Crystal Structure of Tri(*p*-biphenylyl)aminium Perchlorate[1]

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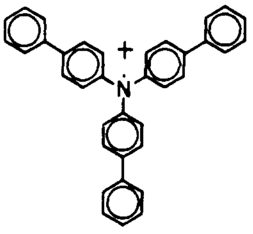
Abstract: Crystals of tri(*p*-biphenylyl)aminium perchlorate, $(p\text{-}C_6H_5C_6H_4)_3\dot{N}^+ClO_4^-$, are monoclinic (space group $P2_1/n$), with $a = 9.842\ (1)$, $b = 24.442\ (1)$, $c = 12.501\ (1)$ Å, $\beta = 106.77\ (1)°$, $Z = 4$, $d_{calcd} = 1.322$ g/cm^3 [$\lambda(\text{Cu K}\alpha_1) = 1.54051$ Å]. With Cu Kα radiation, 6085 reflections were recorded to 161.5° 2θ and corrected for absorption. The structure solution was achieved with Long's multisolution direct-method program. In final least-squares refinement *all* atoms, including hydrogen atoms, were given the usual six anisotropic thermal parameters, and the five atoms of the ClO_4^- ion were each given the ten extra thermal parameters of Johnson's three-cumulant model. Corrections for slight extinction were applied. The final $R(F)$ value was 0.051, and the final standard deviation of fit was 1.55 (all data included). The three N-C bonds are almost exactly coplanar, the N atom being displaced only 0.014 Å from the plane of its three carbon neighbors. The three N-C bonds have lengths of 1.421, 1.418, and 1.386 Å. The twist angles about these bonds from the hypothetical configuration with each six-membered ring attached to N coplanar with the central triangle of C atoms are −43.5, −45.3, and −26.5°, respectively (sign convention as for the Klyne–Prelog torsion angle). The inter-ring C-C bonds in the biphenylyl groups (in same order as the N-C bonds and the angles above) are 1.487, 1.481, and 1.476 Å in length. The twists about these bonds from the coplanar configuration for the two rings are +36.4, −14.5, and +23.0°. The radical cation is generally like a propeller, but each of the six rings has its own pitch. The average Cl-O intermode distance, 1.444 Å, calculated from the third-cumulant parameters, agrees well with Cl-O bond lengths from recent low-temperature determinations of the perchlorate ion structure.

The tri(*p*-biphenylyl)aminium cation (**1**) is representative



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of several known triarylaminium cations,[3] which generally are isolated as the perchlorate salts. These free-radical cations are isoelectronic with the corresponding uncharged triarylmethyl radicals and are expected to be similar in structure to the latter more familiar radicals and also to the triarylcarbonium ions. There exist in all these species similar possibilities for electron delocalization around the aromatic ring systems. The results of diffraction studies[4-8] suggest that, in general, triarylmethyl radicals and carbonium ions have propeller-like structures with essentially plane trigonal arrangements of C-C bonds at the central carbon atoms, which correspond in position to the nitrogen atom in the aminium cation. X-ray analyses on tris(*p*-fluorophenyl)amine and tris(*p*-iodophenyl)amine[9] suggest that even the triarylamines in general have plane or nearly plane arrangements of the valence bonds at nitrogen, at least in the solid state. The study described here was undertaken to determine for the first time the detailed geometry of a triarylaminium radical cation.

The particular compound tri(*p*-biphenylyl)aminium perchlorate was chosen for analysis because of its known stability in the solid state.[3] This compound is of interest also because of the opportunity it affords of observing varying effects of crystal environment on the twist from coplanarity of the two rings in the biphenylyl group. It is known that the twist angle varies widely among various crystalline biphenyl derivatives[10] even when there are no substituents ortho to the inter-ring C-C bond.

Experimental Section

Unit Cell and Space Group. Dark colored, almost black, six-sided prisms of tri(*p*-biphenylyl)aminium perchlorate were obtained by crystallization from an acetone–ether solution (green in color).[3] A crystal specimen with minimum and maximum diameters of about 0.25 and 0.50 mm was cut from a prism and mounted. From preliminary x-ray precession photographs, the space group was established as $P2_1/n$ (systematic absences: $h0l$ for $h + l$ odd and $0k0$ for k odd), and approximate unit-cell parameters were established. The prism axis was found to be along **a**. Precise values for the cell parameters were obtained by the method of least squares from angle data recorded at about 19 °C with the Oak Ridge computer-controlled diffractometer.[11] Data for six reflections in the range 124 to 133° 2θ for Cu Kα_1 radiation ($\lambda = 1.54051$ Å) yielded the following parameters (and standard errors in parentheses): $a = 9.842\ (1)$ Å, $b = 24.442\ (1)$ Å, $c = 12.501\ (1)$ Å, $\beta = 106.77\ (1)°$. The reasonable value 1.322 g/cm^3 is obtained for the calculated density on the assumption of four formula units per cell.

