

The Crystal Structure of a Stable Carbonium Ion, Tri-(*p*-aminophenyl)carbonium Perchlorate, $(\text{H}_2\text{NC}_6\text{H}_4)_3\text{C}^+ \cdot \text{ClO}_4^-$

BY LIP LIN KOH* AND KLAAS ERIKS

Department of Chemistry, Boston University, Boston, Massachusetts 02215, U.S.A

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The crystal structure of tri-(*p*-aminophenyl)carbonium perchlorate, $(\text{H}_2\text{NC}_6\text{H}_4)_3\text{C}^+ \cdot \text{ClO}_4^-$ has been determined from three-dimensional X-ray data. The monoclinic cell, space group $P2_1/c$ with $a = 8.469$ (8), $b = 21.190$ (21), $c = 10.371$ (12) Å, $\beta = 103.9$ (1)°, contains four molecules of the ionic compound. Observed and calculated densities are 1.408 and 1.426 g.cm⁻³. Least-squares refinement of the structure has led to a final value R of 0.097 for the 1513 observed reflections. The carbonium ion has the propeller form, with phenyl rings twisted 27, 34 and 34° out of the plane of the four coplanar central carbon atoms. The phenyl rings show pronounced quinoid structure. The twist angles are the result of steric effects in the ion. The amino groups form hydrogen bonds to the oxygen atoms of the tetrahedral ClO_4^- ions.

Introduction

The present structure determination constitutes a continuation of structural studies of triarylcation ions. The first structure reported was that of triphenylcarbonium perchlorate (Gomes de Mesquita, MacGillavry & Eriks, 1965). The study of the structure of the tri-*p*-amino substituted derivative was undertaken in order to determine (*a*) the possible influence of substituents on the triphenylcarbonium ion configuration and (*b*) the influence of crystal symmetry. In the triphenylcarbonium ion the threefold symmetry of the cation was required by the cubic symmetry of the space group, while crystals of the compound presented here display a much lower symmetry.

In addition the structures of triarylcation ions provide information about steric hindrance effects in molecules that contain closely approaching aromatic rings.

Experimental

A. Preparations and analyses

Three substances were initially prepared for possible structure determination. The three compounds were (I) crystal violet perchlorate, $[p-(\text{H}_3\text{C})_2\text{NC}_6\text{H}_4]_3\text{C} \cdot \text{ClO}_4$, (II) malachite green perchlorate, $[p-(\text{H}_3\text{C})_2\text{NC}_6\text{H}_4]_2(\text{C}_6\text{H}_5)\text{C} \cdot \text{ClO}_4$ and (III) tri-(*p*-aminophenyl)carbonium perchlorate or pararosaniline perchlorate, $[p-\text{H}_2\text{NC}_6\text{H}_4]_3\text{C} \cdot \text{ClO}_4$. The structure of compound (III) is reported in detail below. In this section preparational and structural details are given for compounds (I) and (II) as well.

In each case the perchlorates were prepared by adding a 0.1 M aqueous solution of NaClO_4 to a 0.1 M solution of the dye, in the chloride form, containing 10 to 15% acetic acid. The precipitates of the per-

chlorate dyes were filtered, washed with 0.05 M NaClO_4 solution and then with water, and dried over anhydrous CaSO_4 or P_2O_5 . The products were recrystallized from dioxane in the case of (I) and (II) and from absolute ethanol in the case of (III). Green needles were obtained from the crystallization of compounds (I) and (II). The crystals of (III) are described below. Analyses were obtained for compounds (I) and (III), with the following results:

Compound (I). Calculated percentages for $[(\text{H}_3\text{C})_2\text{NC}_6\text{H}_4]_3\text{C} \cdot \text{ClO}_4$: C, 63.63; N, 8.91; Cl, 7.53; H, 6.36; calculated for $[(\text{H}_3\text{C})_2\text{NC}_6\text{H}_4]_3\text{C} \cdot \text{ClO}_4 \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}_2$: C, 62.85; N, 8.14; Cl, 6.89; H, 6.60. Found: C, 62.7; N, 8.55; Cl, 7.00; H, 6.65.

Compound (III). Calculated for $(\text{H}_2\text{NC}_6\text{H}_4)_3\text{C} \cdot \text{ClO}_4$: C, 58.8; N, 10.84; Cl, 9.16; H, 4.65. Found: C, 59.0; N, 10.6; Cl, 9.05; H, 4.80.

