Organic Semiconductors: Donor–Acceptor Complexes of Conjugated Bases with a Repeating Structural Unit

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Due to mesomeric stabilization, *p*-phenylenediamine and its *N*-alkyl derivatives have the property of readily forming cation-radicals; several complexes of these compounds are known as organic semiconductors. Stable cation-radicals are known also from derivatives of 4,4′-diaminodiphenylamine;[1] the same behaviour in a more pronounced form is expected in derivatives of *NN*′- di-(4-aminophenyl)-*p*-phenylenediamine and 4,4′-di-(4-aminoanilino)diphenylamine.

Complexes containing cation-radicals with a repeating structural unit were prepared by reaction with a small acceptor molecule, and it was shown that in general the electrical conductivity increases with increasing length of the base chain. Both magnitude and sign of the thermoelectric power varied unsystematically within the limits 1—2000μv/°c.

Base (VIII) (m.p. 198°) was prepared by catalytic hydrogenation of *NN*′-di-(4-nitrophenyl)-*p*-phenylenediamine;[4] base (IX) (m.p. 173°) by oxidising a mixture of 4-dimethylamino-4′-aminodiphenylamine and dimethylaniline, and base (X) (m.p. 154°) by oxidising a mixture of 4′-amino-4-dimethylaminodiphenylamine with 4-dimethylaminodiphenylamine.

Iodine complexes were prepared by reaction of leuco-base and iodine in an appropriate oxygen- and water-free solvent, whilst the radical perchlorate salts were formed by oxidation of the leuco-bases with silver perchlorate in acetone. The d.c. electrical conductivity and thermoelectric power were then measured *in vacuo* at temperatures in the range -20—$+90°$ on pressed pellets with vacuum-deposited gold electrodes, with the exception of samples 3—5 for which silver paste electrodes were used. The time stability of all the complexes was good with the exception of samples 1—5. Spin

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[1] O. Neunhoeffer and P. Heitman, *Chem. Ber.*, 1959, **92**, 245.

[2] L. Brüll and M. Minchilli, *Gazzetta*, 1939, **69**, 41.

[3] K. Huml, forthcoming publication.

[4] R. Lantz and P. Obellianne, *Bull. Soc. chim. France*, 1956, 311.

concentrations were determined by comparison with the 100%-stable free-radical *N*-oxide of 2,2,5,5-tetramethyl-Δ^3-pyrroline-4-carboxylic acid.

The following preliminary conclusions are drawn: elongation of the base chain results in an increase in the conductivity of the complexes; methylation of the amino-groups decreases the conductivity and increases the chemical stability. The influence of chain-elongation on conductivity can be explained by a smaller number of necessary intermolecular transitions and/or by crystal ordering. Although the donor properties of bases are improved by methylation of the amino-groups, a decrease in conductivity is observed. This might be the result of a lower degree of crystal ordering due to the bulk of the dimethylamino-groups or to the impossibility of hydrogen-bond formation.

