

The Crystal Structure of Some Conducting Organic Substances. IV. The Chlorate of 4,4'-Bis(dimethylamino)diphenylamine Radical

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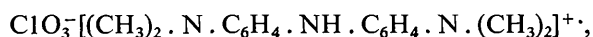
The structure of the chlorate of 4,4'-bis(dimethylamino)diphenylamine radical has been determined and compared with the structures of the iodide and perchlorate of the same cation-radical. The introduction of various anions does not influence the conjugation of bonds in the cation-radical or the packing of the molecules in the crystal lattice, but has a strong influence on the planarity of the cation-radical. Angles between the normals to the planes of the benzene rings in the iodide, perchlorate and chlorate are 23, 45 and 52° respectively.

Introduction

The chlorate of 4,4'-bis(dimethylamino)diphenylamine radical (DADA) belongs to a group of derivatives of diphenylamine which exhibit comparatively high conductivity ($\sim 10^{-6} \text{ohm}^{-1} \cdot \text{cm}^{-1}$). The crystal structures of the iodide and perchlorate of the DADA radical have already been determined (Toman & Očenášková, 1966; Toman, Očenášková & Huml, 1967); it was found that while the bond distances in the cation radical are very similar in both salts, the cation is much more planar in the iodide than in the perchlorate. The present work was undertaken in order to obtain more detailed evidence on the influence of various anions on the conformation of the DADA radical.

Experimental

Crystals of the chlorate of the DADA radical, having the formula



were prepared by Dr J. Honzl of this Institute. A solution of 8g of leuco base in 500 ml of absolute methanol was added to 6g of silver chlorate and stirred for 1 hour. The solution was filtered from the separated silver and crystallized overnight at the sublimation temperature of CO_2 . Dark violet, hygroscopic, explosive crystals about $0.7 \times 0.7 \times 1.0$ mm in size were obtained by the flow recrystallization method. (Tichý & Honzl, 1968).

The unit-cell dimensions were derived from Weissenberg photographs and remeasured on a single-crystal diffractometer as follows: $a = 10.37$, $b = 9.89$, $c = 8.88 \text{ \AA}$, $\alpha = 79.5$, $\beta = 106.6$ and $\gamma = 100.2^\circ$. The space group $P\bar{1}$ was suggested by statistical tests (Dragonette & Karle, 1965; Howells, Phillips & Rogers, 1950).

The observed density of 1.33 g.cm^{-3} corresponds to 2 stoichiometric units per cell, and is in good agreement with the calculated value, 1.323 g.cm^{-3} . The intensities were collected on a manual Hilger & Watts diffractometer with $\text{Mo K}\alpha$ radiation. The measure-

ment was performed by the 'normal beam, ω -scan' technique; a scintillation counter and pulse height analyser were used. The intensities of 3006 independent reflexions, 2042 of which were non-zero, were measured within the limit $0 < 2\theta \leq 50^\circ$. The intensities were corrected in the usual way for the Lorentz and polarization effects. No absorption correction was applied (the linear absorption coefficient μ for $\text{Mo K}\alpha$ radiation is 2.55 cm^{-1}).

Structure determination and refinement

Normalized structure amplitudes were calculated with scale and temperature factors obtained by the method of Wilson (1942) and the structure solved by the symbolic addition procedure (Karle & Karle, 1966). The search for the set of reflexions which satisfy the Σ_1 and Σ_2 relationships was carried out on 186 reflexions for which $E \geq 1.55$, the origin specification being made by the three largest reflexions 021, $\bar{2}12$ and $\bar{1}44$. In order to use the Σ_1 formula the $\bar{2}44$ reflexion was assigned a positive value. Four additional symbols were assigned to reflexions belonging to the remaining parity groups. All these symbols became known as the phase determination proceeded. An E map calculated with these 186 reflexions gave the positions of the Cl, N and C atoms. Signs of 530 reflexions with $E \geq 1.0$ were calculated from the positions of these atoms and a second E map calculated; this gave the positions of all atoms except those of hydrogen.

Structure factors calculated for this model, assuming an overall isotropic temperature factor $B_0 = 5.95 \text{ \AA}^2$, gave $R = \sum w||F_o| - |F_c|| / \sum w|F_o| = 0.274$. Five cycles of block-diagonal least-squares with refinement of the coordinates only, and five more cycles with refinement of individual isotropic temperature factors B_i , led to an R index of 0.189. The R index was reduced to 0.131 after 6 cycles of refinement with anisotropic thermal parameters.