It appears from these analyses that the crystal violet perchlorate (I) crystallizes with $\frac{1}{2}$ mole of dioxane solvent per mole of the organic compound, while the crystals of pararosaniline perchlorate (III) are solvent-free.

The densities of the crystallized substances, determined by flotation method, were 1.226 g.cm⁻³ for I and 1.408 g.cm⁻³ for (III).

The crystals of all three substances were stable in air and highly colored with metallic lustre.

B. Crystal data

Rotation and Weissenberg photographs were taken of the three compounds. The first two were found to have the following approximate cell dimensions:

(I). Monoclinic with $a = 50.8$, $b = 8.48$, $c = 29.8$ Å and $\beta = 118^\circ$, space group Cc or $C2/c$. $Z = 16$. D_x approximately 1.21 g.cm⁻³.

* Present address: Department of Chemistry, Nanyang University, Singapore.

(II). Triclinic with $d_{100}=14.3$, $b=9.7$, $d_{001}=17.5$ Å and $\beta=99^\circ$. $Z=4$ gives a D_x of approximately 1.16 g.cm $^{-3}$.

The crystals of (I) and (II) were not investigated further.

The pararosanine perchlorate, (III) (hereafter indicated by PRA) gave well-formed crystals with external monoclinic symmetry and well-developed faces {100}, {011} and {010}. The absorption of light in the crystals was too high to allow determination of optical properties. Preliminary cell dimensions were determined from rotation and Weissenberg diagrams. For the determination of accurate cell parameters a powder diagram was used.

It was found that powder samples obtained by grinding yielded very poor powder diagrams, indicating that the compound decomposed or the lattice deformed as a result of the heat liberated in grinding. Good diagrams were obtained from samples prepared by rapid cooling of a saturated solution in absolute ethanol. The powder diagrams, taken with a Norelco powder diffractometer, and Cu $K\alpha_1$ radiation ($\lambda=1.5405$ Å) exhibited 29 resolved peaks up to $2\theta=40^\circ$. Cell parameters were calculated by minimizing $\Sigma(\sin^2\theta_{\text{obs}}-\sin^2\theta_{\text{calc}})^2$.

The crystal data for PRA are as follows:

$$a=8.486(8), b=21.232(21), c=10.392(12) \text{ \AA}; \\ \beta=103.9^\circ \pm 0.1^\circ;$$

Table 1. Atomic coordinates, anisotropic temperature parameters ($\times 10^4$) and their standard deviations ($\times 10^4$) after final refinement

All hydrogen atoms were assigned the same temperature parameters, which were equivalent to $B=10.0$ for the isotropic expression. The expression for the anisotropic temperature factor for each atom is