Reflection Data. Intensity data for 6094 independent reflections were recorded with the automatic diffractometer and Cu Kα radiation to the limit 161.5° in 2θ. A combination of ω and θ-2θ scan techniques was used, as described by Brown.[12] The crystal specimen was measured accurately to obtain the necessary data for making absorption corrections[13] and for computing mean path lengths to be used later in applying corrections for extinction. The value of the absorption coefficient used was 10.88 cm^{-1}; the absorption correction factors on the observed intensities ranged from 1.25 to 1.41. From the raw intensity data and corresponding standard errors, the structure-factor squares, F_o^2's, were calculated in the usual preliminary data processing, along with standard errors, $\sigma(F_o^2)$'s. The latter were obtained after the variances of the F_o^2 data were corrected empirically by the addition of the term $(0.03\ F_o^2)^2$ to each variance from counting statistics.[14] The weights used later in least-squares refinement with the F_o^2's as observations were the reciprocals of these corrected variances. The reflection data were put on an approximately absolute scale by the Wilson[15] method, and the normalized structure factors,[16] E's, were computed.

Structure Solution and Refinement. The solution for the structure was obtained through use of Long's multisolution direct method[17] based on iterative use of the Σ_2 relation.[16] All of the 42 atoms of carbon, nitrogen, oxygen, and chlorine in the asymmetric unit were identifiable with peaks in the E map[18] computed with the "best" sign combination for the 730 E's of magnitude $\geqslant 1.50$.

Least-squares refinement[19] was started at once and proceeded smoothly to convergence. After some preliminary cycles, starting coordinates for the hydrogen atoms were computed according to chemical-structural considerations, and both the coordinates and the thermal parameters of the hydrogen atoms were adjusted thereafter. In several full-matrix cycles individual isotropic thermal parameters were adjusted for the 27 hydrogen atoms, along with the anisotropic

Table I. Measures of Goodness of Fit[21] at Three Stages in the Least-Squares Refinement[a]

Stage	$R(F)$	$R(F^2)$	$R_w(F^2)$	σ_1
1	0.057	0.067	0.102	1.811
2	0.055	0.054	0.094	1.679
3	0.051 (0.043)	0.050 (0.049)	0.087 (0.086)	1.549 (1.640)

[a] Values in parentheses for stage 3 do not include reflections for which $F_o^2 \leq \sigma(F_o^2)$.

Table II. Fractional Atomic Coordinates and Thermal Parameters β_{ij} for Tri(*p*-biphenyl)aminium Perchlorate (Hydrogen Atoms Excluded)[a]