A difference Fourier synthesis calculated at this stage yielded the positions of all the hydrogen atoms, with one exception (see Table 1). An additional peak

of height $0.86 \text{ e.}\text{\AA}^{-3}$ appeared, which might correspond to splitting of one of the oxygen atoms. This splitting was assigned to O(3) because of its comparatively small maximum on the electron density map, large shifts of its atomic coordinates and increasing values of their estimated standard deviations during the refinement process, and high temperature factor compared with the other oxygen atoms ($B_i = 15.5 \text{ \AA}^2$). Initially we considered that O(3) was disordered in an approximate ratio of 2:1, judged by the heights on the electron density map of peaks belonging to the other oxygen atoms, the favoured position being the original one. The occupancy factor for this atom was introduced as a refinable parameter. On the basis of the dependence of ΔF on F_o and $\sin^2 \theta$ a weighting scheme

$$w = 1 / [\{10 + |F_o| - (F_o/20)^2\} \{0.12/\sin^2 \theta\}^{1/4}]$$

was applied and five cycles with anisotropic temperature factors were performed in which contributions of the hydrogen atoms to the structure factors were taken into account, but their positions were not refined. (O3) was found to be split in a ratio of 72:28. A final difference Fourier synthesis was computed, in which the last hydrogen atom H(7) (see Table 1) appeared. The electron density maxima on this map did not exceed $0.33 \text{ e.}\text{\AA}^{-3}$. The final R index was 0.098. Calculations were carried out on MINSK 22 and NE503 computers with programs written in our laboratory by K. Tichý and D. Očenašková, and on an IBM computer with a set of NRC programs written by F. R. Ahmed and A. W. Hanson.

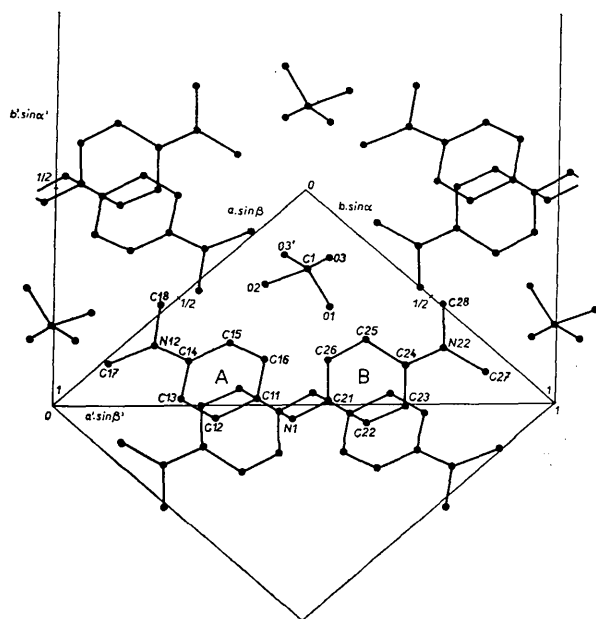


Fig. 1. Projection of the structure along c' . Axes a' , b' , c' of a unit-cell with double volume correspond to the monoclinic axes of the iodide and perchlorate of the DADA radical; a, b, c are actual triclinic axes [$a = \frac{1}{2}(a' + b')$, $b = \frac{1}{2}(b' - a')$, $c = c'$].

Table 1. Fractional coordinates of the hydrogen atoms

Bound to	x/a	y/b	z/c	
H(1)	C(12)	0.22	0.57	0.08
H(2)	C(13)	0.17	0.75	-0.11
H(3)	C(15)	0.60	0.85	-0.09
H(4)	C(16)	0.64	0.66	0.13
H(5)	C(17)	0.17	0.92	-0.33
H(6)	C(17)	0.22	0.08	-0.39
H(7)	C(17)	0.16	0.98	-0.21
H(8)	C(18)	0.43	0.12	-0.37
H(9)	C(18)	0.55	0.98	-0.25
H(10)	C(18)	0.54	0.09	-0.21
H(11)	C(22)	0.50	0.26	0.38
H(12)	C(23)	0.72	0.20	0.57
H(13)	C(25)	0.85	0.61	0.57
H(14)	C(26)	0.66	0.68	0.38
H(15)	C(27)	0.03	0.22	0.79
H(16)	C(27)	0.17	0.86	0.24
H(17)	C(27)	0.93	0.17	0.67
H(18)	C(28)	0.09	0.44	0.86
H(19)	C(28)	0.99	0.55	0.81
H(20)	C(28)	0.09	0.55	0.67
H(21)	N(1)	0.37	0.40	0.22

