The Crystal Structure of some Conducting Organic Substances.
I. The Iodide of 4,4'-Bis(dimethylamino)diphenylamine Radical

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The structure of the iodide of 4,4' bis(dimethylamino)diphenylamine was determined. The crystals are monoclinic, space group $C2c$, $a=12\cdot97$, $b=14\cdot22$, $c=9\cdot60$ Å, $\beta=109\cdot9°$. The unit cell contains 4 stoichiometric units. The cation-radical is roughly planar; the interatomic distances indicate conjugation of bonds.

Introduction

According to Honzl, Ulbert, Hádek & Tlustáková (1966), the electrical conductivity of the iodide and perchlorate of 4,4'-bis(dimethylamino)diphenylamine radical is of the order 10^{-6} ohm^{-1}.cm^{-1}. An understanding of this comparatively high conductivity can be obtained on the basis of the knowledge of its crystal structure. The aim of the present investigation has been to determine the structure of this substance with such precision that not only the general arrangement of ions in the crystal lattice, but also the character of chemical bonds in the organic part of the crystal can be elucidated.

Experimental

The crystals used in this investigation were furnished by Dr J. Honzl of this Institute. As the method of preparation of the iodide of 4,4'-bis(dimethylamino)diphenylamine radical described by Neunhoffer & Heitmann (1959) led to very small crystals, the following alternative procedure was used: the solution of 51 mg of leuco-base in $1\cdot3$ ml of purified dimethylformamide was added (under purified argon) to the solution of $25\cdot4$ mg of iodine in $1\cdot7$ ml of dimethylformamide at $50°C$. After a few hours, dark violet needles appeared. Their composition corresponds to the formula

$$I^-[(CH_3)_2N\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N(CH_3)_2]^+\cdot$$

With these crystals, Weissenberg photographs (with Cu $K\alpha$ radiation) gave the following information. The substance is monoclinic,

$$a=12\cdot97,\quad b=14\cdot22,\quad c=9\cdot60\text{ Å},\quad \beta=109\cdot9°\,.$$

The space group is $C2c$ or Cc. The observed density of $1\cdot54$ g.cm^{-3} corresponds to 4 stoichiometric units in the unit cell (calculated density $1\cdot53$ g.cm^{-3}).

The measurement of intensities of most reflexions was performed on the equator and on the first eight layer lines about the [001] rotation axis, with Mo $K\alpha$ radiation. We confined ourselves to the interval $0<2\theta<50°$. For data collection a counter diffractometer with a scintillation counter and pulse height analyser operated by 'normal beam, ω-scan' technique

was used. Reflexions not measurable about the [001] rotation axis and reflexions having in this orientation a very large Lorentz factor ($Y<10°$) were measured on the equator and on the first three layer lines about the [010] rotation axis by the same technique. In this way 1602 independent reflexions were measured, 357 of which were of zero intensity. Every reflexion was measured at least twice at different settings of the crystal. As the cross section of our crystal was approximately square with a side of $0\cdot1$ mm (linear absorption coefficient $31\cdot5$ cm^{-1}), the absorption correction was neglected.

Determination of the approximate structure and the refinement

Supposing the space group is $C2c$ (the success of the refinement confirmed this hypothesis) the iodide ions can be placed in the following special fourfold positions: (*a*), (*b*), (*c*), (*d*), (*e*) (*International Tables for X-Ray Crystallography*, 1952). The Patterson projection in the direction [001] showed that iodide ions are to be placed in position (*e*) with coordinates $x=0$, $y=0\cdot20$, $z=\frac{1}{4}$.

Neglecting the contributions of all other atoms except iodine, the signs of the structure factors of $hk0$, $hk1$, $hk2$, $hk3$ and $hk4$ reflexions were determined. This enabled us to calculate the generalized projections of electron density in the [001] direction. On these projections we succeeded in recognizing the location and the form of the 4,4'-bis(dimethylamino)diphenylamine cation-radical. The approximate coordinates of the light atoms obtained in this manner, together with coordinates of iodide ions were inserted in the recalculation of signs of the structure factor. Generalized projections of electron density obtained with this set of corrected signs of structure factors showed the organic radical with very good resolution. In Fig. 1 the superposition of the modulus projections $\sum\limits_{i=0}^{4}|\varrho_i|$ is reproduced. The contribution of $|\varrho_0|$ to the sum is taken with half weight. The calculation of the generalized projections was performed on the Ferranti-Sirius machine.

The coordinates obtained in this way were further refined by the least-squares method. The temperature factors of light atoms were taken as different but isotropic. An isotropic temperature factor for the iodide ions was used in the first alternative method of refinement, but in later stages the anisotropy of temperature vibrations was allowed for. The refinement was executed in the initial stages with constant weights. The analysis of the dependence of $(F_o - F_c)^2$ on F_o showed the following weighting scheme to be satisfactory

$$w = 1/(18\cdot54 + 0\cdot1442 |F_o|),\qquad(1)$$

this was later adopted in the last alternative method of refinement. To make the refinement more efficient the whole number of observed structure factors was divided according to indices h and k into four sets:

Set A: first 500 reflexions, reflexions of zero intensity included.

Set B: first 1000 reflexions, reflexions of zero intensity included.

Set C: the whole set of 1602 reflexions.
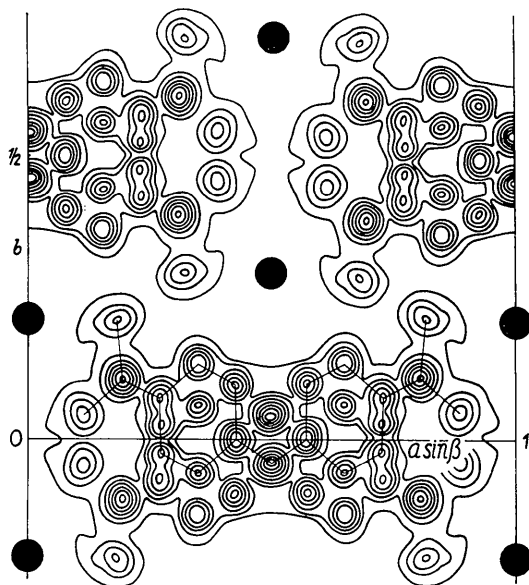
Fig. 1. Superposition of first five generalized modulus projections $\sum\limits_{0}^{4} |\varrho_i|$ along [001].

Set D: the whole set, reflexions of zero intensity omitted.

In the case of reflexions of zero intensity, the half threshold value of the structure factor was inserted into the calculation.

The least-squares refinement was executed in four alternative ways;

Alternative (1): all atoms were refined isotropically, with unit weights.

Alternative (2): iodide ions were refined anisotropically, other atoms isotropically, with unit weights.

