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

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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).

The composition of the crystals corresponds to the formula

$$ClO_4^-[(CH_3)_2.N.C_6H_4.NH.C_6H_4.N.(CH_3)_2]^{+\cdot}.$$

The unit-cell dimensions derived from Weissenberg pictures of these crystals are: $a=15\cdot39$, $b=13\cdot11$, $c=8\cdot82$ Å, $\beta=107\cdot6°$. The probable space group is $C2/c$ (the Cc space group was excluded, not by direct tests but by the success of the refinement of the structure in $C2/c$). The observed density 1·40 g.cm^{-3} corresponds to 4 stoichiometric units per unit cell.

The intensity measurement was performed on a counter goniometer with Mo $K\alpha$ radiation. Our goniometer is operated by the 'normal beam, ω-scan' technique. The diffracted intensity is measured by the scintillation counter with an amplitude analyser. The crystal examined and the counter are set manually in the appropriate positions. During the intensity measurement the counter is stationary, the crystal rotates through the selected ω range with constant velocity and the diffracted intensity is pen recorded. After subtraction of the background, a value proportional to the integrated intensity is obtained by planimetering the diffraction profile. The range of the measurement is extended by using aluminum sheets of known attenuation. Every reflexion was measured twice at different settings of the crystal.

Most reflexions were measured about [001] as the rotation axis. The measuring range was limited to $0° < 2\theta < 40°$ only, because of minute dimensions of the needle-like crystals (cross section 0·05 × 0·05 mm). With this orientation the intensities of 1008 independent reflexions were examined. About 450 of them had measurable intensity. The reflexions non-measurable at this orientation or with $\Upsilon < 10°$ were measured on the equator and four layer lines with rotation axis [010]. With this orientation 189 reflexions were measured. After Lorentz and polarization corrections were applied, both sets of reflexions were set on the same scale. From both these sets a final set of 521 non-equivalent reflexions was compiled, which contained 63 weak reflexions of non-measurable intensity.

3. Determination of the approximate structure and the refinement

The perchlorate of the DADA radical has similar unit-cell dimensions to those of the iodide, and the same space group. In addition, the distribution of the intensity in reciprocal space exhibits considerable similarity in the two salts. This observation led us to the belief that the arrangement and the form of molecules in the two compounds were also closely similar. We supposed, therefore, that the chlorine atoms and the nitrogen atoms of the NH group are located in the special fourfold positions on the twofold rotation axes, whereas the remaining atoms are placed in the general eightfold positions. For the DADA radical in the perchlorate the same symmetry is therefore supposed as was found in the iodide (symmetry 2).

A Patterson projection calculated for $h0l$ reflexions did not contradict this assumption and enabled us to locate the chlorine atoms approximately. The very strong reflexion 14,0,0 demands that the x coordinates of most atoms of the radical be approximately equal to multiples of 1/14 of the cell edge. This strongly confirms our hypothesis that the form and orientation of the organic radical in both salts is similar. A more detailed examination of the intensities of the $0k0$ reflexions led us to a small shift in the y coordinate of the whole DADA radical.

Based on these considerations we deduced approximate x and z coordinates of the carbon, nitrogen and chlorine atoms. With these we calculated the probable signs for $F(h0l)$. In this calculation the contributions from oxygen atoms were omitted, as we had then no information about the orientation of the ClO_4^- groups. Moreover, at this stage, we could not exclude the presence of complete or partial disorder in their orientations, as reported previously by Prosen & Trueblood (1956) for the dioxane complex with silver perchlorate, or by Coulter, Gantzel & McCullough (1963) for trimethyloxonium perchlorate and by McCullough (1964) for tetramethylammonium perchlorate.

After this the projection of the electron density along [001] was calculated. This projection again confirmed our assumption regarding the similarity of the structure of both salts. Better coordinates for the C and N atoms were obtained from this projection. In addition, in the neighbourhood of the chlorine atom we found four maxima, which could possibly be interpreted as the oxygen atom positions of the perchlorate ion.