Results and discussion

Final atomic positional and thermal parameters are listed in Table 2. Observed and calculated structure factors are given in Table 3. The atomic scattering

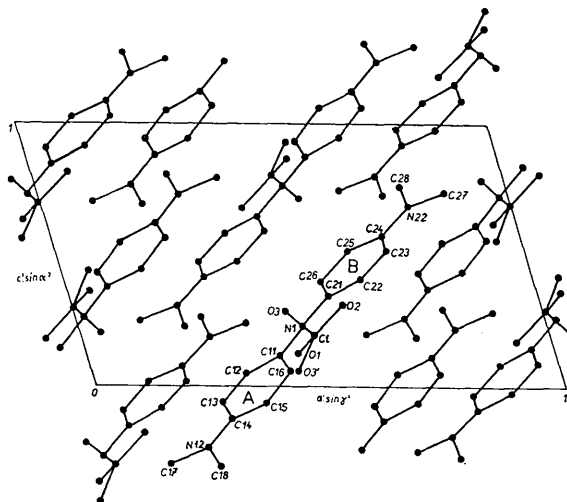


Fig. 2. Projection of the structure along b' .

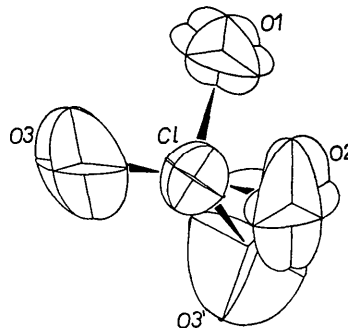


Fig. 3. 50% probability thermal motion ellipsoids of the chlorate anion.

factors used were those given in *International Tables for X-ray Crystallography* (1962).

The thermal motions of several groups of atoms have been analysed in terms of rigid-body tensors of translation (**T**) and libration (**L**) (Cruickshank, 1956). The root-mean-square discrepancies between the $(U_{ij})_{\text{obs}}$ and $(U_{ij})_{\text{calc}}$ (corrected appropriately for the number of degrees of freedom), $\sigma(U_{ij})$, were taken as a measure of the extent to which the rigid-body approximation applied to a group of atoms. Only one

model, embodying the carbon atoms of the benzene rings and all nitrogen atoms, appeared to be acceptable giving a $\sigma(U_{ij})$ value of 0.0052 which may be compared with an average e.s.d. of 0.0024 for the observed U_{ij} values. The rigid-body thermal parameters are given in Table 4. It is seen that the molecular translation vibrations are nearly isotropic, whereas the libration motion is markedly anisotropic. The greatest amplitude of libration is inclined at 3° to the long axis of the molecule.

Table 2. *Final parameters and e.s.d.'s of non-hydrogen atoms*

The temperature factor is in the form:

$$\exp [-2\pi(U_{11}a^*2h^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + U_{22}b^*2k^2 + 2U_{23}b^*c^*kl + U_{33}c^*2l^2)].$$

B_i are the principal axes of thermal ellipsoids of 50% probability.