Alternative (3): iodide ions were refined anisotropically, other atoms isotropically, with unit weights, hydrogen contributions included.

Alternative (4): as alternative 3 but with weights according to formula (1).

In alternatives (3) and (4) the contributions of the hydrogen atoms were included only in the calculation of F_c. Their positions were not refined. Assumed hydrogen coordinates are summarized in Table 1. The positions of hydrogen atoms of aromatic nuclei were chosen so that the C–H bonds were 1·08 Å long and pointing to the center of the aromatic nucleus. In the case of methyl groups, six hydrogens of half weight were placed on the surface of a cone with an axis coinciding with the C–N bond and having an apex angle of 142°. The C–H distance in this case was taken to be 1·09 Å. The hydrogen atom of the NH group was not considered.

In Table 2, the final values of the reliability index $R = \sum ||F_o| - |F_c||/\sum |F_o|$ for different alternative methods of refinement are shown. It is evident from this table, that the anisotropic treatment of the iodine contributions resulted in a striking improvement of the reliability index. On the other hand, the introduction of the correction for hydrogen contributions to structure factors brought no significant improvement. The

Table 2. *Progress of refinement*

Alternative	Set A	Set B	Set C	Set D
(1)	0·139	0·155	—	—
(2)	0·068	—	—	—
(3)	0·066	—	0·102	—
(4)	—	—	0·108	0·072

Table 1. *Assumed fractional coordinates of hydrogen atoms*

	x	y	z		x	y	z
H(2)	0·349	−0·137	0·072	H(5)	0·354	0·208	0·914
H(3)	0·212	−0·080	0·830	H(6)	0·490	0·150	0·152

Hydrogen atoms attached to C(7)

0·049	0·077	0·562		0·029	0·055	0·644
0·083	−0·009	0·706		0·135	−0·031	0·666
0·151	−0·009	0·603		0·094	0·055	0·527

Hydrogen atoms attached to C(8)

0·111	0·223	0·623		0·183	0·223	0·586
0·251	0·227	0·662		0·254	0·241	0·775
0·193	0·244	0·803		0·121	0·238	0·729

Table 3. *Organic part of the crystal. Fractional coordinates, isotropic temperature parameters and their standard deviations*

Atom	x	y	z	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
C(1)	0·4286	0·0018	0·1245	3·66 Å²	0·009 Å	0·010 Å	0·010 Å	0·17 Å²
C(2)	0·3502	0·0599	0·5270	3·74	0·009	0·010	0·010	0·17
C(3)	0·2729	0·0265	0·4018	4·20	0·010	0·011	0·011	0·19
C(4)	0·2709	0·0711	0·8637	3·82	0·009	0·010	0·010	0·16
C(5)	0·3521	0·1305	0·9590	4·07	0·010	0·010	0·010	0·18
C(6)	0·4286	0·0959	0·0818	3·61	0·009	0·010	0·010	0·17
C(7)	0·1121	0·0423	0·6390	6·24	0·014	0·014	0·014	0·29
C(8)	0·1872	0·2065	0·7063	6·04	0·015	0·014	0·015	0·31
N(1)	0·5000	0·0378	0·7500	3·24	—	0·009	—	0·18
N(2)	0·1940	0·1045	0·7389	4·92	0·009	0·010	0·010	0·19

final agreement between calculated and observed structure factors (alternative (4), set C and D) is very satisfactory. We can therefore consider the use of the space group $C2c$ as sufficiently substantiated.

In Table 3, the final fractional coordinates and the isotropic temperature parameters B of atoms of the organic part of the crystal (from alternative (3) on set C) are collected. Standard deviations, shown in the last four columns of this table, are based on diagonal elements of normal equations only. Temperature coefficients B used here are related to the temperature factors as usual by the expression $\exp(-B\sin^2\theta/\lambda^2)$.

Table 4 shows the fractional coordinates of iodide ions, the standard deviation $\sigma(y)$, the anisotropic temperature parameters β_{ij} and their standard deviations. Temperature parameters β_{ij} are used in the expression for the temperature factor, $\exp(-\sum_{ij}\beta_{ij}h_ih_j)$.

Table 4. *The iodide ion. Fractional coordinates, anisotropic temperature parameters and standard deviations*

	$x=0$	$y=0·2041$	$z=\frac{1}{4}$	$\sigma(y)=0·004$ Å	
ij	β_{ij}	$\sigma(\beta_{ij})$	ij	β_{ij}	$\sigma(\beta_{ij})$
11	0·00832	0·00006	22	0·00337	0·00004
12	0	—	23	0	—
13	0·00100	0·00008	33	0·01536	0·00014

Analysing the results shown in Table 3, we were astonished by the fact that the atom C(8) runs appreciably out of the plane of the aromatic nucleus, whilst the atom C(7), the second carbon atom of the dimethylamino group, does not deviate. Considering the possibility that the refinement, with respect to C(8), reached a wrong minimum, we placed C(8) in the position $x=0·1940$, $y=0·2065$, $z=0·6970$ and calculated three further cycles of least-squares refinement (alternative (4) on set C). The coordinates of C(8) after refinement returned to the original values as given in the Table 3. Therefore we consider these as final. The observed and calculated structure factors are summarized in Table 5.

The least-squares calculations were performed on the National Elliott 803B machine. The method adopted by us uses block-diagonal approximation of normal equations in a similar way to that described by Cruickshank *et al.* (1961) for the Ferranti Pegasus machine.

Our program is written in Autocode, with only the most frequently repeating loops in machine code. One cycle (alternative 4 on set C) took about 100 minutes.

Bond distances and angles, calculated from values from Table 3, are collected in Table 6.

Some shorter intermolecular distances are summarized in Table 7. Estimated standard deviations of the interatomic distances are close to 0·017 Å [with the exception of those involving atoms I, C(7) and C(8)]. Estimated standard deviation of the valence angles is 1·5°.

The best plane through the atoms of the aromatic nucleus [C(1) to C(6)] corresponds to the equation:

$$-10·883\,X+2·834\,Y+7·395\,Z+0·067=0,$$

where X, Y and Z are the fractional coordinates referred to the monoclinic axes of the direct crystal lattice. The origin is placed in the position of atom N(1). The calculation was performed by the method of Schomaker, Waser, Marsh & Bergman (1959). The deviations of atoms from this plane are listed in Table 8. The r.m.s. deviation of atoms of the benzene ring from the mean plane is 0·007 Å, but in spite of that we do not believe that the deviations from planarity of the aromatic nucleus are significant. It is of interest that the nitrogen atom and one of the two carbon atoms of the dimethylamino group are located in the plane of the benzene ring, whereas the second carbon atom of this group is very significantly displaced. It seems that the nitrogen atom of the central NH group deviates significantly from the plane of the benzene ring.