$$\exp [-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	0.0623 (3)	0.0309 (1)	0.2223 (2)	167 (4)	20 (1)	124 (3)	6 (1)	58 (3)	3 (1)
O(1)	0.0698 (8)	-0.0361 (3)	0.2289 (7)	308 (16)	27 (2)	222 (12)	5 (5)	25 (11)	9 (4)
O(2)	0.1261 (10)	0.0525 (4)	0.1181 (9)	466 (21)	59 (3)	340 (15)	43 (7)	296 (16)	66 (6)
O(3)	0.1553 (12)	0.0565 (4)	0.3358 (8)	597 (28)	39 (3)	191 (12)	43 (8)	-114 (14)	-40 (5)
O(4)	-0.0994 (8)	0.0532 (4)	0.1961 (8)	222 (14)	55 (3)	249 (13)	59 (5)	125 (11)	39 (5)
N(1)	0.5570 (8)	0.4873 (4)	0.3566 (8)	349 (22)	27 (3)	174 (13)	-25 (6)	156 (15)	-8 (4)
N(2)	0.7413 (9)	0.0320 (4)	0.4266 (8)	208 (15)	29 (2)	155 (12)	11 (11)	62 (11)	-10 (4)
N(3)	-0.1541 (9)	0.2121 (4)	0.7451 (8)	156 (16)	55 (4)	176 (13)	-3 (6)	72 (12)	21 (5)
C(1)	0.3665 (9)	0.2438 (4)	0.4963 (8)	132 (14)	22 (2)	88 (11)	-12 (5)	45 (11)	16 (4)
C(2)	0.4124 (9)	0.3070 (4)	0.4608 (7)	147 (13)	20 (2)	39 (8)	1 (4)	29 (8)	-1 (3)
C(3)	0.2968 (8)	0.3549 (4)	0.4122 (7)	168 (16)	25 (2)	59 (10)	-3 (5)	52 (10)	-6 (4)
C(4)	0.3447 (10)	0.4137 (4)	0.3762 (8)	167 (18)	24 (2)	88 (11)	-8 (5)	59 (12)	4 (4)
C(5)	0.5127 (11)	0.4274 (4)	0.3948 (8)	233 (20)	25 (3)	92 (12)	-22 (6)	92 (14)	-9 (4)
C(6)	0.6307 (10)	0.3806 (4)	0.4451 (8)	147 (17)	26 (3)	94 (12)	-27 (6)	49 (12)	-20 (5)
C(7)	0.5811 (9)	0.3221 (4)	0.4738 (7)	110 (14)	28 (3)	71 (10)	-1 (5)	34 (10)	-7 (4)
C(8)	0.4585 (8)	0.1903 (3)	0.4742 (7)	86 (13)	20 (2)	77 (10)	0 (4)	22 (9)	3 (4)
C(9)	0.5359 (9)	0.1873 (4)	0.3691 (8)	145 (14)	26 (2)	85 (10)	-5 (5)	36 (10)	-4 (4)
C(10)	0.6260 (8)	0.1358 (4)	0.3477 (8)	140 (15)	24 (2)	88 (10)	-3 (5)	28 (10)	0 (4)
C(11)	0.6481 (9)	0.0848 (4)	0.4400 (8)	133 (15)	23 (3)	107 (12)	5 (5)	45 (11)	-12 (4)
C(12)	0.5698 (10)	0.0878 (4)	0.5470 (8)	156 (15)	24 (2)	88 (11)	3 (5)	33 (11)	3 (4)
C(13)	0.4795 (9)	0.1386 (4)	0.5638 (8)	142 (13)	19 (2)	68 (8)	5 (5)	28 (9)	3 (4)
C(14)	0.2257 (8)	0.2374 (4)	0.5512 (7)	107 (13)	21 (2)	56 (8)	-2 (4)	28 (9)	5 (3)
C(15)	0.1361 (8)	0.1796 (4)	0.5372 (8)	124 (14)	21 (2)	98 (10)	-5 (5)	0 (10)	2 (4)
C(16)	0.0092 (10)	0.1724 (4)	0.5981 (8)	162 (13)	22 (2)	101 (11)	-13 (5)	36 (11)	14 (4)
C(17)	-0.0308 (9)	0.2206 (4)	0.6791 (8)	92 (13)	34 (3)	109 (11)	-1 (5)	41 (10)	9 (5)
C(18)	0.0508 (10)	0.2791 (4)	0.6879 (8)	146 (15)	29 (3)	80 (10)	8 (5)	40 (10)	1 (4)
C(19)	0.1772 (9)	0.2875 (4)	0.6253 (7)	132 (14)	26 (2)	70 (10)	8 (5)	31 (10)	0 (4)
H(1)	0.175	0.345	0.385	370	56	247	0	73	0
H(2)	0.250	0.445	0.340						
H(3)	0.475	0.515	0.340						
H(4)	0.665	0.485	0.400						
H(5)	0.750	0.365	0.465						
H(6)	0.660	0.290	0.520						
H(7)	0.520	0.225	0.305						
H(8)	0.690	0.135	0.270						
H(9)	0.850	0.040	0.410						
H(10)	0.640	0.030	0.400						
H(11)	0.590	0.050	0.610						
H(12)	0.415	0.140	0.640						
H(13)	0.170	0.145	0.490						
H(14)	-0.050	0.130	0.590						
H(15)	-0.150	0.170	0.750						
H(16)	-0.160	0.240	0.810						
H(17)	0.020	0.315	0.740						
H(18)	0.220	0.330	0.640						

$Z=4$;
 $D_x=1.426 \text{ g.cm}^{-3}$, $D_m=1.408 \text{ g.cm}^{-3}$;
 space group $P2_1/c$.

Intensity data were collected with a Weissenberg camera using Cu $K\alpha$ radiation. Two crystals were used, one oriented around the a and one around the c axis. These crystals were ground to approximately ellipsoidal shape with dimensions $0.24 \times 0.16 \times 0.13$ mm, small enough so that absorption effects could be neglected. Data were collected of $0kl$ through $5kl$ around

the a axis and $hk0$ through $hk6$ around the c axis. Intensities were estimated visually. Systematic extinctions, *viz.* $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$, determined the space group uniquely as $P2_1/c$. For Cu $K\alpha$ radiation the absorption coefficient μ is 21 cm^{-1} , so that for the crystals used μr is about 0.20.

