEM = semiquinone (radical ion); OX = oxidized form; E_1 and E_2 are redoxpotentials; and K_{SEM} = semiquinone formation constant.

Scheme 3. General Synthesis of DCNQIs (3) from *p*-Quinones (4)

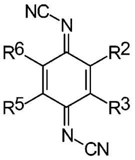


Because 1,4-benzoquinones (**4**) are easily accessible with a great variety of substituents, a one pot procedure was developed according to Scheme 3, which afforded DCNQIs (**3**) in a simple procedure and good yields.[1,19,20]

Because of the wide scope (e.g., applicable to DCNNIs and DCNAIs), this simple transformation advanced to the general accepted method for almost all DCNQI derivatives collected in Tables 1−5 and Scheme 5. The multistep approach, cyanation of *p*-phenylene diamines, proved to be rather cumbersome due to solubility problems with the precursors.[1,19,20]

As well, the potentials E_1 and E_2 and also K_{SEM} of the parent DCNQI match those of TCNQ rather closely.[21] Besides, AM1 calculations of DCNQI and TCNQ predict similar symmetries but lowest unoc-

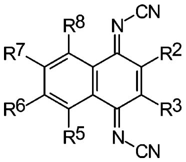
Table 1. DCNQIs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, nBu$_4$N$^+$BF$_4^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})



entry	no.	R^2	R^3	R^5	R^6	E_1	E_2	lg K_{SEM}	ref
1	**5**	H	H	H	H	−0.25	+0.39	10.75	1, 19, 21[a]
2	**6**	Me	H	H	H	−0.31	+0.31	10.54	21
3	**7**	*b*	H	H	H	−0.32	+0.30	10.51	32
4	**8**	Cl	H	H	H	−0.05	+0.49	9.29	21
5	**9**	SMe	H	H	H	−0.63[c,d]	+0.04[c,d]	11.36	41
6	**10**	Me	Me	H	H	−0.38	+0.23	10.32	21, 33
7	**11**	Pr	Pr	H	H	−0.38	+0.23	10.33	33
8	**12**	$-(CH_2)_3-$		H	H	−0.33	+0.31	10.85	33
9	**13**	$-(CH_2)_4-$		H	H	−0.39	+0.22	10.31	33
10	**14**	OMe	OMe	H	H	−0.28	+0.33	10.34	33
11	**15**	Cl	Cl	H	H	−0.05	+0.62	11.38	21, 33
12	**16**	Br	Br	H	H	−0.03	+0.62	11.02	33
13	**17**	$-S-C(CN)_2-S-$		H	H	+0.11	+0.78	11.37[e]	21
14	**18**	Me	H	Me	H	−0.38	+0.21	10.10	1, 21
15	**19**	Me	H	Et	H	−0.38	+0.23	10.30	22
16	**20**	Me	H	^{i}Pr	H	−0.41	+0.20	10.30	22
17	**21**	Pr	H	Pr	H	−0.42	+0.22	10.80	22
18	**22**	*b*	H	Me	H	−0.38	+0.22	10.17	32
19	**23**	*f*	H	*f*	H	−0.55[g]	+0.06[g]	10.33	42, 43
20	**24**	tBu	H	tBu	H	−0.42	+0.16	10.71	1, 21
21	**25**	Ph	H	Ph	H	−0.27	+0.34	10.35	21
22	**26**	Me	H	CF_3	H	−0.14	+0.55	11.60	27
23	**27**	CH_2F	H	CH_2F	H	−0.35[d]	+0.33[d]	11.50	27
24	**28**	CH_2Cl	H	CH_2Cl	H	irr.[d]	+0.35[d]		27
25	**29**	CF_3	H	CF_3	H	+0.06	+0.83	13.10	27
26	**30**	Me	H	OMe	H	−0.40	+0.19	10.10	22
27	**31**	OMe	H	CF_3	H	−0.15	+0.53	11.40	27
28	**32**	Cl	H	Me	H	−0.20	+0.43	10.59	21
29	**33**	Me	H	Br	H	−0.19	+0.42	11.30	22
30	**34**	Me	H	I	H	−0.25	+0.42	11.40	22
31	**35**	Ph	H	Cl	H	−0.13	+0.51	10.90	22
32	**36**	*b*	H	Br	H	−0.20	+0.43	10.68	32
33	**37**	Me	H	SMe	H	−0.62[c,d]	+0.03[c,d]	11.02	41
34	**38**	OMe	H	OMe	H	−0.42	+0.15	9.69	1, 21
35	**39**	Cl	H	OMe	H	−0.19	+0.43	10.50	27
36	**40**	Br	H	OMe	H	−0.20	+0.44	10.90	27
37	**41**	I	H	OMe	H	−0.20	+0.40	10.20	27
38	**42**	SMe	H	OMe	H	−0.60[c,d]	−0.02[c,d]	9.83	41
39	**43**	Cl	H	Cl	H	0.00	+0.65	11.02	19, 21[h]
40	**44**	Cl	H	Br	H	−0.02	+0.63	11.00	22
41	**45**	Cl	H	I	H	+0.01	+0.64	10.70	27
42	**46**	Br	H	Br	H	−0.02	+0.63	10.95	21
43	**47**	Br	H	I	H	+0.02	+0.65	10.70	27
44	**48**	I	H	I	H	(0.00	+0.63	10.70	27
45	**49**	Cl	H	SMe	H	−0.45[c,d]	+0.20[c,d]	11.02	41
46	**50**	SMe	H	SMe	H	−0.55[c,d]	+0.05[c,d]	1.17	41
47	**51**	SPh	H	SPh	H	*i*			44
48	**52**	Me	H	H	Me	−0.37	+0.21	9.71	21
49	**53**	Et	H	H	Et	−0.42	+0.16	10.17	21
50	**54**	Cl	H	H	Cl	−0.12	+0.55	11.42	21
51	**55**	Me	Me	Me	H	−0.38	+0.25	10.78	21
52	**56**	Me	Me	Cl	H	−0.36[g,j]	+0.20[g,j]	9.49	45
53	**57**	Me	Me	Me	Me	−0.39	+0.05	7.42	1, 21
54	**58**	Me	Me	Me	Br	−0.27	+0.26	9.00	46
55	**59**	Me	Me	Cl	Cl	−0.25[g,j]	+0.27[g,j]	8.81	45
56	**60**	Cl	Me	Cl	Me	−0.14	+0.43	9.61	21
57	**61**	Me	Me	Br	Br	−0.24	+0.42	11.20	46
58	**62**	Cl	Me	Cl	Cl	−0.13[g,j]	+0.45[g,j]	9.83	45
59	**63**	OMe	OMe	OMe	OMe	−0.33	+0.22	9.27	1, 21
60	**64**	F	F	F	F	+0.11	+0.79	11.61	21
61	**65**	Cl	Cl	Cl	Cl	+0.13	+0.76	10.83	1, 21
62	**66**	$-S-(CH_2)_2-S-$		$-S-(CH_2)_2-S-$		−0.23	+0.19	7.12	47
63	**67**	$-S-(CH_2)_3-S-$		$-S-(CH_2)_3-S-$		−0.20	+0.22	7.12	47

[a] $E_1 = -0.14$, $E_2 = +0.18$, and MeCN solution 0.5 M in $LiClO_4$ vs calomel electrode. [b] $R = -(CH_2)_{11}-CH_3$. [c] Electrolyte $Bu_4N^+PF_6^-$. [d] In MeCN. [e] Compound **17** additionally shows two irreversible oxidation peaks at +1.08 and +1.28 V. [f] $R = -(CH_2)_3-Ph$. [g] vs glassy carbon electrode. [h] $E_1 = -0.13$, $E_2 = +0.04$, and MeCN solution 0.5 M in $LiClO_4$ vs calomel electrode. [i] Potentials not given. [j] Electrolyte $Bu_4N^+ClO_4^-$.

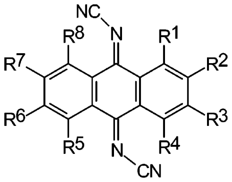
Table 2. DCNNIs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, nBu$_4$N$^+$BF$_4$$^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})



entry	no.	R^2	R^3	R^5	R^6	R^7	E_1	E_2	lg K_{SEM}	ref
64	**68**	H	H	H	H	H	−0.35	+0.19	9.13	1, 21
65	**69**	Me	H	H	H	H	−0.38	+0.10	8.10	21
66	**70**	Cl	H	H	H	H	$-0.34^{a,b}$	$+0.15^{a,b}$	8.31	45
67	**71**	Cl	Cl	H	H	H	−0.11	+0.37	8.14	21, $45^{a,c}$
68	**72**	$-S-(CH_2)_2-S-$		H	H	H	−0.36	+0.05	6.95	47
69	**73**	$-S-(CH_2)_3-S-$		H	H	H	−0.36	+0.02	6.44	47
70	**74**[d]	H	H	OMe	H	H	−0.48	+0.01	8.22	21
71	**75**	H	H	H	$-(CH{=}CH)_2-$		−0.38	+0.11	8.24	21, $48^{b,e,f}$
72	**76**	Me	H	H	$-(CH{=}CH)_2-$		$-0.62^{b,e}$	$-0.17^{b,e}$	7.62	48, 49
73	**77**	OMe	H	H	$-(CH{=}CH)_2-$		$-0.53^{b,e}$	$-0.12^{b,e}$	7.06	48, 49
74	**78**	Cl	H	H	$-(CH{=}CH)_2-$		$-0.55^{b,e}$	$-0.09^{b,e}$	6.27	48
75	**79**	Me	Me	H	$-(CH{=}CH)_2-$		$-0.53^{b,e}$	$-0.17^{b,e}$	6.10	48, 49
76	**80**	Me	Br	H	$-(CH{=}CH)_2-$		$-0.48^{b,e}$	$-0.11^{b,e}$	7.96	48, 49
77	**81**	Cl	Cl	H	$-(CH{=}CH)_2-$		$-0.47^{b,e}$	$-0.06^{b,e}$	7.06	48
78	**82**	Br	Br	H	$-(CH{=}CH)_2-$		$-0.42^{b,e}$	$-0.05^{b,e}$	6.27	48, 49
79	**83**	Me	Me	H	*g*		$-0.45^{b,e}$	$-0.12^{b,e}$	5.59	48

[a] vs glassy carbon electrode. [b] Electrolyte $Bu_4N^+ClO_4^-$. [c] $E_1 = -0.26$, $E_2 = +0.20$. [d] R^8 = OMe. [e] In MeCN. [f] $E_1 = -0.64$, $E_2 = -0.13$. [g] R = $-CH{=}C(OMe)-C(OMe){=}CH-$.

Table 3. DCNAIs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, nBu$_4$N$^+$BF$_4$$^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})



entry	no.	R^1	R^2	R^3	R^4	R^5	E_1	E_2	lg K_{SEM}	ref
80	**84**	H	H	H	H	H	−0.46	−0.11	5.97	1, 21, $50^{a,b}$
81	**85**	Cl	H	H	H	H	−0.62	−0.32	5.08	50^a
82	**86**	H	Me	H	H	H	−0.52	−0.18	5.85	21
83	**87**	H	Et	H	H	H	−0.69	−0.30	6.61	50^a
84	**88**	H	^{t}Bu	H	H	H	*c*			51
85	**89**	H	Cl	H	H	H	−0.62	−0.22	6.78	50^a
86	**90**	$-(CH{=}CH)_2-$		H	H	H	-0.21^d	-0.48^d	4.65	52
87	**91**	OMe	H	H	OMe	H	−0.59	−0.39	3.37	21
88	**92**	Cl	H	H	H	Cl	−0.43	−0.20	3.93	21
89	**93**[e]	Cl	H	H	H	H	−0.59	−0.38	3.56	50^a
90	**94**	H	Me	Me	H	H	−0.55	−0.20	5.93	21
91	**95**	H	$-(CH{=}CH)_2-$		H	H	-0.32^d	-0.62^d	5.17	52
92	**96**[f]	H	$-(CH{=}CH)_2-$		H	H	-0.67^d	-0.43^d	4.13	52

[a] Solvent not given. [b] $E_1 = -0.71$, $E_2 = -0.31$. [c] Potentials not given. [d] Electrolyte $Bu_4N^+ClO_4^-$. [e] R^8 = Cl. [f] $R^6/R^7 = -(CH{=}CH)_2-$.

cupied molecular orbital (LUMO) energies of 0.4 eV lower for the latter (Figure 1).[22]

However, for DCNQI, the atom coefficients of the LUMO π^* orbitals are larger. This may cause higher solvation energies of DCNQI radical anions and may explain the similarity of E_1 for both acceptors.[6] The higher electron density in the end group nitrogen atom may be important for complexation with metal ions in the corresponding radical salts (Section 5).

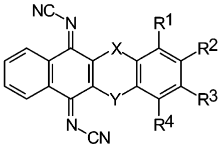
The flexibility of the N−C≡N bond angle is expressed by syn/anti conversions in solution with only ≈10−14 kcal/mol activation energies,[20,23−26] but even then, planarity is conserved.[21] For radical anions from 2,5-DMeO-DCNQI (**38**), the expected smaller energy barrier of 6.8 kcal/mol was determined in dimethylformamide (DMF) at room temperature.[24]

3. *N,N′*-Dicyanoquinone Diimines and Their Redox Properties in Solution

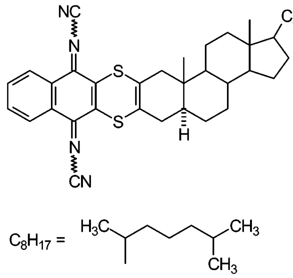
The acceptors in Tables 1−5 are grouped according to the parent quinones from which the *N,N′*-dicyanoimines are derived. Special cases are collected in Scheme 5. The redox potentials E_1 and E_2 (see Scheme 2) were determined vs Ag/AgCl in acetonitrile, either in dichloromethane or in acetonitrile, with only small solvent effects. Therefrom, K_{SEM} was calculated according to Scheme 2.

The general redox equilibrium is given in Scheme 4 together with a typical example for its determination from the cyclovoltammogram. Redox potentials E_2 and E_1 are calculated from the peak potentials by $E_{2pa} + E_{2pc}/2$ and $E_{1pa} + E_{1pc}/2$.

Table 4. DCNHIs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, $nBu_4N^+BF_4^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})



97–112



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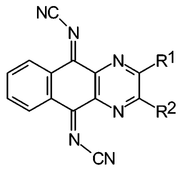
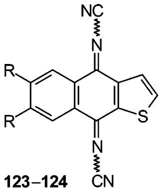


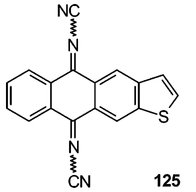
114–122

	R1	R2
114	H	H
115	Ph	Ph
116	2-pyridyl	H
117	3-pyridyl	H
118	4-pyridyl	H
119	2-pyridyl	2-pyridyl
120	3-(*N*-methylpyridinium)	H
121	4-(*N*-methylpyridinium)	H
122	2-(*N*-methylpyridinium)	2-pyridyl



123–124

	R
123	H
124	Cl



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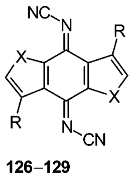
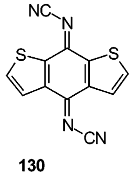


126–129

	X	R
126	O	H
127	S	H
128	S	CH_3
129	S	Br



130

entry	no.	X	Y	R^1	R^2	R^3	E_1	E_2	lg K_{SEM}	ref
93	**97**	O	O	H	H	H	-0.44^a	$+0.07^a$	8.64	37, 39
94	**98**	O	O	Me	H	H	-0.45^a	$+0.02^a$	7.97	39
95	**99**	O	O	OMe	H	H	-0.42^a	-0.04^a	6.44	39
96	**100**	O	O	H	Me	H	-0.45^a	$+0.02^a$	7.97	37, 39
97	**101**	O	O	H	^{t}Bu	H	-0.43^a	-0.03^a	6.78	37, 39
98	**102**	O	O	H	CN	H	-0.38^a	$+0.11^a$	8.31	37, 39
99	**103**	O	O	H	NO_2	H	-0.34^a	$+0.17^a$	8.64	37, 39
100	**104**	O	O	^{t}Bu	H	^{t}Bu	-0.43^a	$+0.02^a$	7.63	37, 39, 53
101	**105**	O	O	H	$-(CH{=}CH)_2-$		-0.44^a	-0.03^a	6.95	39
102	**106**	O	S	H	H	H	-0.42^b	$+0.03^b$	7.63	54, 55
103	**107**	O	S	H	Me	H	-0.43^b	$+0.03^b$	7.79	54
104	**108**	O	S	H	H	Me	-0.44^b	$+0.02^b$	7.79	54
105	**109**	O	S	Me	H	Me	-0.42^b	$(0.00^b$	7.12	54
106	**110**	S	S	H	H	H	-0.36^b	$+0.05^b$	7.01	54, 55
107	**111**	S	S	H	Me	H	-0.34^b	$+0.05^b$	6.61	54
108	**112**	N−CH_3	O	H	H	H	-0.11^a	$+0.51^a$	6.78	56

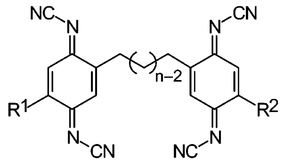
entry	no.	E_1	E_2	lg K_{SEM}	ref
109	**113**	-0.44^c	-0.11^c	5.59	57
110	**114**	$-0.61^{d,e}$	$-0.14^{d,e}$	7.97	40
111	**115**	$-0.62^{d,e}$	$-0.15^{d,e}$	7.97	40
112	**116**	$-0.51^{d,f}$	$+0.02^{d,f}$	8.98	40
113	**117**	$-0.53^{d,f}$	$+0.01^{d,f}$	9.15	40
114	**118**	$-0.50^{d,f}$	$+0.03^{d,f}$	8.98	40
115	**119**	$-0.59^{d,e}$	$-0.11^{d,e}$	8.14	40
116	**120**	$-0.41^{d,f,g}$	$+0.10^{d,f}$	8.64	40
117	**121**	$-0.36^{d,f,g}$	$+0.12^{d,f}$	8.14	40
118	**122**	$-0.45^{d,f,g}$	$+0.09^{d,f}$	9.15	40
119	**123**	$-0.61^{a,e,h}$	$-0.11^{a,e,h}$	8.62	58
120	**124**	$-0.50^{a,e,h}$	$-0.04^{a,e,h}$	7.93	58
121	**125**	$-0.68^{a,e,h}$	$-0.33^{a,e,h}$	6.03	58
122	**126**	-1.00^i	-0.37^i	10.68	25
123	**127**	-0.42^f	$+0.10^f$	8.81	25,[i,k] 59, 60,[f,h,j] 61
124	**128**	-0.60^l	-0.07^l	8.98	61
125	**129**	-0.47^l	$+0.12^l$	10.00	58
126	**130**	-0.42^f	$+0.11^f$	8.98	59

[a] Electrolyte $Bu_4N^+ClO_4^-$. [b] vs glassy carbon electrode. [c] Electrolyte $Bu_4N^+PF_6^-$; the measurements were performed in a single-compartment cell with a disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. [d] V vs SCE, 0.1 mol dm^{-3} Et_4NClO_4, Pt electrode. [e] In MeCN. [f] In DMF. [g] These compounds form stable zwitterionic radicals with two additional potentials: 120, $E_{ox} = +0.10$, $E_{red} = -1.22$; 121, $E_{ox} = +0.12$, $E_{red} = -1.01$; 122, $E_{ox} = +0.09$, $E_{red} = -1.33$. [h] vs SCE. [i] vs Fc/Fc$^+$, 0.1 M $^nBu_4NBF_4$ solution in benzonitrile. [j] $E_1 = -0.42$, $E_2 = +0.13$. [k] $E_1 = -0.99$, $E_2 = -0.43$. [l] In benzonitrile.