The isotropic temperature factors of atoms in the organic cation-radical increase slightly with the distance from the central atom N(1). This perhaps can be attributed to the librational motion of the molecule about an axis going through N(1). We did not examine this matter further as the presence of heavy iodide ions makes a further investigation of this more subtle point rather uncertain.

Discussion

The form of the 4,4'-bis(dimethylamino)diphenylamine radical is shown in Fig. 2. The radical has twofold symmetry and is approximately planar. If the plane through the atoms C(1), N(1) and C(1') is considered as the plane of the molecule, then the aromatic nuclei

Table 5. *Observed and calculated structure factors*

h	k	l	Fo	Fc
0	0	2	200.1	-199.0
0	0	4	139.9	111.7
0	0	6	111.5	-106.4
0	0	8	69.9	65.8
2	0	0	108.9	100.3
2	0	2	171.7	-174.1
2	0	-2	129.3	-121.1
2	0	4	128.4	136.8
2	0	-4	100.0	88.7
2	0	6	86.8	-63.7
2	0	-6	89.4	-77.6
2	0	8	40.7	36.3
2	0	-8	58.4	45.9
4	0	0	142.5	140.3
4	0	2	118.6	-117.2
4	0	-2	291.3	-314.8
4	0	4	79.7	51.9
4	0	-4	94.3	97.7
4	0	6	80.6	-76.8
4	0	-6	94.7	-93.2
4	0	8	31.9	30.2
4	0	-8	93.0	75.2
6	0	0	123.9	119.9
6	0	2	114.9	-113.0
6	0	-2	130.1	-133.8
6	0	4	131.9	128.4
6	0	-4	160.2	172.9
6	0	6	60.2	-47.4
6	0	-6	62.0	-53.0
6	0	8	31.9	26.5
6	0	-8	32.0	24.1
8	0	0	79.7	76.0
8	0	2	49.6	-50.6
8	0	-2	83.2	-44.6
8	0	4	44.3	49.7
8	0	-4	72.6	71.8
8	0	6	34.5	-32.1
8	0	-6	11.9	-24.9
8	0	-8	34.5	33.3
1	1	0	43.6	-13.6
1	1	1	134.9	-155.4
1	1	-1	155.8	149.2
1	1	2	94.8	-88.1
1	1	-2	107.1	-103.6
1	1	3	117.7	117.9
1	1	-3	164.7	-169.0
1	1	4	47.8	45.4
1	1	-4	28.3	24.1
1	1	5	76.1	-84.1
1	1	-5	139.3	127.9
1	1	6	21.3	-21.1
1	1	-6	15.9	7.3
1	1	7	46.9	44.0
1	1	-7	70.8	-60.0
1	1	-8	13.9	9.1
3	1	0	39.8	36.4
3	1	1	214.2	-210.8
3	1	-1	205.4	194.2
3	1	2	74.4	-44.7
3	1	-2	193.9	206.2
3	1	3	156.7	164.1
3	1	-3	197.4	-212.2
3	1	4	10.6	9.5
3	1	-4	47.8	47.8
3	1	5	75.3	-81.5
3	1	-5	101.8	97.8
3	1	6	25.7	19.8
3	1	-6	47.8	-41.7
3	1	7	77.0	69.2
3	1	-7	67.3	-57.9
3	1	8	2.7	7.0
3	1	-8	13.3	0.5
5	1	0	30.1	31.2
5	1	1	113.3	-111.8
5	1	-1	103.6	101.7
5	1	2	29.2	-28.1
5	1	-2	53.1	-54.8
5	1	3	81.4	86.8
5	1	-3	67.3	-44.9
5	1	4	33.6	29.3
5	1	-4	58.4	63.8
5	1	5	53.1	-58.0
5	1	-5	72.6	70.6
5	1	6	29.2	-20.3
5	1	-6	22.1	-26.0
5	1	7	46.0	39.5
5	1	-7	61.1	-53.2
5	1	8	4.4	-7.0
7	1	0	37.2	36.2
7	1	1	111.5	-104.5
7	1	-1	122.2	120.2
7	1	2	24.8	-25.9
7	1	-2	12.4	-11.2
7	1	3	62.0	60.1
7	1	-3	82.3	-89.5
7	1	4	26.6	-23.5
7	1	5	45.2	-50.0
7	1	-5	58.4	-57.3
7	1	-5	92.1	108.3
7	1	6	20.4	-15.3
7	1	-6	18.6	-18.3
7	1	7	30.1	26.2
7	1	-7	46.9	-46.9
7	1	8	12.4	9.9
0	2	0	24.8	15.0
0	2	1	12.4	-0.4
0	2	2	172.6	176.4
0	2	3	49.6	52.7
0	2	4	147.0	-150.7
0	2	5	27.4	-31.2
0	2	6	61.1	55.9
0	2	7	46.0	61.3
0	2	8	19.5	-15.4
2	2	0	149.6	-139.5
2	2	1	100.0	-102.8
2	2	-1	216.0	224.5
2	2	2	97.4	110.3