ATOM	10^5 X	10^5 Y	10^5 Z	10^5 β_{11}	10^5 β_{22}	10^5 β_{33}	10^5 β_{12}	10^5 β_{13}	10^5 β_{23}
CL	-11942(9)	38894(4)	24521(8)	953(4)	152(1)	846(3)	10(1)	201(3)	38(1)
	-11934(4)	38905(2)	24527(4)	955(4)	153(1)	849(3)	11(1)	203(3)	38(1)
O(1)	-11665(25)	41430(10)	14338(19)	1936(20)	252(3)	864(10)	72(6)	306(11)	106(4)
	-11694(15)	41461(6)	14258(11)	1940(22)	253(3)	866(11)	70(6)	311(12)	104(5)
O(2)	-16281(32)	42732(12)	31213(24)	2885(31)	305(4)	1671(18)	191(9)	1347(20)	-53(7)
	-16276(19)	42787(7)	31296(15)	2921(33)	307(4)	1667(19)	190(9)	1364(21)	-49(7)
O(3)	1839(24)	37016(10)	30219(19)	1180(15)	336(3)	1106(12)	156(6)	180(11)	154(5)
	1973(13)	37005(6)	30181(12)	1175(16)	335(4)	1113(13)	150(6)	181(11)	155(5)
O(4)	-21450(31)	34471(11)	22264(28)	1969(24)	253(3)	2232(23)	-312(7)	-39(18)	151(7)
	-21581(18)	34432(7)	22296(17)	1988(25)	256(3)	2244(25)	-312(8)	-51(20)	154(8)
N	22821(11)	28662(4)	25892(9)	905(12)	147(2)	595(8)	-28(4)	249(8)	29(3)
C(1,1)	16217(14)	24317(5)	30065(11)	909(14)	140(2)	658(10)	-22(4)	302(9)	22(4)
C(2,1)	23976(14)	21008(6)	38770(11)	870(14)	167(2)	671(10)	-15(5)	245(1)	32(4)
C(3,1)	17325(14)	16675(6)	42405(11)	1019(16)	155(2)	640(10)	24(5)	256(10)	49(4)
C(4,1)	2883(14)	15616(5)	37504(11)	993(15)	132(2)	646(10)	-10(4)	350(10)	-9(4)
C(5,1)	-4642(14)	19039(6)	28890(12)	833(14)	162(2)	777(11)	-22(5)	239(10)	13(4)
C(6,1)	1826(14)	23327(6)	25122(12)	906(15)	159(2)	704(10)	6(5)	192(10)	57(4)
C(1,1')	-4456(14)	10999(5)	41254(12)	1063(16)	127(2)	754(11)	5(5)	402(10)	0(4)
C(2,1')	-1056(16)	9515(6)	52445(12)	1249(18)	153(2)	751(11)	9(5)	377(12)	11(4)
C(3,1')	-8313(18)	5279(6)	55842(14)	1701(24)	161(3)	884(13)	20(6)	589(15)	63(5)
C(4,1')	-18748(19)	2439(6)	48066(16)	1757(25)	137(3)	1175(17)	-53(6)	714(17)	27(5)
C(5,1')	-22089(18)	3823(6)	36951(15)	1506(22)	150(3)	1090(16)	-118(6)	476(15)	-57(5)
C(6,1')	-15083(17)	8097(6)	33504(13)	1350(19)	158(3)	796(12)	-68(6)	390(12)	-24(4)
C(1,2)	19164(13)	29286(5)	14130(11)	888(14)	148(2)	627(10)	-36(4)	257(9)	16(4)
C(2,2)	18708(15)	24681(6)	7470(12)	1160(17)	133(2)	734(11)	15(5)	212(11)	24(4)
C(3,2)	15144(15)	25214(6)	-3944(12)	1152(17)	142(2)	701(11)	11(5)	196(11)	-30(4)
C(4,2)	11536(13)	30305(5)	-9210(11)	808(14)	152(2)	669(10)	-10(4)	258(9)	-1(4)
C(5,2)	11982(15)	34856(6)	-2291(12)	1266(18)	136(2)	702(11)	8(5)	336(11)	29(4)
C(6,2)	15864(15)	34403(6)	9202(12)	1281(18)	136(2)	671(10)	-4(5)	357(11)	-2(4)
C(1,2')	7180(14)	30802(6)	-21542(12)	866(14)	173(2)	665(10)	-7(5)	254(10)	2(4)
C(2,2')	9702(16)	26580(7)	-28240(13)	1238(19)	198(3)	768(12)	-9(6)	412(12)	-27(5)
C(3,2')	5758(19)	27087(8)	-39793(14)	1532(23)	291(4)	745(12)	-44(8)	499(14)	-69(6)
C(4,2')	-481(19)	31799(9)	-44848(14)	1451(23)	353(5)	660(12)	-64(9)	341(13)	28(6)
C(5,2')	-3072(20)	36009(8)	-38441(15)	1593(25)	275(4)	829(14)	54(8)	204(15)	114(6)
C(6,2')	640(18)	35500(7)	-26908(14)	1420(21)	211(3)	760(12)	88(7)	218(13)	23(5)
C(1,3)	32122(13)	32264(5)	32924(11)	885(14)	146(2)	623(10)	-13(4)	227(9)	25(4)
C(2,3)	42532(14)	35030(6)	29287(12)	1034(16)	176(3)	635(10)	-22(5)	332(10)	29(4)
C(3,3)	51832(14)	38543(6)	36319(12)	1013(16)	159(2)	813(11)	-48(5)	385(11)	34(4)
C(4,3)	51264(14)	39520(6)	47205(12)	949(15)	139(2)	779(11)	1(5)	268(10)	3(4)
C(5,3)	40596(15)	36805(6)	50639(12)	1091(16)	174(3)	662(10)	-22(5)	327(11)	0(4)
C(6,3)	31318(14)	33249(6)	43799(12)	942(15)	174(2)	699(10)	-44(5)	349(10)	24(4)
C(1,3')	61332(15)	43237(6)	54884(14)	1002(16)	147(2)	959(13)	-10(5)	318(12)	-47(4)
C(2,3')	68578(18)	47306(7)	50860(16)	1374(21)	164(3)	1239(17)	-64(6)	368(15)	0(6)
C(3,3')	78207(20)	50704(7)	58270(21)	1563(26)	168(3)	1766(26)	-124(7)	444(21)	-73(7)
C(4,3')	80753(22)	50086(9)	69648(21)	1709(29)	248(4)	1582(24)	-151(9)	400(21)	-280(9)
C(5,3')	73756(22)	46076(9)	73647(18)	1783(29)	338(5)	1134(19)	-166(10)	399(18)	-277(8)
C(6,3')	64208(19)	42648(8)	66405(15)	1495(23)	252(4)	947(15)	-134(8)	424(15)	-135(6)

[a] The second line for each atom of the ClO_4 ion gives the parameters for stage 2 of the refinement. All other parameters are from stage 3. The symbol C(2,1') means carbon atom 2 in ring 1', etc. (see Figure 2).