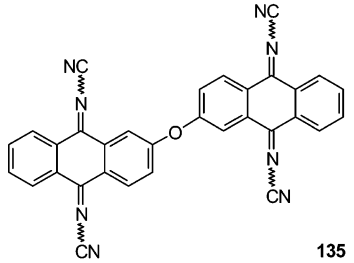
Starting with the parent DCNQI (**5**), up to four substituents were introduced with a great individual variety. In all cases with known Hammett σ-constants, clear-cut correlations with E_1 and E_2 were obtained especially for the most important 2,5-disubstituted DCNQIs by applying $(\sigma_m + \sigma_p)/2$,[27,28] according to the same correlation for 1,4-benzoquinones,[21] which are somewhat more sensitive to substituent effects.

The long alkyl chains in **22** and **36** (entries 18 and 32) were prepared for Langmuir–Blodgett investigations with films on a water surface. However, the badly reproducible results are partly bothered by hydrolysis of the cyanoimine groups.[29,30] From the

Table 5. Tethered DCNQIs together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, $nBu_4N^+BF_4^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})



	n	a	b	c	d	e
		R1 / R2				
131	3	H/H	CH_3/CH_3	Br/Br	H/CH_3	Br/CH_3
132	4	H/H	CH_3/CH_3	Br/Br	-	-
133	5	H/H	CH_3/CH_3	Br/Br	-	-
134	6	H/H	CH_3/CH_3	Br/Br	-	-



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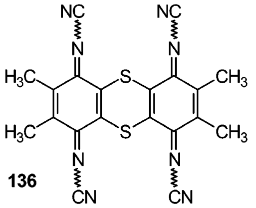

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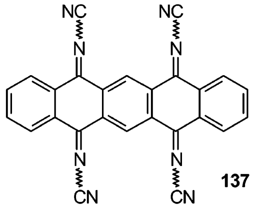


137

entry	no.	E_1[a]	E_2[a]	lg K_{SEM}	ref
127	**131a**	−0.33	+0.33	11.19	31, 32
128	**131b**	−0.39	+0.25	10.85	31, 32
129	**131c**	−0.19	+0.47	11.19	31, 32
130	**131d**	−0.32	+0.33	11.02	31
131	**131e**	−0.19	+0.47	11.19	31
132	**132a**	−0.32	+0.32	10.85	31, 32
133	**132b**	−0.39	+0.24	10.68	31, 32
134	**132c**	−0.17	+0.45	10.51	31, 32
135	**133a**	−0.32	+0.31	10.68	31, 32
136	**133b**	−0.40	+0.22	10.51	31, 32
137	**133c**	+0.45	−0.18	10.68	31, 32
138	**134a**	−0.30	+0.32	10.51	31, 32
139	**134b**	−0.38	+0.23	10.34	31, 32
140	**134c**	−0.18	+0.45	10.68	31, 32
141	**135**	−0.23[b]	−0.54[b]	5.25	62
142	**136**	*c*			62,[d] 63
143	**137**[e]	−0.15[b,f,g]	+0.10[b,f]	4.24	62, 64

[a] Average potentials from the two DCNQI moieties. [b] SCE vs Pt, electrolyte $Bu_4N^+ClO_4^-$. [c] Potentials not available. [d] Potentials not given. [e] CT complex; see chapter 4.1. [f] In DMF. [g] Further potentials $E_1 = -1.11$, $E_2 = -0.91$.

tethered DCNQIs **131**–**134** (Table 5),[31,32] special effects were expected in the crystal lattices of their radical anion salts; however, they were not observed.

According to ^1H NMR data in solution, all 2,5-disubstituted DCNQIs **18**–**51**, entries 14–47, exist in their anti configuration,[1,19,20] whereas two substituents in 2,3-positions (**10**, **11**, and **13**–**17**, entries 6, 7, and 9–13) force the cyano groups into a syn arrangement;[33] only in the case of $R^2/R^3 = -(CH_2)_3-$ (**12**, entry 8), 20% of the anti configuration is observed.[33]

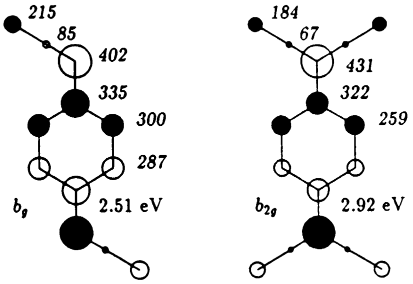
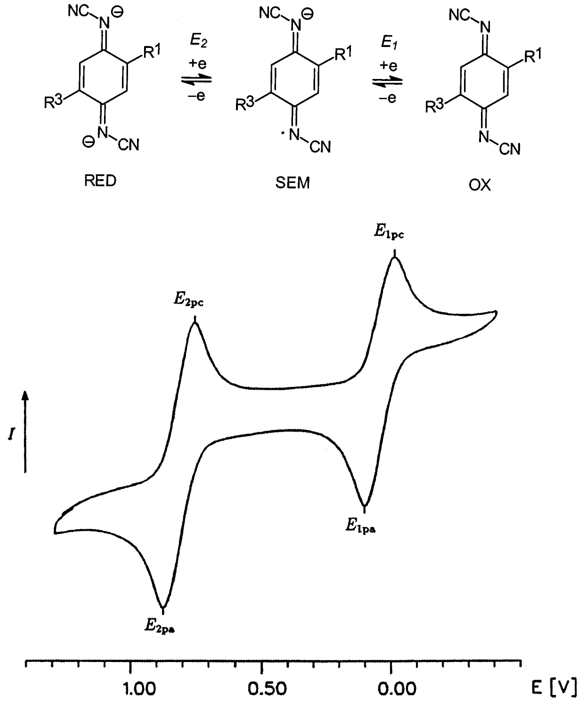


Figure 1. LUMO energies and symmetries of DCNQI (left) and TCNQ (right) from AM1 calculations. For comparison, the p_z coefficients are given in units of 10^{-3}. Reprinted with permission from ref 6. Copyright 1991 Wiley-VCH.

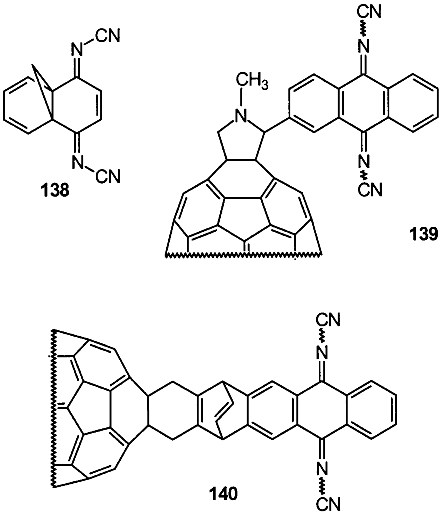
Scheme 4.[196] General Redox Equation for DCNQIs, Exemplified by the Two-Step Cyclovoltammogram for R^2, R^5 = CF_3 (ref 29, cf. Table 1).



The first reduction potentials E_2 of all DCNQIs in Table 1 range from +0.83 mV in **29** (entry 25) to +0.15 mV in **38** (entry 34) indicating a broad range of acceptor strengths. Interestingly, these limits are set by the most important 2,5-disubstituted DCNQIs. LUMO orbital energies from AM1 calculations of various 2,5-disubstituted DCNQIs correlate very well with the corresponding reduction potentials E_2.[27,34–36] In DCNNIs, **68**–**83** (Table 2) and even more in DCNAIs **84**–**96** (Table 3), the range of E_1 and E_2 moves to more negative potentials and the difference becomes smaller, i.e., the thermodynamic stability of the anion radicals, expressed by K_{SEM}, is diminished. Besides, the effect of substituents on the potentials is less pronounced. All of these features are in line with those of the corresponding quinones.

The DCNQIs **97**–**112** (Table 4, entries 93–108) were designed for donor effects from the heterocyclic residues.[37–39] They are accompanied by other heterocyclic DCNQI type acceptors (**113**–**130**, entries 109–

Scheme 5. Special Derivatives of DCNQI Type Acceptors[a]



Nr.	E_1	E_2	lg K_{SEM}	Ref.
138	–[a]	–	–	65
139	−0.98	−0.32	11.19	66,67
140	−1.13	−0.78	5.93	68

[a] Potentials not given. [b] Further reduction potentials; −0.64, −1.07, and −1.78, are due to the fullerene group; all potentials in V vs SCE; GCE as working electrode, toluene:MeCN (5:1), 0.1 M $Bu_4N^+ClO_4^-$. [c] Further reduction potentials; −1.52, −2.09, and −2.48 are due to the fullerene group; *E* values were measured as the average of the anodic and cathodic peak potentials vs the potential for the redox couple of internally added Fc/Fc$^+$.

126). Compounds **120**−**122** (entries 116−118) carrying cationic substituents, i.e., the corresponding radicals, are zwitterions.[40]

Table 5 informs us about tethered DCNQI type acceptors. In examples **131**−**137**, the tether between two DCNQI moieties varies from long, flexible, and insulating (**131a**−**134c**, entries 127−140) over short and flexible (**135**, entry 141) to rigid with weak and strong π-interactions, especially in the radical anion state (**136** and **137**, entries 142 and 143, respectively). In Scheme 5, a variety of DCNQI derived acceptors are collected, which are difficult to categorize.

4. CT Complexes from DCNQI Type Acceptors

Tables 6−8 demonstrate that most of the CT complexes employ DCNQI as acceptors (Table 6 and Scheme 6), whereas only three CT complexes with DCNNIs have been reported (Table 7). In most cases, powder conductivities ranging from 10^{-1} to 10^{-3} S cm^{-1} have been observed pointing to segregated stacks in these solid materials. This assumption was substantiated in quite a few cases by X-ray analysis of single crystals, for which some examples are presented below. Only arrangements with mixed stacks were found (e.g., TTF CT complexes of **6**, **8**, **18**, **19**, **21**, and **55**, entries 2, 3, 11, 12, 15, and 35).[69,70] Out of these, 2,5-DMe-DCNQI (**18**)/TTF (**2**) undergoes a pressure-induced neutral−ionic transition around 1 GPa at room temperature[71] with electron molecular vibration coupling.[72] As already known from CT complexes with TCNQ,[73] segregated stacks of acceptors and donors provoke conductivity, a black color of the solid material, and a uniform, unstructured IR absorption with only a weak peak for the CN frequence. Mixed stack complexes, however, are insulators (σ < 10^{-7} S cm^{-1}) with light colors and normally resolved IR spectra.

4.1. CT Complexes with TTF-Derived Donors

Most of the CT complexes contain TTF and its derivatives as donors, including the corresponding selenium system (Table 6, entries 44 and 45) and the dimeric tellurium derivative (TTFTe)$_2$ (Table 6, entry 46). Because DCNQIs had been developed as substitutes for TCNQ, a comprehensive comparison between the classic TCNQ/TTF (**1**/**2**, $\sigma \approx 500$ S cm^{-1}; Scheme 1 and Figures 1 and 2) and DCNQI/TTF·2H$_2$O (**5**/**2**, ≈ 10 S cm^{-1}; Table 6, entry 1 and Figure 2) was performed.[74]

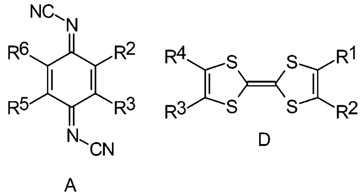
The latter complex could be obtained only from incompletely dried solvents. Apparently, the water molecules occupy the space of the missing second CN group present in **1**. Whereas in **1**/**2** the segregated stacks are arranged in sheets, in **5**/**2**, they are ordered chessboard-like. Water is not found in CT complexes of substituted DCNQIs.

Typical structural properties of the conducting CT complexes in Tables 6−8 are also demonstrated by DCNNI/TTF (Table 7, entry 47).[2,75] The structure (Figure 3) reveals still a different arrangement of the stacks, namely, sheets of ···A−D−D···A. Figure 3 demonstrates the temperature-dependent conductivity,[75] the pattern being typical for most of the CT complexes under discussion. The conductivity of 20−30 S cm^{-1} at 300 K increases slightly down to ≈130 K (metal-like semiconductor) with a smooth transition into a semiconducting state (Figure 3). With the exception of temperatures <70 K, data obtained from the conventional four point dc measurements and the contactless ac microwave measurements[76,77] match each other very closely. From electron spin resonance (ESR) and NMR measurements, a CT of $\rho \approx 0.5$ was derived.[75]

The electronic properties may differ in the individual CT complexes. For 2,5-DBr-DCNQI/[TM-TSF]$_2$ (entry 45),[78] it was found that in this one-dimensional conductor hopping electrons of the TM-TSF are mainly responsible for conduction, whereas the susceptibility is dominated by the 2,5-DBr-DCNQI anion radicals.[78]

From Tables 6−8, no correlations can be deduced between conductivities and (i) the nature and the number of the DCNQI substituents and (ii) the substituent pattern vs TTF: 2,3-substitution (entries 4−10), 2,5-substitution (entries 11−33 and the tethered DCNQIs in Table 8), and the same substituent pattern 2,3 vs different substituted TTFs (entries 4−10 vs 38−44). A better understanding would need crystal structures and single-crystal conductivities of all of these CT complexes. Such data could serve as a touchstone for three-dimensional Hartree−Fock crystal orbital calculations offered to be of crucial importance for designing organic crystals with specific physical properties. This method has been applied so far to TCNQ/TTF (**1**/**2**), DCNQI/TTF (**2**/**5**), and 2,5-DMe-DCNQI/TTF.[79] In connection with Table