h	k	l	Fo	Fc
2	2	-2	90.3	90.2
2	2	3	44.3	50.8
2	2	-3	97.4	-107.1
2	2	4	63.7	-70.3
2	2	-4	94.5	-98.2
2	2	5	6C.2	-63.4
2	2	-5	51.4	61.4
2	2	-6	71.7	66.0
2	2	6	53.1	51.2
2	2	7	26.6	21.9
2	2	-7	51.4	-45.1
2	2	8	36.3	-33.3
2	2	-8	44.3	-38.8
4	2	0	120.4	-119.0
4	2	1	57.5	-61.5
4	2	2	100.6	97.0
4	2	-1	117.7	117.1
4	2	-2	67.3	68.7
4	2	3	47.8	52.0
4	2	-3	21.3	-17.5
4	2	4	66.4	-49.7
4	2	5	63.7	-65.5
4	2	-5	39.0	39.4
4	2	6	21.3	19.9
4	2	-6	72.6	70.7
4	2	7	16.8	12.8
4	2	-7	17.7	-14.6
4	2	-8	33.6	-29.7
4	2	8	26.6	-25.7
4	2	0	144.3	-132.9
6	2	-1	29.2	-30.2
6	2	1	43.4	42.6
6	2	2	86.5	81.9
6	2	-2	93.8	90.2
6	2	3	43.4	44.6
6	2	-3	71.7	-78.4
6	2	4	15.1	-7.3
6	2	5	4.4	-4.3
6	2	-5	4.4	4.0
6	2	6	41.6	38.0
6	2	-6	72.6	56.5
6	2	7	23.9	19.0
6	2	-7	33.6	-31.9
6	2	8	23.0	-23.5
6	2	-8	35.4	-33.4
8	2	0	62.0	-56.2
8	2	1	52.2	-48.9
8	2	2	39.8	39.4
8	2	-2	67.3	63.3
8	2	-2	41.6	39.3
8	2	3	62.0	57.5
8	2	-3	58.4	-43.5
8	2	-4	35.4	-33.0
8	2	4	54.0	-55.2
8	2	5	25.7	-22.2
8	2	-5	34.5	28.2
8	2	-6	42.5	43.4
8	2	6	17.7	12.0
8	2	-7	34.5	-31.9
8	2	-8	18.6	-28.0
1	3	0	161.1	-163.3
1	3	1	123.9	123.8
1	3	-1	129.3	-130.9
1	3	2	158.5	159.3
1	3	-2	155.8	153.4
1	3	3	50.5	-50.8
1	3	-3	94.7	90.2
1	3	4	107.1	-107.3
1	3	-4	83.2	-87.9
1	3	5	59.3	58.1
1	3	-5	46.0	-47.1
1	3	6	68.2	61.8
1	3	7	71.7	69.2
1	3	-7	53.1	-47.4
1	3	-7	60.2	50.0
3	3	0	57.5	-56.4
3	3	-3	30.1	-29.6
3	3	0	123.1	-121.2
3	3	-1	93.0	93.0
3	3	-1	99.2	-101.9
3	3	2	23.0	32.0
3	3	-2	172.6	176.7
3	3	3	59.3	-59.2
3	3	-3	21.3	18.6
3	3	4	74.4	-76.0
3	3	-4	62.3	-63.4
3	3	5	57.5	62.1
3	3	-5	49.6	-50.2
3	3	6	67.3	60.6
3	3	-6	46.9	43.5
3	3	7	4.4	1.9
3	3	-7	36.3	34.0
3	3	8	32.8	-28.8
3	3	-8	42.5	-36.5
5	3	0	154.9	-148.9
5	3	1	35.4	38.0
5	3	-1	91.2	-92.7
5	3	2	119.5	116.3
5	3	-2	100.9	104.6
5	3	3	77.0	-74.3
5	3	-3	99.2	102.8
5	3	4	53.1	-53.8
5	3	-4	115.1	-117.4
5	3	5	52.2	54.6
5	3	-5	56.7	53.8
5	3	6	56.7	54.7
5	3	7	33.6	-30.3
5	3	-7	35.4	28.6
5	3	8	22.1	-20.4
5	3	-8	39.8	-38.2
7	3	0	39.8	-39.9
7	3	1	39.8	42.5
7	3	-1	43.4	-45.9

h	k	l	Fo	Fc
7	3	2	73.5	66.3
7	3	-2	76.1	74.9
7	3	-2	55.8	-51.7
7	3	-3	70.8	72.5
7	3	4	72.6	-68.3
7	3	-4	67.3	-69.8
7	3	5	4.4	10.6
7	3	-5	4.4	1.8
7	3	6	33.6	29.7
7	3	-6	39.0	36.1
7	3	7	15.1	-6.6
7	3	-7	24.6	29.5
7	3	8	15.1	-14.7
7	3	-8	26.1	-15.2
0	4	0	65.9	66.6
0	4	1	175.7	184.5
0	4	2	91.2	-86.3
0	4	-2	134.6	-139.5
0	4	4	4.4	6.6
0	4	5	72.6	62.2
0	4	7	50.5	-51.0
0	4	8	31.0	28.0
2	4	0	84.3	85.4
2	4	1	146.1	150.1
2	4	-1	176.2	-168.6
2	4	2	90.3	-9.3
2	4	-2	88.5	-86.2
2	4	3	147.8	-155.4
2	4	-3	108.0	111.5
2	4	4	65.5	63.2
2	4	5	61.1	66.7
2	4	-5	100.9	-118.4
2	4	6	23.0	-21.7
2	4	-6	38.1	-35.6
2	4	7	45.2	-47.4
2	4	-7	59.3	59.3
2	4	8	33.6	32.5
2	4	-8	20.4	21.6
4	4	0	77.0	74.1
4	4	1	160.2	164.8
4	4	-1	101.8	-100.8
4	4	2	26.6	-26.5
4	4	-2	40.7	-42.0
4	4	3	101.8	-105.1
4	4	-3	125.7	138.1
4	4	4	43.4	36.9
4	4	-4	69.9	69.8
4	4	5	61.1	64.6
4	4	-5	66.4	-78.9
4	4	6	48.7	-43.6
4	4	-6	21.3	-23.4
4	4	7	54.9	-51.6
4	4	-7	46.0	49.0
6	4	0	18.6	20.0
6	4	1	104.5	105.4
6	4	-1	89.4	-92.3
6	4	2	45.2	-44.7
6	4	-2	45.2	-47.4
6	4	3	61.1	-43.1
6	4	-3	87.6	98.0
6	4	4	25.7	22.0
6	4	-4	58.4	63.0
6	4	5	59.3	67.4
6	4	-5	76.1	-92.5
6	4	6	27.4	-25.0
6	4	-6	14.2	-15.3
6	4	7	35.4	-30.3
6	4	-7	45.2	51.8
8	4	0	42.5	40.4
8	4	1	68.2	64.8
8	4	-1	114.2	-111.2
8	4	2	30.1	-26.7
8	4	-2	48.7	-52.0
8	4	3	46.0	-48.7
8	4	-3	58.4	60.1
8	4	4	37.2	35.1
8	4	-4	22.1	22.1
8	4	5	29.2	33.2
8	4	-5	46.0	-53.3
8	4	6	22.1	-16.2
8	4	-6	41.6	-43.7
8	4	7	29.2	-26.0
1	5	0	178.8	171.4
1	5	1	35.4	27.9
1	5	-1	78.8	68.0
1	5	2	127.5	-132.0
1	5	-2	100.0	-100.4
1	5	3	57.5	58.7
1	5	-3	23.9	-22.0
1	5	4	126.6	126.4
1	5	-4	86.5	90.8
1	5	5	14.2	-17.8
1	5	-5	26.6	27.7
1	5	6	69.9	-65.0
1	5	-6	78.8	-75.3
1	5	7	4.4	6.3
1	5	-7	17.7	-13.2
1	5	8	20.4	18.6
1	5	-8	38.1	37.6
3	5	0	117.7	119.3
3	5	1	23.0	-0.9
3	5	-1	67.3	63.6
3	5	3	141.6	-139.0
3	5	-2	140.8	-142.0
3	5	3	10.6	10.0
3	5	-3	27.4	-28.1
3	5	4	93.8	95.2
3	5	5	102.7	102.6
3	5	5	4.4	-9.6
3	5	6	22.1	25.4
3	5	6	64.6	-41.7
3	5	7	93.8	-55.2
3	5	7	23.9	20.1
3	5	-7	4.4	-6.2