The x and z fractional coordinates of the C, N and Cl atoms obtained at this stage were further refined by the least-squares method in two dimensions. The calculation was performed with the same isotropic temperature factor for all atoms. In this way we hoped to obtain better information about the orientation of the ClO_4^- group. The calculation was therefore done for two models of the ClO_4^- group:

1. In the first the orientation of the ClO_4^- group was supposed to be completely random; the electron density of this group was assumed to have spherical symmetry. The scattering factor used here had the form $f_{Cl}+4f_O$ $(\sin rs)/rs$, where $s=4\pi \sin\theta/\lambda$ and $r=1\cdot42$ Å. The final R value obtained for this model was rather unsatisfactory, 0·34.

2. In the second the orientation of the ClO_4^- group was supposed to be ordered; the x and z coordinates of the oxygen atoms were taken from the electron density projection, and this led to an R value of 0·19.

These results completely ruled out the disordered model for the perchlorate ion and simultaneously confirmed our initial hypothesis regarding the similarity of the form and packing of the DADA radicals in both salts. We now proceeded to the three-dimensional least-squares refinement of the structure. For this purpose we used the x and z coordinates as obtained from the two-dimensional refinement and for the y coordinates we used those of the corresponding iodide. The x and z coordinates of the oxygen atoms resulting from the two-dimensional least-squares refinement admitted two different orientations of the ClO_4^- tetrahedron:

1. The interatomic vector O(2)–O(2′) between both atoms O(2) in the ClO_4^- group is perpendicular to the plane of the DADA radical.
2. The vector O(2)–O(2′) is parallel to the plane of the DADA radical.

The least-squares refinement of the structure involving the first model was unsuccessful, the final R value being 0·41. The second alternative turned out to be correct.

The least-squares refinements were now performed in four steps differing mainly in the allowances made for the temperature vibrations. In the first three steps the hydrogen atom contributions were neglected. In the first step the same isotropic temperature factor was given to all atoms. In the second step, individual isotropic temperature factors were used, and in the third step individual anisotropic temperature factors were used. After this last refinement a three-dimensional $(F_o - F_c)$ map was calculated.

Table 1. *The fractional coordinates of the hydrogen atoms*

	Bound to	Fractional coordinates x	y	z
H(1)	N(1)	½	0·12	¾
H(2)	C(2)	0·16	0·39	0·39
H(3)	C(3)	0·22	0·03	0·42
H(4)	C(5)	0·13	0·26	0·08
H(5)	C(6)	0·50	0·17	0·13
H(6)	C(7)	0·36	0·48	0·27
H(7)	C(7)	0·42	0·35	0·33
H(8)	C(7)	0·42	0·39	0·18
H(9)	C(8)	0·23	0·25	0·34
H(10)	C(8)	0·35	0·22	0·37
H(11)	C(8)	0·26	0·19	0·18

Table 2. *The progress of the refinement*

Step	Number of cycles	Final R
I	3	0·250
II	4	0·159
III	5	0·118
IV	5	0·091

This difference Fourier synthesis confirmed the proposed model of the structure, and the orientation of the ClO_4^- group. It also enabled us to locate the hydrogen atoms. However these hydrogen coordinates were not refined by least-squares analysis. Table 1 gives their atomic parameters.

A final least-squares refinement was carried out with anisotropic temperature factors for the Cl, C, N and O atoms, and an isotropic temperature factor ($B = 6$ Å^2) for the H atoms. As can be seen from Table 2, the value of R was improved when the hydrogen atoms were included in the refinement.

Resultant fractional coordinates of the N, C, O and Cl atoms together with their standard deviations are shown in Table 3, and Table 4 gives the temperature parameters β_{ij} for all atoms excluding the hydrogen atoms. They refer to the temperature factor expressed in the form $\exp\,[-\sum_{ij} \beta_{ij}h_ih_j]$.

The average standard deviations of the temperature parameters β_{ij} are given in Table 5.