Structure determination

The visually estimated intensities for each individual level were scaled by least squares (Rollett & Sparks,

Table 2. *Interatomic distances and bond angles within the ions*

Distances	Corrected* value		
Cl—O(1)	1.422 Å	1.44 Å	C(1)—C(8)
Cl—O(2)	1.397	1.47	C(8)—C(9)
Cl—O(3)	1.361	1.45	C(9)—C(10)
Cl—O(4)	1.412	1.44	C(10)—C(11)
N(1)—C(5)	1.404		C(11)—C(12)
N(2)—C(11)	1.395		C(12)—C(13)
N(3)—C(17)	1.391		C(13)—C(8)
C(1)—C(2)	1.466		C(1)—C(14)
C(2)—C(3)	1.416		C(14)—C(15)
C(3)—C(4)	1.389		C(15)—C(16)
C(4)—C(5)	1.419		C(16)—C(17)
C(5)—C(6)	1.415		C(17)—C(18)
C(6)—C(7)	1.365		C(18)—C(19)
C(7)—C(2)	1.438		C(19)—C(14)
C(7)—C(9)	3.047		C(7)—H(7)
C(13)—C(15)	2.984		C(9)—H(6)
C(3)—C(19)	3.005		C(13)—H(13)
H(6)—H(7)	2.6		C(15)—H(12)
H(12)—H(13)	2.4		C(19)—H(1)
H(1)—H(18)	2.7		C(3)—H(18)

Estimated standard deviations in

C—C and C—N bonds	0.012 Å
in Cl—O bonds	0.010
	0.02 (Corrected)
in C—H bonds	0.12
in H—H bonds	0.2

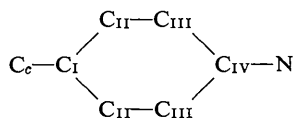
* Corrected according to Cruickshank (1956).

Angles			
O(1)—Cl—O(2)	110.1°	C(2)—C(3)—C(4)	121.1°
O(1)—Cl—O(3)	110.3	C(3)—C(4)—C(5)	119.7
O(1)—Cl—O(4)	111.9	C(4)—C(5)—C(6)	120.2
O(2)—Cl—O(3)	106.7	C(5)—C(6)—C(7)	119.3
O(2)—Cl—O(4)	106.2	C(6)—C(7)—C(2)	122.1
O(3)—Cl—O(4)	111.4	C(7)—C(2)—C(3)	117.4
N(1)—C(5)—C(4)	117.8	C(8)—C(9)—C(10)	122.8
N(1)—C(5)—C(6)	122.0	C(9)—C(10)—C(11)	118.7
N(2)—C(11)—C(10)	121.6	C(10)—C(11)—C(12)	118.6
N(2)—C(11)—C(12)	119.6	C(11)—C(12)—C(13)	121.2
N(3)—C(17)—C(16)	120.9	C(12)—C(13)—C(8)	120.9
N(3)—C(17)—C(18)	119.7	C(13)—C(8)—C(9)	117.7
C(2)—C(1)—C(8)	119.9	C(14)—C(15)—C(16)	120.1
C(2)—C(1)—C(14)	118.6	C(15)—C(16)—C(17)	121.1
C(8)—C(1)—C(14)	121.6	C(16)—C(17)—C(18)	119.3
C(1)—C(2)—C(7)	119.8	C(17)—C(18)—C(19)	120.1
C(1)—C(2)—C(3)	122.8	C(18)—C(19)—C(14)	120.6
C(1)—C(8)—C(9)	122.5	C(19)—C(14)—C(15)	118.5
C(1)—C(8)—C(13)	119.7		
C(1)—C(14)—C(15)	120.5		
C(1)—C(14)—C(19)	120.9		

Estimated standard deviation for all angles = 1.0°

Table 2 (cont.)