Table 6. CT Complexes from DCNQIs with TTF Derivatives[a]



entry	no.	R^2	R^3	R^5	R^6	D	A/D[b]	σ (S cm^{-1})	ref
1	**5**	H	H	H	H	TTF	1/1	9×10^{-2} (p)	19, 69, 74[c], 80, 81
2	**6**	Me	H	H	H	TTF	1/1	5×10^{-7} (p)	69,[d] 80
3	**8**	Cl	H	H	H	TTF	1/1	3×10^{-7} (p)	69,[d] 80
4	**10**	Me	Me	H	H	TTF	2/3	3×10^{-1} (p)	33, 69
5	**11**	Pr	Pr	H	H	TTF	2/3	2×10^{-3} (p)	69
6	**12**	$-(CH_2)_3-$		H	H	TTF	1/1	3×10^{-3} (p)	33
7	**13**	$-(CH_2)_4-$		H	H	TTF	1/1	2×10^{-3} (p)	33[d,e]
8	**14**	OMe	OMe	H	H	TTF	1/1	$\leq 10^{-8}$ (p)	33
9	**15**	Cl	Cl	H	H	TTF	1/1	5×10^{-1} (p)	33, 69
10	**16**	Br	Br	H	H	TTF	2/3	2×10^{-3} (p)	33
11	**18**	Me	H	Me	H	TTF	1/1	$<10^{-7}$ (p)	69,[d] 70,[d,f] 80, 81
12	**19**	Me	H	Et	H	TTF	1/1	$<10^{-7}$ (p)	69,[d] 80
13	**20**	Me	H	^{i}Pr	H	TTF	1/1	$<10^{-7}$ (p)	69, 80
14	**20**	Me	H	^{i}Pr	H	TTF	2/3	1×10^{-2} (p)	69, 80
15	**21**	Pr	H	Pr	H	TTF	1/1	$<10^{-7}$ (p)	69,[d] 80
16	**26**	Me	H	CF_3	H	TTF	1/1	1×10^{-2} (p)	82
17	**30**	Me	H	OMe	H	TTF	1/1	2×10^{-2} (p)	69, 80, 81
18	**31**	OMe	H	CF_3	H	TTF	1/1	1×10^{-3} (p)	82
19	**32**	Me	H	Cl	H	TTF	1/1	2×10^{-1} (p)	69, 80[g]
20	**33**	Me	H	Br	H	TTF	1/1	6×10^{-1} (p)	69, 80, 81[g]
21	**34**	Me	H	I	H	TTF	1/1	3×10^{-2} (p)	69, 80, 81[g]
22	**35**	Ph	H	Cl	H	TTF	1/1	3×10^{-4} (p)	69
23	**38**	OMe	H	OMe	H	TTF	1/1	9×10^{-2} (p)	69, 80
24	**39**	Cl	H	OMe	H	TTF	1/1	3×10^{-2} (p)	82
25	**40**	Br	H	OMe	H	TTF	1/1	3×10^{-2} (p)	82
26	**41**	I	H	OMe	H	TTF	1/1	2×10^{-2} (p)	82
27	**43**	Cl	H	Cl	H	TTF	1/1	7×10^{-2} (p)	19, 69, 80
28	**44**	Cl	H	Br	H	TTF	1/1	5×10^{-2} (p)	69, 80
29	**45**	Cl	H	I	H	TTF	1/1	1×10^{-3} (p)	82
30	**46**	Br	H	Br	H	TTF	1/1	5×10^{-3} (p)	69, 80
31	**47**	Br	H	I	H	TTF	1/1	2×10^{-2} (p)	82
32	**48**	I	H	I	H	TTF	1/1	2×10^{-3} (p)	82
33	**50**	SMe	H	SMe	H	TTF	1/1	400 (s)	83[h]
34	**54**	Cl	H	H	Cl	TTF	1/1	2×10^{-6} (p)	69
35	**55**	Me	Me	Me	H	TTF	1/1	$\leq 10^{-7}$ (p)	69
36	**59**	Me	Me	Cl	Cl	TTF	2/3	$<10^{-6}$ (p)	45
37	**62**	Me	Cl	Cl	Cl	TTF	1/1	$<10^{-6}$ (p)	45
38	**12**	$-(CH_2)_3-$		H	H	TM-TTF	1/1	$\leq 10^{-8}$ (p)	33
39	**15**	Cl	Cl	H	H	TM-TTF	2/3	4×10^{-2} (p)	33
40	**16**	Br	Br	H	H	TM-TTF	1/1	2×10^{-2} (p)	33
41	**15**	Cl	Cl	H	H	DB-TTF	1/1	1×10^{-3} (p)	33
42	**16**	Br	Br	H	H	DB-TTF	1/1	8×10^{-3} (p)	33
43	**15**	Cl	Cl	h	H	BEDT-TTF	1/1	3×10^{-2} (p)	33
44	**16**	Br	Br	H	H	TM-TSF	2/3	8×10^{-3} (p)	33
45	**46**	Br	H	Br	H	TM-TSF	1/2	3×10^{-2} (p)	78,[i] 84[i]
46	**5**	H	H	H	H	$(TTFTe)_2$	*j*	*k*	85

[a] TM-TTF, tetramethyl-TTF; DB-TTF, dibenzo-TTF; BEDT-TTF, bis(ethanedithio)-TTF; TM-TSF, tetramethyltetraselenofulvalene; (p) S cm^{-1} or (s) S cm^{-1}, powder or single crystal conductivity. [b] Stoichiometry acceptor/donor. [c] Space group of 5/2·$2H_2O$: $P2_1/c$. [d] Mixed stacks. [e] Space group: $P1$. [f] Space group: $P2_1/c$. [g] Space group: $P2_1/n$. [h] Space group: $P\bar{1}$. [i] Contactless microwave method. [j] Stoichiometry not given. [k] This CT complex is an insulator; space group: $P\bar{1}$.

8, the CT complex of **137**/TTF [σ = 6 S cm^{-1} (p)][64] should be mentioned here.

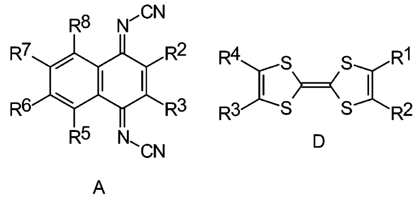
4.2. CT Complexes with Various Donors Except TTF Derivatives

Aromatic diamines constitute interesting donors (Scheme 6). Actually, CT complexes **141** and **142** were the first to be reported.[19] The neutral complex of 2-chloro-5-methyl-1,4-phenylene-diamine (**143**) and 2,5-DMe-DCNQI (**18**) changes continuously to an ionic state on lowering the temperature. This process is preceded by a dimerization of the partners.[86,87] These effects have been studied by applying the extended Hubbard model.[88]

5. Anion Radical Salts Derived from DCNQI Type Acceptors

The most important conducting materials are obtained from partly reduced DCNQIs with monovalent metallic cations and to a lesser extent with organic cations. The outstanding properties of nu-

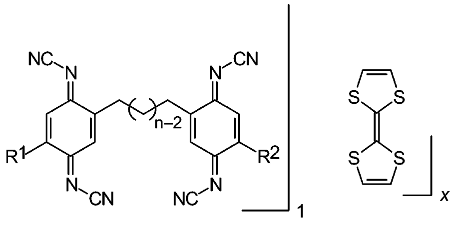
Table 7. CT Complexes from DCNNIs with TTF Derivatives



entry	no.	R^2	R^3	D	A/D	σ (S cm^{-1})	ref
46	**68**	H	H	TTF	1/1	25 (s)	2,[a] 75[a]
47	**70**	Cl	H	TTF	1/2	$<10^{-6}$ (p)	45
48	**71**	Cl	Cl	TTF	1/2	6×10^{-4} (p)	45

[a] Space group: C2/*c*.

Table 8. CT Complexes from Tethered DCNQI Derivatives with TTF Derivatives



	n	R^1 / R^2 a	R^1 / R^2 c
131	3	H/H	Br/Br
132	4	H/H	Br/Br
133	5	H/H	Br/Br
134	6	H/H	Br/Br

entry	DCNQI[a]	*x*	σ (S cm^{-1})[b]	ref
49	**131a**	2.0	8×10^{-3}	31, 32
50	**132a**	2.8	4×10^{-2}	31, 32
51	**133a**	2.5	8×10^{-3}	31, 32
52	**134a**	1.9	1×10^{-4}	31, 32
53	**131c**	2.0	1×10^{-2}	31, 32
54	**132c**	2.0	3×10^{-4}	31, 32
55	**133c**	2.2	4×10^{-5}	31, 32
56	**134c**	2.0	5×10^{-5}	31, 32

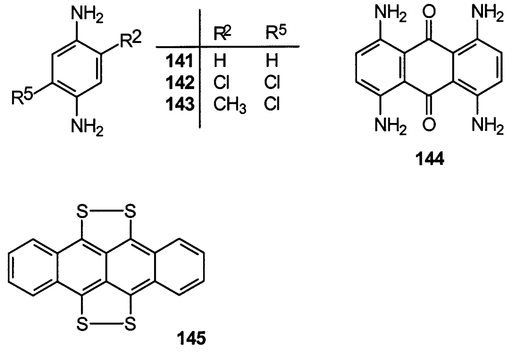
[a] Cf. Table 5. [b] Powder conductivity.

merous DCNQI–Cu^{1+} salts deserve special treatment.

5.1. DCNQI Type Anion Radical Salts with Monovalent Cations Except Copper

In Table 9, so far, published anion radical salts of the general composition (DCNQI type)$_2$$M^+$ are collected. A different stoichiometry is rarely observed. The cations comprise Li^+, Na^+, K^+, NH_4^+, Tl^+, and Ag^+ (for Cu^+, see section 5.2). These salts are prepared by either the classical electrochemical reduction of the acceptor in the presence of the appropriate cation, where often single crystals are obtained, or the reaction of solutions of DCNQIs and the metal iodides, which rapidly yields microcrystalline dark precipitates. Slow diffusion of solutions of the two components into one another affords single crystals as well. The most convenient way for preparing single crystals of DCNQI type anion radical salts consists of immersing a metal wire into a solution of the acceptor. Silver works well,[91] but with copper, it becomes the method of choice (vide infra). As far as checked, all of these routes lead to products of the same composition and structure.

Scheme 6. CT Complexes of DCNQI Derivatives with Non-TTF Donors



	R^2	R^5
141	H	H
142	Cl	Cl
143	CH_3	Cl

144

145

DCNQI[a]	D	σ	Ref.
5	**141**	1.7×10^{-6} (p)	19
43	**141**	4.9×10^{-5} (p)	19
43	**142**	4.1×10^{-5} (p)	19
18	**143**	–[b]	86,87,89
5	**144**	7.0×10^{-3} (p)	90
71	**144**	4.2×10^{-3} (p)[c]	90
66	**145**	2×10^{-2} (p)	47

[a] Cf. Table 1. [b] Space group: *P*1, mixed stacks. [c] Temperature dependence of the conductivity could not be attained, and σ was measured at 304 K.

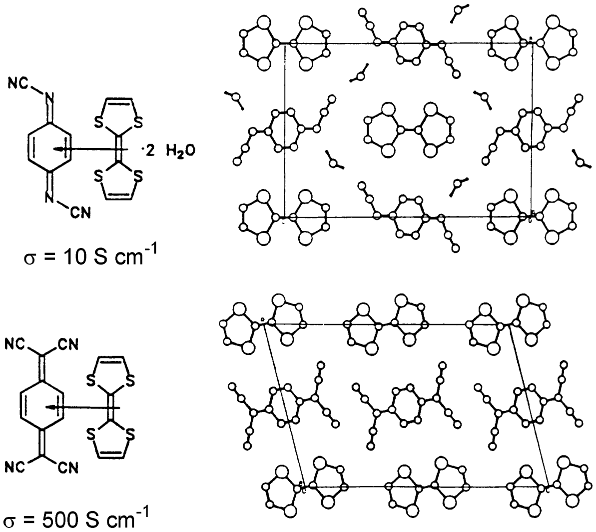


Figure 2. Comparison of the crystal structures by the *b*/*c* projection: TCNQ/TTF (**1/2**; lower), space group $P2_1/_c$; DCNQI/TTF·2 H_2O (**5/2**; upper), space group $P2_1/_c$. Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

In all, the salts of Table 9 acceptors are derived from the parent DCNQI, which may be substituted by various numbers and types of substituents. As can be judged from Table 9 (entries 1–12, 14–17, and 19–38), 2,5-disubstituted DCNQIs constitute by far the most valuable acceptors, since all of the salts derived therefrom display both the same stoichiometry of acceptor:M^+ = 2:1 and the closely related space groups $I4_1/a$ [Li^+, Ag^+, and Cu^+ (see below)], *C*2/*c* (Na^+), and *P*4/*n* (K^+, NH_4^+, Rb^+, and Tl^+) (exception: entry 39, different stoichiometry and space group). These similarities allow us to compare

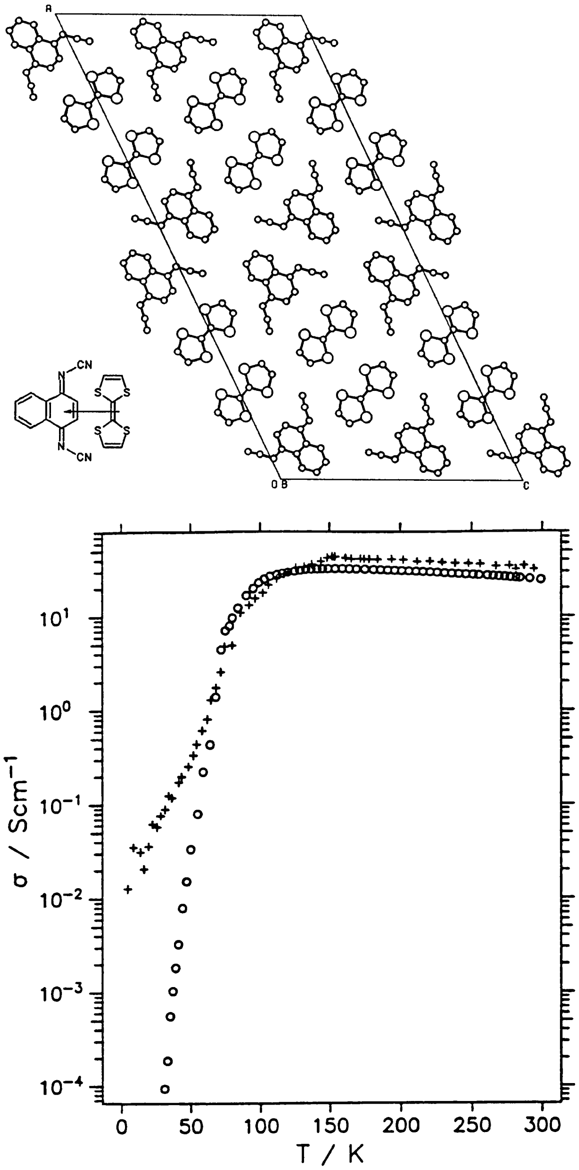


Figure 3. Top: *a*/*c* projection of the crystal structure. Bottom: Temperature dependence of the electrical conductivity of DCNQI/TTF: crosses, ac conductivity at 10.3 GHz; open circles, corrected dc data. Reprinted with permission from ref 75. Copyright 1989 Verlag Z. Naturforsch.

the effect of various metal ions on a given acceptor as well as the effect of differently substituted acceptors on a given metal ion with respect to conductivities and other physical properties.

In the thin black needles of these anion radical salts, the metal ions are arranged like a string of pearls. Each metal ion is surrounded by four DCNQI ligands whereby four stacks of ligands are produced (Figure 4).

A cross-section of these needles reveals a pattern according to Figure 4 demonstrating the bridging function of the DCNQI moieties between the columns of metal ions. The circles in Figure 4 stand for the four tubes of free space into which the 2- and 5-substituents of the acceptor ligands can be incorporated. This open space is missing in the crystal lattice of TCNQ anion radical salts, e.g., TCNQ-Na$^+$ (stoichiometry 1:1!).[7,105]

Although in [2,5-DMe-DCNQI]$_2$Tl (space group *P*4/*n*, Table 9, entry 27) the packing pattern approaches that of Figure 4, the Tl$^+$ ion is coordinated to eight cyano groups in a slightly distorted cubic arrangement.[8,100] In agreement with their crystal structures, all of these anion radical salts are one-dimensional metal-like semiconductors with single-crystal conductivities ranging from 50 to 300 S cm^{-1} at room temperature (Table 9, entries 27 and 1 and 2). The temperature dependence reveals an activation energy of $E \approx 30-70$ meV[6,106] with only slight changing conductivity down to ≈150 K. Typical temperature/conductivity correlations are presented in Figure 5.[102]

So far, there seems to exist only one exception. [2,5-DCl-DCNQI]$_2$Ag shows metallic conductivity down to ca. 100 K, after which a broad transition into the semiconducting state occurs.[107] This salt, therefore, bridges the gap to the M→I (metal→insulator) group of DCNQI copper salts (see below).

The rather special bis-DCNQI derivative **137** afforded not only alkali metal salts but also salts with organic cations. Interestingly, the stoichiometry 1:1 is preserved for all examples[64] (Table 10), which corresponds to the stoichiometry of the usual DCNQI salts.

5.2. DCNQI Type Anion Radical Copper Salts[109]

5.2.1. General Properties

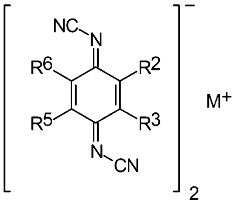
In Table 11 (entries 6−25) are collected salts of the composition [2,5-X,Y-DCNQI]$_2$Cu.[110] They all belong to the space group *I*4$_1$/*a* and display various unique properties, especially metallic conductivities. Besides high conductivities along the stacks of 100−1000 S cm^{-1}, perpendicular conductivities of 1/10 to 1/100 are still observed.[35,111] This latter conductivity must be due to the copper ions, which may oscillate between Cu^{1+} and Cu^{2+}. Thus, an average charge of +1.3 (···Cu$^+$, Cu$^+$, and Cu^{2+}···) has been ascribed to the copper ions[112−114] (cf. section 5.5, Photoelectron Spectroscopy).