All calculations were carried out on the National Elliott 803B and National Elliott 503 computers with programs written in this laboratory. The program for the least-squares calculation will be described in detail

Table 4. *The temperature parameters* $10^4\beta_{ij}$

	$10^4\beta_{11}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{22}$	$10^4\beta_{23}$	$10^4\beta_{33}$
C(1)	67	3	22	57	3	176
C(2)	83	22	22	51	17	182
C(3)	64	7	20	86	−2	189
C(4)	47	−6	35	79	−3	194
C(5)	60	−13	28	61	−13	185
C(6)	52	−3	11	59	5	143
C(7)	36	−2	−3	120	32	469
C(8)	62	21	5	78	23	235
N(1)	80	—	18	41	—	163
N(2)	51	8	4	88	−3	217
Cl	56	—	19	54	—	259
O(1)	163	22	166	195	−77	713
O(2)	110	−77	14	206	−72	367

Table 3. *The fractional coordinates x, y, z*

The standard deviations of coordinates $\sigma(x)$, $\sigma(y)$, $\sigma(z)$ are in Å.

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·4309	0·0240	0·1371	0·006 Å	0·005 Å	0·005 Å
C(2)	0·3482	0·0299	0·5699	0·006	0·005	0·005
C(3)	0·2769	0·0135	0·9582	0·006	0·007	0·005
C(4)	0·2815	0·1131	0·9038	0·006	0·005	0·005
C(5)	0·3666	0·1637	0·9663	0·005	0·005	0·005
C(6)	0·4373	0·1238	0·0794	0·006	0·005	0·005
C(7)	0·1239	0·1058	0·7330	0·006	0·008	0·008
C(8)	0·2211	0·2565	0·7227	0·006	0·007	0·006
N(1)	½	0·0233	¾	—	0·005	—
N(2)	0·2118	0·1562	0·7899	0·006	0·005	0·004
Cl	½	0·3238	¾	—	0·003	—
O(1)	0·4532	0·3786	0·8306	0·006	0·005	0·006
O(2)	0·4419	0·2559	0·6418	0·005	0·005	0·005

elsewhere (Očenášková, 1966). For the calculation of the three-dimensional Fourier functions the program by Tichý (1966) was used. The scattering factors used in the refinement are those by Berghuis, Haanappel, Potters, Loopstra, McGillavry & Veenendaal (1955) for the C, O and N atoms and by Dawson (1960) for the Cl atom. In all steps and cycles of the least-squares calculation only constant weights were used. The standard deviations quoted in this paper are based on the diagonal elements of normal equations only. The input set of structure factors consisted of 458 non-zero structure factors to which 63 structure factors of half threshold value were added. These correspond to the reflexions of non-measurable intensity, where the low intensity was caused by the mutual compensation of contributions from different atoms. Table 6 gives the survey of the calculated and observed structure factors.

With the temperature parameters β_{ij} of the Cl, O(1) and O(2) atoms, the $T_{ii}^{1/2}$ and $\omega_{ii}^{1/2}$, the r.m.s. amplitudes of the translational and librational vibrations of the ClO_4^- group were calculated, using the method of Cruickshank (1956). Here the orthogonal molecular axes were used. The axis 2 was chosen identical with the unique axis; the angles between the crystallographic

Table 5. *The average standard deviations of the temperature parameters* $10^4\beta_{ij}$

	$10^4\sigma(\beta_{11})$	$10^4\sigma(\beta_{12})$	$10^4\sigma(\beta_{13})$	$10^4\sigma(\beta_{22})$	$10^4\sigma(\beta_{23})$	$10^4\sigma(\beta_{33})$
C,N,O	7	7	9	10	13	20
Cl	2	—	4	3	—	8

