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The Crystal Structure of Some Conducting Organic Substances. II.
Projection of the Crystal Structure of the Iodide of *N*,*N*′-Diphenyl-*p*-phenylenediamine Radical

By K. Huml

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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The projection of the crystal structure of the iodide of *NN*′-diphenyl-*p*-phenylenediamine radical on the (010) plane has been determined. The two-dimensional space group is *p*2; planar cell parameters are $a=14{\cdot}00$, $c=18{\cdot}31$ Å, $\beta=109°7'$. The crystals are twins with a twinning axis of $T\equiv[401]$, twinning angle $\tau=180°$ and twinning index $n=2$. The iodine atoms are arranged in columns perpendicular to the (010) plane. The individual columns are mutually shifted in a statistically arbitrary manner in the direction of their axis, a fact which is apparent by the formation of diffuse layer lines.

Introduction

The crystals of some iodides of organic radicals have a significant electrical conductivity (Honzl, Ulbert, Hádek & Tlusťáková, 1965). For this reason increased attention is being given to them, and their structure is being studied (Toman & Očenášková, 1966; Toman, Očenášková & Huml, 1967). In this paper a partial solution of the molecular arrangement in crystals of the iodide of *NN*′-diphenyl-*p*-phenylenediamine radical is presented. The crystals obtained showed disorder, manifested by diffuse non-zero layer lines (Fig. 1). For this reason we have limited ourselves to the determination of the structure only in the projection onto the (010) plane and to the explanation of this disorder.

Experimental

Crystals of the iodide of *NN*′-diphenyl-*p*-phenylenediamine radical were prepared by mixing hot solutions of the base and iodine in ethanol (Honzl, Ulbert, Hádek & Tlusťáková, 1965). The composition of the crystals corresponds to the formula

$$12\mathrm{I}\,.\,5(\mathrm{C_6H_5NHC_6H_4NHC_6H_5})\,.$$

The measured density is 2·04 g.cm^{-3}. The crystals are strongly pleochroic, which is evidence for a linear arrangement of iodine atoms in the direction of the longitudinal crystal axis.

The oscillation picture (Cu $K\alpha$ radiation, photograph taken about the longitudinal crystal axis) shows, beside two diffuse layer lines with a common period of 9·43 Å, traces of discrete reflexions, lying on the equator and on one non-zero layer line, corresponding to a period of 3·77 Å (Fig. 1). The intensity of the diffuse layers depends, in a non-monotonic manner, on the ordinary number of the layer line, but not on the coordinates in the given diffuse plane. This means that on Weissenberg pictures of diffuse layers only a continuous diffuse intensity distribution is visible, decreasing monotonically in dependence on the atomic and temperature factors. On the oscillation picture (Fig. 1) the traces of the first two diffuse layer lines are so weak that they fade into the background. On the other hand the third and fourth diffuse layer lines are distinct, and their intensity could be measured in dependence on the ordinary number of the diffuse layer line by means of an optical densitometer. It follows from a Weissenberg picture of the discrete layer line and equator, that in projection the planar symmetry of the crystal is *p*2, with planar cell parameters of $a=14{\cdot}00$, $c=18{\cdot}31$ Å and $\beta=109°7'$. We have carried out measurements on some thirty crystals, finding that all the crystals used were twins which may be characterized by rotation through a twinning angle $\tau=180°$ around the twinning axis $T\equiv[401]$, perpendicular to the (100) plane (Figs. 2, 3). The twinning index is $n=2$, according to the notation used in *International Tables for X-Ray Crystallography* (1959). On the equator $h0l$, owing to systematic absences, only reflexions with $l=2n$ are present. That means that on the equator only those reflexions remain, which correspond to the common lattice of the twin, and to which the two parts of the twin contribute in

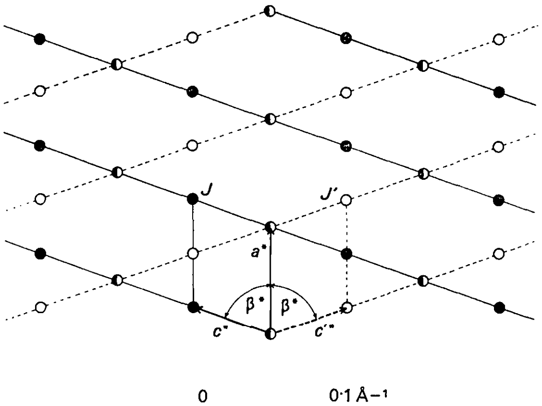

Fig. 1. The non-zero reciprocal lattice section of a normal twin; twin axis normal to the (100) plane. The reciprocal lattice of one individual is denoted with full circles and full lines, of the second individual with open circles and dashed lines. Half-filled circles show points common to both reciprocal lattices. *J*, *J*′ are corresponding points mentioned in text.