h	k	l	Fo	Fc
3	5	-8	31.0	26.4
3	5	-8	39.8	43.0
5	5	0	98.3	97.4
5	5	1	71.7	-64.4
5	5	2	90.3	-92.5
5	5	-1	112.4	-109.3
5	5	3	4.4	6.7
5	5	-2	32.6	-31.8
5	5	4	74.4	73.6
5	5	-3	53.1	55.5
5	5	5	4.4	-13.3
5	5	6	15.9	-7.1
5	5	6	32.1	-26.0
5	5	-6	54.9	-53.4
5	5	7	4.4	2.5
5	5	-7	18.6	-20.0
7	5	0	18.6	8.8
7	5	1	14.5	22.5
7	5	-1	106.2	99.8
7	5	1	15.9	-14.5
7	5	2	18.6	16.5
7	5	-2	75.3	-70.9
7	5	3	79.7	-81.4
7	5	-3	17.7	15.1
7	5	4	4.4	-6.9
7	5	5	52.2	54.8
7	5	5	64.6	73.5
7	5	-5	4.4	-9.1
7	5	-5	23.9	27.5
7	5	6	33.6	-35.6
7	5	6	46.0	-41.6
7	5	7	4.4	7.0
7	5	-7	4.4	-11.0
7	5	-8	30.1	35.3
0	6	0	23.9	-14.0
0	6	1	108.9	-110.9
0	6	2	15.9	-17.3
0	6	3	111.5	113.4
0	6	4	4.4	-1.2
0	6	5	92.1	-95.9
0	6	6	8.0	-7.9
0	6	7	58.4	53.1
2	6	0	58.4	54.8
2	6	1	135.5	-133.7
2	6	-1	87.6	90.3
2	6	2	49.6	-48.8
2	6	3	70.8	75.6
2	6	-3	153.2	-160.4
2	6	4	4.4	-1.7
2	6	5	56.7	-62.4
2	6	-5	60.2	59.6
2	6	6	17.7	-14.4
2	6	7	44.3	39.4
2	6	-7	32.8	-30.3
2	6	-6	20.4	20.2
4	6	0	15.9	16.4
4	6	1	102.7	-102.3
4	6	-1	133.7	133.9
4	6	2	4.4	-2.6
4	6	3	89.4	88.9
4	6	-3	67.3	-69.0
4	6	4	21.3	20.1
4	6	-4	26.6	26.5
4	6	5	55.8	-56.1
4	6	6	18.6	-15.5
4	6	-6	62.0	64.5
4	6	7	18.6	-9.6
4	6	-7	48.7	42.3
4	6	8	46.9	-45.1
4	6	0	33.6	11.3
6	6	-1	66.8	-82.0
6	6	1	91.2	92.4
6	6	2	4.4	-0.8
6	6	-2	23.9	-20.5
6	6	3	69.1	70.1
6	6	-3	58.4	-57.3
6	6	4	14.2	12.3
6	6	5	34.4	-34.9
6	6	-5	69.1	75.5
6	6	6	2.7	-9.2
6	6	-6	6.2	-9.1
6	6	7	31.9	30.8
6	6	-7	39.0	-36.9
8	6	0	17.7	13.7
8	6	1	66.4	-67.2
8	6	-1	47.8	47.6
8	6	2	18.6	-16.3
8	6	3	4.4	-6.6
8	6	-3	56.7	-57.8
8	6	4	17.7	15.5
8	6	-4	15.9	18.4
8	6	5	42.5	-40.6
8	6	-5	36.3	38.3
8	6	6	9.7	-10.3
8	6	-6	23.0	-22.3
8	6	7	4.4	14.9
1	7	0	152.3	142.1
1	7	1	32.8	-33.5
1	7	-1	111.5	110.5
1	7	-2	126.4	118.5
1	7	-2	118.6	117.9
1	7	3	91.2	95.2
1	7	4	58.4	-57.6
1	7	-4	58.4	-66.4
1	7	5	61.1	-6C.1
1	7	-5	41.6	44.5
1	7	6	77.0	74.9
1	7	-6	27.4	30.1

h	k	l	Fo	Fc
1	7	7	31.0	26.4
1	7	-7	33.6	-29.5
1	7	8	36.3	-35.1
1	7	-8	38.2	-38.2
3	7	0	10.6	8.8
3	7	1	46.9	-44.3
3	7	-1	75.3	73.5
3	7	2	93.8	89.9
3	7	-2	91.2	86.5
3	7	3	23.9	3C.1
3	7	-3	27.4	-31.1
3	7	4	59.3	-61.5
3	7	-4	72.6	-80.5
3	7	5	24.6	-26.7
3	7	-5	31.0	31.9
3	7	6	46.9	44.8
3	7	-6	43.4	43.1
3	7	7	20.4	18.4
3	7	-7	26.6	-23.6
3	7	8	28.3	-27.1
3	7	-8	47.8	-47.1
5	7	0	90.3	-89.5
5	7	1	56.7	-57.9
5	7	-1	62.9	63.0
5	7	2	65.5	63.8
5	7	-2	110.7	116.3
5	7	3	48.7	47.2
5	7	-3	65.5	-75.5
5	7	4	68.2	-69.6
5	7	-4	70.0	-84.4
5	7	5	36.3	-37.4
5	7	6	20.4	19.4
5	7	-6	55.8	58.4
5	7	7	16.8	12.1
5	7	-7	23.9	-24.4
5	7	-8	17.7	-9.7
7	7	0	66.4	-63.4
7	7	1	39.0	-35.5
7	7	-1	31.0	27.2
7	7	2	67.3	62.5
7	7	-2	61.1	57.3
7	7	3	29.2	33.5
7	7	-3	27.4	-25.7
7	7	4	46.9	-44.8
7	7	-4	49.6	-49.1
7	7	5	8.9	-12.5
7	7	-5	26.6	26.1
7	7	6	36.3	31.4
7	7	-6	37.2	35.4
7	7	7	15.9	11.9
7	7	-7	22.1	-18.9
7	7	-7	22.1	-18.9
0	8	0	65.0	-67.9
0	8	1	68.2	73.0
0	8	2	83.2	77.3
0	8	3	54.0	-41.0
0	8	4	61.1	-60.2
0	8	5	54.0	57.3
0	8	6	26.6	26.4
0	8	7	28.3	-28.7
0	8	8	23.0	-23.7
2	8	0	70.8	-65.4
2	8	1	120.4	115.4
2	8	-1	147.8	-141.9
2	8	2	95.6	84.7
2	8	-2	21.3	20.1
2	8	3	61.1	-67.1
2	8	-3	64.6	73.6
2	8	4	86.8	-44.2
2	8	-4	56.7	-58.9
2	8	5	58.3	60.1
2	8	-5	60.2	-44.5
2	8	6	25.7	26.9
2	8	-6	76.1	70.5
2	8	7	36.3	-33.1
2	8	-7	64.6	60.2
2	8	8	4.4	-0.8
4	8	0	79.7	-75.8
4	8	1	66.4	63.7
4	8	-1	62.0	-61.8
4	8	-2	56.7	53.9
4	8	3	67.3	75.4
4	8	4	30.1	-29.9
4	8	-4	56.7	-59.9
4	8	5	50.5	52.1
4	8	-5	44.3	-47.8
4	8	6	32.8	31.4
4	8	-6	43.4	37.9
4	8	-7	27.4	-22.9
4	8	7	31.9	32.8
4	8	-8	29.2	-29.1
6	8	0	65.5	-60.6
6	8	1	40.7	39.4
6	8	-1	79.7	-75.0
6	8	2	61.1	56.3
6	8	-2	41.6	39.4
6	8	3	31.9	-36.0
6	8	-3	57.5	66.6
6	8	4	34.5	-31.4
6	8	-4	44.3	-49.4
6	8	5	34.5	35.3
6	8	-5	31.9	-34.6
6	8	-6	31.0	28.2
6	8	6	18.6	-18.5
6	8	-7	31.0	33.0
6	8	-8	2.7	-11.5
8	8	0	29.2	-29.1
8	8	1	62.0	-53.9
8	8	-1	65.5	59.4
8	8	-2	44.7	46.9
8	8	3	31.0	25.2
8	8	-3	56.7	-54.9