Table III. The Third Cumulant Parameters for the Atoms of the Perchlorate Ion

c^{ikl}	Cl $10^{-7}\times$	O(1) $10^{-6}\times$	O(2) $10^{-6}\times$	O(3) $10^{-6}\times$	O(4) $10^{-6}\times$
c^{111}	−53 (88)	20 (41)	234 (74)	−69 (31)	51 (50)
c^{222}	−15 (5)	−13 (2)	−21 (3)	−5 (3)	18 (3)
c^{333}	−132 (51)	28 (16)	−184 (34)	74 (19)	182 (49)
c^{112}	−0 (18)	22 (9)	−8 (16)	−16 (8)	24 (12)
c^{122}	−13 (6)	8 (3)	−10 (5)	−35 (4)	−25 (5)
c^{113}	78 (40)	77 (19)	−218 (42)	−19 (16)	−274 (29)
c^{133}	44 (33)	41 (14)	−244 (32)	−37 (13)	334 (29)
c^{223}	4 (6)	12 (3)	3 (4)	−7 (3)	3 (4)
c^{233}	−42 (13)	15 (5)	−65 (9)	13 (6)	−22 (11)
c^{123}	−20 (10)	26 (5)	−79 (10)	−30 (5)	42 (8)

thermal parameters of the 42 nonhydrogen atoms, the coordinates of all 69 atoms, one scale factor, and one extinction parameter[20] (488 parameters in all). At convergence in refinement with these parameters, the usual discrepancy index,[21] $R(F)$, was 0.057 (see stage 1 in Table I for corresponding values of other conventional measures of goodness of fit[21]).

In the next six least-squares cycles, the parameters of the hydrogen atoms and the parameters of the heavier atoms were refined by turns, anisotropic thermal parameters being used for all atoms. Each cycle was a full-matrix calculation with respect to the set of parameters adjusted. Nine discrepant data were omitted. The index $R(F)$ reached the value 0.055 (see also stage 2 in Table I). Application of the R-factor ratio test[22] showed that the improvement in agreement resulting from use of the anisotropic thermal parameters for the hydrogen atoms is highly significant. The experimental ratio of $R_w(F^2)$ values from rows 1 and 2 of Table II is $\mathcal{R}_{\text{exp}} = 1.077$, to be compared with the considerably smaller value $\mathcal{R}_{135,5460,0.005} = 1.016$ interpolated for the 0.005 probability point from a table of significance points of $\mathcal{R}$.[22b]

In the next two cycles the five atoms of the ClO_4^- ion were each given the ten extra adjustable parameters of the three-cumulant model,[23] in an attempt to represent more faithfully the large amplitude motions (up to 0.46 Å root mean square) of these atoms. The hydrogen parameters were held fixed. After one intervening cycle in which only the hydrogen atom parameters were adjusted, two more cycles on the nonhydrogen atom parameters, again with three-cumulant parameters for the ClO_4^- atoms, completed the refinement. The final $R(F)$ value was 0.051 (see also stage 3 in Table I). The R-factor ratio test showed that the improvement in agreement resulting from use of the three-cumulant parameters is highly significant: $\mathcal{R}_{\text{exp}} = 1.084$; $\mathcal{R}_{50,5412,0.005} = 1.007$.

The largest calculated extinction correction factor on F_o^2 was 1.161; the value found for the Zachariasen[20] extinction parameter r^* was 2.24×10^{-6} cm (esd 0.36×10^{-6} cm). Table II gives for the carbon, nitrogen, oxygen, and chlorine atoms the final values of the coordinates and of the coefficients β_{ij} of the usual temperature-factor expression $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. For the Cl and O atoms, the table also includes the β_{ij} values for the stage of refinement just preceding the introduction of the extra three-cumulant parameters for these atoms. Table III gives the values of these third-cumulant parameters, c^{ijk}'s, as defined by Johnson.[23] See paragraph at end of paper regarding supplementary material.

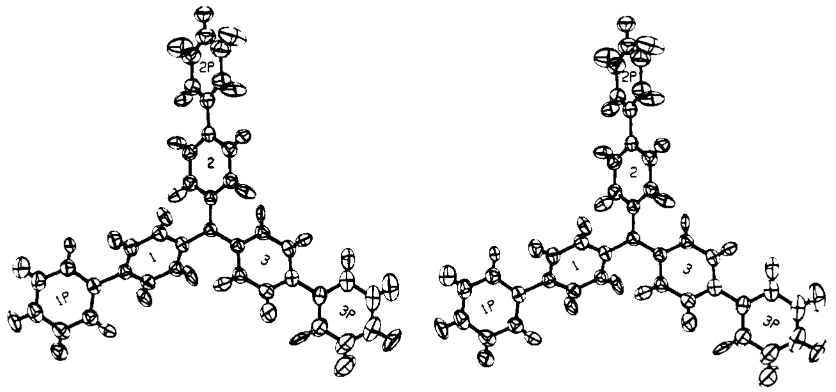

Figure 1. Stereoscopic view of the tri(*p*-biphenylyl)aminium radical cation. Atoms are represented by their thermal ellipsoids of 50% probability. In this figure the ring label 1P means 1′, etc.