Average bond lengths and angles in the carbonium ion



Average distances	C _e —C _I	1.446 ± 0.014 Å
	C _I —C _{II}	1.422 ± 0.010
	C _{II} —C _{III}	1.377 ± 0.011
	C _{III} —C _{IV}	1.418 ± 0.004
	C _{IV} —N	1.397 ± 0.005
Average <i>ortho-ortho</i> distances	C—C	3.01 ± 0.02 Å
	C—H	2.68 ± 0.07
	H—H	2.6 ± 0.2
Average angles	C _{II} —C _I —C _{II}	117.9 ± 0.4 Å
	C _I —C _{II} —C _{III}	121.3 ± 0.8
	C _{II} —C _{III} —C _{IV}	120.2 ± 0.7
	C _{III} —C _{IV} —C _{III}	119.4 ± 0.6

Errors given are the average deviations from the mean values.

1960) with unit weight for each reflection. Lorentz-polarization factors were applied to all reflections and then the different levels were correlated, again using Rollett & Sparks's (1960) method. A total of 1513 independent observed reflections were obtained with $\sin\theta$ ranging up to 0.8. This corresponds to 50% of all possible reflections in the copper sphere. The intensities were brought to an approximate absolute scale using Wilson's (1942) method. The graph yielded an isotropic overall temperature factor $B = 2.5 \text{ \AA}^2$.

Using all observed reflections a sharpened Patterson function was calculated on an IBM 7090 computer, using the *ERFR2* program (Sly, Shoemaker & Van den Hende, 1962). From this vector map the positions of the chlorine atoms could be readily determined and plausible coordinates for the oxygen atoms were found, assuming the ClO_4 group to be tetrahedral. A three-dimensional Patterson superposition was then carried out with the Cl—Cl vector as translation vector. More than half of the carbon and nitrogen atoms could be located directly in this way and the positions for the remaining atoms were assigned by assuming C—C and C—N distances appropriate for a substituted benzene ring structure. These positions were then adjusted to give an optimum fit with the vector map.

Structure factors calculated on the basis of the atomic positions thus found gave an initial R -value of 0.36 for all observed reflections. Hydrogen atoms were excluded and an overall isotropic temperature factor of $B = 2.5 \text{ \AA}^2$ was used, as determined before. A three-dimensional electron density map based on calculated phases showed well resolved atoms, peak heights approximately as expected and a reasonable flat background, all confirming the correctness of the model.

Refinement of the structure was carried out by least-squares, using the full-matrix program of Busing, Martin & Levy (1962) for IBM 7090. Atomic scattering

factors were those from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1949) for C, N and O and that of Dawson (1960) for Cl. Initially unit weights were taken for all reflections, isotropic thermal parameters were used for each atom and hydrogen atoms were excluded from the calculations. Three cycles of refinement brought the R value down to 0.16. At this point a difference electron density map with all observed reflections having $\sin\theta \leq 0.6$ and with the contributions from all the heavier atoms subtracted revealed the positions of all hydrogen atoms. They were included in subsequent calculations, with an isotropic thermal parameter $B = 10 \text{ \AA}^2$, but their positions were not varied. The R value decreased to 0.147 which was the lowest value obtainable with isotropic temperature factors and unit weights.

Least-squares refinement with anisotropic thermal parameters for all atoms except hydrogen reduced the R value to 0.11. In the final cycles weights other than unity were assigned such that

$$w = k_1/|F_o|^2 \quad \text{for } |F_o| \geq 4 F_{\min}$$

$$w = k_2 |F_o|^2 \quad \text{for } |F_o| \leq 4 F_{\min}$$

with the ratio of the two constants $k_1/k_2 = (4|F_{\min}|)^4$ so that the weight is continuous at $|F_o| = 4|F_{\min}|$. Anisotropic refinement was continued with this weighting scheme, giving a final R value of 0.097

$$\text{and } R_w = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right)^{1/2} = 0.11 \text{ for all 1513 ob-}$$

served reflections. When 600 unobserved reflections were included with $F_o = \sqrt{1/3} F_{\min}$ (Hamilton, 1955), R became 0.129 and R_w was 0.123. Positions and thermal parameters for the hydrogen atoms were not refined. Their final positions were determined from a difference electron density map.

C. Packing of the ions

Because of the molecular dissymmetry of the propeller shaped cation it can exist in two forms (enantiomers 1 and 2) which are related by a mirror plane. Each unit cell contains two of each of the enantiomers.

The carbonium ions are stacked in layers parallel to the (102) plane of the crystal. Within each layer a carbonium ion is surrounded by four mirror images. Along the *c* axis the ions are stacked on top of each other with alternating enantiomers.

The ClO_4^- ions form zigzag chains along the *c* axis.