	x/a ($\times 10^5$)	y/b ($\times 10^5$)	z/c ($\times 10^5$)	U_{11} ($\times 10^4$)	U_{12} ($\times 10^4$)	U_{13} ($\times 10^4$)	U_{22} ($\times 10^4$)	U_{23} ($\times 10^4$)	U_{33} ($\times 10^4$)	B_1	B_2	B_3
C(11)	42963 44	60814 46	11921 51	572 Å ² 24	61 Å ² 19	93 Å ² 18	593 Å ² 24	-58 Å ² 18	458 Å ² 24	0.40 Å	0.37 Å	0.31 Å
C(12)	29740 46	64155 50	5285 59	539 24	44 20	129 21	664 27	-84 22	636 29	0.41	0.38	0.36
C(13)	27179 47	75542 52	-6131 60	550 24	72 21	79 21	709 29	-43 23	627 29	0.42	0.39	0.36
C(14)	37756 46	84041 45	-11867 54	625 25	112 19	123 20	545 24	-54 19	540 26	0.41	0.36	0.34
C(15)	51037 45	80465 48	-5300 55	548 24	86 19	137 19	653 26	-46 20	531 26	0.40	0.38	0.34
C(16)	53517 45	69048 48	6220 54	569 24	136 19	163 19	661 26	-48 20	507 25	0.40	0.38	0.33
C(17)	21819 64	99784 70	-29188 94	727 35	265 31	104 35	887 40	202 38	1263 56	0.58	0.47	0.37
C(18)	46188 58	3647 51	-29655 65	876 34	109 24	245 27	564 26	30 23	693 32	0.48	0.40	0.35
N(12)	35401 43	95357 42	-23148 51	725 25	152 19	147 20	637 25	43 18	682 26	0.44	0.42	0.36
C(21)	56624 46	46567 44	34692 52	650 25	71 19	158 19	525 22	-56 18	479 24	0.42	0.35	0.32
C(22)	58233 52	32695 47	41314 55	782 30	4 21	69 21	540 24	-55 19	485 26	0.49	0.35	0.32
C(23)	69757 55	29349 47	52525 59	849 32	79 22	102 24	503 24	-49 21	590 29	0.49	0.36	0.34
C(24)	80496 51	39817 49	58319 55	731 29	154 22	143 21	630 26	-18 21	502 27	0.44	0.38	0.33
C(25)	78487 50	53930 48	52246 58	696 28	38 21	116 22	566 25	-76 21	580 28	0.45	0.37	0.35
C(26)	66862 48	57012 45	40870 55	658 26	83 20	122 21	516 23	-13 19	563 27	0.42	0.36	0.34
C(27)	94068 88	21944 73	75038 99	1395 63	578 43	-292 49	800 40	-80 39	1250 60	0.73	0.48	0.34
C(28)	2449 56	47553 65	76294 70	667 30	94 27	49 26	955 39	-120 30	741 36	0.48	0.46	0.38
N(22)	92188 46	36936 46	69312 55	768 27	221 21	50 22	708 26	-13 21	736 28	0.48	0.42	0.36
N(1)	44833 39	49231 38	23222 43	645 21	74 16	103 17	578 21	-51 16	497 22	0.42	0.38	0.33
Cl	15519 13	16270 14	19996 19	644 7	37 5	45 7	635 7	-7 7	951 10	0.51	0.40	0.38
O(1)	20232 51	30230 47	12919 64	1068 33	-58 24	66 28	803 27	191 25	1199 37	0.65	0.48	0.39
O(2)	27132 57	11363 83	31756 79	941 36	441 40	56 33	2219 63	581 48	1341 48	0.80	0.56	0.41
O(3)	6783 84	17741 85	28742 147	1168 56	30 45	1367 74	1183 57	-34 67	2901 123	0.83	0.54	0.36
O(3')	16023 305	10158 390	6746 371	1690 229	577 240	-295 197	2899 219	-1468 275	1801 253	0.94	0.67	0.43

Table 3 (cont.)

