9:1. Each solution was washed successively with 5% hydrochloric acid, 5% aqueous sodium carbonate, and water, and then was dried (MgSO$_4$). The solvent was evaporated and the residues were analyzed by tlc.[3] Both iodine vapor and iodine–thiocyanate[4a] visualization showed that the two samples had identical 85:15 (±3) exo/endo ratios.

Kinetic Measurements. Experimental details of the kinetic measurements and the treatment of data were identical with those described previously[4a] with one exception. Initially we observed inconsistent and high infinity titers. The problem was traced to leaching of acidic substances from the red rubber serum caps used to seal our reaction flasks. Use of an all glass anaerobic sampling device[33] gave consistent infinity titers which were never outside the range 95–105% of theory.

Solvolysis Product Identification. Minor products were identified and the compositions of the crude solvolysis products were determined by the tlc method previously described.[3] Small samples of the dinitrobenzoate esters ($3 \times 10^{-3} M$ in 80% aqueous acetone) were heated in sealed tubes for at least 10 half-lives. After quenching and addition of 5% aqueous sodium carbonate to the solvolysis solution, the organic products were extracted into ethyl ether, dried (MgSO$_4$) for 10 min, and analyzed immediately. In cases where the similar R_f values of an uncomplexed dienol and the corresponding ψ-exo complexed dienol caused ambiguity, the iodine–thiocyanate visualization method which is specific for iron compounds[4a] was employed. Control experiments demonstrated that all product alcohols were stable under both solvolysis and work-up conditions.

Major products were isolated using a work-up identical with that described above followed by recrystallization and/or alumina chromatography as necessary. Isolated materials were shown to be identical with authentic samples. Results are listed below in the form: "ester solvolyzed → % yield product," **4b** → 50% **4a**, **5b** and/or **6b** → 45–50% **6a**, **10b** → 70% **10a**,[34] **11b** → 24% **11a** + 17% **12a**, **12b** → 71% **12a**.

Acknowledgment. We wish to thank Dr. Nye A. Clinton for many stimulating discussions about this work during which he proposed the steric retardation of the solvolysis of **6b** described above. We also gratefully acknowledge grants for partial support of this research from the National Science Foundation and from the Petroleum Research Fund.

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(33) See D. E. Kuhn, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1969, for details.

(34) Tlc showed traces of unsolvolyzed ester. Ir analysis suggests no major contamination by allylic isomers.

X-Ray Studies on Cyclopropenyl Cations.[1] II. Crystal and Molecular Structure of 1,2,3-Trisdimethylaminocyclopropenium Perchlorate

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Contribution from the Crystallography Laboratory, Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706. *Received August 11, 1971*

Abstract: The crystal structure of 1,2,3-trisdimethylaminocyclopropenium perchlorate has been determined using 829 reflections recorded on a diffractometer. The crystals are orthorhombic with space group *Pnma*. The unit cell dimensions are $a = 14.232$ (4), $b = 10.304$ (3), and $c = 9.196$ (3) Å. The calculated and observed densities are consistent with the presence of four molecules in the unit cell. Therefore, the molecule is bisected by the crystallographic mirror plane reducing the asymmetric unit to half the molecule. The structure was determined by the heavy atom technique and refined by the method of full-matrix least squares to a final R value of 0.076. The cyclopropenium ring is symmetrical with a C–C bond length of 1.363 Å. This value is significantly shorter than the C–C bond in benzene and appears to be characteristic of cyclopropenyl cations. The average exocyclic C–N bond length is 1.333 Å which is considerably shorter than the normal C–N single bond and the cyclopropenyl C–C bond. The nitrogen atoms show small deviations from the plane of the cyclopropenium ring. Two of the nitrogen atoms are displaced on one side of the ring, while the other to the opposite side. All of the six methyl groups are displaced toward the same side of the cyclopropenium ring to a slightly larger extent than the nitrogen atoms. The planes of the symmetry related dimethylamino groups are twisted at angles of 20.8° to the plane of the cyclopropenium ring, while the plane of the third amino group makes a dihedral angle of 9.9°. The nonplanarity of the molecule as a whole is due to the hydrogen–hydrogen interactions between the methyl groups on adjacent nitrogen atoms.