The shortest interionic distances are $\text{C}(19)\text{--}\text{C}(9) = 3.49 \text{ \AA}$, $\text{N}(1)\text{--}\text{N}(1) = 3.38 \text{ \AA}$, $\text{C}(10)\text{--}\text{O}(3) = 3.37 \text{ \AA}$, $\text{N}(1)\text{--}\text{O}(2) = 2.98 \text{ \AA}$ and $\text{N}(2)\text{--}\text{O}(4) = 3.05 \text{ \AA}$. These distances are indicated by dashed lines in Fig. 2.

Discussion

Some interesting conclusions can be drawn about this structure and valuable comparisons can be made with results of determinations of other carbonium ion structures.

The framework of 19 carbon atoms forms an extended conjugated system, in spite of the twist angles of the benzene rings. This can be concluded from the average distance from the central carbon atom C(1) to its three neighboring carbon atoms, C(2), C(8), C(14) of $1.446 \pm 0.014 \text{ \AA}$, indicating appreciable double bond character. For comparison the single bond distance between two sp^2 carbon atoms is 1.47 to 1.52 Å. Also the benzene rings show pronounced quinoid character: $\text{C}_I\text{--}\text{C}_{II} = 1.422 \pm 0.010 \text{ \AA}$, $\text{C}_{II}\text{--}\text{C}_{III} = 1.377 \pm 0.011 \text{ \AA}$, $\text{C}_{III}\text{--}\text{C}_{IV} = 1.418 \pm 0.004 \text{ \AA}$ (average bond lengths). The C–C bond lengths in this conjugated system can in fact be compared with empirical values calculated using an expression proposed by Cruickshank (1962)

$$r_{\text{C--C}} = 1.477 - (1.477 - 1.377) \frac{1.333 p}{0.333 p + 1}$$

where *p* is the π bond order and *r* the bond length in Å. The bond order can be estimated simply from the possible resonating structures I to IV and assigning equal weights to each:

Table 4. Planarity of the carbonium ion and the benzene rings*

Plane 1. Plane around central carbon atom, containing atoms C(1), C(2), C(8), and C(14)							
$0.5882x + 0.1048y + 0.8019z - 5.8346 = 0$							
Distance to plane†	C(1)	C(2)	C(8)	C(14)			
	0.006	-0.002	-0.002	-0.002			
Plane 2. Plane through the carbonium ion							
$0.6035x + 0.1127y + 0.7894z - 5.9193 = 0$							
Distance to plane	C(1)	C(2)	C(8)	C(14)	C(5)	C(11)	C(17)
	-0.041	-0.027	-0.041	-0.079	0.057	0.062	0.069
Plane 3. Plane through the carbonium ion including the nitrogen atoms							
$0.6078x + 0.1201y + 0.7849z - 5.9801 = 0$							
Distance to plane	C(1)	C(2)	C(8)	C(14)	C(5)	C(11)	C(17)
	-0.076	-0.048	-0.079	-0.123	0.062	0.018	0.004
Distance to plane	N(1)	N(2)	N(3)				
	0.049	0.091	0.101				
Plane 4. Plane containing ring I							
$0.0575x + 0.3130y + 0.9480z - 5.9574 = 0$							
Distance to plane	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	
	0.006	0.012	-0.019	0.010	0.021	-0.012	
Plane 5. Plane containing ring II							
$0.8150x + 0.4357y + 0.3821z - 6.3524 = 0$							
Distance to plane	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	
	-0.003	0.012	-0.015	0.010	-0.002	-0.003	
Plane 6. Plane containing ring III							
$0.6489x - 0.3466y + 0.6773z - 2.9961 = 0$							
Distance to plane	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	
	0.024	-0.004	-0.025	0.032	-0.013	-0.015	
Angles between normals of pairs of planes, numbering of planes as above.							
	Planes	Angle	Planes	Planes	Angle		
	1	4	34.2°	4	5	57.0°	
	1	5	33.8	4	6	55.2	
	1	6	27.3	5	6	50.5	

* Equations based on Cartesian coordinate system with *y* along the *b* axis, *z* along the *c* axis, *x* perpendicular to *yz* plane. *x*, *y*, *z* in units of Å.

† All distances are in Å. Atoms with negative distances are on the same side of the plane as the origin of the coordinate system, those with positive distances on the other side.