H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c
0	8	0	7.3	-5.4	-6	6	0	3.5	-1.0	1	5	0	16.0	17.6	9	4	0	5.4	5.0	-7	2	0	0.7	-0.7
1	8	0	0.7	0.1	-5	6	0	3.1	2.9	2	5	0	12.9	13.4	-10	1	0	5.1	5.1	-6	2	0	20.1	-20.5
2	8	0	5.1	-5.7	-4	6	0	9.3	-8.3	3	5	0	4.5	-13.8	-9	1	0	10.2	9.1	-5	2	0	25.8	24.1
3	8	0	1.4	-1.5	-3	6	0	11.6	-12.9	4	5	0	11.3	-10.5	-8	1	0	1.4	-0.4	-1	2	0	5.8	-6.4
4	8	0	6.2	5.2	-2	6	0	0.7	-0.5	5	5	0	12.2	-11.1	-7	1	0	9.3	-9.0	-3	2	0	12.6	13.5
5	8	0	1.7	1.6	-1	6	0	21.7	-18.6	6	5	0	1.9	-1.1	-6	1	0	13.6	-13.2	-2	2	0	38.0	35.7
-9	7	0	1.1	1.8	0	6	0	22.4	22.9	8	5	0	6.0	5.9	-5	1	0	0.7	0.6	-1	2	0	19.7	17.5
-8	7	0	0.7	1.4	1	6	0	15.5	14.9	-11	4	0	2.0	2.2	-4	1	0	25.0	24.7	0	2	0	3.8	-4.9
-7	7	0	8.3	7.8	2	6	0	12.4	11.8	-9	4	0	4.1	4.3	-3	1	0	7.8	-5.4	1	2	0	59.2	-57.7
-6	7	0	4.2	3.3	3	6	0	14.2	-14.3	-8	4	0	5.2	-3.8	-2	1	0	18.8	-17.2	2	2	0	18.3	-16.3
-5	7	0	9.3	9.5	4	6	0	5.8	-5.1	-7	4	0	8.9	-8.3	-1	1	0	15.3	-14.3	3	2	0	6.1	-5.6
-4	7	0	13.8	-12.4	5	6	0	2.7	2.9	-6	4	0	0.7	-0.1	0	1	0	17.9	-18.2	4	2	0	13.9	12.0
-3	7	0	4.8	-4.8	6	6	0	8.2	7.1	-5	4	0	20.6	19.7	1	1	0	33.2	-31.5	5	2	0	7.1	7.2
-2	7	0	2.7	2.2	7	6	0	5.6	5.0	-4	4	0	8.4	8.0	2	1	0	15.8	-14.5	6	2	0	11.0	11.5
-1	7	0	12.1	12.6	-11	5	0	1.5	1.9	-3	4	0	2.5	1.1	3	1	0	28.1	27.5	7	2	0	6.6	-6.1
0	7	0	7.0	4.8	-10	5	0	2.9	2.7	-2	4	0	6.6	6.9	4	1	0	7.1	-5.7	8	2	0	13.0	-13.0
1	7	0	8.0	-8.1	-9	5	0	7.3	-7.2	-1	4	0	27.4	-27.0	5	1	0	4.9	-3.5	9	2	0	13.6	13.0
2	7	0	23.2	-23.7	-8	5	0	7.1	-5.7	0	4	0	0.9	-2.7	6	1	0	4.7	-3.4	11	2	0	3.5	3.1
3	7	0	3.3	-3.2	-7	5	0	9.7	-8.7	1	4	0	5.4	6.1	7	1	0	5.8	-5.2	-10	1	0	4.8	-3.9
4	7	0	2.2	2.4	-6	5	0	7.7	7.1	2	4	0	16.0	15.2	8	1	0	6.8	-7.1	-9	1	0	1.4	0.5
5	7	0	1.2	1.4	-5	5	0	9.0	7.5	3	4	0	4.4	5.1	9	1	0	2.6	2.2	-8	1	0	9.8	10.2
6	7	0	5.5	6.1	-4	5	0	3.1	-3.0	4	4	0	25.7	27.9	-10	1	0	4.3	4.1	-7	1	0	6.1	6.1
-10	6	0	0.7	-1.4	-3	5	0	2.3	-1.6	5	4	0	12.9	-11.4	-11	2	0	3.3	-2.9	-6	1	0	7.1	5.1
-9	6	0	0.7	-0.9	-2	5	0	13.3	-12.2	6	4	0	4.6	-4.4	-10	2	0	3.2	-2.8	-5	1	0	17.7	-15.0
-8	6	0	1.4	2.1	-1	5	0	6.4	4.8	7	4	0	0.7	0.4	-9	2	0	7.7	7.0	-4	1	0	37.6	-37.0
-7	6	0	0.7	1.4	0	5	0	6.8	6.9	8	4	0	5.9	5.4	-8	2	0	9.8	9.0	-3	1	0	19.2	-17.4

Table 4. Rigid-body thermal parameters for carbon atoms of benzene rings and nitrogen atoms

$$\mathbf{T} \times 10^4 = \begin{pmatrix} 578 (20) & 15 (17) & 28 (17) \\ & 519 (20) & -21 (17) \\ & & 481 (18) \end{pmatrix} \text{ \AA}^2$$

$$\mathbf{L} \times 10 = \begin{pmatrix} 63 (16) & -32 (13) & 77 (19) \\ & 80 (16) & -83 (20) \\ & & 183 (30) \end{pmatrix} \text{ deg}^2$$