The existence of carbonium ions as reaction intermediates has long been recognized, and there has been exhaustive studies in this area in the literature. Moreover, direct observations of carbonium ions in solution by nmr spectroscopy have been reported by a number of workers.[3] However, little X-ray structural studies on carbonium ions have been reported. Some of the carbonium ions whose structures have been determined by X-ray diffraction techniques are as follows: triphenylmethyl perchlorate,[4] *sym*-triphenylcyclopropenium perchlorate,[1] 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate,[5] methyloxocarbonium hexafluoroantimonate,[6] methyl-, ethyl-, and isopropyloxocarbonium hexachloroantimonate,[7] tetraanisyl-

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(1) For part I, see M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966); **85**, 3302 (1963).

(2) To whom correspondence should be addressed.

(3) For a review, see G. A. Olah, *Science*, **168**, 1298 (1970).

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ethylene dichloroiodate,[8] triazidocarbonium hexachloroantimonate,[9] and an aryl dication.[10]

Carbonium ions with Hückel-type aromatic system are relatively stable. The best known examples of aromatically stabilized carbonium ions are the cycloheptatrienyl (tropylium)[11–14] and the cyclopropenyl cations.[1,15] The first derivative of the parent cyclopropenyl cation, triphenylcyclopropenium perchlorate was prepared[16] in 1957 and the X-ray crystal structural study[1] of it was reported in 1966. As an extension of this study, we now report the crystal and molecular structure of another two-π-electron aromatic system, 1,2,3-trisdimethylaminocyclopropenium perchlorate.[17]

Experimental Section

A sample of 1,2,3-trisdimethylaminocyclopropenium perchlorate was provided by Professor Zen-ichi Yoshida of Kyoto University, Japan. The compound gave crystals elongated along *b* on recrystallization from aqueous ethanol. Oscillation and Weissenberg photographs established the crystal system to be orthorhombic. The systematic absences $h00$, $h = 2n + 1$; $0kl$, $k = 2n + 1$; $00l$, $l = 2n + 1$; $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$ indicated that the space group is either *Pnma* (centric) or *Pn*2₁*a* (noncentric). Intensity statistics favored the centrosymmetric space group, *Pnma*. The cell constants measured on a diffractometer are $a = 14.232$ (4) $b = 10.304$ (3), $c = 9.196$ (3) Å ($\lambda_{\mathrm{Cu}K\alpha}$ 1.5418 Å). The density of the crystal measured by flotation in a mixture of cyclohexane and carbon tetrachloride is 1.319 g cm^{-3}, which is in good agreement with the calculated density of 1.318 g cm^{-3} for four molecules of $C_9H_8N_3ClO_4$ in the unit cell. Since there are eight equivalent positions in this space group, the molecule should lie on the mirror plane; thus the molecular symmetry should be C_{2v}. Three-dimensional intensity data were collected on a Picker FACS-I diffractometer with Ni-filtered Cu radiation ($\lambda_{\mathrm{Cu}K\alpha}$ 1.5418 Å, μ = 26.4 cm^{-1}) using a crystal of dimensions 0.15 × 0.20 × 0.3 mm^3. The θ–2θ scan technique was employed with a scan speed of 2°/min. The Weissenberg photographs indicated that the intensities showed a precipitous drop-off around $2\theta = 120°$. Therefore, reflections were scanned out to a 2θ value of 120°. A total of 1065 independent reflections were recorded. A reflection with intensity greater than 1.5 times its standard deviation was considered observed. Accordingly there were 829 observed reflections. The structure analysis was carried out using these reflections after correcting for the usual Lorentz–polarization effects.