Table 6. *Observed and calculated structure factors*

h	k	l	F_o	F_c
0	0	2	111	-110
0	0	4	23	22
0	0	6	35	-39
0	2	0	19	-23
0	2	1	5	6
0	2	2	87	84
0	2	3	5	4
0	2	4	20	-13
0	2	5	18	11
0	2	6	5	-5
0	4	0	27	-23
0	4	1	54	53
0	4	2	19	17
0	4	3	27	-21
0	4	4	5	-6
0	4	5	24	25
0	4	6	5	10
0	6	0	65	63
0	6	1	14	-15
0	6	2	5	5
0	6	3	27	24
0	6	4	32	33
0	6	5	16	14
0	8	0	64	61
0	8	4	21	-19
0	8	5	19	20
0	10	0	16	-6
0	10	1	12	9
0	10	3	19	-19
0	10	5	23	18
0	12	3	16	9
1	1	0	45	-44
1	1	1	124	-123
1	1	-1	38	33
1	1	2	74	-73
1	1	-2	89	-88
1	1	3	11	-4
1	1	-3	29	-28
1	1	4	32	32
1	1	-4	14	14
1	1	5	5	-5
1	1	-5	5	7
1	1	6	27	19
1	1	-6	5	-4
1	3	0	128	-124
1	3	1	15	-12
1	3	-1	78	-80
1	3	2	61	61
1	3	-2	138	140
1	3	3	39	41
1	3	-3	21	17
1	3	4	15	-13
1	3	-4	27	-26
1	3	5	5	-9
1	3	-5	5	7
1	3	6	5	8
1	3	-6	14	16
1	5	0	41	-35
1	5	1	61	59
1	5	-1	45	44
1	5	2	5	7
1	5	-2	8	7
1	5	3	42	-42
1	5	-3	5	1
1	5	4	5	6
1	5	-4	5	7
1	5	5	10	11
1	5	-5	5	8
1	5	6	30	-26
1	7	0	20	-17
1	7	1	22	-22
1	7	-1	19	23
1	7	2	12	-15
1	7	-2	24	-20
1	7	3	32	30
1	7	-3	15	-16
1	7	5	64	-61
1	7	-5	20	19
1	9	0	23	-12
1	9	-1	12	-9
1	9	2	10	15
1	9	-2	17	12
1	9	-4	17	-15
1	9	-6	19	18
1	11	0	19	18
1	11	2	18	-19
1	13	1	15	-14
1	13	3	11	-11
2	0	0	47	44
2	0	2	22	-24
2	0	-2	131	-128
2	0	4	16	-10
2	0	-4	17	-18
2	0	6	19	-18
2	0	-6	5	11
2	2	0	20	-20
2	2	1	84	-83
2	2	-1	197	191
2	2	2	35	-35
2	2	-2	98	-93
2	2	3	5	12
2	2	-3	43	43
2	2	4	27	26
2	2	-4	15	-14
2	2	5	23	-28
2	2	-5	5	9
2	2	-6	5	2
2	4	0	40	-35
2	4	1	20	22
2	4	-1	75	-74
2	4	2	22	26
2	4	-2	61	-55
2	4	3	72	-71
2	4	-3	29	27
2	4	4	20	-23
2	4	-4	20	-21
2	4	5	23	22
2	4	-5	17	-18
2	4	-6	15	13
2	6	0	17	18
2	6	1	20	16
2	6	-1	45	-43
2	6	2	34	-36
2	6	-2	47	-47
2	6	3	15	-14
2	6	-3	25	-26
2	6	-4	29	26
2	6	-5	5	9
2	6	6	17	-16
2	6	-6	20	-13
2	8	0	15	-13
2	8	1	23	-22
2	8	-1	28	25
2	8	2	12	18
2	8	3	12	12
2	8	4	15	-13
2	8	-4	27	-30
2	8	5	16	11
2	10	1	11	11
2	10	-1	15	-15
2	10	2	20	-22
2	10	-2	11	-14
2	10	3	45	-46
2	10	-3	33	34
2	10	-5	16	-19
2	12	-1	15	12
3	1	0	51	46
3	1	1	117	-113
3	1	-1	127	115
3	1	2	35	-33
3	1	-2	184	183
3	1	3	56	53
3	1	-3	133	-128
3	1	4	19	-15
3	1	-4	5	5
3	1	5	11	-9
3	1	-5	5	4
3	1	6	5	-7
3	1	-6	5	-2
3	3	0	49	-47
3	3	1	5	-7
3	3	-1	30	-33
3	3	2	33	36
3	3	-2	48	45
3	3	3	50	49
3	3	-3	27	-19