Principal axes of T

Eigenvalue	Direction cosines ($\times 10^4$)		
0.0587 \AA^2	9632	1462	2257
0.0529	375	-9041	4258
0.0464	-2663	4017	8762

Principal axes of L

Eigenvalue	Direction cosines ($\times 10^4$)		
26.4 deg ²	3823	-4367	8143
4.0	-5365	-8224	-1892
2.2	7523	-3645	-5488

$$\sigma(U_{ij}) \leq 0.0052 \text{ \AA}^2$$

Tensors \mathbf{T} and \mathbf{L} are related to an orthogonal set of axes X, Y, Z , where X is parallel to a , Y lies in the ab plane, and Z is parallel to c^* .

The whole DADA radical cannot be described in terms of the rigid-body model [which yields a negative minor-axis libration amplitude and a $\sigma(U_{ij})$ value of 0.0130] probably because of non-rigidity of the dimethylamino groups [see the high $(U_{ij})_{\text{obs}}$ of the C(17), C(18), C(27), C(28) atoms]. Also an attempt to calculate the rigid-body tensors for the chlorate anion failed, giving a $\sigma(U_{ij})$ value about 10 times as great as the average e.s.d. for the observed U_{ij} values. Bond distances and valence angles with their e.s.d.'s are given in Table 5. The bond distances were not corrected for libration motion, because the calculated corrections are comparable with the coordinate e.s.d.'s. Some shorter intermolecular distances and their e.s.d.'s are listed in Table 6. The equations:

$$0.1641X - 0.6857Y - 0.7091Z + 4.3493 = 0$$

$$0.6830X - 0.1479Y - 0.7153Z - 0.0027 = 0$$

define the mean planes through the carbon atoms of the benzene rings A and B respectively. The equations are referred to the orthogonal axes X, Y, Z , with X along the a axis, Y in the ab plane, and Z along the c^* axis, Atoms C(17), C(18) and C(27), C(28) belonging to the dimethylamino groups do not lie in the planes of the benzene rings. The angles between the normals to the plane determined by N(12), C(17) and C(18) and the plane of the benzene ring A , and between the normals to the plane of N(22), C(27) and C(28) and the benzene ring B are $4^\circ 18'$ and $4^\circ 22'$ respectively. The deviations of the ring and extra-ring atoms from these planes are given in Table 7. The dihedral angle between the benzene rings is 52° .

Table 5. Bond distances and valence angles

N(1)—C(11)	1.380 (6) \AA	N(1)—C(21)	1.381 (6) \AA
C(11)—C(12)	1.401 (7)	C(21)—C(22)	1.409 (6)
C(12)—C(13)	1.379 (7)	C(22)—C(23)	1.367 (8)
C(13)—C(14)	1.416 (7)	C(23)—C(24)	1.427 (7)
C(14)—C(15)	1.414 (7)	C(24)—C(25)	1.430 (7)
C(15)—C(16)	1.385 (7)	C(25)—C(26)	1.374 (7)
C(11)—C(16)	1.403 (7)	C(21)—C(26)	1.407 (7)
C(14)—N(12)	1.365 (6)	C(24)—N(22)	1.360 (7)
N(12)—C(17)	1.471 (9)	N(22)—C(27)	1.505 (9)
N(12)—C(18)	1.459 (7)	N(22)—C(28)	1.444 (8)
Cl—O(1)	1.470 (5)		
Cl—O(2)	1.442 (7)		
Cl—O(3)	1.391 (10)		
Cl—O(3')	1.435 (33)		
N(1)—C(11)—C(12)	118.24 (41) $^\circ$		
C(11)—C(12)—C(13)	121.09 (46)		
C(12)—C(13)—C(14)	121.22 (46)		
C(13)—C(14)—C(15)	117.33 (43)		
C(14)—C(15)—C(16)	121.02 (44)		
C(15)—C(16)—C(11)	121.02 (43)		
C(16)—C(11)—C(12)	118.28 (43)		
C(15)—C(14)—N(12)	120.69 (43)		
C(18)—N(12)—C(17)	117.04 (47)		
C(16)—C(11)—N(1)	123.42 (42)		
C(13)—C(14)—N(12)	121.97 (44)		
C(14)—N(12)—C(17)	121.15 (46)		
C(14)—N(12)—C(18)	121.81 (43)		

Table 5 (cont.)