h	k	l	Fo	Fc
0	0	-1	48.7	60.6
0	0	4	31.0	-25.6
0	0	-2	23.9	-17.8
8	0	5	18.6	21.8
8	0	6	10.6	-45.2
8	0	6	14.2	14.1
8	0	-6	28.3	27.3
8	0	7	4.4	-16.4
8	0	-7	23.0	18.2
10	0	0	63.7	53.5
10	0	2	100.0	-98.4
10	0	-2	53.1	-58.6
10	0	4	27.4	30.2
10	0	-4	69.9	70.5
10	0	6	18.8	-17.8
10	0	-6	63.7	-70.1
10	0	8	4.4	15.9
10	0	-8	25.7	27.5
9	1	0	23.9	22.2
9	1	1	71.7	-68.3
9	1	-1	69.9	70.6
9	1	2	15.9	11.5
9	1	-2	29.2	-29.7
9	1	3	57.5	54.1
9	1	-3	60.2	-60.3
9	1	4	12.4	14.1
9	1	-4	13.3	12.1
9	1	5	38.1	-36.2
9	1	-5	35.4	34.9
9	1	6	4.4	-7.6
9	1	-6	4.4	3.9
9	1	7	33.6	22.9
9	1	-7	39.8	-33.7
9	1	8	4.4	-0.6
9	1	-8	4.4	11.5
11	1	0	32.8	29.4
11	1	1	26.6	-26.1
11	1	2	43.4	40.7
11	1	-2	14.2	-12.1
11	1	3	32.8	31.0
11	1	-3	43.4	-44.4
11	1	1	4.4	9.6
11	1	-4	4.4	-3.7
11	1	5	22.1	-23.1
11	1	-5	26.7	26.7
11	1	6	4.4	-5.2
11	1	7	4.4	-3.3
11	1	-7	31.9	-31.6
11	1	8	2.7	2.4
11	1	-8	2.7	9.7
10	2	0	52.2	-49.1
10	2	1	23.0	-22.7
10	2	2	21.3	16.8
10	2	-2	8.9	9.9
10	2	3	4.4	8.7
10	2	-2	95.8	65.2
10	2	-3	16.8	-13.1
10	2	4	23.9	-88.6
10	2	5	16.8	-14.3
10	2	-5	26.6	26.8
10	2	6	29.2	21.5
10	2	7	4.4	7.5
10	2	-7	4.4	8.2
10	2	-7	4.4	16.4
10	2	8	19.5	-19.2
9	3	0	56.7	-54.4
9	3	1	33.4	43.8
9	3	2	34.5	-29.4
9	3	3	45.2	46.8
9	3	3	29.2	-26.8
9	3	4	33.6	-36.1
9	3	5	33.4	42.6
9	3	-5	22.1	22.3
9	3	-5	31.9	-37.2
9	3	6	20.4	17.1
9	3	7	58.4	64.1
9	3	-7	4.4	-11.0
9	3	-7	5.5	5.5
10	4	0	26.6	26.4
10	4	-1	56.7	-54.9
10	4	2	23.9	-17.5
10	4	-2	4.4	-4.2
10	4	3	47.8	44.9
10	4	-3	37.2	4C.C
10	4	4	13.3	15.3
10	4	-4	16.8	17.0
10	4	-5	29.2	27.7
10	4	-6	29.2	-29.5
10	4	-6	23.9	-22.3
10	4	7	39.8	46.3
9	5	0	58.4	52.6
9	5	1	4.4	10.6
9	5	2	23.0	25.0
9	5	-2	56.7	-54.3
9	5	-2	64.6	-60.3

Table 5 (cont.)

h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc
9	5	3	19.5	19.3		3	9	-8	2.7	6.8		8	10	0	24.6	20.0		12	0	4	23.0	22.7		16	4	2	4.4	-2.0		4	12	0	55.8	-56.9
9	5	-3	4.4	-5.1		5	9	0	84.8	78.4		8	10	1	4.4	-0.4		12	0	-4	24.6	27.1		16	4	-2	4.4	-7.5		4	12	1	15.9	-15.0

(Numerical structure-factor data table continues — dense tabulation of h, k, l, Fo, Fc values across six column groups.)

Table 5 (cont.)