Structure Determination and Refinement. The structure was solved by the heavy atom method. Since there are only four molecules of $C_9H_{18}N_3ClO_4$ in a unit cell, both the cation and the anion must occupy the mirror plane. Consequently, the following atoms, Cl, O(1), O(3), C(1), and N(1), lie on the mirror plane. The asymmetric unit of the structure contains 11 nonhydrogen atoms and 9 hydrogen atoms. The chlorine coordinates were obtained from a sharpened three-dimensional Patterson map. From the initial chlorine phases and successive rounds of structure factor and Fourier calculations the remaining atoms in the structure were located. The initial R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ value for all of the atoms included in the structure factor calculation was 0.32, where F_o is the observed and F_c is the calculated structure factors. The anomalous dispersion correction for the chlorine atom was made including both the real and imaginary parts. Three cycles of isotropic full-matrix least-squares refinement followed by two cycles of anisotropic refinement reduced the R value to 0.12. The hydrogen atoms were then obtained from difference electron density maps. Two additional cycles of anisotropic refinement on the nonhydrogen atoms with the hydrogen atom parameters fixed, dropped the R value to 0.096. Refinement of the hydrogen atom positions with fixed isotropic temperature factors of 5.0 Å followed by a final cycle of refinement of the nonhydrogen atoms dropped the R value to 0.076 and the weighted R to 0.097 for the observed reflections. The R value for all of the 1065 reflections was 0.089 and the weighted R was 0.11. The average ratio of the shifts to the standard deviations in the parameters was 0.04 with a maximum of 0.4. In the final refinement cycles the three reflections, 202, 022, and 020, which were suspected of suffering from secondary extinction, were given zero weight.

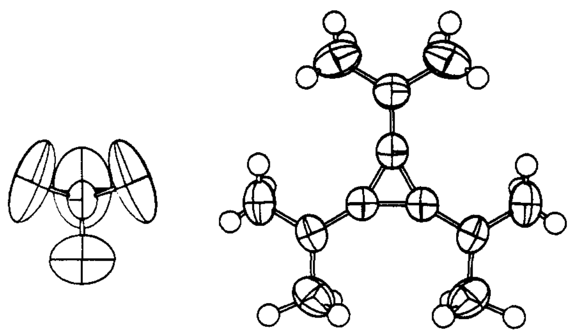

Figure 1. The ellipsoids of vibration of 1,2,3-trisdimethylaminocyclopropenium perchlorate. The drawing was made using the ORTEP program of Johnson.[21] Note the large vibrations executed by the perchlorate oxygen atoms.

The weighting scheme used was $1/\sqrt{w} = 1.20$ for $|F_o| < 8.11$ and $1/\sqrt{w} = 0.821 + 0.047|F_o|$ for $|F_o| > 8.11$. For scattering factors for C, O, N, and Cl were those from Cromer and Waber,[18] and that for H was from Stewart, Davidson, and Simpson.[19] The anomalous dispersion correction terms for chlorine scattering factors were those from the "International Tables for X-Ray Crystallography."[20]

The above successful refinement was based on the centric space group *Pnma*. Refinement based on the noncentric space group *Pn*2₁*a* was also tried. Although three cyeles of anisotropic refinement of the nonhydrogen atoms using the final coordinates from the previous refinement dropped the R value to 0.064, the shifts in the parameters were oscillating. In addition the chemically equivalent bond lengths and bond angles showed considerable distortions. This further confirms that the correct space group is *Pnma*.

Results

The ellipsoids of vibration for 1,2,3-trisdimethylaminocyclopropenium perchlorate viewed perpendicularly to the cyclopropenium ring are shown in Figure 1.[21] The perchlorate group under the cyclopropenium ring is shown alongside the cation. The positional coordinates and the thermal parameters for all atoms are listed in Table I. A list of the observed and calculated structure amplitudes will appear in the microfilm edition of this journal.[22] Bond lengths and bond

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(22) Microfilm copies of this table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche. Copies can also by obtained from the ASIS National Auxiliary Publication Service, c/o CCM, Information Corp., 909 3rd Ave., New York, N. Y. 10022.