coincidence. Assuming that both parts of the twin reflect independently, then intensities may be calculated from the measured intensities of the twin, which would correspond to a single-crystal of the substance (Huml, 1966). For simplifying the following calculations, let us select an auxiliary orthogonal coordinate system in such a way, that the $\bar{a}$ axis is parallel to the twinning axis T. The intensities of compound reflexions with respect to this axis may then be written as the superposition of the intensities from the two parts of the twin:

$$\begin{aligned} J &= (1-v)J_H + vJ_{\bar{H}} \\ J' &= vJ_H + (1-v)J_{\bar{H}} \qquad (1) \end{aligned}$$

where J, J' are the intensities of compound reflexions accessible to measurement, J_H and $J_{\bar{H}}$ being the desired compound intensities of the corresponding single-crystal. Assuming that the total volume of the twin is unity, then v denotes the volume of one part of the twin. The value of v may be estimated, for example, from the asymmetry of compound reflexions, using the relations

$$\begin{aligned} &0 \le v \le J/(J+J')\,, \\ &0 \le v \le J'/(J+J')\,, \qquad (2) \end{aligned}$$

which follow from equations (1), using the assumption that the intensity measured is always a non-negative quantity. In our case we have estimated that the sample measured has a value of $v=15\%$. Intensities on the equator $h0l$ were measured in the normal-beam arrangement with a Hilger & Watts diffractometer (Mo $K\alpha$ radiation) by means of the ω-scan method, in which the crystal is rotated and the counter remains stationary during the measurement. Each reflexion was measured in two positions, coupled by the Friedel law. The intensities of very strong reflexions were attenuated by means of aluminum filters of known absorption.

Determination of the crystal structure in the projection onto the (010) plane

We have determined the position of iodine atoms from the Patterson projection, calculated with intensities modified according to equations (1) and (2). The phase problem has been solved by the heavy-atom method. From an electron-density projection on the (010) plane (Fig. 3) we obtained input data for the position of atoms for refining the structure by means of the least-squares method (Table 1). With respect to the small contribution of the organic part of the crystal to the dif-

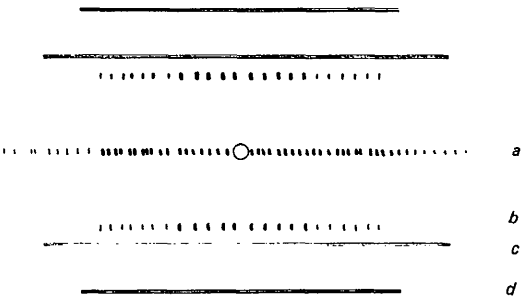

Fig. 2. Schematic diagram of the oscillation photograph taken about the longitudinal crystal axis. a – equatorial discrete layer line; b – non-zero discrete layer line; c, d – diffuse layer lines. The layers are perpendicular to the oscillation axis.