The 2:1 stoichiometry is bound to copper salts from 2,5-disubstituted DCNQIs. Other substituent patterns prefer different stoichiometries: 1:1 (entries 1, 2, 5, 9, 27, 28, 32, and 33), 1.33:1 (entry 3), and 1.5:1 (entry 4, 8, 10, and 30), all of unknown crystal structure. Expectedly, salts with a 1:1 stoichiometry are insulators (entries 2 and 28). However, the exceptions [entry 1, $\sigma = 2 \times 10^{-2}$ S cm^{-1} (p), and entry 27, $\sigma = 4 \times 10^{-3}$ S cm^{-1} (p)] are as difficult to explain as the state of an insulator for the 1.5:1 stoichiometry in entry 4.[91] Small deviations from the exact 1:1 stoichiometry may be screened by the accuracy of the elemental analysis. Again, the structural basis for the good conductivity of the reported DCNNI/Cu salts is not known.[91]

5.2.2. Anion Radical Copper Salts Derived from DCNNI, DCNAI, and Heterocyclic Derivatives (DCNHI)

A comparatively small number of these salts have been published (Tables 12 and 13), emphasizing the key positions of 2,5-X,Y-DCNQIs as acceptors for the special properties of the copper salts. Accordingly, the stoichiometry acceptor:Cu = 2:1 is only seldom found

Table 9. Anion Radical Salts from DCNQIs and Monovalent Metallic Cations (Including NH_4^+, Excluding Cu^+) of the General Stoichiometry 2:1[a]



entry	M^+	DCNQI[b] no.	R^1	R^2	R^3	R^4	σ (S cm^{-1})	ref
1	Li^+	**18**	Me	H	Me	H	300 (s)	80, 82,[d] 92,[c] 93
2	Li^+	**32**	Me	H	Cl	H	300 (s)	82,[e] 92,[c] 93, 94
3	Li^+	**33**	Me	H	Br	H	1×10^{-1} (p)	82,[c] 93
4	Li^+	**34**	Me	H	I	H	7×10^{-2} (p)	82,[c] 93
5	Li^+	**38**	OMe	H	OMe	H	200 (s)[f]	22,[c,e] 82,[c,d] 94, 95[c]
6	Li^+	**46**	Br	H	Br	H		96
7	Na^+	**18**	Me	H	Me	H	60−130 (s)	82,[d] 92,[g] 93, 97, 98[h]
8	Na^+	**30**	Me	H	OMe	H	3×10^{-3} (p)	82
9	Na^+	**32**	Me	H	Cl	H	2×10^{-2} (p)	93
10	Na^+	**33**	Me	H	Br	H	1×10^{-3} (p)	93
11	Na^+	**34**	Me	H	I	H	1×10^{-1} (p)	93
12	Na^+	**38**	OMe	H	OMe	H	100 (s)	82,[d,i] 93, 95
13	Na^+ [j]	**66**	$-S-(CH_2)_2-S-$		$-S-(CH_2)_2-S-$		4×10^{-8} (p)	47
14	K^+	**18**	Me	H	Me	H	100 (s)	82,[d] 92,[k] 93
15	K^+	**34**	Me	H	I	H	7×10^{-2} (p)	93
16	K^+	**19**	Me	H	Et	H	1×10^{-1} (p)	93
17	K^+	**38**	OMe	H	OMe	H	2×10^{-2} (p)	82
18	K^+[j]	**66**	$-S-(CH_2)_2-S-$		$-S-(CH_2)_2-S-$		4×10^{-6} (p)	47
19	NH_4^+	**18**	Me	H	Me	H	60 (s)	82,[k] 93−95
20	NH_4^+	**32**	Me	H	Cl	H	70 (s)	92,[k] 94
21	NH_4^+	**33**	Me	H	Br	H	2×10^{-2} (p)	93
22	NH_4^+	**34**	Me	H	I	H	4×10^{-2} (p)	93
23	Rb^+	**18**	Me	H	Me	H	80 (s)	82,[d,k] 93, 97
24	Rb^+	**30**	Me	H	OMe	H	3×10^{-3} (p)	82[k]
25	Rb^+	**38**	OMe	H	OMe	H	1×10^{-4} (p)	82[k]
26	Cs^+	**18**	Me	H	Me	H		99[l]
27	Tl^+	**18**	Me	H	Me	H	50 (s)	93, 100[d,k]
28	Tl^+	**33**	Me	H	Br	H	2×10^{-2} (p)	97
29	Tl^+	**34**	Me	H	I	H	4×10^{-2} (p)	97
30	Ag^+	**18**	Me	H	Me	H	100 (s)	80[d], 92,[c] 93, 98,[h] 101
31	Ag^+	**32**	Me	H	Cl	H	100 (s)	80,[d] 93,[c] 95
32	Ag^+	**33**	Me	H	Br	H	100 (s)	80,[d] 93[c]
33	Ag^+	**34**	Me	H	I	H	20 (s)	93,[c,d] 102
34	Ag^+	**43**	Cl	H	Cl	H	2×10^{-2} (p)	93
35	Ag^+	**44**	Cl	H	Br	H	2×10^{-2} (p)	93
36	Ag^+	**46**	Br	H	Br	H	1×10^{-2} (p)	93
37	Ag^+	**47**	Br	H	I	H	6×10^{-3} (p)	82
38	Ag^+	**48**	I	H	I	H		103
39	Ag^+ [m]	**50**	SMe	H	SMe	H	100 (s)	41[n]

[a] Crystal structures of space groups $I4_1/a$ or closely related structures. (p) S cm^{-1} and (s) S cm^{-1} = powder or single-crystal conductivities at room temperature. All salts are metal-like semiconductors. [b] Cf. Table 1. [c] Space group: I_1/a. [d] Temperature-dependent conductivity given. [e] Contains 1.4 H_2O. [f] For nonohmic conductivity, see ref 104. [g] Space group: $C2/c$. [h] Temperature dependence of the polarized reflectance spectra given. [i] Space group: $I2/a$. [j] Stoichiometry 1/1. [k] Space group: $P4/n$. [l] Prepared in situ, usual technics yield solutions only.[82] [m] Stoichiometry 1/1.2. [n] Space group: $Pban$.

in the examples of Tables 12 and 13 and also for the tethered DCNQIs in Table 14.

5.2.3. Specific Properties of [2,5-DMe-DCNQI]$_2$Cu[121]

5.2.3.1. Temperature Dependence of Conductivity. Increasing metallic conductivities are observed on lowering the temperature in all cases. However, only one group (M) stays metallic down to the lowest temperatures, whereas a second group (M→I) shows a sharp phase transition into a semiconducting or insulating state at ca. 200−170 K (Figure 6).[34] These differences have been analyzed as a subtle balance between the size and the electronic properties of the substituents;[34] thereby, the very first example published, [2,5-DMe-DCNQI]$_2$Cu,[3] is characterized as a borderline case: The rather small methyl groups should allow a phase transition, which is counteracted by their acceptor qualities, thus stabilizing the crucial coordination at the copper ion (α = 124.8°) as found for different compounds already (cf. Figure 10).[35]

Already, the left side of Figure 6 documents the special position of [2,5-DMe-DCNQI]$_2$Cu starting with the highest conductivity of 1000 S cm^{-1} at ambient temperature and approaching 500000 S cm^{-1} at ca. 10 K.[3] This conductivity corresponds to that of copper metal when based on the number of mobil electrons per unit volume and is the highest found for an organic conductor so far.

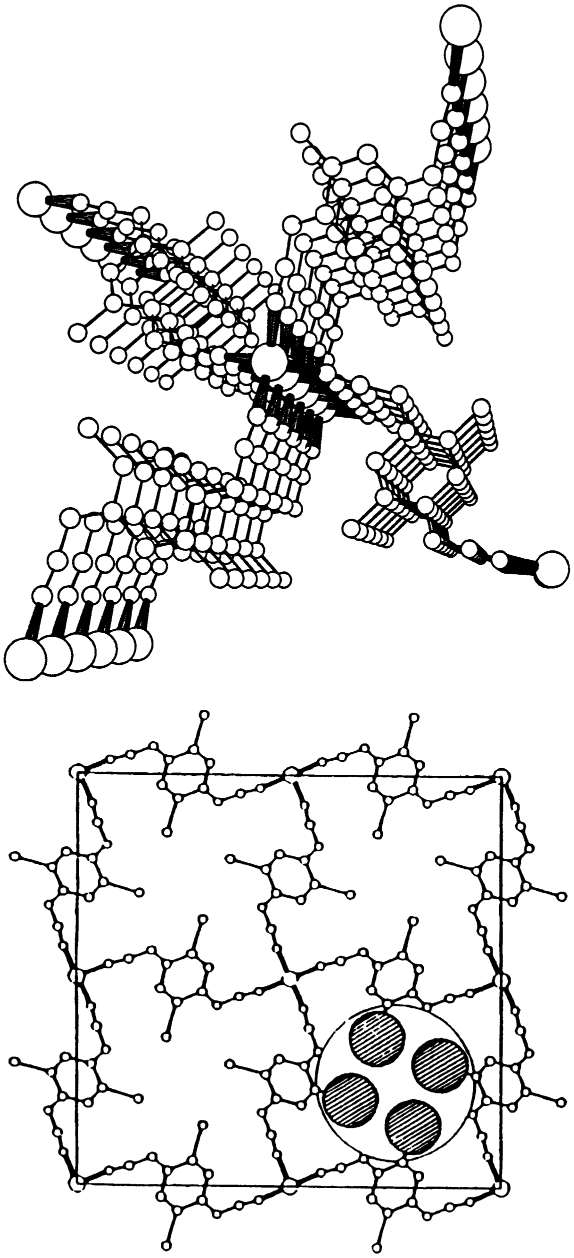


Figure 4. Crystal lattice of $[R^1,R^3\text{-DCNQI}]_2Cu$, space group $I4_1/a$. Top: View along one chain of copper ions, surrounded by four stacks of ligands (c-axis). Bottom: ab-plane. Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

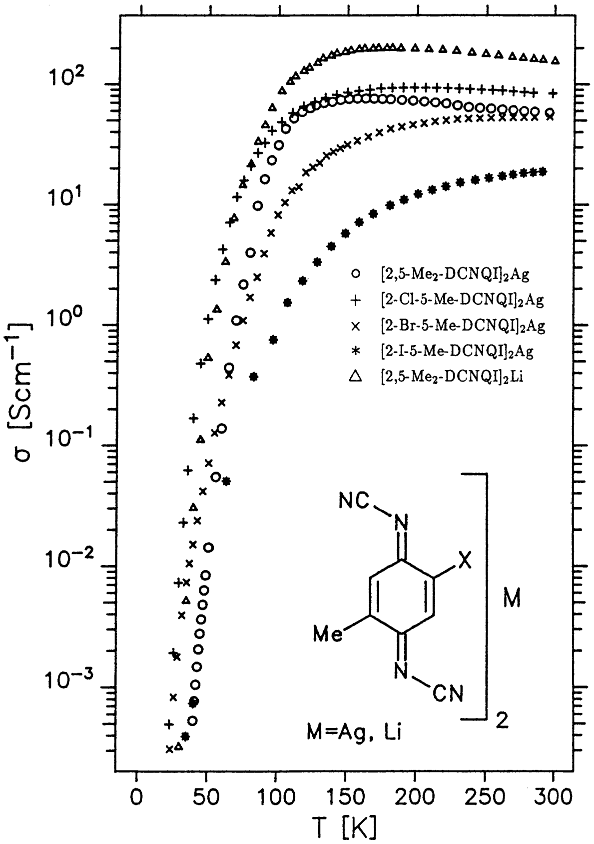
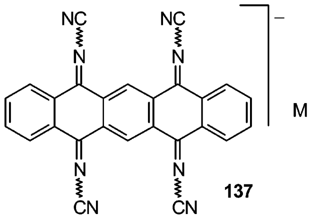


Figure 5. Temperature-dependent conductivities of [2-X,5-Me-DCNQI]$_2$Ag salts and [2,5-DMe-DCNQI]$_2$Li. Reprinted with permission from ref 6. Copyright 1991 Wiley-VCH.

Table 10. Anion Radical Salts from the DCNQI 137 and Monovalent Cations of General Stoichiometry 1:1[64]



137

entry	cation	σ_{rt} (S cm^{-1})
1	Li^{+a}	3×10^{-1} (p)
2	Na^+	4×10^{-1} (p)^b
3	K^+	5×10^{-2} (p)^b
4	Me_4N^+	1×10^{-2} (p)
5	$Bu_4N^{+\,c}$	1×10^{-4} (p)^b

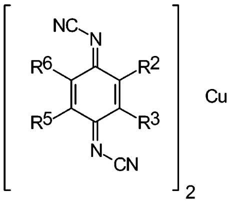
[a] Conductivities as high as 4 S cm^{-1} were obtained but not reproducibly. [b] Ref 108. [c] Space group: $P2_1/n$.

5.2.3.2. Pressure Dependence of Conductivity. Both lowering of temperature and increasing pressure cause crystals to shrink. Therefore, a phase transition at a certain temperature will move to higher temperatures on applying pressure. This normal behavior is exemplified by [2-Cl,5-Me-DCNQI]$_2$Cu[122] in Figure 7.

However, [2,5-DMe-DCNQI]$_2$Cu behaves differently. (i) A metal/insulator transition (M→I) is induced by pressure. (ii) In a certain pressure/temperature range, reentrance to the metallic state occurs (I→M). As can be seen in Figure 7, this compound first follows the normal trend. However, at ca. 50 K, an increase of pressure by as little as ca. 100 bar triggers a phase transition that does not approach a final $T_{M\rightarrow I}$ value at lower temperatures: Instead, the curve turns around at lower temperatures and the pressure for an M→I transition has to be increased. In other words, by a constant pressure of ca. 200 bar, [2,5-DMe-DCNQI]$_2$Cu becomes an insulator at ca. 70 K and regains its metallic character if cooled below ca. 25 K ($T_{I\rightarrow M}$).[123-125] The rapid response to even small pressure alterations on conductivity and ESR spectra of deuterated [2,5-DMe-DCNQI]$_2$Cu may be turned into sensitive sensors.[126,127]

5.2.3.3. Effect of Light. In each given case of temperature- and/or pressure-induced phase transitions M→I, the reversed process I→M shows a typical hysteresis. As shown in Figure 8, this gap can be

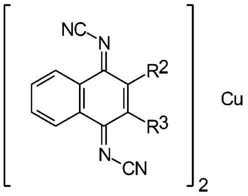
Table 11. Radical Anion Salts from DCNQIs and Cu^{+a}



		DCNQI					
entry	DCNQI/Cu	R^2	R^3	R^5	R^6	σ (S cm^{-1})	ref
1	1/1	H	H	H	H	2 × 10^{-2} (p)	91
2	1/1[b]	Cl	H	H	H	<10^{-7} (p)	91
3	1.33/1	Me	Me	H	H	1 × 10^{-4} (p)	91
4	1.5/1	−(CH$_2$)$_4$−		H	H	<10^{-7} (p)	22
5	1/1	Cl	Cl	H	H	7 × 10^{-5} (p)	22
6	2/1	Me	H	Me	H	1000−2000 (s)[e]	3,[c,d] 80,[c,d] 91−93,[c] 98,[g] 101[f]
7	2/1	Me	H	Et	H	1 × 10^{-1} (p)	22
8	1.5/1	Me	H	^{i}Pr	H	7 × 10^{-2} (p)	22
9	1/1	Et	H	Et	H	5 × 10^{-3} (p)	22
10	1.5/1	Pr	H	Pr	H	6 × 10^{-2} (p)	22
11	2/1	Me	H	CF$_3$	H	1 × 10^{-3} (p)	82
12	2/1	Me	H	OMe	H	80 (s)	82,[c,d] 91, 93
13	2/1	Me	H	Cl	H	700 (s)	92,[c] 91, 80,[d] 93,[c] 101[f]
14	2/1	Me	H	Br	H	1000 (s)	80,[d] 91, 93,[c] 95, 98,[g] 115[c]
15	2/1	Me	H	I	H	500 (s)[h]	22, 82,[d] 91, 93,[c] 116[c]
16	2/1	OMe	H	OMe	H	700 (s)	82,[d] 93, 95, 115,[c] 117,[c] 118[i]
17	2/1	OMe	H	Cl	H	500 (s)	82,[d] 119
18	2/1	OMe	H	Br	H	500 (s)	82,[d] 93
19	2/1	OMe	H	I	H	4 × 10^{-2} (p)	82
20	2/1	Cl	H	Cl	H	700 (s)	22, 82, 91, 93, 95, 115,[c] 117[c]
21	2/1	Cl	H	Br	H	600 (s)	91, 93,[d] 115,[c] 117[c]
22	2/1	Cl	H	I	H	70 (s)[j]	34,[d,k] 82[c,d]
23	2/1	Br	H	Br	H	700 (s)	22, 82,[c,d] 91, 93, 95, 115,[c] 117[c]
24	2/1	Br	H	I	H	500 (s)	82,[c,d] 93
25	2/1	I	H	I	H	70 (s)[j]	82,[c,d] 93
26	2/1	Me	Me	Cl	H	<10^{-6} (p)	45
27	1/1	Me	Me	Me	Me	4 × 10^{-3} (p)	91
28	1/1	Me	Me	Me	Br	<10^{-7} (p)	91
29	2/1	Me	Me	Cl	Cl	<10^{-6} (p)	45
30	1.5/1	Me	Me	Br	Br	1 × 10^{-7} (p)	91
31	2/1	Me	Cl	Cl	Cl	1 × 10^{-6} (p)	45[d]
32	1/1	−S−(CH$_2$)$_2$−S−		−S−(CH$_2$)$_2$−S−		10 × 10^{-7} (p)	47
33	1/1	−S−(CH$_2$)$_3$−S−		−S−(CH$_2$)$_3$−S−		6 × 10^{-10} (p)	47

[a] (p) S cm^{-1} and (s) S cm^{-1} = powder or single-crystal conductivities at room temperature. [b] Contains 1.2 H$_2$O. [c] Space group: I_1/a. [d] Temperature-dependent conductivity given. [e] Highest conductivity of 5 × 10^5 S cm^{-1} at temperatures ≤10 K. [f] Pressure-dependent conductivity given. [g] Temperature dependence of the polarized reflectance spectra given. [h] Highest conductivity of 2500 S cm^{-1} at 1.2 K. [i] Pressure dependence of the resistivity given. [j] Microwave measurements. [k] Microwave conductivity.

Table 12. Radical Anion Salts from DCNQIs and Cu$^+$ with the Stoichiometry 2:1^a



entry	DCNNI[b]	R^2	R^3	σ (S cm^{-1})	ref
1	**68**[c]	H	H	4 × 10^{-2} (p)	91
2	**70**	Cl	H	<10^{-6} (p)	45
3	**71**	Cl	Cl	1 × 10^{-3} (p)[d]	45

[a] Conductivities (S cm^{-1}) at room remperature are given. [b] Cf. Table 2. [c] Stoichiometry DCNNI/Cu 1.25:1. [d] Temperature dependence revealed semiconductor.

shifted to lower temperatures by light.[126−128] In films of such salts, light causes multicomponent conductivity changes.[129] The very fast and strong response of reflection of microwaves on illumination of partly deuterated [2,5-DMe-DCNQI]$_2$Cu allows the design of fast switches.[130]

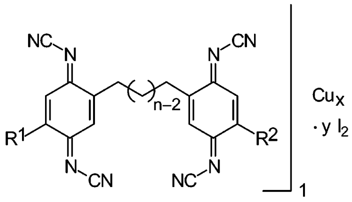
Table 13. Radical Anion Salts from DCNHIs and Cu$^+$ with Various Stoichiometry^a

entry	DCNHI/Cu	DCNHI[b]	σ (S cm^{-1})	ref
1		**98**	1 × 10^{-1} (p)	37
2	2/3	**101**	1 × 10^{-4} (p)	37
3	*b*	**102**	≈1 (p)	37[d]
4	1/1	**103**	1 × 10^{-1} (p)	37
5	1/2	**104**	1 × 10^{-5} (p)	37
6	2/1[e]	**127**	72.5 (p)[f]	59, 120

[a] Conductivities (S cm^{-1}) at room temperature are given. [b] Cf. Table 4. [c] Stoichiometry: Cu(**102**)Br·MeCN. [d] Space group: $P2(1)/c$. [e] Contains 1 H$_2$O. [f] Temperature dependence revealed semiconductor.