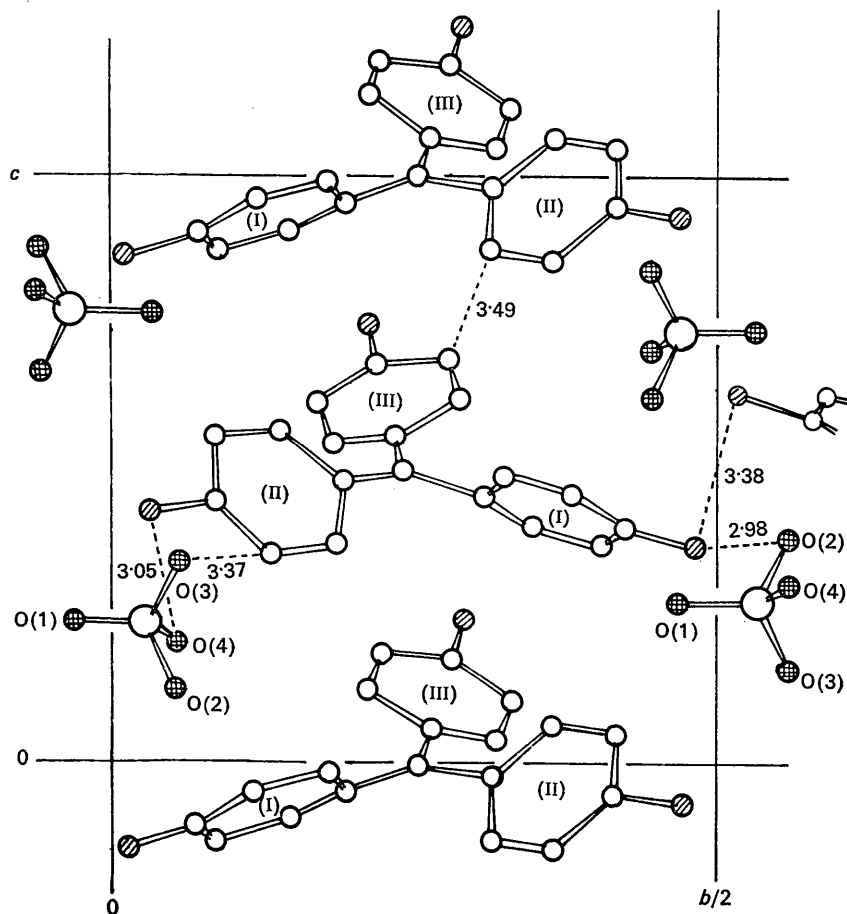
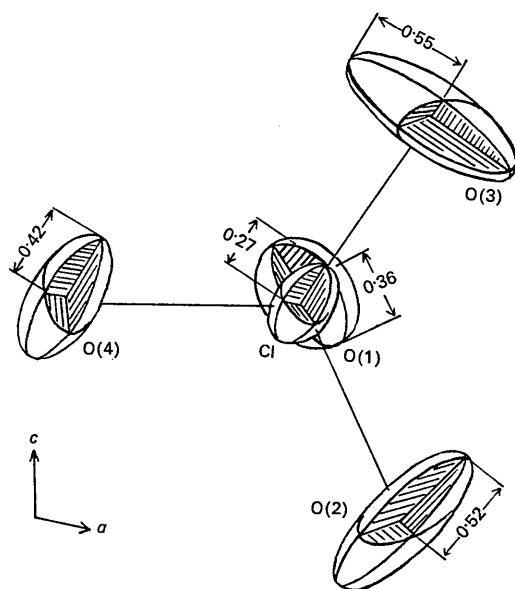
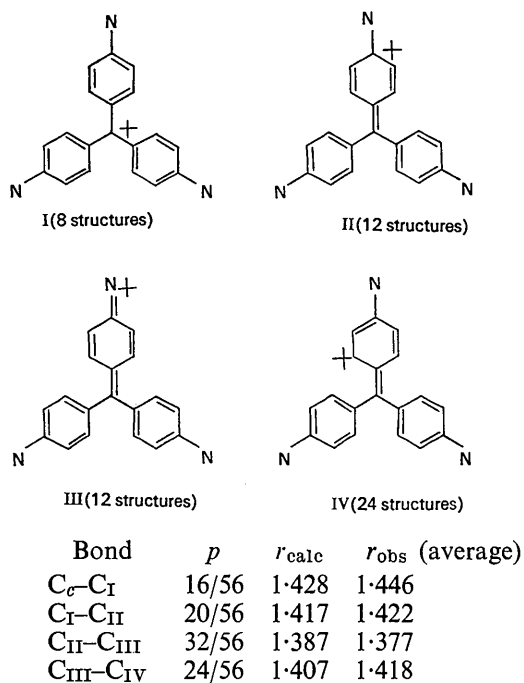

 Fig. 2. Projection of the structure along the *a* axis.