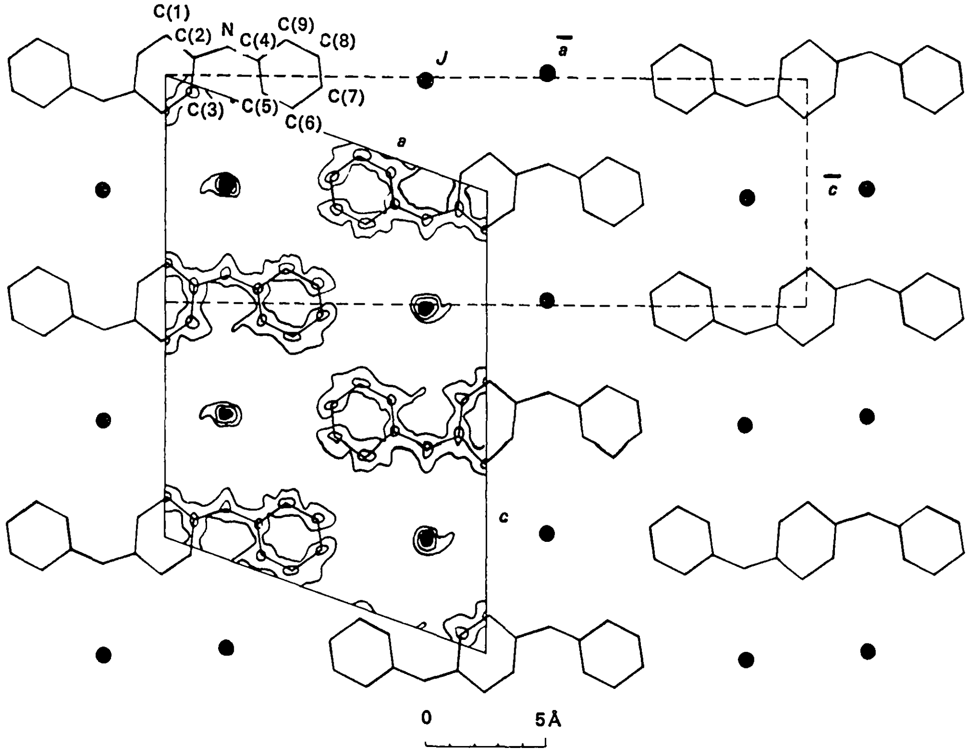

Fig. 3. The electron density projection on (010). a, c – the true cell axes (full lines); $\bar{a}, \bar{c}$ – the orthogonal cell axes (dashed lines).

fracted radiation the organic part was taken as constant in the refining process, with an isotropic temperature factor of $B=3$ Å^2. The refinement was limited to the position of iodine atoms, with the assumption that iodine atoms have anisotropic temperature vibrations. 240 non-zero structure factors were included in the calculation. In five cycles of the refinement the R index was reduced to 0·136. The resulting coordinates and anisotropic temperature parameters of the iodine atom are given in Table 2. The input and calculated structure factors are given in Table 3. Values of scattering factors for the C and N atoms have been taken from the study by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), values for iodine atoms from Thomas & Umeda (1957). In refinement we assumed that the weight of all structure factors is unity. The calculations were carried out on the National Elliott 803 B computer. The program for the Fourier synthesis was written by Tichý (1966). For the least-squares refinement, the program by Očenášková (1966) was used.

Table 1. *Orthogonal input coordinates (fractional)*

	$\bar{x}$	$\bar{z}$
C(1)	0·002	−0·150
C(2)	0·045	−0·070
C(3)	0·037	0·080
C(4)	0·144	−0·060
C(5)	0·148	0·070
C(6)	0·196	0·130
C(7)	0·242	0·050
C(8)	0·237	−0·080
C(9)	0·187	−0·140
N	0·095	−0·110
I	0·402	0·012

Table 2. *Refined orthogonal coordinates (fractional), thermal parameters, and their standard deviations,* for *the iodine atoms*

$\bar{x}=0{\cdot}4032$	$\sigma(\bar{x})=0{\cdot}0027$ Å
$\bar{z}=0{\cdot}0146$	$\sigma(\bar{z})=0{\cdot}0018$
$B_{11}=9{\cdot}95$ Å^2	$\sigma(B_{11})=0{\cdot}26$ Å^2
$B_{33}=4{\cdot}28$	$\sigma(B_{33})=0{\cdot}13$
$B_{13}=0{\cdot}53$	$\sigma(B_{13})=0{\cdot}15$

Determination of disorder in the crystal

We see from a projection of the crystal structure on the (010) plane, and in agreement with the crystal pleochroism, that iodine atoms are arranged in columns perpendicular to the (010) plane, while the organic part of the molecule is located in successive layers, with a period of 3·77 Å. The NH groups of the planar organic molecule are oriented in the direction towards the iodine atom, agreeing with our earlier communication (Toman & Očenášková, 1966). It may be shown, on the basis of elementary diffraction theory, that the disorder of the crystal, manifested by diffuse layer lines, may be explained by a statistically random mutual shift of the iodine columns in the direction of the longitudinal axis of the columns, the organic part of the molecule remaining three-dimensionally perfectly arranged, with discrete layer lines corresponding to it.