3	3	4	38	-38
3	3	-4	5	-2
3	3	5	14	11
3	3	-5	5	4
3	3	6	5	9
3	3	-6	5	7
3	5	0	35	29
3	5	1	45	49
3	5	-1	5	4
3	5	2	20	19
3	5	-2	14	-14
3	5	3	5	5
3	5	-3	43	36
3	5	4	30	28
3	5	-4	23	22
3	5	-5	19	-16
3	5	6	15	-11
3	5	-6	5	-8
3	7	0	5	5
3	7	1	14	-11
3	7	-1	5	8
3	7	2	12	-11
3	7	-2	54	58
3	7	3	33	33
3	7	-3	31	-32
3	7	-5	25	22
3	9	0	19	-15
3	9	-2	32	27
3	9	3	21	21
3	9	4	23	-26
3	11	0	17	15
3	11	-2	19	-18
3	11	3	19	17
3	13	-1	15	15
3	13	2	8	11
3	13	3	20	21
3	13	-3	16	-17
4	0	0	87	92
4	0	2	15	-17
4	0	-2	175	-168
4	0	4	44	45
4	0	-4	5	-5
4	0	6	28	-26
4	0	-6	5	-6
4	2	0	40	-41
4	2	1	39	-41
4	2	-1	74	65
4	2	2	45	45
4	2	-2	77	79
4	2	3	15	17
4	2	-3	27	-25
4	2	4	5	-3
4	2	-4	5	-4
4	2	5	19	-20
4	2	-5	24	20
4	2	-6	5	11
4	4	0	25	16
4	4	1	28	27
4	4	-1	20	-23
4	4	2	17	22
4	4	-2	48	-44
4	4	3	11	-12
4	4	-3	25	27
4	4	-4	85	84
4	4	5	15	13
4	4	-5	36	-32
4	4	-6	5	4
4	6	0	23	25
4	6	1	13	12
4	6	-1	16	14
4	6	2	53	-55
4	6	-2	23	-27
4	6	3	26	-22
4	6	-3	14	-15
4	6	4	28	29
4	6	-4	11	12
4	6	-5	5	3
4	6	6	15	-13
4	8	1	16	14
4	8	2	33	38
4	8	3	30	-30
4	8	-4	20	-23
4	10	1	28	29
4	10	2	16	20
4	10	-2	13	11
4	10	-3	18	13
4	10	-5	19	-21
4	12	2	11	-15
4	12	-2	11	-13
5	1	0	16	-12
5	1	1	16	-16
5	1	-1	10	14
5	1	2	13	-14
5	1	-2	5	-2
5	1	3	5	5
5	1	-3	14	12
5	1	-4	29	-27
5	1	-5	27	23
5	1	-6	5	-6
5	3	0	72	-68
5	3	1	111	-115
5	3	-1	21	-20
5	3	2	46	47
5	3	-2	5	2
5	3	3	20	23
5	3	-3	56	55
5	3	4	19	-15
5	3	-4	95	-97
5	3	-5	17	15
5	3	6	24	25
5	3	-6	5	-3
5	5	0	34	25
5	5	-1	5	-9
5	5	2	19	-20
5	5	-2	38	-39
5	5	3	35	-33
5	5	-3	31	-26
5	5	4	16	16
5	5	-4	5	-4
5	5	-5	21	-6
5	5	-6	20	-18
5	7	1	23	-23
5	7	-1	19	20
5	7	2	19	-18
5	7	3	35	36
5	7	-3	19	-23
5	9	0	44	-43
5	9	-1	28	-29
5	9	-2	23	21
5	9	3	15	-17
5	9	-3	18	19
5	9	-4	23	-27
5	11	1	45	-41
5	11	-2	21	-19
5	11	-3	9	8
6	0	0	23	-18
6	0	2	5	-4
6	0	-2	43	-43
6	0	4	18	20
6	0	-4	66	67
6	0	6	25	-22
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6	2	1	5	-7
6	2	-1	17	14
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6	2	-2	23	24
6	2	3	36	37
6	2	-3	17	-16
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6	2	-4	19	20
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6	2	-6	5	5
6	4	0	5	-4
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6	4	-1	5	-2
6	4	2	17	17
6	4	-2	12	-9