Fig. 3. Ellipsoids of thermal motion of the perchlorate group. Values given are root-mean-square displacements along the longest axis, in Å.

The agreement is quite good, with the possible exception of C_c-C_l . The high observed value for the latter bond length is to be expected, however, since for these two atoms the sp^2 planes are not coplanar as a result of the twist angles of about 30° , and thus the overlap of the π -orbitals is decreased.

The angles of twist of the benzene rings of 34, 34 and 27° are close to the value of 31° found in the triphenylcarbonium ion (Gomes de Mesquita *et al.*, 1965). It may be noted that benzene ring (III) with the 27° twist angle is also the one carrying the amino group that does not form a hydrogen bond with a perchlorate oxygen atom. The nonbonding *ortho-ortho* C-C, C-H and H-H contacts of 3.01, 2.7 and 2.6 Å respectively between adjacent benzene rings agree closely with the values of 3.04, 2.7 and 2.6 Å for the same distances in the triphenylcarbonium ion. Assuming van der Waals radii for C and H of 1.5 and 1.2 Å respectively, these nonbonding distances correspond to contact distances and it follows that the angles of twist of the benzene rings are determined strictly by steric hindrance. This is further confirmed by the fact that the twist angles of phenyl rings in the triphenylcyclopropenium ion are only 21° (Sundaralingam & Jensen, 1963). The central cyclopropenium ring replacing a single carbon atom moves the phenyl rings appreciably farther apart and thus allows a smaller twist angle, determined by contact distances. In the 3-Cl-1,2,3,4-tetraphenylcyclobutenium ion (Bryan, 1964) there is no steric hindrance left for the two phenyl rings that form the conjugated system (rings 2 and 4) and these rings are found to be coplanar with the cyclobutene ring.

The three *p*-amino groups in the present structure

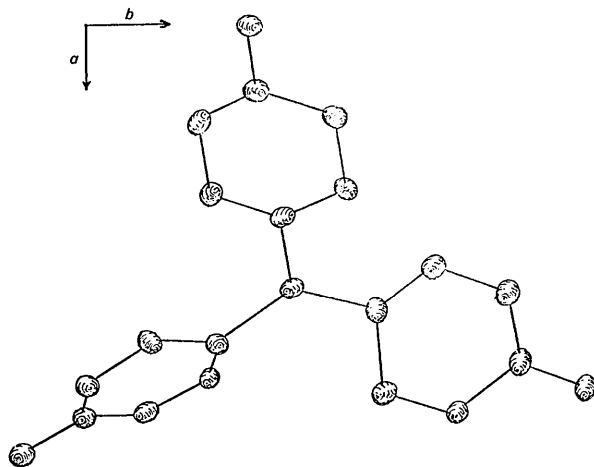


Fig. 4. Thermal motion ellipsoids of the atoms of the carbonium ion.

do not influence the structure of the ion appreciably when compared with the unsubstituted trityl perchlorate (Gomes de Mesquita *et al.*, 1965); bond lengths and angles of twist do not differ significantly. Also, within the PRA carbonium ion, the 7° difference in twist angle between rings I, II and ring III produces no observable changes in bond lengths. The packing of ions in the trityl perchlorate and in PRA is entirely different, however. Trityl perchlorate crystals contain two groups of crystallographically different ClO_4^- ions, one of which is disordered and located near the centers of four carbonium ions, the other (ordered) is surrounded by twelve protruding benzene rings all from different carbonium ions. In PRA all perchlorate ions are equivalent, ordered and all are located close to amino groups, presumably held in place by hydrogen bonding to these NH_2 groups.

Another major difference between the two crystalline substances is that trityl perchlorate, with the noncentric space group $F4_132$, can contain only one enantiomeric form of the carbonium ion and the individual crystals must be optically active. PRA on the other hand, with the centrosymmetric space group $P2_1/c$, has two ions of each enantiomeric form in the unit cell. The reasons for this totally different behavior of crystallization of the two substances will be studied in the future.

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