5.2.3.4. Deuterated [2,5-DMe-DCNQI] Copper Salts. Apart from DCNQI chemistry, deuteration of some CT complexes[131−134] and cation radical salts[135−138] revealed the expected small secondary deuterium effect on phase transition and transition tempera-

Table 14. Radical Anion Salts from Tethered DCNQIs and Cu^{+a}



	n	R^1/R^2 a	b	c	d	e
131	3	H/H	CH_3/CH_3	Br/Br	H/CH_3	Br/CH_3
132	4	H/H	CH_3/CH_3	Br/Br	-	-
133	5	H/H	CH_3/CH_3	Br/Br	-	-
134	6	H/H	-	Br/Br	-	-

entry	DCNQI	x	y	σ (S cm^{-1})	ref
1	**131a**	2.0		5×10^{-5} (p)	32
2	**132a**	1.8	0.2	3×10^{-5} (p)	32
3	**133a**	1.6	0.2	9×10^{-5} (p)	32
4	**134a**	1.8	0.2	1×10^{-3} (p)	32
5	**131b**	1.9		8×10^{-3} (p)	32
6	**132b**	1.8	0.2	4×10^{-2} (p)	32
7	**133b**	1.8	0.6	1×10^{-1} (p)	32
8	**131c**	1.8		3×10^{-5} (p)	32
9	**132c**	1.0	0.2	1×10^{-3} (p)	32
10	**133c**	1.8	0.2	1×10^{-6} (p)	32
11	**134c**	1.6	0.1	9×10^{-4} (p)	32
12	**131d**	1.7	0.3	8×10^{-3} (p)	32
13	**131e**	1.7	0.3	8×10^{-3} (p)	32

[a] Conductivities (S cm^{-1}) at room temperature are given.

tures to superconductivity, respectively. Deuteration of [2,5-DMe-DCNQI]$_2$Cu, however, provokes an unprecedented dramatic effect, as demonstrated in Figure 9.

Unusually sharp reversible phase transitions (within 1−2 K) with a drop of conductivity by a factor of 10^7−10^8 are connected with one CD_3 group at 58 K, with two CD_3 groups at 78 K, whereas additional deuteration of the ring shifts the phase transition to 82 K.[139] An impressive reentrant phenomenon is seen in Figure 9: The alloy prepared from 2,5-$(CH_3)_2$-DCNQI and 2,5-$(CD_3)_2$-DCNQI ("H_8/D_6" = 70:30) loses its conductivity at ca. 60 K completely but regains it at ca. 26 K at an even higher level.[140] On warming, hysteresis is observed.[141] These phenomena have been corroborated by a systematic deuteration study,[26,142−146] which reveals already the effect of one CH_2D group (Table 15).

Unexpectedly, even the isotopes ^{13}C and ^{15}N[148−150] in the =N−CN groups of [2,5-DMe-DCNQI]$_2$Cu and its deuterated derivatives alter the transition temperatures.[148,149,151−153] Special attention was given to the deuterium effect on the reentrance phenomenon,[154−167] magnetic properties,[168−171] specific heat,[166,172,173] and the type of charge transport.[26,174,175] Inspired by these results, numerous experiments with copper and noncopper DCNQI salts have been performed in order to learn about the factors that induce or alter phase transitions by pressure.[176−188] In the case of DCNQI copper salts, charge ordering with the Cu^{2+} local moment appears at the M→I transition,[111,177,188] which occurs already with pressure in the M→I group copper salts.[113]

5.2.3.5. Effects of the Crystal Structure. Obviously, the crystal lattice of these 2,5-DMe-DCNQI copper salts is extremely sensitive to slight distortions, which disturb the equal distant arrangement of the ligands (dimerization), causing a metal semiconductor transition, which must also include the copper ions. Probably, the $I4_1/a$ crystal structure, which is known to contain hidden superadamantane units,[189] plays a decisive role.[35]

As shown in Figure 10, an electron travelling from the top Cu^+ ion to the next one in the same position at the bottom has to pass the distance of seven c-units (extension of the unit cell along the c-axis of the crystal). Because seven superadamantane units are intercalated, as shown in Figure 10, the ligands themselves are in close contact. These arrangements may also be viewed as a "spring", which can be compressed by lowering the temperature or/and pressure. Indeed, the same effects are observed if a single thin crystal needle is compressed, influencing the c-axis only.[126,127,190] Shortening of the c-axis is inevitable connected with an expansion of the a,b-axis. Thereby, the nearly tetrahedral coordination angles at the copper ions may be enlarged beyond a crucial number causing phase transition. Actually, the phase transition temperature and the coordination angle α_{co} could be correlated for seven 2-X,5-Y-DCNQI copper salts, together with the borderline case of [2,5-DMe-DCNQI]$_2$Cu and the changes in its $(CD_3)_2$ derivative.[35] According to this correlation, deuteration causes a somewhat greater flexibility, which by cooperation of innumerous units of stacked [2-X,5-Y-DCNQI]$_2$Cu moieties in the crystal lead to the observed dramatic bulk effects.[35]

5.2.3.6. Effect of Gases. The special crystal lattice of DCNQI copper salts seems to be responsible for the diminishing of conductivity by increasing the partial pressure of oxygen[31,50,191] and nitrogen oxide due to their free spins. The oxygen effect has also been observed in films of DCNQI copper salts.[192] The effect of hydrogen,[193,194] however, cannot be explained on this basis. Sensors for hydrogen and oxygen have been proposed.[193−195]

5.3. Alloys of 2-X,5-Y-DCNQI Copper Salts

In principle, two variations of alloying are possible within the $I4_1/a$ lattice of a given [2-X,5-Y-DCNQI]$_2$Cu salt: (i) Partial substitution of the Cu^+ ions by other monovalent cations and (ii) partial substitution of a given DCNQI ligand by one or more ligand types. The special case of isotopic alloying has been treated already in section 5.2.3.4.

5.3.1. Alloys with Different Metal Ions

The similarity between the effective ionic radii[196] of Cu^+ (55 pm) and Li^+ (62 pm) (e.g., [DBr-DCNQI]$_2$Cu and [DBr-DCNQI]$_2$Li are isostructural[197]) has provoked intensive studies with different copper salts of the M→I and M groups under variation of the Cu^+/Li^+ ratio. The observed effects on the phase diagrams (either suppression or induction of phase transitions) have been explained by the inability of Li^+ to deliver electrons to the ligand.[148,197,198−209]

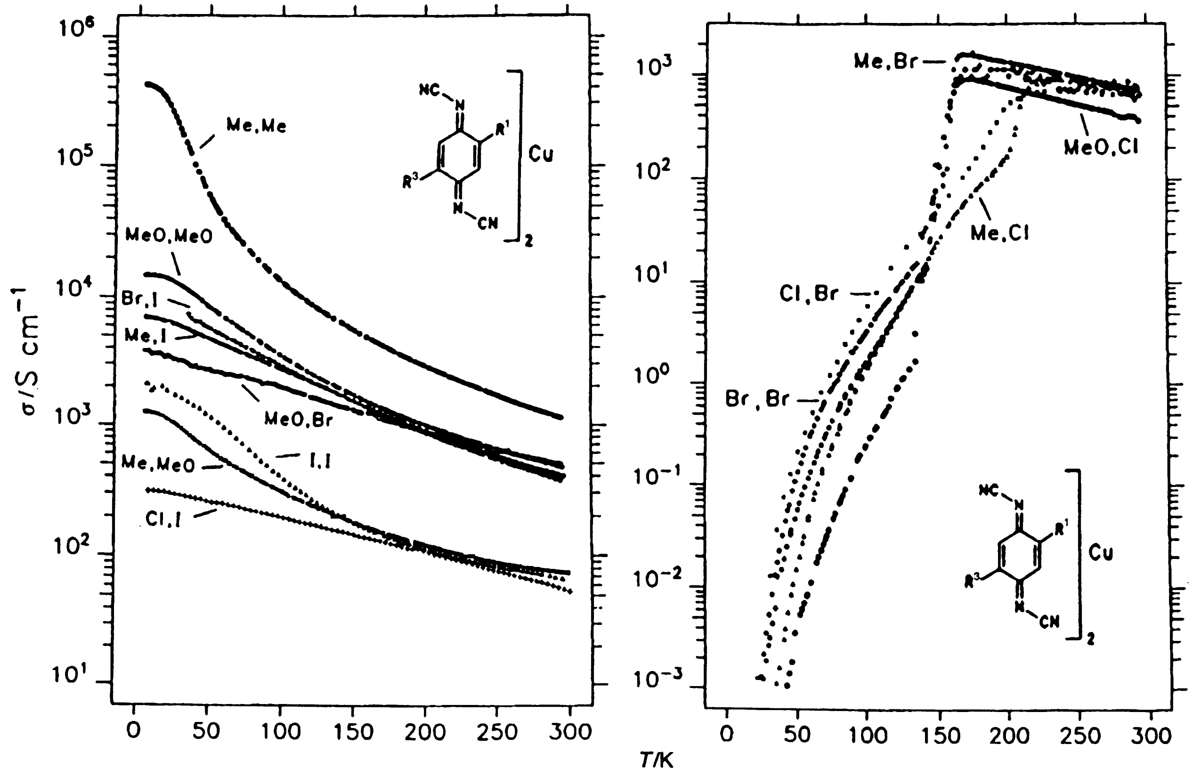


Figure 6. Temperature dependence of conductivity for [R^1,R^3-DCNQI]$_2$Cu, ordered for salts without (left) and with (right) phase transition. Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

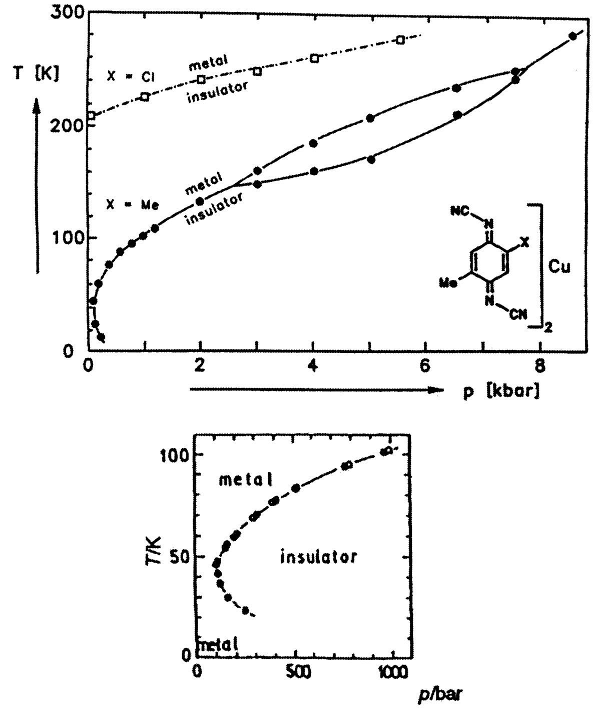


Figure 7. Top: Temperature/pressure phase diagram for [2-X,5-Me-DCNQI]$_2$Cu, X = Cl and Me. Bottom: Pressure-induced phase transitions of [2,5-DMe-DCNQI]$_2$Cu on cooling; low pressure phase diagram with p fixed and T variable; cooling (○) and warming (●). Top: Reprinted with permission from ref 6. Copyright 1991 Wiley-VCH. Bottom: Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

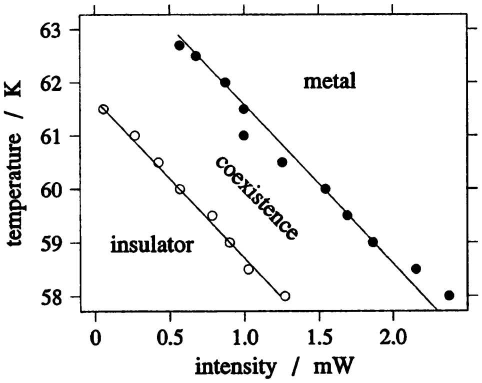


Figure 8. Light/temperature diagram for the insulating and metallic phase of [2,5-DCD$_3$-DCNQI]$_2$Cu by illumination with light of increasing (●)/decreasing (○) intensity. The parameter is the temperature T. Reprinted with permission from ref 126. Copyright 1996 American Institute of Physics.

The alloys of [2-Br,5-Me-DCNQI]$_2$Cu$_{1-x}$Li$_x$ present a typical example[10,210] with $x = 0.25-0.50$. The high single-crystal conductivity of ca. 1000 S cm^{-1} is preserved down to the lowest temperatures although the pure Cu$^+$ and Li$^+$ salts both undergo phase transitions (vide supra).[210] Figure 11 demonstrates this situation for $x = 0.35$. By contrast, the alloy with $x = 0.1$ starts with diminished conductivity, which on lowering the temperature is sharply increased down to 130 K, where a phase transition occurs. Alloys from Cu$^+$/Ag$^+$ DCNQIs have also been reported.[211,212]

5.3.2. Alloys with Different DCNQI Ligands

A great variety of copper salts have been prepared in which the alloy consists of two different 2,5-disubstituted DCNQI ligands. Substituents were varied according to their size and/or electronic properties.[213]

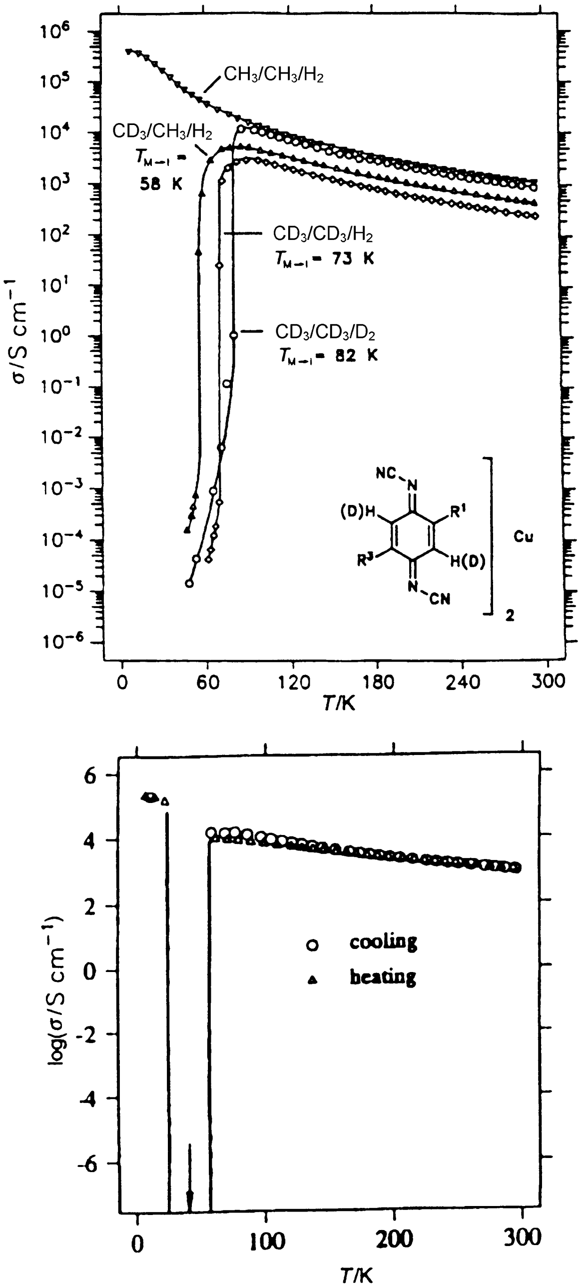


Figure 9. Top: Effect of H–D exchange on the temperature-dependent conductivity of three differently deuterated [2,5-DMe-DCNQI]$_2$Cu salts. Bottom: Temperature-dependent conductivity of a [2,5-DMe-DCNQI]$_2$Cu, D$_6$–H$_8$ alloy (0.6:1.4). Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

Starting from conductivities of 130–400 S cm^{-1} at ambient temperature, the temperature-dependent phase diagrams can be grouped as follows: (i) metallic behavior down to lowest temperatures (Table 16, entries 1, 13, 25, 32, 33, and 35); (ii) metallic behavior with sharp (Table 16, entries 6, 9, 26, 36, and 37) and broad phase transitions (Table 16, entry 14) at low temperatures; and (iii) metallic semiconductors similar to those of noncopper DCNQI salts (Table 16, entries 4, 20, 27, and 34).

Alloys from DCNQI copper salts without and with phase transitions are of special interest. In Table 16, the alloys from [(2-Me,5-Br-DCNQI)$_m$/(2-Me,5-I-DCNQI)$_n$]Cu with the ratio m:n = 1.2:0.8 (entry 25) still show no phase transition down to the lowest temperatures. By contrast, the ratio m:n = 1.5:0.5 (entry 26) displays a sharp phase transition at ca. 130 K.

Besides, an alloy with three different ligands {Figure 12F, [(2,5-DMe-DCNQI)$_{1.0}$(2-MeO,5-Me-DCNQI)$_{0.8}$(2-I,5-Me-DCNQI)$_{0.2}$]Cu} is shown, which displays a nearly constant conductivity of ca. 70 S cm^{-1} down to 4 K, although the conductivities of the single three DCNQI salts increase steeply (cf. Figure 12).

5.4. Thin Films of DCNQI Type Acceptors and Their Salts

By sublimation of DCNQI type acceptors on to a surface, films from ultrathin to up to ca. 60 layers can be produced. This way, the charge transport in layers of 2-*tert*-butyl-DCNAI was studied.[51]

Thorough spectroscopical investigations are reported for films of DMe-DCNQI on surfaces of Ag(111), Ag (100) and Cu(111), Cu(110).[36,192,216–226] The same protocol was applied to surfaces of alkali metals, freshly prepared on an inert support.[219,220,222,227,228] In all cases, highly structured films are obtained, variable by the conditions applied, including annealing, which may produce the corresponding anion radical metal salts in highly ordered arrangements. Strong pressure dependence of conductivity and oxygen adsorption[192] of such [DMe-DCNQI]$_2$Cu layers on copper may be of practical importance.