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6	4	-3	25	29
6	4	-4	17	14
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6	4	-6	19	15
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6	6	2	16	-18
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6	6	-4	27	33
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6	6	-6	28	-23
6	8	0	40	-37
6	8	-2	18	18
6	8	3	12	10
6	8	-3	19	-19
6	8	-6	19	14
6	10	1	46	48
6	10	2	9	-11
6	10	-3	22	17
6	10	5	18	-17
6	12	0	14	11
6	12	-2	11	-10
7	1	0	26	26
7	1	1	36	-35
7	1	-1	49	52
7	1	2	11	-13
7	1	-2	41	37
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7	1	-3	28	-31
7	1	4	17	-18
7	1	-4	5	-2
7	1	5	30	-27
7	1	-5	38	37
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7	1	-6	5	-3
7	3	0	5	5
7	-3	-1	20	-19
7	3	2	25	25
7	3	-2	17	15
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7	5	2	14	-16
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7	7	3	14	10
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7	7	-5	17	15
7	9	0	17	17
7	9	-2	32	31
7	9	-3	10	11
7	11	-3	11	12
7	13	-1	16	20
8	0	0	20	18
8	0	2	12	-13
8	0	-2	39	-39
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8	0	-4	29	30
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9	5	1	24	22
9	5	-2	20	-19
9	5	-5	16	-15
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9	7	-1	23	28
9	7	3	20	18
9	7	-3	41	-41
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10	4	1	17	14
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10	4	-3	10	7
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10	6	-1	14	10
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10	6	-4	20	27
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10	8	-3	17	15
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11	1	0	17	15
11	1	1	23	-23
11	1	-1	12	16
11	1	2	28	32
11	1	3	30	28
11	1	-3	32	-31
11	1	-5	14	12
11	3	0	20	-19
11	3	-2	9	10
11	3	-4	19	-14
11	3	-6	16	17
11	5	0	20	17
11	5	-4	16	21
11	7	1	15	-12
11	7	-3	20	-18
11	9	-3	14	-8
12	2	1	39	-40
12	2	-3	15	-13
12	2	-5	21	24
12	4	1	19	17
12	4	-3	18	-17
12	4	-5	19	19
12	6	0	15	15
12	6	-2	17	-17
12	8	0	12	-14
12	8	-2	12	12
13	1	0	17	-17
13	1	-1	19	21
13	3	0	19	-17
13	5	-1	18	-20
13	5	-3	14	14
14	0	0	45	42
14	2	2	12	11