N(1)—C(21)—C(22)	118.62 (41)°
C(21)—C(22)—C(23)	121.47 (46)
C(22)—C(23)—C(24)	121.24 (47)
C(23)—C(24)—C(25)	117.10 (45)
C(24)—C(25)—C(26)	120.49 (46)
C(25)—C(26)—C(21)	121.86 (44)
C(26)—C(21)—C(22)	117.66 (43)
C(25)—C(24)—N(22)	119.75 (46)
C(28)—N(22)—C(27)	118.91 (51)
C(26)—C(21)—N(1)	123.62 (42)
C(23)—C(24)—N(22)	123.14 (46)
C(24)—N(22)—C(27)	118.05 (50)
C(24)—N(22)—C(28)	122.97 (47)
C(11)—N(1)—C(21)	127.12 (39)
O(1)—Cl—O(2)	106.48 (36)
O(1)—Cl—O(3)	107.50 (48)
O(1)—Cl—O(3')	92.22 (140)
O(2)—Cl—O(3)	104.31 (52)
O(2)—Cl—O(3')	100.08 (141)
O(3)—Cl—O(3')*	142.36 (145)

* Not a valence angle.

Table 6. Intermolecular distances less than 3.6 Å

* Denotes an atom from the molecule related to the original one by a centre of symmetry. Hydrogen atom contacts are excluded.

O(1)—N(1)	2.911 Å	O(3')—C(15*)	3.410 Å
O(1)—C(11)	3.494	O(3')—C(27)	3.248
O(1)—C(12)	3.327	O(3')—C(27*)	3.422
O(1)—C(28)	3.546	C(14)—C(22*)	3.492
O(2)—C(18)	3.456	C(15)—C(22*)	3.448
O(2)—C(18*)	3.425	C(16)—N(1*)	3.496
O(3)—C(17*)	3.166	C(21)—C(21*)	3.589
O(3)—C(25*)	3.430		

Table 7. Deviations from the best planes through the benzene rings

Ring A		Ring B	
C(11)	-0.011 (4) Å	C(21)	0.028 (5) Å
C(12)	0.010 (5)	C(22)	-0.019 (5)
C(13)	-0.003 (5)	C(23)	-0.005 (5)
C(14)	-0.002 (5)	C(24)	0.020 (5)
C(15)	0.000 (5)	C(25)	-0.011 (5)
C(16)	0.006 (5)	C(26)	-0.012 (5)
N(1)	0.012 (4)	N(1)	0.033 (4)
N(12)	-0.016 (4)	N(22)	0.051 (5)
C(17)	-0.120 (7)	C(27)	0.124 (9)
C(18)	0.060 (5)	C(28)	-0.056 (6)

The structure of the chlorate of the DADA radical is very similar to the structures of the iodide and perchlorate, in spite of the fact that the title compound crystallizes in space group $P\bar{1}$ and the others in $C2/c$. The similarity of the packing is obvious from Figs. 1 and 2, where the molecules are placed in a double-volume unit cell, corresponding to the monoclinic unit cells of the iodide and perchlorate. In the chlorate the conjugation of the cation-radical was found to be similar to the iodide and perchlorate. This means that there are two shorter C—C bonds and four longer ones in the benzene rings and the C(11)—N(1), C(21)—N(1),

C(14)—N(12) and C(24)—N(22) bonds are shortened compared with the single bond between a nitrogen atom and a benzene ring, but the difference between these bonds is less than in the iodide and perchlorate. The average lengths of the shorter C—C bonds (1.38 Å) and of the longer ones (1.41 Å) are closer to the C—C bond in benzene, 1.395 Å (*International Tables for X-ray Crystallography*, 1962), than to the C—C bond lengths in benzoquinone, 1.32 and 1.48 Å (Trotter, 1960), in contrast to the iodide of this radical.

Corresponding to the reduced conjugation of the cation-radical there is a larger dihedral angle (52°) between the planes of the benzene rings. This angle is 23° in the iodide, 45° in the perchlorate, and 61 or 65° in the neutral diphenylamines (Toman & Očenášková, 1966; Toman, Očenášková & Huml, 1967).