TABLE I

Base*	Radical No.	form I†	Solvent used in prepn‡	σ_{23}(ohm^{-1}cm.$^{-1}$)		Unpaired electrons/g.		Actn. energy (ev)	
				air	vac.	air	vac.	air	vac.
(I) $HX\cdot NH\cdot X\cdot NH_2$	1	1·3	A	$4{\cdot}3\times10^{-8}$		$1{\cdot}2\times10^{19}$		0·52	
	2	2·0	A	$1{\cdot}7\times10^{-7}$		$2{\cdot}3\times10^{19}$		0·43	
(II) $H_2N\cdot[X\cdot NH]_2\cdot H$	3	1·0	A	$1{\cdot}4\times10^{-6}$					
	4	3·2	A	$1{\cdot}6\times10^{-5}$					
(III) $Me_2N\cdot[X\cdot NH]_2\cdot H$	5	1·0	A	$1{\cdot}2\times10^{-9}$					
(IV) $Me_2N\cdot X\cdot NH\cdot X\cdot NMe_2$	6	1·0	B	$6{\cdot}2\times10^{-6}$	$7{\cdot}4\times10^{-6}$	$1{\cdot}3\times10^{20}$	$1{\cdot}2\times10^{20}$	0·31	0·25
	7	1·0	A	$4{\cdot}5\times10^{-6}$	$5{\cdot}0\times10^{-6}$	$1{\cdot}2\times10^{20}$	$1{\cdot}3\times10^{20}$	0·32	0·30
	8	(1)	C	$4{\cdot}3\times10^{-6}$	$2{\cdot}0\times10^{-6}$	$1{\cdot}4\times10^{20}$	$1{\cdot}7\times10^{20}$	0·25	0·29
(V) $Me_2N\cdot X\cdot NMe\cdot X\cdot NMe_2$	9	2·8	D	$7{\cdot}6\times10^{-8}$		$4{\cdot}8\times10^{20}$		0·4	
(VI) $(Me_2N\cdot X)_3N$	10	2·9	E	$9{\cdot}2\times10^{-6}$	$1{\cdot}1\times10^{-5}$	$1{\cdot}7\times10^{20}$	$1{\cdot}4\times10^{20}$	0·28	0·26
	11	(1)	C	$7{\cdot}8\times10^{-5}$		$1{\cdot}4\times10^{20}$	$5\ \times10^{19}$	0·28	
(VII) $H\cdot[X\cdot NH]_2\cdot XH$	12	**	F	$1{\cdot}3\times10^{-2}$		$6{\cdot}6\times10^{19}$		0·065	
	13	(1)	C	$5{\cdot}2\times10^{-8}$	$5{\cdot}2\times10^{-8}$	$1{\cdot}4\times10^{20}$	$7\ \times10^{19}$	0·38	0·36
(VIII) $H_2N\cdot[X\cdot NH]_3\cdot H$	14	1·2	E	$3{\cdot}5\times10^{-2}$	$3{\cdot}5\times10^{-2}$	$1{\cdot}5\times10^{20}$		0·052	0·05
	15	2·0	E	$3\ \times10^{-1}$	$4\ \times10^{-1}$	$1{\cdot}6\times10^{20}$	$1{\cdot}4\times10^{20}$	0·043	0·034
(IX) $Me_2N\cdot[X\cdot NH]_2\cdot X\cdot NMe_2$	16	1·0	A	$1{\cdot}9\times10^{-4}$	$1{\cdot}9\times10^{-4}$	$9{\cdot}6\times10^{19}$	$4{\cdot}4\times10^{19}$	0·26	0·26
	17	1·0	F	$1{\cdot}3\times10^{-4}$	$1{\cdot}3\times10^{-4}$			0·28	0·28
	18	2·0	A	$1{\cdot}0\times10^{-3}$	$1{\cdot}0\times10^{-3}$	$6{\cdot}5\times10^{19}$		0·16	0·16
	19	2·0	F	$1{\cdot}3\times10^{-3}$		$8{\cdot}8\times10^{19}$		0·17	
(X) $Me_2N\cdot[X\cdot NH]_3\cdot X\cdot NMe_2$	20	1·0	A	$2{\cdot}7\times10^{-2}$	$2{\cdot}7\times10^{-2}$	$6{\cdot}7\times10^{18}$	$8{\cdot}2\times10^{19}$	0·16	0·16
	21	1·2	F		$1{\cdot}6\times10^{-2}$	$5{\cdot}5\times10^{19}$	$5{\cdot}3\times10^{19}$		0·09
	22	2·0	A	$4{\cdot}4\times10^{-4}$	$4{\cdot}4\times10^{-4}$	$3{\cdot}2\times10^{19}$	$3{\cdot}5\times10^{19}$	0·19	0·19
	23	3·1	A	$1{\cdot}5\times10^{-3}$	$1{\cdot}5\times10^{-3}$	$3{\cdot}7\times10^{19}$	$3{\cdot}5\times10^{19}$	0·13	0·13

* X = *p*-C_6H_4

† Number of I (or if given in parentheses, ClO_4) per molecule of base

‡ A = 1,2-Dichloroethane, B = methanol, C = acetone, D = cyclohexane, E = dioxan, F = nitromethane

** We have not succeeded in preparing the complex $(Ph\cdot NH\cdot C_6H_4\cdot NH\cdot Ph)_2\ I_3$ by the method given in reference 2. According to the chemical and *X*-ray structural analyses[3] (of a single crystal) our complex has the stoicheiometry $(Ph\cdot NH\cdot C_6H_4\cdot NH\cdot Ph)_5\ I_{12}$.

The coincidence of conductivities and concentrations of unpaired electrons in the iodine complex and perchlorate salt of base (IV) may be a consequence of the great similarity of the crystal structure of the two compounds,[5] *viz.* identical unit-cell dimensions and the same type of symmetry.

The high conductivity of the iodine complex derived from the relatively weak donor (VII) may be connected with the polyiodide character of this compound,[3] in which a smaller mean distance between iodine atoms was found. The perchlorate salt, with a substantially higher concentration of unpaired electrons than the corresponding iodine complex, exhibits an electrical conductivity which is six orders of magnitude smaller.

The results obtained indicate that substances with a low resistivity have a low activation energy of conductivity and a low thermo-e.m.f. The solvents from which the samples were prepared have little influence upon the conductivity and its activation energy, but they do influence the value, and even the sign, of the thermo-e.m.f. From the sign of the vacuum thermo-e.m.f. it is evident that both electrons and holes may act as carriers of electric current in these compounds. The concentration of unpaired electrons is in no direct simple relationship to the electrical conductivity at room temperature.

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[5] K. Toman, forthcoming publication.