Table I. Positional and Thermal Parameters of Atoms in 1,2,3-Trisdimethylaminocyclopropenium Perchlorate[a]

Atom	X	Y	Z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	2132 (1)	2500	385 (2)	69 (1)	93 (2)	169 (3)	0	18 (2)	0
O(1)	1331 (9)	2500	−459 (15)	208 (12)	441 (26)	574 (31)	0	−156 (17)	0
O(2)	2019 (5)	1398 (6)	1201 (9)	229 (7)	222 (8)	520 (16)	95 (7)	181 (9)	180 (10)
O(3)	2905 (8)	2500	−473 (15)	177 (9)	399 (22)	646 (31)	0	241 (15)	0
N(1)	1626 (4)	2500	5186 (7)	61 (4)	128 (8)	179 (10)	0	−11 (5)	0
N(2)	−26 (3)	723 (4)	2846 4)	67 (2)	98 (4)	160 (6)	−9 (3)	9 (3)	13 (4)
C(1)	940 (5)	2500	4210 (7)	47 (3)	99 (7)	137 (9)	0	15 (5)	0
C(2)	320 (3)	1839 (4)	3357 (5)	51 (3)	103 (4)	117 (6)	14 (3)	13 (3)	−3 (4)
C(4)	2075 (4)	1289 (8)	5616 (6)	60 (3)	228 (10)	232 (10)	22 (5)	−15 (5)	29 (9)
C(8)	−709 (4)	771 (6)	1669 (6)	95 (4)	180 (8)	155 (8)	−22 (5)	−13 (5)	−30 (7)
C(9)	502 (4)	−474 (5)	3056 (7)	95 (4)	105 (6)	220 (10)	1 (4)	26 (5)	−15 (6)
H(41)	174 (3)	59 (10)	547 (6)	5.0 (Å)^2					
H(42)	222 (4)	132 (5)	656 (7)	5.0					
H(43)	262 (4)	134 (7)	520 (11)	5.0					
H(81)	−44 (4)	110 (5)	87 (5)	5.0					
H(82)	−106 (4)	−24 (5)	161 (6)	5.0					
H(83)	−122 (3)	136 (5)	197 (6)	5.0					
H(91)	82 (4)	−46 (5)	391 (6)	5.0					
H(92)	19 (4)	−113 (5)	290 (9)	5.0					
H(93)	118 (6)	−51 (8)	254 (6)	5.0					

[a] Positional parameters of heavy atoms are multiplied by 10^4. Positional parameters of hydrogen atoms are multiplied by 10^3. Anisotropic thermal parameters are multiplied by 10^4. Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Estimated standard deviations are in parentheses. Parameters without standard deviations were not refined (symmetry constrained).

angles for the nonydrogen atoms are shown in Figure 2. The average standard deviations in bond lengths are C–C = N–C = 0.007 Å and Cl–O = 0.010 Å. The average standard deviations in bond angles are C–C–C = 0.27, N–C–C = 0.38, and O–Cl–O = 0.45°.

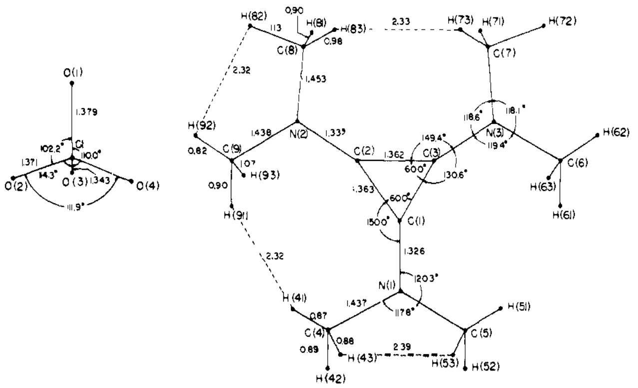

Figure 2. Bond lengths and bond angles in the 1,2,3-trisdimethylaminocyclopropenium perchlorate. The estimated standard deviations in the bonds are C–C = C–N = 0.007 Å, Cl–O = 0.010 Å, and in the angles, C–C–C = 0.27°, N–C–C = 0.38°, and O–Cl–O = 0.45°.

The larger errors in the bond distances and bond angles involving the chlorine atom are due to the large thermal vibration executed by the perchlorate group. The bond lengths and bond angles involving hydrogen atoms are in the normal range and are summarized in Table II.

Table II. Bond Lengths and Bond Angles Involving H Atoms

	Min	Max	Av	σ^a
C–H (9)[b]	0.82 Å	1.15 Å	0.94 Å	0.06 A
N–C–H(9)	103°	116°	110°	2°
H–C–H(9)	86°	118°	108°	3°

[a] Average estimated standard deviation. [b] Numbers in parentheses indicate the number of such bonds or angles in the structure.