axes *a* and *c* and the molecular axes 1 and 3 are approximately 10° and −10°, respectively. The resulting r.m.s. amplitudes are given in Table 7.

Table 7. *The r.m.s. amplitudes of translational and librational vibrations of the* ClO_4^- *group relative to the molecular axes*

Axis	$T_{ii}^{1/2}$	$\omega_{ii}^{1/2}$
1	0·20 Å	15°
2	0·22	18
3	0·29	16

In Table 8 the bond distances and valence angles are summarized. To the bond distances Cl–O(1) and Cl–O(2) calculated with the coordinates from Table 3 the librational correction 0·06 Å was added.

Table 8. *Some bond distances and valence angles*

N(1)–C(1)	1·366 Å	C(1)–N(1)–C(1)	126·0°
N(2)–C(4)	1·352	C(2)–C(1)–C(6)	117·3
N(2)–C(7)	1·452	C(3)–C(2)–C(1)	121·4
N(2)–C(8)	1·467	C(4)–C(3)–C(2)	121·7
C(2)–C(3)	1·358	C(5)–C(4)–C(3)	115·6
C(5)–C(6)	1·340	C(6)–C(5)–C(4)	123·5
C(3)–C(4)	1·400	C(1)–C(6)–C(5)	120·0
C(4)–C(5)	1·422		
C(1)–C(2)	1·419		
C(1)–C(6)	1·418		
Cl—O(1)	1·42		
Cl—O(2)	1·47		

In Table 9 some shorter intermolecular distances are given. Estimated standard deviations of interatomic distances and bond angles shown in Tables 8 and 9 are about 0·008–0·010 Å and about 0° 50′ respectively.

Table 9. *Some shorter intermolecular distances*

Cl—N(1)	3·94 Å	O(1)–C(5)		3·48 Å
O(1)–O(1′)	2·31	O(1)–C(7)		3·19
O(2)–O(2′)	2·19	N(1)–C(6)	*AB′*	3·58
O(2)–N(1)	3·24	N(2)–C(5)	*BA*	3·64
O(2)–C(2)	3·27	C(2)–C(4)	*AB*	3·57
O(2)–C(6)	3·53	C(5)–C(8)	*C′D′*	3·56

The equation:

$$-9{\cdot}037X+4{\cdot}882Y+7{\cdot}603Z+0{\cdot}017=0$$

corresponds to the best-fit plane through the carbon atoms of the benzene ring [atoms C(1)–C(6)]. Here X,Y,Z are the fractional coordinates referred to the crystallographic axes of the direct lattice. The origin is placed at the atom N(1). The deviations of atoms from this plane are given in Table 10.

Table 10. *The deviations from the best-fit plane through the benzene ring*

N(1)	−0·017 Å	C(5)	−0·020 Å
C(1)	0·017	C(6)	0·002
C(2)	−0·012	C(7)	0·119
C(3)	−0·006	C(8)	−0·107
C(4)	0·024	N(2)	−0·002

The atoms C(7) and C(8) of the dimethylamino group deviate symmetrically from the plane of the benzene ring. The angle between the normals to the plane of the benzene ring and to the plane determined by atoms N(2), C(7) and C(8) is 8° 50′.

4. Discussion

The results of this structure determination can be summarized as follows. The form and the conformation of the DADA radical in the perchlorate and iodide is roughly similar. The most striking difference is the much larger angle between the normals to the planes of the benzene ring in the perchlorate. The DADA radical is therefore much less planar in the perchlorate than in the iodide. The dihedral angle between the planes of both benzene rings amounts to 23° in the iodide and to 45° in the perchlorate. This can be compared with 65° found in some different neutral diphenylamine compounds, summarized in our previous paper.

The bond distances and the valence angles in the DADA radical, on the other hand, are practically identical in both salts, and indicate a high degree of conjugation of bonds.

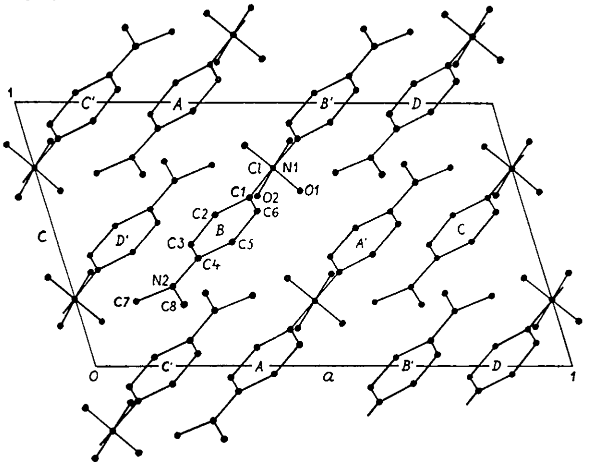

Fig. 1. Projection of the structure along [010].