The ClO₃ tetrahedron occupies two positions, one of which is preferred to the other in a ratio of 72:28. The positions of Cl, O(1) and O(2) are common for both tetrahedra. Thus the resultant effect appears as a splitting of the third oxygen atom into O(3) and O(3'). This is obviously why the calculation of rigid-body tensors of libration and translation for both the Cl, O(1), O(2), O(3) and Cl, O(1), O(2), O(3') groups failed, since the anisotropic temperature factors of Cl, O(1) and O(2) involve the thermal motion of both tetrahedra. Both tetrahedra are oriented with their O(1)—O(2) edge strictly parallel to the long axis of the cation radical. The position of O(1) is fixed by a hydrogen bond to N(1) [the O(1)···H(21) and H(21)—N(1) distances are 1.83 and 1.14 Å respectively]. O(2) is probably attracted to the cation radical by its positive charge; the intermolecular distances are too great to invoke overlap of atomic orbitals. The two different orientations of the chlorate anion can be explained by electrostatic attraction of the dimethyl-amino groups (see Fig. 1).

The thermal ellipsoids of the chlorate anion and the DADA radical are shown in Figs. 3 and 4 respectively.

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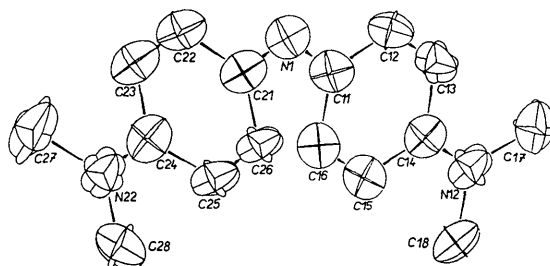


Fig. 4. 50% probability thermal motion ellipsoids of the DADA radical.

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X-ray Structure Analysis of Cubic Tetracyanoethylene and the Length of the C≡N Bond. Application of a Double-Atom Refinement Method

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The crystal structure of a cubic modification of tetracyanoethylene has been studied. The space group is $Im\bar{3}$ and the cell edge is 9.736 (5) Å. The bond lengths agree well with those in the monoclinic modification, but there are significant differences between the bond angles in the two forms. The central C=C bond is 1.344 (2) Å which is not significantly different from the corresponding bond length in ethylene and considerably shorter than predicted from INDO calculations. A new double-atom refinement method has been applied which, from the X-ray data alone, corrects for the apparent shortening of the C≡N bond length, as previously found by comparison of X-ray and neutron diffraction data. The corrected value for C≡N (1.166 (2) Å) is close to the electron diffraction result on tetracyanoethylene. The molecular packing in the crystal is such that large cavities surround the positions (0,0,0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

Introduction

Tetracyanoethylene (TCNE) is a compound of considerable interest, as it forms charge-transfer complexes with a large number of organic molecules.

As part of a research program on the charge distribution in aromatic hydrocarbon molecules and their charge-transfer complexes with TCNE, we have made a study of a cubic modification of tetracyanoethylene, crystals of which were obtained accidentally during an attempt to prepare some charge-transfer complexes. The cubic form of TCNE has not been described in the scientific literature, but we discovered after a substantial part of this work had been completed that it had been studied several years ago by Coulter & Trueblood (1963). The present results are fully compatible with those obtained earlier, but no detailed comparison between the two data sets has been attempted.

A monoclinic modification of TCNE has been described by Bekoe & Trueblood (1960, 1964), while Hope (1968) performed an electron diffraction analysis

of the molecule in the gas phase. The thermodynamic relationship between the two solid modifications is not known.

Experimental

A large mass of the cubic form of TCNE was obtained from ethyl acetate solutions. When a saturated solution in the same solvent was seeded with this material, nicely formed cubic crystals of TCNE showing the form {100} were obtained. The density was determined as 1.375 g.cm⁻³ by flotation in hexane-carbon tetrachloride mixtures. This compares with a measured density of 1.318 g.cm⁻³ for the monoclinic modification, indicating that the molecules are more closely packed in the cubic form.

There are six molecules in the body-centered unit cell, while the Laue symmetry of the X-ray photographs is $m\bar{3}$. The only cubic space groups compatible with the body-centering and the Laue symmetry, which will accommodate six molecules of TCNE in the unit cell are $I23$ (no. 197) and $Im\bar{3}$ (no. 204). The latter centric space group was selected on the basis of the structure analysis. Crystallographic data are summarized in Table 1.

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