Discussion

The two independent C–C bond lengths in the 1,2,3-trisdimethylaminocyclopropenyl cation (**1**) are identical within experimental errors. Thus, the cyclopropenium ring is symmetrical indicating that the resonance structures I to III make equal contributions. The C–C bond distance of 1.363 Å is significantly shorter than the C–C bond distance of 1.398 Å in benzene.[23] This finding is in accord with the results obtained previously on the crystal structure of *sym*-triphenylcyclopropenyl cation (**2**).[1] West, Sadö, and Tobey[24] have found from a normal coordinate analysis of the vibrational spectrum of trichlorocyclopropenyl cation (**3**) that the cyclopropenyl C–C stretching force constant of 6.32 mdyn/Å was considerably greater than that of benzene, 5.59 mdyn/Å. Again they also suggested that the cyclopropenyl C–C bond was shorter than the benzene C–C bond. The shortening in the C–C bonds of the cyclopropenium ring can be explained by the concept of the "bent" or "banana" bonds[25] as proposed for cyclopropane.

The Hückel molecular orbital and CNDO calculations have been performed for the unsubstituted trisaminocyclopropenium cation (**4**).[26] The C–C bond orders were 0.79 and 0.864, respectively, corresponding to C–C bond lengths of 1.370 and 1.360 Å[27] for the cyclopropenium ring. Both these values are in good agreement with our experimental values. It should be noted that the C–C bond length of **1** is about 0.010 Å shorter than that in **2**, 1.373 Å. Although this difference is barely significant, it might be related to the fact that the amino groups are stronger electron donating groups than the phenyl groups.

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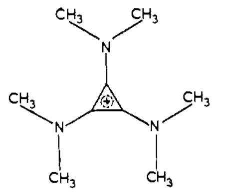

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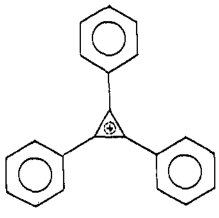

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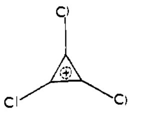

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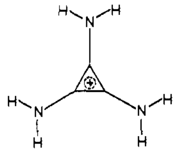

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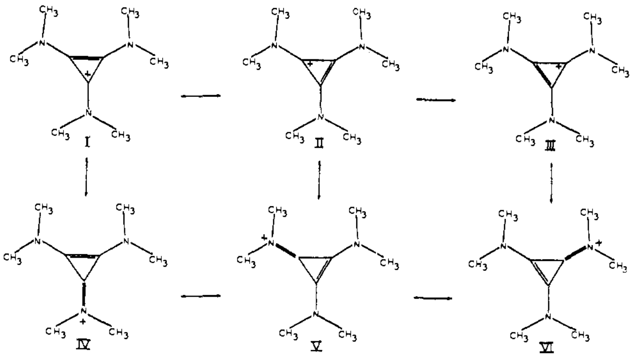
The average exocyclic C–N bond length of 1.333 Å is also considerably shorter than the normal C–N single bond distance of 1.47 Å,[28a] but close to the C–N double bond distance of 1.29 Å,[28a] and the C–N bond (1.302 Å) in *N*,*N*-dimethylisopropylideniminium perchlorate[29] $[(CH_3)_2N^+{=}C(CH_3)_2 \leftrightarrow (CH_3)_2NC^+(CH_3)_2]$, and the C–N bond distances (1.32 Å)[28b] in peptides and amides. The strong delocalization of the lone-pair electrons of the nitrogen atoms into the cyclopropenium ring, as shown in the resonance structures III–VI accounts for the shortening of this bond. The ^{13}C–H coupling constant of the parent cyclopropenyl cation found by Breslow and Groves[15] indicates that the orbital used for bonding with hydrogen is sp hybridized. Thus the shortening of the exocyclic C–N bond in **1** may also be partly due to the sp hybrid character of the ring carbon atoms. Similar shortening of the exocyclic bonds has been observed in cyclopropane derivatives.[30]



Also, the average N–C (methyl) distance of 1.457 Å is shorter than the normal C–N single bond distance of 1.47 Å.[28a] This again indicates that the resonance structures III to VI with the positive charge delocalized into the nitrogen atoms are important contributors to the overall resonance of the molecule.