Table 3. *Observed and calculated structure factors*

h	k	l	$\|F_o\|$	F_c
0	0	2	273	287
0	0	-2	273	287
0	0	4	90	96
0	0	-4	90	96
0	0	6	69	66
0	0	-6	69	66
0	0	8	49	39
0	0	-8	49	39
0	0	10	11	13
0	0	-10	11	13
1	0	1	96	-91
1	0	-1	96	-92
1	0	3	210	-191
1	0	-3	162	-151
1	0	5	164	-166
1	0	-5	95	-89
1	0	7	89	-96
1	0	-7	36	-28
1	0	9	48	-54
1	0	-9	6	-8
2	0	0	54	66
2	0	2	127	120
2	0	-2	32	0
2	0	4	108	107
2	0	-4	32	-10
2	0	6	90	79
2	0	-6	34	-16
2	0	8	67	56
2	0	-8	40	-24
2	0	10	46	37
2	0	-10	13	-18
3	0	1	22	19
3	0	-1	29	30
3	0	3	38	15
3	0	-3	96	79
3	0	5	19	-14
3	0	-5	92	93
3	0	7	28	-29
3	0	-7	70	64
3	0	9	27	-20
3	0	-9	35	37
4	0	0	126	-141
4	0	2	120	-108
4	0	-2	186	-188
4	0	4	80	-68
4	0	-4	156	-158
4	0	6	37	-30
4	0	-6	101	-96
4	0	8	9	-12
4	0	-8	64	-63
4	0	10	0	0
4	0	-10	47	-40
5	0	1	236	243
5	0	-1	247	244
5	0	3	144	136
5	0	-3	151	142
5	0	5	97	95
5	0	-5	118	114
5	0	7	58	56
5	0	-7	82	83
5	0	9	0	15
5	0	-9	31	35
6	0	0	157	-165
6	0	2	197	-194
6	0	-2	156	-148
6	0	4	140	-145
6	0	-4	95	-96
6	0	6	87	-74
6	0	-6	58	-38
6	0	8	49	-49
6	0	-8	19	-17
6	0	10	33	-36
6	0	-10	0	-7
7	0	1	83	82
7	0	-1	75	76
7	0	3	96	89
7	0	-3	56	49
7	0	5	93	93
7	0	-5	22	3
7	0	7	78	68
7	0	-7	42	-31
7	0	9	36	35
7	0	-9	27	-29
8	0	0	58	43
8	0	2	29	-5
8	0	-2	85	89
8	0	4	36	-22
8	0	-4	78	82
8	0	6	11	-27
8	0	-6	50	44
8	0	8	36	-25
8	0	-8	0	22
8	0	9	11	-18
8	0	-9	11	22
9	0	1	110	-105
9	0	-1	117	-110
9	0	3	95	-83
9	0	-3	127	-119
9	0	5	31	-27
9	0	-5	99	-92
9	0	7	20	3
9	0	-7	61	-57
9	0	9	15	4
9	0	-9	38	-36
10	0	0	123	126
10	0	2	77	71
10	0	-2	95	101
10	0	4	72	60
10	0	-4	81	81
10	0	6	81	77
10	0	-6	90	93
10	0	8	42	47
10	0	-8	67	66
10	0	10	11	9
10	0	-10	11	24
11	0	1	134	-144
11	0	-1	133	-133
11	0	3	143	-143
11	0	-3	128	-121
11	0	5	69	-67
11	0	-5	50	-51
11	0	7	11	-13
11	0	-7	11	-3
11	0	9	11	-13
11	0	-9	11	-2
12	0	0	78	70
12	0	2	76	73
12	0	-2	25	31
12	0	4	57	55
12	0	-4	36	18
12	0	6	11	49
12	0	-6	11	10
12	0	8	42	37
12	0	-8	0	-7
12	0	10	11	19
12	0	-10	11	-13
13	0	1	28	14
13	0	-1	6	10
13	0	3	15	-3
13	0	-3	38	35
13	0	5	50	-34
13	0	-5	61	52
13	0	7	0	-37
13	0	-7	46	33
13	0	9	11	-20
13	0	-9	11	15
14	0	0	72	-71
14	0	2	36	-35
14	0	-2	88	-84
14	0	4	25	-15
14	0	-4	53	-55
14	0	6	0	-8
14	0	-6	33	-31
14	0	8	0	-3
14	0	-8	31	-29
14	0	10	11	3
14	0	-10	11	-24
15	0	1	65	59
15	0	-1	60	69
15	0	3	56	42
15	0	-3	69	61
15	0	5	52	45
15	0	-5	64	63
15	0	7	31	33
15	0	-7	45	48
15	0	9	11	8
15	0	-9	11	16
16	0	0	76	-65
16	0	2	73	-82
16	0	-2	63	-59
16	0	4	47	-55
16	0	-4	47	-44
16	0	6	18	-13
16	0	-6	18	-18
16	0	8	11	-9
16	0	-8	11	-12
16	0	10	11	-14
16	0	-10	11	-12
17	0	1	38	31
17	0	-1	33	28
17	0	3	42	30
17	0	-3	16	21
17	0	5	38	36
17	0	-5	11	18
17	0	7	11	29
17	0	-7	22	4
17	0	9	11	10
17	0	-9	11	-5
18	0	0	27	-22
18	0	2	11	-16
18	0	-2	11	-5
18	0	4	16	-11
18	0	-4	16	22
18	0	6	27	-10
18	0	-6	27	26
18	0	8	9	-10
18	0	-8	22	16
18	0	10	11	-7
18	0	-10	11	13
19	0	1	31	-24
19	0	-1	11	-35
19	0	3	20	-12
19	0	-3	40	-34
19	0	5	0	-1
19	0	-5	35	-25
19	0	7	11	3
19	0	-7	11	-20
19	0	9	11	3
19	0	-9	11	-14
20	0	0	60	67
20	0	2	32	32
20	0	-2	44	52
20	0	4	15	7
20	0	-4	27	22
20	0	6	20	8
20	0	-6	20	15
20	0	8	11	4
20	0	-8	11	11
20	0	10	11	-1
20	0	-10	11	4
21	0	1	11	0
21	0	-1	11	6
21	0	3	25	-36
21	0	-3	25	-28
21	0	5	33	-32
21	0	-5	33	-33
21	0	7	11	-15
21	0	-7	11	-14
21	0	9	11	-12
21	0	-9	11	-7
22	0	0	40	36
22	0	2	27	29
22	0	-2	6	11
22	0	4	11	9
22	0	-4	11	-3
22	0	6	11	7
22	0	-6	11	2
22	0	8	11	4
22	0	-8	11	2
22	0	10	11	1