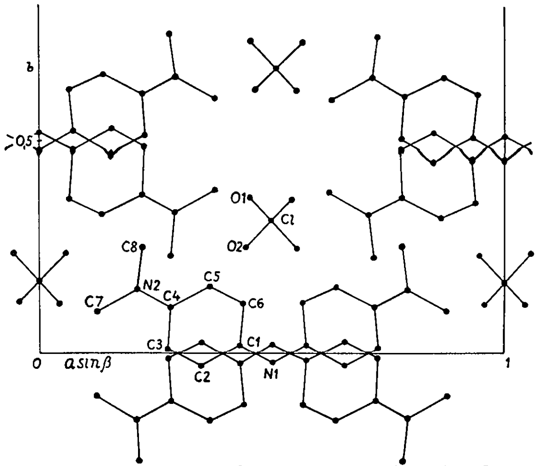

Fig. 2. Projection of the structure along [001].

The molecular packing of the DADA radicals (Figs. 1 and 2) is very similar in the iodide and the perchlorate. Contrary to the case of the iodide of the DADA radical, we did not find any abnormally short intermolecular distances in the perchlorate, except the distance C(7)–O(1).

It is noteworthy that the tetrahedral group ClO_4^- is oriented with the edge O(2)–O(2′) approximately parallel to the plane of the DADA radical. The explanation of this remarkable feature is at present not clear.

The authors are very grateful to Dr J. Honzl for providing the crystals and for numerous interesting discussions. We are also highly indebted to Dr B. Sedláček for his continuous interest in this work.

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A Reinvestigation of the Structure of Sodium Metasilicate, Na_2SiO_3

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New data have been used in a refinement which gives the mean dimensions of the metasilicate chain as Si–O (bridging) $1{\cdot}672 \pm 0{\cdot}002$ Å, Si–O (non-bridging) $1{\cdot}592 \pm 0{\cdot}002$ Å and ∠Si–O–Si 133·7°. These dimensions are interpreted in terms of π-bonding effects. The angular distortions in the tetrahedra in chlorate, sulphate, phosphate and silicate structures are examined, and distortions in silicates are shown to be consistent with non-bridging oxygen atoms having larger electronic charges than bridging oxygen atoms.

Introduction

The crystal structure of sodium metasilicate was determined by Grund & Pizy (1952). Their analysis used partial three-dimensional data, which were obtained photographically, and gave a residual R of 27%. They showed that the structure consists of infinite chains of silicate tetrahedra, with the chains linked together by coordination to sodium. The two types of Si–O bond were found to have lengths of 1·57 and 1·67 Å; the difference is unusually large for silicate structures but it could occur in this type of chain. However, the residual shows that the accuracy is likely to be low. The present reinvestigation was undertaken in order to determine accurately the Si–O bond lengths and angles, which are relevant to the discussion of π-bonding in second-row elements (Cruickshank, 1961).

Crystal data

Na_2SiO_3. $M = 122{\cdot}07$. Orthorhombic, $a = 10{\cdot}48$, $b = 6{\cdot}07$, $c = 4{\cdot}82$ Å; $V = 306{\cdot}6$ Å^3, $Z = 4$, $D_c = 2{\cdot}64$. $F(000) = 240$. Space group $Cmc2_1$ (no. 36). μ for Mo $K\alpha$ radiation $= 8{\cdot}5$ cm^{-1}.

Experimental

Crystals of Na_2SiO_3 were kindly supplied by Dr F. Liebau. They were prepared by fusion of equi-molar quantities of SiO_2 and Na_2CO_3 at 1100° and slow cooling of the melt. For the present work an approximately equi-dimensional crystal of mean diameter about 0·3 mm ($\mu R = 0{\cdot}13$) was selected and sealed in a Lindemann-glass capillary.

Cell dimensions were reported by Grund & Pizy (1952), and by Seeman (1956). In this work they were remeasured from precession photographs and on the linear diffractometer (Arndt & Phillips, 1961). The various measurements are given in Table 1. The

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