5.5. Evaluation of the Electronic State of DCNQI Type Anion Radical Salts

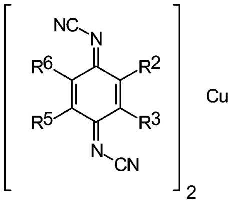
Together with the dependence of conductivity on temperature, pressure, and light, the electronic state, charge transport, etc. in DCNQI type anion radical salts—especially copper salts with their phase transitions—have been evaluated by various methods. Normally, structured IR spectra are obtained with DCNQI salts of Li$^+$,[96,229] Ag$^+$,[229,230] and Cu^{9+} [8,197,204,229,231–239] only in the low conducting range, where the CN frequency becomes visible. High conductivity, however, is connected to weekly resolved IR spectra.

By NMR spectroscopy of the counterions ^{7}Li$^+$[240],[205] Tl$^+$, [40–242] and ^{63}Cu$^+$,[240–245] metal-like Knight shifts were observed in DMe-DCNQI radical salts. Corresponding shifts were found in the anionic ligands for ^{13}C[151,152,212,246–253] and ^{15}N,[212,250–252] where increasing relaxation times below M→I transitions point to charge ordering. Similarly, ^{1}H NMR spectra have been analyzed according to relaxation rates.[102,254,255] By employing ESR spectroscopy, insight has been gained about charge densities and mobilities together with dynamic susceptibilities in DCNQI type radical metal salts.

Metal-like 1d semiconductors of, i.e., all noncopper salts, behave similarly: Li$^+$,[95,195,256–264] Na$^+$,[85,95,259,260,265] K$^+$,[95,258,260,265] NH$_4^+$,[95] Rb$^+$,[258,259,265] Tl$^+$,[241,242,258] and Ag$^+$,[4,95,150,258,266–269] combined with different DCNQIs. However, mostly 2,5-DMe-DCNQI was studied.

Because of their nearly 3d conductivity, the corresponding Cu salts behave quite differently.[4,33,95,102,266,267,270–274] In the conducting region,

Table 15. Deuterated [2,5-DMe-DCNQI] Copper Salts[143,147]



					transition temperature			
					on cooling		on warming	
entry	R^2	R^5	R^3	R^6	$T_{\mathrm{M\to I}}$	$T_{\mathrm{I\to M}}$	$T_{\mathrm{I\to M}}$	$T_{\mathrm{M\to I}}$
1	CH_3	CH_3	H	H[a]	*b*	*b*	*b*	*b*
2	CH_3	CH_3	D	H	*b*	*b*	*b*	*b*
3	CH_3	CH_3	D	D	ca. 40 (slight sh)[c]	ca. 50 (slight sh)[c]		
4	CH_2D	CH_3	H	H	ca. 40 (sh)[c]	ca. 50 (sh)[c]		
5	CH_2D	CH_3	D	H	ca. 40 (sh)[c]	ca. 50 (sh)[c]		
6[d]	CH_2D	CH_3	D	D	51	28	54	41
7	CH_2D	CH_2D	H	H	55	21	56	35
8	CHD_2	CH_3	H	H	55	20	58	35
9	CH_2D	CH_2D	D	H	57	16	63	30
10	CH_2D	CH_2D	D	D	61	13	59	33
11[e]	CD_3	CH_3	H	H[a]	62	10	66	22
					64	*b*	67	*b*
12	CD_3	CH_3	D	D	66	*b*	70	*b*
13	CHD_2	CHD_2	H	H	68	*b*	71	*b*
14	CD_3	CD_3	H	H[a]	75	*b*	78	*b*
15	CD_3	CD_3	D	H	77	*b*	80	*b*
16	CD_3	CD_3	D	D[a]	80	*b*	82	*b*

[a] Refs 35 and 139. [b] Transition is not observed. [c] sh stands for shoulder; some samples do not indicate any anomaly. [d] Some samples indicate no sharp reentrant transition but only a shoulder at ca. 50 K. [e] Some samples do not indicate the reentrant transition.

these copper salts are ESR silent caused by extreme line broadening due to 3d movement of the electrons by coupling with the Cu d states. Below the M→I transition, ESR line widths narrow strongly with losing their intensity (together with conducting, which means spin pairing). The now observed anisotropy of the ESR signal corresponds to that of Cu^{2+} with localized spin states.

Magnetic measurements have been applied to DCNQI type copper salts mostly in combination with ESR spectroscopy. The data, which depend on the direction of the crystal needles in the magnetic field, reveal strong static susceptibilities for the conducting range. Around the M→I transition, antiferromagnetic and partly ferromagnetic ordering is observed.[50,114,200,232,235,270,275−289] The effect of uniaxial stacking has also been studied.[290]

Variants of photoelectronspectroscopy have been applied to $[2\text{-X},5\text{-Y-DCNQI}]_2Cu$ to find out how far the orbitals C 2p and N 2p of the cyano groups and especially Cu 3d are involved in the conducting process and/or the insulator state of these salts. Thus, X-ray photospectroscopy absorptions[115,291−296] and emissions were studied.[294,297−302]

If the salts were prepared and handled under complete exclusion of oxygen, the oxidation state of copper was found +1;[300] otherwise, it was +1.3.[115] In some cases, synchrotron[99,292,303] or cyclotron radiation[304] was employed. Results from near edge X-ray absorption fine structure have also been reported.[305,306] Some of these studies were complemented by valence bond UV photoelectron spectroscopy.[221,293,300,307,308] Results from Raman[309] and scanning tunneling electron microscopy[310,311] have also been reported. Some noncopper salts were included as follows: Rb^{+}[307] and especially Ag^{1+}[88,307,310] for comparison with copper salts.

5.6. Theoretical Approaches

The various physical investigations have been backed by theoretical calculations. Ab initio results were offered for DCNQI itself[312] but also for Li^+ and Ag^+ salts.[313] Charge ordering[314] and electron correlations were calculated for one-dimensional conductors (Li^+, Ag^+)[315−318] together with their energy band structures.[319] The main effort is focused on the peculiar copper salts: ground state,[320] energy band structures,[319,321] metallic state,[316,317,322] M→I transitions,[323−327] and charge ordering.[328]

5.7. Conclusions

The temperature- and pressure-dependent conductivities of the anion radical salts $[2\text{-X},5\text{-Y-DCNQI}]_2M$ have been thoroughly studied by physical methods outlined above. The interplay between densities of charge carriers and their mobility is modified by the substituents X and Y and by the metal ions. The semiconducting noncopper salts form one group with similar properties (e.g., Li^{+}[104,263,329−331] and Ag^{1+}[04,330,332−336]). Most investigations are focused on the metallic copper salts with their unprecedented unique properties, especially the sharp M→I transitions and the reentrance of conductivity (I→M) in some cases. According to their temperature/pressure phase diagrams at low temperatures, three groups of DCNQI copper salts can be discerned depending on the size of substituents, isotope effects, and doping as shown in Figure 13.

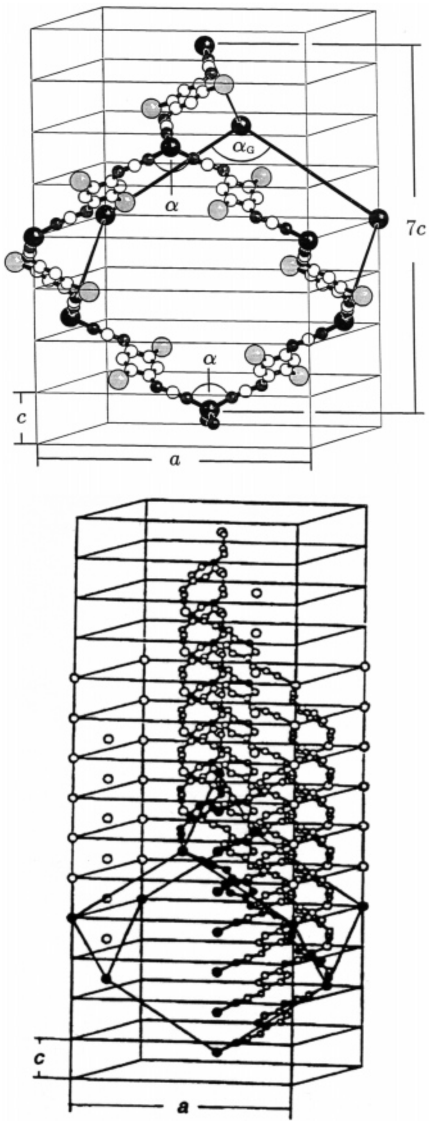


Figure 10. Top: Superadamantane unit in the crystal lattice of [2,5-DMe-DCNQI]$_2$Cu. The distance 7*c* encloses two Cu ions of the same column. Bottom: Seven intercalating superadamantane units in the crystal lattice of [2,5-DMe-DCNQI]$_2$Cu. Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

Members of group I stay metallic down to the lowest temperatures. Members of group II undergo a metallic/insulator (M→I) transition, which is reversed into a I→M transition on lowering temperatures or increasing pressure. Members of group III only undergo a M→I transition. A comprehensive review on this topic is already available.[10]

The very subtle interplay of ligand 2p and copper 3d orbitals expressed in different bond distances and coordination angles[35] leads to complicated Fermi levels and 2k Peierls distortions (formation of clusters from the equidistant subunits in a stack with smaller internal distances but larger gaps between these clusters) with admixed 4k spin Peierls transformations.[195,265,337−344]

6. Anion Radical Salts of DCNQIs with Organic Cations

As shown above, the high conductivity of the salts [2-X,5-Y-DCNQI]$_2$M$^+$ is strongly dependent on their crystal structures. These are bound to a certain size of the ligands and nearly tetrahedral coordination angles of the metal ions. Organic cations will not allow such specific coordinations by both their structure and their size. Therefore, the radical salts with cations **146**−**154** and varying stoichiometry have to be considered as individuals (Table 17).

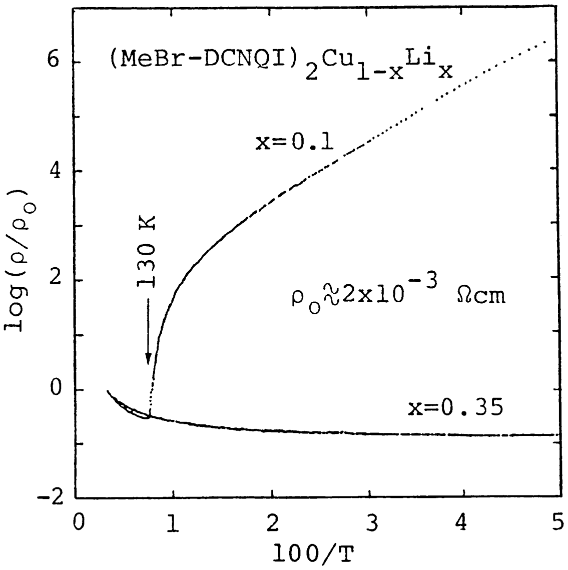


Figure 11. Resistivity vs temperature of [2-Br,5-Me-DCNQI]$_2$Cu$_{1-x}$Li$_x$ for $x = 0.1$ and $x = 0.35$ (note the different plotting). Reprinted with permission from ref 210. Copyright 1991 The Chemical Society of Japan.

In [2,5-DCl-DCNQI]$_2$[NMe$_4$], the 2:1 stoichiometry of the metal salts is preserved. However, the anion radicals are now arranged in parallel zigzag stacks, the holes filled by the spheric cations (Figure 14).[352,353]

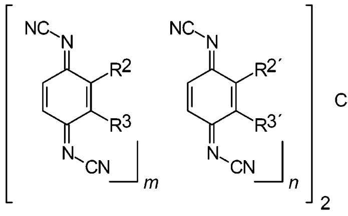
This structure still allows the rather high conductivity of 10^{-2} S cm^{-1}. However, **6**/TMA (2:1) with unknown structure shows only 9×10^{-7} S cm^{-1} (Table 17, entry 1). From TCNQ, the much larger but flat *N*-methylquinolinium (**147**) and *N*-methylphenazinium (**148**) cations had already yielded conducting salts.[352,354] DCNQIs behave similarly (Table 17, entries 4−6 and 7−9).

Organic dications offer the opportunity to place two positive charges in a definite distance. This was done (Table 17) with *N*,*N*′-hexamethyl-1,2-ethane-diammonium ion (**149**), *N*,*N*′-dimethyl-4,4′-bipyridinium ion (DMBP^{2+}, **150**), *N*,*N*′-ethylene-2,2′-bipyridinium ion (**151**), and 2,2′-ethenediylbis(3-methylbenzothiazolium) ion (**152**) by electrocrystallization. It should be mentioned that the latter three cations may accept electrons reversibly (violene systems, cf. Scheme 2).

In all cases, crystalline salts were obtained with reasonable conductivities (Table 17, entries 10−28). Their weakly resolved IR spectra point to segregated stacks. This arrangement is shown in a typical pattern by the crystal structure of **33**/DMBP (**150**) (Figure 15).[347]

The conducting anions are arranged along the *c*-axis in skewed stacks, where this well-known "ring over bond" packing[355] allows favorable orbital overlaps. The DMBP dications are located also along the same axis, forming flat isolating walls between the conducting stacks. All of these salts (Table 17, entries

Table 16. Powder (p) or Single-Crystal (s) Conductivities at Room Temperature of Alloys with Different DCNQI Ligands from Electrocrystallization (Method A) or by Growing on a Copper Wire (Method B)[82,214,215]



entry	R^2	R^3	*m*	$R^{2¢}$	$R^{3¢}$	n	method	σ (S cm^{-1})
1	Me	Me	0.8	Me	OMe	1.2	B	2×10^{-1} (p)
2	Me	Me	0.5	Me	Cl	1.5	A	200 (s)
3	Me	Me	0.9	Me	Cl	1.1	B	3×10^{-1} (p)
4	Me	Me	0.24	Me	Br	1.76	A	900 (s)
5	Me	Me	0.5	Me	Br	1.5	A	200 (s)
6	Me	Me	0.9[a]	Me	Br	1.1	B	400 (s)
7	Me	Me	0.6	Me	I	1.4	A	200 (s)
8	Me	Me	1.0	Me	I	1.0	B	2×10^{-1} (p)
9	Me	Me	1.0	Cl	Cl	1.0	B	130 (s)
10	Me	Me	1.1	Cl	Br	0.9	B	3×10^{-1} (p)
11	Me	Me	1.0	Br	Br	1.0	B	
12	Me	Me	1.2	Me	OMe	0.8	B	40 (s)
13	Me	Me	1.0	OMe	OMe	1.0	B	220 (s)
14	Me	Me	1.2	Br	OMe	0.8	B	180 (s)
15	Me	OMe	1.4	Br	Br	0.6	B	4×10^{-1} (p)
16	Me	Cl	0.8	Me	Br	1.2	A	400 (s)
17	Me	Cl	1.0	Me	Br	1.0	B	2×10^{-1} (p)
18	Me	Cl	1.0	Me	I	1.0	A	400 (s)
19	Me	Cl	1.5	Me	I	0.5	B	400 (s)
20	Me	Cl	0.8	Cl	Cl	1.2	B	230 (s)
21	Me	Cl	1.0	Cl	Br	1.0	B	
22	Me	Cl	1.1	Br	Br	0.9	B	2×10^{-1} (p)
23	Me	Br	1.0	Me	OMe	1.0	B	2×10^{-1} (p)
24	Me	Br	1.0[b]	Me	I	1.0	B	1×10^{-1} (p)
25	Me	Br	1.2	Me	I	0.8	A	200 (s)
26	Me	Br	1.5[c]	Me	I	0.5	A	700 (s)
27	Me	Br	1.4	OMe	OMe	0.6	B	220 (s)
28	Me	Br	1.8	Br	OMe	0.2	B	2×10^{-1} (p)
29	Me	Br	1.0	Cl	Cl	1.0	B	1×10^{-1} (p)
30	Me	Br	1.0	Cl	Br	1.0	B	2×10^{-1} (p)
31	Me	Br	1.0	Br	Br	1.0	B	2×10^{-1} (p)
32	Me	I	0.8	Me	OMe	1.2	B	260 (s)
33	Me	I	1.3	OMe	OMe	0.7	B	200 (s)
34	Me	I	1.0	Cl	Cl	1.0	B	280 (s)
35	Me	I	1.3	Br	Br	0.7	B	140 (s)[d]
36	Me	Me	1.0	CD_3	CD_3	1.0	A	490 (s)[e]
37	Me	Me	1.4	CD_3	CD_3	0.6	A	130 (s)[e]

[a] Neutron activation: *m*/*n* 0.90/1.10. [b] Neutron activation: *m*/*n* 1.15/0.85. [c] Neutron activation: *m*/*n* 1.37/0.63. [d] Ref 97. [e] Ref 140.

10–28) are typical semiconductors, whose conductivity drops steadily on cooling.