h	k	l	Fo	Fc
7	13	-4	9.7	9.0
7	13	7	4.4	-4.8
7	13	-7	4.4	5.9
9	13	1	33.6	26.9
9	13	-1	22.1	-21.5
9	13	2	18.6	15.6
9	13	-2	14.2	12.7
9	13	-3	20.4	22.7
9	13	4	4.4	-10.0
9	13	-4	9.7	-10.6
9	13	5	4.4	8.6
9	13	-5	16.8	-17.4
9	13	6	4.4	2.7
9	13	-6	4.4	11.3
11	13	1	19.5	16.1
11	13	-1	4.4	-11.4
11	13	2	4.4	11.6
11	13	-2	4.4	5.5
11	13	3	4.4	-14.6
11	13	-3	21.3	20.9
11	13	4	4.4	-7.0
11	13	-4	4.4	-9.8
0	14	0	47.8	39.4
0	14	1	35.4	35.9
0	14	2	29.2	-27.0
0	14	3	54.0	-52.0
0	14	4	18.6	21.0
0	14	5	16.8	23.0
0	14	6	9.7	-9.4
2	14	0	33.6	31.8
2	14	1	47.8	45.4
2	14	-1	45.2	-43.0
2	14	2	28.3	-28.8
2	14	-2	39.8	-36.0
2	14	3	30.1	-32.7
2	14	-3	38.1	39.3
2	14	4	19.5	23.2
2	14	-4	23.0	27.1
2	14	5	19.5	26.2
2	14	-5	26.6	-30.1
2	14	6	4.4	-21.8
2	14	-6	13.3	-17.2
2	14	7	4.4	-16.2
2	14	-7	18.6	17.1
4	14	0	28.3	27.1
4	14	1	49.6	44.1
4	14	-1	38.1	-34.9
4	14	2	31.0	-25.5
4	14	-2	39.8	-36.1
4	14	3	34.5	-30.7
4	14	-3	26.6	29.5
4	14	4	4.4	12.3
4	14	-4	15.9	21.0
4	14	5	17.7	22.6
4	14	-5	32.8	-34.9
4	14	6	4.4	-15.2
4	14	-6	4.4	-8.0
6	14	0	25.7	23.6
6	14	1	33.6	32.3
6	14	-1	34.5	-33.1
6	14	2	17.7	-17.2
6	14	-2	16.8	-14.9
6	14	3	23.0	-23.2
6	14	-3	23.9	25.9
6	14	4	15.1	20.2
6	14	-4	19.5	20.9
6	14	-5	16.8	-20.3
6	14	6	4.4	-11.2
6	14	-6	9.7	-15.1
8	14	0	19.5	18.0
8	14	1	30.1	24.3
8	14	-1	23.9	-23.6
8	14	2	15.1	-15.3
8	14	-2	17.7	-15.8
8	14	3	4.4	-18.3
8	14	-3	24.8	21.4
8	14	4	4.4	13.9
8	14	-4	20.4	19.4
8	14	5	4.4	13.3
8	14	-5	17.7	-16.8
8	14	6	4.4	-8.5
8	14	-6	4.4	-12.5
10	14	1	16.8	13.3
10	14	-1	24.8	-22.1
10	14	2	4.4	-12.5
10	14	-2	4.4	-10.7
10	14	3	4.4	-10.3
10	14	-3	15.1	12.9
10	14	4	4.4	8.5
10	14	-4	4.4	6.0
1	15	0	43.4	43.7
1	15	1	20.4	-18.8
1	15	-1	21.3	15.4
1	15	2	47.8	-45.8
1	15	-2	52.2	-50.0
1	15	3	19.5	17.7
1	15	-3	22.1	-18.3
1	15	4	28.3	36.7
1	15	-4	31.0	38.2
1	15	5	4.4	-9.6
1	15	-5	4.4	8.4
3	15	0	58.4	55.6
3	15	1	24.8	-19.7
3	15	-1	18.6	12.0
3	15	2	39.8	-38.2
3	15	-2	39.0	-35.2
3	15	3	4.4	12.4
3	15	-3	16.8	-12.0
3	15	4	35.4	41.8
3	15	-4	32.8	35.8
3	15	5	4.4	-10.1
5	15	0	41.6	39.5
5	15	1	14.2	-12.9
5	15	-1	15.9	14.8
5	15	2	37.2	-34.9
5	15	-2	37.2	-36.6
5	15	3	10.6	13.4
5	15	-3	9.7	-11.2
5	15	-4	30.1	29.3
5	15	5	4.4	-8.1
5	15	-5	14.2	11.6
7	15	0	27.4	27.3
7	15	1	4.4	-10.8
7	15	-1	4.4	11.6
7	15	2	45.2	-36.1
7	15	-2	40.7	-37.3
7	15	3	4.4	6.3
7	15	-3	4.4	4.4
7	15	-4	17.7	19.5
7	15	5	4.4	-5.3
7	15	-5	4.4	6.9
9	15	0	28.3	23.9
9	15	1	4.4	-8.8
9	15	-1	4.4	9.6
9	15	2	11.5	-17.0
9	15	-2	22.1	-21.7
9	15	3	4.4	5.2
9	15	-3	4.4	-6.8
11	15	0	22.1	17.9
0	16	1	45.2	-46.2
0	16	2	14.2	10.6
0	16	3	39.8	40.9
0	16	4	4.4	-3.7
2	16	0	4.4	-6.4
2	16	1	43.4	-42.3
2	16	-1	47.8	46.2
2	16	2	4.4	4.2
2	16	-2	4.4	1.4
2	16	3	34.5	37.5
2	16	-3	33.6	-35.6
2	16	4	4.4	-7.8
2	16	-4	4.4	-3.4
4	16	0	15.9	-10.4
4	16	1	46.0	-39.2
4	16	-1	37.2	35.5
4	16	2	4.4	0.5
4	16	-2	4.4	0.3
4	16	3	30.1	32.6
4	16	-3	31.0	-34.9
4	16	4	4.4	-9.2
4	16	-4	4.4	-4.7
6	16	1	31.0	-31.9
6	16	-1	32.8	32.3
6	16	2	15.9	10.1
6	16	-2	15.1	10.9
6	16	-3	30.1	-33.3
6	16	4	4.4	-0.6
6	16	-4	4.4	-0.8
8	16	1	22.1	-21.5
8	16	-1	31.0	26.1
8	16	2	4.4	3.7
8	16	-2	4.4	5.8
1	17	0	43.4	-39.5
1	17	1	4.4	-11.5
1	17	-1	4.4	5.4
1	17	2	30.1	30.8
1	17	-2	40.7	35.2
1	17	3	4.4	4.0
1	17	-3	4.4	0.2
3	17	0	29.2	-29.8
3	17	1	4.4	-0.1
3	17	-1	4.4	2.9
3	17	2	32.8	32.4
3	17	-2	39.8	33.9
3	17	3	4.4	3.0
3	17	-3	4.4	-6.0
5	17	0	29.2	-27.3
5	17	1	4.4	-3.2
5	17	-1	4.4	8.5
5	17	2	24.8	24.7
5	17	-2	34.5	29.3
5	17	3	4.4	8.1
5	17	-3	4.4	-3.9
7	17	0	28.3	-25.2
7	17	1	4.4	-0.8
7	17	-1	4.4	2.0
0	18	0	21.3	-14.0
0	18	1	26.6	27.6
0	18	2	15.9	14.0

are not coplanar with the molecule but are rotated about an axis going through atoms C(1) and C(4). The angle of rotation is $\pm 12.5°$. The atoms C(7) and N(2) also lie in the plane of the aromatic nucleus. The atom C(8) is displaced from this plane by 0·133 Å, but the cause of this displacement is not clear.