Distances of the iodine atoms are modulated in the column, following from the fact that the intensity of the diffuse layer lines depends non-monotonically on their ordinary number. It follows from a measurement of the intensity of diffuse layer lines in dependence on their ordinary number, that iodine atoms are built into the columns in the form of triiodide ions; the distance of atoms in the triiodide ion is approximately 2·99 Å and the shortest distance between iodine atoms in neighbouring triiodide ions along the chain is 3·44 Å.

Discussion

All the crystals we have measured so far have been disordered. Notwithstanding the difficulties mentioned, we succeeded in solving the projection of the crystal structure on the (010) plane and in explaining the disorder in the crystal. It may be shown (Huml, 1966) that, with respect to the special position of the iodine atoms close to the twinning axis, the calculation of the structure in the projection is not very sensitive to the precision of the estimation of volumes of the parts of the twin. It has been found in the course of the study that the degree of disorder in the crystals depends on the method of their preparation; *e.g.* crystals grown from nitromethane were nearly ordered. The diffuse reflexions disintegrate into discrete traces, and more discrete layer lines appear. A common period of 18·86 Å may be ascribed to all the layer lines. We hope to succeed in preparing perfect crystals, so as to allow a complete three-dimensional structure of this substance to be determined.

I wish to thank Dr K. Toman for guidance in this study, and Dr J. Honzl for preparation of the crystals and fruitful discussions of the chemical problems involved. I also wish to thank D. Očenášková and K. Tichý for kindly placing the computer programs at my disposal. Finally I have the honour of thanking Dr Ing. B. Sedláček DSc. for his lasting interest in my work.

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The Crystal Structure of Some Conducting Organic Substances. III. Perchlorate of 4,4′-Bis(dimethylamino)diphenylamine Radical

BY K. TOMAN, D. OČENÁŠKOVÁ AND K. HUML

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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The structure of the perchlorate of 4,4′-bis(dimethylamino)diphenylamine radical was determined. The form and conformation of the radical is described and its dependence on the nature of the anion stated. The cation-radical in the perchlorate is much less planar than in the iodide. The bond distances in the radical do not depend on the nature of the anion.

1. Introduction

According to Honzl, Ulbert, Hádek & Tlusťáková (1965), the perchlorate of the 4,4′-bis(dimethylamino)diphenylamine radical (DADA) shows similar electrical properties to its iodide. The crystal and molecular structure of the iodide of the DADA radical have been described by two of us previously (Toman & Očenášková 1966). In considering the relations between the physical properties of this substance, the bonding state of the radical and the packing of the radical molecules, the knowledge of the crystal structure of the perchlorate of the DADA radical appeared to be desirable. It was particularly interesting to find out whether, and in what degree, the substitution of the iodide anion by the perchlorate anion changes the character of bonds, the conformation and the packing of the DADA radicals.

2. Experimental

The crystals used in this work were provided by Dr J. Honzl of this Institute; they were prepared according to Neunhoeffer & Heitmann (1959).