The sources of the x-ray scattering factors used (all for neutral atoms) are as follows: *f*(Cl), *f*(O), and *f*(N) from "International Tables";[24] *f*(C) from Berghuis et al.;[25] *f*(H) from Stewart et al.[26]

Discussion

Structure of the Radical Cation. The geometrical configuration of the tri(*p*-biphenylyl)aminium cation is shown in the stereoscopic drawing of Figure 1, in which the atoms are represented by their thermal ellipsoids of 50% probability. [27] The configuration is generally that of a propeller, but each of the six aromatic rings which make up the blades has its own particular pitch. In Figure 2 the following metrical details of the geometry are displayed: the intracationic distances C···C, C···H (average), and H···H between neighboring atoms in ortho positions relative to the N atoms; deviations of atoms from the least-squares best planes[28] through the individual rings and from the plane (Δ) through the central triangle of carbon atoms C(1,1), C(1,2), and C(1,3); all bond lengths and valence angles not involving the hydrogen atoms; twist angles about the N-C bonds and about the inter-ring C-C bonds of the biphenylyl groups. A positive deviation of an atom from a plane is in the perpendicular direction outward from the plane on the side visible to the viewer of Figure 2. The zero of twist angle for each bond is taken to be the configuration in which the planes of the two atom groups connected by the bond coincide. The signs of the twist angles conform to the convention of Klyne and Prelog[29] for torsion angles. For example, for a twist about a C-C bond the sign associated with an angle is taken as positive if the best plane of the particular primed six-carbon ring would have to be turned clockwise through that angle to make it coincident in trace with the best plane of the unprimed ring when one looks along the biphenylyl group axis from the primed to the unprimed ring. Of course, the signs given in Figure 2 apply only to the radical cation for whch the coordinates are given in Table II and to the cation related to it by the 2_1 screw axis parallel to **b**; the twist angles have *opposite* signs for the other two cations in the centrosymmetric cell, which are mirror images of the first two.

The configuration of the nitrogen atom and the three sets of axial carbon atoms of the biphenylyl groups is approximately but not exactly planar. The largest deviation among these atoms from the plane Δ is 0.110 Å. The distance of the nitrogen atom from the plane Δ is 0.014 Å, about ten times the standard error, $\sigma_\perp$, of position of the atom along the perpendicular to the plane. This is a significant displacement in the formal mathematical sense, but it is clear that the geometry of the valence bonds at the N atom is essentially plane trigonal, as expected. The small displacement of the N atom corresponds to bending of each N-C bond by only 0.6° from an exactly plane configuration for the central NC_3 grouping. No carbon atom is displaced from the best least-squares plane through its own ring by more than 0.009 Å, about $6\sigma_\perp$, an amount hardly to be regarded as structurally significant. On the other hand, generally for all six rings the atoms directly attached to the rings are displaced somewhat more, indicating small but significant effects of packing in the crystal.

The twists of −43.5, −45.3, and −26.5° about the N-C bonds are all within the range of values found for the corresponding twists in triphenylamines,[9] triphenylmethyls,[4,5] and triphenylcarbonium ions.[6-8] Some such large twists all in the same sense about these bonds are required, of course, to prevent or minimize interference among the rings 1, 2, and 3 at the positions ortho to the N atom. The ortho-ortho C···C, C···H, and H···H distances found (Figure 2) are all slightly longer than those in triphenylcarbonium ion,[7] and in tris(*p*-aminophenyl)carbonium ion,[8] even though the N-C bonds are slightly shorter than the corresponding C-C bonds in the latter compounds, consistent with the fact that the average N-C twist is larger than the corresponding C-C twist in either of the latter. The three different twist angles, +36.4, −14.5, and +23.0°, about the inter-ring C-C bonds of the biphenylyl groups are within the range known from studies of other biphenyl derivatives[10] with no substituents on the carbon atoms ortho to the inter-ring bond.

The hybridization of the nitrogen valence orbitals must be very nearly the ideal sp^2 plane trigonal hybridization. Presumably the nearly planar configuration signifies some stabilization through electron delocalization and π-orbital overlap between the nitrogen atom and the attached carbon atoms, even though all of the rings are twisted far from the configuration allowing maximum overlap. There is a most interesting correlation for the N-C bonds among their lengths, interbond angles, and twist angles. The bond N-C(1,3), at 1.386 Å, is shorter than the average of bonds N-C(1,1) and N-C(1,2) by 0.035 Å, about 17 times the standard error of its length. This significant difference is probably related to the fact that the ring 3 is twisted about 20° less than 1 or 2 from the plane Δ. The lesser twist should make bond N-C(1,3) stronger and shorter than the other two, since the π-orbital overlap integral is proportional to the cosine of the twist angle.[30] It follows from the valence-shell electron-pair repulsion theory of directed valency[31,32] that the C-N-C angle opposite C(1,3) should be the smallest of the three C-N-C angles, as is observed. In agreement with the same theory,[32] the interior ring angle C(2,3)-C(1,3)-C(6,3) is smaller than the corresponding angles in the other two biphenylyl groups, and the bonds C(1,3)-C(2,3) and C(1,3)-C(6,3) are slightly longer than the corresponding bonds in the other groups.