A special case is given by the metalocenium salts **153** and **154**, which had to be prepared at low temperatures. These salts exhibit ferromagnetic coupling as evidenced by their fit to the Curie–Weiss expression. For **153**, dominant ferromagnetic interactions are supported by Mössbauer spectra.[349] [Fe(C_5Me_5)$_2$]DMe DCNQI crystallizes in the triclinic space group *P*1 with mixed stacks as shown in Figure 16.[351]

7. Special Metal DCNQI Complexes

All of the metal salts discussed in sections 5.1, 5.2.1, and 5.2.2 have in common that the DCNQI type moieties only are coordinated to the metal ion. A different approach employs DCNQIs in the oxidized form or as the dianion of the reduced form as an electron transferring linker between two transition

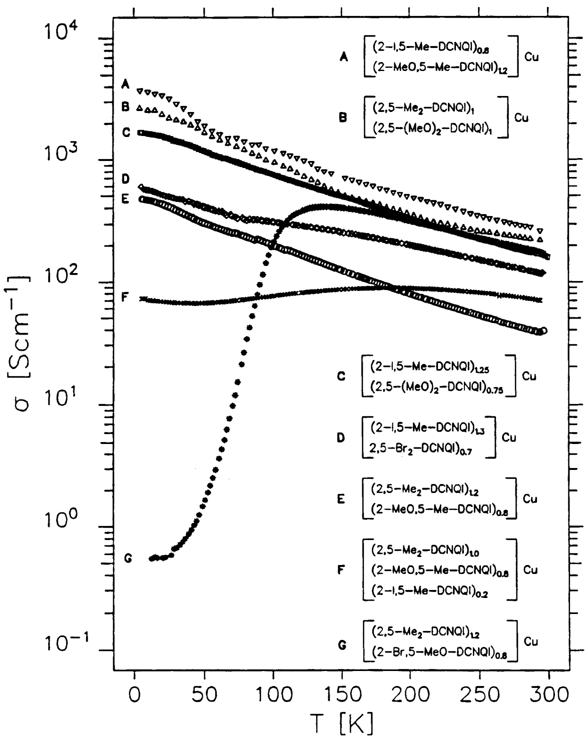


Figure 12. Temperature-dependent conductivity of Cu salt alloys from Table 16: A, entry 32; B, entry 13; C, entry 33; D, entry 35; E, entry 1; F, not given in Table 16; and G, entry 14). Examples for groups 1 and 2 are presented in Figure 12. The subtle substituent effects of the mixed ligands on the crystal lattice of the copper salts are seen in compounds D and G of Figure 12. In D, the phase transition connected to Br/Br is supressed, whereas in G the broad phase transition is produced by two components, which both belong to the M group.

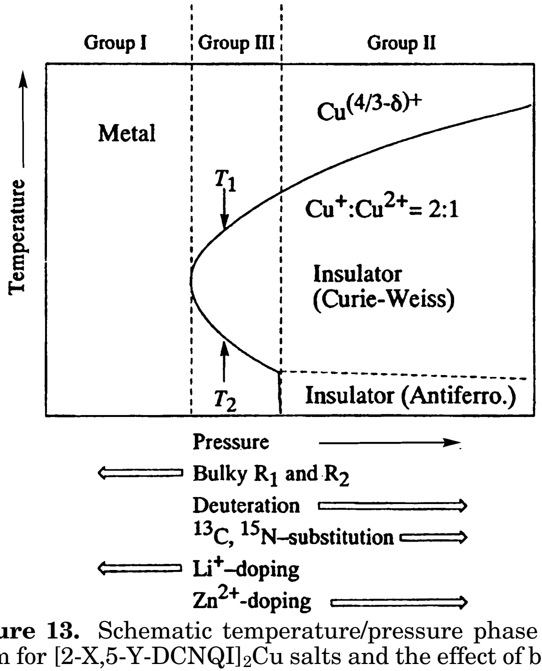
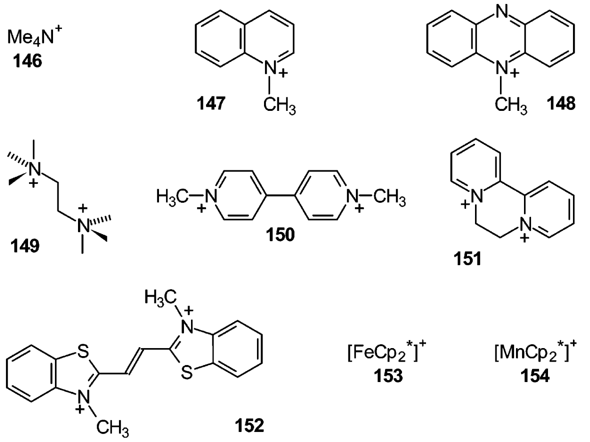


Figure 13. Schematic temperature/pressure phase diagram for [2-X,5-Y-DCNQI]$_2$Cu salts and the effect of bulky substituents, isotopes, and doping by metal ions. The variation of the pressure of these factors on the phase transitions has been called the "effective" pressure. Reprinted with permission from ref 10. Copyright 2000 The Chemical Society of Japan.

Table 17. Anion Radical Salts of DCNQIs with Organic Cations



entry	no.^{a}	R^2	R^3	R^5	cation	m:n^b	σ (S cm^{-1})	ref
1	**6**	Me	H	H	**146**	2:1	9×10^{-7} (p)	393
2	**43**	Cl	H	Cl	**146**	2:1^c	2×10^{-2} (p)	93,^{d} 345, 346
3	**46**	Br	H	Br	**146**	3:2^c		346^e
4	**43**	Cl	H	Cl	**147**	5:3^c	1×10^{-1} (s)	346
5	**46**	Br	H	Br	**147**	5:4^c		346
6	**46**	Br	H	Br	**147**	3:2^f		346
7	**5**	H	H	H	**148**	2:1^g		346
8	**43**	Cl	H	Cl	**148**	1:1^c		346
9	**46**	Br	H	Br	**148**	1:1^g		346
10	**15**	Cl	Cl	H	**149**	8:3^g	2×10^{-5} (p)	347
11	**16**	Br	Br	H	**149**	3:1^g	3×10^{-4} (p)	347, 348
12	**43**	Cl	H	Cl	**149**	3:1^g	4×10^{-4} (p)	347, 348
13	**46**	Br	H	Br	**149**	8:3^g	8×10^{-4} (p)	347, 348
14	**15**	Cl	Cl	H	**150**	3:1^c	3×10^{-3} (p)	347, 348
15	**16**	Br	Br	H	**150**	3:1^h	7×10^{-3} (p)	347, 348
16	**43**	Cl	H	Cl	**150**	3:1^h	7×10^{-4} (p)	347, 348
17	**46**	Br	H	Br	**150**	3:1^h	3×10^{-2} (p)	347, 348
18	**32**	Cl	H	Me	**150**	3:1^h	3×10^{-3} (p)	347, 348
19	**33**	Br	H	Me	**150**	3:1^c	1×10^{-1} (s)	347,^{i,j} 348^i
20	**15**	Cl	Cl	H	**151**	3:1^g	3×10^{-2} (p)	347, 348
21	**16**	Br	Br	H	**151**	3:1^h	2×10^{-5} (p)	347, 348
22	**43**	Cl	H	Cl	**151**	5:2^c	2×10^{-2} (p)	347, 348
23	**46**	Br	H	Br	**151**	3:1^h	5×10^{-2} (p)	347, 348
24	**32**	Cl	H	Me	**151**	3:1^c	1×10^{-1} (s)	347,^{i,k} 348^{i,j}
25	**33**	Br	H	Me	**151**	3:1^c	2×10^{-2} (p)	347, 348
26	**34**	I	H	Me	**151**	3:1^g	7×10^{-5} (p)	347, 348
27	**46**	Br	H	Br	**152**	3:1^g	3×10^{-2} (p)	347
28	**33**	Br	H	Me	**152**	8:3^g	1×10^{-2} (p)	347
29	**18**	Me	H	Me	**153**	1:1		349−351
30	**25**	Ph	H	Ph	**153**	1:1		350
31	**30**	MeO	H	Me	**153**	1:1		349
32	**32**	Cl	H	Me	**153**	1:1		349
33	**18**	Me	H	Me	**154**	1:1		349

[a] Cf. Table 1. [b] Stoichiometry m:n of [DCNQI] and the mono- or dication. [c] Needles. [d] Space group: $C2/m$. [e] Space group: $P\bar{1}$. [f] Cubes. [g] Amorphous solid. [h] Polycrystalline solid. [i] Temperature-dependent conductivity given. [j] Crystal structure given. [k] Space group: $P1$.

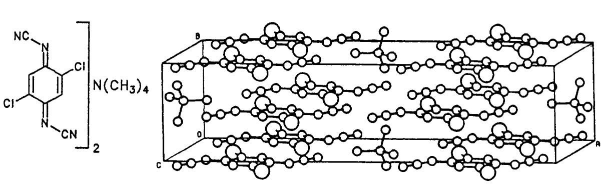


Figure 14. Unit cell of [2,5-DCl-DCNQI]$_2$[NMe$_4$], space group $C2/m$; $\sigma = 10^{-2}$ S cm^{-1}. Reprinted with permission from ref 8. Copyright 1995 The Royal Society of Chemistry.

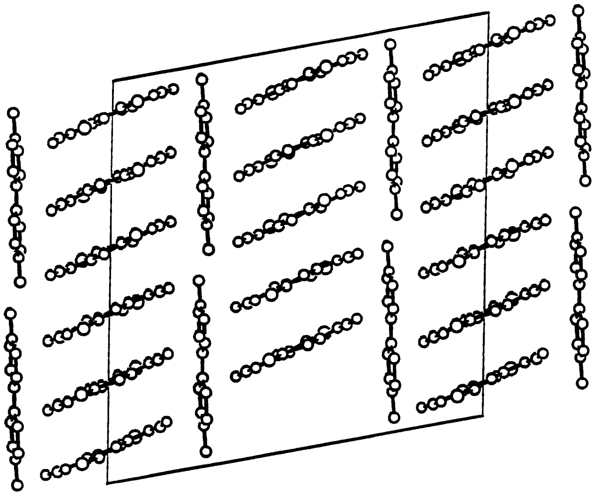


Figure 15. Crystal structure of [2-Br,5-Me-DCNQI]$_3$DMBP (**150**). View onto the a,c-plane (along [0$\bar{1}$0]). Reprinted with permission from ref 347. Copyright 1998 Wiley-VCH.

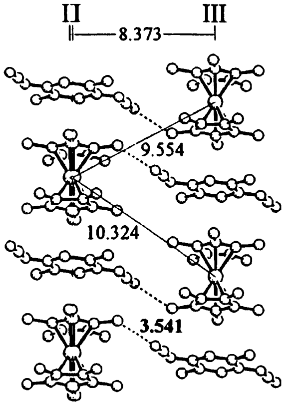


Figure 16. Out-of-registry arrangement of chains II and III. The solid lines show the interchain separations and the closest interchain M−M distances. The thick dotted lines show the closest interchain interionic distances (hydrogen atoms are omitted for clarity). Reprinted with permission from ref 351. Copyright 2001 Elsevier.

metal centers. These centers are partly protected by ligands that way to produce (mostly) polymeric chains from the metal ions and the dianionic donor according to the general structure ···M−D−M−D···. Interest in these complexes has been focused on antiferromagnetic superexchange effects (Table 18).

A deep blue carbonyl manganese complex has been reported (Table 18, entry 2) for which σ−N coordination of the cyano group could be derived from the shifted CO frequencies.[356] Polymeric one-dimensional complexes result from Mo$_2$(O$_2$CCF$_3$)$_4$[163] and Rh$_2$(O$_2$CCF$_3$)$_4$[357] with 2,5-DMe DCNQI (anti CN groups provide streched chains) (Table 18, entries 1, 12, 14, and 15) whereas syn CN arrangements in the DCNNI produce zigzag chains (Table 18, entry 13).[357] The brownish yellow color together with the visible CN frequency points to a neutral acceptor, which is σ−N bonded (X-ray). By substitution, two or four trifluoromethyl acetate ligands in Rh$_2$(O$_2$CCF$_3$)$_4$ result in deep blue polymers, in which by N,N'-di-p-tolylformamidinate one electron has been transferred to the acceptor (CN frequency no longer visible[358]) (Table 18, entries 14−16).

In the case of Rh$_2$(O$_2$CCR)$_4$/2,5-DMe DCNQI (Table 18, entry 7), the linear polymer has been demonstrated to contain the bridging acceptor as a radical anion.[359] A rather unusual donor is provided by [Fe$_2$(C$_5$Me$_5$)$_2$-(μ-SEt)$_2$(CO)$_2$] in which two iron moi-

Table 18. Polymeric CT Complexes from DCNQI Derivatives 5, 6, 18, 32, 43, 65, and 68 with Transition Metal Complexes[a]

entry	formula	ref
1	$[Mo_2(O_2CCF_3)_4(\mathbf{18})\cdot C_6H_6]_n$	361[b]
2	$[(h^1\text{-}\mathbf{18})Mn(CO)_2(h^5\text{-}C_5Me_5)]_n$	356
3	$[Fe_2(h\text{-}C_5Me_5)_2(m\text{-}SEt)_2(CO)_2][\mathbf{18}]$	362[c]
4	$[Fe_2(h\text{-}C_5Me_5)_2(m\text{-}SEt)_2(CO)_2][\mathbf{32}]$	362
5	$[Fe_2(h\text{-}C_5Me_5)_2(m\text{-}SEt)_2(CO)_2][\mathbf{6}]$	362
6	$[Fe_2(h\text{-}C_5Me_5)_2(m\text{-}SEt)_2(CO)_2][\mathbf{5}]$	362
7	$[Ru_2(O_2CR)_4(\mathbf{18})]_n$; R = H, Me, Et, Pr, Ph, *p*-tolyl	359, 363
8	$[m\text{-}\mathbf{5}\{(NH_3)_5Ru\}_2][ClO_4]\cdot 4H_2O$	360[d]
9	$[m\text{-}\mathbf{18}\{(NH_3)_5Ru\}_2][ClO_4]\cdot$1/6acetone	360
10	$[m\text{-}\mathbf{43}\{(NH_3)_5Ru\}_2][Cl_4]\cdot 3H_2O$	360
11	$[m\text{-}\mathbf{65}\{(NH_3)_5Ru\}_2][Cl_4]$	360, 364
12	$[Rh_2(O_2CCF_3)_4(\mathbf{18})]_n\cdot(C_6H_6)$	357[e]
13	$[Rh_2(O_2CCF_3)_4(\mathbf{68})]_n\cdot(C_7H_8)$	357[f]
14	$[Rh_2(form)_4(\mathbf{18})]$	358
15	$[Rh_2(form)_2(O_2CCF_3)_2(\mathbf{18})]_n$	358
16	$[Rh_2(form)_2(O_2CCF_3)_2(\mathbf{68})]_n$	358
17	$[\{Ru(bpy)(terpy)\}_2(m\text{-}\mathbf{5})][PF_6]\cdot$DMF	365

[a] bpy, 2,2′-bipyridine; form, *N*,*N*′-di-*p*-tolylformamidinate; terpy, 2,2′,2″-terpyridine. [b] Space group: *C*2/*c*. [c] Space group: *C*2/*c*. [d] Space group of $[\mu\text{-}\mathbf{5}\{(NH_3)_5Ru\}_2][OTs]_4\cdot$acetone: $P2_1/c$. [e] Space group: $P\bar{1}$. [f] Space group: *P*2/*c*.

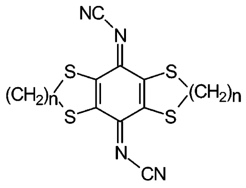
eties are bridged by two thioethyl groups. With various DCNQI derivatives, blue–black solids are formed due to one electron transfer. The mixed stacks are arranged as $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}\cdots$. The temperature dependence of the magnetic susceptibility follows the Curie–Weiss law (Table 18, entries 3–6).

For comparison with the complexes from entries 8–11 (Table 18), the salts from the dianions of the reduced DCNQIs **5**, **18**, **43**, and **65** with two $[AsPh_4]^+$ as counterions have been prepared.[360] For comparison of some Ru complexes of Table 18, the copper complexes **155**–**157** (dications) and **158**–**160** (neutral) have been prepared with dianions of DCNQIs/RED (i.e., dianions of the corresponding biscyanoimides) as linkers and trident ligands filling the residual coordination positions of Cu^{2+} (Scheme 7). The dianions of DCNQIs/RED (cf. Scheme 4) act as bifunctional electron donors. These structures prevent polymerization.[366]

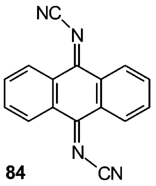
Another class of compounds deserves special attention. As mentioned above, on cooling, acetonitrile solutions of the DCNQIs from Table 11 and CuI black salts $(DCNQI)_2Cu$ are precipitated. In sharp contrast with the heterocyclic acceptors **66**, **67**, and **127**–**130** and also DCNAI **84**, the black precipitates consist of the addition compounds acceptor·2CuI (Table 19). Obviously, decreasing the electron affinity and increasing the steric demand of these acceptors prevent the formation of the normal anion radical salts with their typical crystal lattice.

The black color of these adducts points to charge delocalization, although the powder conductivities of **66**·2CuI and **67**·2CuI (Table 19, entries 1 and 2) are rather low. By contrast, the unexpected high powder conductivities of 45 (**127**·2CuI)[59,60] and 100 S cm^{-1} (**130**·2CuI)[59] (Table 19, entries 4 and 7) together with their metallic behavior down to 170 K deserve special attention.

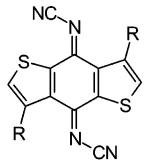
Table 19. Addition Complexes from Acceptors 66, 67, and 127–130 with Copper Iodide (A/2 CuI) and Their Powder Conductivities σ



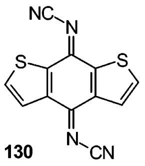
66 (n =2), **67** (n =3)



84



R	H	CH_3	Br
	127	**128**	**129**



130

entry	no.	σ (S cm^{-1})	ref
1	**66**·2CuI	2×10^{-5} (p)	47
2	**67**·2CuI	3×10^{-8} (p)	47
3	**84**·2CuI	4×10^{-3} (p)	61
4	**127**·2CuI	45 (s)	59, 60
5	**128**·2CuI	8×10^{-3} (p)	61[a]
6	**129**·2CuI	8×10^{-3} (p)	61
7	**130**·2CuI	100 (p)	59[b]

[a] Space group: $P2_1/a$. [b] Temperature dependence of conductivity given.