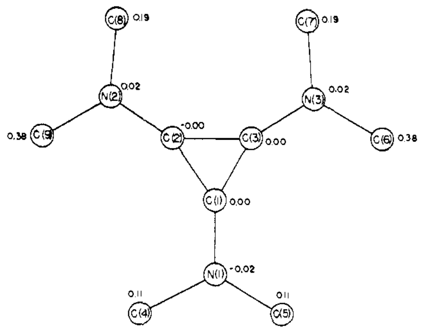


Figure 3. The deviations of the atoms from the plane through C(1)–C(2)–C(3) in 1,2,3-trisdimethylaminocyclopropenium cation.

Planarity of the Cation. The three nitrogen atoms attached to the ring carbon atoms are slightly displaced from the plane of the cyclopropenium ring. Two of the nitrogen atoms, N(2) and N(3), are displaced on one side of the ring, while N(1) is on the opposite side (Table III, plane 1). On the other hand, all of the six methyl groups are displaced toward the same side of the cyclopropenium plane, to a slightly larger extent than the nitrogen atoms (Figure 3). The least-squares plane through all the nonhydrogen atoms C(1), C(2), C(3), N(1), N(2), N(3), C(4), C(5), C(6), C(7), C(8), and C(9) is shown in Table III, plane 2. It is clear that these atoms do not lie in a perfect plane. The D_{3h} symmetry of the cation breaks down in going outward from the cyclopropenium ring to the substituents on the nitrogen atoms. The symmetry related amino groups on C(2) and C(3) are twisted at angles of 20.8° to the plane of the cyclopropenium ring, while the plane of the amino group on C(1) makes a dihedral angle of 9.9° to the cyclopropenium ring. The out-of-plane deviations of the amino groups tend to minimize the hydrogen–hydrogen interactions of the methyl groups on adjacent nitrogen atoms. In spite of these deviations, the intramolecular distances between the hydrogen atoms of the adjacent methyl groups are 2.32–2.39 Å (Figure 2).

Table III. Deviations of the Atoms from the Least-Squares Planes[a]

	Planes					
Atoms	1	2	3	4	5	6
N(1)	−0.022	*−0.096*	−0.091	*−0.068*	0.099	0.146
N(2)	0.023	*−0.111*	0.119	0.146	−0.162	*−0.121*
N(3)	0.023	*−0.111*	0.119	0.146	0.412	0.458
C(1)	*0.000*	*−0.099*	*−0.000*	*0.025*	0.113	0.158
C(2)	*−0.000*	*−0.121*.	0.061	0.087	*0.000*	*0.043*
C(3)	*0.000*	*−0.121*	0.061	0.087	0.213	0.258
C(4)	0.107	*0.048*	*−0.000*	*0.022*	0.035	0.080
C(5)	0.107	*0.048*	*0.000*	*0.022*	0.426	0.475
C(6)	0.378	*0.257*	0.438	0.464	0.960	1.009
C(7)	0.186	*0.025*	0.357	0.386	0.558	0.602
C(8)	0.186	*0.025*	0.357	0.386	*−0.000*	*0.039*
C(9)	0.378	*0.257*	0.438	0.464	*−0.000*	*0.039*
Coefficients[b]						
l	0.665	0.679	0.625	0.624	0.661	0.661
m	0.000	0.000	0.000	0.000	0.157	0.158
n	−0.747	−0.730	−0.781	−0.781	−0.734	−0.733
d	−2.003	−1.836	−2.186	−2.215	−1.668	−1.705

[a] Atoms italicized denote atoms used in calculating the plane. [b] The equation to the plane is $lx + my + nz = d$, where l, m, n are the direction cosines of the normal to the plane and d is the distance of the plane from the origin in ångströms. x, y, and z are coordinates in ångström units.