The same kind of correlation appears to hold in crystalline tris(*p*-fluorophenyl)amine.[9] The average N-C bond length of 1.408 Å in the tri(*p*-biphenylyl)aminium cation is shorter by 0.011 Å than in this amine, though the average twist angles

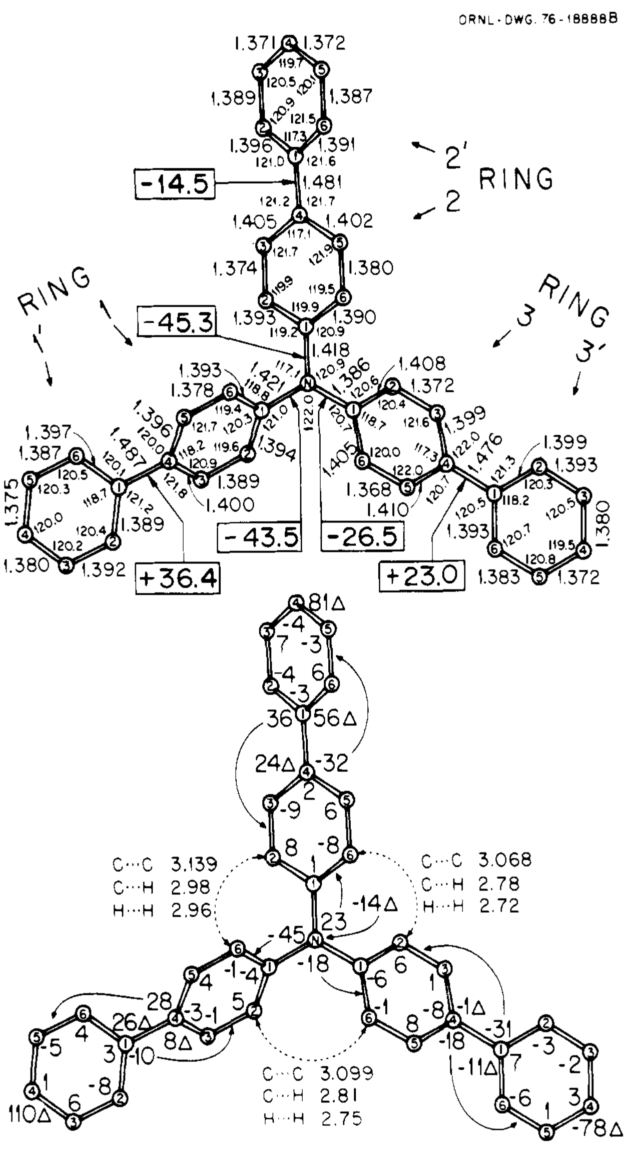

Figure 2. Geometry of the tri(*p*-biphenylyl)aminium radical cation. (Bottom) Distances (Å) C···C, C···H (average), and H···H between neighboring atoms in ortho positions relative to the N atom. Also shown are deviations, in units of 10^{-3} Å, of atoms from the least-squares best planes through the individual rings and from the plane (Δ) through the central triangle of carbon atoms. Deviations of atoms from their own rings are shown inside the rings. The reference planes for other deviations are indicated either by arrows or by Δ symbols; for example, atom C(1,3') is displaced −0.031 Å from the plane of ring 3 and −0.011 Å from the plane of the central triangle. (Top) Bond lengths (Å) and valence angles (deg) not involving hydrogen atoms and twist angles (deg) about the N-C and the inter-ring C-C bonds. The esd's of the bond lengths are 0.002-0.003 Å, and those of the valence angles are ~0.2°. See text for further explanation.

differ by only ~2°. Some such shortening is to be expected because electron delocalization is much more favored energetically in the radical cation, where it is not accompanied by charge separation.

The geometrical parameters discussed so far for the tri(*p*-biphenylyl)aminium radical anion seem generally reasonable in relation to those found for bis(*p*-dimethylaminophenyl)aminium iodide,[33] perchlorate,[34] and chlorate.[35] In each of these compounds the radical cation has twofold symmetry. The twist angles (between aromatic ring plane and C-N-C plane) are 12.7, 25.4, and 29.3°, respectively; the N-C bond lengths are 1.363 (17), 1.366 (8), and 1.380 (6) Å; the C-N-C angles are 131.2 (1.5), 126.0 (8), and 127.1 (4)°.