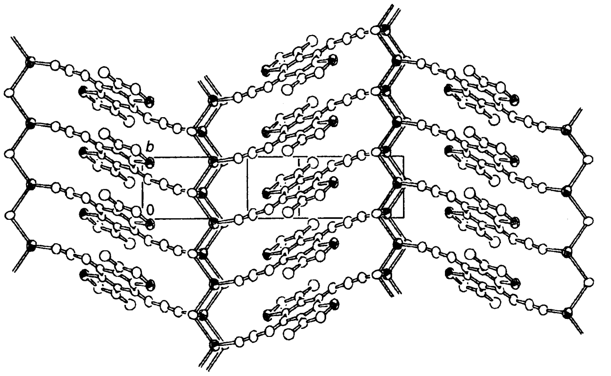
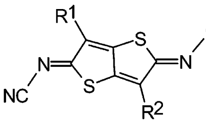


Figure 17. Crystal structure of **128**·2CuI, showing the Cu ladder and the stacking of molecules of **128**. Reprinted with permission from ref 61. Copyright 1996 The Royal Society of Chemistry.

The structure in Figure 17 seems to be typical for all of these adducts: zigzaging ladders of CuI units along the *b*-axis are connected by stacks of the bidentate acceptors. The π-overlap of the planes of the acceptors along the *b*-axis is larger (*d* = 356 pm) than that in DCNQI copper salts (*d* = 322 in $[2,5\text{-}DMe\text{-}DCNQI]_2Cu$). However, whereas the Cu–Cu distance in the latter amounts to 388 pm, in adducts according to Figure 17, only 289 pm are found, rather close to metallic copper (256 pm). Therefore, in contrast to DCNQI copper salts, charge transport in the adducts with CuI is mainly ascribed to the CuI ladders.[61] Besides, structures according to Figure 17 can be considered within the framework of crystal engineering of CuI.[367]

Table 20. DCNTTs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, $n$$Bu_4N^+BF_4^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})[384,385]



161−171

entry	no.	R^1	R^2	E_1	E_2	lg K_{SEM}
1	**161**	H	H	−0.33	+0.10	7.29
2	**162**	Me	H	−0.42	+0.01	7.29
3	**163**	Br	H	−0.23	+0.21	7.46
4	**164**	Me	Me	−0.46	−0.05	6.95
5	**165**	Me	Cl	−0.32	+0.12	7.46
6	**166**	Me	Br	−0.32	+0.12	7.46
7	**167**	Me	SMe	−0.38	+0.01	6.61
8	**168**	Br	Br	−0.14	+0.31	7.63
9	**169**	I	I	−0.14	+0.29	7.29
10	**170**	Br	SMe	−0.22	+0.18	6.78
11	**171**	SMe	SMe	−0.28	+0.09	6.27

8. Applications of DCNQI Type Acceptors

The conductivity of the acceptors, their CT complexes, and the anion radical salts discussed in sections 1−6 have been exploited for several applications. Electrophotographic layers have been described, containing various DCNQI type acceptors.[108,190,368−373] They also have been proposed as electron transferring reagents in polymeric cathodes, especially for lithium batteries.[374]

In situ preparation of DCNQI type copper salts can be used for the fabrication of conductive plastic moldings,[68] as well as DCNQI-derived CT complexes.[375] Very efficient solid capacitators are claimed to result from DCNQI type/TTF CT complexes.[376,377] Imaging of [2,5-DMe-DCNQI]$_2$Cu (crystals and films) by scanning tunneling microscopy (STM) is thought to be important for nanotechnologies.[378] For STM, materials containing DCNQI type metal salts are described as media for electron density memories.[379]

Various sensors have been designed as follows: (i) thin films of DCNQI type alkali salts for the contactless determination of spin-carrying gases, e.g., O_2 and NO;[228] (ii) DCNQI type copper salts on the surface of conducting SnO_2 as a sensor for hydrogen;[192,380] and (iii) pressure sensors from DCNQI type films.[192]

9. Other Acceptors Carrying =NCN End Groups

The exceptional features of DCNQI type acceptors have triggered the search for further variants.

9.1. 2,5-Bis(Cyanimino)-2,5-dihydrothiopheno-[3,2b]thiophenes (DCNTTs)

This variation of the quinoid backbone (R^1, R^2 = H, Br) and =C(CN)$_2$ end groups was already demonstrated to yield conducting CT complexes.[381−383] Therefore, DCNTTs **161**−**171** were prepared for the same purpose.[384,385] They also behave as two-step reversible redox systems (Table 20).

By the employed substituents, the first reduction potential E_2 can be shifted by 0.35 V. Lg K_{SEM} of ca. 7 is still large but definitely smaller than in the DCNQI series, probably due to lower Coulomb repulsion of the two negative charges in the reduced form of this longer π-system.[15,386]

Table 21. CT Complexes from DCNTTs[a]

entry	no.[b]	R^1	R^2	D	A:D[c]	σ (S cm^{-1})	ref
1	**168**	Br	Br	TTF	1:1	25 (s)	384[d]
2	**169**	I	I	TTF	1:1	6 × 10^{-2} (p)	387
3	**170**	Br	SMe	TTF	1:1	4 × 10^{-1} (p)	387
4	**165**	Me	Cl	TM-TTF	1:2	1 × 10^{-2} (p)	387
5	**166**	Me	Br	TM-TTF	1:1	2.0 (p)	384
6	**168**	Br	Br	TM-TTF	1:1	1.2 (p)	384
7	**169**	I	I	TM-TTF	1:1	2 × 10^{-1} (p)	387
8	**168**	Br	Br	BEDT-TTF	1:1	2 × 10^{-5} (p)	384
9	**169**	I	I	BEDT-TTF	1:1	2 × 10^{-6} (p)	387
10	**168**	Br	Br	TM-TSF	1:1	200 (s)[e]	384
11	**169**	I	I	TM-TSF	1:1	2 × 10^{-6} (p)	387
12	**168**	Br	Br	TTT (**145**)[f]	5:2	5 × 10^{-2} (p)	384
13	**169**	I	I	TTT (**145**)[f]	2:3	1 × 10^{-2} (p)	387

[a] TM-TTF, tetramethyl-TTF; DB-TTF, dibenzo-TTF; BEDT-TTF, bis(ethanedithio)-TTF; TM-TSF, tetramethyltetraselenofulvalene; TTT, tetrathiotetracene; (p) S cm^{-1} or (s) S cm^{-1}, powder or single-crystal conductivity. [b] cf. Table 20. [c] Stoichiometry acceptor:donor. [d] Space group: *Pccn*. [e] Mixture of conducting and insulating phases. [f] cf. Scheme 6.

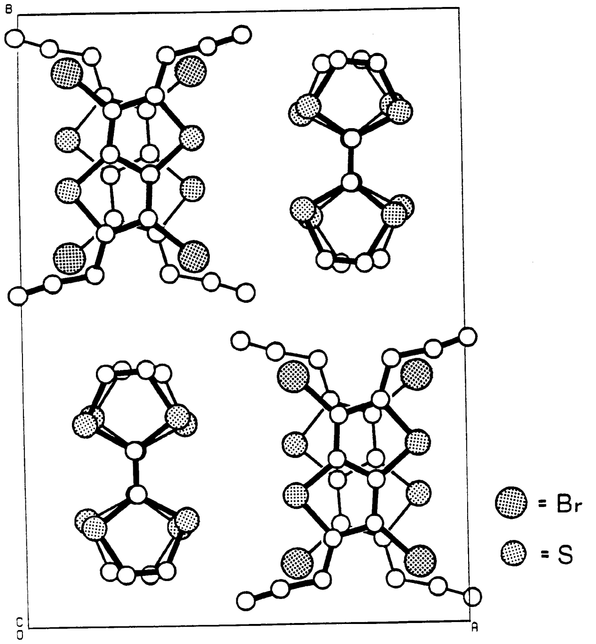


Figure 18. *a*,*b*-Projection of the crystal lattice of **168**/TTF. Reprinted with permission from ref 387. Copyright 1992 Wiley-VCH.

DCNTTs form CT complexes with various donors (Table 21). Because of powder conductivities of 0.01−2.0 S cm^{-1} for most of the CT complexes, crystal lattices with segregated stacks are to be expected. For single crystals of **168**/TTF (σ = 25 S cm^{-1}), this arrangement could be verified (Figure 18).

In contrast to known CT complexes from TCNQ and DCNQIs, the stacks are not skewed but arranged in a parallel fashion to the *c*-axis of the unit cell. Besides, the molecules of both components are centered and not ordered in the common "ring over bond" array. The DCNTT molecules are stacked showing alternation of the large atoms S and Br on one side.

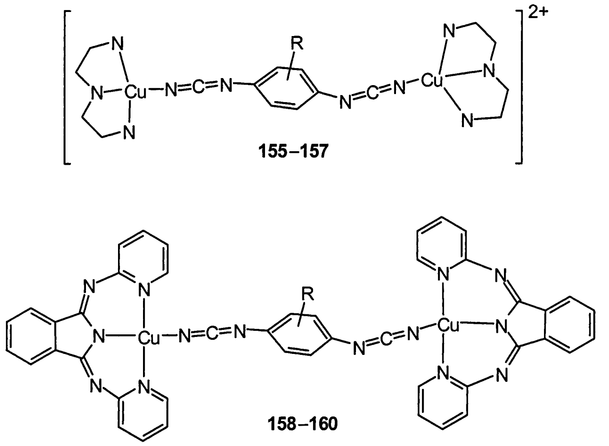
The powder conductivity of **168**/TM-TSF (entry 10) should be higher, since crystallization disclosed two

Table 22. Radical Anion Salts of DCNTTs with Organic Cations and Their Conductivities[119]

entry	no.[a]	R^1	R^2	cation[b]	*m*:*n*[c]	σ (S cm^{-1})
1	**166**	Br	Me	**146**	2:1	9×10^{-2} (s)
2	**168**	Br	Br	**146**	5:3	7×10^{-2} (s)
3	**169**	I	I	**146**	2:1	1×10^{-2} (p)
4	**168**	Br	Br	**150**	7:3	5 (p)

[a] Cf. Table 20. [b] Cf. Table 17. [c] Stoichiometry *m*:*n* of [DCNTT] and the mono- or dication.

Scheme 7. DCNQI Copper Salts with Trident Ligands

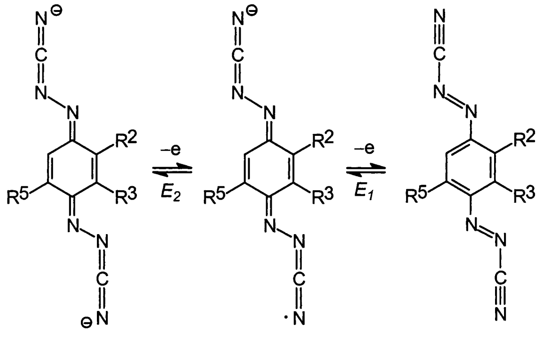


155–157

158–160

	R^1	R^2
155,158	H	H
156,159	2-Me	5-Me
157,160	2-Cl	3-Cl

Scheme 8. Two-Step Redox Systems from BDACNs



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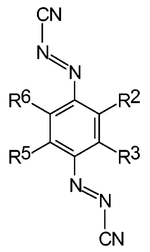
phases: an insulating one (mixed stacks, space group $P\bar{1}$) and one of unknown structure but with a conductivity of σ = 200 S cm^{-1}).[387] Preparations of DCNTT anion radical metal salts suffered from ill reproducibility and impure products.[388] However, the organic cations **146** and **150** revealed definite radical anion salts (Table 22). The structure of these well-conducting salts is unknown.

9.2. Benzene-bis(diazocyanides) (BDACNs)

An important subgroup of the violene systems (cf. Scheme 8) is represented by Wurster type redox systems in which the oxidized state contains a quinoid core.[389] TCNQs and DCNQIs are striking examples. BDACNs, however, belong to the inverse Wurster type, in which the reduced state becomes quinoid. This behavior was verified by electrochemical data of the BDACNs in Table 23.

Table 23. BDACNs Together with Their Redox Potentials E_1 and E_2 (mV, in CH_2Cl_2 vs Ag/AgCl/MeCN, $nBu_4N^+BF_4^-$) and the Corresponding Semiquinone Formation Constants (lg K_{SEM})[390]



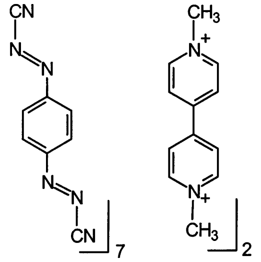
172–175

entry	no.	R^2	R^3	R^5	E_1	E_2	lg K_{SEM}
1	**172**	H	H	H	−0.15	+0.22	6.10
2	**173**	Me	H	Me	−0.15	+0.20	5.92
3	**174**	Cl	H	Cl	+0.07	+0.47	6.82
4	**175**	−(CH=CH)$_2$−		H	−0.01	+0.32	6.49

The somewhat lower LUMO energies of **172** (2.16 eV) and the naphthoderivative **175** (−2.30 eV) as compared to DCNQI (−2.51, E_2 = +0.39 V) are reflected in their lower potentials E_2. A series of dark CT complexes with weakly resolved IR spectra and good conductivities were obtained, pointing to segregated stacks in the crystals (Table 24). This ordering was substantiated for single crystals of **173**/TTF (σ = 120 S cm^{-1}) as shown in Figure 19.[390−392]

The temperature-dependent conductivity characterizes **173**/TTF as a metal-like semiconductor with a band gap of only $\Delta E \approx 40$ meV. The narrow bandwidth of the ESR signal of 2 G at 300 K points to a charge transport by BDACN molecules since cooperation with the donor TTF would produce broad ESR bands.[259]

The preparation of anion radical salts derived from BDACNs met with difficulties mainly due to high solubilities of the radical salts;[393] so far, only salt **172**/**156** was obtained with a reasonable powder conductivity.



172/**156**: σ (p) = 1×10^{-2} S cm^{-1}

The classical synthesis of diazocyanides from diazonium salts and cyanides[393,394] did not meet the expectations. A new approach was developed, starting from arylamides **176**, which are transformed to *N*-nitroso compounds **177**, a class well-known to rearrange to *O*-aryldiazoesters **178**.[243] In the presence of trimethylsilylcyanide, these esters react smoothly to the diazocyanides **179**. The reaction sequence was

Table 24. CT Complexes from BDACNs[a]

entry	no.[b]	R^2	R^3	R^5	D	A:D[c]	σ (S cm^{-1})	ref
1	**172**	H	H	H	TTF	1:1	3×10^{-1} (p)	390, 391,[d] 392[d]
2	**173**	Me	H	Me	TTF	1:1	120 (s)	390[e]
3	**174**	Cl	H	Cl	TTF	1:1	2×10^{-4} (p)	390
4	**172**	H	H	H	TM-TTF	1:1	3×10^{-3} (s)	390
5	**174**	Cl	H	Cl	TM-TTF	1:2	1×10^{-2} (p)	390
6	**174**	Cl	H	Cl	DB-TTF	1:2	2×10^{-5} (p)	390
7	**174**	Cl	H	Cl	TM-TSF	1:2	4×10^{-2} (p)	390
8	**175**	$-(CH{=}CH)_2-$		H	TTF	1:1	1 (p)	390
9	**175**	$-(CH{=}CH)_2-$		H	TM-TTF	1:1	1 (p)	390

[a] TM-TTF, tetramethyl-TTF; DB-TTF, dibenzo-TTF; BEDT-TTF, bis(ethanedithio)-TTF; TM-TSF, tetramethyltetraselenofulvalene; (p) S cm^{-1} or (s) S cm^{-1}, powder or single-crystal conductivity. [b] Cf. Table 23. [c] Stoichiometry acceptor:donor. [d] Space group: $P\bar{1}$. [e] Space group: $P1$.

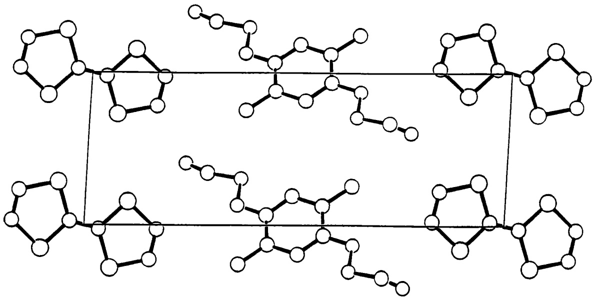
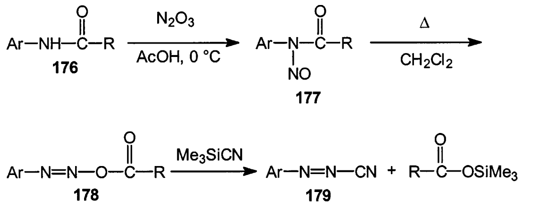


Figure 19. Crystal structure of **173**/TTF; view along [100]. Reprinted with permission from ref 390. Copyright 1991 Wiley-VCH.

adopted to the syntheses of BDACNs **173**−**175**, which were obtained in 50−70% yield.[395]



Ar = C_6H_5, p-ClC_6H_4, R = CH_3

10. Conclusions

The DCNQI type acceptors reviewed above have been proven to be powerful acceptors, which may be varied with both regard to the backbone structure and nature, number, and pattern of substituents. Besides numerous conducting CT complexes, a great variety of anion radical metal salts are available. High conductivities characterize these metal-like semiconductors. Unprecedented properties are displayed by DCNQI copper salts, especially by their temperature- and pressure-dependent conducting and magnetic behavior.

All of these properties of DCNQI metal salts can be modified in (ultra) thin films with definite structure ordering on metallic and nonmetallic conducting surfaces. Therefore, above the cited applications (section 8), these compounds should be closely considered for the developments of materials for charge transport including photovoltaic cells. Although the subject is correctly categorized under low molecular weight conductors, the special properties of these DCNQI-derived materials arise from self-organization of the subunits in specific crystal lattices.

11. Acknowledgment

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