Interatomic distances in the molecule (Table 6) point to extensive conjugation of bonds in the cation-radical. For example, the lengths of bonds N(1)–C(1) and

N(2)–C(4) are comparable to the value of 1·352 Å which is tabulated for the bond length of the partial double bond (*International Tables for X-Ray Crystallography*, 1962) and are very significantly shorter than 1·426 Å, which is the value given in the same tables for the single bond between a nitrogen atom and a benzene ring. Bond lengths between different carbon atoms in the benzene ring are not equal and exhibit very significant differences. There are two short bonds (mean length 1·35 Å) and four longer ones (mean length 1·42 Å) distributed in a similar manner as in the case of benzoquinone (Trotter, 1960). On the other hand, bond lengths of methyl carbon atoms to nitrogen N(2) are normal.

Table 6. Bond distances and valence angles in the organic radical

N(1)–C(1)	1·363 Å			
N(2)–C(4)	1·354	C(1)–N(1)–C(1')	131·2°	
N(2)–C(7)	1·460	C(2)–C(1)–C(6)	118·0	
N(2)–C(8)	1·480	C(3)–C(2)–C(1)	120·6	
C(1)–C(6)	1·400			
C(2)–C(3)	1·359	C(4)–C(3)–C(2)	120·4	
C(5)–C(6)	1·346	C(5)–C(4)–C(3)	118·0	
C(3)–C(4)	1·433	C(6)–C(5)–C(4)	120·6	
C(4)–C(5)	1·414	C(1)–C(6)–C(5)	122·0	
C(1)–C(2)	1·424	C(7)–N(2)–C(8)	118·5	

Table 8. Deviations of atoms from the plane of the benzene ring

N(1)	0·067 Å	C(5)	0·002 Å
C(1)	0·028	C(6)	-0·021
C(2)	-0·014	N(2)	0·021
C(3)	-0·004	C(7)	-0·003
C(4)	0·012	C(8)	0·133

Table 7. Some shorter intermolecular distances

I–N(1)		3·67 Å	N(1)–C(6)	BA	3·69 Å	C(8)–C(3)	AD'	4·01 Å
I–C(8)	BA'	4·13	N(2)–C(1)	BA	3·87	C(1)–C(1)	BA'	3·48
I–C(5)	BA'	3·98	N(2)–C(2)	BA	3·38	C(1)–C(6)	BA'	3·43
I–C(7)	BC'	4·19	C(7)–C(7)	BA'	3·42	C(1)–C(5)	BA'	3·72
I–C(8)	BC'	4·19	C(7)–C(2)	BA	3·61	C(6)–C(2)	BA'	3·41
N(1)–C(3)	BA	3·81	C(7)–C(3)	BA	3·57			
N(1)–C(4)	BA	3·53	C(8)–C(2)	BA	3·77			
N(1)–C(5)	BA	3·47	C(8)–C(2)	AD'	3·95			

The angle between benzene rings in 4,4'-bis(dimethylamino)diphenylamine cation-radical is abnormally small as compared with other diphenylamine compounds of known crystal structure. This again can be interpreted as the result of the large conjugation of bonds. Numerical values are given in Table 9.

Table 9. *Dihedral angles between planes of benzene rings in some diphenylamine compounds*

p,p'-Dichlorodiphenylamine (Plieth & Ruban, 1961)	61°
N-Picryl-p-iodoaniline (Grison, 1949)	65
4,4'-Bis(dimethylamino)diphenylamine radical (present work)	23

For the interpretation of the electrical conductivity of the iodide of 4,4'-bis(dimethylamino)diphenylamine cation-radical not only the electronic structure of the cation-radicals, but also their arrangement in the lattice, may be of importance. This is shown in Fig. 3. Cation-radicals are oriented approximately parallel with planes (30$\bar{2}$). Beside this, cation-radicals denoted *A* and *B* are in close contact, so that they form a layer placed on both sides of the glide plane $y=0$. Cation-radicals *C* and *D* form a second layer placed on both sides of the glide plane $y=\frac{1}{2}$. As can be seen from Table 7, there are some interesting short contacts between radicals *A* and *B* (similarly between *C* and *D*); these are especially:

(a) Contacts between atoms in benzene rings (3·48, 3·43, 3·41 Å).

(b) Contact between methyl groups through the center of symmetry (3·42 Å).

Between radicals lying in different layers we did not observe any abnormally short contacts.

Iodide ions are located approximately midway between layers of cation-radicals in such a way that every I⁻ is coordinated to one NH group, probably through an I–H–N bridge. The distance between I⁻ and NH is 3·67 Å, somewhat less than we have found in the case of the polyiodide complex with *N*-methylacetamide (3·74 Å) (Toman, Honzl & Ječný, 1965). The temperature vibrations of I⁻ are markedly anisotropic; the mean-square amplitudes of vibrations in the directions of the principal axes and the directions of principal axes (vectors Q_j) are given in Table 10. This shows that the largest amplitude of vibrations of I⁻ is oriented approximately perpendicular to the plane of the cation-radical.

Table 10. *Mean-square amplitudes (Å²) and the directions of principal axes of vibrations of iodide ions*

j	$\overline{u_j^2}$	Q_j*
1	0·052	705
2	0·035	010
3	0·085	40$\bar{3}$

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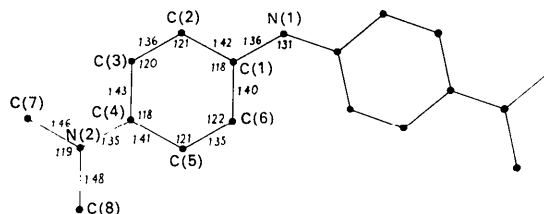TROTTER, J. (1960). *Acta Cryst.* **13**, 86.

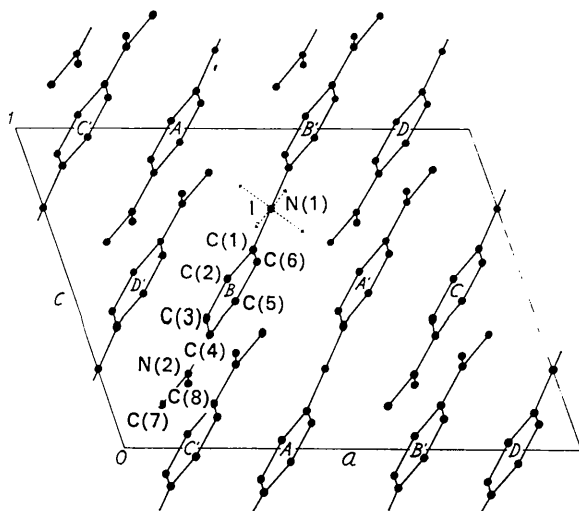Fig. 2. Intramolecular bond lengths and angles in the cation-radical.

Fig. 3. Projection of the structure along [010]. Iodide ions coinciding with the nitrogen atoms N(1) are not drawn. The arrows indicate principal axes of anisotropic vibrations of the iodide ion.