For the inter-ring C-C bonds of the biphenylyl groups, the correlation of lengths with the corresponding twist angles is not so obvious. The spread of the bond lengths is only 0.011 Å, though the twists vary from −14.5 to +36.4°. The smallest twist from coplanarity is associated with the intermediate bond length, 1.481 Å. The reason is probably that at a twist angle of 14.5° repulsion between neighboring ortho hydrogen atoms prevents the C-C bond from shortening quite as much as it would otherwise. Calculations by Casalone et al.[36] of the energy of an isolated biphenyl molecule suggest that the inter-ring C-C distance should decrease with increasing twist angle as the strain of the H···H contacts is released until an angle of 20° is reached and then increase again at about 50° because of the diminished π conjugation. There are indications that there are such significant H···H repulsions in crystalline *p*-terphenyl[37] and in the *p*-terphenyl molecule in the 1:1 complex of *p*-terphenyl with 7,7,8,8-tetracyanoquinodimethane.[38] In the latter case, there is a 12° twist about the C-C bond connecting the center ring to each end ring, and the bond length is 1.482 (1) Å. In crystalline biphenyl the inter-ring C-C bond length has been reported as 1.494 (3) Å at room temperature[39] and 1.496 (3) Å at 110 K,[40] and the molecule appears to have coplanar rings as a requirement of its location on a symmetry center. It seems likely from the thermal parameters,[40] however, that the molecule is actually slightly twisted, but that the twisting is masked by disorder that satisfies the symmetry requirement.

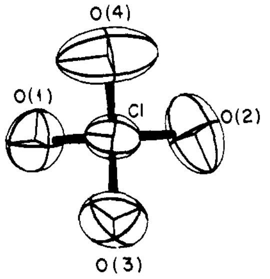

Figure 3. The perchlorate ion, showing the thermal ellipsoids of 50% probability.

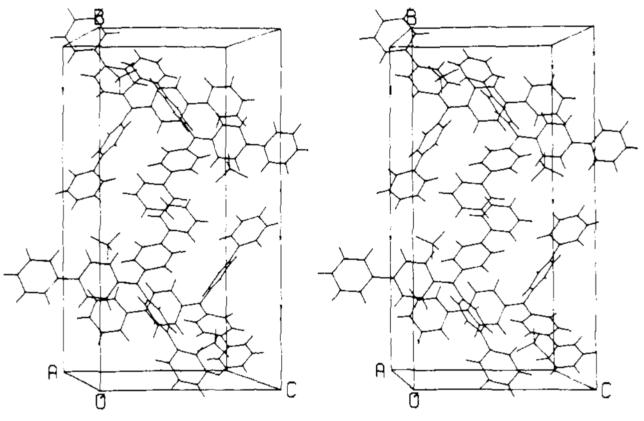

Figure 4. Stereoscopic drawing of the crystal structure of tri(*p*-biphenylyl)aminium perchlorate.

In the biphenylyl groups the average of the six interior ring angles at the ends of the C–C bonds joining the rings is 117.8°. Similar angles significantly less than 120° have been found in biphenyl,[39,40] *p,p*-bitolyl,[10b] and *p*-terphenyl.[37,38] The value of 117.8° is not significantly different from the mean value 117.6° reported by Domenicano et al.[41] for the angle α within a benzene ring at the point of attachment of a phenyl group. The averages of the two angles α for the three different C–C inter-ring bonds for biphenylyl groups 1, 2, and 3 are 118.5, 117.2, and 117.8°, respectively. Though the differences are not large, the smallest average angle is associated with the smallest C–C twist angle and vice versa, as is reasonable.

The particular pattern of twist angles found may be considered to result from the perturbation of crystal packing upon the equilibrium conformation (possibly conformations) that an isolated cation would have. Intuitively one might expect an isolated tri(*p*-biphenylyl)aminium ion to have point-group symmetry 3 exactly, at least for the inner portion of the ion including only the three unprimed six-membered rings. The asymmetry found in the pattern of twists about the N–C bonds may reasonably be attributed to the energetic requirements of packing. It is, however, possible that this pattern represents with some faithfulness the actual conformation of an isolated cation. In the case of triphenylphosphine, analogous except for the absence of electron delocalization, Brock and Ibers[42] have calculated by a semiempirical energy minimization procedure that the isolated molecule should have a number of different conformations of similar energy, including one conformation quite close to the unsymmetrical one observed in that crystal structure.

The fact that the twist angles about the three inter-ring C–C bonds have three widely different values, +36.4, −14.5, and +23.0°, can only result from the effects of crystal packing in perturbing the cation from whatever equilibrium of preferred conformations there may be about these bonds in isolation. Our results tell nothing about the functional form for the variation with twist angle of the internal energy of a single biphenylyl group, except to suggest that the curve must be rather flat, perhaps with either a low maximum or a shallow minimum at 0°, depending on the relative importance of the repulsion energy between nonbonded atoms ortho to the inter-ring bond and the electron delocalization energy. In relation to these questions of conformation we plan detailed potential energy calculations for the cation and for the crystal.