Atom N(1) is displaced by 0.090 Å from the plane formed by atoms C(1), C(4), and C(5) while N(2) (and N(3)) is displaced by 0.162 Å from the plane formed by atoms C(2), C(8), C(9) (and C(3), C(6), C(7)). The

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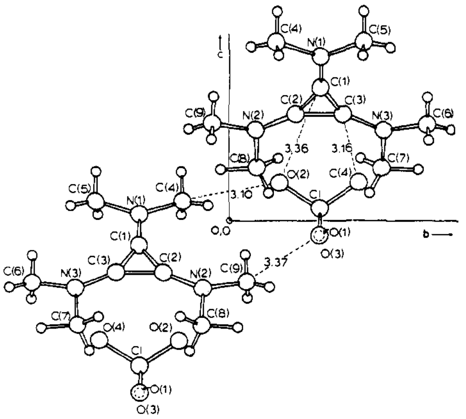

Figure 4. The shorter intermolecular oxygen–carbon distances. The molecules are viewed down the *a* axis.

sum of the bond angles around N(1) is 358.8° while that around N(2) (and N(3)) is 357.1°. Both these values are significantly smaller than 360°. Therefore, the nitrogen atoms possess some pyramidal character.

Perchlorate Group. The perchlorate ion executes a large vibrational motion, as seen from the β_{ij} values of the oxygen atoms (Table I and Figure 1). Especially the β_{11} values are considerably larger for the oxygen atoms as compared to the atoms in the cation. The shortening of the Cl–O bond distances from the expected length of 1.46 Å[31] is attributable to the thermal vibration.

Crystal Packing. The crystal structure can be described as being composed of the cations **1** and the perchlorate anions in a roughly zigzag arrangement along the *a* axial direction. As in the case of *sym*-triphenylcyclopropenium perchlorate,[1] the carbonium ions are sandwiched by the ClO_4^- groups, while the ClO_4^- groups are held tightly by pairs of cations. The shortest distances between the cations and anions are indicated in Figure 4. The top molecule is the reference molecule, while the lower one is related by the symmetry operation $^1/_2 - x, \bar{y}, z - {}^1/_2$; $^1/_2 - x, y - {}^1/_2, z - {}^1/_2$. The crystal packing of the contents of the unit cell viewed down the *c* axis is shown in Figure 5.

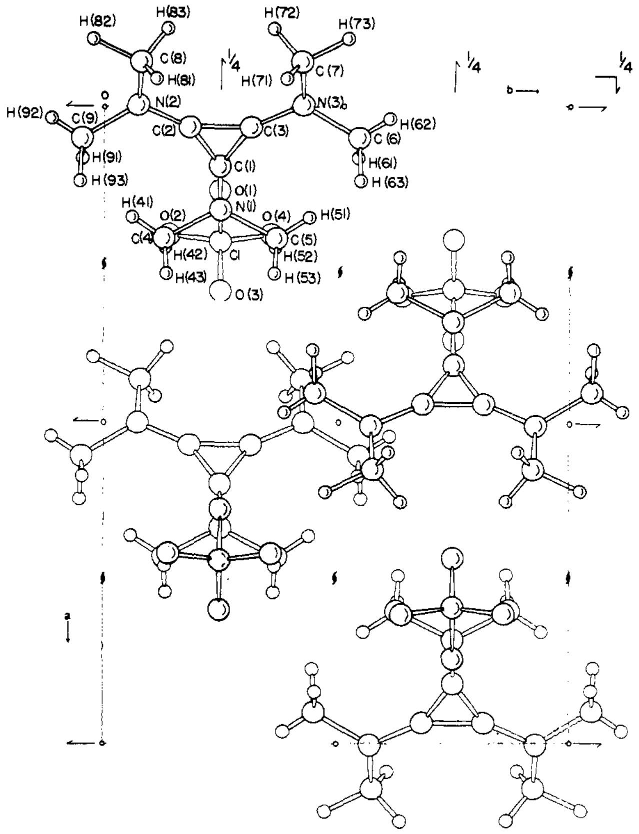

Figure 5. Packing diagram of 1,2,3-trisdimethylaminocyclopropenium perchlorate as viewed down the *c* axis.

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