The apparent C–H bond lengths show the systematic error of shortening usually observed for them in x-ray analysis, attributable to the shifting of the centroids of the hydrogen electron clouds from the proton positions as a result of chemical bonding.[26] In the present case the mean apparent C–H bond length is 0.970 Å, and the root mean square deviation is 0.028. The minimum and maximum lengths are 0.904 and 1.030 Å, respectively. The actual C–H internuclear distance is known to be about 1.08 Å in aromatic compounds.[38] The C–C–H angles are all in the range 116–124°, and the average displacement of the H atoms from their ring best planes is 0.034 Å (maximum displacement, 0.110 Å).

It is of interest that we were able to refine successfully the anisotropic thermal parameters of the 27 hydrogen atoms, that is, to have the exponents of the temperature factors remain negative-definite quadratic forms. This has been done only rarely,[43] partly because of the extra computer time required and partly because the quality of the diffraction data often does not allow it. No detailed analysis of the thermal parameters of the hydrogen atoms has been attempted, but their ellipsoids depicted in Figure 1 are generally physically reasonable, though certainly not to the degree that those of the heavier atoms are.

Perchlorate Ion. Perchlorate ions are often found to be in a disordered arrangement that makes it impossible to determine their atomic parameters precisely. In the present case the ions are in an ordered arrangement, though, as can be seen from Figure 3, the oxygen atoms are characterized by rather large root mean square vibrational amplitudes (up to 0.46 Å in magnitude). It was these large amplitudes which suggested the use of the three-cumulant refinement for the atoms of the perchlorate ion. The extra parameters obtained in this refinement allowed calculation of the intermode Cl–O distances,[23b] which should be better approximations to the actual Cl–O bond lengths than the uncorrected distances from the two-cumulant refinement. The O–Cl–O valence angles defined by the intermode vectors were also computed. For comparison, we also made corrections on the bond lengths and angles through a rigid-body analysis,[44] using the program of C. K. Johnson[45] and the coordinates and anisotropic thermal parameters from the last refinement cycle before the three-cumulant model was introduced. The fit of the calculated to the observed U_{ij} parameters was rather good, the standard deviation of an observation of unit weight being 0.0011 Å^2. The root mean square amplitudes associated with the three principal axes of libration of the ion were calculated to be 12.9, 9.8, and 7.7°.

Table IV shows the intermode distances and angles and the uncorrected and corrected bond lengths and angles from the two-cumulant refinement. At first sight the corrections by the rigid-body calculation seeem extraordinarily satisfactory, in that the spread of the corrected distances is reduced to only 0.003 Å, though the corrections range from 0.038 to 0.054 Å. However, the average corrected distance of 1.471 Å is too high in comparison with the results from a number of recent and apparently reliable crystallographic determinations of the perchlorate ion structure,[46] most of them done at −188 °C or below and therefore relatively free from the perturbations of thermal motion. The average from these determinations is 1.443 Å, almost the same as the average intermode distance

Table IV. Bond Lengths and Valence Angles in the Perchlorate Ion[a]

	From two-cumulant refinement		From mode calculation
	Uncor	Cor	
	Bond Lengths, Å		
Cl-O(1)	1.434	1.472	1.453
Cl-O(2)	1.417	1.471	1.431
Cl-O(3)	1.425	1.469	1.447
Cl-O(4)	1.422	1.472	1.446
Av	1.425	1.471	1.444
	Angles, deg		
O(1)-Cl-O(2)	109.2	109.6	108.7
O(1)-Cl-O(3)	108.9	108.5	108.6
O(1)-Cl-O(4)	110.0	109.5	110.1
O(2)-Cl-O(3)	109.5	109.3	110.5
O(2)-Cl-O(4)	109.4	109.7	109.5
O(3)-Cl-O(4)	109.8	110.2	109.3

[a] The standard errors of the uncorrected bond lengths and angles from the two cumulant refinement are about 0.002 Å and 0.2°.

in Table IV. It appears, therefore, that intermode distances may be expected to be more reliable than corrected distances from a rigid-body analysis when the librational amplitudes are large. The assumption of simple harmonic motion implicit in the rigid-body analysis is evidently not valid for the large amplitudes.

The packing of the perchlorate ions with the aminium ions is shown in the stereoscopic drawing of Figure 4. There are no unusually short contacts. Atom O(3) of the perchlorate ion is in close contact with the aminium ion near its center, with O(3)···C(6,3), O(3)···N, and O(3)···C(1,3) distances of 3.05, 3.06, and 3.13 Å, respectively.

Supplementary Material Available: A table of coordinates and thermal parameters of the hydrogen atoms and a listing of observed and calculated structure factors, with standard errors of the former (26 pages). Ordering information is given on any current masthead page.

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